Table II. Phosphorus Analyses

polymer	% P	% 5 in 6
6a	1.59	4.67
6b	1.83	5.38
6c	1.55	4.56

disappeared by shaking with D_2O), 3.60 (m, 3 H), 4.25 (d, J = 5.5 Hz, 2 H), 5.62 (dd, J = 1.4, 1.4 Hz, 1 H), 6.17 (dd, J = 1.0, 1.3 Hz, 1 H); ^{13}C NMR δ 18.1, 63.5, 65.4, 70.3, 126.2, 135.9, 166.7; IR (neat) 3400, 2960, 2890, 1720, 1645, 1335, 1300, 1175, 1050, 945, 820 cm^{-1}. Anal. Calcd for $C_7H_{12}O_4$: C, 52.53; H, 7.50. Found: C, 52.50; H, 7.52.

(2RS)-2,3-Dihydroxypropyl Methacrylate [(R,S)-2]. The racemic isomer was prepared in 80% yield from (2RS)-(2,3-isopropylidenedioxy)propyl methacrylate as described for the S isomer: bp 95–97 °C (0.05 mmHg). Anal. Calcd for $C_7H_{12}O_4$: C, 52.53; H, 7.50. Found: C, 52.45; H, 7.45. The spectroscopic data were identical with those reported for the S isomer.

(2R)-2,3-Dihydroxypropyl Methacrylate [(R)-2]. The R isomer was prepared in 69% yield from (2R)-(2,3-isopropylidenedioxy)propyl methacrylate as described for the S isomer: bp 85–86 °C (0.025 mmHg); $[\alpha]^{22}_D$ +11.91° (c 2.15, CH_3OH). Anal. Calcd for $C_7H_{12}O_4$: C, 52.53; H, 7.50. Found: C, 52.70; H, 7.60. The spectroscopic data were identical with those reported for the S isomer.

Preparation of Copolymer 6a. To a resin kettle equipped with an efficient overhead stirrer, a condenser, and a nitrogen inlet was added 5 mL of benzene, which was then heated to 65 °C. The monomers (S,S)-**5** (0.18 g, 0.32 mmol), (S)-**2** (0.93 g, 5.80

mmol), and ethylene dimethacrylate (0.064 g, 0.32 mmol) and AIBN (20 mg) were dissolved in 5 mL of benzene, and this solution was added to the resin kettle. The mixture was stirred at 65 °C for 15 h, cooled to room temperature, and filtered. The copolymer was washed with (5 × 10 mL) benzene and dried overnight at 0.10 mmHg to yield 0.99 g (85%) of **6a** as a white powder.

The above procedure was used for the preparation of **6b** and **6c**. The elemental analyses of copolymers **6a–c** are reported in Table II.

General Procedure for Asymmetric Hydrogenation Using Polymer-Supported Catalysts. To an argon-filled flask were added 68 mg (0.018 mequiv of diphosphine) of **6a**, 3.0 mg (0.012 mequiv of Rh) of chloro(1,5-cyclooctadiene)rhodium(I) dimer, and 10 mL of ethanol. The mixture was stirred for 36 h and then filtered. The copolymer was washed with 10 mL of ethanol and dried overnight under 0.05 mmHg to give the light yellow polymer-bound catalyst. The catalyst was transferred to a Fischer–Porter tube containing 0.6 mmol of substrate, and 10 mL of solvent was added via a syringe. The apparatus was then pressurized to 1 atm with hydrogen, and the mixture was stirred at room temperature. The workup consisted of filtration to remove the catalyst and evaporation of the solvet under reduced pressure. The ratio of N-acylamino acid to unsaturated N-acylamino acid was determined by NMR, and the enantiomeric excess was determined by optical rotation on the basis of the mole percent amino acid as described previously.[12,13]

Palladium-Catalyzed Olefination of Vinyl Triflates

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The olefination of vinyl trifluoromethanesulfonates (triflates) takes place under mild reaction conditions in polar solvents to give high yields of conjugated dienes. The reaction of 4-*tert*-butylcyclohexenyl triflate with Michael acceptors in the presence of a catalytic amount of bis(triphenylphosphine)dichloropalladium(II) and an excess of triethylamine gave high yields of the expected regioisomer. The reaction conditions are sufficiently mild that acrolein gave (*E*)-3-(4-*tert*-butylcyclohexenyl)propenal in 86% yield without appreciable polymerization. Acetylenes also undergo the reaction to give high yields of enynes. Less reactive olefins may be employed with the use of palladium(0) catalysts and, in some cases, added lithium salts.

The palladium-catalyzed olefination of organic halides with alkenes (the Heck reaction) is a unique method of carbon–carbon bond formation in which the organic halide is homologated by two or more carbons.[1,2] The alkene insertion is largely regiospecific with the organic halide adding to the least hindered position of the alkene. The organic halides are limited mostly to aryl, vinyl, and benzyl halides, since alkyl halides containing an sp³ hydrogen β to the carbon bearing the halogen undergo a facile β-hydride elimination in preference to alkene insertion.

The palladium-catalyzed reaction of alkenes with vinyl halides has been practically limited to the reactions of vinyl bromides and iodides. While the synthesis of acyclic vinyl halides from alkynes has been well worked out,[3–7] the

generation of cyclic vinyl iodides from cyclic ketones[8–10] proceeds with variable regioselectivity. In general, 2-substituted cyclic vinyl iodides are unavailable from the corresponding 2-substituted ketone or enone.

The ease of preparation of vinyl trifluoromethanesulfonates (triflates) in high regioselective purity from ketones[11,12] and enones[12,13] and the availability of the starting materials have expanded their use as vinyl cation synthons. For example, organocopper reagents react with vinyl triflates to yield coupled products.[14–16] More re-

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(3) Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967,** *89,* 2753–2755.
(4) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967,** *89,* 4245–4247.
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(11) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982,** 85–126.
(12) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983,** *24,* 979–982.
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(14) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1980,** *21,* 4313–4316.

Table I. Effect of Solvent on the Palladium(II)-Catalyzed Coupling of 4-*tert*-Butylcyclohexenyl Triflate with Methyl Acrylate[a]

entry	solvent	h at 75 °C	isolated yield, % product[b]	recvd triflate
1	CHCl$_3$	17	d	66
2	THF (argon)	c	57	1
3	THF (air)	c	59	2
4	DME	c	66	6
5	CH$_3$CN	10	78	3
6	ethanol	17	83	1
7	HMPA	9	75	1
8	Me$_2$SO	17	93	1
9	DMF	9	91	1

[a] Reaction of 2.5 mmol of 4-*tert*-butylcyclohexenyl triflate with 5.0 mmol of methyl acrylate in a mixture of 8.0 mmol of Et$_3$N, 2.1 mol % of Pd(PPh$_3$)$_2$Cl$_2$, and 10 mL of solvent. All reactions except that in entry 3 were run under an argon atmosphere. [b] Only the *E* isomer was observed. [c] Reaction run at 75 °C for 24 h and then warmed to 90 °C for 24 h. No improvement in conversion was noticed at the higher temperature. [d] Trace.

cently, we have shown that vinyl triflates are capable of undergoing palladium-catalyzed coupling reactions with a wide variety of organostannanes under mild conditions.[17] When this coupling is carried out in the presence of carbon monoxide, carbon monoxide is inserted between the coupling partners, producing vinyl ketones.[18]

In the coupling reaction of vinyl triflates with organotin reagents, a key step in the catalytic cycle is the rapid oxidative addition of the vinyl triflate to a palladium(0) complex to generate a vinylpalladium(II) species. This suggested that vinyl triflates could be utilized in other palladium-catalyzed reactions requiring an organopalladium(II) complex produced via an oxidative addition. In particular, it became apparent that vinyl triflates could replace vinyl halides in the Heck reaction. While this work was in progress, such an olefination reaction was reported.[19] We wish to report our results in the olefination reaction of vinyl triflates and more clearly define the scope and limitations of the reaction.
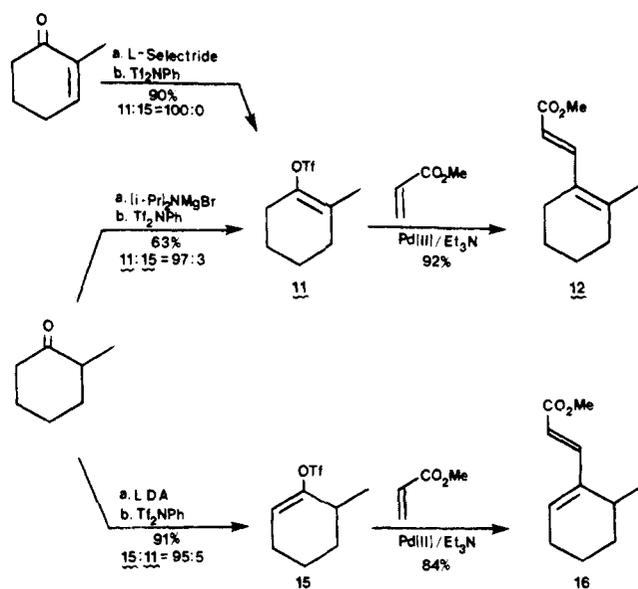
Results and Discussion

Initially, a brief survey of palladium complexes as catalysts for the reaction of vinyl triflate **1** with methyl acrylate (**2**) in the presence of 3 equiv of triethylamine
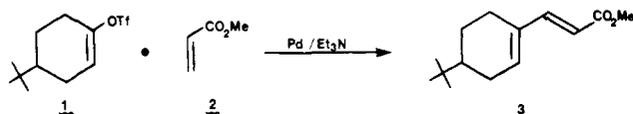
using tetrahydrofuran as the solvent was conducted. While all of these reactions proceeded in good to moderate conversions, it was apparent from monitoring the reaction mixtures (GC) that bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh$_3$)$_2$Cl$_2$) was slightly superior to other catalysts. As shown in Table I, the reaction proceeded well with this catalyst in most common solvents. While the presence of air did not seem detrimental to the course of the reaction (entry 3), all reactions were routinely conducted under an argon atmosphere. Although triethylamine is not particularly soluble in dimethyl sulfoxide at

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(17) Scott, W. J.; Crisp, G. T.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4630–4632.

(18) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500–7506.

(19) Cacchi, S.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1984**, *25*, 2271–2274.

Scheme I

room temperature, the reaction mixture became homogeneous on heating, and yields of **3** with this solvent were excellent (entry 8). The olefination also works well in protic solvents (entry 6).

This reaction proved to be quite general for activated olefins (Table II). While olefins such as methyl acrylate and acrylonitrile are commonly used in the Heck reaction, it has been pointed out that acrolein cannot be used because it polymerizes under the reaction conditions.[1] In contrast, a good yield of (*E*)-3-(4-*tert*-butylcyclohexenyl)propenal (**6**) was isolated in this case, with none of the *Z* isomer being observed (entry 9). The reaction also is insensitive to steric hindrance about the vinyl triflate (entries 18 and 19). The regioselective conversion of ketones into dienes was demonstrated by the two-step conversion of 2-methylcyclohexanone into either β-(2-methylcyclohexenyl)acrylate (**12**) or β-(6-methylcyclohexenyl)acrylate (**16**) via the corresponding vinyl triflates (Scheme I).

In order to determine whether the stereochemistry of the products isolated was representative of that formed on reductive elimination or whether it was the result of an equilibration process, the reaction of **1** with acrylonitrile was monitored by gas chromatography in both DMF (Table II, entry 5) and ethanol (Table II, entry 8). Early in the reaction, the product mixture was largely composed of the *E* isomer (80%, Table III). However, as the reaction progressed, the *E*:*Z* ratio dropped to the ratios that were isolated. Prolonged reaction times did not change the product ratios significantly. Thus, it would appear that the product ratio reflects equilibrium conditions in this case, a finding similar to that observed in the standard Heck reaction.[1]

While activated olefins appear quite reactive, unactivated olefins afford poor to moderate yields of products. Thus, while styrene normally is considered to be an excellent olefin for the Heck reaction,[1,2] only traces of product could be isolated in the reaction of styrene with **1** (Table II, entry 21). Similarly, 1-hexyne gave only moderate yields of product (Table II, entry 12).

Previous studies of the palladium-catalyzed reactions of vinyl triflates indicated that the oxidative addition of the vinyl triflate takes place readily, yielding a palladium complex which is incapable of proceeding further in the catalytic cycle. This problem was circumvented by the

Table II. Palladium(II)-Catalyzed Olefination of Vinyl Triflates[a]

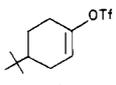| entry	triflate	olefin	solvent	product	isolated yield, %
1	1	CO_2Me	DMF	3 (CO_2Me)	91
2			Me$_2$SO	3 (CO_2Me)	93
3	1	(methyl vinyl ketone)	DMF	4	89
4			Me$_2$SO	4	88
5	1	CN	DMF	5 E:Z = 73:27	99
6			Me$_2$SO	5 E:Z = 77:23	97
7			CH$_3$CN	5 E:Z = 76:24 + 1	49, 36[b]
8			ethanol	5 E:Z = 74:26 + 1	21, 74[b]
9	1	CHO	DMF	6 (CHO)	86
10	1	H—≡—Ph	DMF	7 (≡Ph)	91
11	1	NH_2 (acrylamide)	DMF	8 (NH_2, O)	95
12	1	H—≡—Bu	DMF	9 (≡Bu)	50
13	1	H—≡—C(CH$_3$)$_2$OH	DMF	10 (≡, OH)	100
14	11	CO_2Me	DMF	12 (CO_2Me)	92
15	13	CO_2Me	DMF	14 (CO_2Me)	88

Table II *(Continued)*

entry	triflate	olefin	solvent	product	isolated yield, %
16	15	CO2Me	DMF	16	84
17	15		DMF	17	90
18	18	CO2Me	DMF	19	89
19	18		DMF	20	83
20	1		DMF	1	60 [b]
21	1	Ph	DMF [c]	21	3

[a] Reactions were run with 3 equiv of triethylamine and 2 mol % of Pd(PPh$_3$)$_2$Cl$_2$ at 75 °C, except where noted. [b] Isolated yield of starting vinyl triflate. [c] Reaction was run at 75 °C for 4 h and then heated to 115 °C for 24 h. The yield of isolated starting material was not quantified.

Table III. Palladium(II)-Catalyzed Reaction of 4-*tert*-Butylcyclohexenyl Triflate with Acrylonitrile

solvent	reactn time at 75 °C,h	yield of 1, %	yield of product	*E:Z* ratio GC	*E:Z* ratio NMR
DMF	0.5		3[a]	5:1	
	1.5		75[a]	3.5:1	
	6.5		100[a]	2.9:1	
	6.5	1[b]	94[b]	3.2:1	3.4:1
	17	1[b]	99[b]	3.1:1	2.7:1
ethanol	6.5		22[a]	4.7:1	
	24		47[a]	2.5:1	
	24	74[b]	21[b]	2.4:1	2.8:1

[a] Conversion of starting vinyl triflate to product as determined by peak height ratios. These numbers are included to indicate the progress of the reaction and have not been calibrated to show molar ratios. [b] Isolated yields (%).

addition of lithium chloride to the reaction mixture, which presumably acted to form a more stable palladium(II) chloride species.[17,18] However, no improvement in the consumption of 1 in the presence of styrene was observed on the addition of 3 equiv of either lithium chloride[17,18] or lithium acetate[20] to the reaction mixture.

The Heck reaction is preceded by the reduction of the palladium(II) catalyst to a palladium(0) species, presumably by the olefin.[1,2] The resulting palladium(0) species is then capable of entering the catalytic cycle (Scheme II) by oxidative addition of an electrophile (in this case, the triflate) and coordination with the olefin to afford a pal-

(20) Spencer, A. *J. Organomet. Chem.* **1984**, *270*, 115–120.

Scheme II. Proposed Mechanism for the Olefination of Vinyl Triflates
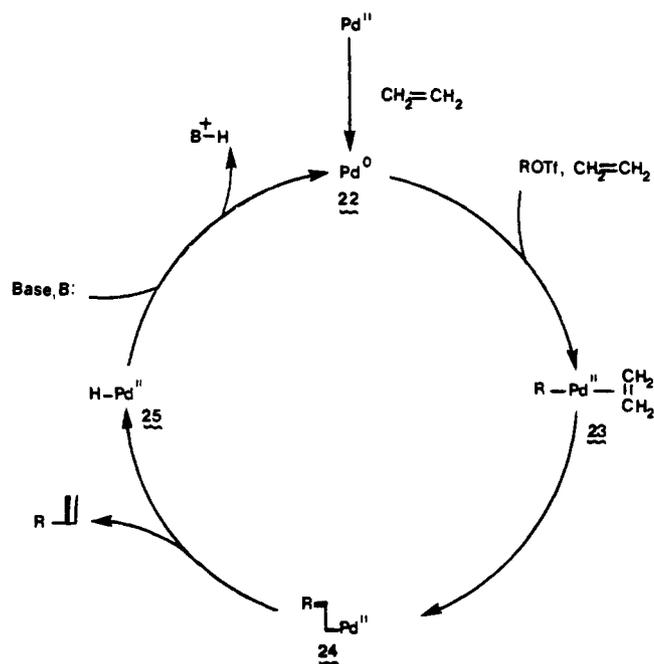
ladium(II) species, such as **23**. On the assumption that the low conversion of 1 to products was due to the inability of the olefin to reduce Pd(PPh$_3$)$_2$Cl$_2$, the reaction of 1 with styrene was carried out in the presence of the tetrakis-(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$) and 3 equiv

Table IV. Palladium(0)-Catalyzed Olefination of Vinyl Triflates

entry	triflate	olefin	LiCl, equiv	product	isolated yield, %
1			0.0		57
2			0.0		50
3			3.0		78
4			0.0		53

of triethylamine. Under these conditions the yield of **21** in the olefination of **1** with styrene increased from 3% (Table II, entry 21) to 57% (Table IV, entry 1). Similarly, dihydropyran gave a much improved yield of **28**, in which the unsaturation in the pyran ring has migrated out of conjugation with the cyclohexenyl double bond (Table IV, entry 4). Such a migration is also seen in the palladium-(II)-catalyzed coupling of iodobenzene with dihydropyran.[21]

Surprisingly, 1-hexyne showed no increase in yield when Pd(PPh₃)₄ was used in the reaction (compare Table II, entry 12 and Table IV, entry 2). However, on addition of 3 equiv of lithium chloride to the reaction mixture, **1** was totally consumed and the desired product could be isolated in good yield (Table IV, entry 3).

Conclusions

Because the oxidative addition of vinyl triflates to palladium(0) complexes takes place readily, they are excellent substrates for the Heck olefination, providing the rapid conversion of a ketone into a diene or an enzyne. Such a conversion can be performed regioselectively by using known enolate chemistry.[12,13] The palladium-catalyzed reaction is unaffected by steric hindrance in the vinyl triflate.

The reaction conditions necessary for the olefination appear to depend on the olefin employed. While good Michael acceptors react well in the presence of a catalyst introduced as Pd(PPh₃)₂Cl₂, less reactive olefins may require a palladium catalyst introduced as Pd(0) and/or the addition of chloride. Finally, the olefination may be carried out in a wide variety of polar solvents, at moderate temperatures, and by employing easily polymerized substrates.

Experimental Section

¹H NMR spectra were recorded on an IBM WP270 spectrometer in CDCl₃ with tetramethylsilane as an internal standard. ¹³C NMR spectra and gated decoupled ¹³C NMR spectra were recorded on an IBM WP 270 spectrometer (68 MHz) using CDCl₃ as solvent and internal standard. Infrared spectra were recorded on a Beckman 4250 spectrometer. Gas chromatographic analyses were conducted with a Varian 3700 equipped with a 0.25 mm × 50 m SE-30 capillary column. Low-resolution mass spectra (LRMS) were performed on a VG Micromass 16 spectrometer. High-resolution mass spectra (HRMS) were obtained from the Midwest Center for Mass Spectrometry at the University of Nebraska. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Tetrahydrofuran (THF) and dimethoxyethane (DME) were distilled from potassium under an argon atmosphere. Triethylamine, acetonitrile, hexamethylphosphoramide (HMPA), dimethyl sulfoxide (Me₂SO), and dimethylformamide (DMF) were distilled from calcium hydride. Thin-layer chromatographic analyses (TLC) were performed on EM silica gel 60 F-254 plates. Column chromatographic purification of reaction mixtures were performed with Woelm 230–400-mesh silica gel. Bulb-to-bulb distillations were conducted by using an Aldrich Kugelrohr apparatus.

Olefination reactions were conducted in 25-mL round-bottom flasks equipped with a single Ace Glass no. 11 threaded joint and stoppered with a solid Ace Glass no. 11 threaded Teflon plug. All reactions were conducted under an argon atmosphere except where stated.

The term "worked up in the usual manner" refers to separation of the reaction mixture between 20 mL of water and 20 mL of a 1:1 ether/hexanes solution, washing of the organic phase with 20 mL of water, back-extraction of the combined aqueous phases with a 1:1 ether/hexanes solution, extraction of the combined organic phases with water (2 × 10 mL) and a saturated sodium chloride solution (2 × 10 mL), drying (MgSO₄), and filtration through a plug of silica gel to remove palladium.

Vinyl Triflates. The following vinyl triflates were prepared according to literature methods: 4-*tert*-butylcyclohexenyl triflate (**1**),[22] 2-methylcyclohexenyl triflate (**11**),[13,18] 5-(2-propenyl)-2-methylcyclohexenyl triflate (**13**),[13] 6-methylcyclohexenyl triflate (**15**),[12] and 2,2,5-trimethylcyclopentenyltriflate triflate (**18**).[18]

Methyl (E)-3-(4-*tert*-Butylcyclohexenyl)propenoate (3). To a slurry of Pd(PPh₃)₂Cl₂ (0.038 g, 2.2 mol %) in DMF (5 mL) was added a solution of **1** (0.712 g, 2.49 mmol), methyl acrylate (0.50 mL, 5.5 mmol), and triethylamine (1.2 mL, 8.6 mmol) in DMF (5 mL). The resulting mixture was heated at 75 °C for 9 h, cooled to room temperature, worked up in the usual manner, and concentrated. Column chromatography of the resulting yellow solids (silica gel; hexanes, 2.5% ethyl acetate/hexanes) gave **3** (0.50 g, 91%): mp 37.5–39 °C; bp (bulb-to-bulb) 100 °C (0.40 mmHg); TLC (10% ethyl acetate/hexanes) Rf 0.67; IR (CDCl₃) 3050, 3020, 1710, 1620 cm⁻¹; ¹H NMR δ 0.77 (s, 9 H), 1.02–1.21 (m, 3 H), 1.77–1.90 (m, 2 H), 2.09–2.16 (m, 2 H), 3.62 (s, 3 H), 5.63 (d, J = 15.8 Hz, 1 H), 6.03–6.06 (m, 1 H), 7.18 (d, J = 15.8 Hz, 1 H); ¹³C NMR δ 23.4, 25.4, 27.0 (3 C), 28.1, 32.0, 43.8, 51.1, 114.4, 134.7, 138.7, 147.5, 167.7; LRMS, m/z 222 (M⁺, 32%). Anal. Calcd for C₁₄H₂₂O₂: C, 75.63; H, 9.97. Found: C, 75.61; H, 9.28.

Other experiments on the reaction of **1** with methyl acrylate were run in an analogous manner. The reaction conditions and solvents employed were as noted in Table I and in Table II, entry 2.

(E)-4-(4-*tert*-Butylcyclohexenyl)but-3-en-2-one (4). A mixture of 0.037 g of Pd(PPh₃)₂Cl₂ (2.1 mol %), 0.704 g of **1** (2.46

(21) Arai, I; Daves, G. D., Jr. *J. Org. Chem.* **1979**, *44*, 21–23.

(22) Scott, W. J. Ph.D. Dissertation, Cornell University, Ithaca, NY, 1983.

mmol), 0.43 mL of methyl vinyl ketone (5.2 mmol), and 1.2 mL of triethylamine (8.6 mmol) in 10 mL of DMF was heated at 75 °C for 5 h, cooled to room temperature, worked up in the usual manner, and concentrated to give yellow solids. Column chromatography of this material (silica gel; hexanes, 2.5% ethyl acetate/hexanes) afforded 0.45 g of **4** (89% yield) as a white solid: mp 75.5–76.5 °C; bp (bulb-to-bulb) 90–95 °C (0.40 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.21; IR (CDCl$_3$) 3040, 1665, 1630, 1595, 1390, 1365 cm^{-1}; ^{1}H NMR δ 0.81 (s, 9 H), 1.04–1.23 (m, 3 H), 1.83–2.05 (m, 2 H), 2.14–2.27 (m, 2 H), 2.20 (s, 3 H), 5.96 (d, J = 16.0 Hz, 1 H), 6.14–6.16 (m, 1 H), 7.06 (d, J = 16.0 Hz, 1 H); ^{13}C NMR (gated decoupled) δ 23.3 (t, J = 131.7 Hz), 25.4 (t, J = 129.7 Hz), 27.0 (q, J = 128.1 Hz, 3 C), 27.1 (q, J = 131.8 Hz), 28.2 (t, J = 129.7 Hz), 32.0 (s), 43.7 (d, J = 130.5 Hz), 124.3 (d, J = 157.6 Hz), 135.0 (s), 140.0 (d, J = 151.9 Hz), 146.3 (dd, J = 7.1, 151.8 Hz), 198.6 (s); LRMS, m/z 206 (M$^+$, 39%). Anal. Calcd for C$_{14}$H$_{22}$O: C, 81.49; H, 10.75. Found: C, 81.23; H, 10.65.

The reaction of 1 with methyl vinyl ketone in Me$_2$SO was run in an analogous manner (Table II, entry 4).

(E)- and (Z)-3-(4-*tert*-Butylcyclohexenyl)acrylonitrile (5). To a slurry of 0.038 g of Pd(PPh$_3$)$_2$Cl$_2$ (2.2 mol %) in DMF (5 mL) was added a solution of 0.702 g of 1 (2.45 mmol), 0.40 mL of acrylonitrile (6.1 mmol), and 1.2 mL of triethylamine (8.6 mmol) in DMF (5 mL). This was heated to 75 °C for 6.5 h, cooled to room temperature, worked up in the usual manner, and concentrated. The resulting oil was purified by column chromatography (silica gel; hexanes, 2.5% ethyl acetate/hexanes) to give a mixture of (E)-5 and (Z)-5 in a 73:27 ratio (0.46 g, 99%) as a waxy white solid: bp (bulb-to-bulb) 95–100 °C (0.50 mmHg); TLC (2.5% ethyl acetate/hexanes) R_f 0.23; IR (CDCl$_3$) 3060, 3010, 2200, 1655, 1595, 1390, 1360 cm^{-1}; ^{1}H NMR δ 0.89 (s, 9 H), 1.01–1.41 (m, 3 H), 1.87–2.85 (m, 4 H), 5.04 (d, J = 12.1 Hz, 0.28 H), 5.17 (d, J = 16.3 Hz, 0.72 H), 6.15–6.17 (m, 1 H), 6.61 (d, J = 12.1 Hz, 0.26 H), 7.16 (d, J = 16.3 Hz, 0.74 H); LRMS, (GC-MS) (Z)-5 m/z 189 (M$^+$, 3%), (E)-5 m/z 189 (M$^+$, 0.7%). Anal. (E/Z mixture) Calcd for C$_{13}$H$_{19}$N: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.26; H, 10.06; N, 7.34.

Other reactions of acrylonitrile with 1 were run in an analogous manner. In cases where unreacted 1 was isolated, it was recovered during chromatography while eluting with hexanes.

(E)-3-(4-*tert*-Butylcyclohexenyl)propenal (6). To a slurry of 0.040 g of Pd(PPh$_3$)$_2$Cl$_2$ (2.3 mol %) in DMF (5 mL) was added a solution of 0.701 g of 1 (2.45 mmol), 0.33 mL of freshly distilled acrolein (4.9 mmol), and 1.2 mL of triethylamine (8.6 mmol) in 5 mL of DMF. The resulting solution was heated at 75 °C for 1.5 h, cooled to room temperature, worked up in the usual manner, and concentrated to give a yellow oil. Column chromatography of this material (silica gel; hexanes, 5% ethyl acetate/hexanes) gave 6 as an oil, which solidified on standing (0.41 g, 86%): mp 58–59.5 °C; bp (bulb-to-bulb) 70–75 °C (0.20 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.17; IR (CDCl$_3$) 3030, 2740, 2710, 1675, 1625, 1605, 1390, 1365 cm^{-1}; ^{1}H NMR δ 0.90 (s, 9 H), 1.00–1.38 (m, 3 H), 1.92–2.17 (m, 2 H), 2.26–2.37 (m, 2 H), 6.06 (dd, J = 7.9, 15.6 Hz, 1 H), 6.31–6.33 (m, 1 H), 7.11 (d, J = 15.6 Hz, 1 H), 9.55 (d, J = 8.0 Hz, 1 H); ^{13}C NMR δ 23.3, 25.5, 27.0 (3 C), 28.4, 32.1, 43.6, 125.9, 135.3, 141.5, 155.5, 194.0; LRMS, m/z 192 (M$^+$, 11%); HRMS, calcd for C$_{13}$H$_{20}$O 192.1515; found 192.1507. Anal. Calcd for C$_{13}$H$_{20}$O: C, 81.20; H, 10.48. Found: C, 81.37; H, 10.28.

1-(4-*tert*-Butylcyclohexenyl)-2-phenylacetylene (7). A mixture of 0.040 g (2.3 mol %) of Pd(PPh$_3$)$_2$Cl$_2$, 0.710 g (2.48 mmol) of 1, 0.42 mL (3.8 mmol) of phenylacetylene, and 1.2 mL (8.6 mmol) of triethylamine in 10 mL of DMF was heated to 75 °C for 0.5 h, cooled to room temperature, worked up in the usual manner, and concentrated to give a thick brown oil. Column chromatography of this material (silica gel; hexanes) afforded 7 as a colorless oil (0.54 g, 91%), which crystallized on standing: mp 43–45 °C; bp (bulb-to-bulb) 115–120 °C (0.35 mmHg); TLC (hexanes) R_f 0.35; IR (neat) 3080, 3060, 3030, 2200, 1600, 1570, 1395, 1365, 750, 685 cm^{-1}; ^{1}H NMR δ 0.87 (s, 9 H), 1.10–1.34 (m, 3 H), 1.81–1.94 (m, 2 H), 2.13–2.30 (m, 2 H), 6.19–6.21 (m, 1 H), 7.22–7.53 (m, 5 H); ^{13}C NMR δ 23.9, 27.1 (3 C), 27.5, 30.8, 32.2, 43.3, 87.0, 91.1, 120.6, 123.9, 127.6, 128.2 (2 C), 131.5 (2 C), 135.3; LRMS, m/z 238 (M$^+$, 65%). Anal. Calcd for C$_{18}$H$_{22}$: C, 90.70; H, 9.30. Found: C, 90.63; H, 9.53.

(E)-3-(4-*tert*-Butylcyclohexenyl)acrylamide (8). To a slurry of 0.044 g (2.5 mol %) of Pd(PPh$_3$)$_2$Cl$_2$ in 5 mL of DMF

was added a solution of 0.714 g (2.49 mmol) of 1, 0.33 g (4.6 mmol) of acrylamide, and 1.2 mL (8.6 mmol) of triethylamine in 5 mL of DMF. This was heated at 75 °C for 8 h, cooled to room temperature, worked up in the usual manner, and concentrated to give an off-white solid. Recrystallization of this material (ethyl acetate/hexanes) gave 8 as white needles (0.49 g, 95%): mp 169–170 °C; TLC (ethyl acetate) R_f 0.39; IR (paraffin oil) 3400, 3180, 3040, 1670, 1640, 1600, 1390, 1365, 975 cm^{-1}; ^{1}H NMR δ 0.89 (s, 9 H), 1.16–1.31 (m, 3 H), 1.90–2.22 (m, 2 H), 2.26–2.34 (m, 2 H), 5.55 (br s, 2 H), 5.77 (d, J = 15.4 Hz, 1 H), 6.15–6.17 (m, 1 H), 7.24 (d, J = 15.3 Hz, 1 H); ^{13}C NMR δ 23.6, 25.7, 27.2 (3 C), 28.1, 32.2, 44.0, 116.3, 134.4, 138.2, 145.0, 168.9; LRMS, m/z 207 (M$^+$, 1.6%). Anal. Calcd for C$_{13}$H$_{21}$NO: C, 75.31; H, 10.21; N, 6.76. Found: C, 75.06; H, 10.02; N, 6.86.

1-(4-*tert*-Butylcyclohexenyl)hex-1-yne (9). To a slurry of 0.070 g (2.4 mol %) of Pd(PPh$_3$)$_4$ and 0.32 g (7.6 mmol) of lithium chloride in 5 mL of DMF was added a solution of 0.706 g (2.47 mmol) of 1, 0.40 mL (3.5 mmol) of 1-hexyne, and 1.2 mL (8.6 mmol) of triethylamine. This mixture was heated to 75 °C for 24 h, cooled to room temperature, worked up in the usual manner, and concentrated to give a tan oil. Column chromatography of this material (silica gel; hexanes) gave 0.42 g (78%) of slightly yellow oil: bp (bulb-to-bulb) 109–114 °C (0.35 mmHg); TLC (hexanes) R_f 0.39; IR (neat) 3030, 2210 w, 1640, 1390, 1365 cm^{-1}; ^{1}H NMR δ 0.85 (s, 9 H), 0.91 (t, J = 7.1 Hz, 3 H), 1.08–2.28 (m, 13 H), 5.99–6.00 (m, 1 H); ^{13}C NMR δ 13.5, 19.0, 21.9, 23.9, 27.1 (3 C), 27.2, 31.2 (2 C), 32.2, 43.4, 82.0, 87.5, 121.0, 133.1; LRMS, m/z 218 (M$^+$, 54%); HRMS, calcd for C$_{16}$H$_{26}$ 218.2036; found 218.2028.

Other reactions of 1-hexyne with 1 were run in an analogous manner without lithium chloride (Table IV, entry 2) or with Pd(Ph$_3$)$_2$Cl$_2$ substituted for Pd(Ph$_3$)$_4$ and without lithium chloride (Table II, entry 12).

2-Methyl-4-(4-*tert*-butylcyclohexenyl)but-3-yn-2-ol (10). A mixture of 0.039 g of Pd(PPh$_3$)$_2$Cl$_2$ (2.2 mol %), 0.716 g of 1 (2.50 mmol), 0.36 mL of 2-methylbut-3-yn-2-ol (3.7 mmol), and 1.2 mL of triethylamine (8.6 mmol) in 10 mL of DMF was heated at 75 °C for 5.5 h to give a burgundy red solution. This was cooled to room temperature, worked up in the usual manner, and concentrated to give a dark brown oil. Bulb-to-bulb distillation of this material [110 °C (0.07 mmHg)] gave a viscous yellow oil, which slowly crystallized on standing (0.55 g, 100%). Alternatively, column chromatography (silica gel; 2.5% ethyl acetate/hexanes) gave the same product as a yellow oil, which solidified on standing, however, in lower yield (55%) due to decomposition in the presence of silica gel: mp 65–66 °C; TLC (10% ethyl acetate/hexanes) R_f 0.18; IR (CDCl$_3$) 3580 br, 3030, 2215, 1640, 1395, 1370 cm^{-1}; ^{1}H NMR δ 0.88 (s, 9 H), 1.11–1.29 (m, 3 H), 1.53 (s, 6 H), 1.78–1.88 (m, 2 H), 2.07–2.21 (m, 3 H), 6.06–6.09 (m, 1 H); ^{13}C NMR (gated decoupled) δ 23.8 (t, J = 124.2 Hz), 27.1 (q, J = 124.7 Hz, 3 C), 27.4 (t, J = 120.5 Hz), 30.7 (t, J = 122.6 Hz), 31.6 (q, J = 125.2 Hz, 2 C), 32.1 (s), 43.3 (d, J = 126.8 Hz), 65.5 (s), 83.6 (s), 91.5 (s), 120.0 (s), 135.0 (d, J = 163.5 Hz); LRMS, m/z 220 (M$^+$, 13%); HRMS, calcd for C$_{15}$H$_{24}$O 220.1828; found 220.1824. Anal. Calcd for C$_{15}$H$_{24}$O: C, 81.76; H, 10.98. Found: C, 81.78; H, 11.05.

Methyl (E)-3-(2-Methylcyclohexenyl)acrylate (12). A mixture of 0.038 g (2.2 mol %) of Pd(PPh$_3$)$_2$Cl$_2$, 0.614 g (2.51 mmol) of 2-methylcyclohexenyl triflate (11), 0.50 mL (5.6 mmol) of methyl acrylate, and 1.2 mL (8.6 mmol) of triethylamine in 10 mL of DMF was heated at 75 °C for 19 h, cooled to room temperature, worked up under the usual conditions, and concentrated to give a yellow oil. Column chromatography of this material (silica gel; hexanes, 2.5% ethyl acetate/hexanes) gave 0.42 g (92%) of 12 as a colorless oil: bp (bulb-to-bulb) 78–82 °C (0.25 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.40; IR (neat) 3075, 2995, 1725, 1620 cm^{-1}; ^{1}H NMR δ 1.58–1.66 (m, 4 H), 1.90 (s, 3 H), 2.12–2.14 (m, 4 H), 3.74 (s, 3 H), 5.77 (d, J = 15.6 Hz, 1 H), 7.85 (d, J = 15.6 Hz, 1 H); ^{13}C NMR (gated decoupled) δ 19.4 (q, J = 126.2 Hz), 22.2 (br t, J = 126.3 Hz, 2 C), 24.9 (t, J = 125.3 Hz), 33.3 (t, J = 126.4 Hz), 50.9 (q, J = 145.9 Hz), 113.9 (d, J = 162.0 Hz), 127.0 (s), 142.6 (d, J = 154.0 Hz), 143.1 (s), 168.0 (s); LRMS, m/z 180 (M$^+$, 74%). Anal. Calcd for C$_{11}$H$_{16}$O$_2$: C, 73.30; H, 8.95. Found: C, 73.21; H, 9.11.

Methyl (E)-3-(2-Methyl-5-(2-propenyl)cyclohexenyl)acrylate (14). A mixture of 0.039 g (2.2 mol %) of Pd(PPh$_3$)$_2$Cl$_2$,

0.733 g (2.58 mmol) of 2-methyl-5-(2-propenyl)cyclohexenyl triflate (**13**), 0.50 mL (5.6 mmol) of methyl acrylate, and 1.2 mL (8.6 mmol) of triethylamine in 10 mL of DMF was heated at 75 °C for 19 h, cooled to room temperature, worked up in the usual manner, and concentrated. The resulting yellow oil was purified by column chromatography (silica gel; hexanes, 2.5% ethyl acetate/hexanes) to give **14** as a colorless oil (0.50 g, 88%): bp (bulb-to-bulb) 95–105 °C (0.50 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.40; IR (neat) 3070, 3010, 1720, 1645, 1625, 1615 cm^{-1}; ^{1}H NMR δ 1.73–1.82 (m, 1 H), 1.76 (s, 3 H), 1.91 (s, 3 H), 1.98–2.33 (m, 6 H), 3.74 (s, 3 H), 4.72 (br s, 1 H), 4.75 (br s, 1 H), 5.80 (d, J = 15.7 Hz, 1 H), 7.85 (d, J = 15.7 Hz, 1 H); ^{13}C NMR δ 19.2, 20.5, 27.0, 30.4, 33.7, 40.7, 51.0, 108.9, 114.2, 126.6, 142.4, 142.8, 148.8, 168.0; LRMS, m/z 220 (M$^+$, 39%). Anal. Calcd for C$_{14}$H$_{20}$O$_2$: C, 76.33; H, 9.15. Found: C, 76.16; H, 9.19.

Methyl (*E*)-3-(6-Methylcyclohexenyl)acrylate (16). To a slurry of Pd(Ph$_3$)$_2$Cl$_2$ (0.037 g, 1.7 mol%) in DMF (5 mL) was added a solution of 6-methylcyclohexenyl triflate (0.778 g, 3.19 mmol), methyl acrylate (0.50 mL, 5.6 mmol), and triethylamine (1.2 mL, 8.6 mmol) in DMF (5 mL). This was heated to 75 °C for 1 h, cooled to room temperature, worked up in the usual manner, and concentrated to give a yellow oil. Column chromatography of this mixture (silica gel; hexanes, 5% ethyl acetate/hexanes) afforded **16** as a colorless oil (0.49 g, 84%): bp (bulb-to-bulb) 80–83 °C (0.45 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.34; IR (neat) 3070, 3010, 1720, 1630 cm^{-1}; ^{1}H NMR δ 1.09 (d, J = 6.9 Hz, 3 H), 1.57–1.74 (m, 4 H), 2.10–2.20 (m, 2 H), 2.52–2.56 (m, 1 H), 3.74 (s, 3 H), 5.82 (d, J = 15.7 Hz, 1 H), 6.09 (t, J = 4.0 Hz, 1 H), 7.20 (d, J = 16.0 Hz, 1 H); ^{13}C NMR δ 17.0, 19.4, 26.3, 27.3, 29.2, 51.1, 114.1, 138.0, 139.7, 147.5, 167.8; LRMS, m/z 180 (M$^+$, 54%). Anal. Calcd for C$_{11}$H$_{16}$O$_2$: C, 73.30; H, 8.95. Found: C, 73.17; H, 8.79.

(*E*)-4-(6-Methylcyclohexenyl)but-3-en-2-one (17). A mixture of 0.046 g (2.1 mol %) of Pd(Ph$_3$)$_2$Cl$_2$, 0.751 g (3.07 mmol) of 6-methylcyclohexenyl triflate (**15**), 0.45 mL (5.4 mmol) of methyl vinyl ketone, and 1.2 mL (8.6 mmol) of triethylamine in 10 mL of DMF was heated at 75 °C for 1 h, cooled to room temperature, worked up in the usual manner, and concentrated to give a yellow oil. Column chromatography of this material (silica gel; hexanes, 5% ethyl acetate/hexanes) afforded **17** as a colorless oil (0.46 g, 90%): bp (bulb-to-bulb) 75–80 °C (0.50 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.20; IR (neat) 3050, 3010, 1690, 1670, 1625, 1600 cm^{-1}; ^{1}H NMR δ 1.10 (d, J = 6.9 Hz, 3 H), 1.59–1.73 (m, 4 H), 2.14–2.30 (m, 2 H), 2.29 (s, 3 H), 2.52–2.58 (m, 1 H), 6.11 (d, J = 16.4 Hz, 1 H), 6.14–6.17 (m, 1 H), 7.04 (d, J = 16.2 Hz, 1 H); ^{13}C NMR δ 16.9, 19.3, 26.4, 26.7, 27.3, 29.2, 124.1, 138.8, 139.9, 146.2, 198.4; LRMS, m/z 164 (M$^+$, 50%). Anal. Calcd for C$_{11}$H$_{16}$O: C, 80.44; H, 9.82. Found: C, 80.39; H, 9.71.

Methyl (*E*)-3-(2,5,5-Trimethylcyclopentenyl)acrylate (19). To a slurry of 0.045 g (2.2 mol %) of Pd(PPh$_3$)$_2$Cl$_2$ in 5 mL of DMF was added a solution of 0.768 g (2.97 mmol) of 2,5,5-trimethylcyclopentenyl triflate (**18**), 0.50 mL (5.6 mmol) of methyl acrylate, and 1.2 mL (8.6 mmol) of triethylamine in 5 mL of DMF. This was heated at 75 °C for 18 h, cooled to room temperature, worked up in the usual manner, concentrated, and purified by column chromatography (silica gel; hexanes, 2.5% ethyl acetate/hexanes) to give 0.52 g (89% yield) of **19** as a white solid: mp 48–50 °C; bp (bulb-to-bulb) 80–85 °C (0.30 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.44; IR (CDCl$_3$) 3080, 3020, 1720, 1630 cm^{-1}; ^{1}H NMR δ 1.20 (s, 6 H), 1.71 (t, J = 7.3 Hz, 2 H), 1.89 (br s, 3 H), 2.36 (br t, J = 7.3 Hz, 2 H), 3.76 (s, 3 H), 5.99 (d, J = 16.3 Hz, 1 H), 7.48 (d, J = 16.3 Hz, 1 H); ^{13}C NMR δ 15.2, 26.9 (2 C), 36.1, 40.0, 46.2, 51.0, 115.9, 137.8, 139.7, 147.5, 168.0; LRMS, m/z 194 (M$^+$, 32%). Anal. Calcd for C$_{12}$H$_{18}$O$_2$: C, 74.19; H, 9.33. Found: C, 74.29; H, 9.48.

(*E*)-4-(2,5,5-Trimethylcyclopentenyl)but-3-en-2-one (20). A mixture of Pd(PPh$_3$)$_2$Cl$_2$ (0.036 g, 2.0 mol %), 2,5,5-trimethylcyclopentenyl triflate (0.653 g, 2.53 mmol), methyl vinyl ketone (0.45 mL, 5.4 mmol), and triethylamine (1.2 mL, 8.6 mmol)

in DMF (10 mL) was heated at 75 °C for 18 h, cooled to room temperature, worked up in the usual manner, concentrated, and purified by column chromatography (silica gel; hexanes, 5% ethyl acetate/hexanes) to give **20** as a colorless oil (0.38 g, 83%): bp (bulb-to-bulb) 85–90 °C (0.30 mmHg); TLC (5% ethyl acetate/hexanes) R_f 0.23; IR (neat) 3065, 3020, 1695, 1665, 1610, 1590 cm^{-1}; ^{1}H NMR δ 1.19 (s, 6 H), 1.70 (t, J = 7.5 Hz, 2 H), 1.88 (br s, 3 H), 2.29 (s, 3 H), 2.36 (br t, J = 7.3 Hz, 2 H), 6.28 (d, J = 16.5 Hz, 1 H), 7.31 (d, J = 16.5 Hz, 1 H); ^{13}C NMR δ 15.4, 27.0 (2 C), 31.4, 36.4, 40.1, 46.4, 125.9, 136.5, 140.0, 148.5, 198.3; LRMS, m/z 178 (M$^+$, 10%); HRMS, calcd for C$_{12}$H$_{18}$O 178.1358, found 178.1359.

β-(4-*tert*-Butylcyclohexenyl)styrene (21). A mixture of 0.055 g (1.9 mol %) of Pd(PPh$_3$)$_4$, 0.53 mL (4.8 mmol) of freshly distilled styrene, 0.70 g (2.4 mmol) of **1**, and 1.2 mL (8.6 mmol) of triethylamine in 10 mL of DMF was heated to 75 °C for 29 h, cooled to room temperature, worked up in the usual manner, and concentrated to give a yellow oil. This material was further concentrated under a high vacuum to remove unreacted styrene and then purified by column chromatography (silica gel; hexanes) to give **21** (0.33 g, 57%) closely followed by an unidentified material (0.14 g). On standing, **21** solidified: mp 56–57 °C; bp (bulb-to-bulb) 103–108 °C (0.75 mmHg); TLC (hexanes) R_f 0.27; IR (paraffin oil) 3040, 1645, 1609, 1503, 1391, 1386, 956 cm^{-1}; ^{1}H NMR δ 0.88 (s, 9 H), 1.11–1.34 (m, 3 H), 1.88–2.00 (m, 2 H), 2.10–2.22 (m, 1 H), 2.40–2.48 (m, 1 H), 5.87 (t, J = 3.1 Hz, 1 H), 6.40 (d, J = 16.2 Hz, 1 H), 6.76 (d, J = 16.2 Hz, 1 H), 7.12–7.39 (m, 5 H); ^{13}C NMR δ 23.9, 26.0, 27.2 (3 C), 27.8, 32.8, 44.0, 124.9, 126.1, 126.8, 128.5 (2 C), 131.9 (2 C), 132.1, 135.7, 138.1; LRMS, m/z 240 (M$^+$, 24%). Anal. Calcd for C$_{18}$H$_{24}$: C, 89.93; H, 10.06. Found: C, 89.71; H, 10.28.

6-(4-*tert*-Butylcyclohexenyl)-Δ²-dihydropyran (28). A mixture of Pd(PPh$_3$)$_4$ (0.039 g, 1.4 mol %), **1** (0.705 g, 2.46 mmol), dihydropyran (0.45 mL, 4.9 mmol), and triethylamine (1.2 mL, 8.6 mL) in DMF (10 mL) was heated to 115 °C for 23 h, cooled to room temperature, worked up in the usual manner, and concentrated to give a brown oil. Column chromatography of this material (silica gel; hexanes) afforded **1** (0.13 g, 19%) followed by **28** (0.29 g, 53%): bp (bulb-to-bulb) 87–90 °C (0.14 mmHg); TLC (hexanes) R_f 0.21; IR (neat) 3060, 1650, 1395, 1365, 1240 cm^{-1}; ^{1}H NMR δ 0.86 (s, 9 H), 1.09–1.30 (m, 3 H), 1.73–2.14 (m, 8 H), 4.13 (br d, J = 7.7 Hz, 1 H), 4.64–4.66 (m, 1 H), 5.73–5.74 (m, 1 H), 6.42 (d, J = 6.1 Hz, 1 H) (irradiation at δ 4.65 collapsed the doublet at δ 6.42, irradiation at δ 4.13 caused no visible effect between δ 4.0 and 7.0); ^{13}C NMR δ 20.1, 24.0, 26.5, 26.8, 27.2 (3 C), 30.1, 32.1, 44.2, 78.5, 100.0, 123.1, 137.6, 144.2; LRMS, m/z 220 (M$^+$, 7%). Anal. Calcd for C$_{15}$H$_{24}$O: C, 81.76; H, 10.98. Found: C, 81.71; H, 10.75.

Registry No. 1, 77412-96-5; 2, 96-33-3; 3, 96575-55-2; 4, 96575-56-3; (*E*)-5, 96575-57-4; (*Z*)-5, 96575-58-5; 6, 96575-59-6; 7, 76794-69-9; 8, 96575-60-9; 9, 96575-61-0; 10, 96575-62-1; 11, 32363-21-6; 12, 96575-63-2; 13, 86544-75-4; 14, 96615-38-2; 15, 76605-82-8; 16, 96575-64-3; 17, 41437-89-2; 18, 91158-82-6; 19, 96575-65-4; 20, 96575-66-5; 21, 96575-67-6; 28, 96575-68-7; CH$_2$=CHCOCH$_3$, 78-94-4; CH$_2$=CHCN, 107-13-1; CH$_2$=CHCHO, 107-02-8; HC≡CPh, 536-74-3; CH$_2$=CHCONH$_2$, 79-06-1; HC≡CBu, 693-02-7; HC≡CC(CH$_3$)$_2$OH, 115-19-5; CH$_2$=CHPh, 100-42-5; 2*H*-3,4-dihydropyran, 110-87-2; 2-methyl-2-cyclohexenone, 1121-18-2; 2-methylcyclohexanone, 583-60-8.