Palladium-Catalyzed Arylation of Allylic Benzoates Using Hypervalent Siloxane Derivatives†

Reuben Correia and Philip DeShong*

Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

pd10@umail.umd.edu

Received June 19, 2001

Palladium-catalyzed cross-coupling of hypervalent arylsiloxane derivatives proceeded in good to excellent yields with allylic benzoates. Arylation occurred with complete inversion of configuration. The scope and limitations of this reaction, an alternative to the Stille coupling, is summarized.

Introduction

Palladium-catalyzed carbon−carbon bond forming reactions of allylic esters have been widely used in organic synthesis.[1−6] Particularly notable has been the development of couplings of stabilized nucleophiles such as malonate. Carbon−carbon bond couplings of more basic nucleophiles have proven to be problematic. One solution to this limitation has been to employ stannanes as nucleophilic surrogates (Stille coupling).[7] Stille couplings of aryl- and vinylstannanes with allylic acetates and halides have been used widely due to the excellent yields of adducts and the regioselectivity of the coupling process.[4,7] However, stannanes have several limitations for practical organic synthesis: tin(IV) derivatives are toxic, the removal of tin byproducts is problematic, and the coupling reaction displays modest stereoselectivity.[4,8] Other coupling reagents have been developed in an effort to overcome the limitations of stannanes. Fiaud and Legros have performed palladium-catalyzed couplings of sodium tetraphenylborate with allylic acetates.[9] Hiyama and Hatanaka have carried out fluoride-promoted palladium-catalyzed couplings of allylfluorosilanes with aryl halides,[10−14] as well as couplings of allylic carbonates with aryl- and vinyl- fluorosilanes.[15,16] The limitations of this method are that the synthesis of fluorosilanes is a multistep process and fluorosilanes are hydrolytically unstable.

Our lab had previously demonstrated that hypervalent silicate anions such as tetrabutylammonium triphenyldifluorosilicate (TBAT) coupled with allylic benzoates in the presence of a palladium catalyst to afford products in good yields.[8] However, there were two limitations of the TBAT methodology, the first being that only one phenyl group of the three present in the reagent was transferred. Also, the preparation of TBAT and similar reagents is a multistep process.[17] These limitations were overcome by preparing hypervalent silicates in situ from arylsiloxanes.[18] The methodology employing siloxanes[18−22] and other silane derivatives[23−29] has been used to prepare unsymmetrical biaryls from aryl halides. Similarly, it was demonstrated that siloxanes[18] and other silane derivatives[23,30−39] could be used to transfer vinyl groups to aryl

* To whom correspondence should be addressed. Telephone: 301-405-1892. Fax: 301-314-9121.

† This manuscript is dedicated to Steven M. Weinreb on the occasion of his 60th birthday.

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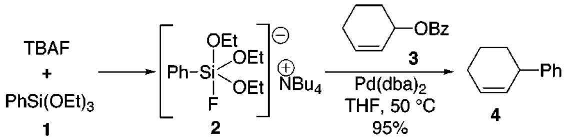
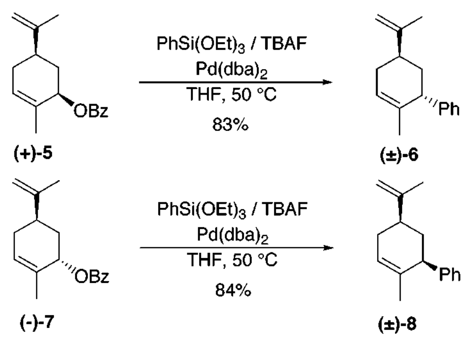
10.1021/jo010627f CCC: $20.00
Published on Web 09/27/2001

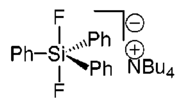
Scheme 1



Scheme 2



and vinyl halides. In this paper, we report that the hypervalent silicates derived from arylsiloxanes undergo aryl transfer to allylic benzoates in excellent yields. The coupling is highly regio- and stereoselective.



TBAT

Results and Discussion

Treatment of phenyl triethoxysilane (**1**) with an equimolar amount of tetrabutylammonium fluoride (TBAF) resulted in the in situ formation of hypervalent fluorosilicate anion **2** (Scheme 1).[17−20,40−42] Subsequent coupling of silicate **2** with benzoate **3** in the presence of a Pd(0) catalyst afforded phenylated product **4** in 95% yield.

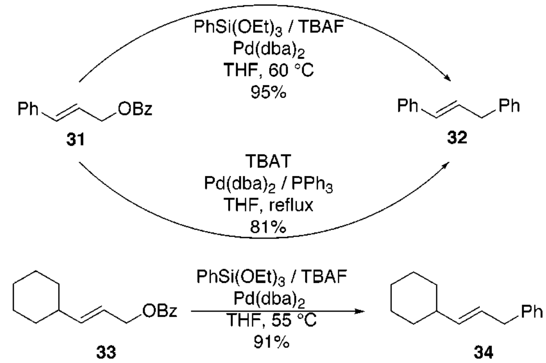
To assess the stereoselectivity of the cross-coupling reaction, carvyl benzoates **5** and **7** were employed as substrates (Scheme 2). *cis*-Benzoate (+)-**5** coupled with $PhSi(OEt)_3$/TBAF to afford exclusively *trans*-arene (±)-**6**, the product of inversion of configuration. Analogously, *trans*-benzoate (−)-**7** was transformed with complete inversion of configuration to *cis*-arene (±)-**8** in 84% yield. It should be noted that alkenes **6** and **8** were racemic since a *meso* π-allyl−Pd complex was an intermediate in each transformation.

The scope and limitations of the coupling reaction were assessed employing a variety of arylsiloxane derivatives, and the results are summarized in the table. The yields of arylated products were generally excellent with siloxanes having methyl and methoxy substituents on the phenyl group. In addition, the position of substitution was generally inconsequential for the coupling. For example, benzoate **3** coupled with *o*-, *m*- and *p*-tolylsiloxanes in high yields (entries 1−3) with no significant reduction in yield due to steric factors from the ortho-substituent. Similarly, benzoate **3** underwent arylation with *m*- and *p*- anisolylsiloxanes in high yields (entries 4−6). However, *o*-anisolylsiloxane **21** gave only 9% of alkene **22** (entry 7). The major products were 1,3-cyclohexadiene and anisole. Previous studies in our lab had demonstrated that the silicate derived from siloxane **21** was particularly prone to protodesilylation.[43,44] The unique behavior of siloxane **21** has been attributed to coordination of the *o*-methoxy group to silicon.

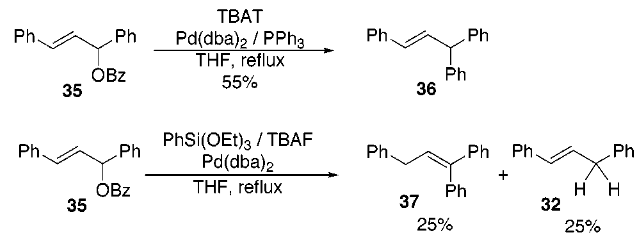
This coupling reaction also worked well with siloxanes having chloro or disubstituted amino substituents on the phenyl group. Thus, benzoate **3** coupled with siloxanes **23** and **25** in yields of 87% and 84%, respectively (entries 8 and 9). However, aniline siloxane **27** produced only 34% of the expected product **28** (entry 10).

To confirm that these arylations occurred in a highly stereoselective manner, benzoate (+)-**5** was allowed to react with siloxanes **9** and **15**, respectively. In each case, the anticipated product resulting from inversion of configuration was the only product obtained (entries 11 and 12).

Scheme 3



Scheme 4



The regioselectivity of the coupling reaction was investigated using acyclic allylic ester derivatives. As summarized in Scheme 3, *trans*-cinnamoyl benzoate (**31**) coupled with both $PhSi(OEt)_3$/TBAF and TBAT to give alkene **32** in 95% and 81% yields, respectively. In both cases, only regioisomer **32**, derived from attack of phenyl at the less-substituted terminus of the allyl system, was observed. The yields of arylation of this substrate were excellent; by comparison, Stille coupling of benzoate **31** with phenyl trimethylstannane, gave 57% of alkene **32**.[7] Finally, benzoate **33** coupled with $PhSi(OEt)_3$/TBAF to afford alkene **34** in 91% yield. In this coupling, traces of the alternative regioisomer were detected by ^{1}H NMR

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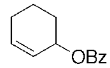
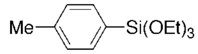
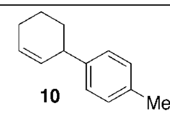
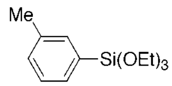
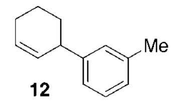
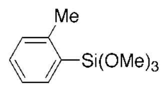
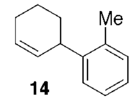
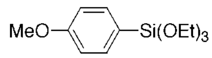
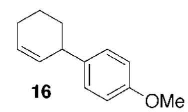
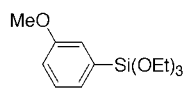
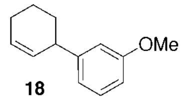
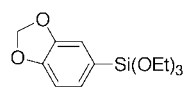
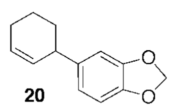
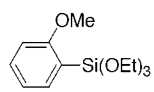
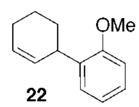
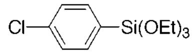
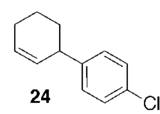
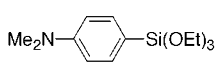
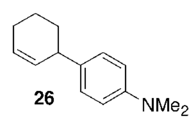
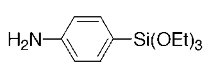
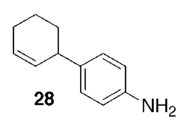
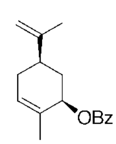
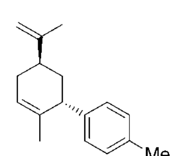
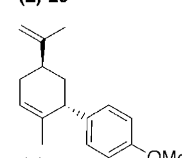
(44) The following control experiments have been performed: heating equimolar quantities of siloxane **21** and TBAF in the absence of benzoate **3** gave anisole rapidly and in high yield. On the other hand, when equimolar quantities of siloxane **15** and TBAF were heated in THF, no trace of anisole was detected.

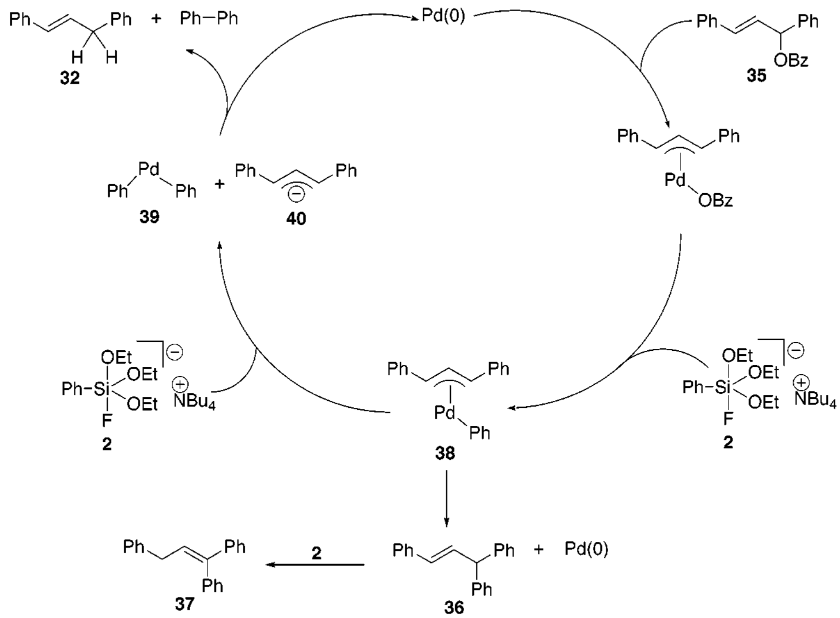
Table 1. Palladium-Catalyzed Arylation of Cyclic Allylic Benzoates

Entry	Allylic Benzoate	Siloxane	Product	Yield (%)
1	 **3**	 **9**	 **10**	87
2	**3**	 **11**	 **12**	86
3	**3**	 **13**	 **14**	77
4	**3**	 **15**	 **16**	88
5	**3**	 **17**	 **18**	88
6	**3**	 **19**	 **20**	87
7	**3**	 **21**	 **22**	9[a]
8	**3**	 **23**	 **24**	87
9	**3**	 **25**	 **26**	84
10	**3**	 **27**	 **28**	34[b]
11	 **(+)-5**	**9**	 **(±)-29**	84
12	**(+)-5**	**15**	 **(±)-30**	78

[a] 50% of 1,3-cyclohexadiene formed. [b] 27% starting material recovered.

analysis of the crude reaction mixture. The coupling reaction of silicates with allylic esters that proceed through highly stabilized π-allyl complexes was less efficient. For example, benzoate **35** coupled with TBAT, an isolable silicate, to give a moderate yield of the expected adduct **36** (Scheme 4). On the other hand, benzoate **35** coupled with the in situ-derived silicate from $PhSi(OEt)_3$/TBAF to produce alkenes **32** and **37** in low yield, respectively. A control experiment demonstrated that the formation of alkene **37** resulted from isomeriza-

Scheme 5



tion of the alkene **36**, the expected product of the coupling reaction, under the basic reaction conditions. Formation of alkene **32**, the reduction product of benzoate **35** was unexpected and is attributed to intermediacy of highly conjugated allylic anion **40** generated by displacement from palladium−allyl complex **38** as shown in Scheme 5. This remarkable displacement was observed only with benzoate **35** and indicated that formation of a highly stabilized anion (i.e., **40**) was a requirement for the reaction. Support for this mechanistic hypothesis was production of biphenyl in equimolar amounts to the alkene **32** (see Scheme 5). Attempts to trap anion **40** with deuterium (D_2O), benzaldehyde, or methyl iodide were unsuccessful.

Conclusion

The results summarized above demonstrate that hypervalent siloxane derivatives are versatile reagents in transferring aryl groups to allylic benzoates in a highly regio- and stereoselective manner. There are several advantages of siloxane couplings compared to Stille couplings with allylic systems, including mild reaction conditions, stability, low toxicity and ease of preparation of siloxane reagents,[47,48,50] and the high stereoselectivity of arylation with net inversion of configuration. The scope and limitations of this methodology for the synthesis of natural products will be reported in due course.

Experimental Section

General Methods. Nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a 400 MHz spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts are reported in parts per million (δ) relative to the nondeuterated solvent peak. Coupling constants (*J* values) are reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br s (broad singlet). Infrared spectra were recorded as solutions in CCl_4. Band positions are given in reciprocal centimeters (cm^{-1}) and relative intensities are listed as br (broad), s (strong), m (medium), or w (weak). Thin-layer chromatography (TLC) was performed with the compounds being identified in one or more of the following manners: UV (254 nm), iodine, or vanillin/sulfuric acid charring. Flash chromatography data is reported as (column diameter in mm, column height in cm, solvent). The enantiomeric composition of all compounds was determined by HPLC analysis using a Chiralpak AD column. In all cases, a baseline separation of the enantiomers was obtained.

Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Pyridine and methylene chloride (CH_2Cl_2) were distilled from calcium hydride. Methanol (MeOH) was stored over molecular sieves. Glassware used in the reactions described below was dried for a minimum of 12 h in an oven at 120 °C. All reactions were run under an atmosphere of argon unless otherwise noted. Phenyl triethoxysilane (**1**), tetrabutylammonium fluoride (TBAF, 1.0 M solution in THF), and cerium chloride heptahydrate ($CeCl_3{\cdot}7H_2O$) were purchased from Aldrich. Bis(dibenzylideneacetone)palladium ($Pd(dba)_2$) was purchased from Acros. Sodium borohydride ($NaBH_4$) was purchased from Fisher. Tetrabutylammonium triphenyldifluorosilicate (TBAT) was synthesized according to the procedure of DeShong and Handy.[17] All reported compounds were >95% pure as determined by ^{1}H and ^{13}C NMR spectroscopy.

General Procedure for the Cross-Coupling Reactions Utilizing Allylic Benzoates. To a solution of 0.10 g (1.0 equiv) of the allylic benzoate, 0.10 equiv of $Pd(dba)_2$, and 2.0 equiv of arylsiloxane in 10 mL of THF was added 2.0 equiv of TBAF via syringe. The reaction mixture was degassed to remove oxygen via two freeze−pump−thaw cycles and heated at 50−60 °C under an argon atmosphere for 12−48 h. The reaction mixture was quenched by the addition of 50 mL of water. The aqueous layer was extracted with 4 × 50 mL of Et_2O, and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash chromatography yielded the cross-coupled adduct. The spectral data of the individual compounds are reported below.

3-Benzoylcyclohexene (3). The benzoate **3** was prepared according to the procedure of DeShong and Mowery.[18] The IR, ^{1}H NMR, and ^{13}C NMR data were identical to the data reported by DeShong and Mowery.[18]

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3-Phenylcyclohexene (4). Alkene **4** was prepared according to the general procedure for the cross-coupling reaction employing 0.081 g (0.40 mmol) of benzoate **3**. The reaction mixture was heated at 50 °C for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.060 g (95%) of alkene **4**. The IR, ^{1}H NMR, and ^{13}C NMR data were identical to the data reported by DeShong and Mowery.[18]

(+)-(*R,R*)-*cis*-Carvyl Benzoate (5). The benzoate (+)-**5** was prepared according to the procedure of DeShong and Mowery:[18] IR (CCl_4) 3073 (m), 2971 (m), 2920 (m), 1720 (s), 1646 (m), 1452 (m), 1270 (s), 1112 (s); ^{1}H NMR ($CDCl_3$) δ 1.58−1.69 (m, 1H), 1.71 (s, 3H), 1.73 (s, 3H), 1.96−2.20 (m, 2H), 2.27−2.44 (m, 2H), 4.74 (s, 2H), 5.62−5.74 (m, 2H), 7.43 (t, J = 7.5, 2H), 7.55 (t, J = 7.5, 1H), 8.07 (d, J = 7.5, 2H); ^{13}C NMR ($CDCl_3$) δ 19.0, 20.5, 30.8, 34.0, 40.2, 73.8, 109.4, 126.0, 128.3, 129.6, 130.5, 132.9, 133.1, 148.2, 166.4; $[\alpha]^{24}_D = +17.1$ (c = 1.25, EtOH). The ^{1}H NMR data were consistent with the data reported by Utagawa et al. recorded at 60 MHz.[45]

(±)-*trans*-2-Methyl-3-phenyl-5-isopropenyl-1-cyclohexene (6). Alkene (±)-**6** was prepared according to the general procedure for the cross-coupling reaction employing 0.101 g (0.395 mmol) of benzoate (+)-**5**. The reaction mixture was heated at 50 °C for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.070 g (83%) of alkene (±)-**6**. The IR, ^{1}H NMR, and ^{13}C NMR data were identical to the data reported by DeShong and Brescia.[8] HPLC analysis and the optical rotation of alkene (±)-**6** confirmed that it was racemic.

(−)-(*R,S*)-*trans*-Carvyl Benzoate (7). The benzoate (−)-**7** was prepared according to the procedure of Uesaka et al.[46] The IR and ^{1}H NMR data were identical to the data reported by Uesaka et al.[46] ^{13}C NMR ($CDCl_3$) δ 20.7, 20.9, 30.9, 33.7, 36.0, 71.2, 109.2, 127.9, 128.3, 129.6, 130.6, 131.0, 132.8, 148.6, 166.3; $[\alpha]^{26}_D = -224.1$ (c = 1.28, EtOH).

(±)-*cis*-2-Methyl-3-phenyl-5-isopropenyl-1-cyclohexene (8). Alkene (±)-**8** was prepared according to the general procedure for the cross-coupling reaction employing 0.100 g (0.391 mmol) of benzoate (−)-**7**. The reaction mixture was heated at 54 °C for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.070 g (84%) of alkene (±)-**8**. The IR, ^{1}H NMR, and ^{13}C NMR data were identical to the data reported by DeShong and Brescia.[8] HPLC analysis and the optical rotation of alkene (±)-**8** confirmed that it was racemic.

4-(Triethoxysilyl)toluene (9). The siloxane **9** was prepared according to the procedure of Masuda.[47] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by Masuda.[47]

3-(4-Methylphenyl)cyclohexene (10). Alkene **10** was prepared according to the general procedure for the cross-coupling reaction employing 0.090 g (0.45 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 12 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.067 g (87%) of alkene **10** as a colorless oil: TLC R_f = 0.59 (pentane); IR (CCl_4) 3021 (m), 2931 (s), 2858 (m), 2837 (m), 1512 (m), 1446 (m); ^{1}H NMR ($CDCl_3$) δ 1.46−1.78 (m, 3H), 1.93−2.10 (m, 3H), 2.31 (s, 3H), 3.36 (br s, 1H), 5.69 (dd, J = 9.9, 2.0, 1H), 5.82−5.90 (m, 1H), 7.10 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 21.0, 21.2, 25.0, 32.7, 41.4, 127.6, 128.1, 128.9, 130.4, 135.4, 143.6; LRMS (EI) 173 ((M + 1), 14), 172 ((M^+), 100), 157 (60), 129 (87); HRMS (EI) calcd for $C_{13}H_{16}$ 172.1252 (M^+), found 172.1248. The ^{1}H NMR data were consistent with the data reported by Kamigata et al. recorded at 60 MHz.[49]

3-(Triethoxysilyl)toluene (11). The siloxane **11** was prepared according to the procedure of DeShong and Manoso.[48] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by DeShong and Manoso.[48]

3-(3-Methylphenyl)cyclohexene (12). Alkene **12** was prepared according to the general procedure for the cross-coupling reaction employing 0.086 g (0.43 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 10 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.063 g (86%) of alkene **12** as a colorless oil: TLC R_f = 0.64 (pentane); IR (CCl_4) 3022 (m), 2932 (s), 2859 (m), 2838 (m), 1608 (m), 1558 (m), 1487 (m), 1447 (m); ^{1}H NMR ($CDCl_3$) δ 1.47−1.79 (m, 3H), 1.94−2.12 (m, 3H), 2.33 (s, 3H), 3.36 (br s, 1H), 5.70 (dd, J = 10.3, 2.0, 1H), 5.84−5.91 (m, 1H), 6.98−7.04 (m, 3H), 7.18 (t, J = 7.2, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 21.4, 25.0, 32.6, 41.8, 124.8, 126.7, 128.1, 128.2, 128.4, 130.3, 137.8, 146.6; LRMS (EI) 173 ((M + 1), 11), 172 (M^+), 74), 157 (47), 144 (32), 129 (100), 128 (37), 115 (32); HRMS (EI) calcd for $C_{13}H_{16}$ 172.1252 (M^+), found 172.1244.

2-(Trimethoxysilyl)toluene (13). The siloxane **13** was prepared according to the procedure of DeShong and Ahn.[50] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by DeShong and Ahn.[50]

3-(2-Methylphenyl)cyclohexene (14). Alkene **14** was prepared according to the general procedure for the cross-coupling reaction employing 0.085 g (0.42 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 15 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.056 g (77%) of alkene **14** as a colorless oil: TLC R_f = 0.69 (pentane); IR (CCl_4) 3021 (m), 2933 (s), 2858 (m), 2837 (m), 1487 (m), 1460 (m); ^{1}H NMR ($CDCl_3$) δ 1.42−1.79 (m, 3H), 1.94−2.17 (m, 3H), 2.34 (s, 3H), 3.61 (br s, 1H), 5.67 (dd, J = 9.9, 2.0, 1H), 5.87−5.94 (m, 1H), 7.06−7.22 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 19.2, 21.1, 25.0, 30.6, 37.7, 125.8, 125.9, 127.5, 128.3, 130.2, 130.4, 135.4, 144.3; LRMS (EI) 173 ((M + 1), 4), 172 ((M^+), 34), 129 (100), 128 (42), 115 (48); HRMS (EI) calcd for $C_{13}H_{16}$ 172.1252 (M^+), found 172.1256.

4-(Triethoxysilyl)anisole (15). The siloxane **15** was prepared according to the procedure of Masuda.[47] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by Masuda.[47]

3-(4-Methoxyphenyl)cyclohexene (16). Alkene **16** was prepared according to the general procedure for the cross-coupling reaction employing 0.084 g (0.42 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 16 h. Purification of the residue by flash chromatography (25 mm, 15 cm, 10% CH_2Cl_2/pentane) gave 0.069 g (88%) of alkene **16**. The ^{1}H NMR, ^{13}C NMR, and MS data were identical to the data reported by Goering et al.[51]

3-(Triethoxysilyl)anisole (17). The siloxane **17** was prepared according to the procedure of DeShong and Manoso.[48] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by DeShong and Manoso.[48]

3-(3-Methoxyphenyl)cyclohexene (18). Alkene **18** was prepared according to the general procedure for the cross-coupling reaction employing 0.081 g (0.40 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 12 h. Purification of the residue by flash chromatography (25 mm, 15 cm, 10% CH_2Cl_2/pentane) gave 0.066 g (88%) of alkene **18** as a colorless oil: TLC R_f = 0.42 (10% CH_2Cl_2/pentane); IR (CCl_4) 3023 (m), 2935 (s), 2859 (m), 2836 (m), 1601 (s), 1485 (s), 1265 (s), 1057 (m); ^{1}H NMR ($CDCl_3$) δ 1.49−1.80 (m, 3H), 1.94−2.15 (m, 3H), 3.37 (br s, 1H), 3.78 (s, 3H), 5.70 (dd, J = 10.3, 2.0, 1H), 5.84−5.91 (m, 1H), 6.71−6.84 (m, 3H), 7.20 (t, J = 7.5, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 25.0, 32.5, 41.8, 55.1, 111.1, 113.5, 120.2, 128.3, 129.1, 130.0, 148.3, 159.6; LRMS (EI) 189 ((M + 1), 14), 188 ((M^+), 100), 159 (41), 134 (33); HRMS (EI) calcd for $C_{13}H_{16}O$ 188.1201 (M^+), found 188.1203.

1,2-Methylenedioxy-4-(triethoxysilyl)benzene (19). The siloxane **19** was prepared according to the procedure of DeShong and Manoso.[48] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by DeShong and Manoso.[48]

3-(3,4-Methylenedioxyphenyl)cyclohexene (20). Alkene **20** was prepared according to the general procedure for the cross-coupling reaction employing 0.086 g (0.42 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, 10% CH_2Cl_2/pentane) gave 0.075 g (87%) of alkene **20** as a colorless oil: TLC R_f = 0.44 (10% CH_2Cl_2/pentane); IR (CCl_4) 3016 (m), 2926 (m), 2878 (m), 1508 (m), 1487 (s), 1442 (m), 1252 (m), 1232 (m), 1042 (m); ^{1}H NMR ($CDCl_3$) δ 1.45−1.78 (m, 3H), 1.91−2.13 (m, 3H), 3.32 (br s, 1H), 5.66 (dd, J =

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9.9, 2.0, 1H), 5.83−5.89 (m, 1H), 5.90 (s, 2H), 6.64−6.76 (m, 3H); ^{13}C NMR (CDCl$_3$) δ 21.1, 25.0, 32.8, 41.5, 100.7, 108.0, 108.3, 120.5, 128.3, 130.3, 140.7, 145.7, 147.5; LRMS (EI) 203 ((M + 1), 15), 202 ((M$^+$), 100), 174 (28), 116 (20); HRMS (EI) calcd for $C_{13}H_{14}O_2$ 202.0994 (M$^+$), found 202.1002.

2-(Triethoxysilyl)anisole (21). The siloxane **21** was prepared according to the procedure of DeShong and Ahn.[50] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by DeShong and Ahn.[50]

3-(2-Methoxyphenyl)cyclohexene (22). Alkene **22** was prepared according to the general procedure for the cross-coupling reaction employing 0.083 g (0.41 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 36 h. Purification of the residue by flash chromatography (25 mm, 15 cm, 10% CH_2Cl_2/pentane) gave 0.007 g (9%) of alkene **22**. The ^{1}H NMR data were identical to the data reported by Kocovsky et al.[52] GC analysis of the crude reaction mixture indicated the formation of 50% of 1,3-cyclohexadiene by comparison with an authentic sample. Anisole (0.10 g) was isolated and compared with an authentic sample by TLC, GC, and ^{1}H NMR spectroscopy.

4-Chloro(triethoxysilyl)benzene (23). The siloxane **23** was prepared according to the procedure of Masuda.[47] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by Masuda.[47]

3-(4-Chlorophenyl)cyclohexene (24). Alkene **24** was prepared according to the general procedure for the cross-coupling reaction employing 0.082 g (0.41 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 12 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.068 g (87%) of alkene **24** as a colorless oil: TLC R_f = 0.70 (pentane); IR (CCl$_4$) 3023 (m), 2933 (s), 2860 (m), 2833 (m), 1490 (s), 1446 (m), 1408 (m); ^{1}H NMR (CDCl$_3$) δ 1.44−1.76 (m, 3H), 1.93−2.14 (m, 3H), 3.36 (br s, 1H), 5.66 (dd, J = 9.9, 2.0, 1H), 5.86−5.93 (m, 1H), 7.13 (d, J = 8.3, 2H), 7.25 (d, J = 8.3, 2H); ^{13}C NMR (CDCl$_3$) δ 21.0, 25.0, 32.6, 41.2, 128.3, 128.8, 129.1, 129.6, 131.6, 145.1; LRMS (EI) 194 (26), 193 ((M + 1),12), 192 ((M$^+$), 78), 157 (52), 129 (100); HRMS (EI) calcd for $C_{12}H_{13}Cl$ 192.0706 (M$^+$), found 192.0697.

4-(Triethoxysilyl)-*N*,*N*-dimethylaniline (25). The siloxane **25** was prepared according to the procedure of Masuda.[47] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by Masuda.[47]

3-(4-*N*,*N*-Dimethylaminophenyl)cyclohexene (26). Alkene **26** was prepared according to the general procedure for the cross-coupling reaction employing 0.080 g (0.40 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, 5% EtOAc/hexane) gave 0.067 g (84%) of alkene **26** as a yellow oil: TLC R_f = 0.33 (5% EtOAc/hexane); IR (CCl$_4$) 3020 (m), 2932 (m), 2857 (m), 1615 (m), 1518 (m); ^{1}H NMR (CDCl$_3$) δ 1.47−1.79 (m, 3H), 1.91−2.14 (m, 3H), 2.90 (s, 6H), 3.31 (br s, 1H), 5.70 (dd, J = 9.9, 2.0, 1H), 5.80−5.87 (m, 1H), 6.70 (d, J = 8.7, 2H), 7.09 (d, J = 8.7, 2H); ^{13}C NMR (CDCl$_3$) δ 21.2, 25.0, 32.7, 40.8, 40.9, 112.8, 127.7, 128.3, 130.9, 134.8, 149.1; LRMS (EI) 202 ((M + 1),16), 201 ((M$^+$), 100), 173 (61), 172 (47); HRMS (EI) calcd for $C_{14}H_{19}N$ 201.1517 (M$^+$), found 201.1518.

4-(Triethoxysilyl)aniline (27). The siloxane **27** was prepared according to the procedure of DeShong and Manoso.[48] The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by DeShong and Manoso.[48]

3-(4-Aminophenyl)cyclohexene (28). Alkene **28** was prepared according to the general procedure for the cross-coupling reaction employing 0.075 g (0.37 mmol) of benzoate **3**. The reaction mixture was heated at 60 °C for 36 h. Purification of the residue by flash chromatography (25 mm, 15 cm, 25% EtOAc/hexane) gave 0.022 g (34%) of alkene **28** as a yellow oil: TLC R_f = 0.23 (25% EtOAc/hexane); IR (CCl$_4$) 3473 (w), 3391 (w), 3021 (m), 2931 (m), 1622 (m), 1514 (m); ^{1}H NMR (CDCl$_3$) δ 1.45−1.80 (m, 3H), 1.90−2.15 (m, 3H), 3.29 (br s, 1H), 3.57 (br s, 2H), 5.68 (dd, J = 9.9, 2.0, 1H), 5.81−5.88 (m, 1H), 6.64 (d, J = 8.3, 2H), 7.01 (d, J = 8.3, 2H); ^{13}C NMR (CDCl$_3$) δ 21.1, 25.0, 32.7, 41.0, 115.2, 127.9, 128.5, 130.8, 136.8, 144.4; LRMS (EI) 174 ((M + 1),14), 173 ((M$^+$), 100), 145 (70), 144 (79); HRMS (EI) calcd for $C_{12}H_{15}N$ 173.1204 (M$^+$), found 173.1203.

(±)-*trans*-2-Methyl-3-(4-methylphenyl)-5-isopropenyl-1-cyclohexene (29). Alkene (±)-**29** was prepared according to the general procedure for the cross-coupling reaction employing 0.105 g (0.410 mmol) of benzoate (+)-**5**. The reaction mixture was heated at 60 °C for 48 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.078 g (84%) of alkene (±)-**29** as a colorless oil: TLC R_f = 0.58 (pentane); IR (CCl$_4$) 3085 (m), 2966 (m), 2917 (s), 2859 (m), 1644 (m), 1510 (m), 1448 (m); ^{1}H NMR (CDCl$_3$) δ 1.58 (s, 3H), 1.63 (s, 3H), 1.70−1.81 (m, 1H), 1.83−2.01 (m, 2H), 2.10−2.28 (m, 2H), 2.32 (s, 3H), 3.32 (d, J = 5.2, 1H), 4.61 (s, 1H), 4.64 (s, 1H), 5.70 (br s, 1H), 7.09 (s, 4H); ^{13}C NMR (CDCl$_3$) δ 20.9, 21.0, 22.6, 31.1, 34.6, 36.4, 45.2, 108.4, 123.8, 128.4, 128.8, 134.0, 135.2, 141.7, 149.8; LRMS (EI) 227 ((M + 1), 6), 226 ((M$^+$), 34), 183 (100), 143 (50); HRMS (EI) calcd for $C_{17}H_{22}$ 226.1722 (M$^+$), found 226.1729. HPLC analysis and the optical rotation of alkene (±)-**29** confirmed that it was racemic.

(±)-*trans*-2-Methyl-3-(4-methoxyphenyl)-5-isopropenyl-1-cyclohexene (30). Alkene (±)-**30** was prepared according to the general procedure for the cross-coupling reaction employing 0.100 g (0.391 mmol) of benzoate (+)-**5**. The reaction mixture was heated at 60 °C for 20 h. Purification of the residue by flash chromatography (25 mm, 15 cm, 10% CH_2Cl_2/pentane) gave 0.073 g (78%) of alkene (±)-**30** as a colorless oil: TLC R_f = 0.49 (10% CH_2Cl_2/pentane); IR (CCl$_4$) 3035 (m), 2934 (m), 2914 (m), 2835 (m), 1610 (m), 1509 (s), 1247 (s), 1042 (m); ^{1}H NMR (CDCl$_3$) δ 1.58 (s, 3H), 1.63 (s, 3H), 1.69−1.77 (m, 1H), 1.82−1.99 (m, 2H), 2.09−2.27 (m, 2H), 3.31 (d, J = 5.2, 1H), 3.78 (s, 3H), 4.61 (s, 1H), 4.64 (s, 1H), 5.69 (br s, 1H), 6.83 (d, J = 8.7, 2H), 7.11 (d, J = 8.7, 2H); ^{13}C NMR (CDCl$_3$) δ 20.9, 22.6, 31.1, 34.7, 36.6, 44.9, 55.2, 108.4, 113.5, 123.8, 129.4, 134.2, 136.9, 149.8, 157.8; LRMS (EI) 243 ((M + 1), 8), 242 ((M$^+$), 42), 199 (100), 159 (39), 121 (35); HRMS (EI) calcd for $C_{17}H_{22}O$ 242.1671 (M$^+$), found 242.1679. HPLC analysis and the optical rotation of alkene (±)-**30** confirmed that it was racemic.

***trans*-Cinnamoyl Benzoate (31).** To a solution of 2.0 g (15 mmol) of *trans*-cinnamaldehyde and 6.7 g (18 mmol) of $CeCl_3 \cdot 7H_2O$ in 25 mL of anhydrous MeOH kept at 0 °C was added 0.69 g (18 mmol) of $NaBH_4$ via a solid addition funnel. The $NaBH_4$ was slowly added over a period of 15 min. The reaction was stirred at room temperature for 1 h and was quenched by the addition of 50 mL of saturated NH_4Cl. The aqueous layer was washed with 3 × 50 mL of Et_2O. The combined organics were washed with 50 mL of saturated NaCl and 2 × 50 mL of water, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash chromatography (50 mm, 15 cm, 50% EtOAc/hexane) gave 1.2 g (60%) of *trans*-cinnamyl alcohol. The ^{1}H NMR and ^{13}C NMR data were identical to the data reported by Singaram et al.[53]

To a solution of 1.1 g (8.2 mmol) of *trans*-cinnamyl alcohol and 2.1 mL (25 mmol) of pyridine in 40 mL of CH_2Cl_2 kept at 0 °C was added 3.0 mL (25 mmol) of benzoyl chloride via syringe. The reaction was stirred at room temperature for 12 h and quenched by the addition of 50 mL of water. The aqueous layer was washed with 3 × 50 mL of Et_2O. The combined organic layers were washed with 50 mL of each of the following: 10% HCl, saturated $NaHCO_3$, saturated NaCl and water, dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash chromatography (50 mm, 15 cm, 10% EtOAc/hexane) gave 1.9 g (96%) of benzoate **31** as a colorless oil: TLC R_f = 0.42 (10% EtOAc/hexane); IR (CCl$_4$) 3057 (m), 3026 (m), 2948 (m), 1719 (s), 1601 (m), 1492 (m), 1451 (m), 1269 (s), 1176 (m), 1117 (m), 966 (m); ^{1}H NMR

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($CDCl_3$) δ 4.98 (d, *J* = 6.4, 2H), 6.41 (dt, *J* = 15.9, 6.4, 1H), 6.74 (d, *J* = 15.9, 1H), 7.22−7.59 (m, 8H), 8.09 (d, *J* = 7.9, 2H); ^{13}C NMR ($CDCl_3$) δ 65.4, 123.2, 126.6, 128.0, 128.3, 128.5, 129.6, 130.1, 132.9, 134.2, 136.1, 166.3; LRMS (EI) 239 ((M + 1), 2), 238 ((M^+), 16), 133 (43), 115 (83), 105 (100), 77 (45); HRMS (EI) calcd for $C_{16}H_{14}O_2$ 238.0994 (M^+), found 238.1003.

***trans*-1,3-Diphenyl-1-propene (32).** Alkene **32** was prepared according to the general procedure for the cross-coupling reaction employing 0.101 g (0.424 mmol) of benzoate **31**. The reaction mixture was heated at 60 °C for 12 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.078 g (95%) of alkene **32**. The IR, ^1H NMR, and MS data were identical to the data reported by Lawrence and Muhammad.[54] ^{13}C NMR (DMSO-d_6) δ 38.6, 126.0, 126.1, 127.1, 128.4, 128.5, 128.6, 129.4, 130.5, 137.0, 140.0.

***trans*-3-Benzoyl-1-cyclohexyl-1-propene (33).** The benzoate **33** was prepared from the corresponding alcohol, which was prepared according to the procedure of Chini et al.[55] The IR and ^1H NMR data of the alcohol were identical to the data reported by Chini et al.[55] To a solution of 1.2 g (8.6 mmol) of *trans*-1-cyclohexylpropen-3-ol and 2.3 mL (27 mmol) of pyridine in 40 mL of CH_2Cl_2 kept at 0 °C was added 3.8 mL (27 mmol) of benzoyl chloride via syringe. The reaction was stirred at room temperature for 12 h and quenched by the addition of 50 mL of water. The aqueous layer was washed with 3 × 50 mL of Et_2O. The combined organic layers were washed with 50 mL of each of the following: 10% HCl, saturated $NaHCO_3$, saturated NaCl and water, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash chromatography (50 mm, 15 cm, 17% CH_2Cl_2/pentane) gave 1.9 g (90%) of benzoate **33** as a colorless oil: TLC R_f = 0.37 (17% CH_2Cl_2/pentane); IR (CCl_4) 2927 (m), 2847 (m), 1722 (s), 1449 (m), 1270 (s), 1107 (m), 973 (m); ^1H NMR ($CDCl_3$) δ 1.02−1.34 (m, 5H), 1.60−1.80 (m, 5H), 2.00 (br s, 1H), 4.76 (d, *J* = 6.4, 2H), 5.63 (dt, *J* = 15.5, 6.4, 1H), 5.80 (dd, *J* = 15.5, 6.4, 1H), 7.43 (t, *J* = 7.5, 2H), 7.54 (t, *J* = 7.5, 1H), 8.06 (d, *J* = 7.5, 2H); ^{13}C NMR ($CDCl_3$) δ 26.0, 26.1, 32.5, 40.4, 66.0, 121.3, 128.3, 129.6, 130.4, 132.8, 142.1, 166.4; LRMS (FAB) 245 ((M + 1), 3), 244 ((M^+), 3), 123 (63), 105 (100), 81 (50); HRMS (FAB) calcd for $C_{16}H_{20}O_2$ 244.1463 (M^+), found 244.1468.

***trans*-1-Cyclohexyl-3-phenyl-1-propene (34).** Alkene **34** was prepared according to the general procedure for the cross-coupling reaction employing 0.102 g (0.418 mmol) of benzoate **33**. The reaction mixture was heated at 55 °C for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.077 g (91%) of alkene **34** as a colorless oil: TLC R_f = 0.70 (pentane); IR (CCl_4) 3029 (m), 2926 (s), 2852 (s), 1603 (w), 1543 (m), 1495 (m), 1449 (m), 970 (m); ^1H NMR ($CDCl_3$) δ 1.00−1.32 (m, 5H), 1.58−1.77 (m, 5H), 1.94 (br s, 1H), 3.32 (d, *J* = 5.6, 2H), 5.43−5.56 (m, 2H), 7.15−7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 26.1, 26.2, 33.1, 39.1, 40.6, 125.8, 126.1, 128.3, 128.5, 138.1, 141.2; LRMS (EI) 201 ((M + 1), 3), 200 ((M^+), 16), 117 (45), 109 (100), 108 (34), 104 (95), 91 (45), 67 (74), 55(39); HRMS (EI) calcd for $C_{15}H_{20}$ 200.1565 (M^+), found 200.1557. In this coupling reaction, traces (<2%) of the alternative regioisomer were detected by GC and ^1H NMR analysis of the crude reaction mixture.

***trans*-3-Benzoyl-1,3-diphenyl-1-propene (35).** The benzoate **35** was prepared from the corresponding alcohol, which was prepared according to the procedure of Bosnich et al.[56] The ^1H NMR and ^{13}C NMR data of the alcohol were identical to the data reported by Baba et al.[57] To a solution of 1.4 g (6.7 mmol) of *trans*-1,3-diphenylpropen-3-ol and 1.6 mL (19 mmol) of pyridine in 50 mL of CH_2Cl_2 kept at 0 °C was added 2.3 mL (19 mmol) of benzoyl chloride via syringe. The reaction was stirred at room temperature for 12 h and quenched by the addition of 50 mL of water. The aqueous layer was washed with 4 × 50 mL of Et_2O. The combined organic layers were washed with 50 mL of each of the following: 10% HCl, saturated $NaHCO_3$, saturated NaCl and water, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue by flash chromatography (50 mm, 15 cm, 10% EtOAc/hexane) gave 1.9 g (90%) of benzoate **35**: TLC R_f = 0.42 (10% EtOAc/hexane); IR (CCl_4) 3068 (m), 3026 (m), 1724 (s), 1608 (m), 1496 (m), 1451 (m), 1265 (s), 1176 (m), 1107 (m), 963 (m); ^1H NMR ($CDCl_3$) δ 6.47 (dd, *J* = 15.9, 6.8, 1H), 6.67−6.77 (m, 2H), 7.21−7.61 (m, 13H), 8.13 (d, *J* = 7.9, 2H); ^{13}C NMR ($CDCl_3$) δ 76.6, 126.7, 127.0, 127.5, 128.0, 128.2, 128.4, 128.5, 128.6, 129.7, 130.3, 132.8, 133.0, 136.1, 139.2, 165.5; LRMS (EI) 314 ((M^+), 2), 209 (36), 193 (33), 192 (100), 191 (33); HRMS (EI) calcd for $C_{22}H_{18}O_2$ 314.1307 (M^+), found 314.1313.

1,3,3-Triphenyl-1-propene (36). A solution of 0.094 g (0.30 mmol) of benzoate **35**, 0.018 g (0.03 mmol) of $Pd(dba)_2$, 0.008 g (0.03 mmol) of PPh_3, and 0.324 g (0.60 mmol) of TBAT in 10 mL of THF was degassed via two freeze−pump−thaw cycles. The reaction mixture was heated under reflux under an argon atmosphere for 36 h and quenched by the addition of 50 mL of water. The aqueous layer was extracted with 4 × 50 mL of Et_2O, and the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash chromatography (25 mm, 15 cm, 10% CH_2Cl_2/hexane) gave 0.045 g (55%) of alkene **36**: TLC R_f = 0.32 (10% CH_2Cl_2/hexane); IR (CCl_4) 3085 (m), 3063 (m), 3028 (m), 2870 (w), 1601 (m), 1494 (s), 1450 (m), 966 (m); ^1H NMR ($CDCl_3$) δ 4.89 (d, *J* = 7.5, 1H), 6.34 (d, *J* = 15.9, 1H), 6.67 (dd, *J* = 15.9, 7.5, 1H), 7.16−7.39 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 54.2, 126.3, 126.5, 127.3, 128.5, 128.6, 128.7, 131.4, 132.6, 137.3, 143.5. The ^1H NMR data were consistent with the data reported by Whitesides et al. recorded at 60 MHz.[58]

1,1,3-Triphenyl-1-propene (37). Alkene **37** was prepared according to the general procedure for the cross-coupling reaction employing 0.094 g (0.30 mmol) of benzoate **35**. The reaction mixture was heated under reflux for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.021 g (25%) of alkene **37**. The IR and ^1H NMR data were identical to the data reported by Saito et al.[59] Alkene **32** (0.015 g, 25%) was isolated and compared with an authentic sample by TLC and ^1H NMR spectroscopy. Biphenyl (0.012 g, 26%) was isolated and compared with an authentic sample by TLC and ^1H NMR spectroscopy.

Isomerization of Alkene 36 to Alkene 37. Alkene **36** (0.024 g, 0.089 mmol) was subjected to the standard conditions for the cross-coupling reaction employing 0.006 g (0.01 mmol) of $Pd(dba)_2$, 0.048 g (0.20 mmol) of $PhSi(OEt)_3$, and 0.20 mL (0.20 mmol) of TBAF in 10 mL of THF. The reaction mixture was degassed to remove oxygen via two freeze−pump−thaw cycles and heated under reflux for 14 h. Purification of the residue by flash chromatography (25 mm, 15 cm, pentane) gave 0.022 g (92%) of alkene **37** which was compared with an authentic sample by TLC and ^1H NMR spectroscopy.

Attempted Trapping of Anion 40. Attempts to trap anion **40** by addition of trace quantities of D_2O to the reaction mixture, or by quenching the reaction with D_2O, methyl iodide, or benzaldehyde under a variety of conditions failed to provide the expected adducts.

Acknowledgment. We thank Dr. Yiu-Fai Lam and Ms. Caroline Ladd for their assistance in obtaining NMR and mass spectral data. The financial support of the National Cancer Institute (CA-82169) is also acknowledged.

Supporting Information Available: ^1H NMR and ^{13}C NMR spectra of compounds whose spectra have been reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

JO010627F

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