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# Articles

## Regioselectivity in the Palladium-Catalyzed Addition of Carbon Nucleophiles to Carbocyclic Derivatives‡

Molly E. Hoke, Marc-Raleigh Brescia, Suzanne Bogaczyk, and Philip DeShong*

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

Bryan W. King and Michael T. Crimmins§

*Department of Chemistry and Biochemistry, The University of North Carolina at Chapel Hill, Venable and Kenan Laboratories CB 3290, Chapel Hill, North Carolina 27599-3290*

*pd10@umail.umd.edu*

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The regioselectivity of Pd-catalyzed malonate additions and arylations to cycloalkenyl esters can be predicted by completing a stereochemical analysis of the Pd−$\pi$-allyl complex. The Pd-catalyzed malonate additions which have the greatest degree of regioselectivity are in which substituents have a steric influence in blocking the incoming nucleophile. Cyclopentenyl substrates displayed lower regioselectivity than the cyclohexyl counterparts presumably due to increased planarity of the system. Arylations using tin and hypervalent silicon reagents were compared.

### Introduction

Palladium-catalyzed allylic substitution is an efficient and highly stereoselective method for formation of carbon−carbon bonds, and the alkylation with stabilized carbon nucleophiles has been widely applied in organic synthesis.[1−8] The major characteristic of alkylation using stabilized nucleophiles is that it proceeds with retention of configuration at the least hindered site of the intermediate $\pi$-allyl complex.[8]

Our group[9] and others[3,10−12] have investigated factors controlling the regioselectivity of Pd(0)-catalyzed alkylations of heterocyclic (i.e., carbohydrate and pyranose) derivatives. In many cases, it was found that both elec-

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

‡ This paper is dedicated to Richard W. Franck on the occasion of his 65th birthday.

§ Phone: 919-962-2172. Fax: 919-962-2388. E-mail: crimmins@email.unc.edu.

(1) Diederich, F.; Stang, P. J.; Eds. In *Metal-catalyzed Cross-coupling Reactions*; Wiley-VCH: Weinheim, 1998.

(2) Tsuji, J. *Palladium Reagents and Catalysts. Innovations in Organic Synthesis*; John Wiley & Sons: New York, 1995; pp 290−422.

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(5) Hegedus, L. S. *Coord. Chem. Rev.* **1996**, *147*, 443−545.

(6) (a) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771−1780. (b) Stille, J. K.; Hegedus, L. S.; Del Valle, L. *J. Org. Chem.* **1990**, *55*, 3019−3023.

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(8) (a) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615−2649. (b) Trost, B. M. *Pure Appl. Chem.* **1979**, *51*, 787−800. (c) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385−393. (d) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395−422.

(9) (a) Brescia, M.-R.; Shimshock, Y. C.; DeShong, P. *J. Org. Chem.* **1997**, *62*, 1257−1263. (b) Class, Y. J.; DeShong, P. *Tetrahedron Lett.* **1995**, *36*, 7631−7634.

(10) Curran, D. P.; Suh, Y.-G. *Carbohydr. Res.* **1987**, *171*, 161−191.

(11) Dunkerton, L. V.; Serino, A. J. *J. Org. Chem.* **1982**, *47*, 2812−2814.

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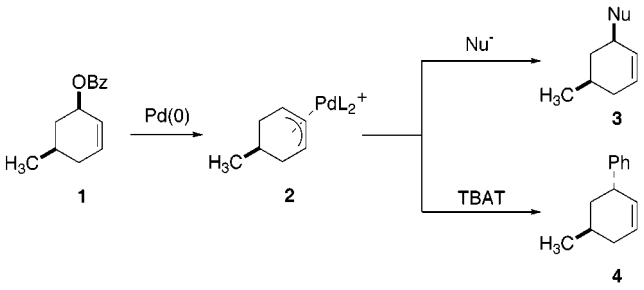
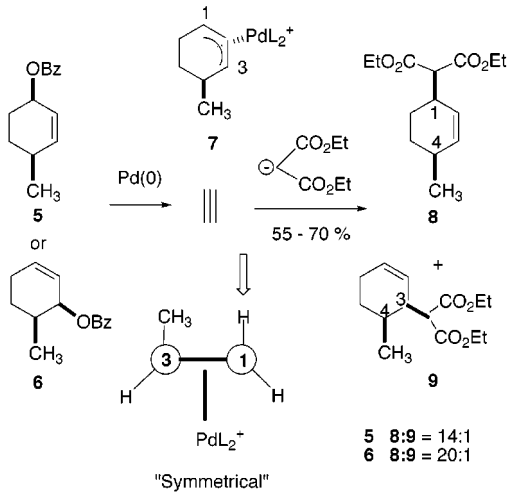
**Scheme 1**




**Scheme 2**

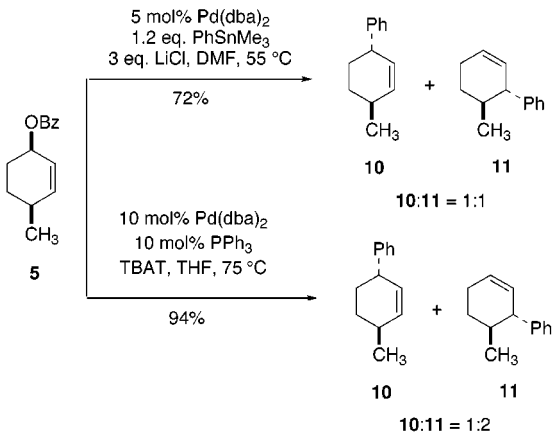



tronic and steric factors influenced the regioselectivity of the reaction. However, a systematic investigation of the regioselectivity of the substitution of cyclohexenyl and cyclopentenyl systems has not been reported. In this paper, we report a systematic study of the regioselectivity and stereoselectivity of Pd(0)-catalyzed alkylation reactions using both stabilized nucleophiles and silyl derivatives. In addition, the effectiveness of tin and hypervalent silicon reagents as arylation agents in the substitution reaction will be compared and contrasted.[13]

Pd-catalyzed substitution of a cyclohexenyl allylic ester such as **1** with stabilized nucleophiles (i.e., malonate) is known to occur with overall retention of configuration.[2] Employing the standard mechanism for this process, the reaction proceeds via displacement of the benzoate by Pd with inversion of configuration to provide Pd−$\pi$-allyl complex **2**. Attack of the stabilized nucleophile onto this intermediate occurs on the face opposite to Pd resulting in overall retention of configuration (Scheme 1). On the other hand, arylation of complex **2** using silyl (or stannyl) derivatives occurs with overall inversion presumably due to aryl transfer from silicon to Pd followed by reductive elimination.

The complex formed from benzoate **1** is symmetrical with respect to the methyl group and Pd and there is no regiochemistry associated with the substitution. Substitution of unsymmetrical complexes such as complex **7** (Scheme 2) is expected to provide a mixture of regioisomeric substitution products. Allylic benzoates such as **5** and **6** are known to provide "symmetrical" Pd−$\pi$-allyl complex **7**.[2] That is, the metal resides symmetrically over the allyl function due to the substituent residing on the opposite face of the complex.Subsequent malonate addition to this "symmetrical" complex should occur with high stereoselectivity at C-1 due to the steric bias provided by the methyl substituent during approach of the nucleophile. Arylation of this "symmetrical" complex, on the other hand, should occur with low stereoselectivity due to the altered mechanism involved in this process, i.e., aryl transfer to the metal followed by reductive elimination. Since the substituent is on the opposite face of the ring, it does not bias the arylation process.

**Scheme 3**




## Results and Discussion

Benzoates **5** and **6** were individually subjected to a standard set of alkylation conditions employing malonate, and, as predicted by the model, gave diester **8** as the major product along with a small amount of diester **9**. The structures of the regioisomers produced in each alkylation reaction were confirmed by homonuclear decoupling experiments.

In the arylation studies, cis-1,4-allylic benzoate **5** (Scheme 3) again gives trans Pd−$\pi$-allyl intermediate **7** (Scheme 2) and therefore it would be expected that reductive elimination of the phenyl group could occur equally toward C-1 or C-3. Using standard Stille protocol[6b] (top, Scheme 3) gave an equal distribution of regioisomers **10** and **11** (resulting from attack at C-1 and C-3, respectively). The structures of the regioisomers of each arylation product were confirmed by homonuclear decoupling experiments. The stereochemistries of the arylation products were determined by reduction (5% Pd/C) and comparing the experimental spectral data to published spectral data.[19]

The arylation reactions were also performed using tetrabutylammonium triphenyldifluorosilicate (TBAT, Figure

(13) For more information on the use of silicon reagents as sources of arylation, see: (a) Denmark, S. E.; Wu, Z. *Org. Lett.* **1999**, *1*, 1495−1498. (b) Shibata, K.; Miyazawa, K.; Goto, Y. *Chem. Commun.* **1997**, 1309−1310. (c) Corriu, R. J. P.; Chuit, C.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (d) Horn, A. H. *Chem. Rev.* **1995**, *95*, 1317−1350. (e) Nolan, S. P.; Lee, H. M. *Org. Lett.* **2000**, *2*, 2053−2055. (f) Correia, R.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7159−7165.

(14) It should be noted that structures depicted in the cyclohexenyl series in this article are not absolute stereochemistries, but are relative stereochemistries. For the cyclopentenyl series, the structures are absolute, and the compounds were enantiomerically pure.

(15) DeShong, P.; Handy, C. J.; Lam, Y.-F. *J. Org. Chem.* **2000**, *65*, 3542−3543.

(16) Brescia, M.-R.; DeShong, P. *J. Org. Chem.* **1998**, *63*, 3156−3157.

(17) Mowery, M. E.; DeShong, P. *J. Org. Chem.* **1999**, *64*, 3266−3270.

(18) Definitive information as to why TBAT gives a more regioselective reaction is not available as of yet.

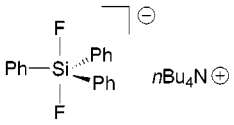
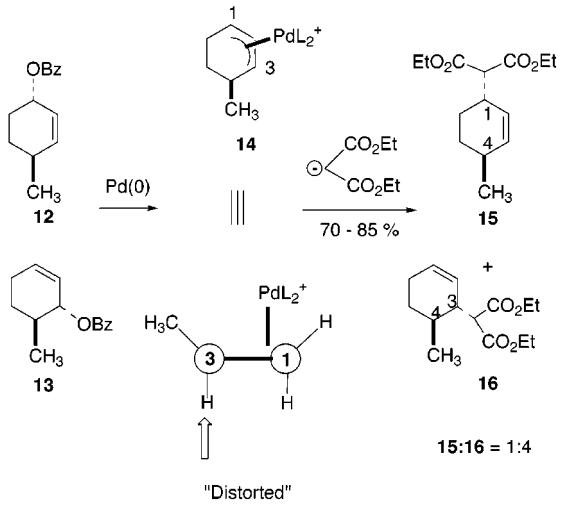


**Figure 1.** Tetrabutylammonium triphenyldifluorosilicate (TBAT).

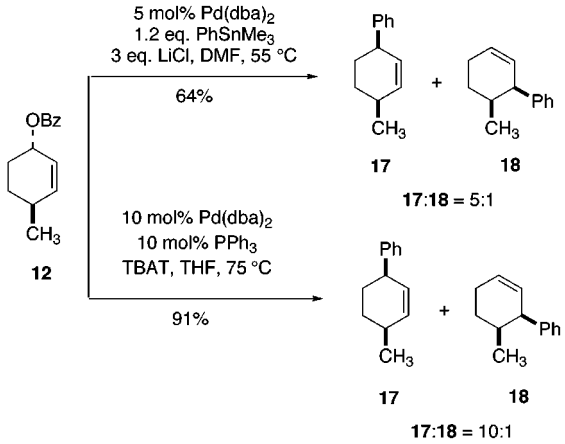
**Scheme 4**




1).[15] Previous studies in our lab have shown that TBAT is an effective cross coupling reagent for allylic benzoates[16] as well as aryl iodides, bromides, and triflates.[17] The arylation of allylic benzoate **5** (bottom, Scheme 3) was performed with TBAT, and in this case a ratio of 1:2 of phenylated adducts **10** and **11** were obtained. In this case, there is a slight preference for formation of the regioisomer resulting from attack at C-3.[18] It should be noted that the TBAT reaction is higher yielding and more regioselective than the Stille counterpart.

The corresponding set of trans-allylic benzoates **12** and **13** (Scheme 4) was also synthesized.[20] In this case, the intermediate Pd−$\pi$-allyl complex **14** is syn. It was anticipated that there would be a steric interaction between the methyl group and Pd, and that the Pd−$\pi$-allyl complex would be distorted away from the methyl group in an attempt to minimize this steric interaction (Scheme 4). The complex is best described as $\sigma$-$\eta^2$. It was predicted that attack of the distorted Pd−$\pi$-allyl complex **14** would occur in an $S_N2'$-like fashion, and attack at C-3 would be favored to give the 1,2-regioisomer **16** as the major product. Benzoates **12** and **13** were individually subjected to a standard set of alkylation conditions, and both gave a 1:4 ratio of diesters **15** and **16**. The major regioisomer resulted from attack at C-3, as expected from the proposed model. Malonate additions in the cis series of allylic benzoates gave a higher degree of regioselectivity (Scheme 2) than the corresponding trans series (Scheme 4). In the cis series, the methyl group played a direct role in influencing the regioselectivity of attack by the incoming malonate anion. In the trans series, the methyl group had an indirect role by distorting the position of the metal in the Pd−$\pi$-allyl complex.

**Scheme 5**




Regioselectivity of the arylation of *trans*-1,4-allylic benzoate **12** (Scheme 5) was also investigated and found to be significantly more regioselective than the cis-isomer. Employing the proposed model for regioselectivity in malonate additions, the Pd−$\pi$-allyl complex formed from benzoate **12** is distorted due to steric interactions between the methyl group and the metal−ligand moiety (**14**, Scheme 4). Accordingly, reductive elimination of the aryl group from Pd in complex **14** would occur preferentially distal to the methyl group at C-3 to provide alkene **17** as the major regioisomer (Scheme 5). The arylation was also performed using Stille conditions to give a 5:1 ratio of regioisomers **17** and **18**, respectively (Scheme 5). Again, the reaction employing TBAT gave higher yield of the adducts, in addition to being more regioselective than the stannane.[18]

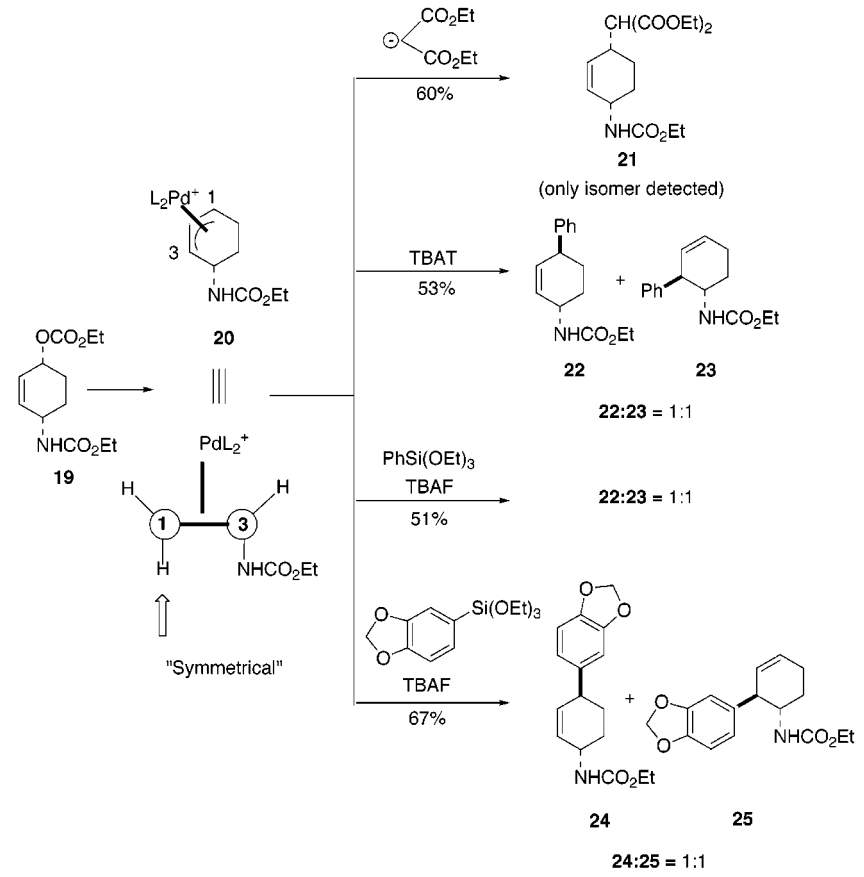
As part of our ongoing project to apply this methodology to the synthesis of alkaloidal natural products, we investigated the coupling reaction with carbonate **19**. This more complex cyclohexenyl system was studied to determine whether the established model was valid with heterosubstituents. Carbonate **19** was synthesized by Diels−Alder cycloaddition of α-chloronitrosocyclohexane with 1,4-cyclohexadiene followed by reduction of the N,O-bond and functionalization of the resulting amino and hydroxyl groups.[21] On the basis of the analogues discussed above, it was anticipated that coupling reactions would proceed via "symmetrical" $\pi$-allyl complex **20** (Scheme 6). Malonate addition to carbonate **19** occurred regiospecifically to afford diester **21**. In this instance, the reaction was even more regioselective than the methyl counterpart (compare to benzoate **5** in Scheme 2). In our systems, steric factors are apparently the dominant factor that controls whether "distorted" or "symmetrical" $\pi$-allyl complexes are formed. It should be noted that Szabó and Bäckvall have demonstrated that electronic effects of substitutents on the face *opposite* the palladium also play a role in the outcome of the nucleophilic attack on $\pi$-allyl

(19) $^1$H and $^{13}$C NMR spectral data for *cis*- and *trans*-4-methyl-1-phenylcyclohexanes can be found in Eliel, E. K.; Manoharan, M. *J. Org. Chem.* **1981**, *46*, 1959−1962. Actual spectral data for these compounds is shown in Garbisch, E. E., Jr.; Patterson, D. B. *J. Am. Chem. Soc.* **1963**, *85*, 3228−3231.

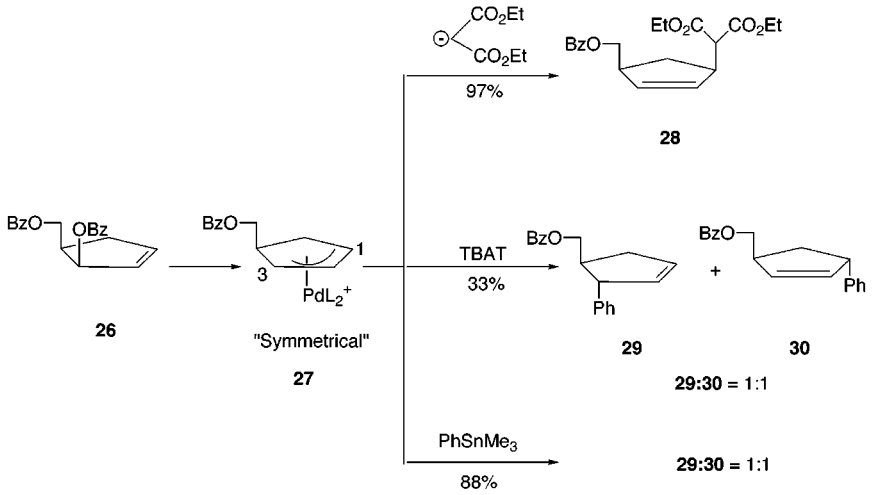
(20) The stereochemistries of allylic benzoates **5** and **12** were indirectly determined by comparing the preparation methods with the preparation method of crystalline 1,4-trans allylic *p*-nitrobenzoate.

(21) For the synthesis of α-chloronitrosocyclohexane using hypochlorous acid, see Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1980**, *21*, 1117−1120. The preparation of the amino alcohol derivative preceding carbamate **19** is described in Nelsen, S. F.; Thompson-Colon, J. A.; Kirste, B.; Rosenhouse, A.; Kaftory, M. *J. Am. Chem. Soc.* **1987**, *109*, 7128−7136. Protection of the amino alcohol derivative is performed using ethyl chloroformate as described in Hall, A.; Bailey, P. D.; Rees, D. C.; Rosair, G. M.; Wightman, R. H. *J. Chem. Soc., Perkin Trans. 1* **2000**, 329−343.

**Scheme 6**




**Scheme 7**




complexes.[22] They too have proposed the intermediacy of "distorted" palladium complexes.

On the other hand, arylation of carbonate **19** with a variety of silicon-based aryl transfer reagents[23] displayed no selectivity and gave a 1:1 mixture of regioisomeric adducts in all cases (Scheme 6). The lack of regioselectivity in the arylation reaction was consistent with the intermediacy of the "symmetrical" Pd-complex.

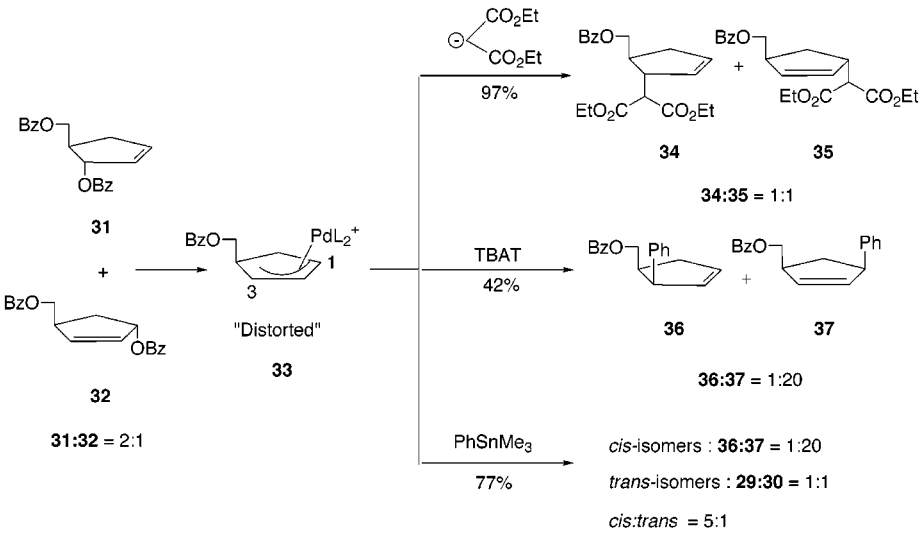
Having established a model that explained the regioselectivity of Pd(0)-catalyzed alkylation and arylation of cyclohexenyl derivatives, we studied cyclopentenyl substrates to determine if the model would also be applicable to these systems. On the basis of the model, cis-allylic benzoate **26** was predicted to produce "symmetrical" Pd–$\pi$-allyl complex **27** (Scheme 7). Subsequent malonate addition to **27** was expected to occur selectively at C-1 to avoid steric interactions with the bulky ester side chain at C-4. In fact, malonate addition to dibenzoate **26** gave exclusively the *cis*-1,4-cyclopentene adduct **28**.

Arylation reactions of *cis*-dibenzoate **26** were expected to display limited regioselectivity due to the "symmetrical" Pd-complex (**27**, Scheme 7). Arylation of **26**

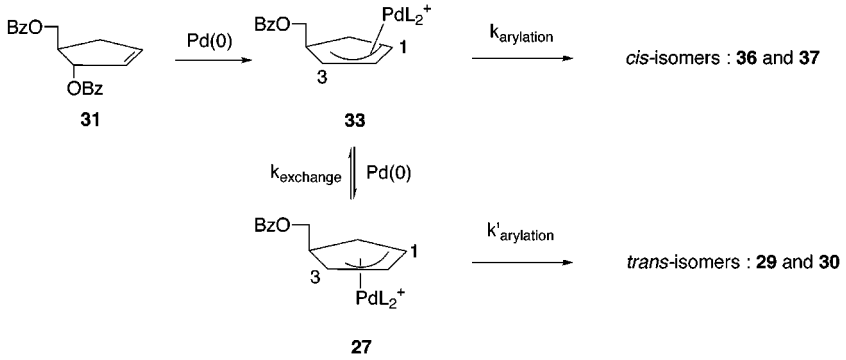
(22) Jonasson, C.; Kritikos, M.; Bäckvall, J.-E.; Szabó, K. *Chem. Eur. J.* **2000**, *6*, 432–436, and references therein.

(23) (a) Manoso, A. S.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7449–7455. (b) DeShong, P.; Mowery, M. E. *J. Org. Chem.* **1999**, *64*, 1684–1688. (c) DeShong, P.; Mowery, M. E. *Org. Lett.* **1999**, *1*, 2137–2140. (d) DeShong, P.; Handy, C. J.; Mowery, M. E. *Pure Appl. Chem.* **2000**, *72*, 1655–1658.

**Scheme 8**



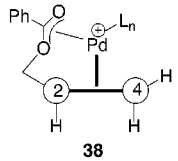

**Scheme 9**




using standard Stille protocol[6b] gave a 1:1 ratio of arylated adducts **29** and **30**. Similarly, arylation of dibenzoate **26** utilizing TBAT gave an identical distribution of products (Scheme 7).

Unexpected results were obtained when coupling reactions of trans allylic benzoates were studied. Coupling reactions of *trans*-dibenzoates **31** and **32** proceeded via the "distorted" Pd−$\pi$-allyl complex **33** (Scheme 8). Accordingly, it was anticipated that malonate addition would occur with high regioselectivity at C-3. To our surprise, the mixture of benzoates **31** and **32** gave a 1:1 mixture of adducts **34** and **35** (Scheme 8). This result is consistent with a "symmetrical", rather than "distorted", intermediate Pd−$\pi$-allyl complex. A possible explanation for this unusual result involves ligation of the Lewis-basic ester functionality to the electron-deficient palladium to form a "symmetrical" Pd−$\pi$-allyl complex as depicted in Figure 2.

Even though malonate addition to trans allylic benzoates **31** and **32** appeared to occur via a "symmetical" Pd−$\pi$-allyl complex (**38**, Figure 2), we anticipated that arylation of benzoates **31** and **32** would afford adducts




**38**

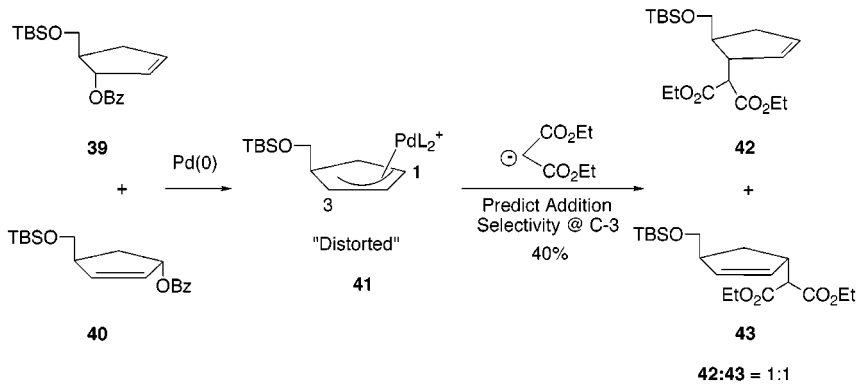
**Figure 2.** "Symmetrical" Pd−$\pi$-allyl complex.

with strong regioselectivity for coupling at C-1 since *reductive elimination of the aryl group from the metal to the substrate must proceed distal to the bulky ester side chain at C-4, irrespective of whether the benzoate group is ligated to Pd*. In other words, Pd-complex **38** is a "symmetrical" complex with regard to malonate addition, but is "distorted" when considering the arylation reaction. This hypothesis was supported by the subsequent results. Arylation with TBAT showed excellent regioselectivity with the C-1 adduct as the major product (Scheme 8).

Stille arylation of dibenzoates **31** and **32** (Scheme 8) also gave a 1:20 ratio of arenes **36** and **37** (arylation at C-3 and C-1, respectively). However, the Stille protocol also gave a mixture of arenes **29** and **30** resulting from a loss of stereochemical integrity of the Pd−$\pi$-allyl complex according to the process outlined in Scheme 9.[24] On the basis of the precedents of Cook and Bäckvall, it is proposed that Pd(0) attacks complex **33** to give diastereomeric complex **27** (Scheme 9). If the rate of arylation of complex **33** is faster than the rate of conversion to **27**, then the arylation will occur stereospecifically to afford cis-isomers **29** and **30**, respectively. However, if the rates of arylation and Pd attack are comparable, then mixtures of regio- and stereoisomers are obtained. These

(24) This loss of stereochemical integrity is best explained by a second Pd coming in and attacking the Pd−$\pi$-allyl complex. Fore more information regarding the phenomenon, please see: (a) Cook, G. R.; Shanker, P. S.; Pararajasingham, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 110−112. (b) Granberg, K. L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1992**, *114*, 6858−6863. (c) Bäckvall, J.-E.; Granberg, K.; Heumann, A, *Isr. J. Chem.* **1991**, *31*, 17−24.

**Scheme 10**




results indicate that the aryl transfer from silicates to Pd proceeded faster than the tin counterparts.

We had proposed that ligation of the benzoate functionality in complex **38** was responsible for the lack of regioselectivity observed in malonate addition to this complex (see Scheme 8 and Figure 2). Silyl-protected primary alcohol derivatives **39** and **40**, derivatives that should not be able to serve as ligands for the metal, were subjected to additions, and the results are summarized in Scheme 10. With the side chain unable to participate via coordination to Pd, the Pd−$\pi$-allyl intermediate predicted from the model should be "distorted" (Scheme 10) and malonate anion should couple preferentially at C-3. However, reaction with malonate afforded a 1:1 mixture of adducts **42** and **43**, exactly the same results that were obtained with the benzoate derivative (Scheme 8).[25] These results suggest that malonate addition in the cyclopentenyl system does not proceed through a "distorted" Pd−$\pi$-allyl complex as anticipated. Therefore, conformational factors of the intermediate cyclopentenyl complex must play a more significant role than has been anticipated in the model outlined above.

## Conclusions

The results summarized above indicate that steric factors in the intermediate Pd−$\pi$-allyl complexes exert significant control of the regioselectivity of Pd(0)-catalyzed malonate additions and arylations of cyclohexenyl and cyclopentenyl derivatives. Substituents on the carbocyclic systems lead to formation of either "symmetrical" or "distorted" Pd-complexes. The regioselectivity of the subsequent attack on the complex (i.e., malonate addition or arylation) can be correctly predicted in most instances using mechanistic considerations. The resulting model performs well with cyclohexenyl derivatives, but is limited with cyclopentenyl analogues due to conformational factors that have yet to be fully understood. We are currently investigating the conformations of the intermediate cyclohexenyl and cyclopentenyl Pd-complexes computationally, and the results will be reported at a later date.

(25) The regiochemistries of the products **42** and **43** formed from the malonate addition shown in Scheme 10 were determined in the following manner: Diesters **42** and **43** were deprotected using HF and $H_2SiF_6$ to give a 1:1 ratio of alcohols. The alcohols were then esterified with benzoyl chloride to give a 1:1 mixture of previously characterized diesters **34** and **35** (Scheme 8). These diesters were identical by $^1$H NMR to the diesters previously synthesized in Scheme 8. The procedures and yields are fully explained in the Experimental Section under the heading "Diesters **42** and **43** using $Pd(PPh_3)_4$".

## Experimental Section

**General Methods.** Nuclear magnetic resonance ($^1$H and $^{13}$C NMR) spectra were recorded on a 200 or 400 MHz spectrometer in $CDCl_3$. Chemical shifts are reported in parts per million ($\partial$) 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). $Et_2O$ was distilled from sodium/benzophenone ketyl while methylene chloride ($CH_2Cl_2$) was distilled from calcium hydride. Dimethylformamide (DMF) was distilled from 4Å Linde-type molecular sieves. Reagent grade methanol was stored over 4Å Linde-type molecular sieves. Absolute ethanol (EtOH) was used without further purification. 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 $N_2$ at room temperature unless otherwise noted. All ratios given were determined by GC or $^1$H NMR unless otherwise indicated.

Benzoic acid ($PhCO_2H$), benzoyl chloride (BzCl), ethyl chloroformate, bromine ($Br_2$), *tert*-butyldimethylsilyl chloride (TBDMS-Cl), diethyl malonate, diphenylphosphinoethane (dppe), lithium chloride (LiCl), 4-methylcylcohexanone, *p*-nitrobenzoyl chloride (*p*-NBzCl), palladium acetate ($Pd(OAc)_2$), palladium on carbon (5%, Pd/C), sodium borohydride ($NaBH_4$), sodium hydride (60% dispersion in oil, NaH), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), and trimethyl(phenyl)tin ($PhSnMe_3$) were purchased from Aldrich and used as received. Bis(dibenzylidene acetone)palladium ($Pd(dba)_2$) and diethyl azodicarboxylate (DEAD) were purchased from Acros and used as received. Lithium carbonate ($Li_2CO_3$) was purchased from Baker and used as received. Fluorosilicic acid ($H_2SiF_6$) was purchased from Fischer and used as received. Triphenylphosphine ($PPh_3$) was purchased from Aldrich and recrystallized from pentane prior to use. Tetrabutylammonium triphenyldifluorosilicate (TBAT) was synthesized according to the literature procedure.[15] The corresponding diol precursor for dibenzoate **26** was provided by Prof. Michael Crimmins.

**Diesters 8 and 9. Using $Pd(PPh_3)_4$. Substrate: *cis*-4-Methylcyclohex-2-en-1-yl Benzoate (5).** Sodium hydride (0.12 g of a 60% dispersion in oil, 2.9 mmol) was washed with 2 × 2 mL of hexane and 2 mL of THF. To a suspension of oil-free NaH in 3 mL of THF was added 0.90 mL (5.9 mmol) of diethyl malonate. The resulting diethyl malonate anion was added via syringe to a degassed solution of 0.10 g (0.46 mmol) of allylic benzoate **5**, 48 mg (0.042 mmol) of $Pd(PPh_3)_4$, and 0.11 g (0.42 mmol) of $PPh_3$ in 11 mL of THF. The resulting yellow solution was heated at 78 °C. The reaction mixture was

quenched after 25 h. with 40 mL of $H_2O$. The layers were separated, and the aqueous phase was extracted with 3 × 50 mL of $Et_2O$. The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (15 mm, 20 cm, 5% EtOAc/hexane) gave 65 mg (55%) of diesters **8** and **9** as a colorless oil. The ratio of diesters **8** to **9** was 14:1. Approximately 8% of diester **16** was obtained and this was attributed to the presence of 8% of benzoate **12** in the starting material. TLC $R_f$ = 0.62 (20% EtOAc/hexane); IR ($CCl_4$) 3025 (w), 2988 (s), 2963 (s), 2931 (s), 2868 (s), 1750 (s), 1738 (s), 1656 (w), 1481 (m), 1463 (m), 1400 (m), 1369 (s), 1338 (m), 1300 (s), 1275 (s), 1244 (s), 1231 (s), 1156 (s), 1181 (s), 1100 (s), 1038 (s); $^1$H NMR ($CDCl_3$, major isomer **8**) 0.95 (d, 3H, $J$ = 7.1), 1.01−2.15 (m, 11H), 2.83−2.85 (br m, 1H), 3.24 (d, 1H, $J$ = 9.8), 4.17 (q, 4H, $J$ = 7.1), 5.51 (B of ABq, 1H, $J_{AB}$= 10.2), 5.66 (A of ABq, 1H, $J_{AB}$=10.2); $^{13}$C NMR ($CDCl_3$, major isomer **8**) 14.1, 21.0, 23.0, 23.9, 27.9, 29.7, 57.1, 61.0, 126.6, 135.6, 168.5, 168.6; GC/MS (diester **8**) 254 ($M^+$, 6), 180 (100), 161 (41), 151 (47), 134 (24), 115 (44), 107 (28), 95 (73), 94 (75), 91 (24), 79 (56), 77 (29); (diester **9**) 254 ($M^+$, 5), 180 (100), 161 (30), 152 (37), 115 (35), 107 (30), 95 (71), 79 (37).

**Substrate: *cis*-6-Methylcyclohex-2-en-1-yl Benzoate (6).** The preparation of diesters **8** and **9** was performed in the same manner as described for the *cis*-1,4-benzoate **5**. The Pd(0)-catalyzed addition of the diethyl malonate anion to 12 mg (0.055 mmol) of allylic benzoate **6** gave 10 mg (71%) of diesters **8** and **9** as a colorless oil following, and the ratio of diesters **8** to **9** was 20:1. Approximately 4% of diester **16** was obtained, and this was attributed to the presence of 4% of benzoate **13** in the starting material. The spectral data was identical to the above-reported results.

**Arenes 10 and 11. Using $PhSnMe_3$.** To a yellow mixture of 30 mg (0.14 mmol) of allylic benzoate **5**, 6 mg (10 $\mu$mol) of $Pd(dba)_2$, and 24 mg (0.57 mmol) of LiCl in 3 mL of DMF was added 40 $\mu$L (0.22 mmol) of $PhSnMe_3$. The mixture was degassed via a single freeze−pump−thaw cycle. The brown solution was heated at 55 °C for 21 h. The resulting dark-brown suspension was quenched by the addition of 50 mL of $H_2O$ and extracted with 4 × 50 mL of $Et_2O$. The combined organics were dried over $MgSO_4$ and concentrated in vacuo. Column chromatography (15 mm, 21 cm, hexanes) gave 17 mg (72%) of arenes **10** and **11** with a ratio of 1:1. TLC $R_f$ = 0.53 (hexanes); IR ($CCl_4$, arene **10** only) 3063 (w), 3025 (m), 2963 (s), 2931 (s), 2863 (s), 1681 (m), 1514 (s), 1456 (m), 1256 (m), 1113 (m), 1013 (m), 900 (s); $^1$H NMR (arene **10** only) 1.01 (d, 3H, $J$ = 7.1), 1.17−2.24 (m, 5H), 3.32 (br s, 1H), 5.66 (dd, 2H, $J$ = 19.0, 10.6), 7.15−7.35 (m, 5H); $^{13}$C NMR (arene **10** only) 21.9, 30.4, 31.4, 32.7, 42.4, 126.0, 127.6, 128.3, 129.7, 134.5, 146.8; $^{13}$C NMR (arene **11** only) 20.2, 25.3, 30.6, 36.7, 50.6, 128.1, 128.2, 128.3, 130.9, 135.8, 145.9; GCMS (arene **11**) 173 172 ($M^+$, 37), 157 (8), 131 (17), 130 (100), 129 (68), 128 (23), 115 (36), 91 (21), 77 (10), 51 (12); (arene **10**) 172 ($M^+$, 66), 157 (28), 143 (28), 130 (85), 124 (86), 128 (30), 117 (18), 115 (51), 104 (100), 91 (39), 79 (12), 78 (11), 77 (19), 65 (13), 51 (19).

**Using TBAT.** A solution of 17 mg (30 $\mu$mol) of $Pd(dba)_2$, 9.0 mg (34 $\mu$mol) of $PPh_3$, and 60 mg (0.28 mmol) of allylic benzoate **5** in 5 mL of THF was degassed via a single freeze−pump−thaw cycle. Then, 0.32 g (0.60 mmol) of TBAT was added to the reaction which was degassed by a second freeze−pump−thaw cycle. The dark yellow solution was heated at 70 °C for 17 h. The reaction was quenched by the addition of 50 mL of $H_2O$ and extracted with 4 × 50 mL of $Et_2O$. The combined organics were dried over $MgSO_4$ and concentrated in vacuo. Purification of the residue by column chromatography (20 mm, 20 cm, hexanes) gave 45 mg (94%) of arenes **10** and **11** as a 1:2 mixture. The spectral data was identical to the preceding results.

**Diesters 15 and 16. Using $Pd(PPh_3)_4$. Substrate: *trans*-4-Methylcyclohex-2-en-1-yl Benzoate (12).** The preparation of diesters **15** and **16** was performed in the same manner as described for diesters **8** and **9** (benzoate **5**). The Pd(0)-catalyzed addition of the diethyl malonate anion to 0.11 g (0.527 mmol) of allylic benzoate **12** gave 0.11 g (87%) of diesters **15** and **16** as a colorless oil. The ratio of diesters **15** to **16** was 1:4. Approximately 5% of diester **8** was observed due to the presence of 5% of benzoate **5** in the starting material. Integration of the doublets at 3.17 (diester **15**) and 3.46 (diester **16**) of the malonate proton in the $^1$H NMR spectrum gave a ratio of 1:3.8. TLC $R_f$ = 0.77 (33% EtOAc/hexane); IR ($CDCl_3$) 3038 (w), 2988 (m), 2962 (m), 2931 (m), 2875 (m), 2856 (w), 1759 (s), 1731 (s), 1606 (w), 1462 (w), 1369 (m), 1361 (m), 1269 (m), 1231 (m), 1181 (s), 1156 (s), 1106 (s); $^1$H NMR ($CDCl_3$, major isomer **16**) 0.99 (d, 3H, $J$ = 6.6), 1.17−1.99 (m, 11H), 2.53 (br s, 1H), 3.47 (d, 1H, $J$ = 7.1), 4.14−4.42 (m, 4H), 5.58 (B of ABq, 1H, $J_{AB}$= 10.2), 5.74 (A of ABq, 1H, $J_{AB}$=10.2) $^{13}$C NMR ($CDCl_3$, major isomer **16**) 14.1, 19.3, 23.0, 27.8, 30.2, 41.8, 55.2, 61.3, 126.3, 128.7, 168.4, 169.1; GC/MS (diester **16**) 254 ($M^+$, 5), 209 (3), 180 (100), 161 (40), 151 (40), 133 (21), 115 (54), 95 (94), 94 (47), 79 (74); (diester **15**) 254 ($M^+$, 4), 209 (1), 180 (37), 161 (34), 151 (20), 133 (13), 115 (30), 95 (58), 94 (100), 79 (61), 77 (18).

**Substrate: *trans*-6-Methylcyclohex-2-en-1-yl Benzoate (13).** The preparation of diesters **15** and **16** was performed in the same manner as for diesters **8** and **9** (benzoate **5**). The Pd(0)-catalyzed addition of the diethyl malonate anion to 20 mg (0.092 mmol) of allylic benzoate **13** gave 16 mg (67%) of diesters **15** and **16** as a colorless oil following purification by column chromatography (15 mm, 17 cm, 12.5% EtOAc/hexane). The ratio of diesters **15** to **16** was 1:4 by GC. Approximately 11% of diester **8** was observed due to a 5% impurity of benzoate **6** in the starting material. Integration of the doublets at 3.18 (diester **15**) and 3.47 (diester **16**) of the malonate proton gave a ratio of 1:5.0. The spectral data was identical to the above-reported results.

**Arenes 17 and 18. Using $PhSnMe_3$.** Using the previously described procedure for the synthesis of arenes **10** and **11** using $PhSnMe_3$, but substituting benzoate **12** gave 15 mg (64%) of arenes **17** and **18** as a 5:1 ratio by GC. TLC $R_f$ = 0.58 (hexanes); IR ($CCl_4$) 3088 (w), 3063 (w), 3025 (m), 2963 (s), 2925 (s), 2875 (m), 2856 (m), 1563 (s), 1544 (s), 1456 (w), 1250 (m), 1219 (m), 1138 (m), 1117 (m), 1081 (m), 1006 (s), 981 (m), 838 (s); $^1$H NMR ($CDCl_3$)1.04 (d, 3H, $J$ = 7.1), 1.63−1.69 (m, 2H), 1.87−1.93 (m, 2H), 2.24 (br s, 1H), 3.37 (br s, 1H), 5.73 (dt, 2H, $J$ = 39.8, 10.0, 2.5) 7.15−7.35 (m, 5H); $^{13}$C NMR 21.4, 27.7, 29.6, 29.7, 41.1, 125.9, 128.0, 128.2, 128.6, 134.7, 151.0; GCMS (arene **18**) 172 ($M^+$, 42), 157 (11), 131 (19), 130 (100), 129 (72), 128 (23), 115 (38), 91 (21); (arene **17**) 172 ($M^+$, 81), 157 (33), 143 (29), 130 (85), 129 (92), 128 (30), 117 (18), 115 (52), 104 (100), 91 (37), 77 (19), 51 (21).

**Using TBAT.** Using the previously described procedure for the synthesis of arenes **10** and **11** using TBAT, but substituting benzoate **12**, gave 43 mg (91%) of arenes **17** and **18** as a 10:1 mixture. The spectral data was identical to the preceding results.

**Diester 21.** Sodium hydride (93 mg of a 60% dispersion in oil, 2.33 mmol) was washed with 2 × 2 mL of hexane and 2 mL of THF. To a suspension of oil-free NaH in 3 mL of THF was added 355 $\mu$L (2.33 mmol) of diethyl malonate. The resulting diethyl malonate anion was added via syringe to a degassed solution of 200 mg (0.778 mmol) of carbonate **19** and 40 mg (0.039 mmol) of $Pd_2(dba)_3$·$CHCl_3$ in 10 mL of THF. The resulting yellow solution was heated at 50 °C. The reaction mixture was quenched after 25 h with 40 mL of $H_2O$. The layers were separated, and the aqueous phase was extracted with 3 × 40 mL of $Et_2O$. The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (15 mm, 20 cm, 3:1 hexanes:EtOAc) gave 150 mg (60%) of diester **21** as a colorless oil. TLC $R_f$ = 0.19 (3:1 hexanes:EtOAc); IR ($CCl_4$) 3455 (w) 2960 (m), 2922 (m), 2871 (m), 1736 (m), 1459 (m), 1242 (m); $^1$H NMR ($CDCl_3$) 1.18−1.24 (m, 9H), 1.43−1.49 (m, 1H), 1.67−1.73 (m, 3H), 2.76−2.82 (m, 1H), 3.25 (d, 1H, $J$ = 7.4), 4.04 (q, 2H, $J$ = 7.0), 4.06−4.17 (m, 5H), 4.76 (d, 1H, $J$ = 8.0), 5.70 (s, 2H); $^{13}$C NMR ($CDCl_3$) 14.1, 14.6, 22.2, 27.7, 35.0, 44.7, 56.1, 60.6, 61.4, 128.8, 131.5, 155.7, 168.1, 168.2; FAB mass spectrum *m*/*z* (relative intensity) 328 ((M + H), 9), 239 (28), 161 (100), 79 (38); HRMS (FAB) calcd for $C_{16}H_{26}O_6N$ (M + H) 328.1760, found 328.1773.

**Arenes 22 and 23. Using $PhSi(OEt)_3$.** To a solution of 100 mg (0.389 mmol) of carbonate **19** and 20 mg (0.020 mmol) $Pd_2(dba)_3 \cdot CHCl_3$ in 10 mL THF was added 190 $\mu$L (0.778 mmol) $PhSi(OEt)_3$, followed by 778 $\mu$L (0.778 mmol, 1.0 M solution in THF) TBAF. The solution was degassed via a single freeze−pump−thaw cycle. After 10 min., a color change from maroon to amber was noticed. The reaction mixture was quenched after 48 h. with 40 mL $H_2O$. The layers were separated and the aqueous phase was extracted with 3 × 40 mL $Et_2O$. The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (20 mm, 20 cm, 5% EtOAc/ hexanes) gave 48 mg (51%) of arenes **22:23** as a white solid. The ratio of diesters **22** to **23** was 1:1. The pure regioisomers were separated using preparative HPLC (3:1 hexanes:EtOAc). Arene **22**: TLC $R_f$ = 0.35 (3:1 hexanes:EtOAc); IR ($CCl_4$) 3454 (w), 3026 (w), 2943 (w), 1728 (s), 1500 (s); $^1$H NMR ($CDCl_3$) 1.25 (t, 3H, $J$ = 6.7), 1.47−1.52 (m, 1H), 1.58−1.63 (m, 1H), 2.07−2.09 (m, 2H), 3.36−3.38 (m, 1H), 4.12 (q, 2H, $J$ = 6.7), 4.32−4.34 (m, 1H), 4.63 (br s, 1H), 5.77 (d, 1H, $J$ = 9.9), 5.82 (d, 1H, 9.9), 7.16−7.31 (m, 5H); $^{13}$C NMR ($CDCl_3$) 14.6, 29.6, 31.0, 41.8, 47.0, 60.7, 126.3, 127.5, 128.4, 129.6, 133.1, 145.2, 156.0; FAB mass spectrum *m*/*z* (relative intensity) 246 ((M + H), 17), 157 (66), 91 (100); HRMS (FAB) calcd for $C_{15}H_{20}O_2N$ (M + H) 246.1494, found 246.1491. Arene **23**: $R_f$ = 0.35 (3:1 hexanes:EtOAc); IR ($CCl_4$) 3447 (w), 3029 (w), 2933 (w), 1729 (s), 1552 (s); $^1$H NMR ($CDCl_3$) 1.16 (t, 3H, $J$ = 6.8), 1.58−1.62 (m, 1H), 1.87−1.92 (m, 1H), 2.14−2.24 (m, 2H), 3.29−3.33 (m, 1H), 3.78−3.83 (m, 1H), 4.01 (q, 2H, $J$ = 6.8), 4.80 (br s, 1H), 5.62 (ddd, 1H, $J$ = 2.0, 3.6, 9.9), 5.89 (ddd, 1H, $J$ = 2.0, 4.0, 9.9), 7.21−7.29 (m, 5H); $^{13}$C NMR ($CDCl_3$) 14.5, 23.0, 25.5, 48.0, 52.6, 60.6, 126.7, 127.9, 128.3, 128.4 (2C), 142.6, 156.0; FAB mass spectrum *m*/*z* (relative intensity) 246 ((M + H), 17), 102 (100), 91 (25); HRMS (FAB) calcd for $C_{15}H_{20}O_2N$ (M + H) 246.1494, found 246.1491.

**Using TBAT.** To a solution of 100 mg (0.389 mmol) of carbonate **19** and 20 mg (0.020 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$ in 10 mL of THF was added 420 mg (0.778 mmol) of TBAT. The solution was degassed via a single freeze−pump−thaw cycle and then heated to 55 °C. The reaction was quenched by the addition of 20 mL of $H_2O$ and extracted with 3 × 20 mL of $Et_2O$. The combined organics were dried over $MgSO_4$ and concentrated in vacuo. Purification of the residue by column chromatography (20 mm, 20 cm, 9:1 hexanes:EtOAc) gave 50 mg (53%) of arenes **22** and **23** as a 1:1 mixture. The spectral data was identical to the preceding results.

**Arenes 24 and 25.** To a solution of 220 mg (0.778 mmol) of 1,2-methylenedioxyphenyl siloxane in 10 mL of THF were added 100 mg (0.389 mmol) of carbonate **19**, 20 mg (0.019 mmol) of $Pd_2(dba)_3 \cdot CHCl_3$, and 780 $\mu$L (1.05 mmol, 1.0 M solution in THF) of TBAF. The reaction mixture was heated to 55 °C. After 10 min, a color change from maroon to amber was noticed. The reaction mixture was quenched after 20 h with 40 mL of $H_2O$. The layers were separated, and the aqueous phase was extracted with 3 × 40 mL of $Et_2O$. The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (20 mm, 20 cm, 9:1 hexanes:EtOAc) gave 75 mg (67%) of a 1:1 mixture of arenes **24:25** as a white solid. The ratio of diesters **24** to **25** was 1:1. The pure regioisomers were separated using preparative HPLC (3:1 hexanes:EtOAc). Arene **24**: recrystallized from $CH_2Cl_2$/ hexanes, mp = 90−92 °C. TLC $R_f$ = 0.22 (3:1 hexanes:EtOAc); IR ($CCl_4$) 3441 (w), 3033 (w), 2926 (w), 1721 (s), 1542 (s); $^1$H NMR ($CDCl_3$) 1.23 (t, 3H, $J$ = 7.0), 1.41−1.54 (m, 2H), 2.01−2.07 (m, 2H), 3.28−3.29 (m, 1H), 4.10 (q, 2H, 7.0), 4.28−4.30 (m, 1H), 4.63 (br s, 1H), 5.75 (m, 2H), 5.90 (s, 2H), 6.60−6.64 (m, 2H), 6.72 (d, 1H, $J$ = 7.9); $^{13}$C NMR ($CDCl_3$) 14.6, 29.5, 31.1, 41.5, 46.9, 60.7, 100.8, 108.0, 108.2, 120.4, 129.6, 133.2, 139.2, 146.0, 147.6, 156.1; FAB mass spectrum *m*/*z* (relative intensity) 290 ((M + H), 46), 201 (100), 174 (24), 135 (60), 73 (48); HRMS (FAB) calcd for $C_{16}H_{20}O_4N$ (M + H) 290.1392, found 290.1390. Arene **25**: $R_f$ = 0.22 (3:1 hexanes:EtOAc); IR ($CCl_4$) 3447 (w), 3029 (w), 2933 (w), 1729 (s), 1552 (s); $^1$H NMR ($CDCl_3$) 1.18 (t, 3H, $J$ = 7.2), 1.53−1.62 (m, 1H), 1.86−1.90 (m, 1H), 2.04−2.20 (m, 2H), 3.21−3.23 (m, 1H), 3.71−3.74 (m, 1H), 4.03 (q, 2H, 7.2), 4.74−4.76 (m, 1H), 5.66 (d, 1H, 10.0), 5.87 (d, 1H, 10.0), 5.91 (s, 2H), 6.67−6.73 (m, 3H); $^{13}$C NMR ($CDCl_3$) 14.5, 22.9, 25.5, 47.6, 52.7, 60.6, 100.9, 108.0, 108.7, 121.5, 127.9, 136.5, 146.2, 147.6, 156.0; FAB mass spectrum *m*/*z* (relative intensity) 290 ((M + H), 21), 201 (100), 174 (31), 135 (81), 73 (90); HRMS (FAB) calcd for $C_{16}H_{20}O_4N$ (M + H) 290.1392, found 290.1379.

**Diester 28. Using $Pd(PPh_3)_4$.** The preparation of diester **28** was performed in the same manner as for diesters **8** and **9** (benzoate **5**). The Pd(0)-catalyzed addition of the diethyl malonate anion to 30 mg (0.085 mmol) of allylic benzoate **26** gave 32 mg (97%) of diester **28** as a colorless oil. TLC $R_f$ = 0.44 (10% EtOAc/hexane); IR ($CCl_4$) 3069 (w), 2988 (s), 2963 (s), 2944 (m), 2906 (w), 2889 (w), 2875 (w), 1756 (s), 1731 (s), 1606 (w); $^1$H NMR ($CDCl_3$) 1.23 (t, 6, $J$ = 7.1), 1.37 (dt, 1, $J$ = 7.5, 13.5), 2.39 (dt, 1, $J$ = 8.3, 13.5), 3.14−3.17 (m, 1), 3.26 (d, 1, $J$ = 9.6), 3.37−3.42 (m, 1), 4.15−4.27 (m, 6), 5.77−5.80 (m, 2), 7.42 (t, 2, $J$ = 7.5), 7.53 (t, 1, $J$ = 7.5), 8.01 (d, 2, $J$ = 7.5); $^{13}$C NMR ($CDCl_3$) 14.1, 31.7, 45.0, 45.1, 57.3, 61.3, 68.1, 128.3, 129.6, 130.2, 132.8, 132.9, 133.6, 166.5, 168.4; LRMS (EI) 361 ((M + 1), 3), 238 (45), 164 (87), 105 (100), 77 (35); HRMS (EI) calcd for $C_{20}H_{25}O_6$ (M + 1) 361.1651, found 361.1641.

**Arenes 29 and 30. Using $PhSnMe_3$.** To a yellow mixture of 30 mg (0.093 mmol) of allylic benzoate **26**, 3 mg (5 $\mu$mol) of $Pd(dba)_2$ and 12 mg (0.28 mmol) of LiCl in 3 mL of DMF was added 34 mg (0.14 mmol) of phenyltrimethyltin. The mixture was degassed and stirred at room temperature for 72 h. The reaction mixture was then partitioned between 15 mL of distilled $H_2O$ and 15 mL of $Et_2O$. The organic layer washed with an additional 15 mL of distilled $H_2O$, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash chromatography (10 mm, 16 cm, 0−10% $CH_2Cl_2$/hexane) gave 23 mg (88%) of a 1:1 ratio of arenes **29** and **30** as a yellow oil. TLC $R_f$ = 0.33 (25% EtOAc/hexane); IR ($CCl_4$) 3063 (w), 3038 (w), 2956 (s), 2899 (s), 2869 (s), 1725 (s), 1606 (w); $^1$H NMR ($CDCl_3$) for arene **29** 1.97−2.05 (m, 1), 2.26−2.31 (m, 1), 3.33−3.35 (m, 1) 4.01−4.05 (m, 1), 5.72−5.96 (m, 2), 7.18−7.58 (m, 6), 7.96−8.06 (m, 2); $^1$H NMR ($CDCl_3$) for arene **30** 2.32−2.35 (m, 1), 2.60−2.66 (m, 1), 2.70−2.75 (m, 1) 3.74−3.76 (m, 1), 5.72−5.96 (m, 2), 7.18−7.58 (m, 6), 7.96−8.06 (m, 2); GCMS (arene) 130 (100), 129 (98), 128 (84), 115 (95), 91 (67), 77 (46), 51 (59); (arene) 160 (40), 115 (51), 91 (100), 77 (47), 51 (72).

**Using TBAT.** A solution of 3.0 mg (5.0 mmol) of $Pd(dba)_2$, 1.0 mg (5.0 mmol) of $PPh_3$, and 30 mg (0.093 mmol) of allylic benzoate **26** in 5 mL of THF was degassed by three freeze−pump−thaw cycles. The solution stirred at room temperature for 30 min before 97 mg (0.18 mmol) of TBAT was added. The reaction mixture was then heated at reflux for 12 h. The resulting black mixture was filtered through a silica gel plug before it was partitioned between 5 mL of water and 5 mL of $Et_2O$. The aqueous layer was then extracted with 3 × 5 mL of $Et_2O$. The organic layers were combined, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by column chromatography using pentane gave 8 mg (33%) of a 1:1 ratio of arenes **29** and **30** as a pale yellow oil.

**Diesters 34 and 35. Using $Pd(PPh_3)_4$.** The preparation of diesters **34** and **35** was performed in the same manner as for diesters **8** and **9** (benzoate **5**). The Pd(0)-catalyzed addition of the diethyl malonate anion to 30 mg (0.085 mmol) of allylic benzoates **31** and **32** gave 32 mg (97%) diesters **34** and **35** as a 1:1 ratio of a colorless oil. TLC $R_f$ = 0.44 (10% EtOAc/ hexane); IR ($CCl_4$) 3069 (w), 2988 (s), 2963 (s), 2944 (m), 2906 (w), 2889 (w), 2875 (w), 1756 (s), 1731 (s), 1606 (w); $^1$H NMR ($CDCl_3$) 1.23 (t, 6, $J$ = 7.1), 1.37 (dt, 1, $J$ = 7.5, 13.5), 2.39 (dt, 1, $J$ = 8.3, 13.5), 3.14−3.17 (m, 1), 3.26 (d, 1, $J$ = 9.6), 3.37−3.42 (m, 1), 4.15−4.27 (m, 6), 5.77−5.80 (m, 2), 7.42 (t, 2, $J$ = 7.5), 7.53 (t, 1, $J$ = 7.5), 8.01 (d, 2, $J$ = 7.5); GCMS (diester) 238 (29), 165 (69), 164 (88), 118 (59), 105 (96), 91 (81), 79 (97), 78 (74), 77 (100), 51 (49); (diester) 238 (60), 165 (81), 164 (95), 118 (45), 105 (98), 91 (61), 79 (94), 78 (72), 77 (100), 51 (54).

**Arenes 36 and 37. Using $PhSnMe_3$.** Using the previously described procedure for the synthesis of arenes **29** and **30** via $PhSnMe_3$, but substituting a 2:1 mixture of benzoates **31** and **32** gave 20 mg (77%) of a 1:20:2:2 ratio of arenes **36**, **37**, **29**, and **30** as yellow oil.

**Using TBAT.** Using the previously described procedure for the synthesis of arenes **29** and **30** via TBAT, but substituting a 2:1 mixture of benzoates **31** and **32** gave 11 mg (42%) of a 1:20 ratio of arenes **36** and **37** as a light yellow oil. TLC $R_f$ = 0.47 (10% EtOAc/hexane); IR ($CCl_4$) 3063 (w), 3031 (w), 2956 (s), 2938 (s), 2898 (s), 2868 (s), 1725 (s), 1600 (w); $^1$H NMR ($CDCl_3$) 1.52−1.61 (m, 2), 2.63−2.78 (m, 1), 3.21−3.36 (m, 1), 3.97−4.15 (m, 1), 4.32−4.44 (m, 2), 5.88−5.94 (m, 2), 7.18−7.72 (m, 8), 7.95−8.11 (m, 2); $^{13}$C NMR ($CDCl_3$) 37.6, 45.7, 51.2, 68.2, 126.2, 127.1, 127.3, 128.3, 128.4, 128.5, 129.6, 132.4, 132.9, 136.0, 166.6; LRMS (EI) 278 ($M^+$, 3), 201 (17), 156 (100), 105 (53), 77 (39); HRMS calcd for $C_{19}H_{18}O_2$ ($M^+$) 278.1307, found 278.1308. The experiment was repeated with dppe as the ligand, and a 1:21 ratio of arenes **36** and **37** was obtained.

**Diesters 42 and 43. Using $Pd(PPh_3)_4$.** The preparation of diesters **42** and **43** was performed in the same manner as for diesters **8** and **9** (benzoate **5**). The Pd(0)-catalyzed addition of the diethyl malonate anion to 10 mg (31 mmol) of allylic benzoates **39** and **40** gave an oil which was transferred to a polyethylene test tube in 5 mL of $CH_3CN$. To this solution were added 10 $\mu$L (49% aq solution, 0.31 mmol) of HF and 15 $\mu$L (25% aq solution, 0.03 mmol) of $H_2SiF_6$ via Eppendorf pipet. Within 5 min, the solution became light yellow. The reaction mixture was stirred for 20 min and quenched by the addition of 1 mL of saturated of $K_2CO_3$ solution and 1 mL of saturated NaCl solution solution. The aqueous phase was extracted with 3 × 2 mL EtOAc. The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. Purification of the residue by flash chromatography (5 mm, 3 cm, 40% EtOAc/hexane) gave 6 mg (80%) of a 1:1 ratio of deprotected diesters as a colorless oil. The deprotected diesters were then esterified with BzCl and pyridine using conditions previously described (benzoate **12**). The esterification gave 4 mg (50%) of a 1:1 ratio of diesters **42** and **43** as a colorless oil. The overall yield of transformations was 40%. TLC $R_f$ = 0.23 (40% EtOAc/hexane); IR ($CCl_4$) 3038 (m), 3550 (m), 2988 (m), 2962 (m), 2938 (m), 2875 (m), 1756 (s), 1738 (s); $^1$H NMR ($CDCl_3$) 1.25 (t, 6, $J$ = 6.9), 1.79−1.83 (m, 1), 1.90−1.93 (m, 1), 2.85−3.02 (m, 1), 3.22 (d, 1, $J$ = 9.5), 3.42−3.44 (m, 1), 3.54 (d, 2, $J$ = 5.6), 4.17 (q, 4, $J$ = 6.9), 5.76 (d, 1, $J$ = 5.8), 5.81 (d, 1, $J$ = 5.8); $^{13}$C NMR ($CDCl_3$) 14.1, 30.9, 44.9 47.7, 57.0, 61.3, 66.1, 133.4, 134.0, 168.6; LRMS (EI) 256 ($M^+$, 2), 238 (12), 226(11), 166 (23), 164 (55), 151 (87), 114 (30), 79 (100); HRMS (EI) calcd for $C_{13}H_{20}H_5$ ($M^+$) 256.1311, found 256.1302.

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**Supporting Information Available:** Synthetic procedures and spectroscopic data for compounds **5**, **6**, **12**, **13**, **19**, **26**, **31**, **32**, **39**, and **40** are contained in the Supporting Information, along with $^1$H and $^{13}$C NMR spectra for compounds **8**, **21**, **22**, **23**, **24**, **25**, **28**, and **37**. This material is available free of charge via the Internet at http://pubs.acs.org.

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