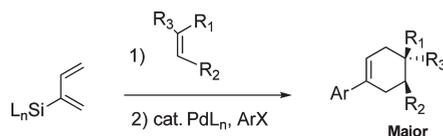# Preparation of 2-Silicon-Substituted 1,3-Dienes and Their Diels−Alder/Cross-Coupling Reactions

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2-Triethoxysilyl-substituted 1,3-butadiene has been prepared in 30-g quantities from chloroprene via a simple synthetic procedure. Silatrane- and catechol-substituted analogues of this main group element substituted diene were then prepared on a 10-g scale by ligand exchange and characterized by X-ray crystallography in addition to standard spectroscopic techniques. 2-Dimethylphenylsilyl-1,3-butadiene has also been prepared from chloroprene on an 8-g scale. Diels−Alder reactions of these dienes are reported as well as subsequent TBAF-assisted/Pd-catalyzed Hiyama cross-coupling reactions of those Diels−Alder adducts. Silicon-substituted cycloadducts and cross-coupled products were also characterized by NMR spectroscopy and, in two cases, by X-ray crystallography.

Introduction

Reports of main group element substituted 1,3-dienes and their reaction chemistry are not widespread in organic chemistry. In 2008, we published a review which covered boron- and silicon-substituted diene preparation and reaction chemistry up through 2007.[1] In general, reports of 2-trialkylsilyl-substituted 1,3-dienes[2] are 3- to 4-fold less frequent than their 1-substituted counterparts, and reports of 2-trialkoxysilyl-1,3-dienes are rarer still. We found a report of the use of the Ganem and Batt protocol[3] to make 2-trimethoxysilyl- and 2-triethoxysilyl-1,3-butadiene in 1984[4] and then a report of the polymerization of these materials in 1989.[5] There are a few other reports of some chemistry of 2-silyl-substituted 1,3-dienes.[6,7] Given the

known propensity of trialkoxysilyl aryls and alkenyls to participate in fluoride-assisted, metal-catalyzed cross-coupling reactions,[8] we felt that an easily accessible preparation of 2-trialkoxysilyl 1,3-dienes would be subsequently useful for tandem Diels−Alder/cross-coupling chemistry. We reported our initial studies in this area in 2007[9] and in the work that follows we provide more details of our subsequent work in this area of chemistry. Roush's group has also independently reported related intramolecular Diels−Alder chemistry of silicon substituted dienes and dienophiles.[10,11]

Results and Discussion

2-Trialkoxysilyl-Substituted 1,3-Diene Preparation and Characterization. 2-Triethoxysilyl-1,3-butadiene (**2**) was prepared in high yield by the nucleophilic addition of 1,3-butadienyl-2-magnesium chloride (generated in situ from chloroprene (**1**) and Mg) to triethoxysilyl chloride.[5,12] The title compound (**2**) was isolated as a colorless liquid after distillation under reduced pressure. This compound slowly polymerized on standing at room temperature over a period

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of 10−15 days but is quite stable at low temperature (−20 °C). In practice, for the larger scale ligand-exchange reactions we report here, we made this diene on ∼30 g scale and used it subsequently at ∼90% purity (contained ∼10% residual reaction solvent). 2-Triethoxysilyl-1,3-butadiene (**2**) can be used in ligand-exchange reactions to make other siloxy dienes (**3**, **4**) as air-stable crystalline solids, and here we report their preparation on a 10- to 15-g scale. Alcoholysis of compound **2** with triethanolamine in the presence of a catalytic amount of KOH resulted in the formation of (buta-1,3-dien-2-yl)silatrane (**3**) as a white solid. Treatment of **2** with catechol in the presence of KOH yielded potassium [bis(1,2-benzenediolato)-1,3-butadien-2-yl]silicate (**4**) as a white amorphous powder. At room temperature, compounds **3** and **4** show no signs of decomposition over a period of months.

We also used the same general synthetic sequence which provided compound **2** to produce a 2-dimethylphenylsilyl-substituted diene (**5**) in 97% yield on an 8-g scale. This diene is a liquid rather than the solid forms of **3** and **4** so it has some practical disadvantages compared to them. However, we wanted to compare a 2-alkyl- or arylsilyl-substituted diene to these 2-trialkoxysilyl dienes in Diels−Alder chemistry. All of the silyl butadienes (**2−5**) (Scheme 1) were structurally characterized by 1D and 2D NMR techniques, and compounds **3** and **4** were also characterized by X-ray crystallography.[6]

SCHEME 1
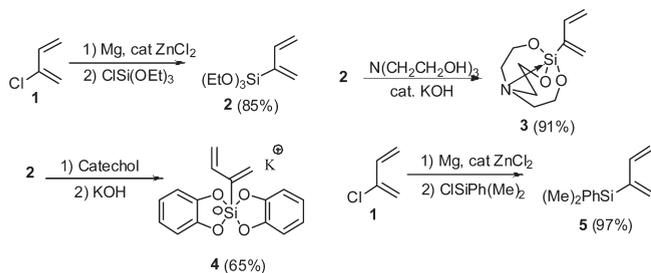
Diels−Alder Reactions. We initially compared dienes **2−5** in reactions with N-phenylmaleimide. We found that while the 2-triethoxysilyl diene (**2**) showed only a 2% conversion to cycloadduct **6** by ^{1}H NMR after 30 min at 25 °C in THF, the silatrane (**3**) and catechol containing dienes (**4**) showed complete conversion to cycloadducts **7** and **8** under the same conditions by ^{1}H NMR, and the cycloadducts were subsequently isolated in almost quantitative yield (Scheme 2). The 2-dimethylphenylsilyl diene (**5**) proved unreactive at 25 °C;

SCHEME 2
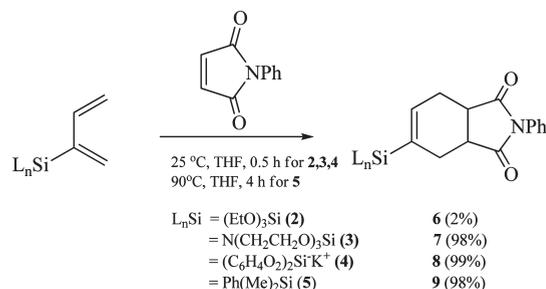
however, we isolated an almost quantitative yield of cycloadduct **9** from the reaction after heating in a sealed tube at 90 °C for 4 h.

Cycloadduct **8** was also characterized by X-ray crystallography (for details, see the Supporting Information). The Si−sp^{2}C bond length (Si(1)−C(13)) in this compound (1.876(4) Å) was slightly shorter than what we had seen in the starting diene (**4**) (1.889(5) Å).[9] In this cycloadduct, as in the original diene (**4**), the O−Si−O bond angles between adjacent oxygens are all in the 85−88° range. The overall geometry around silicon here is a significantly distorted square-based pyramid as can be seen from the O(4)−Si−O(1) and O(3)−Si−O(2) bond angles of 133.91(15) and 163.90(15)°, respectively. For comparison, these same bond angles in diene **4** were 136.48(15) and 162.32(16)°.[13]

Next, we wanted to get an idea of the relative reactivity of the most reactive silicon substituted dienes (**3** or **4**) in comparison to known, reactive dienes such as Danishefsky's diene (1-methoxy-3-trimethylsiloxy-1,3-butadiene).[14] We found that silatrane diene (**3**) reacted with N-phenylmaleimide at 0 °C with a k_{obs} of 3.7×10^{-2} min^{-1} and $t_{1/2}$ of 18.8 min whereas Danishefsky's diene reacted under identical conditions with a k_{obs} of 2.1×10^{-2} min^{-1} and a $t_{1/2}$ of 33 min. This data suggests the silatrane diene (**3**) is almost twice as reactive as Danishefsky's diene.

Single point energy, semiempirical (AM1) calculations of HOMO energies for a number of dienes while constraining the 1,3-diene dihedral angles to 0°, were also performed using SPARTAN 2.0. 1,3-Butadiene, 2-methoxybutadiene, and Danishefsky's diene have HOMO energies of −9.35, −9.09, and −8.82 eV respectively. Dienes **2**, **3**, and **4** have HOMO energies of −9.21, −7.87, and −5.04 eV respectively. These energies are consistent with our observations that **2** is less reactive than Danishefsky's diene, where **3** is more reactive than Danishefsky's diene, and diene **3** is less reactive than diene **4**.

SCHEME 3
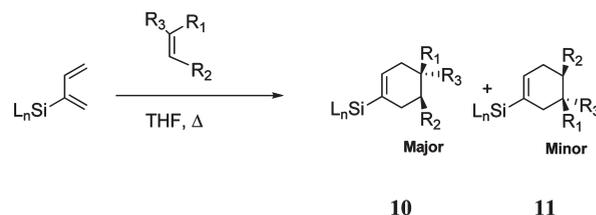
Additional Diels−Alder reactions with symmetrical and unsymmetrical dienophiles were then performed to assess any differences in rate or regioselectivity of cycloaddition reactions. The silatrane substituted diene (**3**) produced a 2.0:1 mixture of para:meta regioisomers (**10a:11a**) in 78% isolated yield after heating to 120 °C in THF for 48 h with citraconic anhydride (Scheme 3, Table 1, entry a). The catechol silane substituted diene (**4**) reacted under slightly milder conditions (90 °C for 36 h) to produce a 4.8:1 mixture of **10b:11b** with this same dienophile in 78% isolated yield (Table 1, entry b). The aforementioned general trend of the bis catechol silyl diene (**4**) being slightly more reactive than

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TABLE 1. Diels−Alder Reactions

entry	L_n	R_1	R_2	R_3	temp (°C)	time (h)	**10:11**	% yield
a)	$N(CH_2CH_2O)_3$	$-C(O)-$	$-OC(O)-$	Me	120	48	2.0:1	78
b)	$(C_6H_4O_2)_2K^+$	$-C(O)-$	$-OC(O)-$	Me	90	36	4.8:1	78
c)	$N(CH_2CH_2O)_3$	CO_2Et	H	H	150	90	4.0:1	99
d)	$(C_6H_4O_2)_2K^+$	CO_2Et	H	H	90	28	3.6:1	94
e)	$N(CH_2CH_2O)_3$	CO_2Et	CO_2Et	H	150	110	NA	73
f)	$(C_6H_4O_2)_2K^+$	CO_2Et	CO_2Et	H	90	29	NA	70

SCHEME 4
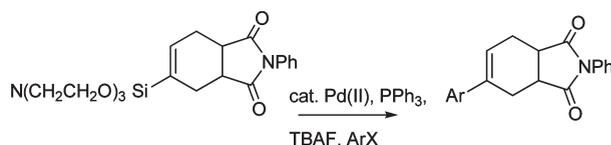
ArX = iodobenzene, 84%, **12**
ArX = 2-iodoanisole, 57%, **13**
ArX = 3-iodoanisole, 88%, **14**
ArX = 4-iodoanisole, 68%, **15**
ArX = 2-fluoro-iodobenzene, 84%, **16**
ArX = 2-trifluoromethyl-iodobenzene, 75%, **17**
ArX = 3-trifluoromethyl-iodobenzene, 90%, **18**
ArX = 4-trifluoromethyl-iodobenzene, 89%, **19**
ArX = 3-iodobenzonitrile, 54%, **20**
ArX = 2-iodothiophene, 51%, **21**

the silatrane diene (**3**) was noted for the two other dienophiles tried here as well (compare Table 1 entries c and d as well as e and f). These dienes are similar in reactivity and regioselectivity to previously reported thermal Diels−Alder reactions of 2-phenyl-1,3-butadiene.[13,15] This diene is known to react with di- and trisubstituted dienophiles at 80−110 °C for 24−36 h. The synthetic advantage here is that one cycloadduct can be converted to a variety of aryl substituted cycloadducts via the cross-coupling chemistry described below.

Major and minor isomer regiochemistry assignments for **10a** and **11a** were originally performed using NOESY data, and this assignment was subsequently confirmed for the major isomer (**10a**) by X-ray crystallography.[9] The regiochemistry of the major isomer from the reactions with ethyl acrylate (Supporting Information, **10c** and **10d**) was confirmed by the presence of a strong HMBC cross peak between C2 and H4 of the major cycloadduct.

Diels−Alder/Cross Coupling. Recent papers from the Lee group[16] as well as from Yorimitsu, Oshima, et al.[17] have demonstrated that it is possible to effect palladium-catalyzed cross couplings of 1,3-butadienyl species. We have demonstrated that it is possible to effect Hiyama cross-coupling reactions of silicon-substituted Diels−Alder cycloadducts as well. Silatrane-substituted cycloadduct (**7**) was treated with a wide variety of aryl iodides substituted with electron-donating and electron-withdrawing substituents in the presence of $Pd(II)$, PPh_3, and TBAF (Scheme 4). Most of these cross-coupling reactions proceeded in excellent yield with the exception of the reactions with 2-iodoanisole (**13**), 3-iodo-

benzonitrile (**20**), and 2-iodothiophene (**21**), which produced cross-coupled cycloadducts in more moderate yields around 50−60%. All these cross-coupled products were characterized by ^1H and ^{13}C NMR techniques, and the cross-coupled product from 2-fluoroiodobenzene (**16**) was also characterized by X-ray crystallography (for details, see the Supporting Information).

However, when we tried these cross-coupling conditions with a biscatechol silyl substituted cycloadduct such as **10d** and iodobenzene, we isolated the desired cross-coupled product (**22d**) as well as the homocoupled product, biphenyl, in a 1:1 ratio. We subsequently optimized cross-coupling conditions to the use of $[Pd(allyl)Cl]_2$, S-Phos, and KF in DMF for the biscatechol silyl substituted cycloadduct **10d** and then used these optimized conditions for cross coupling cycloadducts **10c−f** to produce cross-coupled products **22c−f** Scheme 5).

SCHEME 5
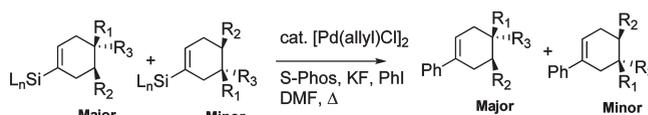
10-11 c-f

22c	70%,	3.8:1
22d	70%,	3.9:1
22e	66%	
22f	35%	

Conclusions

In summary, we have prepared new, stable, crystalline silyl-substituted dienes in high yield and find that they readily participate in Diels−Alder/cross-coupling tandem reactions. We will report the transition-metal-catalyzed reaction chemistry of these main group element substituted dienes in much more detail in due course.

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(16) Kim, S.; Seomoon, D.; Lee, P. H. *Chem. Commun.* **2009**, 1873–1875.
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Experimental Section

General experimental details can be found in the preliminary communication on this work.[9] Silatrane containing compounds should be handled with care with appropriate skin protection inside a fume hood.[18] For all $^1H-^1H$ 2-D spectra, the spectral width was 4432.6 Hz. 2-D $^1H-^1H$ gradient selected COSY and NOESY spectra were acquired with 2048 complex points in t_2, 256 points in t_1, and 16 transients with a pulse repetition delay of 1.5 s. The 2-D NOESY spectra were collected with a mixing time of $t_m = 600$ ms. Data sets were multiplied with a 90° phase shifted squared-sinebell apodization function and zero-filled to 512 × 512 data points before Fourier transformation.

Large-Scale Synthesis of Buta-1,3-dien-2-yltriethoxysilane 2. To a dried 250-mL two-neck round-bottom flask equipped with a stir bar, reflux condenser, and addition funnel and charged with magnesium turnings (7.271 g, 0.299 mol) was added 1,2-dibromoethane (1.8 mL, 0.02 mol) dissolved in THF (25 mL). After 5 min, anhydrous zinc chloride (1.413 g, 0.010 mol) dissolved in THF (10 mL) was added dropwise, followed by additional THF (35 mL). The reaction mixture was then brought to reflux, and a solution of chloroprene (**1**) in 50% xylenes (36.5 mL, 0.207 mol) and 1,2-dibromoethane (4.0 mL, 0.05 mol) in THF (40 mL) was added dropwise over 30 min. The reaction mixture was refluxed for an additional 45 min and then cooled to room temperature. The mixture was then transferred via double-ended needle into a 500-mL round-bottom flask equipped with a stir bar and containing triethoxy-chlorosilane (36.0 mL, 0.180 mol) dissolved in THF (125 mL) and brought to reflux. After 1 h, the reaction was cooled to room temperature and the solution poured into a separatory funnel containing 0.5 M HCl (150 mL). The organic components were extracted with pentane (2 × 100 mL) and washed successively with 0.5 M HCl (250 mL) and distilled H₂O (350 mL). The organic extracts were then dried over MgSO₄ and concentrated by rotary evaporation. The resulting light yellow liquid (52.703 g) contains buta-1,3-dien-2-yltriethoxysilane (**2**) (33.71 g, 0.156 mol, 86.6% by ^1H NMR integration) (identical by spectroscopic comparison to material we have reported previously)[9] in xylenes and residual THF. This crude mixture was used in the syntheses described below without further purification.

Large-Scale Synthesis of (Buta-1,3-dien2-yl)silatrane 3. To a dried 500-mL round-bottom flask equipped with a stir bar and reflux condenser were added buta-1,3-dien-2-yltriethoxysilane (**2**) in xylenes (29.85 g) described above (containing the diene (19.28 g, 0.089 mol) by ^1H NMR integrations), triethanolamine (10.51 g, 0.070 mol), and a catalytic amount of KOH (0.439 g, 7.825 mmol), and the mixture was dissolved in THF (250 mL). The solution was brought to reflux and, after 2.5 h, cooled to room temperature and condensed by rotary evaporation to remove approximately half of the solvent. The product was then precipitated with pentane (100 mL) and collected by vacuum filtration followed by drying overnight under high vacuum to yield a white, fluffy solid (13.34 g, 0.059 mol, 83.4%) identical by spectroscopic comparison to material we have reported previously.[9]

Large-Scale Synthesis of Potassium Bis(5,5′-benzenediolato)-(1,3-butadien-2-yl)silicate (4). To a dried 500-mL round-bottom flask equipped with a stir bar and reflux condenser was added catechol (10.21 g, 0.092 mol), and the mixture was dissolved in THF (125 mL). Buta-1,3-dien-2-yltriethoxysilane (**2**) in xylenes (18.18 g) described above (containing the diene (11.74 g, 0.054 mol) by ^1H NMR integrations) and KOH (2.66 g, 0.047 mol) were then added, and the solution

was brought to reflux. After 2.5 h, reflux was stopped, and the hot solution was gravity filtered. Precipitation with pentane (50 mL) yielded a white solid which was collected and dried by vacuum filtration. The white powder (11.89 g, 0.035 mol, 76.3%) was recrystallized by dissolving in a minimum quantity of hot THF, cooling to room temperature, and cooling at −40 °C for 1 h. The resulting white flaky solid was collected and dried by vacuum filtration followed by drying overnight under high vacuum (8.49 g, 0.025 mol, 54.5%).

Synthesis of (Buta-1,3-dien-2-yl)dimethyl(phenyl)silane (5). General Main Group Diene Synthesis Procedure. An oven-dried, 100 mL, two-neck, round-bottom flask equipped with a magnetic stir bar, addition funnel, and reflux condenser was charged with magnesium (1.6 equiv) followed by the addition of dibromoethane (11.0 mol %) in THF (5 mL). After the mixture was stirred for ~ca. 5 min (initiation of magnesium activation can be noticed by its silver color and ethane gas liberation), 3.0 mol % of anhydrous ZnCl₂ in THF (5 mL) was added. This mixture was added with additional THF (30 mL) and resulted in a whitish-gray solution which was brought to gentle reflux over a period of 15 min. Chloroprene (in 50% xylenes) (1.0 equiv) and dibromoethane (23.0 mol %) in THF (25 mL) were added dropwise to the refluxing reaction mixture over 30 min. After the addition, refluxing was continued for another 45 min. The greenish-gray Grignard solution was transferred by canula into a 250-mL, one-neck, round-bottom flask containing triethoxychlorosilane (0.95 equiv) in THF (25 mL) at room temperature. The reaction mixture was refluxed (1 h), poured into 0.5 M HCl solution (100 mL), and extracted with pentane (2 × 75 mL). The combined colorless, clear organic layers were washed successively with 0.5 M HCl (75 mL) and water (2 × 100 mL). After drying over MgSO₄, the solvent was removed under reduced pressure to yield the 2-substituted silyl diene with xylenes as a colorless liquid. This compound was subjected to fractional vacuum distillation to remove xylenes and then purified by flash chromatography. Chloroprene (**1**) (4.575 g, 51.69 mmol) and phenyldimethylchlorosilane (8.034 g, 47.06 mmol) were used according to the procedure above to yield a light yellow crude product (14.38 g) as a mixture of diene and xylenes. The crude product was subjected to fractional distillation at reduced pressure (20 mm, 45 °C) to produce a brown liquid, which was further purified by flash chromatography (100% pentanes) to yield the title compound as a light yellow liquid in pure form (**5**) (8.36 g, 44.39 mmol, 96.8%): R_f 0.63 (100% pentanes); ^1H NMR (500 MHz, CDCl₃) δ 7.49−7.55 (m, 2H), 7.31−7.37 (m, 3H), 6.46 (dd, J = 17.7, 10.9 Hz, 1H), 5.88 (d, J = 3.2 Hz, 1H), 5.51 (d, J = 3.2 Hz, 1H), 5.10 (d, J = 17.7 Hz, 1H), 5.00 (d, J = 10.9 Hz, 1H), 0.43 (s, 9H); ^{13}C NMR (75 MHz, CDCl₃) δ 147.6, 141.1, 138.2, 133.9, 130.4, 129.0, 127.8, −2.3; HRMS calcd for C₁₂H₁₆Si (M⁺) 188.1021, found 188.1020.

Synthesis of 3a,4,7,7a-Tetrahydro-5-[dimethyl(phenyl)silyl]-2-phenyl-2H-isoindole-1,3-dione (9). Diene **5** (0.302 g, 1.603 mmol) and N-phenylmaleimide (0.103 g, 0.595 mmol) were dissolved in THF (5 mL) in a sealed tube and purged with N₂. After being heated for 4 h at 90 °C, the reaction mixture was filtered through a cotton plug, and volatiles were removed by rotary evaporation. The resulting yellow residue was purified by flash chromatography with the excess diene eluting as a light yellow solution (0.151 g, 0.802 mmol, 50% recovery: R_f 0.84, pentane/diethyl ether, 1:1) followed by the cycloadduct **9** which after solvent removal was isolated as a colorless, clear viscous liquid (0.204 g, 0.564 mmol, 97.6%): R_f 0.29 (pentane/diethyl ether, 1:1); ^1H NMR (500 MHz, CDCl₃) δ 7.41−7.54 (m, 4H), 7.29−7.41 (m, 4H), 7.09−7.20 (m, 2H), 6.34 (p, J = 3.2 Hz, 1H), 3.18−3.30 (m, 2H), 2.71−2.88 (m, 2H), 2.22−2.36

(18) Seganish, W. M.; DeShong, P. *J. Org. Chem.* **2004**, *69*, 6790−6795.

(m, 2H), 0.36 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 179.1, 178.7, 140.7, 138.4, 137.0, 133.9, 132.0, 129.2, 129.0, 128.4, 127.8, 126.3, 39.3, 39.2, 26.4, 25.0, -3.88, -3.89; HRMS calcd for C$_{22}$H$_{23}$NO$_2$Si (M$^+$) 361.1498, found 361.1490. Anal. Calcd for C$_{22}$H$_{23}$NO$_2$Si: C, 73.10; H, 6.42. Found: C, 72.63; H, 6.38.

Synthesis of Potassium Bis(7,7′-benzenediolato)-[4-(ethoxycarbonyl)cyclohex-1-enyl]silicate (10d) and Potassium Bis(7,7′-benzenediolato)[3-(ethoxycarbonyl)cyclohex-1-enyl)-silicate (11d).

Major Isomer (10d)   **Minor Isomer (11d)**
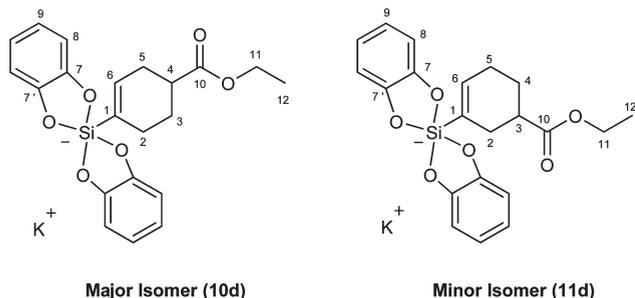
Diene (**4**) (0.500 g, 1.48 mmol) and ethyl acrylate (245 μL, 2.25 mmol) were dissolved in THF (20 mL) in a sealed tube and purged with N$_2$. After being stirred for 28 h at 90 °C, the reaction vessel was cooled to room temperature, and the solvent was removed by rotary evaporation. Additional drying under vacuum overnight to remove excess ethyl acrylate produced cycloadducts **10d** and **11d** as a light brown fluffy powder (0.610 g, 1.39 mmol, 94.1%): mp 239 °C dec. Major isomer (**10d**): ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.54−6.52 (m, 4H), 6.45−6.43 (m, 4H), 5.85 (m, 1H), 3.99 (q, J = 6.9 Hz, 2H), 2.31−2.25 (m, 1H), 2.09−1.99 (m, 3H), 1.94−1.83 (m, 1H), 1.77−1.70 (m, 1H), 1.32−1.24 (m, 1H), 1.12 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 175.3, 150.7, 150.6, 139.8, 131.8, 117.2, 117.1, 109.5, 109.4, 59.6, 38.6, 28.4, 27.3, 25.4, 14.0; HRMS [M+K]$^+$ calcd for C$_{21}$H$_{21}$KO$_6$Si 475.0382, found 475.0382. Regioisomer ratio 3.6:1.0 (based on ^{1}H NMR integrations).

Synthesis of [4-(Ethoxycarbonyl)cyclohex-1-enyl]silatrane (10c) and [3-(Ethoxycarbonyl)cyclohex-1-enyl]silatrane (11c).

Major Isomer (10c)   **Minor Isomer (11c)**
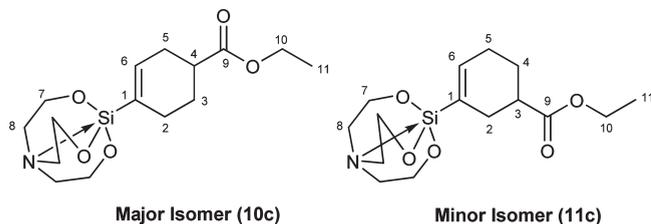
Diene **3** (0.520 g, 2.28 mmol) and ethyl acrylate (360 μL, 3.30 mmol) were dissolved in THF (20 mL) in a sealed tube and purged with N$_2$. After being stirred for 90 h at 150 °C, the reaction vessel was cooled to room temperature and the solution condensed by rotary evaporation. Additional drying under vacuum overnight to remove excess ethyl acrylate led to the formation of the cycloadducts **10c** and **11c** as a white, flaky solid (0.745 g, 2.27 mmol, 99.4%): mp 77−80 °C. Major isomer **10c**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.24 (m, 1H), 4.10 (q, J = 7.0 Hz, 2H), 3.80 (t, J = 5.8 Hz, 6H), 2.82 (t, J = 5.9 Hz, 6H), 2.52−2.44 (m, 1H), 2.36−2.23 (m, 3H), 2.20−2.10 (m, 1H), 2.00−1.91 (m, 1H), 1.66−1.54 (m, 1H), 1.23 (t, J = 7.0, 4H); ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 176.8, 138.9, 132.6, 60.1, 58.0, 51.2, 39.7, 29.0, 27.7, 26.0, 14.4. Minor isomer **11c**, diagnostic peaks: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.74 (t, J = 5.7 Hz, 6H), 2.78 (t, J =

5.7 Hz, 6H); ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 177.0, 137.7, 133.7, 57.9, 40.3, 30.6, 26.3, 25.2, 14.4; HRMS [M + Na]$^+$ calcd for C$_{15}$H$_{25}$NO$_5$Si + Na 350.1400, found 350.1394. Regioisomer ratio 4.0:1.0 (based on GC integrations). Anal. Calcd for C$_{15}$H$_{25}$NO$_5$Si: C, 55.02; H, 7.70. Found: C, 55.50; H, 8.14.

Synthesis of Potassium Bis(7,7′-benzenediolato)[3,4-bis-(ethoxyxarbonyl)cyclohex-1-enyl]silicate (10f). Diene **4** (0.98 g, 2.91 mmol) and diethyl maleate (731 μL, 4.50 mmol) were dissolved in THF (40 mL) and used in the cycloaddition reaction according to the general procedure. After being stirred for 29 h at 90 °C, the reaction vessel was cooled to room temperature and the solution condensed by rotary evaporation. Additional drying under high vacuum resulted in a dark brown flaky solid (1.53 g). Based on ^{1}H NMR integrations, this product contains the title compound **10f** (1.04 g, 2.04 mmol, 70.3%) and excess diethyl maleate. **10f**: ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.54−6.52 (m, 4H), 6.46−6.43 (m, 4H), 5.83 (m, 1H), 3.97−3.87 (m, 4H), 2.81−2.74 (m, 2H), 2.45−2.37 (m, 1H), 2.35−2.27 (m, 1H), 2.26−2.12 (m, 2H), 1.06 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125.7 MHz, DMSO-d_6) δ 173.0, 172.9, 150.6, 150.5, 137.8, 131.8, 117.1, 117.1, 109.5, 109.4, 59.6, 59.4, 38.5, 28.6, 26.4, 13.8, 13.8. This crude product was used as is for the cross-coupling reactions described below.

Synthesis of [3,4-Bis(ethoxycarbonyl)cyclohex-1-enyl]silatrane (10e). Diene **3** (0.546 g, 2.40 mmol) and diethyl maleate (414 μL, 2.55 mmol) were dissolved in THF (25 mL) in a sealed tube purged with N$_2$. After being stirred for 110 h at 150 °C, the reaction vessel was cooled to room temperature and the solution condensed by rotary evaporation. Additional drying under reduced pressure resulted in a light yellow residue (0.995 g). On the basis of ^{1}H NMR integrations, this product contains the title compound **10e** (0.695 g, 1.74 mmol, 72.5%) and excess diethyl maleate. This crude product was used as is for the cross-coupling reactions described below.

General Procedure for the Cross-Coupling Reactions of Cycloadduct 7. Diels−Alder cycloadduct (1.0 equiv), Pd(OAc)$_2$ (10 mol %), PPh$_3$ (20 mol %), and aryl halide (1.2 equiv) were taken up in a sealed tube charged with a micro stir bar and DMF (5 mL). This transparent yellow reaction mixture was stirred followed by addition of TBAF (1.2 equiv) dissolved in THF (0.5 mL). The reaction mixture turned dark brown, was purged with N$_2$, and was heated in an oil bath for 2 h at 90 °C. During the course of the reaction, the reaction mixture turned to dark black, and the formation of active palladium species (Pd^{II} → Pd^0) was also noticed as the catalyst slowly turned to a black solid. The reaction mixture was then quenched with water (50 mL) and extracted with Et$_2$O (4 × 30 mL). The combined organic layers were again washed with water (2×75 mL) and dried over MgSO$_4$, and volatiles were removed by rotary evaporation. The resulting cross-coupled cycloadduct residue was purified by flash chromatography.

Synthesis of (3aR,7aS)-5-(2-Methoxyphenyl)-2-phenyl-3a,4,-7,7a-tetrahydro-1H-isoindole-1,3(2H)-dione (13). Cycloadduct **7** (0.101 g, 0.252 mmol), Pd(OAc)$_2$ (0.020 g, 0.034 mmol), PPh$_3$ (0.024 g, 0.092 mmol), 2-iodoanisole (0.084 g, 0.359 mmol), and TBAF (0.110 g, 0.349 mmol) were used according to the general procedure mentioned above. The resulting brown oily crude reaction mixture was subjected to flash chromatography to yield the cross-coupled product **13** as a brownish-yellow crystalline solid (0.048 g, 0.144 mmol, 57.1%): mp 128−132 °C dec; R_f 0.42 (diethyl ether/hexanes, 2:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (t, J = 8.1 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.18−7.25 (m, 3H), 7.08 (d, J = 7.5 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.03 (p, J = 3.4 Hz, 1H), 3.67 (s, 3H), 3.36 (ddd, J = 9.1, 7.7, 2.4 Hz, 1H), 3.32 (ddd, J = 9.1, 6.7, 2.6 Hz, 1H), 3.07 (dd, J = 15.4, 2.4 Hz, 1H), 2.94 (ddd, J = 15.4, 6.7, 2.6 Hz, 1H), 2.63 (ddt, J = 15.4, 7.7,

2.4 Hz, 1H), 2.37−2.50 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 179.2, 178.8, 156.5, 139.5, 132.3, 130.9, 129.2, 129.0, 128.8, 128.5, 126.7, 125.1, 120.6, 110.5, 54.9, 40.0, 39.8, 28.9, 24.5; HRMS calcd for C$_{21}$H$_{19}$NO$_3$Cs (M + Cs$^+$) 466.0419, found 466.0430.

Synthesis of (3a*R*,7a*S*)-5-(3-Methoxyphenyl)-2-phenyl-3a,-4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (14). Cycloadduct **7** (0.100 g, 0.250 mmol), Pd(OAc)$_2$ (0.028 g, 0.047 mmol), PPh$_3$ (0.024 g, 0.088 mmol), 3-iodoanisole (0.126 g, 0.538 mmol), and TBAF (0.128 g, 0.406 mmol) were used according to the general procedure mentioned above. The resulting brown oily crude reaction mixture was subjected to flash chromatography to yield the cross-coupled product **14** as a brown oil (0.073 g, 0.219 mmol, 87.7%): R_f 0.15 (diethyl ether/hexanes, 2:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 (at, *J* = 8.1 Hz, 2H), 7.35 (at, *J* = 8.1 Hz, 1H), 7.19−7.25 (m, 1H), 7.16 (ad, *J* = 8.1 Hz, 2H), 6.91−7.02 (m, 1H), 6.90 (at, *J* = 2.1 Hz, 1H), 6.81 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.22 (p, *J* = 3.4 Hz, 1H), 3.80 (s, 3H), 3.44 (ddd, *J* = 9.4, 7.0, 2.5 Hz, 1H), 3.34 (ddd, *J* = 9.4, 7.2, 2.5 Hz, 1H), 3.24 (dd, *J* = 15.3, 2.5 Hz, 1H), 2.93 (ddd, *J* = 15.3, 7.0, 2.5 Hz, 1H), 2.64 (ddt, *J* = 15.3, 7.0, 2.3 Hz, 1H), 2.37−2.51 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 179.0, 178.8, 159.8, 141.9, 140.0, 132.0, 129.5, 129.1, 128.6, 126.4, 123.4, 118.0, 113.1, 111.2, 55.5, 40.1, 39.5, 27.7, 25.3; HRMS calcd for C$_{21}$H$_{19}$NO$_3$Cs (M + Cs$^+$) 466.0419, found 466.0444.

Synthesis of (3a*R*,7a*S*)-5-(2-Fluorophenyl)-2-phenyl-3a,4,7,-7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (16). Cycloadduct **7** (0.135 g, 0.337 mmol), Pd(OAc)$_2$ (0.023 g, 0.039 mmol), PPh$_3$ (0.024 g, 0.092 mmol), 1-iodo-2-fluorobenzene (0.126 g, 0.568 mmol), and TBAF (0.132 g, 0.418 mmol) were used according to the general procedure mentioned above. The resulting brown oily crude reaction mixture was subjected to flash chromatography to yield the cross-coupled product **16** as a light-yellow, amorphous solid (0.091 g, 0.283 mmol, 84.3%): mp (neat) 110−112 °C; R_f 0.27 (diethyl ether/hexanes, 1:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.44 (t, *J* = 7.6 Hz, 2H), 7.37 (tt, *J* = 7.6, 1.3 Hz, 1H), 7.15−7.25 (m, 4H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 7.04 (ddd, *J* = 10.7, 8.2, 1.0 Hz, 1H), 6.21 (p, *J* = 3.2 Hz, 1H), 3.41 (ddd, *J* = 9.5, 6.9, 2.5 Hz, 1H), 3.35 (ddd, *J* = 9.5, 6.9, 2.5 Hz, 1H), 3.16 (dd, *J* = 15.5, 1.6 Hz, 1H), 2.94 (ddd, *J* = 15.5, 6.9, 2.5 Hz, 1H), 2.73 (ddq, *J* = 15.5, 7.3, 1.3 Hz, 1H), 2.47 (dddd, *J* = 15.5, 6.6, 3.5, 2.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 178.9, 178.7, 159.7 (d, $^1J_{C-F}$ = 247.7 Hz), 135.3, 132.0, 129.1, 128.99 (d, $^3J_{C-F}$ = 5.7 Hz), 128.91 (d, $^3J_{C-F}$ = 5.7 Hz), 128.79, 128.6, 127.2 (d, $^4J_{C-F}$ = 3.4 Hz), 126.4, 124.2 (d, $^4J_{C-F}$ = 3.4 Hz), 115.9 (d, $^2J_{C-F}$ = 22.4 Hz), 40.0, 39.3, 28.6 (d, $^4J_{C-F}$ = 2.3 Hz), 25.0; ^{19}F NMR (300 MHz, CDCl$_3$) δ −116.3; HRMS calcd for C$_{20}$H$_{16}$FNO$_2$Cs (M + Cs$^+$) 454.0219, found 454.0238. Anal. Calcd for C$_{20}$H$_{16}$FNO$_2$: C, 74.75; H, 5.02. Found: C, 74.47; H, 5.08.

Synthesis of (3a*R*,7a*S*)-2-Phenyl-5-(2-(trifluoromethyl)phe-nyl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (17). Cycloadduct **7** (0.158 g, 0.394 mmol), Pd(OAc)$_2$ (0.022 g, 0.037 mmol), PPh$_3$ (0.020 g, 0.076 mmol), 1-iodo-2-(trifluor-omethyl)benzene (0.122 g, 0.448 mmol), and TBAF (0.126 g, 0.399 mmol) were used according to the general procedure mentioned above. The resulting brown oily crude reaction mixture was subjected to flash chromatography to yield the cross-coupled product **17** as a yellow-brown liquid (0.11 g, 0.296 mmol, 75.1%): R_f 0.68 (diethyl ether/hexanes, 1:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.43−7.54 (m, 3H), 7.40 (tt, *J* = 7.6, 2.0 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.29 (dt, *J* = 7.6, 2.0 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 5.95 (p, *J* = 3.4 Hz, 1H), 3.40 (ddd, *J* = 9.4, 7.0, 2.6 Hz, 1H), 3.39 (ddd, *J* = 9.4, 7.0, 2.6 Hz, 1H), 2.81−2.98 (m, 2H), 2.66−2.80 (m, 1H), 2.40−2.57 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 179.0, 178.8, 141.2 (q, $^3J_{C-F}$ = 2.3 Hz), 138.4, 132.0, 131.8, 129.9, 129.1, 128.6, 127.8 (q, $^2J_{C-F}$ = 29.9 Hz), 127.3, 126.5 (q, $^5J_{C-F}$ = 1.7 Hz),

126.3, 126.1 (q, $^3J_{C-F}$ = 5.2 Hz), 124.2 (q, $^1J_{C-F}$ = 273.6 Hz), 39.9, 38.8, 29.6 (q, $^5J_{C-F}$ = 1.7 Hz), 24.7; ^{19}F NMR (300 MHz, CDCl$_3$) δ −58.2; HRMS calcd for C$_{21}$H$_{16}$F$_3$NO$_2$Cs (M + Cs$^+$) 504.0187, found 504.0219.

Synthesis of (3a*R*,7a*S*)-2-Phenyl-5-(3-(trifluoromethyl)phe-nyl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (18). Cycloadduct **7** (0.100 g, 0.25 mmol), Pd(OAc)$_2$ (0.018 g, 0.030 mmol), PPh$_3$ (0.018 g, 0.069 mmol), 1-iodo-3-(trifluoromethyl)benzene (0.096 g, 0.353 mmol), and TBAF (0.092 g, 0.292 mmol) were used according to the general procedure mentioned above. The resulting brown oily crude reaction mixture was subjected to flash chromatography to yield the cross-coupled product **18** as a brown liquid (0.084 g, 0.226 mmol, 90.3%): R_f 0.16 (diethyl ether/hexanes, 1:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60 (s, 1H), 7.54 (d-overlapped, *J* = 7.9 Hz, 1H), 7.52 (d-overlapped, *J* = 8.1 Hz, 1H), 7.39−7.48 (m, 3H), 7.36 (att, *J* = 7.3, 1.4 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 2H), 6.30 (p, *J* = 3.5 Hz, 1H), 3.47 (ddd, *J* = 9.4, 6.9, 2.7 Hz, 1H), 3.37 (ddd, *J* = 9.4, 7.5, 2.5 Hz, 1H), 3.25 (dd, *J* = 15.4, 2.7 Hz, 1H), 2.97 (ddd, *J* = 15.6, 6.9, 2.5 Hz, 1H), 2.67 (ddt, *J* = 15.4, 6.9, 2.5 Hz, 1H), 2.47 (dddd, *J* = 15.6, 6.2, 3.7, 2.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 178.8, 178.6, 141.1, 138.9, 131.8, 131.0 (q, $^2J_{C-F}$ = 32.2 Hz), 129.13, 129.11, 128.7 (q, $^4J_{C-F}$ = 1.7 Hz), 128.6, 126.3, 125.0, 124.2 (q, $^3J_{C-F}$ = 4.0 Hz), 124.0 (q, $^1J_{C-F}$ = 273.0 Hz), 122.4 (q, $^3J_{C-F}$ = 4.0 Hz), 40.0, 39.2, 27.5, 25.3; ^{19}F NMR (300 MHz, CDCl$_3$) δ −63.2; HRMS calcd for C$_{21}$H$_{17}$F$_3$NO$_2$ (M + H)$^+$ 372.1211, found 372.1211.

Synthesis of (3a*R*,7a*S*)-2-Phenyl-5-(4-(trifluoromethyl)phe-nyl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (19). Cycloadduct **7** (0.099 g, 0.247 mmol), Pd(OAc)$_2$ (0.023 g, 0.039 mmol), PPh$_3$ (0.024 g, 0.092 mmol), 1-iodo-4-(trifluoromethyl)benzene (0.132 g, 0.485 mmol), and TBAF (0.098 g, 0.311 mmol) were used according to the general procedure mentioned above. The resulting brown oily crude reaction mixture was subjected to flash chromatography to yield the cross-coupled product **19** as a yellow-brown liquid (0.082 g, 0.221 mmol, 89.3%): R_f 0.35 (diethyl ether/hexanes, 2:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.31 (p, *J* = 3.4 Hz, 1H), 3.47 (ddd, *J* = 9.4, 6.7, 2.5 Hz, 1H), 3.38 (ddd, *J* = 9.4, 7.1, 2.3 Hz, 1H), 3.27 (dd, *J* = 15.3, 2.5 Hz, 1H), 2.99 (ddd, *J* = 15.6, 7.1, 2.3 Hz, 1H), 2.65 (ddt, *J* = 15.3, 6.7, 2.5 Hz, 1H), 2.37−2.54 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 178.8, 178.7, 143.7 (q, $^5J_{C-F}$ = 1.1 Hz), 139.1, 131.8, 129.5 (q, $^2J_{C-F}$ = 32.8 Hz), 129.1, 128.6, 126.3, 125.8, 125.5 (q, $^3J_{C-F}$ = 4.0 Hz), 125.4, 124.1 (q, $^1J_{C-F}$ = 271.8 Hz), 40.0, 39.2, 27.4, 25.3; ^{19}F NMR (300 MHz, CDCl$_3$) δ −63.0; HRMS calcd for C$_{21}$H$_{16}$F$_3$NO$_2$Cs (M + Cs$^+$) 504.0187, found 504.0222.

Synthesis of 3-[(3a*R*,7a*S*)-1,3-Dioxo-2-phenyl-2,3,3a,4,7,7a-hexahydro-1*H*-isoindol-5-yl]benzonitrile (20). Cycloadduct **7** (0.15 g, 0.375 mmol), Pd(OAc)$_2$ (0.027 g, 0.046 mmol), PPh$_3$ (0.024 g, 0.088 mmol), 3-iodobenzonitrile (0.118 g, 0.515 mmol), and TBAF (0.143 g, 0.453 mmol) were used according to the general procedure mentioned above. The resulting brown oily crude reaction mixture was subjected to flash chromatography to yield the cross-coupled product **20** as light yellow solid (0.066 g, 0.201 mmol, 53.7%): mp (neat) 157−159 °C; R_f 0.51 (100% diethyl ether); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (t, *J* = 1.5 Hz, 1H), 7.58 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.54 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.39−7.48 (m, 3H), 7.63 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.15 (app d, *J* = 7.4 Hz, 2H), 6.29 (p, *J* = 3.4 Hz, 1H), 3.48 (ddd, *J* = 9.4, 6.8, 2.5 Hz, 1H), 3.38 (ddd, *J* = 9.4, 7.6, 2.5 Hz, 1H), 3.22 (dd, *J* = 15.3, 2.5 Hz, 1H), 2.98 (ddd, *J* = 15.7, 7.0, 2.5 Hz, 1H), 2.64 (ddt, *J* = 15.3, 6.8, 2.5 Hz, 1H), 2.47 (dddd, *J* = 15.7, 7.6, 3.6, 2.5 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 178.7, 178.5, 141.4, 138.3, 131.8, 131.0, 129.8, 129.5, 129.2, 128.7, 126.3, 125.7, 118.7, 112.9, 40.0, 39.1, 27.2, 25.4; HRMS calcd for C$_{21}$H$_{16}$N$_2$O$_2$Cs (M + Cs$^+$) 461.0266, found 461.0280.

Synthesis of (3a*R*,7a*S*)-2-Phenyl-5-(thiophene-2-yl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (21). Cycloadduct 7 (0.15 g, 0.375 mmol), Pd(OAc)$_2$ (0.022 g, 0.037 mmol), PPh$_3$ (0.026 g, 0.099 mmol), 2-iodothiophene (0.126 g, 0.60 mmol), and TBAF (0.129 g, 0.409 mmol) were used according to the general procedure mentioned above. The oily crude reaction mixture was purified by flash chromatography to yield the cross-coupled product 21 as a brown oily substance (0.059 g, 0.191 mmol, 50.9%): R_f 0.22 (diethyl ether/hexanes, 1:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.30−7.47 (m, 3H), 7.10−7.22 (m, 3H), 7.05 (ad, *J* = 3.4 Hz, 1H), 6.97 (at, *J* = 4.3 Hz, 1H), 6.28 (p, *J* = 3.4 Hz, 1H), 3.40 (ddd, *J* = 9.6, 7.0, 2.8 Hz, 1H), 3.31 (ddd, *J* = 9.6, 7.0, 2.6 Hz, 1H), 3.22 (dd, *J* = 15.3, 2.8 Hz, 1H), 2.87 (ddd, *J* = 15.8, 7.0, 2.6 Hz, 1H), 2.67 (ddt, *J* = 15.3, 7.0, 2.3 Hz, 1H), 2.38−2.55 (m, 1H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 178.8, 178.4, 143.9, 133.3, 131.9, 129.0, 128.5, 127.5, 126.4, 124.2, 123.0, 121.4, 39.7, 39.3, 27.5, 24.8; HRMS calcd for C$_{18}$H$_{15}$NO$_2$SCs (M + Cs$^+$) 441.9878, found 441.9891.

General Procedure for Optimized Cross-Coupling Reactions of 10−11(c−f). Diels−Alder cycloadduct (compounds 10−11-(c−f)), [Pd(allyl)Cl]$_2$, and 2-dicyclohexylphosphino-2′,6′-dimethoxy-1,1′-biphenyl (S-Phos) were taken up in a single-neck round-bottom flask fitted with a reflux condenser and dissolved in DMF. After the solution was purged with argon for 5 min, iodobenzene and the fluoride source were added, and the reaction was heated to 100 °C. After the specified time, the reaction was quenched with distilled water (100 mL) and extracted with Et$_2$O (4 × 75 mL). The combined organic layers were washed with distilled water (2 × 150 mL), dried over MgSO$_4$, and condensed by rotary evaporation. The resulting residue was purified by flash chromatography on silica gel.

Cross-Coupling Reaction of 10d and 11d Resulting in the Synthesis of Ethyl 4-Phenylcyclohex-3-enecarboxylate (22d Major) and Ethyl 3-Phenylcyclohex-3-enecarboxylate (22d Minor). Compounds 10d and 11d (0.220 g, 0.504 mmol), [Pd(allyl)Cl]$_2$ (0.026 g, 0.071 mmol), S-Phos (0.105 g, 0.220 mmol), iodobenzene (67.0 μL, 0.600 mmol), KF (0.099 g, 1.70 mmol), and DMF (20 mL) were used according to the general procedure mentioned above. The resulting brown residue was subjected to flash chromatography using silica gel and 10:1 hexane/ethyl acetate as eluent to yield the cross-coupled product (22d major and minor) as a colorless oil (0.081 g, 0.352 mmol, 69.8%): R_f 0.30 (hexanes/ethyl acetate, 10:1). Major isomer 22d: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.31 (m, 5H), 6.10 (m, 1H), 4.17 (q, *J* = 7.06 Hz, 2H), 2.73−2.39 (m, 5H), 2.25−2.13 (m, 1H), 1.92−1.76 (m, 1H), 1.28 (t, *J* = 7.07 Hz, 3H); ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 175.0, 142.0, 136.6, 128.5, 127.1, 125.3, 122.9, 60.7, 39.4, 28.5, 27.1, 25.9, 14.6. Minor isomer 22d, diagnostic peaks: ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.18 (q, *J* = 7.06 Hz, 2H), 2.32 (m), 2.05 (m); ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 176.0, 142.1, 135.5, 125.4, 124.2, 40.3, 30.0, 25.5, 25.1; GC/MS *m/z* (relative) (major isomer 22d) 230 (15) [M$^+$], 157 (28), 156 (100), 155 (31), 141 (11), 129 (17), 115 (16), 91 (26), 77 (8); (minor isomer 22d) 231 (6), 230 (38) [M$^+$], 184 (9), 158 (13), 157 (100), 156 (99), 155 (53), 141 (21), 129 (26), 115 (33), 91 (54), 77 (11); HRMS [M + H]$^+$ calcd for C$_{15}$H$_{18}$O$_2$ 231.1385, found 231.1387. Regioisomer ratio 3.8:1.0 (based on GC integrations).

Cross-Coupling Reaction of 10c and 11c Resulting in the Synthesis of Ethyl 4-Phenylcyclohex-3-enecarboxylate (22c Major) and Ethyl 3-Phenylcyclohex-3-enecarboxylate (22c Minor). Compounds 10c and 11c (0.051 g, 0.156 mmol), [Pd(allyl)Cl]$_2$ (0.010 g, 0.027 mmol), S-Phos (0.047 g, 0.099 mmol), iodobenzene (20.5 μL, 0.184 mmol), TBAF (0.45 mL, 0.450 mmol), and DMF (6 mL) were used according to the general procedure mentioned above. The resulting brown residue was subjected to flash chromatography using silica gel and 10:1 hexane/ethyl acetate as eluent to yield the cross-coupled product 22c as a colorless oil (0.025 g, 0.109 mmol, 69.8%). Characterization

data mirror that of the product 22d mentioned above. Regioisomer ratio 3.9:1.0 (based on GC integrations).

Cross-Coupling Reaction of 10f) Resulting in the Synthesis of Diethyl 4-Phenylcyclohex-4-ene-1,2-dicarboxylate (22f). The crude compound 10f (0.304 g) which contains the cycloadduct (0.206 g, 0.405 mmol) by ^{1}H NMR integrations, [Pd(allyl)Cl]$_2$ (0.020 g, 0.055 mmol), S-Phos (0.107 g, 0.224 mmol), iodobenzene (67.0 μL, 0.601 mmol), KF (0.120 g, 2.06 mmol), and DMF (20 mL) were used according to the general procedure mentioned above. The resulting brown residue was subjected to flash chromatography using silica gel and 6:1 hexanes/ethyl acetate to yield the cross-coupled product 22f as a light brown oil (0.043 g, 0.142 mmol, 35.1%): R_f 0.25 (hexanes/ethyl acetate 6:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 (m, 2H), 7.31 (m, 2H), 7.24 (m, 1H), 6.05 (m, 1H), 4.17 (q, *J* = 7.14 Hz, 4H), 3.21−3.18 (td, *J* = 6.30 Hz, 3.62 Hz, 1H), 3.11−3.08 (td, *J* = 6.30 Hz, 3.62 Hz, 1H), 3.03−2.95 (m, 1H), 2.79−2.70 (m, 2H), 2.58−2.51 (m, 1H), 1.25 (t, *J* = 7.12 Hz, 6H); ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 173.0, 173.0, 141.3, 135.2, 128.2, 127.0, 125.2, 122.3, 60.66, 60.63, 40.4, 39.5, 28.0, 26.4, 14.18, 14.16; GC/MS *m/z* (relative) 302 (3) [M$^+$], 257 (8), 228 (29), 199 (2), 156 (16), 155 (100), 154 (19), 153 (8), 141 (3), 129 (5), 128 (6), 115 (8), 103 (1), 91 (7), 77 (9), 51 (2); HRMS [M + H]$^+$ calcd for C$_{18}$H$_{22}$O$_4$ 303.1596, found 303.1595.

Cross-Coupling Reaction of 10e Resulting in the Synthesis of Diethyl 4-Phenylcyclohex-4-ene-1,2-dicarboxylate (22e). Crude compound 10e (0.251 g) which contains the cycloadduct (0.175 g, 0.439 mmol), [Pd(allyl)Cl]$_2$ (0.028 g, 0.077 mmol), S-Phos (0.102 g, 0.214 mmol), iodobenzene (67.0 μL, 0.601 mmol), TBAF (1.5 mL, 1.5 mmol), and DMF (20 mL) were used according to the general procedure mentioned above. The resulting brown residue was subjected to flash chromatography using silica gel and 6:1 hexanes/ethyl acetate to yield the cross-coupled product 22e as a light brown oil (0.088 g, 0.291 mmol, 66.3%). Characterization data mirrors that of the product 22f mentioned above.

Brief Experimental Description of X-ray Characterization of Compound 8. Weakly diffracting colorless needle-shaped crystals of K[Si(O$_2$C$_6$H$_4$)$_2$(C$_{14}$H$_{12}$NO$_2$)]−MeCN are, at 213(2) K, monoclinic, space group $P2_1/c$ − C_{2h}^5 (No. 14) with *a* = 10.141(8) Å, *b* = 12.072(10) Å, *c* = 21.290(14) Å, β = 95.56(2)°, V = 2594(3) Å^3, and Z = 4 [d_{calcd} = 1.410 g cm^{-3}; μ_a(Mo Kα) = 0.298 mm^{-1}]. Repeated recrystallization attempts to obtain better quality crystals were unsuccessful. A full hemisphere of diffracted intensities (1968 30-s frames with an ω scan width of 0.30°) was measured using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART APEX CCD single-crystal diffraction system. X-rays were provided by a fine-focus sealed X-ray tube operated at 50 kV and 30 mA.

Lattice constants were determined with the Bruker SAINT software package using peak centers for 1493 reflections having 7.72° ≤ 2θ ≤ 39.09°. A total of 19509 integrated reflection intensities having 2θ(Mo Kα) ≤ 50.00° were produced using the Bruker program SAINT; 4548 of these were unique and gave R_{int} = 0.106 with a coverage which was 99.6% complete. The data were corrected empirically for scaling and variable absorption effects using Bruker SADABS software; the relative transmission factors ranged from 0.609 to 0.746.

The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 2008/3 software package. The resulting structural parameters have been refined to convergence [R_1 (unweighted, based on F) = 0.0749 for 3164 independent reflections having 2θ(Mo Kα) < 50.00° and F^2 > $2\sigma(F^2)$] [R_1 (unweighted, based on F) = 0.1146 and wR_2 (weighted, based on F^2) = 0.1570 for all 4548 reflections] using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all nonhydrogen atoms. The hydrogen atoms were

included in the structural model as fixed atoms (using idealized sp^2- or sp^3-hybridized geometry and C−H bond lengths of 0.94−0.99 Å) "riding" on their respective carbon atoms. The isotropic thermal parameters for all hydrogen atoms were fixed at a value 1.2(nonmethyl) or 1.5(methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded. A total of 343 parameters were refined using no restraints and 4548 data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.348 and −0.409 $e^-/Å^3$, respectively.

Brief Experimental Description of X-ray Characterization of Compound 16. CIF File Deposition Code CCDC 745626:. Large colorless plate-shaped crystals of $C_{20}H_{16}FNO_2$ are, at 193(2) K, monoclinic, space group $P2_1/n$ [an alternate setting of $P2_1/c - C_{2h}^5$ (No. 14)] (1) with $a = 14.649(1)$ Å, $b = 6.6182(6)$ Å, $c = 17.212(2)$ Å, $\beta = 99.662(1)°$, $V = 1645.1(3)$ Å^3, and $Z = 4$ formula units [$d_{calcd} = 1.297$ g/cm^3; μ_a(Mo Kα) = 0.091 mm^{-1}]. A full hemisphere of diffracted intensities (1968 20 s frames with a ω scan width of 0.30°) was measured for a single domain specimen using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART APEX CCD single crystal diffraction system (2). X-rays were provided by a fine-focus sealed X-ray tube operated at 50 kV and 30 mA.

Lattice constants were determined with the Bruker SAINT software package using peak centers for 4453 reflections having $7.81° \leq 2\theta \leq 53.84°$. A total of 17395 integrated reflection intensities having 2θ(Mo Kα) < 60.10° were produced using the Bruker program SAINT (3); 4776 of these were unique and gave $R_{int} = 0.029$ with a coverage which was 98.8% complete. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.12 software package (4).

The final structural model incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. The hydrogen atoms were included in the structural model as fixed atoms (using idealized sp^2- or sp^3-hybridized geometry and C−H bond lengths of 0.95−1.00 Å) "riding" on their respective carbon atoms. The isotropic thermal parameter of each hydrogen atom was fixed at a value 1.2 times the equivalent isotropic thermal parameter of the carbon atom to which it is covalently bonded. A total of 217 parameters were refined using no restraints and 4776 data. Final agreement factors at convergence are: R_1(unweighted, based on F) = 0.059 for 3533 independent "observed" reflections having 2θ(Mo Kα) < 60.10° and $I > 2\sigma(I)$; R_1(unweighted, based on F) = 0.078 and wR_2(weighted, based on F^2) = 0.169 for all 4776 independent reflections having 2θ(Mo Kα) < 60.10°. The largest shift/su was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.363 and −0.172 $e^-/Å^3$, respectively.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all novel compounds produced. Experimental procedures for many of the Diels−Alder and cross-coupling reactions other than the representative examples included here and X-ray crystallographic data for **8** and **16**. This material is available free of charge via the Internet at http://pubs.acs.org.