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Synthesis of 4-Aryl- and 4-Alkyl-2-silyl-1,3-butadienes and Their Diels−Alder/Cross-Coupling Reactions

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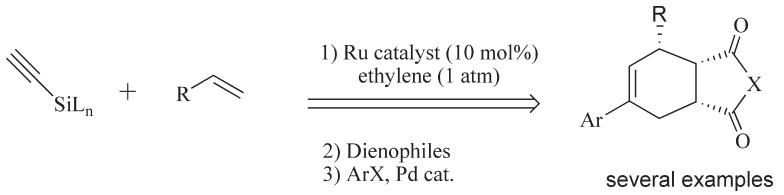

An ene-yne cross methasis of silyl-substituted alkynes and alkenes has been developed as a route to 4-aryl- and 4-alkyl-2-silyl-substituted 1,3-dienes. The dienes prepared were used to affect highly diastereoselective Diels−Alder reactions and then the silicon-substituted Diels−Alder cycloadducts were used in Hiyama cross-coupling reactions. The cross-coupling reactions enable these silicon dienes to be used as synthons for a variety of other dienes one might prepare and need access to. Two of the silicon-substituted Diels−Alder cycloadducts and one of the Hiyama cross-coupling products were also characterized 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 that 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 2-trimethoxysilyl-[3] and 2-triethoxysilyl-1,3-butadiene in 1978 and 1984,[4] respectively, as well as a report of the polymerization of these materials in 1989.[5] In 1988, Tamao, Ito, and co-workers reported the intramolecular hydrosilylation of the alkyne moiety of homopropargyl alcohols to make siloxacyclopentanes containing exocyclic alkenes.[6] Other routes to siloxacycle-containing species used in cross-coupling chemistry have also been reported.[7−9] In 2004, Clark and Woerpel reported the reaction of a "tBu_2Si" source with a protected enynol to produce a siloxacyclopentene containing a silicon substituent at the 1-position of a 1,3-diene moiety[10] that reacted with *N*-phenylmaleimide in a Diels−Alder reaction. Also in 2004, Lee and co-workers synthesized a number of siloxacycles that are part of a 1,3-diene unit via a condensation/metathesis strategy using alkenyl alcohols and alkynyl silanes.[11] No Diels−Alder or cross-coupling reactions of these substrates were reported. Roush's group has made siloxacyclopentenes containing pendant dienophiles and demonstrated that they could be used in intramolecular Diels−Alder reactions that were followed by protiodesilylation.[12−14] Most recently, the Soderquist group has reported a preparation of 2-(10-TMS-9-borabicyclo[3.3.2]decane)-substituted 1,3-dienes and their use in the asymmetric synthesis of pentadienols[15] and

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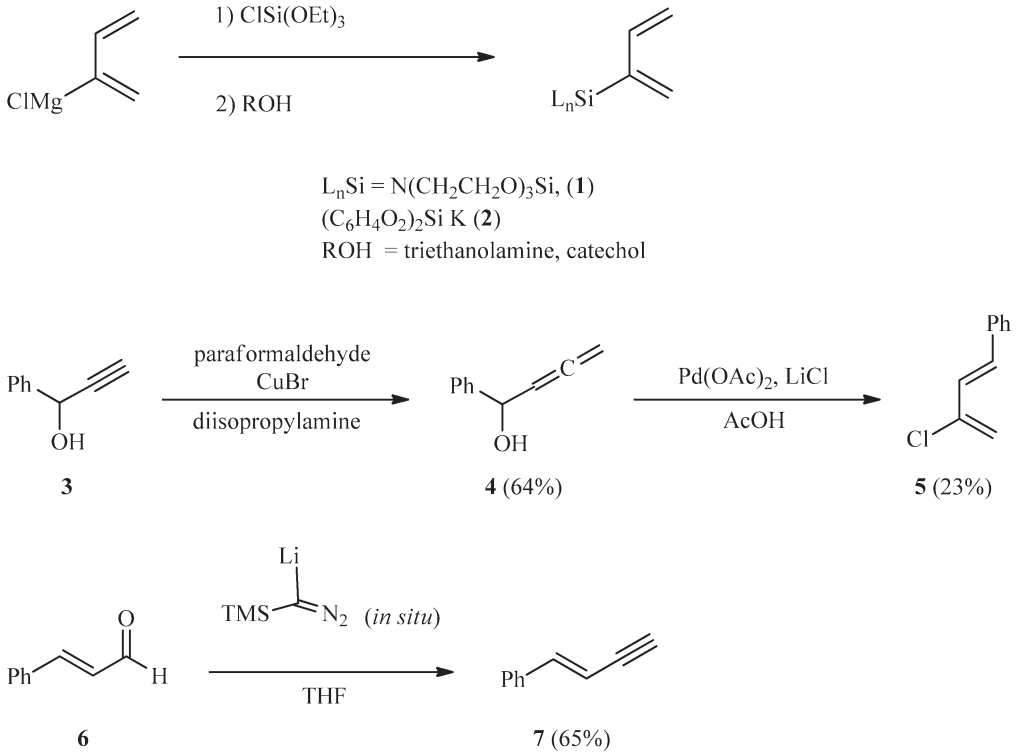
SCHEME 1



the Suginome group has reported a nickel-catalyzed silaborative dimerization of alkynes to prepare 1,4-silicon,boron-substituted 1,3-dienes.[16]

Given the known propensity of trialkoxysilyl aryls and alkenyls to participate in fluoride-assisted, metal-catalyzed cross-coupling reactions (Hiyama couplings),[17] we felt that an easily accessible preparation of 4-aryl- and alkyl-substituted-2-silyl-1,3-dienes would be subsequently useful for tandem Diels–Alder/cross-coupling chemistry. We reported our initial studies in this area in 2007[18,19] and 2009[20] for 2-trialkoxysilyl-1,3-butadienes and in the work that follows we provide more details of our subsequent work. Here we disclose a general method for the preparation of a number of substituted silicon dienes, their diastereoselective Diels–Alder reactions, and the participation of those Diels–Alder cycloadducts in subsequent cross-coupling chemistry. Through the cross-coupling chemistry these silicon dienes end up serving as synthons for a host of organic dienes that one might otherwise prepare independently and use in Diels–Alder chemistry.

Results and Discussion

Silyl-Substituted 1,3-Diene Preparation and Characterization. Given our success in preparing silyl-substituted butadienes (**1**, **2**) from the reaction of a dienyl Grignard reagent and a silyl halide we sought to prepare more highly substituted silicon dienes by using this same protocol (Scheme 1).[18] We prepared (*E*)-2-chloro-4-phenyl-1,3-butadiene (**5**) from the corresponding phenyl propargyl alcohol (**3**).[21] Attempts to prepare the Grignard reagent of that halodiene (**5**) and then treat it with chlorotriethoxysilane resulted in diene decomposition. (*E*)-4-Phenyl-3-buten-1-yne (**7**) was then prepared via a Colvin rearrangement from *trans*-cinnamaldehyde (**6**)[22] and ruthenium-catalyzed hydrosilyation of the yne (**7**) functional group was attempted with triethoxysilane.[23] While the ^{1}H NMR spectra of the crude product indicated dienes were formed, it appeared to be a mixture of regio- and stereoisomers and these triethoxysilyl dienes were not stable to chromatographic separation.

Since the unsubstituted silatrane diene (**1**) we reported earlier[18] was quite stable, we prepared the siletrane silane (**8**) by modification of a literature preparation[24] and attempted enyne hydrosilyation of (*E*)-4-phenyl-3-buten-1-yne (**7**) but were also unsuccessful (Scheme 2). Our next attempts involved alkene cross metathesis between the unsubstituted dienes (**1** and **2**) and styrene with first generation Grubbs, second generation Grubbs, and Schrock catalysts, but in all cases, unreacted silyl dienes were recovered.

We were finally successful at preparing more highly substituted silicon dienes by using ene-yne cross metathesis (Scheme 3).[25] Initial trials utilized triethylsilylacetylene (**9**, L = Et) and styrene (**10**) with the Grubbs–Hoveyda second generation catalyst to effect the desired reaction (Table 1, entry c). Dimethylphenylsilylacetylene (**9**, L = Me_2Ph) also worked in this cross metathesis (Table 1, entry d) but the isolated yield of

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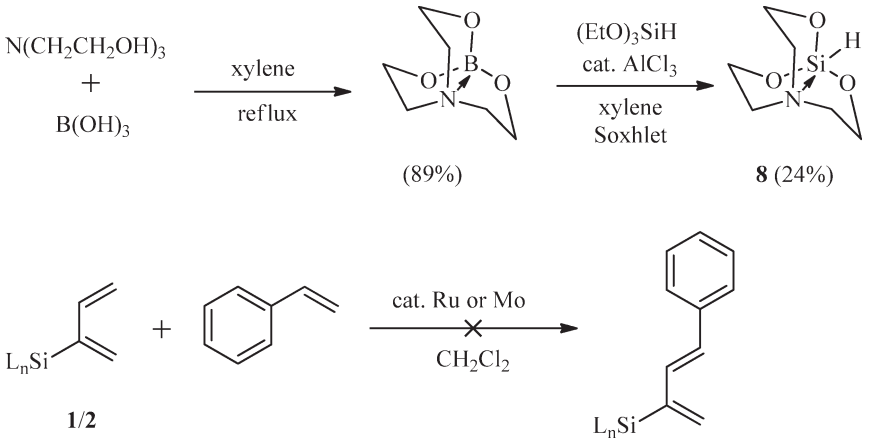
SCHEME 2



SCHEME 3

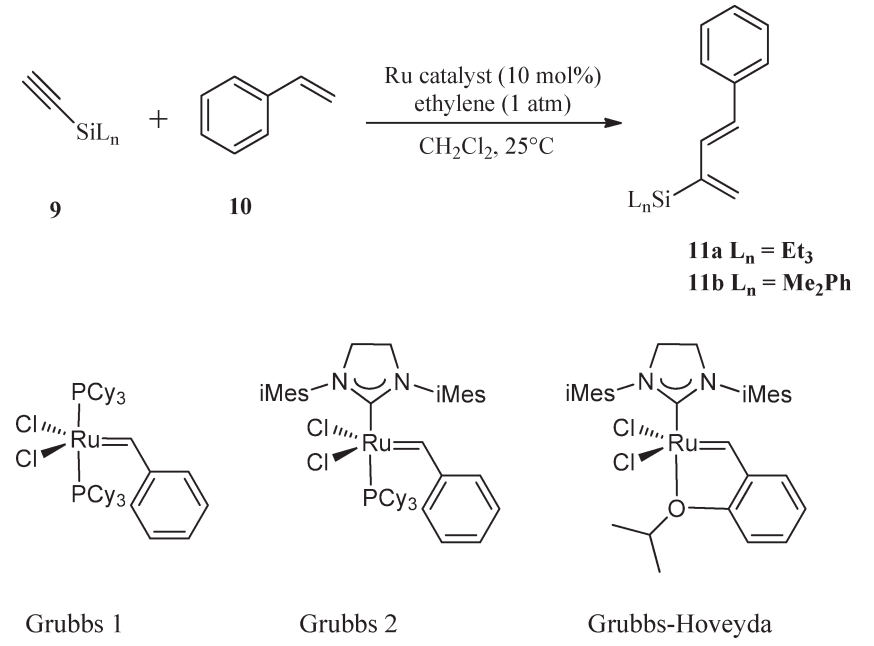


TABLE 1. Silyl Alkyne Cross Metathesis

entry	SiL_n	Ru catalyst	yield (%)
a	$SiEt_3$	Grubbs first	28
b	$SiEt_3$	Grubbs second	57
c	$SiEt_3$	Grubbs–Hoveyda second	69
d	$SiMe_2Ph$	Grubbs–Hoveyda second	47

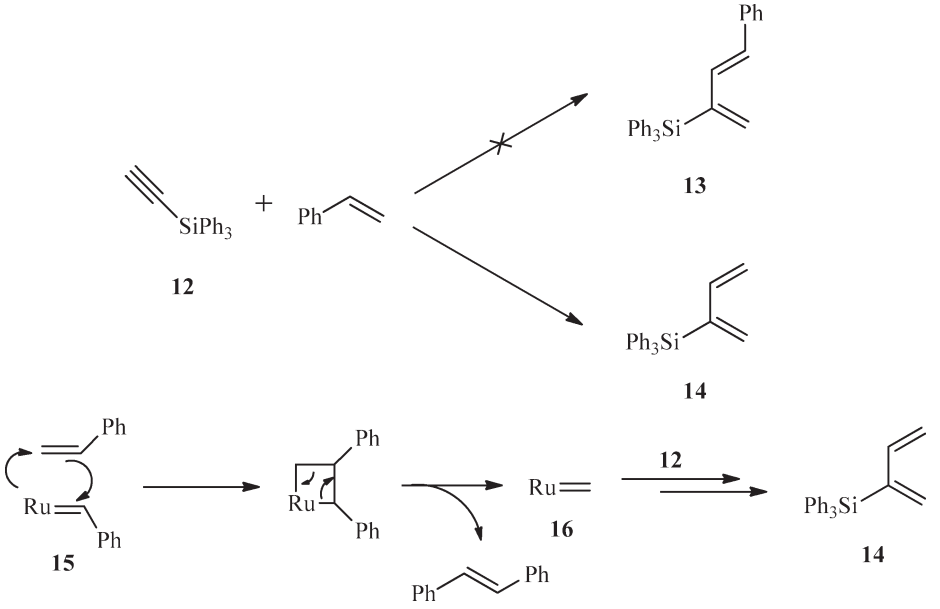
the silyl-substituted diene (**11b**) was not quite as high as the triethylsilyl case (**11a**).

Synthesis of a third diene was also attempted by using triphenylsilylacetylene **12** (Scheme 4). Monitoring of the initial reaction by GC/MS revealed formation of the unsubstituted diene **14**[8] and *trans*-stilbene but none of the desired product **13**. We believed this undesired product was exacerbated by the ethylene gas present; however, in the absence of the ethylene atmosphere the reaction still produces **14**. We now speculate that this occurs through metathesis of styrene with the original catalyst to produce *trans*-stilbene and the unsubstituted ruthenium carbene **16**. Presumably ruthenium carbene **15** is too sterically hindered to undergo metathesis with **12** but **16** is not.

With two dienes of interest now available (**11a**, **11b**), we turned to the Diels–Alder chemistry of these compounds (Scheme 5). The prochiral C-4 of these dienes allowed us to examine any diastereoselectivity in these cycloadditions. Dienes **11a** and **11b** were treated with symmetrical dienophiles maleic anhydride and *N*-phenylmaleimide under an inert atmosphere in sealed tubes (Table 2).

As expected maleic anhydride was more reactive as a dienophile than *N*-phenylmaleimide (compare entries b and e). The reactions are generally *endo*(*syn*) selective to produce the *syn* diastereomers (**17**) and this selectivity increases as the reaction temperature is lowered. The stereochemistry of each major diastereomer was supported by ^{1}H NOE data and the major cycloadduct from entry e (**17e**) was also characterized by X-ray crystallography (for details, see the Supporting Information).

SCHEME 4



SCHEME 5

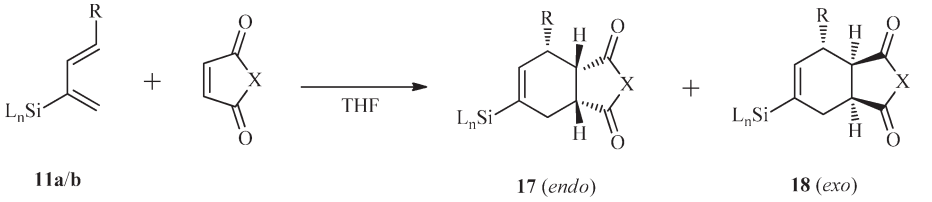


TABLE 2. Reactions of Silicon Dienes 11a and 11b with Dienophiles

entry	SiL_n	X	R	T (°C)	t (h)	% yield[a]	endo:exo[b]
a	$SiEt_3$	O	Ph	90	5	55	1.0:1
b				25	48	70	17.0:1
c				15	66	68	33.0:1
d	$SiEt_3$	*N*-Ph	Ph	90	24	71	3.4:1
e				25	148	85	20.0:1
f	$SiMe_2Ph$	*N*-Ph	Ph	90	16	93	9.0:1
g				50	28	69	17.0:1

[a]Entries b, d, and f are isolated yields. The remainder are calculations based on proton NMR integrations of the vinyl proton chemical shifts of the cycloadduct and excess dienophile. [b]Diasteriomeric ratio based on proton NMR integrations of vinyl proton chemical shifts.

We first tried cross coupling on the maleic anhydride cycloadduct (**17c**) using several previously reported procedures for triethysilyl compounds.[26,27] However, both of these protocols resulted in cycloadduct decomposition. Subsequently, one of Hiyama's protocols[28] with iodobenzene on the triethylsilyl *N*-phenylmaleimide cycloadduct (**17e**) was attempted. However, rather than isolating a cross-coupled product we instead isolated the *anti* diastereomer (**18e**) in high yield (84%). This double epimerization α to both carbonyls presumably results from the basic cross coupling reaction conditions.

Lastly, we attempted cross coupling with the dimethylphenylsilyl cycloadduct (**17g**) since they are known to be more reactive than trialkylsilyl alkenes particularly when they are converted in situ to the corresponding silanol (Scheme 6).[29] However, we again isolated no cross-coupled product (**20**) and instead isolated a 10:1 mixture of regio/stereoisomers of ring-opened product (**19**). Since this was not the desired reaction outcome we did not completely characterize this product mixture.

After having no success trying to cross couple the triethylsilyl- and dimethylphenylsilyl-substituted Diels–Alder cycloadducts (**17a–g**), we synthesized a number of benzyldimethylsilyl-substituted dienes (**22a–d**) by this cross-metathesis reaction (Scheme 7). We started these cross-metathesis reactions by again optimizing on styrene (**10**) as the alkene partner. Isolated yields of the desired cross-metathesis diene product were typically 10–20% higher when 5 rather than 1.1 equiv of styrene was used. Somewhat surprisingly, we found that 3,3-dimethyl-1-butene and *tert*-butoxyethylene did not work in this reaction, but 4,4-dimethyl-1-pentene underwent cross metathesis and provided **22d** as a 3:1 mixture of *E*:*Z* isomers.

These silyl dienes (**22a–d**) reacted with *N*-phenylmaleimide with excellent *endo* diastereoselectivity in high yield to produce cycloadducts (**23a–d**) (Scheme 8). Benzyldimethylsilyldiene (**22a**) was also reacted with citraconic anhydride

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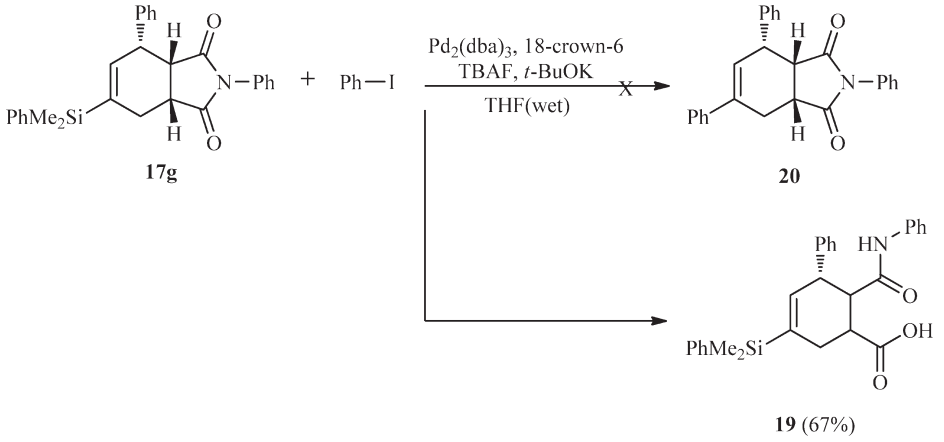
SCHEME 6



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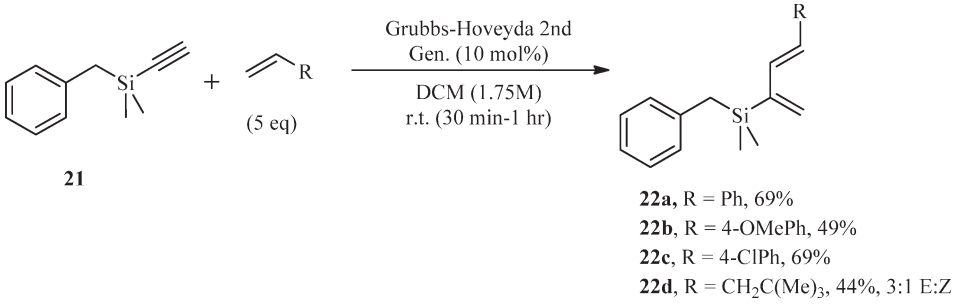
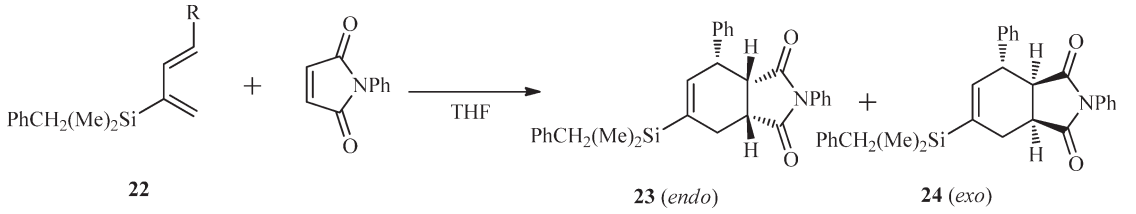
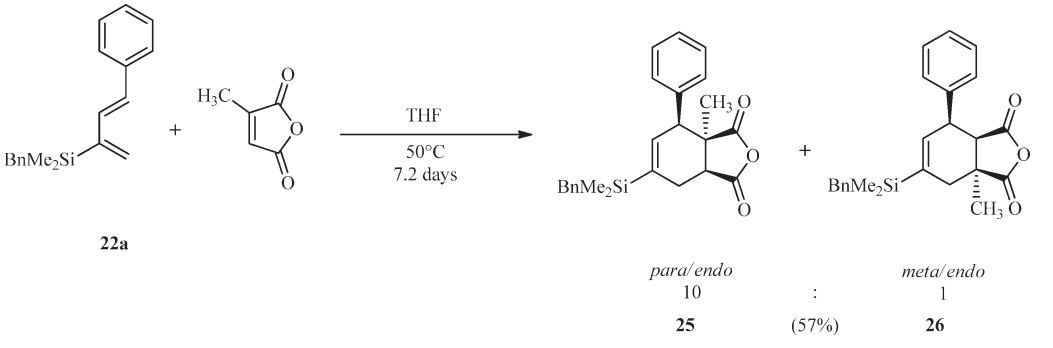


SCHEME 8



SCHEME 9



(Scheme 9; Table 3). Para:meta regioisomers from *endo* transition states **25** and **26** were isolated in 57% yield (10:1 ratio). The major para (*endo*) cycloadduct (**25**) was also characterized by X-ray crystallography (for details, see the Supporting Information). The minor isomer is a meta isomer from NMR data and we presume it was meta (*endo*) though this isomer was not completely characterized.

These benzyldimethylsilyl-substituted cycloadducts also cross coupled with aromatic iodides easily to produce products (**27**) (Scheme 10).[30] Fluoride sources other than TBAF such as KF or AgF proved ineffective in this reaction and

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TABLE 3. Reactions of Silicon Dienes 22 with *N*-Phenylmaleimide

compd	R	temp (°C)	time (h)	% yield	*endo*:*exo*
23a	Ph	50	24	70	14:1
23b	4-OMePh	50	16	33	26:1
23c	4-ClPh	50	18	65	20:1
23d	$CH_2C(CH_3)_3$	50	17	56	>25:1

temperatures higher than 50 °C can lower the reaction times but result in more ring junction epimerization. The cycloadduct that had been prepared from the neopentyl-substituted diene and then cross coupled with iodobenzene (**27f**) was also characterized by X-ray crystallography (for details, see the Supporting Information).

Conclusions

4-alkyl- and 4-aryl-2-silyl-1,3 dienes can be prepared stereoselectively by ene-yne cross metathesis. These silyl dienes then participate in highly stereoselective Diels−Alder reactions and the Diels−Alder cycloadducts participate in cross-coupling reactions. The cross-coupling reactions enable the original silyl dienes to serve as synthons for a host of organic dienes.

Experimental Section

General. The ^{1}H NMR spectra were recorded using a 300 MHz spectrometer and a 500 MHz spectrometer operating at 300.13 and 500.13 MHz, respectively. ^{13}C NMR spectra were also recorded on the previously mentioned spectrometers operating at 75.48 and 125.77 MHz, respectively. The ^{19}F NMR spectrum was recorded on the previously mentioned 300 MHz spectrometer operating at 282.40 MHz. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS) or to residual resonances of the deuterated solvents: benzene (C_6D_6) or chloroform ($CDCl_3$). Coupling constants (J values) were reported in hertz (Hz) and spin multiplicities were indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). When supplied, the number of protons on each carbon was determined by using ^{13}C Attached Proton Test (APT) NMR spectroscopy and reported using the following abbreviations: C (quaternary), CH (tertiary), CH_2 (secondary), and CH_3 (primary). For all ^{1}H−^{1}H 2-D spectra, the spectral width was 4432.6 Hz. 2-D ^{1}H−^{1}H 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. The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Rd., Cambridge CB2 1EZ, UK or via www.ccdc.cam.ac.uk/conts/retrieving.html.

Analytical chromatographic techniques were performed using a gas chromatograph coupled to a mass selection detector run in electron impact mode. The gas chromatograph was run under a 50-split method and used a 5-MS capillary column (30 m, 0.25 μm film, 0.25 mm OD). The temperature sequence of the chromatograph oven was as follows: initial temperature of 50 °C held for 1 min followed by a ramp of 12 deg/min up to 320 °C.

Flash chromatography was performed with use of thick-walled glass chromatography columns and "Ultra Pure" silica gel (40−63 μM).

All reactions were carried out under an inert atmosphere unless otherwise noted. HPLC-grade methylene chloride (DCM) and tetrahydrofuran (THF) were purified by using the centrally located solvent dispensing system. Hexanes for flash chromatography were dried over 4 Å molecular sieves and purified by fractional distillation.

The term "BDMS" is an abbreviation for "benzyldimethylsilyl".

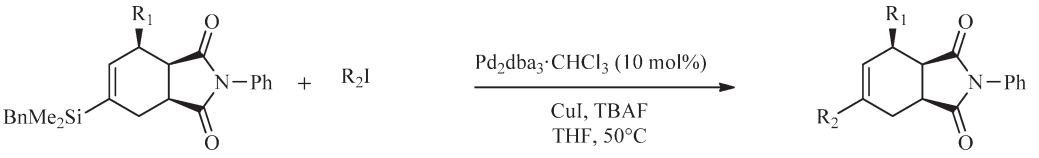
General Procedure for En-Yne Cross-Metathesis Reactions. To a dried round-bottomed flask equipped with a stir bar and 4 Å molecular sieves (40% w/w) was added Hoveyda−Grubbs second generation catalyst (10 mol %), which was dissolved in DCM (1.7 M) and degassed with argon for 5 min. Silyl acetylene and olefin were then added successively to the reaction solution and capped with a rubber septum. The reaction solution quickly changes color from deep translucent green to cloudy brown. The reaction was run under continuous stirring at 25 °C for the stipulated amount of time under argon or ethylene atmosphere.

(*E*)-Triethyl(4-phenylbuta-1,3-dien-2-yl)silane (11a). Triethylsilylacetylene (**9a**) (75.0 μL, 0.419 mmol), styrene (**10**) (480 μL, 4.19 mmol), Hoveyda−Grubbs second generation catalyst (0.029 g, 0.042 mmol), and DCM (1 mL) were used under ethylene atmosphere (1 atm) according to the general procedure. After 1 h the reaction mixture was condensed by rotary evaporation and dried under vacuum. The resulting brown residue was purified by flash chromatography, using silica gel and cyclohexane as eluent, to yield the product as a colorless oil (0.070 g, 0.286 mmol, 69%): R_f 0.5 (cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (m, 2H), 7.31 (m, 2H), 7.21 (m, 1H), 6.76 (d, J = 16.1 Hz, 1H), 6.61 (d, J = 16.1 Hz, 1H), 5.95 (d, J = 3.0 Hz, 1H), 5.46 (d, J = 3.1 Hz, 1H), 0.97 (t, J = 7.4 Hz, 9H), 0.75 (q, J = 7.1 Hz, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 146.20 (C), 138.16 (C), 134.83 (CH), 130.03 (CH), 129.88 (CH_2), 128.93 (CH), 127.63 (CH), 126.65 (CH), 7.77 (CH_3), 3.87 (CH_2). GC/MS: m/z (relative, %) 245.2 (4) [M + 1], 244.2 (17) [M$^+$], 216.1 (31), 215.1 (14), 187.1 (21), 185.1 (9), 159.1 (17), 157.1 (9), 145.1 (9), 131.1 (24), 128.1 (49), 115.1 (68), 105.0 (10), 87.1 (100), 77.1 (4), 51.1 (4).

(*E*)-Dimethyl(phenyl)(4-phenylbuta-1,3-dien-2-yl)silane (11b). Dimethylphenylsilylacetylene (**9b**) (250 μL, 1.41 mmol), styrene (**10**) (0.2 mL, 1.7 mmol), Hoveyda−Grubbs second generation catalyst (0.090 g, 0.144 mmol), and DCM (3 mL) were used under ethylene atmosphere according to the general procedure. After 1 h the reaction mixture was condensed by rotary evaporation and dried under vacuum. The resulting brown residue was purified by flash chromatography with silica gel and 20:1 hexanes/ethyl acetate as eluent to yield the product as a colorless oil (0.175 g, 0.662 mmol, 47%): R_f 0.5 (hexanes/ethyl acetate 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59−7.14 (m, 8H), 6.92 (d, J = 16.4 Hz, 1H, H-3), 6.48 (d, J = 16.2 Hz, 1H, H-4), 6.00 (d, J = 2.9 Hz, 1H, H-1), 5.57 (d, J = 2.9 Hz, 1H, H-1′), 0.49 (s, 6H, H-9). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 146.8 (C), 138.1 (C), 137.5 (C), 133.9 (CH), 133.5 (CH), 131.5 (CH), 130.5 (CH_2, C-1), 129.1 (CH), 128.5 (CH), 127.9 (CH), 127.3 (CH), 126.2 (CH), −2.1 (CH_3, C-9). GC/MS: m/z (relative, %) 265.2 (2) [M + 1], 264.1 (8) [M$^+$], 204.1 (2), 173.1 (3), 171.0 (3), 145.0 (4), 137.1 (4), 136.1 (14), 135.1 (100), 128.1 (27), 121.0 (4), 107.0 (6), 105.0 (8), 91.1 (4), 78,1 (7), 51.1 (3).

(*E*)-Benzyldimethyl(4-phenylbuta-1,3-dien-2-yl)silane (22a). BDMS acetylene (**21**) (2.012 g, 11.54 mmol), styrene (**10**) (6.5 mL, 56.7 mmol), Hoveyda−Grubbs second generation catalyst (0.710 g, 1.13 mmol), and DCM (40 mL) were used under argon atmosphere according to the general procedure. After 1.75 h the reaction mixture was condensed by rotary evaporation. The resulting brown oil was purified by flash chromatography with silica gel and 20:1 hexanes/ethyl acetate as eluent. The combined fractions were then condensed and dried under vacuum overnight to remove excess styrene resulting in a yellow oil (2.22 g, 7.97 mmol, 69%): R_f 0.6 (hexanes/ethyl acetate 20:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43−6.99 (m, 10H), 6.91 (d, J = 16.4 Hz, 1H, H-3), 6.58 (d, J = 16.4 Hz, 1H, H-4), 5.92 (d, J = 2.6 Hz, 1H, H-1), 5.47 (d, J = 2.5 Hz, 1H, H-1), 2.34 (s, 2H, H-10), 0.22 (s, 6H, H-9). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.3 (C), 139.8 (C), 137.7 (C), 133.9 (CH), 130.8 (CH), 129.6 (CH_2), 128.7 (CH), 128.4 (CH), 128.2

SCHEME 10



23a-d

27a R_1 = Ph, R_2 = Ph, 70%
27b R_1 = Ph, R_2 = 3'-CF_3Ph, 36%
27c R_1 = Ph, R_2 = 3'-MeOPh, 32%
27d R_1 = 4'-MeOPh, R_2 = Ph, 42%
27e R_1 = 4'-ClPh, R_2 = Ph, 33%
27f R_1 = $(CH_3)_3CCH_2$, R_2 = Ph, 61%

(CH), 127.5 (CH), 126.4 (CH), 124.3 (CH), 25.9 (CH_2, C-10), −2.7 (CH_3, C-9). GC/MS: *m*/*z* (relative, %) 278.1 (4) [M^+], 187.1 (100), 171.1 (16), 159.0 (17), 149.0 (54), 128.0 (47), 121.0 (44), 115.0 (13), 105.0 (16), 91.1 (28), 77.0 (14), 59.0 (88).

(*E*)-Benzyl(4-(4′-methoxyphenyl)buta-1,3-dien-2-yl)dimethylsilane (22b). BDMS acetylene (**21**) (0.253 g, 1.45 mmol), 4-vinylanisole (0.96 mL, 7.1 mmol), Hoveyda−Grubbs second generation catalyst (0.095 g, 0.152 mmol), and DCM (5 mL) were used under argon atmosphere according to the general procedure. After 1 h the reaction mixture was condensed by rotary evaporation and run through a silica plug with 10:1 hexanes/ethyl acetate as eluent. The resulting oil was triturated with cold methanol (20 mL) and gravity filtered to remove the insoluble (*E*)-1,2-bis(4-methoxyphenyl)-ethene byproduct. The filtrate was condensed by rotary evaporation and purified on silica with 80:1 chloroform/ethyl acetate as eluent resulting in a yellow oil (0.221 g, 0.716 mmol, 49%): R_f 0.7 (chloroform/ethyl acetate, 80:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35−6.81 (m, 9H), 6.78 (d, J = 16.5 Hz, 1H, H-3), 6.52 (d, J = 16.5 Hz, 1H, H-4), 5.86 (d, J = 2.8 Hz, 1H, H-1), 5.41 (d, J = 2.9 Hz, 1H, H-1), 3.83 (s, 3H, H-5′), 2.33 (s, 2H, H-6), 0.21 (s, 6H, H-5). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 159.1 (C), 147.2 (C), 139.8 (C), 131.8 (C), 130.4 (C), 130.2 (CH), 128.5 (CH_2), 128.3 (CH), 128.1 (CH), 127.5 (CH), 124.1 (CH), 114.0 (CH), 55.3 (CH_3, C-5′), 25.85 (CH_2, C-6), −2.8 (CH_3, C-5). GC/MS: *m*/*z* (relative, %) 308.2 (21) [M], 293.1 (12), 217.1 (100), 202.1 (69), 187.0 (15), 175.0 (18), 158.0 (30), 149.1 (91), 121.0 (63), 91.1 (26), 77.0 (10), 59.0 (42).

(*E*)-Benzyl(4-(4′-chlorophenyl)buta-1,3-dien-2-yl)dimethylsilane (22c). BDMS acetylene (**21**) (0.250 g, 1.43 mmol), 4-chlorostyrene (0.91 mL, 7.1 mmol), Hoveyda−Grubbs second generation catalyst (0.093 g, 0.148 mmol), and DCM (5 mL) were used under argon atmosphere according to the general procedure. After 1 h the reaction mixture was condensed by rotary evaporation and purified by flash chromatography with silica gel and 142:7:1 hexanes/ethyl actetate/methanol as eluent. The resulting residue was triturated with cold methanol (20 mL) and gravity filtered to remove the insoluble (*E*)-1,2-bis(4-chlorophenyl)ethene byproduct. The filtrate was then condensed and dried under vacuum to yield an amber oil (0.306 g, 0.978 mmol, 69%): R_f 0.6 (hexanes/ethyl acetate/methanol, 142:7:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.2−7.18 (m, 4H), 7.11−7.02 (m, 5H), 6.85 (d, J = 16.4 Hz, 1H, H-3), 6.47 (d, J = 16.4 Hz, 1H, H-4), 5.92 (d, J = 2.9 Hz, 1H, H-1), 5.49 (d, J = 2.9 Hz, 1H, H-1), 2.32 (s, 2H, H-6), 0.22 (s, 6H, H-5). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 146.9 (C), 139.6 (C), 136.0 (C), 134.3 (CH), 132.9 (C), 129.9 (C), 128.7 (CH), 128.3 (CH), 128.1 (CH), 127.4 (CH), 124.2 (CH), 25.8 (CH_2, C-6), −2.8 (CH_3, C-5). GC/MS: *m*/*z* (relative, %) 312.1 (9) [M], 223.1 (36), 221.1 (100), 164.0 (21), 162.0 (39), 149.1 (93), 121.0 (57), 93.0 (56), 91.1 (53), 77.1 (32), 59.0 (63).

(*E*/*Z*)-Benzyl(6,6-dimethylhepta-1,3-dien-2-yl)dimethylsilane (22d). BDMS acetylene (**21**) (0.247 g, 1.42 mmol), 4,4-dimethyl-1-pentene (1.0 mL, 7.0 mmol), Hoveyda−Grubbs second generation catalyst (0.090 g, 0.143 mmol), and DCM (5 mL) were used under ethylene atmosphere according to the general procedure. After 1 h the reaction mixture was condensed by rotary evaporation and dried under vacuum to remove excess olefin. The resulting brown residue was purified by flash chromatography with silica gel and 20:1 hexanes/ethyl acetate to yield a yellow oil (0.171 g, 0.628 mmol, 44%): R_f 0.5 (hexanes/ethyl acetate, 20:1). **Major isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23−7.18 (m, 2H), 7.09−6.99 (m, 3H), 6.15 (d, J = 15.7 Hz, 1H, H-3), 5.78 (dt, J = 15.7, 7.7 Hz, 1H, H-4), 5.68 (d, J = 3.0 Hz, 1H, H-1), 5.28 (d, J = 3.1 Hz, 1H, H-1), 2.27 (s, 2H, H-9), 1.98 (dd, J = 7.5, 0.9 Hz, 2H, H-5), 0.92 (s, 9H, H-6/7), 0.13 (s, 6H, H-8). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.8 (CH), 130.3 (CH), 128.3 (CH), 128.0 (CH), 127.3 (CH_2, C-1), 127.0 (C), 124.1 (CH), 47.9 (CH_2), 29.4 (CH_3, C-6/7), 25.7 (CH_2), −2.9 (CH_3, C-8). **Minor isomer, diagnostic peaks:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.04 (bd, J = 11.5 Hz, 1H), 5.60 (dd, J = 3.3, 1.8 Hz, 1H), 5.47 (d, J = 3.5 Hz, 1H), 2.17 (s, 2H, H-9), 0.91 (s, 9H, H-6/7), 0.05 (s, 6H, H-8). GC/MS: *m*/*z* (relative, %) (major isomer) 272.2 (20) [M^+], 215.1 (25), 149.1 (40), 125.1 (29), 123.1 (26), 121.1 (51), 109.1 (20), 91.1 (15), 73.1 (20), 57.1 (100); (minor isomer) 272.2 (10) [M^+], 215.1 (9), 181.1 (55), 149.1 (42), 125.1 (25), 123.1 (31), 121.1 (59), 109.1 (20), 91.1 (18), 73.1 (34), 57.1 (100). Isomer ratio 3:1 (*E*):(*Z*) (based on ^{1}H NMR integrations).

General Procedure for Diels−Alder Reactions. To an oven-dried thick-walled sealable tube charged with a mini stir bar was added the diene, which was dissolved in THF (0.5 M). After purging the solution with argon for 2 min, the dienophile was added and the tube was sealed with a Teflon screw cap fitted with an O-ring (or a rubber septum and crimp cap when using the 10-mL tubes). The reaction was run with continuous stirring at a stipulated time and temperature. The reaction vessel was then brought to room temperature and the vial was uncapped.

***endo*-(3a*R*,4*R*,7a*S*)-4-Phenyl-6-(triethylsilyl)-3a,7,7a-tetrahydroisobenzofuan-1,3-dione (17b).** Diene (**11a**) (0.043 g, 0.176 mmol), maleic anhydride (0.025 g, 0.255 mmol), and THF (3 mL) were used according to the general procedure. After 50 h at 25 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting colorless residue was purified by flash chromatography with silica gel and 2:1 hexanes/ethyl acetate as eluent to yield a white powder (0.042 g, 0.123 mmol, 70%): R_f 0.5 (hexanes/ethyl acetate, 2:1); mp 106−107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (m, 2H, H-12), 7.33 (m, 1H, H-13), 7.28 (m, 2H, H-11), 6.55 (t, J = 3.2 Hz, 1H, H-5), 3.68 (m, 1H, H-4), 3.56 (dd, J = 9.6, 6.9 Hz, 1H, H-3a), 3.50 (ddd, J = 9.6, 7.4, 2.1 Hz, 1H, H-7a), 2.96 (dd, J = 15.7, 2.1 Hz, 1H, H-7), 2.34 (dddd, J = 15.7, 7.4, 2.8, 2.1 Hz, 1H, H-7′), 0.93 (t, J = 7.7 Hz, 9H, H-9), 0.65 (q, J = 7.7, 6H, H-8). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 173.76 (C, C-1), 170.60 (C, C-3), 140.59 (C, C-6), 140.51 (CH, C-5), 138.21 (C, C-10), 128.79 (CH, C-11), 128.55 (CH, C-13), 127.59 (CH, C-12), 46.38 (CH, C-3a), 41.57 (CH, C-4), 40.14 (CH, C-7a), 26.62 (CH_2, C-7), 7.25 (CH_3, C-9), 2.18 (CH_2, C-8). GC/MS: *m*/*z* (relative, %) 313.1 (50), 295.1 (5), 285.1 (13), 267.1 (17). 241.1 (4), 216.1 (20), 215.1 (100), 187.1 (16), 185.1 (16), 165.0 (62), 155.1 (16), 145.0 (9), 131.0 (26), 115.1 (61), 103.0 (18), 87.1 (47), 75.0 (18), 59.1 (56). . HRMS [M + Cs]$^+$ calcd for $C_{20}H_{26}O_3Si$, 475.0706, found

475.0721. Diastereomeric ratio 17.0:1 (determined by ^{1}H NMR integrations).

2,4-Diphenyl-6-(triethylsilyl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (17d and 18d). Diene (**11a**) (0.254 g, 1.04 mmol), *N*-phenylmaleimide (0.214 g, 1.24 mmol), and THF (5 mL) were used according to the general procedure. After 24 h at 90 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting yellow residue was purified by flash chromatography with silica gel and 2:1 hexanes/ethyl acetate as eluent to yield the two diastereomers. **Major diastereomer (17d) (*endo*):** white powder (0.236 g, 0.565 mmol, 54%); R_f 0.4 (hexanes/ethyl acetate, 2:1); mp 116−117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.22 (m, 8H), 6.93−6.89 (m, 2H, H-15), 6.55 (dd, J = 4.4, 2.2 Hz, 1H, H-5), 3.84 (m, 1H, H-4), 3.46 (dd, J = 9.1, 6.9 Hz, 1H, H-3a), 3.36 (td, J = 8.8, 2.7 Hz, 1H, H-7a), 3.02 (dd, J = 16.4, 2.6 Hz, 1H, H-7′), 2.47 (ddt, J = 16.3, 8.6, 1.9 Hz, 1H, H-7), 0.944 (t, J = 8.0 Hz, 9H, H-9), 0.662 (q, J = 8.0 Hz, 6H, H-8). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 178.38 (C, C-1), 176.20 (C, C-3), 139.81 (CH, C-5), 139.02 (C, C-10), 138.94 (C, C-6), 131.74 (C, C-14), 129.12 (CH), 128.85 (CH), 128.34 (CH), 128.28 (CH), 127.14 (CH), 126.22 (CH, C-15), 45.28 (CH, C-3a), 42.15 (CH, C-4), 39.10 (CH, C-7a), 25.99 (CH_2, C-7), 7.39 (CH_3, C-9), 2.36 (CH_2, C-8). GC/MS: *m*/*z* (relative, %) 417.3 (2) [M^+], 390.2 (9), 389.2 (32), 388.2 (100), 230.1 (4), 215.1 (25), 187.1 (8), 185.1 (6), 159.1 (10), 157.0 (6), 145.0 (5), 131.0 (14), 129.1 (9), 115.1 (8), 87.1 (15), 59.1 (15). HRMS [M + Cs]$^+$ calcd for $C_{26}H_{31}NO_2Si$ 550.1179, found 550.1192. **Minor diastereomer (18d) (*exo*):** white powder (0.074 g, 0.177 mmol, 17%); R_f 0.5 (hexanes/ethyl acetate, 2:1); mp 78−79 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47−7.25 (m, 10H), 6.41 (dd, J = 5.6, 1.9 Hz, 1H, H-5), 4.12 (dd, J = 5.2, 3.7 Hz, 1H, H-4), 3.44 (dd, J = 9.3, 3.5 Hz, 1H, H-3a), 3.18 (ddd, J = 9.3, 7.6, 4.5 Hz, 1H, H-7a), 2.56 (dd, J = 15.6, 4.5 Hz, 1H, H-7′), 2.49 (ddd, J = 15.6, 7.6, 1.9 Hz, 1H, H-7), 0.929 (t, J = 7.9 Hz, 9H, H-9), 0.642 (q, J = 7.9 Hz, 6H, H-8). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 178.87 (C, C-1), 178.33 (C, C-3), 141.46 (C, C-10), 140.33 (CH, C-5), 139.12 (C, C-6), 131.95 (C, C-14), 129.07 (CH), 128.79 (CH), 128.50 (CH), 127.60 (CH), 126.75 (CH), 126.27 (CH), 46.68 (CH, C-3a), 41.20 (CH, C-4), 39.00 (CH, C-7a), 26.51 (CH_2, C-7), 7.41 (CH_3, C-9), 2.25 (CH_2, C-8). HRMS [M + Cs]$^+$ calcd for $C_{26}H_{31}NO_2Si$ 550.1179, found 550.1197. Diastereomeric ratio 3.4:1 (determined by ^{1}H NMR integrations).

6-(Dimethyl(phenyl)silyl)-2,4-diphenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (17f and 18f). Diene (**11b**) (0.075 g, 0.284 mmol), *N*-phenylmaleimide (0.038 g, 0.219 mmol), and THF (3 mL) were used according to the general procedure. After 16 h at 90 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting colorless residue was purified by flash chromatography with silica gel and 2:1 hexanes/ethyl acetate as eluent to yield the two diastereomers. **Major diastereomer (17f) (*endo*):** colorless residue (0.080 g, 0.183 mmol, 83%); R_f 0.5 (hexanes/ethyl acetate, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53−7.23 (m, 13H), 6.83−6.79 (m, 2H, H-18), 6.62 (dd, J = 4.6, 2.1 Hz, 1H, H-5), 3.84 (m, 1H, H-4), 3.46 (dd, J = 9.0, 6.8 Hz, 1H, H-3a), 3.35 (dt, J = 8.7, 2.5 Hz, 1H, H-7a), 3.03 (dd, J = 16.4, 2.4 Hz, 1H, H-7′), 2.47 (ddt, J = 16.3, 8.6, 1.9 Hz, 1H, H-7), 0.43 (as, 3H, H-8), 0.42 (as, 3H, H-8). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 178.2 (C, C-1), 176.2 (C, C-3), 140.2 (CH, C-5), 140.0 (C, C-13), 138.8 (C, C-6), 136.8 (C, C-9), 133.9 (CH), 131.7 (C, C-17), 129.3 (CH), 129.1 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 127.9 (CH), 127.2 (CH), 126.3 (CH, C-18), 45.3 (CH, C-3a), 42.3 (CH, C-4), 39.1 (CH, C-7a), 25.9 (CH_2, C-7), −3.74 (CH_3, C-8). HRMS [M + Na]$^+$ calcd for $C_{28}H_{27}NO_2SiNa$ 460.1709, found 460.1703. **Minor diastereomer (18f) (*exo*):** colorless residue (0.009 g, 0.021 mmol, 9%); R_f 0.6 (hexanes/ethyl acetate, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.16 (m, 15H), 6.47 (dd, J = 5.7, 1.5 Hz, 1H, H-5), 4.11 (m, 1H, H-4), 3.44 (dd, J = 9.3, 3.6 Hz, 1H, H-3a), 3.17 (ddd, J = 9.3, 7.5, 4.6 Hz, 1H, H-7a), 2.57 (dd, J = 15.8, 4.7 Hz, 1H, H-7′), 2.48 (ddd, J = 15.8, 7.6, 1.8 Hz, 1H, H-7), 0.40 (s, 6H, H-8). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 178.6 (C, C-1), 178.2 (C, C-3), 141.3 (C, C-13), 140.7 (CH, C-5), 140.2 (C, C-6), 133.9 (CH), 131.9 (C, C-17), 129.3 (CH), 129.1 (CH), 128.8 (CH), 128.5 (CH), 128.0 (CH), 127.6 (CH), 126.8 (CH), 126.3 (CH), 46.6 (CH, C-3a), 41.3 (CH, C-4), 39.1 (CH, C-7a), 26.4 (CH_2, C-7), −3.88 (CH_3, C-8). HRMS [M + Na]$^+$ calcd for $C_{28}H_{27}NO_2SiNa$ 460.1709, found 460.1727. Diastereomeric ratio 9.0:1 (determined by ^{1}H NMR integrations).

***endo*-6-(Benzyldimethylsilyl)-2,4-diphenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (23a).** Diene (**22a**) (0.252 g, 0.905 mmol), *N*-phenylmaleimide (0.134 g, 0.774 mmol), and THF (5 mL) were used according to the general procedure. After 24 h at 50 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting yellow residue was purified by flash chromatography with silica gel and 2:1 hexanes/ethyl acetate as eluent to yield a white powder (0.245 g, 0.542 mmol, 70%): R_f 0.4 (hexanes/ethyl acetate, 2:1); mp 135−138 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.18 (m, 10H), 7.12−6.98 (m, 3H), 6.89−6.84 (m, 2H, H-19), 6.55 (dd, J = 4.5, 1.9 Hz, 1H, H-5), 3.83 (m, 1H, H-4), 3.45 (dd, J = 9.0, 6.9 Hz, 1H, H-3a), 3.34 (dt, J = 8.8, 2.6 Hz, 1H, H-7a), 2.98 (dd, J = 16.4, 2.6 Hz, 1H, H-7/7′), 2.42 (ddt, J = 16.4, 8.3, 1.9 Hz, 1H, H-7/7′), 2.26 (d, J = 13.7 Hz, 1H, H-9), 2.19 (d, J = 13.7 Hz, 1H, H-9), 0.14 (s, 6H, H-8). ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 178.3 (C, C-1), 176.2 (C, C-3), 140.0 (C), 139.6 (CH, C-5), 139.4 (C), 138.6 (C), 131.7 (C), 129.1 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 128.1 (CH), 127.2 (CH), 126.2 (CH), 124.2 (CH), 45.2 (CH, C-3a), 42.2 (CH, C-4), 39.1 (CH, C-7a), 25.6 (CH_2, C-7), 24.9 (CH_2, C-9), −4.2 (CH_3, C-8), −4.3 (CH_3, C-8). HRMS [M + Cs]$^+$ calcd for $C_{29}H_{29}NO_2Si$ 584.1022, found 584.1051. Diastereomeric ratio 14.0:1 (determined by ^{1}H NMR integrations).

***endo*-6-(Benzyldimethylsilyl)-4-(4-methoxyphenyl)-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (23b).** Diene (**22b**) (0.174 g, 0.564 mmol), *N*-phenylmaleimide (0.086 g, 0.497 mmol), and THF (2 mL) were used according to the general procedure. After 16 h at 50 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting yellow residue was purified by flash chromatography with silica gel and 4:1 chloroform/ethyl acetate as eluent to yield a white solid (0.079 g, 0.164 mmol, 33%): R_f 0.6 (chloroform/ethyl acetate, 2:1); mp 89−93 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38−7.29 (m, 3H), 7.24−6.97 (m, 7H), 6.91−6.82 (m, 4H), 6.51 (dd, J = 4.7, 1.8 Hz, 1H, H-5), 3.81 (m, 1H, H-4), 3.79 (s, 3H, H-18), 3.40 (dd, J = 9.0, 6.7 Hz, 1H, H-3a), 3.32 (dt, J = 8.5, 2.5 Hz, 1H, H-7a), 2.96 (dd, J = 16.6, 2.5 Hz, 1H, H-7/7′), 2.41 (ddt, J = 16.6, 8.5, 1.8 Hz, 1H, H-7/7′), 2.24 (d, J = 13.7 Hz, 1H, H-9), 2.18 (d, J = 13.7 Hz, 1H, H-9), 0.13 (as, 3H, H-8), 0.12 (as, 3H, H-8). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 178.4 (C, C-1), 176.4 (C, C-3), 158.8 (C), 139.9 (CH), 139.7 (C), 139.5 (C), 131.7 (C), 130.5 (C), 130.1 (CH), 128.9 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 126.2 (CH), 124.2 (CH), 113.8 (CH), 55.3 (CH_3, C-18), 45.3 (CH, C-3a), 41.5 (CH, C-4), 39.0 (CH, C-7a), 25.5 (CH_2, C-7), 24.9 (CH_2, C-9), −4.1 (CH_3, C-8), −4.2 (CH_3, C-8). HRMS [M + Na]$^+$ calcd for $C_{30}H_{31}NO_3$-SiNa 504.1971, found 504.2002. Diastereomeric ratio 26.3:1 (determined by ^{1}H NMR integrations).

***endo*-6-(Benzyldimethylsilyl)-4-(4-chlorophenyl)-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (23c).** Diene (**22c**) (0.920 g, 2.94 mmol), *N*-phenylmaleimide (0.514 g, 2.97 mmol), and THF (12 mL) were used according to the general procedure. After 19 h at 50 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting yellow residue was purified by flash chromatography with silica gel and 2:1 hexanes/ethyl acetate as eluent to yield a white crystalline solid (0.925 g, 1.90 mmol, 65%): R_f 0.3 (hexanes/ethyl acetate, 2:1); mp 102−105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.30 (m, 3H), 7.18 (m, 4H), 7.08 (m, 1H), 6.99 (m, 1H), 6.93 (m, 2H), 6.48 (dd, J = 4.5, 2.2 Hz, 1H, H-5), 3.75 (at, J = 5.5 Hz, 1H,

H-4), 3.43 (dd, J = 9.1, 6.9 Hz, 1H, H-3a), 3.35 (dt, J = 8.8, 2.5 Hz, 1H, H-7a), 2.98 (dd, J = 16.2, 2.6 Hz, 1H, H-7), 2.37 (ddt, J = 16.1, 8.3, 2.2 Hz, 1H, H-7′), 2.23 (d, J = 13.7 Hz, 1H, H-13), 2.17 (d, J = 13.7 Hz, 1H, H-13), 0.12 (s, 6H, H-12). ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 178.1 (C), 176.0 (C), 140.9 (C), 139.33 (C), 139.28 (CH), 137.3 (C), 133.1 (C), 131.6 (C), 130.4 (CH), 129.0 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 126.1 (CH), 124.3 (CH), 45.2 (CH), 41.7 (CH), 39.1 (CH), 26.0 (CH_2), 24.8 (CH_2), −4.2 (CH_3, C-12), −4.3 (CH_3, C-12). HRMS [M + Cs]$^+$ calcd for $C_{29}H_{28}ClCsNO_2Si$ 618.0632, found 618.0686. Diastereomeric ratio 20.0:1 (determined by ^{1}H NMR integrations).

***endo*-6-(Benzyldimethylsilyl)-4-neopentyl-2-phenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (23d).** Diene (**22d**) (0.444 g, 1.63 mmol), *N*-phenylmaleimide (0.284 g, 1.64 mmol), and THF (8 mL) were used according to the general procedure. After 16.5 h at 50 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting yellow oil was purified by flash chromatography with silica gel and 1:1 hexanes/ethyl acetate as eluent to yield a white crystalline solid (0.409 g, 0.918 mmol, 56%): R_f 0.7 (hexanes/ethyl acetate, 1:1); mp 109−112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46−7.41 (m, 2H), 7.37−7.32 (m, 1H), 7.25−7.15 (m, 4H), 7.08−7.03 (m, 1H), 6.96−6.94 (m, 2H, H-14), 6.15 (t, J = 3.1 Hz, 1H, H-5), 3.27 (ddd, J = 8.8, 7.1, 1.9 Hz, 1H, H-7a), 3.15 (dd, J = 8.8, 6.1 Hz, 1H, H-3a), 2.86 (dd, J = 14.7, 1.9 Hz, 1H, H-7), 2.37 (m, 1H, H-4), 2.18 (am, 1H, H-7), 2.16 (ad, J = 13.7 Hz, 1H, H-12), 2.08 (d, J = 13.7 Hz, 1H, H-12), 2.03 (dd, J = 14.5, 1.5 Hz, 1H, H-8), 1.79 (dd, J = 14.5, 9.0 Hz, 1H, H-8), 0.94 (s, 9H, H-10), 0.03 (s, 3H, H-11), 0.01 (s, 3H, H-11). ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 178.7 (C, C-1), 177.4 (C, C-3), 146.5 (CH, C-5), 139.5 (C, C-13), 139.0 (C, C-6), 131.9 (C. C-17), 129.0 (CH), 128.4 (CH), 128.14 (CH), 128.12 (CH), 126.3 (CH), 124.1 (CH), 45.2 (CH_2, C-8), 45.1 (CH, C-3a), 40.3 (CH, C-7a), 33.8 (CH, C-4), 31.2 (CH_2, C-9), 29.8 (CH_3, C-10), 27.1 (CH_2, C-7), 24.9 (CH_2, C-12), −4.3 (CH_3, C-11), −4.5 (CH_3, C-11). HRMS [M + Cs]$^+$ calcd for $C_{28}H_{35}CsNO_2Si$ 578.1491, found 578.1486. Diastereomeric ratio 100:1 (determined by ^{1}H NMR integrations).

***endo*-6-(Benzyldimethylsilyl)-3a-methyl-4-phenyl-3a,4,7,7a-tetrahydroisobenzofuran-1,3-dione (25).** Diene (**22a**) (0.527 g, 1.89 mmol), citraconic anhydride (145 μL, 1.61 mmol), and THF (7 mL) were used according to the general procedure. After 7.2 days at 50 °C the reaction solution was condensed by rotary evaporation and dried under vacuum overnight. The resulting yellow residue was purified by flash chromatography with silica gel and 2:1 hexanes/ethyl acetate as eluent to yield a white crystalline solid (0.358 g, 0.917 mmol, 57.0%): R_f 0.4 (hexanes/ethyl acetate, 2:1); mp 107−110 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 3H), 7.22 (m, 2H, H-16), 7.10 (m, 3H, H-9/17), 7.00 (m, 2H, H-15), 6.28 (dd, J = 4.0, 2.6 Hz, 1H, H-5), 3.25 (dd, J = 4.0, 1.8 Hz, 1H, H-4), 3.05 (dd, J = 7.2, 2.5 Hz, 1H, H-7a), 2.92 (dd, J = 16.4, 2.5 Hz, 1H, H-7), 2.27 (ddt, J = 16.4, 7.2, 2.3 Hz, 1H, H-7′), 2.23 (d, J = 13.7 Hz, H-13), 2.18 (d, J = 13.7 Hz, 1H, H-13), 1.47 (s, 3H, H-18), 0.12 (s, 6H, H-12). ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 173.8 (C, C-3), 172.6 (C, C-1), 141.1 (C, C-6), 140.6 (CH, C-5), 139.2 (C, C-14), 137.7 (C, C-8), 129.7 (CH, C-9), 128.33 (CH), 128.27 (CH), 128.17 (CH), 128.0 (CH), 124.3 (CH, C-17), 50.1 (C, C-3a), 49.8 (CH, C-4), 46.9 (CH, C-7a), 24.8 (CH_2), 24.7 (CH_2), 23.7 (CH_3, C-18), −4.30 (CH_3, C-12), −4.33 (CH_3, C-12). HRMS [M + Cs]$^+$ calcd for $C_{24}H_{26}CsO_3Si$ 523.0706, found 523.0698.

Attempted Cross Coupling of Triethylsilylcycloadduct (17e), Which Resulted in Production of 18e. To a dried 10-mL round-bottomed flask equipped with a stir bar were added the *endo*-silicon-substituted cycloadduct (0.026 g, 0.062 mmol) and allylpalladium chloride dimer (0.003 g, 0.006 mmol), which were dissolved in HMPA (0.3 mL) under argon at 0 °C. Iodobenzene (10.0 μL, 0.090 mmol) and tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF) (0.051 g, 0.185 mmol) dissolved in THF (0.5 mL) were then added to the reaction flask and heated to 50 °C. After 4 h there was no cycloadduct detected by TLC. The reaction was quenched with distilled H_2O (10 mL) and extracted with diethyl ether (4 × 10 mL). The combined organic layers were washed with distilled H_2O (2 × 20 mL), dried over $MgSO_4$, condensed by rotary evaporation, and vacuum dried to yield a brown residue (0.021 g, 84%). ^{1}H NMR analysis of the product revealed a transformation to the *exo*-silicon-substituted cycloadduct. Chemical shifts mirrored those of the purified compound (**18f**) reported above.

Attempted Cross Coupling of Phenyldimethylsilylcycloadduct (17g), Which Produced Ring-Opened Product (19). To a dried 10-mL round-bottomed flask equipped with a stir bar were added potassium *tert*-butoxide (0.056 g, 0.49 mmol), tris(dibenzylideneacetone)-dipalladium(0) (0.013 g, 0.02 mmol), 18-crown-6 (0.088 g, 0.33 mmol), iodobenzene (21.1 μL, 0.19 mmol), and 1.0 M TBAF in THF (0.38 mL, 0.38 mmol), under argon. In a separate vial the *endo*-silicon-substituted cycloadduct (0.083 g, 0.19 mmol) was dissolved in THF (1.5% v/v H_2O) (1 mL) and then added to the reaction flask. After 4.5 h the cycloadduct is no longer detected by TLC. The reaction was then quenched with 0.6 M HCl (25 mL) and extracted with diethyl ether (2 × 25 mL). The combined organic layers were washed with distilled H_2O (30 mL), dried over $MgSO_4$, condensed by rotary evaporation, and vacuum-dried to yield a brown residue (0.079 g). Purification by column chromatography on silica gel with hexanes/ethyl acetate (1:1) as eluent yielded a white solid (0.058 g, 67%): R_f (hexanes/EtOAc 1:1) 0.5. ^{1}H NMR (500 MHz, CD_3CN, δ) 11.10 (bs, 1H, OH), 8.26 (bs, 1H, NH), 7.59−7.09 (m, 9H), 5.99 (m, 1H, H-6), 3.94 (m, 1H, H-1), 3.07 (m, 1H, H-2), 2.98 (dd, J = 8.4, 3.0 Hz, 1H, H-3), 2.76 (m, 1H, H-4), 2.38 (m, 1H, H-4), 0.39 (s, 3H, Me), 0.38 (s, 3H, Me). ^{13}C NMR (75.5 MHz, DMSO-d_6, δ) 174.8 (C), 170.9 (C), 143.7 (C), 139.3 (C), 137.7 (C), 137.2 (CH), 135.8 (C), 133.9 (CH), 129.1 (CH), 128.6 (CH), 128.4 (CH), 127.9 (CH), 126.6 (CH), 123.0 (CH), 119.3 (CH), 48.1 (CH), 43.2 (CH), 37.9 (CH), 27.7 (CH_2), −3.43 (CH_3), −3.44 (CH_3). IR (cm^{-1}) 3625 (NH, amide), 3520 (OH, acid), 1713 (C═O, acid), 1631 (C═O, amide), 1111 (Si-Ph). HRMS [M + Cs]$^+$ calcd for $C_{28}H_{29}NO_3Si$ 588.0940, found 588.0999.

General Procedure for Cross-Coupling Reactions. To a dried round-bottomed flask equipped with a stir bar were added the silicon-substituted cycloadduct (1.0 equiv) and $Pd_2dba_3 \cdot CHCl_3$ (10 mol %), dissolved in THF (1.0 M), and purged with argon. Aryl iodide (1.5 equiv) was then added to the reaction mixture. After 5 min, the reaction mixture changed color from deep purple to cloudy brown. Copper(I) iodide (CuI) (1.5 equiv) and tetrabutylammonium fluoride (TBAF) (3 equiv) were then added successively. Color change from brown to black indicates the formation of elemental Pd(0). The reaction vessel was then sealed with a rubber septum and placed in a 50 °C oil bath for the specified amount of time. After completion, the reaction was quenched with distilled water (5 mL) and extracted with diethyl ether (2 × 30 mL). The organic layers were combined, washed with distilled water (2 × 10 mL), dried over $MgSO_4$, condensed by rotary evaporation, and dried under vacuum.

***endo*-2,4,6-Triphenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (27a).** Diels−Alder cycloadduct (**23a**) (0.201 g, 0.445 mmol), iodobenzene (74.0 μL, 0.664 mmol), $Pd_2dba_3 \cdot CHCl_3$ (0.041 g, 0.040 mmol), CuI (0.126 g, 0.663 mmol), TBAF (1.3 mL, 1.3 mmol), and THF (2 mL) were used according to the general procedure. After 2.5 h at 50 °C and the previously mentioned workup, the resulting tan solid was purified by flash chromatography with silica gel and 1:1 hexanes/ethyl acetate as eluent to yield a white crystalline solid (0.118 g, 0.311 mmol, 70%): R_f 0.5 (hexanes/ethyl acetate, 1:1); mp 73−79 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.33 (m, 2H, H-9), 7.20 (m, 2H, H-13), 7.14−6.90 (m, 11H), 6.23 (dd, J = 5.2, 1.8 Hz, 1H, H-5), 3.55 (at, J = 5.5 Hz, 1H, H-4), 3.37 (dd, J = 16.5, 2.5 Hz, 1H, H-7), 2.84 (dd, J = 8.1, 7.1 Hz, 1H, H-3a), 2.59 (dt, J = 8.8, 2.6 Hz, 1H, H-7a), 2.23 (ddt, J = 16.5, 8.8, 1.8 Hz, 1H, H-7′). ^{13}C NMR (125.5 MHz, C_6D_6) δ 177.8 (C), 175.2 (C), 140.8 (C),

139.4 (C), 139.2 (C), 132.7 (C), 129.7 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.1 (CH), 127.9 (CH), 127.4 (CH), 126.5 (CH), 126.2 (CH), 126.0 (CH), 45.3 (CH), 42.8 (CH), 39.6 (CH), 26.3 (CH_2). HRMS $[M + Cs]^+$ calcd for $C_{26}H_{21}CsNO_2$ 512.0627, found 512.0668.

***endo*-2,4-Diphenyl-6-(3-(trifluoromethyl)phenyl)-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)dione (27b).** Diels−Alder cycloadduct (**23a**) (0.201 g, 0.445 mmol), 3-iodobenzotrifluoride (95.7 μL, 0.664 mmol), $Pd_2dba_3 \cdot CHCl_3$ (0.045 g, 0.043 mmol), CuI (0.137 g, 0.719 mmol), TBAF (1.3 mL, 1.3 mmol), and THF (2 mL) were used according to the general procedure. After 2 h at 50 °C and the previously mentioned workup, the resulting tan solid was purified by flash chromatography with silica gel and 1:1 hexanes/ethyl acetate as eluent to yield a white crystalline solid (0.071 g, 0.159 mmol, 36%): R_f 0.4 (hexanes/ethyl acetate, 1:1); mp 72−75 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 7.67 (s, 1H, H-13), 7.28−6.88 (m, 13H), 6.05 (dd, J = 5.3, 1.5 Hz, 1H, H-5), 3.51 (at, J = 6.2 H, 1H, H-4), 3.20 (dd, J = 16.9, 2.6 Hz, 1H, H-7), 2.81 (dd, J = 8.9, 7.4 Hz, 1H, H-3a), 2.55 (dt, J = 8.9, 2.6 Hz, 1H, H-7a), 2.10 (ddt, J = 16.9, 8.9, 1.5 Hz, 1H, H-7′). ^{13}C NMR (125.5 MHz, C_6D_6) δ 177.5 (C), 175.0 (C), 141.6 (C), 138.8 (C), 137.6 (C), 132.6 (C), 131.2 (q, $^2J_{C-F}$ = 32.0 Hz, C, C-12), 129.7 (CH), 129.4 (CH), 129.2 (CH), 128.8 (CH), 128.7 (CH), 128.3 (CH), 128.1 (CH), 127.9 (CH), 127.6 (CH), 126.4 (CH), 124.9 (q, $^1J_{C-F}$ = 273.1 Hz, C, C-14), 124.4 (q, $^3J_{C-F}$ = 3.7 Hz, CH), 122.7 (q, $^3J_{C-F}$ = 3.6 Hz, CH), 45.0 (CH), 42.7 (CH), 39.3 (CH), 25.6 (CH_2, C-7). ^{19}F NMR (282 MHz, C_6D_6) δ −62.29. HRMS $[M + H]^+$ calcd for $C_{27}H_{21}F_3NO_2$ 448.1524, found 448.1555.

***endo*-6-(3-Methoxyphenyl)-2,4-diphenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (27c).** Diels−Alder cycloadduct (**23a**) (0.209 g, 0.463 mmol), 3-iodoanisole (79.2 μL, 0.664 mmol), $Pd_2dba_3 \cdot CHCl_3$ (0.047 g, 0.045 mmol), CuI (0.128 g, 0.672 mmol), TBAF (1.3 mL, 1.3 mmol), and THF (2 mL) were used according to the general procedure. After 3 h at 50 °C and the previously mentioned workup, the resulting brown residue was purified by flash chromatography with silica gel and 1:1 hexanes/ethyl acetate as eluent to yield an off-white crystalline solid (0.061 g, 0.149 mmol, 32%): R_f 0.4 (hexanes/ethyl acetate, 1:1); mp 75 °C dec. ^{1}H NMR (300 MHz, C_6D_6) δ 7.21−6.98 (m, 12H), 6.91−6.88 (m, 1H), 6.75−6.72 (m, 1H), 6.30 (dd, J = 5.1, 2.0 Hz, 1H, H-5), 3.54 (at, J = 6.2 Hz, 1H, H-4), 3.39 (dd, J = 16.6, 2.6 Hz, 1H, H-7), 3.34 (s, 3H, H-14), 2.84 (dd, J = 8.8, 7.9 Hz, 1H, H-3a), 2.59 (dt, J = 8.7, 2.1 Hz, 1H, H-7a), 2.26 (ddt, J = 16.6, 8.7, 1.8 Hz, 1H, H-7′). ^{13}C NMR (125.5 MHz, C_6D_6) δ 177.7 (C), 175.1 (C), 160.5 (C), 142.4 (C), 139.33 (C), 139.31 (C), 132.8 (C), 129.9 (CH), 129.6 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 127.4 (CH), 126.6 (CH), 126.4 (CH), 118.5 (CH), 113.6 (CH), 111.9 (CH), 54.8 (CH_3, C-14), 45.4 (CH), 42.9 (CH), 39.7 (CH), 26.5 (CH_2, C-7). HRMS $[M + Na]^+$ calcd for $C_{27}H_{23}NaNO_3$ 432.1576, found 432.1576.

***endo*-4-(4-Methoxyphenyl)-2,6-diphenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (27d).** Diels−Alder cycloadduct (**23b**) (0.207 g, 0.430 mmol), iodobenzene (68.8 μL, 0.617 mmol), $Pd_2dba_3 \cdot CHCl_3$ (0.043 g, 0.042 mmol), CuI (0.116 g, 0.609 mmol), TBAF (1.2 mL, 1.2 mmol), and THF (2 mL) were used according to the general procedure. After 2.5 h at 50 °C and the previously mentioned workup, the resulting brown residue was purified by flash chromatography with silica gel and 1:1 hexanes/ethyl acetate as eluent to yield a white crystalline solid (0.074 g, 0.181 mmol, 42%): R_f 0.3 (hexanes/ethyl acetate, 1:1); mp 70−73 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.36 (m, 2H), 7.13−7.00 (m, 9H), 6.90 (m, 1H), 6.75 (m, 2H), 6.26 (dd, J = 5.2, 1.7 Hz, 1H, H-5), 3.59 (at, J = 6.2 Hz, 1H, H-4), 3.37 (dd, J = 16.9, 2.6 Hz, 1H, H-7), 3.28 (s, 3H, H-20), 2.85 (dd, J = 8.9, 7.2 Hz, 1H, H-3a), 2.61 (dt, J = 8.8, 2.5 Hz, 1H, H-7a), 2.27 (ddt, J = 16.8, 8.8, 1.8, Hz, 1H, H-7′). ^{13}C NMR (125.5 MHz, C_6D_6) δ 177.9 (C), 175.4 (C), 159.5 (C), 140.9 (C), 138.8 (C), 132.8 (C), 131.0 (C), 130.7 (CH), 128.8 (CH), 128.7 (CH), 128.3 (CH), 127.9 (CH), 126.6 (CH), 126.0 (CH), 114.2 (CH), 54.8 (CH_3, C-20), 45.4 (CH), 42.1 (CH), 39.5 (CH), 26.0 (CH_2, C-7). HRMS $[M + Na]^+$ calcd for $C_{27}H_{23}NaNO_3$ 432.1576, found 432.1585.

***endo*-4-(4-Chlorophenyl)-2,6-diphenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (27e).** Diels−Alder cycloadduct (**23c**) (0.202 g, 0.416 mmol), iodobenzene (68.8 μL, 0.617 mmol), $Pd_2dba_3 \cdot CHCl_3$ (0.046 g, 0.044 mmol), CuI (0.121 g, 0.635 mmol), TBAF (1.3 mL, 1.3 mmol), and THF (2 mL) were used according to the general procedure. After 2 h at 50 °C and the previously mentioned workup, the resulting brown residue was purified by flash chromatography with silica gel and 1:1 hexanes/ethyl acetate as eluent to yield a white powder (0.056 g, 0.135 mmol, 33%): R_f 0.3 (hexanes/ethyl acetate, 1:1); mp 86−88 °C. ^{1}H NMR (300 MHz, C_6D_6) δ 7.35 (m, 2H), 7.13−6.88 (m, 12H), 6.11 (dd, J = 4.9, 2.1 Hz, 1H, H-5), 3.34 (at, J = 6.0 Hz, 1H, H-4), 3.32 (dd, J = 16.2, 2.1 Hz, 1H, H-7), 2.75 (dd, J = 9.0, 6.8 Hz, 1H, H-3a), 2.61 (dt, J = 8.5, 2.3 Hz, 1H, H-7a), 2.17 (ddt, J = 16.3, 8.1, 2.0 Hz, 1H, H-7′). ^{13}C NMR (125.5 MHz, C_6D_6) δ 177.5 (C), 175.0 (C), 140.5 (C), 139.9 (C), 137.9 (C), 133.3 (C), 132.6 (C), 130.9 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 126.4 (CH), 126.0 (CH), 125.7 (CH), 45.3 (CH), 42.1 (CH), 39.7 (CH), 26.8 (CH_2, C-7). HRMS $[M + Na]^+$ calcd for $C_{26}H_{20}NaClNO_2$ 436.1080, found 436.1079.

***endo*-4-Neopentyl-2,6-diphenyl-3a,4,7,7a-tetrahydro-1*H*-isoindole-1,3(2*H*)-dione (27f).** Diels−Alder cycloadduct (**23d**) (0.202 g, 0.453 mmol), iodobenzene (75.0 μL, 0.673 mmol), $Pd_2dba_3 \cdot CHCl_3$ (0.045 g, 0.043 mmol), CuI (0.130 g, 0.683 mmol), TBAF (1.4 mL, 1.4 mmol), and THF (1.8 mL) were used according to the general procedure. After 21 h at 50 °C and the previously mentioned workup, the resulting brown residue was purified by flash chromatography with silica gel and 2:1 hexanes/ethyl acetate as eluent to yield a white crystalline solid (0.103 g, 0.276 mmol, 61%): R_f 0.3 (hexanes/ethyl acetate, 2:1); mp 127−129 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 7.39 (m, 2H, H-12), 7.23 (m, 2H, H-16), 7.10 (m, 2H, H-13), 7.01 (m, 3H, H14/17), 6.90 (m, 1H, H-18), 5.94 (t, J = 2.7 Hz, 1H, H-5), 3.24 (dt, J = 15.0, 1.6 Hz, 1H, H-7), 2.66 (ddd, J = 8.8, 6.9, 1.8 Hz, 1H, H-7a), 2.56 (dd, J = 8.8, 5.9 Hz, 1H, H-3a), 2.19 (m, 1H, H-4), 2.16 (dd, J = 14.8, 2.6 Hz, 1H, H-8/8′), 2.03 (dddd, J = 15.0, 6.8, 2.7, 1.5 Hz, 1H, H-7′), 1.90 (dd, J = 15.0, 9.7 Hz, 1H, H-8/8′), 0.93 (s, 9H, H-10). ^{13}C NMR (125.5 MHz, C_6D_6) δ 178.1 (C, C-1), 176.4 (C, C-3), 140.5 (C, C-11), 139.3 (C, C-6), 132.9 (C, C-15), 131.6 (CH, C-5), 128.9 (CH, C-13/17), 128.1 (CH, C-18), 127.7 (CH, C-14), 126.8 (CH, C-16), 126.0 (CH, C-12), 45.73 (CH, C-3a), 45.70 (CH_2, C-8), 41.0 (CH, C-7a), 34.6 (CH, C-4), 31.2 (C, C-9), 30.0 (CH_3, C-10), 28.6 (CH_2, C-7). HRMS $[M + Na]^+$ calcd for $C_{25}H_{27}NaNO_2$ 396.1939, found 396.1939.

Brief Experimental Description of X-ray Characterization of Compound 17e. A CIF file has been deposited with the CCDC under code 787685. Colorless crystals of $C_{26}H_{31}NO_2Si$ are, at 193(2) K, orthorhombic, space group $P2_12_12_1$-D_2^4 (No. 19) with a = 8.1254(11) Å, b = 13.4757(18) Å, c = 21.652(3) Å, V = 2370.8(6) Å^3, and Z = 4 {d_{calcd} = 1.170 g cm^{-3}; μ_a(Mo Kα̅) = 0.120 mm^{-1}}. A full hemisphere of diffracted intensities (1968 30-s frames with an ω scan width of 0.30°) was measured for a single-domain specimen, using graphite-monochromated Mo Kα̅ 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 APEX2 software package, using peak centers for 3975 reflections having 7.53° ≤ 2θ ≤ 44.61°. A total of 21111 integrated reflection intensities having 2θ(Mo Kα̅) ≤ 53.44° were produced with the Bruker program SAINT; 2857 of these were unique and gave R_{int} = 0.053 with a coverage that was 99.5% complete (Friedel opposites were merged). The data were corrected empirically for variable scaling and absorption effects with the SADABS program; the estimated minimum and maximum transmission values reported were 0.6129 and 0.7457.

The Bruker software package SHELXTL was used to solve the structure by using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL software package. The resulting structural parameters have been refined to convergence {R_1(unweighted, based on F) = 0.0471 for 2402 independent reflections having 2Θ(Mo K$\overline{\alpha}$) < 53.44° and $F^2 > 2\sigma(F^2)$} {R_1(unweighted, based on F) = 0.0584 and wR_2(weighted, based on F^2) = 0.1217 for all 2857 reflections} using counter-weighted full-matrix least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All methyl groups were incorporated into the structural model as rigid groups (using idealized sp^3-hybridized geometry and a C−H bond length of 0.98 Å) with a "staggered" orientation. The remaining hydrogen atoms were included into the structural model as idealized atoms (assuming sp^2- or sp^3-hybridization of the carbon atoms and C−H bond lengths of 0.95−1.00 Å). The isotropic thermal parameters of all hydrogen atoms were fixed at values 1.2 (nonmethyl) or 1.5 (methyl) times the equivalent isotropic thermal parameter of the carbon atom to which they are covalently bonded.

Two of the ethyl groups identified by carbon atoms $C_{23}-C_{26}$ (and their respective hydrogens) appear to be disordered between two possible orientations. The two alternate orientations designated by $C_{23}-C_{26}$ and $C_{23'}-C_{26'}$ were included in the refinement as half-occupancy sites. All $Si-C^{sp^3}$ and ethyl $C^{sp^3}-C^{sp^3}$ bond lengths were restrained to common values of 1.851 and 1.540 Å, respectively, in the refinement.

A total of 312 parameters were refined using 10 restraints and 2857 data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.315 and −0.139 $e^-/Å^3$, respectively.

Brief Experimental Description of X-ray Characterization of Compound 25. A CIF file has been deposited with the CCDC under code 787686. Colorless crystals of $C_{24}H_{26}O_3Si$ are, at 193(2) K, orthorhombic, space group $P2_12_12_1$-D_2^4 (No. 19) with a = 7.1897(9) Å, b = 10.065(1) Å, c = 29.034(4) Å, V = 2101.0(4) $Å^3$, and Z = 4 {d_{calcd} = 1.235 gcm^{-3}; μ_a(Mo K$\overline{\alpha}$) = 0.133 mm^{-1}}. A full hemisphere of diffracted intensities (1968 30-s frames with an ω scan width of 0.30°) was measured for a single-domain specimen, using graphite-monochromated Mo K$\overline{\alpha}$ 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 APEX2 software package, using peak centers for 3944 reflections having 7.98° ≤ 2θ ≤ 53.82°. A total of 19570 integrated reflection intensities having 2θ(Mo K$\overline{\alpha}$) ≤ 55.00° were produced with the Bruker program SAINT; 4786 of these were unique and gave R_{int} = 0.053 with a coverage that was 99.2% complete. The data were corrected empirically for variable scaling and absorption effects, using the SADABS program; the estimated minimum and maximum transmission values reported were 0.5401 and 0.7460.

The Bruker software package SHELXTL was used to solve the structure by using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted by using F_o^2 data with the SHELXTL software package. The resulting structural parameters have been refined to convergence {R_1(unweighted, based on F) = 0.0571 for 4271 independent reflections having 2Θ(Mo K$\overline{\alpha}$) < 55.00° and $F^2 > 2\sigma(F^2)$} {R_1(unweighted, based on F) = 0.0659 and wR_2(weighted, based on F^2) = 0.1298 for all 4786 reflections} using counter-weighted full-matrix least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All methyl groups were incorporated into the structural model as rigid groups (using idealized sp^3-hybridized geometry and a C−H bond length of 0.98 Å) with a "staggered" orientation. The remaining hydrogen atoms were included into the structural model as idealized atoms (assuming sp^2- or sp^3-hybridization of the carbon atoms and C−H bond lengths of 0.95−1.00 Å). The isotropic thermal parameters of all hydrogen atoms were fixed at values 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 256 parameters were refined with no restraints and 4786 data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.500 and −0.224 $e^-/Å^3$, respectively.

Brief Experimental Description of X-ray Characterization of Compound 27f. A CIF file has been deposited with the CCDC under code 787687. Colorless crystals of $C_{25}H_{27}NO_2$ are, at 193(2) K, monoclinic, space group $P2_1/c$-C_{2h}^5 (No. 14) with a = 11.975(3) Å, b = 16.248(4) Å, c = 21.172(6)Å, β = 95.843(4)°, V = 4097.9(19) $Å^3$, and Z = 8 {d_{calcd} = 1.211 $g\,cm^{-3}$; μ_a(Mo K$\overline{\alpha}$) = 0.076 mm^{-1}}. A full hemisphere of diffracted intensities (1968 40-s frames with an ω scan width of 0.30°) was measured for a mostly single-domain weakly diffracting specimen, using graphite-monochromated Mo K$\overline{\alpha}$ 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 APEX2 software package, using peak centers for 656 reflections having 7.72° ≤ 2θ ≤ 36.02°. A total of 28952 integrated reflection intensities having 2θ(Mo K$\overline{\alpha}$) ≤ 48.22° were produced with the Bruker program SAINT; 6505 of these were unique and gave R_{int} = 0.210 with a coverage that was 99.6% complete. The data were corrected empirically for variable scaling and absorption effects by using the SADABS program; the estimated minimum and maximum transmission values reported were 0.9681 and 0.9985.

The Bruker software package SHELXTL was used to solve the structure by using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted by using F_o^2 data with the SHELXTL software package. The resulting structural parameters have been refined to convergence {R_1(unweighted, based on F) = 0.0869 for 2748 independent reflections having 2Θ(Mo K$\overline{\alpha}$) < 48.22° and $F^2 > 2\sigma F^2$)} {R_1(unweighted, based on F) = 0.2093 and wR_2(weighted, based on F^2) = 0.2255 for all 6505 reflections} using counter-weighted full-matrix least-squares techniques and a structural model that incorporated anisotropic thermal parameters for all nonhydrogen atoms and isotropic thermal parameters for all hydrogen atoms. All methyl groups were incorporated into the structural model as rigid groups (using idealized sp^3-hybridized geometry and a C−H bond length of 0.98 Å) with a "staggered" orientation. The remaining hydrogen atoms were included into the structural model as idealized atoms (assuming sp^2- or sp^3-hybridization of the carbon atoms and C−H bond lengths of 0.95−1.00 Å). The isotropic thermal parameters of all hydrogen atoms were fixed at values 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 511 parameters were refined with no restraints and 6505 data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.341 and −0.306 $e^-/Å^3$, respectively.

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Supporting Information Available: ^1H and ^{13}C NMR spectra of all novel compounds produced and X-ray crystallographic data for compounds **17e**, **25**, and **27f**. This material is available free of charge via the Internet at http://pubs.acs.org.