# Synthesis of Polycyclic Structures by the Diels−Alder Reaction of Inner-Outer-Ring 1,3-Bis(trimethylsilyloxy)dienes

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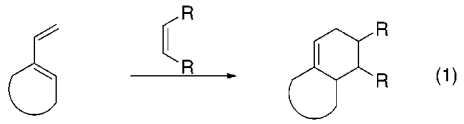
A Diels−Alder reaction of novel inner-outer-ring 1,3-silyloxydienes **5**−**8** with a variety of dienophiles to afford highly functionalized polycyclic structures is reported. The inner-outer-ring 1,3-silyloxydienes **5**−**8** containing five- to seven-membered carbocyclic and heterocyclic rings were prepared in a single reaction vessel from 2-acetylcyclocarbonyls in quantitative yields. The Diels−Alder reaction with 1,4-benzoquinone (BQ), dimethyl acetylenedicarboxylate (DMAD), and methyl vinyl ketone (MVK) proceeded smoothly at room temperature, affording functionalized polycyclic naphthols, phenols, and enones with high regioselectivity and good yields (39−75%). Moreover, dienes **5**−**8** also reacted in a hetero-Diels−Alder reaction with benzaldehyde (BA) and *N*-benzylideneaniline (NBA) in the presence of catalytic amounts of $ZnCl_2$, affording substituted polycyclic pyranones and pyridinones in good yields (40−93%). Overall, our synthetic strategy provides straightforward access to an interesting set of polycyclic structures useful for natural and nonnatural product synthesis.

## Introduction

The Diels−Alder reaction is one of the most fundamental and useful reactions in organic synthesis.[1] Since its discovery over 70 years ago, the synthetic potential of this reaction has been greatly expanded through modifications of the diene and dienophile components.[2] Dienes where the olefins form part of a cyclic structure, such as inner-outer-ring dienes (**1**),[3] are particularly useful for the synthesis of polycyclic structures, since they allow the incorporation of additional rings in the six-membered ring formed in the Diels−Alder reaction (eq 1). Despite this interesting synthetic feature, inner-outer-




(1)

**1**, Inner-outer-ring diene **2**

ring dienes have strong synthetic limitations due to their low reactivity and poor regioselectivity,[4] a problem that can sometimes be overcome by the introduction of substituents[5] in the inner-outer-ring dienes or in the dienophiles.[2e,6]

The oxygenated dienes are an important family of dienes recognized by their high reactivity, selectivity, and usefulness in natural product synthesis. Soon after the discovery of the Diels−Alder reaction, the high reactivity of alkoxydienes was revealed,[7] but the difficulty of their preparation limited their synthetic applications. The development of efficient methods to prepare silyl enol ethers from ketones,[8] led to the extensive employment of silyloxydienes in the Diels−Alder reaction.[9] A particularly useful subgroup is constituted by the 1,3-dioxygenated dienes, due to their increased reactivity with dienophiles, produced from the synergism between the two oxygen substituents, and the ease with which the cycloadducts may be selectively converted to enones and aromatic compounds. The most representative member of this group is 1-methoxy-3-trimethylsilyloxy-1,3-butadiene (**3**), the so-called Danishefsky's diene.[10]

After our participation in the synthesis of furaquinocin C,[11] where the key step was a Diels−Alder reaction between a quinone and an inner-outer-ring 1,3-bis-

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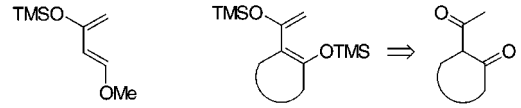


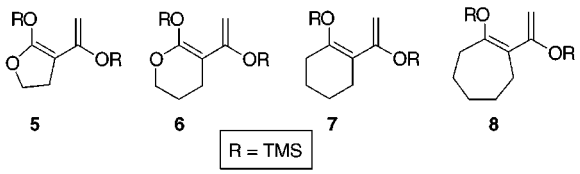

**3**, Danishefsky's diene

**4**, Inner-outer-ring 1,3-bis(trimethylsilyloxy)dienes

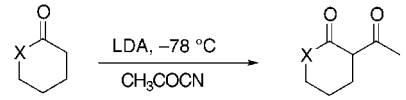
(silyloxy)diene, we became interested in further exploring the Diels−Alder reactivity of this type of diene with dienophiles. Hitherto, the use of 1,3-bis(silyloxy)dienes has been limited to linear dienes[12] and one example of inner-outer ring dienes.[13] In this, a full account,[14] we report on the Diels−Alder reaction of novel inner-outer-ring 1,3-bis(silyloxy)dienes prepared from 2-acetylcyclocarbonyls (**4**) with several types of dienophiles directed to the synthesis of polycyclic structures of interest.

## Results and Discussion

**Preparation of the Dienes.** Our research focused on dienes **5**−**8** containing heterocyclic and carbocyclic rings of five to seven members, with the purpose of studying the effect that the ring size and components had on the Diels−Alder reactivity, and to exploit this to incorporate furane, pyrane, cyclohexane, and medium-sized rings into a polycyclic structure. For the preparation of the dienes, we used 2-acetylcyclocarbonyl compounds that could be prepared by acetylation of the corresponding cyclocarbonyls in one or two steps.[15]




2-Acetylbutyrolactone (**11**) and 2-acetylcyclohexanone (**13**) are commercially available, while 2-acetyl-$\delta$-valerolactone (**12**)[16] and 2-acetylcycloheptanone (**14**)[17] were prepared in 45% and 67% yields from $\delta$-valerolactone (**9**) and cycloheptanone (**10**), respectively, by treatment with LDA at −78 °C, and acetylation with pyruvonitrile in one step following a modified procedure (eq 1).[18] Other reaction conditions and other acylating reagents, such as acetic anhydride or acetyl chloride, gave either lower yields, or mixtures of C- and O-acylation products that were difficult to separate.



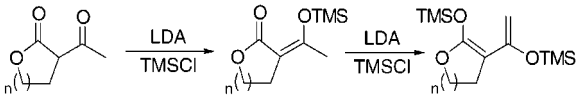

(2)

**9**, X = O
**10**, X = $(CH_2)_2$

**12**, X = O (45%)
**14**, X = $(CH_2)_2$ (67%)

With the 2-acetylcyclocarbonyls in hand, we proceeded to study the preparation of the corresponding dienes. Some years ago, Molander and Cameron[19] prepared some 1,3-bis(trimethylsilyloxy)dienes,[20] including diene **5**, in a two-step process using $Et_3N$ and TMSCl, to prepare the silyl enol ether intermediate, followed by the addition of LDA/TMSCl to synthesize the 1,3-bis(trimethylsilyloxy)-dienes (70% overall yield). In our procedure, diene **5** was obtained in a quantitative yield in a one-pot/two-step process using LDA as a base at low temperature, followed by TMSCl addition (Scheme 1).[21] When the reaction was interrupted after the first addition of LDA and TMSCl, the silyl enol ether **15** intermediate was isolated. The structure of **15** was inferred from the observed homoallylic $^1$H NMR coupling constant ($J$ = 2.0 Hz) between the methyl group and the methylene hydrogen at the $\beta$-position. Silyl enol ether **15** can be transformed into diene **5** by addition of LDA and TMSCl at −78 °C in a quantitative yield. Following the same experimental procedure, 2-acetyl-$\delta$-valerolactone (**12**) was converted to diene **6** in a quantitative yield. The structure of the silyl enol ether intermediate **16** was also assigned based on the data from its $^1$H NMR spectra.

**Scheme 1**




**11**, n = 1
**12**, n = 2

**15**, n = 1
**16**, n = 2

**5**, n = 1
**6**, n = 2

The preparation of carbocyclic dienes **7** and **8** from 2-acetylcyclohexanone and 2-acetylcycloheptanone requires a regioselective deprotonation. Literature precedents[22] have shown that the treatment of 2-acetylcyclohexanone with $Et_3N$ and TMSCl, gives a mixture of dienes **19** and **7** in a ratio of 9:1, **7** being the minor regioisomer (Scheme 2). Following the experimental procedure described for **5** and **6**, we found that treatment of commercial 2-acetylcyclohexanone with LDA at low temperature (−78 °C), followed by addition of TMSCl, resulted in the formation of a single product which was assigned as silyl enol ether **17**, based on the methyl

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(18) Tang, Q.; Sen, S. E. *Tetrahedron Lett.* **1998**, *39*, 2249.

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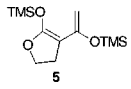
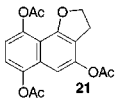
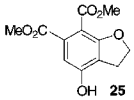
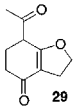
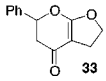
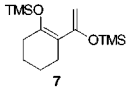
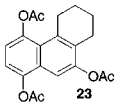
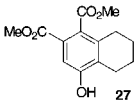
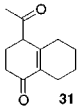
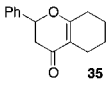
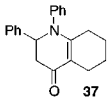
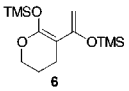
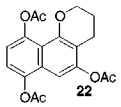
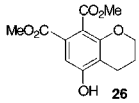
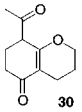
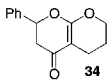
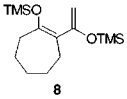
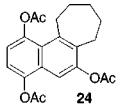
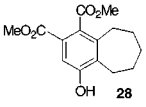
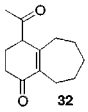
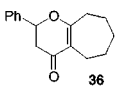
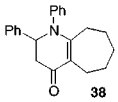
(20) While this manuscript was in preparation, the synthesis of new 1,3-bis(trimethylsilyloxy)dienes was reported: Langer, P.; Schneider, T.; Stoll, M. *Chem. Eur. J.* **2000**, *6*, 3204.

(21) Other experimental conditions, such as the addition of LDA/TMSCl (2.2 equiv) gave lower yields, and at many times gave mixtures of silyl enol ethers.

(22) (a) Babot, O.; Cazeau, P.; Duboudin, F. *J. Organomet. Chem.* **1987**, *326*, C27. (b) Hansson, L.; Carlston, R. *Acta Chem. Scand.* **1989**, *43*, 304.

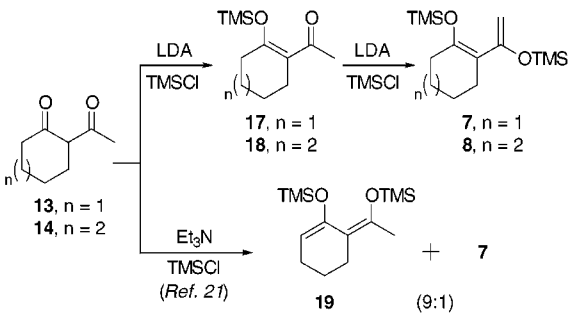
**Table 1. Results of the Diels–Alder Reaction of 1,3-Bis(trimethylsilyloxy)dienes 5–8 with Dienophiles**[a]

| Entry | Diene | Dienophile | Reac. Cond. | Product (yield %) |
|---|---|---|---|---|
| 1 |  **5** | BQ | rt 24 h |  **21** (75) |
| 2 | | DMAD | rt 12 h |  **25** (69) |
| 3 | | MVK | rt 24 h |  **29** (62) |
| 4 | | BA | rt 24 h $ZnCl_2$ (cat) |  **33** (44) |
| 5 |  **7** | BQ | rt 24 h |  **23** (70) |
| 6 | | DMAD | rt 12 h |  **27** (66) |
| 7 | | MVK | 90°C 24 h |  **31** (50) |
| 8 | | BA | rt 24 h $ZnCl_2$ (cat) |  **35** (60) |
| 9 | | NBA | rt 24 h $ZnCl_2$ (cat) |  **37** (93) |
| 10 |  **6** | BQ | rt 24 h |  **22** (72) |
| 11 | | DMAD | rt 20 h |  **26** (66) |
| 12 | | MVK | rt 24 h |  **30** (40) |
| 13 | | BA | rt 24 h $ZnCl_2$ (cat) |  **34** (40) |
| 14 |  **8** | BQ | rt 24 h |  **24** (70) |
| 15 | | DMAD | rt 20 h |  **28** (39) |
| 16 | | MVK | rt 24 h $ZnCl_2$ (cat) |  **32** (46) |
| 17 | | BA | rt 24 h $ZnCl_2$ (cat) |  **36** (41) |
| 18 | | NBA | rt 24 h $ZnCl_2$ (cat) |  **38** (69) |

[a] BQ: 1,4-benzoquinone. DMAD: dimethyl acetylenedicarboxylate. MVK: methyl vinyl ketone. BA: benzaldehyde. NBA: *N*-benzylideneaniline.

singlet observed by $^1$H NMR. Kinetic deprotonation of **17** with LDA, and enolate trapping with TMSCl, led to the desired diene **7**,[23] as the only diene observed by $^1$H NMR, as a distillable colorless oil in a quantitative yield. In this way, diene **7** was prepared for the first time in a pure form by a new regioselective one-pot procedure. The novel diene **8** was also obtained following the same experimental procedure in a quantitative yield from 2-acetylcycloheptanone. The structure of the silyl enol ether intermediate **18** was also determined by $^1$H NMR.

**Scheme 2**



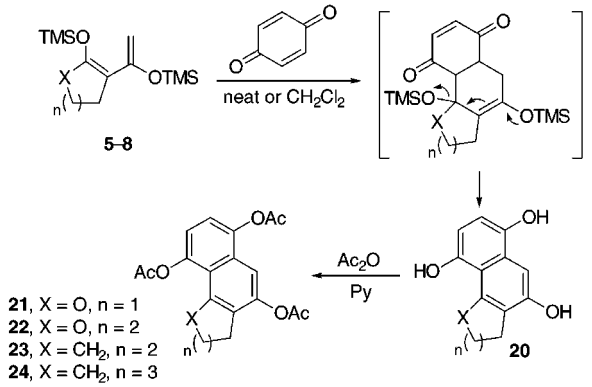

Although 1,3-bis(trimethylsilyloxy)dienes **5**–**8** are moisture-sensitive liquids or oils, they can be stored under argon after distillation and kept for at least 1 week under refrigeration (4–5 °C). The carbocyclic dienes **7** and **8** showed a higher stability than **5** and **6**. Attempts to increase the diene stability by preparing the less labile *tert*-butyldimethylsilyl enol ethers failed.

**Diels–Alder Reactivity.** The Diels–Alder reaction of the inner-outer-ring 1,3-bis(trimethylsilyloxy)dienes **5**–**8** was studied with some of the most common dienophiles with the purpose to access to a diverse array of polycyclic structures and to explore the reactivity of these novel dienes. We assayed the reaction with 1,4-benzoquinone (BQ), dimethyl acetylenedicarboxylate (DMAD), methyl vinyl ketone (MVK), benzaldehyde (BA), and *N*-benzylideneaniline (NBA).

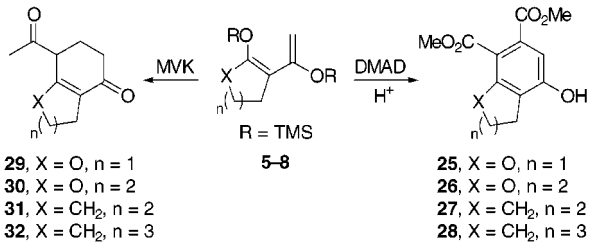
**(a) Reaction with 1,4-Benzoquinone (BQ).** The Diels–Alder reaction of silyloxydienes with quinones has been very useful for the synthesis of several natural products.[9] The inner-outer-ring 1,3-bis(silyloxy)dienes **5**–**8** reacted with 1,4-benzoquinone at room-temperature exothermically, in short reaction times (3–5 h) and good yields (70–75%). Trihydroxy naphthalenes **20** were directly obtained from this reaction, following a general reaction pattern (Scheme 3). However, they proved to be

(23) Krageloh, K.; Simchen, G.; Schweiker, K. *Liebigs Ann. Chem.* **1985**, 2352.

**Scheme 3**




**Scheme 4**



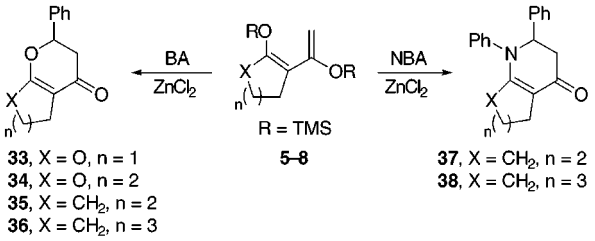

unstable in air and were transformed in situ into the acetylated derivatives (**21**−**24**). In this way, novel naphthofuran, naphthopyran, and phenanthrene structures (see Table 1, entries 1, 5, 10, and 14) were prepared in two steps from the 2-acetylcyclocarbonyls.

**(b) Reaction with Dimethyl Acetylenedicarboxylate (DMAD).** DMAD is an electron-deficient alkyne often used in cycloadditions.[2] The Diels−Alder reaction of DMAD with 1,3-dioxygenated dienes has allowed the preparation of various functionalized phenols.[9] The reaction of dienes **5**−**8** with DMAD proceeded at room temperature to give moderate yields (39−70%) (Scheme 4). While diene **5** affords the benzofurane **25** directly (see Table 1, entry 2), the reaction with other dienes needed acidic conditions to give phenols **26**−**28** (see Table 1, entries 6, 11, and 15). The reaction times were similar for all dienes, but the lowest yields were obtained with diene **8** containing the cycloheptane ring (Table 1, entry 15).

**(c) Reaction with Methyl Vinyl Ketone (MVK).** As an asymmetric dienophile, MVK allows for the study of the regioselectivity of dienes in the Diels−Alder reaction. On the other hand, the reaction of 1,3-oxygenated dienes with MVK has afforded synthetically useful enones.[9] Dienes **5** and **6** react with MVK at room temperature to give enones **29** and **30** in 62% and 40% yields, respectively, as the only regioisomers detected by $^1$H NMR (see Table 1, entries 3 and 12). Dienes **7** and **8** containing the carbocyclic six- and-seven membered rings showed a lower reactivity. Diene **7** needed to be heated with MVK in benzene at 90 °C to give the unstable enone **31** in a 50% yield after 24 h (Table 1, entry 7). The reaction of diene **8** with MVK at 90 °C gave enone **32** in only a 10% yield, but in the presence of catalytic amounts of $ZnCl_2$, the reaction proceeded at room temperature to give a 46% yield after 24 h (Table 1, entry 16). For all the dienes, a single regioisomer was detected by $^1$H NMR (Scheme 4).

**(d) Hetero-Diels−Alder Reaction.** The Diels−Alder reaction of dienes and/or dienophiles containing heteroatoms inserted in the olefins (hetero-Diels−Alder) is

**Scheme 5**




significant in the preparation of heterocyclic compounds.[1,2] Only highly reactive dienes react with heterodienophiles with the assistance of Lewis acids.[2f] For this reason, we decided to explore the hetero-Diels−Alder reaction of the inner-outer-ring 1,3-bis(silyloxy)dienes **5**−**8** with aldehydes and imines. The hetero-Diels−Alder reaction of silyloxydienes with aldehydes and imines has been very useful in the synthesis of pyranes in carbohydrate chemistry and also for other heterocyclic structures.[9,24] Despite the scant reporting of the use of inner-outer-ring silyloxydienes, they should allow for the construction of interesting polyheterocyclic structures.[25]

The Diels−Alder reaction of 1,3-bis(silyloxy)dienes **5**−**8** with benzaldehyde (BA) proceeded smoothly at room temperature in THF and catalytic amounts of $ZnCl_2$ to give interesting bicyclic pyranones (**33**−**36**) in moderate yields (40−60%) (see Scheme 5, and Table 1, entries 4, 8, 13, and 17).[26] The yields were moderate mainly because the 1,3-bis(trimethylsilyloxy)dienes were partially hydrolyzed in the reaction conditions. A considerable quantity of the corresponding 2-acetylcyclocarbonyl compound was recovered (40%). As seen in the reactions with MVK, in the reactions with BA, a single regioisomer was detected by $^1$H NMR.

The reactivity of the inner-outer-ring silyloxydienes **5**−**8** with a nonactivated imine, *N*-benzylideneaniline (NBA), was also studied.[24] The Diels−Alder reaction of dienes **7** and **8** took place in THF with catalytic amounts of $ZnCl_2$ to give the pyridinone derivatives **37** and **38** in yields of 93% and 69%, respectively (Table 1, entries 9 and 18). The Diels−Alder reaction of dienes **5** and **6** did not afford the corresponding pyridinones, the structure of the new products is still under investigation.

## Conclusions

In summary, we have shown that the inner-outer-ring 1,3-bis(trimethylsilyloxy)dienes **5**−**8** containing carbocyclic or heterocyclic rings with different ring sizes can be efficiently prepared from 2-acetylcyclocarbonyls. Dienes **5**−**8** react smoothly with 1,4-benzoquinone, dimethyl acetylenecarboxylate, and methyl vinyl ketone in a efficient and regioselective Diels−Alder reaction. The dienes also participate in a hetero-Diels−Alder reaction with aldehydes such as benzaldehyde, and imines such as *N*-benzylideneaniline. Overall, the Diels−Alder reactivity of **5**−**8** is comparable to other Danishefsky's type dienes, with low dependence on the ring size and diene components used. Our synthetic strategy provides a straightforward access to an interesting set of highly

(24) (a) Kerwin, J. F.; Danishefsky, S. *Tetrahedron Lett.* **1982**, *23*, 3739. (b) Danishefsky, S.; Langer, M. E.; Vogel, C. *Tetrahedron Lett.* **1985**, *26*, 5983.

(25) Veyrat, C.; Wartski, L.; Seyden-Penne, J. *Tetrahedron Lett.* **1986**, *27*, 2981.

(26) The use of other Lewis acids gave similar results.

functionalized polycyclic structures present in natural and nonnatural products with good yields (39−93%).

## Experimental Section

**General Materials and Methods.** Unless otherwise stated, all reactions were conducted in flame-dried glassware under a positive pressure of argon. Reaction temperatures refer to external bath temperatures. All dry solvents were distilled under argon immediately prior to use. Tetrahydrofuran (THF), ether ($Et_2O$), and benzene were distilled from the sodium ketyl of benzophenone. Dichloromethane ($CH_2Cl_2$) and acetic anhydride were distilled from $P_2O_5$. Trimethylsilyl chloride and *i*-$Pr_2NH$ were distilled from $CaH_2$ prior use. Pyridine was distilled from KOH. Methyl vinyl ketone and benzaldehyde were distilled under vacuum prior use. Lithium diisopropylamine (LDA) was prepared as a 0.5−1.0 M solution in THF by addition of *i*-$Pr_2NH$ to a solution of *n*-BuLi in hexanes at −78 °C dilution by adding THF and warming to 0 °C.[27] Organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated using a rotary evaporator at aspirator pressure (20−30 mmHg). Thin-layer chromatography was effected on silica gel 60 $F_{254}$ (layer thickness 0.2 mm), and components were located by observation under UV light and/or by treating the plates with a phosphomolybdic acid or *p*-anisaldehyde reagent followed by heating. Flash column chromatography was performed on silica gel 60 (230−400 mesh) by Still's method.[28] Bulb-to-bulb distillations were performed in a Kugelrohr apparatus, and bp corresponds to the external air bath temperature. $^1$H NMR spectra were recorded on a 200 MHz spectrometer and $^{13}$C NMR spectra at 50 MHz. DEPT was used to assign carbon types. Melting points are uncorrected.

**2-Acetyl-δ-valerolactone (12)**. To a solution of δ-valerolactone (400 μL, 4.32 mmol) in THF (15 mL) at −78 °C was added a solution of LDA in THF (9.2 mL, 5.06 mmol, 0.55 M) dropwise via syringe. After 1 h of stirring, pyruvonitrile (370 μL, 5.18 mmol) was added dropwise over a 10 min period. After 20 min, the reaction mixture was quenched by addition of a few drops of water. The solvent was evaporated and the residue purified by column chromatography (30% AcOEt/hexanes) to give 250 mg of 2-acetyl-δ-valerolactone [**12**, 45%, $R_f$ = 0.35 (30% AcOEt/hexanes)] as a yellow solid: mp 46−48 °C; $^1$H NMR ($CDCl_3$) δ 1.93 (m, 2 H), 2.01 (s, 3 H), 2.42 (t, $J$ = 6.6 Hz, 2 H), 4.29 (t, $J$ = 5.1 Hz, 2 H), 13.70 (s, 1 H); $^{13}$C NMR ($CDCl_3$) δ 18.7 ($CH_3$), 22.5 ($CH_2$), 22.6 ($CH_2$), 68.9 ($CH_2$), 93.2 (C), 172.7 (C), 175.8 (C); MS (EI, 70 eV) *m*/*z* 143 ($M^+$ + 1, 23), 142 ($M^+$, 92), 99 (100).

**2-Acetylcycloheptanone (14).** Following the same experimental procedure as for **12**, reaction of cycloheptanone (300 μL, 2.53 mmol) with LDA in THF (6.4 mL, 0.47 M, 3.04 mmol) and pyruvonitrile (215 μL, 3.04 mmol) afforded after column chromatography (20% AcOEt/hexanes) 263 mg of 2-acetylcycloheptanone [67%, $R_f$ = 0.58 (40% AcOEt/hexanes)] as a yellow oil: $^1$H NMR ($CDCl_3$) δ 1.67 (m, 6 H), 2.12 (s, 3 H), 2.37 (m, 2 H), 2.54 (m, 2 H), 16.48 (s, 1 H); $^{13}$C NMR ($CDCl_3$) δ 22.2 ($CH_3$), 24.7 ($CH_2$), 26.8 ($CH_2$), 28.7 ($CH_2$), 31.6 ($CH_2$), 40.5 ($CH_2$), 111.7 (C), 185.6 (C), 200.4 (C); MS (EI, 70 eV) *m*/*z* 154 ($M^+$, 94), 111 (100), 139 (82).

**3-[1-[(Trimethylsilyl)oxy]ethylidenyl]-4,5-dihydrofuran-2-one (15).** To a cooled (−78 °C) solution of 2-acetylbutyrolactone (170 μL, 1.6 mmol) in THF (5 mL) was slowly added via syringe a solution of LDA in THF (3.7 mL, 1.89 mmol, 0.51 M). The reaction mixture was stirred for 30 min, and TMSCl (300 μL, 2.37 mmol) was added via syringe dropwise. The mixture was warmed to room temperature, the solvent was evaporated at reduced pressure, the residue was dissolved in $Et_2O$ (25 mL) and filtered, and the filtrate was concentrated to afford 315 mg of **15** [99%, $R_f$ = 0.30 (40% EtOAc/hexanes)] as a yellow oil: $^1$H NMR ($CDCl_3$) δ 0.26 (s, 9 H), 2.32 (t, $J$ = 2.0 Hz, 3 H), 2.80 (dt, $J$ = 7.8, 2.0 Hz, 2 H), 4.23 (t, $J$ = 7.8 Hz, 2 H); $^{13}$C NMR ($CDCl_3$) δ 1.0 (3 × $CH_3$), 18.6 ($CH_3$), 26.1 ($CH_2$), 64.3 ($CH_2$), 104.6 (C), 162.5 (C), 172.4 (C); MS (FAB) *m*/*z* 201 ($M^+$ + 1, 43), 181 (100).

**2-Acetyl-1-(trimethylsilyloxy)-5,6-dihydro-4*H*-pyran (16).** Following the same experimental procedure described for **15**, the title compound **16** [94 mg, 85%, $R_f$ = 0.80 (20% EtOAc/hexanes)] was prepared from 3-acetyltetrahydropyran-2-one (74 mg, 0.52 mmol): $^1$H NMR ($CD_2Cl_2$) δ 0.27 (s, 9 H), 1.78 (m, 2 H), 2.31 (t, $J$ = 1.7 Hz, 3 H), 2.38 (m, 2 H), 4.14 (t, $J$ = 5.4 Hz, 2 H); $^{13}$C NMR ($CD_2Cl_2$) δ 0.9 (3 × $CH_3$), 21.8 ($CH_3$), 23.0 ($CH_2$), 23.5 ($CH_2$), 68.4 ($CH_2$), 107.3 (C), 165.1 (C), 168.1 (C).

**2-Acetyl-1-(trimethylsilyloxy)-1-cyclohexene (17)**. Following the same experimental procedure described for **15**, the title compound **17** [302 mg, 99%, $R_f$ = 0.57 (40% EtOAc/hexanes)] was prepared from 2-acetylcyclohexanone (185 μL, 1.42 mmol): $^1$H NMR ($CDCl_3$) δ 0.29 (s, 9 H), 1.61 (m, 4 H), 2.23 (t, $J$ = 5.4 Hz, 2 H), 2.26 (t, $J$ = 5.4 Hz, 2 H), 2.37 (s, 3 H); $^{13}$C NMR ($CDCl_3$) δ 1.2 (3 × $CH_3$), 22.2 ($CH_2$), 22.9 ($CH_2$), 24.1 ($CH_2$), 32.2 ($CH_2$), 32.5 ($CH_3$), 118.4 (C), 161.4 (C), 199.2 (C); MS (FAB) *m*/*z* 197 ($M^+$ − $CH_3$, 30), 181 (100).

**2-Acetyl-1-(trimethylsilyloxy)-1-cycloheptene (18)**. Following the same experimental procedure described for **15**, the title compound **18** [242 mg, 98%, $R_f$ = 0.65 (40% EtOAc/hexanes)] was prepared from 2-acetylcycloheptanone (168 mg, 0.64 mmol): $^1$H NMR ($CD_2Cl_2$) δ 0.23 (s, 9 H), 1.60 (m, 6 H), 2.15 (s, 3 H), 2.38 (m, 2 H), 2.50 (m, 2 H).

**General Experimental Procedure for Preparation of 1,3-Bis(trimethylsilyloxy)dienes.** To a cooled (−78 °C) solution of the 2-acetylcycloalkanone or 2-acetyllactone (3 mmol) in THF was added via syringe a previously prepared solution of LDA in THF (1.2 equiv). The mixture was stirred for 30 min and TMSCl (1.5 equiv) was added over 10 min. The reaction mixture was warmed to room temperature and recooled to −78 °C. Then, a solution of LDA in THF (1.2 equiv) was slowly added via syringe dropwise over 5 min. After 40 min, TMSCl (1.5 equiv) was added over 10 min, and the reaction mixture was allowed to reach room temperature for 1 h. The solvent was evaporated at reduced pressure, the residue was dissolved in $Et_2O$ (25 mL) and filtered, and the filtrate was concentrated to afford the desired diene in quantitative yield.

**1-Trimethylsilyloxy-2-[1-(trimethylsilyloxy)ethylidenyl]-4,5-dihydrofuran (5).**[19] Following the general experimental procedure described previously, diene **5** was obtained from 2-acetylbutyrolactone (500 μL, 4.64 mmol) as a liquid in quantitative yield [1.26 g, $R_f$ = 0.49 (40% AcOEt/hexanes)]: bp (bulb-to-bulb) 129−131 °C (0.5 mmHg); $^1$H NMR ($CD_2Cl_2$) δ 0.19 (s, 9 H), 0.25 (s, 9 H), 2.69 (t, $J$ = 8.8 Hz, 2 H), 3.86 (s, 1 H), 3.92 (s, 1 H), 4.21 (t, $J$ = 8.8 Hz, 2 H); $^{13}$C NMR ($CD_2Cl_2$) δ 0.2 (3 × $CH_3$), 0.5 (3 × $CH_3$), 30.6 ($CH_2$), 66.5 ($CH_2$), 82.2 (C), 87.1 ($CH_2$), 153.7 (C), 155.4 (C); MS (EI, 70 eV) *m*/*z* 273 ($M^+$ + 1, 2), 73 (100).

**2-Trimethylsilyloxy-3-[1-(trimethylsilyloxy)ethylidenyl]-5,6-dihydro-4*H*-pyran (6).** Following the general experimental procedure, diene **6** was obtained from 2-acetyl-δ-valerolactone (**12**, 260 mg, 1.83 mmol) as a liquid in quantitative yield [519 mg, $R_f$ = 0.81 (50% AcOEt/hexanes)]: bp (bulb-to-bulb) 124−126 °C (0.7 mmHg); $^1$H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.22 (s, 9 H), 1.79 (m, 2 H), 2.17 (t, $J$ = 6.6 Hz, 2 H), 4.00 (t, $J$ = 5.4 Hz, 2 H), 4.21 (s, 1 H), 4.41 (s, 1 H); $^{13}$C NMR ($CDCl_3$) δ 0.1 (3 × $CH_3$), 0.5 (3 × $CH_3$), 22.3 ($CH_2$), 22.7 ($CH_2$), 66.9 ($CH_2$), 90.4 ($CH_2$), 105.0 (C), 152.9 (C), 155.2 (C); MS (EI, 70 eV) *m*/*z* 286 ($M^+$, 5), 271 (11), 73 (100).

**1-Trimethylsilyloxy-2-[1-(trimethylsilyloxy)ethylidenyl]-1-cyclohexene (7).**[23] Following the general experimental procedure, diene **7** was obtained from 2-acetylcyclohexanone (550 μL, 4.23 mmol) as a yellow oil in quantitative yield (1.2 g, $R_f$ = 0.71 (40% AcOEt/hexanes)]: bp (bulb-to-bulb) 119−121 °C (0.1 mmHg); $^1$H NMR ($CDCl_3$) δ 0.20 (s, 9 H), 0.21 (s, 9 H), 1.60 (m, 4 H), 2.08 (t, $J$ = 6.5 Hz, 2 H), 2.14 (t, $J$ = 6.5 Hz, 2 H), 4.36 (s, 1 H), 4.53 (s, 1 H); $^{13}$C NMR ($CDCl_3$) δ 0.1

(27) Vedejs, E.; Engler, D. A.; Telschow, J. E. *J. Org. Chem.* **1978**, *43*, 188.
(28) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(3 × $CH_3$), 0.9 (3 × $CH_3$), 22.7 ($CH_2$), 23.1 ($CH_2$), 26.3 ($CH_2$), 31.2 ($CH_2$), 93.9 ($CH_2$), 114.3 (C), 147.1 (C), 154.9 (C); MS (EI, 70 eV) *m*/*z* 285 ($M^+ + 1$, 9), 284 ($M^+$, 36), 269 (90), 73 (100).

**1-Trimethylsilyloxy-2-[1-(trimethylsilyloxy)ethylidenyl]-1-cycloheptene (8).** Following the general experimental procedure, diene **8** was obtained from 2-acetylcycloheptanone (209 mg, 1.36 mmol) as a liquid in quantitative yield [402 mg, $R_f$ = 0.74 (30% AcOEt/hexanes)]: bp (bulb-to-bulb) 129−131 °C (0.7 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 0.18 (s, 9 H), 0.20 (s, 9 H), 1.54 (m, 4H), 1.66 (m, 2H), 2.17 (m, 2 H), 2.31 (m, 2 H), 4.30 (s, 1 H), 4.39 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 0.2 (3 × $CH_3$), 0.8 (3 × $CH_3$), 25.0 ($CH_2$), 27.0 ($CH_2$), 28.6 ($CH_2$), 32.1 ($CH_2$), 36.1 ($CH_2$), 93.5 ($CH_2$), 119.5 (C), 152.5 (C), 155.3 (C); MS (EI, 70 eV) *m*/*z* 299 ($M^+ + 1$, 14), 298 ($M^+$, 6), 283 (18), 73 (100).

**4,6,9-Triacetoxy-2,3-dihydronaphtho[1,2-*b*]furan (21).** 1,4-Benzoquinone (114 mg, 1.05 mmol) was added to neat diene **5** (430 mg, 1.58 mmol) in portions at room temperature during 15 min. The exothermic mixture was stirred for 2 h, and $CH_2Cl_2$ (2 mL), pyridine (2 mL), and $Ac_2O$ (600 $\mu$L, 6.35 mmol) were successively added. After the mixture was stirred overnight, the solvent was evaporated and the residue was purified by column chromatography (40% AcOEt/hexanes) to give 270 mg of **21** [75%, $R_f$ = 0.45 (60% AcOEt/hexanes)] as a light brown solid: mp 160−162 °C ($CH_2Cl_2$/hexanes); IR (KBr) 1770−1750, 1610, 1590, 1525, 1210, 1190, 1170 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.35 (s, 3 H), 2.37 (s, 3 H), 2.43 (s, 3 H), 3.21 (t, $J$ = 9.0 Hz, 2 H), 4.78 (t, $J$ = 9.0 Hz, 2 H), 7.00 and 7.19 (2 d, AB system, $J$ = 7.8 Hz, 2 H), 7.14 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 20.9 (2 × $CH_3$), 21.1 ($CH_3$), 27.8 ($CH_2$), 72.6 ($CH_2$), 105.4 (CH), 114.5 (C), 117.3 (CH), 117.5 (C), 118.4 (CH), 129.4 (C), 143.2 (C), 144.2 (C), 146.7 (C), 156.3 (C), 168.5 (C), 169.0 (C), 170.1 (C); MS (EI, 70 eV) *m*/*z* 345 ($M^+ + 1$, 1), 344 ($M^+$, 7), 218 (100). Anal. Calcd for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68. Found: C, 62.81; H, 4.67.

**5,7,10-Triacetoxy-2,3-dihydronaphtho[1,2-*b*]-4*H*-pyran (22).** Following the same experimental procedure as for **21**, 1,4-benzoquinone (55 mg, 0.56 mmol) was added to diene **6** (240 mg, 0.84 mmol) and stirred for 5 h. Pyridine (1 mL) and $Ac_2O$ (160 $\mu$L, 1.69 mmol) were added. Purification by column chromatography (30% AcOEt/hexanes) afforded 145 mg of **22** [72%, $R_f$ = 0.27 (50% AcOEt/hexanes)] as a yellow solid: mp 145−147 °C ($CH_2Cl_2$/hexanes); $^1$H NMR ($CDCl_3$) $\delta$ 2.05 (m, 2 H), 2.34 (s, 3 H), 2.36 (s, 3 H), 2.42 (s, 3 H), 2.69 (t, $J$ = 6.6 Hz, 2 H), 4.27 (t, $J$ = 5.4 Hz, 2 H), 6.99 and 7.21 (2 d, AB system, $J$ = 8.3 Hz, 2 H), 7.15 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.9 ($CH_2$), 20.78 ($CH_2$), 20.82 ($CH_3$), 20.9 ($CH_3$), 21.1 ($CH_3$), 66.5 ($CH_2$), 105.2 (CH), 113.2 (C), 118.2 (CH), 118.3 (CH), 127.7 (C), 143.9 (C), 144.0 (2 × C), 148.6 (C), 151.6 (C), 168.9 (C), 169.0 (C), 170.1 (C); MS (EI, 70 eV) *m*/*z* 359 ($M^+ + 1$, 5), 358 ($M^+$, 24), 232 (100); HRMS calcd for $C_{19}H_{18}O_7$ 358.1053 ($M^+$), found 358.1060.

**1,4,9-Triacetoxy-5,6,7,8-tetrahydrophenanthrene (23).** Following the same experimental procedure as for **21**, 1,4-benzoquinone (109 mg, 1.01 mmol) was added to a solution of diene **7** (431 mg, 1.52 mmol) in $CH_2Cl_2$ (1 mL). After the mixture was stirred for 4 h, pyridine (1 mL) and $Ac_2O$ (290 $\mu$L, 3.07 mmol) were added. Purification by column chromatography (50% AcOEt/hexanes) afforded 247 mg of **23** [70%, $R_f$ = 0.29 (40% AcOEt/hexanes)] as a brown solid: mp 186−188 °C ($CH_2Cl_2$/hexanes); IR (neat) 1760, 1610, 1200 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.82 (m, 4 H), 2.37 (s, 3 H), 2.39 (s, 3 H), 2.44 (s, 3 H), 2.70 (m, 2 H), 3.27 (m, 2 H), 7.06 and 7.21 (2 d, AB system, $J$ = 8.3 Hz, 2 H), 7.42 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 20.9 ($CH_3$), 21.1 ($CH_3$), 21.2 ($CH_2$), 21.6 ($CH_3$), 23.1 ($CH_2$), 24.7 ($CH_2$), 29.0 ($CH_2$), 111.1 (CH), 117.4 (CH), 119.8 (CH), 126.1 (C), 127.4 (C), 130.8 (C), 134.7 (C), 144.3 (C), 144.8 (C), 148.5 (C) 169.1 (C), 169.3 (C), 169.8 (C); MS (EI, 70 eV) *m*/*z* 357 ($M^+ + 1$, 1), 356 ($M^+$, 7), 272(53), 230 (100). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.16; H, 5.68.

**1,4,6-Triacetoxycyclohepta[*a*]naphthalene (24).** Following the same experimental procedure as for **21**, 1,4-benzoquinone (95 mg, 0.88 mmol) was added to diene **8** (400 mg, 1.34 mmol). After the mixture was stirred for 20 h, pyridine (1 mL) and $Ac_2O$ (250 $\mu$L, 2.64 mmol) were added. Purification by column chromatography (30% AcOEt/hexanes) afforded 230 mg of **24** [70%, $R_f$ = 0.33 (30% AcOEt/hexanes)] as a brown solid: mp 165−167 °C ($CH_2Cl_2$/hexanes); $^1$H NMR ($CDCl_3$) $\delta$ 1.76 (m, 6 H), 2.38 (s, 3 H), 2.39 (s, 3 H), 2.44 (s, 3 H), 2.88 (m, 2 H), 3.44 (m, 2 H), 7.07 and 7.20 (2 d, AB system, $J$ = 8.3 Hz, 2 H), 7.43 (s, 1 H). $^{13}$C NMR ($CDCl_3$) $\delta$ 20.9 ($CH_3$), 21.1 ($CH_3$), 21.4 ($CH_3$), 25.9 ($CH_2$), 26.4 ($CH_2$), 26.7 ($CH_2$), 30.8 ($CH_2$), 31.4 ($CH_2$), 111.5 (CH), 117.0 (CH), 119.6 (CH), 125.4 (C), 127.9 (C), 137.7 (C), 140.9 (C), 144.3 (C), 144.5 (C), 147.4 (C), 169.1 (C), 169.5 (2 × C); MS (EI, 70 eV) *m*/*z* 370 ($M^+$, 8), 328 (19), 244 (100); HRMS (EI) calcd for $C_{21}H_{22}O_6$ 370.1416 ($M^+$), found 370.1426.

**Dimethyl 2,3-Dihydro-4-hydroxybenzofuran-6,7-dicarboxylate (25).** Dimethyl acetylenedicarboxylate (77 $\mu$L, 0.26 mmol) was added to diene **5** (509 mg, 1.87 mmol) at room temperature. After 12 h, the reaction mixture was directly purified by column chromatography (50% AcOEt/hexanes) to give 108 mg of **25** [69%, $R_f$ = 0.23 (40% AcOEt/hexanes)] as a white solid: mp 138−140 °C ($Et_2O$/hexanes); IR (KBr) 3390, 1730, 1700, 1600, 1280, 1250 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.17 (t, $J$ = 8.8 Hz, 2 H), 3.85 (s, 3H), 3.88 (s, 3H), 4.69 (t, $J$ = 8.8 Hz, 2 H), 6.80 (s, 1 H), 6.89 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 26.5 ($CH_2$), 52.6 ($CH_3$), 52.8 ($CH_3$), 72.9 ($CH_2$), 107.4 (C), 110.2 (CH), 117.5 (C), 132.0 (C), 154.6 (C), 160.6 (C), 167.1 (C), 168.1 (C); MS (EI, 70 eV) *m*/*z* 253 ($M^+ + 1$, 12), 252 ($M^+$, 83), 221 (100). Anal. Calcd for $C_{12}H_{12}O_6$: C, 57.0; H, 4.8. Found: C, 57.20; H, 4.53.

**Dimethyl 2,3-Dihydro-5-hydroxybenzo[*b*]-4*H*-pyran-7,8-dicarboxylate (26).** Dimethyl acetylenedicarboxylate (60 $\mu$L, 0.49 mmol) was added to diene **6** (220 mg, 0.77 mmol) at room temperature. After the mixture was stirred for 20 h, $CH_2Cl_2$ (6 mL) and HCl (10 mL, 18%) were added and the resulting mixture stirred for 5 h. The organic phase was extracted, dried, and filtered, and the filtrate was concentrated. The residue was purified by column chromatography (30% AcOEt/hexanes) to give 90 mg of **26** [66%, $R_f$ = 0.18 (60% AcOEt/hexanes)] as a white solid: mp 137−139 °C ($Et_2O$/hexanes); $^1$H NMR ($CDCl_3$) $\delta$ 2.02 (m, 2 H), 2.69 (t, $J$ = 6.6 Hz, 2 H), 3.83 (s, 3 H), 3.91 (s, 3 H), 4.18 (t, $J$ = 5.1 Hz, 2 H), 6.41 (br s, 1 H), 6.97 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 19.3 ($CH_2$), 20.9 ($CH_2$), 52.5 ($CH_3$), 52.7 ($CH_3$), 66.6 ($CH_2$), 107.8 (CH), 115.3 (C), 116.6 (C), 126.5 (C), 153.2 (C), 154.9 (C), 166.1 (C), 168.8 (C); MS (EI, 70 eV) *m*/*z* 267 ($M^+ + 1$, 6), 266 ($M^+$, 41), 235 (100); HRMS (EI) calcd for $C_{13}H_{14}O_6$ 266.0790 ($M^+$), found 266.0799.

**Dimethyl 4-Hydroxy-5,6,7,8-tetrahydronaphtho-1,2-dicarboxylate (27).** Following the same experimental procedure as for **26**, reaction of dimethyl acetylenedicarboxylate (90 $\mu$L, 0.73 mmol) and diene **7** (304 mg, 1.07 mmol) afforded after purification by column chromatography (50% AcOEt/hexanes) 128 mg of **27** [66%, $R_f$ = 0.28 (40% AcOEt/hexanes)] as a white solid: mp 132−134 °C ($Et_2O$/hexanes); $^1$H NMR ($CDCl_3$) $\delta$ 1.80 (m, 4 H), 2.68 (t, $J$ = 6.4 Hz, 2 H), 2.72 (t, $J$ = 6.4 Hz, 2 H), 3.87 (s, 3 H), 3.91 (s, 3 H), 5.12 (s, 1 H), 7.23 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 21.7 ($CH_2$), 22.1 ($CH_2$), 23.4 ($CH_2$), 26.5 ($CH_2$), 52.4 ($CH_3$), 52.5 ($CH_3$), 113.0 (CH), 125.5 (C), 127.8 (C), 129.7 (C), 136.3 (C), 154.1 (C), 166.4 (C), 170.6 (C); MS (EI, 70 eV) *m*/*z* 264 ($M^+$, 3), 233 (46), 174 (100). Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.67; H, 6.03.

**Dimethyl 4-Hydroxycyclohepta[*a*]benzene-1,2-dicarboxylate (28).** Following the same experimental procedure as for **26**, reaction of dimethyl acetylenedicarboxylate (120 $\mu$L, 0.98 mmol) and diene **8** (171 mg, 0.57 mmol) afforded after purification by column chromatography (15% AcOEt/hexanes) 62 mg of **28** [39%, $R_f$ = 0.70 (30% AcOEt/hexanes), white solid] and 37 mg of 2-acetylcycloheptanone (**14**, 41%). **28**: mp 155−157 °C ($Et_2O$/hexanes); $^1$H NMR ($CDCl_3$) $\delta$ 1.61 (m, 6 H), 1.79 (m, 4 H), 2.72 (t, $J$ = 5.7 Hz, 2 H), 2.90 (t, $J$ = 5.6 Hz, 2 H), 3.85 (s, 3 H), 3.91 (s, 3 H), 5.60 (s, 1 H), 7.29 (s, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.7 ($CH_2$), 26.7 ($CH_2$), 27.1 ($CH_2$), 31.97 ($CH_2$), 32.02 ($CH_2$), 52.4 ($CH_3$), 52.5 ($CH_3$), 114.7 (CH), 125.5 (C), 127.5 (C), 135.7 (C), 143.1 (C), 152.8 (C), 166.2 (C), 170.8 (C); MS (EI, 70 eV) *m*/*z* 278 ($M^+$, 4), 247 (12), 160 (16), 71 (100); HRMS (EI) calcd for $C_{15}H_{18}O_5$ 278.1154 ($M^+$), found 278.1152.

**7-Acetyl-2,3,4,5,6,7-hexahydrobenzofuran-4-one (29).** Methyl vinyl ketone (55 $\mu$L, 0.65 mmol) was added to diene **5**

(529 mg, 1.94 mmol) via syringe, and the reaction mixture was stirred for 24 h and purified by column chromatography (60% AcOEt/hexanes) to afford 74 mg of **29** [62%, $R_f$ = 0.20 (60% AcOEt/hexanes)] as a yellow oil: IR (neat) 1715, 1660 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.10−2.50 (m, 4 H), 2.26 (s, 3 H), 2.81 (dt, $J$ = 8.8, 2.0 Hz, 2 H), 3.49 (t, $J$ = 4.6 Hz, 1H), 4.58 (t, $J$ = 9.8 Hz, 2 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 24.4 ($CH_2$), 25.7 ($CH_2$), 29.5 (CH), 34.4 ($CH_2$), 47.9 ($CH_3$), 73.4 ($CH_2$), 114.7 (C), 173.0 (C), 194.6 (C), 203.6 (C); MS (EI, 70 eV) $m/z$ 181 ($M^+$ + 1, 5), 180 ($M^+$, 33), 137 (100); HRMS (EI) calcd for $C_{10}H_{12}O_3$ 180.0786 ($M^+$), found 180.0788.

**8-Acetyl-2,3,5,6,7,8-hexahydrobenzo[*b*]-4*H*-pyran-5-one (30).** Following the same experimental procedure as for **29**, reaction of diene **6** (67 mg, 0.24 mmol) with methyl vinyl ketone (30 $\mu$L, 0.36 mmol) for 24 h gave after purification by column chromatography (35−40% AcOEt/hexanes) 18 mg of **30** [40%, $R_f$ = 0.35 (80% AcOEt/hexanes)] as a colorless oil: $^1H$ NMR ($CDCl_3$) $\delta$ 1.86 (m, 2 H), 2.10−2.52 (m, 6 H), 2.26 (s, 3 H), 3.41 (t, $J$ = 5.6 Hz, 1 H), 4.13 (t, $J$ = 5.4 Hz, 2 H). $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.5 ($CH_2$), 21.2 ($CH_2$), 23.5 ($CH_2$), 29.1 (CH), 33.9 ($CH_2$), 51.9 ($CH_3$), 67.7 ($CH_2$), 113.4 (C), 167.2 (C), 196.9 (C), 205.6 (C); MS (EI, 70 eV) $m/z$ 195 ($M^+$ + 1, 6), 194 ($M^+$, 39), 152 (100); HRMS (EI) calcd for $C_{11}H_{14}O_2$ 194.0943 ($M^+$), found 194.0942.

**5-Acetylbicyclo[4.4.0]dec-1(6)-en-2-one (31).** A solution of methyl vinyl ketone (60 $\mu$L, 0.72 mmol) and diene **7** (284 mg, 1.00 mmol) in benzene (1 mL) was heated at 90 °C in a sealed tube for 24 h. The reaction mixture was purified by column chromatography (40% AcOEt/hexanes), affording 69 mg of **31** [50%, $R_f$ = 0.37 (60% AcOEt/hexanes)] as a yellow oil: IR (neat) 1705, 1660 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.60 (m, 4 H), 2.18 (m, 4 H), 2.25 (s, 3 H), 2.32 (m, 4 H), 3.31 (t, $J$ = 4.9 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.8 ($CH_2$), 21.9 ($CH_2$), 22.2 ($CH_2$), 25.4 ($CH_2$), 29.4 (CH), 31.0 ($CH_2$), 34.4 ($CH_2$), 54.3 ($CH_3$), 134.6 (C), 152.3 (C), 197.6 (C), 207.7 (C); MS (EI, 70 eV) $m/z$ 193 ($M^+$ + 1, 3), 192 ($M^+$, 12), 149 (100); HRMS (EI) calcd for $C_{12}H_{16}O_2$ 192.1150 ($M^+$), found 192.1142.

**11-Acetylbicyclo[5.4.0]undec-1(7)-en-8-one (32).** Following the same experimental procedure as for **29**, reaction of diene **8** (130 mg, 0.44 mmol) and methyl vinyl ketone (55 $\mu$L, 0.66 mmol) afforded after purification by column chromatography (30% AcOEt/hexanes) 41 mg of the diketone **32** [46%, $R_f$ = 0.53 (30% AcOEt/hexanes)] as a yellow oil: $^1H$ NMR ($CDCl_3$) $\delta$ 1.65 (m, 6 H), 2.17−2.33 (m, 6 H), 2.27 (s, 3 H), 2.55 (t, $J$ = 5.6 Hz, 2 H), 3.49 (t, $J$ = 4.6 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 24.2 ($CH_2$), 25.2 ($CH_2$), 25.4 ($CH_2$), 25.7 ($CH_2$), 29.4 ($CH_3$), 32.1 ($CH_2$), 33.8 ($CH_2$), 36.5 ($CH_2$), 56.2 (CH), 140.6 (C), 157.8 (C), 196.9 (C), 207.4 (C); MS (EI, 70 eV) $m/z$ 206 ($M^+$, 13), 164 (100); HRMS (EI) calcd for $C_{13}H_{18}O_2$ 206.1307 ($M^+$), found 206.1314.

**6-Phenyl-2,3,5,6-tetrahydrofuran[2,3-*b*]-4*H*-pyran-4-one (33).** To a solution of diene **5** (475 mg, 1.74 mmol) in THF (2 mL) at room temperature were added benzaldehyde (120 $\mu$L, 1.18 mmol) and a catalytic amount of $ZnCl_2$. After the mixture was stirred for 20 h, the reaction mixture was diluted with $CH_2Cl_2$ (30 mL) and washed with a solution of HCl (10 mL, 5%). The organic layer was dried and filtered, and the filtrate was concentrated. The residue was purified by column chromatography (50% AcOEt/hexanes), affording 112 mg of **33** [44%, $R_f$ = 0.25 (80% AcOEt/hexanes), white solid] and 176 mg of 2-acetylbutyrolactone (44%). **33**: mp 123−125 °C ($CH_2Cl_2$); $^1H$ NMR ($CD_3OD$) $\delta$ 2.58 (dd, $J$ = 17.1, 3.9 Hz, 1 H), 2.89 (m, 2 H), 3.30 (m, 1 H), 4.67 (m, 2 H), 5.74 (dd, $J$ = 12.7, 3.9 Hz, 1 H), 7.42 (m, 5 H); $^{13}C$ NMR ($CD_3OD$) $\delta$ 26.1 ($CH_2$), 43.2 ($CH_2$), 74.6 ($CH_2$), 86.3 (CH), 91.3 (C), 128.6 (2 × CH), 130.9 (2 × CH), 131.2 (CH), 139.7 (C), 179.9 (C), 189.9 (C); MS (EI, 70 eV) $m/z$ 216 ($M^+$, 27), 188 (11), 131 (100); HRMS (EI) calcd for $C_{13}H_{12}O_3$ 216.0786 ($M^+$), found 216.0795.

**2-Phenyl-2,3,6,7-tetrahydro-4*H*-pyrane[2,3-*b*]-4*H*-pyran-4-one (34).** Following the experimental procedure described for **33**, diene **6** (180 mg, 0.63 mmol) reacted with benzaldehyde (100 $\mu$L, 0.98 mmol) in the presence of a catalytic amount of $ZnCl_2$ to give, after 24 h of stirring and purification by column chromatography (50% AcOEt/hexanes), 58 mg of **34** [40%, $R_f$ = 0.23 (50% AcOEt/hexanes), yellow oil] and 35 mg of 2-acetyl-$\delta$-valerolactone (**12**, 40%). **34**: $^1H$ NMR ($CDCl_3$) $\delta$ 1.95 (m, 2 H), 2.34 (m, 2 H), 2.66 (dd, $J$ = 17.1, 3.6 Hz, 1 H), 2.80 (dd, $J$ = 17.1, 13.4 Hz, 1 H), 4.18 (m, 1 H), 4.41 (m, 1H), 5.48 (dd, $J$ = 13.4, 3.6 Hz, 1 H), 7.40 (m, 5 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 17.3 ($CH_2$), 21.6 ($CH_2$), 42.3 ($CH_2$), 69.6 ($CH_2$), 80.3 (CH), 91.3 (C), 126.1 (2 × CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 137.6 (C), 169.9 (C), 190.5 (C); MS (EI, 70 eV) $m/z$ 230 ($M^+$, 10), 212 (7), 104 (100); HRMS (EI) calcd for $C_{14}H_{14}O_3$ 230.0943 ($M^+$), found 230.0935.

**2-Phenyl-2,3-dihydrocyclohexa[*b*]-4*H*-pyran-4-one (35).** Following the experimental procedure described for **33**, diene **7** (430 mg, 1.51 mmol) reacted with benzaldehyde (230 $\mu$L, 2.26 mmol) during 21 h in the presence of a catalytic amount of $ZnCl_2$ to give, after purification by column chromatography (20% AcOEt/hexanes), 207 mg of **35** [60%, $R_f$ = 0.30 (30% AcOEt/hexanes)] as a white solid (mp 56−57 °C): IR (neat) 1660, 1610, 1400, 1295 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.65 (m, 4 H), 2.32 (m, 4 H), 2.64 (dd, $J$ = 16.6, 3.4 Hz, 1 H), 2.72 (dd, $J$ = 16.6, 14.2 Hz, 1 H), 5.35 (dd, $J$ = 14.2, 3.4 Hz, 1 H), 7.39 (m, 5 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.7 ($CH_2$), 21.9 ($CH_2$), 22.1 ($CH_2$), 28.6 ($CH_2$), 43.1 ($CH_2$), 79.8 (CH), 112.4 (C), 126.1 (2 × CH), 128.6 (CH), 128.7 (2 × CH), 138.7 (C), 171.3 (C), 191.9 (C); MS (EI, 70 eV) $m/z$ 229 ($M^+$ + 1, 8), 228 ($M^+$, 22), 151 (14), 104 (100); HRMS (EI) calcd for $C_{15}H_{16}O_2$ 228.1150 ($M^+$), found 228.1148.

**2-Phenyl-2,3-dihydrocyclohepta[*b*]-4*H*-pyran-4-one (36).** Following the same experimental procedure as for **33**, diene **8** (200 mg, 0.67 mmol) reacted with benzaldehyde (110 $\mu$L, 1.08 mmol) during 48 h, in the presence of a catalytic amount of $ZnCl_2$, to give, after purification by column chromatography (5−15% AcOEt/hexanes), 67 mg of **36** [41%, $R_f$ = 0.18 (5% AcOEt/hexanes), white solid] and 42 mg of 2-acetylcycloheptanone (**14**, 40%). **36**: mp 45−47 °C; IR (neat) 1660, 1610, 1400 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.52 (m, 2 H), 1.73 (m, 4 H), 2.55 (m, 5 H), 2.83 (dd, $J$ = 16.6, 14.2 Hz, 1 H), 5.32 (dd, $J$ = 14.2, 3.9 Hz, 1 H), 7.38 (m, 5 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 22.0 ($CH_2$), 24.9 ($CH_2$), 26.9 ($CH_2$), 31.7 ($CH_2$), 34.9 ($CH_2$), 42.3 ($CH_2$), 80.1 (CH), 116.8 (C), 126.1 (2 × CH), 128.6 (CH), 128.7 (2 × CH), 138.6 (C), 177.0 (C), 190.9 (C); MS (EI, 70 eV) $m/z$ 243 ($M^+$ + 1, 16), 242 ($M^+$, 23), 104 (100); HRMS (EI) calcd for $C_{16}H_{18}O_2$ 242.1307 ($M^+$), found 242.1305.

***N*,2-Diphenyl-1,2,3,4,5,6,7,8-octahydroquinolin-4-one (37).** To diene **7** (380 mg, 1.34 mmol) were added at room temperature *N*-benzylideneaniline (136 mg, 0.75 mmol) and a catalytic amount of $ZnCl_2$ in THF (2 mL). After being stirred for 20 h, the reaction mixture was diluted with AcOEt (40 mL) and washed with water (20 mL). The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography (30% AcOEt/hexanes), affording 215 mg of ketone **37** [93%, $R_f$ = 0.28 (50% AcOEt/hexanes)] as a white solid: mp 160−162 °C ($CH_2Cl_2$/hexanes); IR (neat) 1630, 1560, 1280 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.63 (m, 4 H), 2.07 (m, 2 H), 2.37 (m, 2 H), 2.84 (dd, $J$ = 16.4, 7.1 Hz, 1 H), 3.12 (dd, $J$ = 16.4, 6.1 Hz, 1 H), 4.91 (t, $J$ = 6.6 Hz, 1 H), 7.03 (m, 2 H), 7.21 (m, 8 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.7 ($CH_2$), 22.1 ($CH_2$), 22.7 ($CH_2$), 30.0 ($CH_2$), 43.3 ($CH_2$), 65.4 (CH), 110.0 (C), 126.7 (CH), 127.1 (2 × CH), 127.5 (CH), 127.6 (2 × CH), 128.5 (2 × CH), 129.0 (2 × CH), 139.9 (C), 144.1 (C), 158.4 (C), 189.9 (C); MS (EI, 70 eV) $m/z$ 304 ($M^+$ + 1, 14), 303 ($M^+$, 44), 226 (15), 77 (100). Anal. Calcd for $C_{21}H_{21}NO$: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.04; H, 7.13; N, 4.73.

***N*,2-Diphenyl-1,2,3,4-tetrahydrocyclohepta[*b*]pyridin-4-one (38).** Following the same experimental procedure as for **37**, reaction of diene **8** (138 mg, 0.46 mmol) with *N*-benzylideneaniline (60 mg, 0.33 mmol) and a catalytic amount of $ZnCl_2$ in THF (2 mL) at room temperature during 20 h afforded, after purification by column chromatography (40% AcOEt/hexanes) 72 mg of **38** [69%, $R_f$ = 0.26 (40% AcOEt/hexanes)] as a white solid: mp 122−124 °C ($CH_2Cl_2$/hexanes); IR (neat) 1625, 1550, 1185 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.46 (m, 2 H), 1.66 (m, 4 H), 2.43 (m, 2 H), 2.67 (m, 1 H), 2.80 (dd, $J$ = 16.1, 4.4 Hz, 1 H), 3.20 (dd, $J$ = 16.4, 6.6 Hz, 1 H), 4.98 (dd, $J$ = 6.6, 4.4 Hz,

1 H), 7.03 (m, 2 H), 7.27 (m, 8 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 23.3 ($CH_2$), 26.1 ($CH_2$), 27.5 ($CH_2$), 31.9 ($CH_2$), 33.0 ($CH_2$), 41.6 ($CH_2$), 65.0 (CH), 116.8 (C), 125.9 (2 × CH), 126.1 (CH), 126.6 (2 × CH), 127.5 (CH), 128.5 (2 × CH), 129.3 (2 × CH), 139.6 (C), 145.3 (C), 163.5 (C), 188.3 (C); MS (EI, 70 eV) *m*/*z* 318 ($M^+ + 1$, 13), 317 ($M^+$, 46), 289 (11), 77 (100). Anal. Calcd for $C_{22}H_{23}NO$: C, 83.24; H, 7.30; N, 4.41. Found: C, 83.27; H, 7.54; N, 4.54.

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**Supporting Information Available:** $^1$H NMR and $^{13}$C NMR for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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