Reaction of Pentadienyltrimethylsilane with N-Acyliminium Ion Intermediates. A Convenient Route to Pentadienyl-Substituted Lactams

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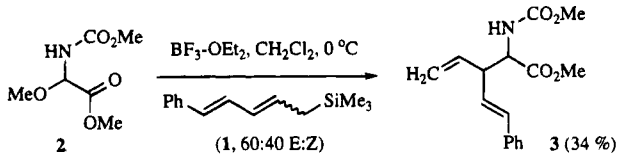
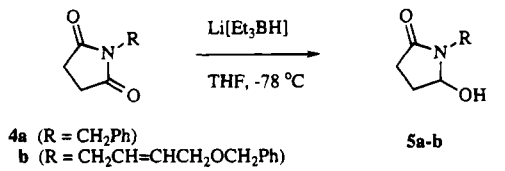
The generation of *N*-acyliminium ion intermediates via the Lewis acid promoted ionization of α-alkoxy- or α-hydroxy lactams and -amides, and their reactions with weak carbon nucleophiles, provide exceptionally useful methods for carbon-carbon bond formation, both in intermolecular[1] and intramolecular[2] cases. The use of allyltrimethylsilane as the weak carbon nucleophilic trap for an *N*-acyliminium ion intermediate was first reported by Kraus.[3] Since that initial report a wide variety of allysilane derivatives have been utilized, and the methodology has found significant use in organic synthesis; for example, in recent applications to the synthesis of alkaloids[4–6] and amino acids.[7]

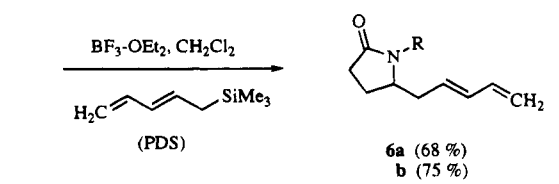
Our interest in the catalytic metal-mediated carbocyclizations of 1,3-diene-containing substrates[8,9] led us to ask whether *N*-acyliminium ion chemistry could be efficiently used for the preparation of dienylated substrates. 1-(Trimethylsilyl)-2,4-pentadiene (pentadienyltrimethylsilane, PDS) was originally prepared by Seyferth and co-workers,[10–14] and to date has found rather limited use in synthesis. The substitutions of allylsilanes occur regioselectively at the γ position (S_E' substitution), and generally, the reactions of PDS proceed regioselectively, substituting in an S_E'' fashion (ϵ with respect to the silyl group), rather than S_E' (γ substitution) or S_E (α substitution). For example, the Lewis acid-promoted reactions of PDS with a variety of aldehydes, ketones, acetals, and ketals are reported to give predominantly S_E'' products of the type $R^1R^2C(OR)CH_2CH{=}CH{-}CH{=}CH_2$.[12,13] More highly substituted dienylsilanes behave similarly,[15–17] and such substitution products have found some use in organic synthesis. For example, the adduct derived from the addition of PDS to hexanal is the starting point in a total synthesis of anhydrocannabisativene,[18] and the addition of PDS to a ketal is a key step in a synthesis of anthracyclinone C-glycosides.[19] In contrast to these dienylation reactions, the Lewis acid-promoted reactions of PDS with quinones,[20] and certain enones,[12] afford Diels–Alder cycloadducts and/or the product of conjugate addition.

Speckamp and co-workers[21] reported that the phenyl-substituted dienylsilane **1** undergoes reaction with the *N*-acyliminium ion derived from gylcidyl cation equivalent **2** to afford the 1,4-diene **3** in modest yield (34%, 2:1 mixture of diastereomers). Substitution of **1** occurs regioselectively, but via the S_E' rather than the desired S_E'' pathway. In spite of this discouraging precedent, we pursued an investigation into the BF_3-catalyzed addition of PDS to *N*-acyliminium ion intermediates and now report the full experimental details. The resulting methodology provides a convenient route to pentadienyl-substituted lactams.



α-Hydroxy lactams are conveniently prepared via the half-reduction of substituted imides.[22–24] For example, treatment of 1-benzylsuccinimide (**4a**) with $Li[Et_3BH]$[23] (1.7 equiv, THF, −78 °C, 20 min) affords the corresponding α-hydroxy lactam **5a**. The α-hydroxy lactams are relatively easily handled, but their purification can be somewhat problematic. Consequently, it is more practical to use the crude α-hydroxy lactam directly or to convert it to the corresponding α-methoxy lactam. In the case of **5a**, treatment of the crude α-hydroxy lactam with PDS (1.5 equiv, 1.4 equiv of $BF_3{-}OEt_2$, CH_2Cl_2, −78 to 25 °C, 12 h) affords 1-benzyl-5-((2*E*)-2,4-pentadienyl)-2-pyrrolidinone (**6a**) in 68% overall yield from 1-benzylsuccinimide. By a similar sequence succinimide **4b** affords the pentadienyl derivative **6b** in an overall yield of 75%. In our hands $BF_3{-}Et_2O$ is generally the Lewis acid of choice, although other strong Lewis acids (*e.g.*, $SnCl_4$, $TiCl_4$) afford similar results.





Two aspects of the chemistry are of particular note. (1) The $S_E'':S_E'$ regioselectivity (ϵ-: γ-substitution) in the addition reaction is quite good (>95:5), provided that the reaction mixture is warmed relatively slowly (over 6–10 h) from −78 °C. When the dienylation is carried out at higher temperatures (ca. 0 °C), S_E' reaction (addition at the γ-position of PDS) competes and the formation of a substantial amount of the isomeric addition product **7** is

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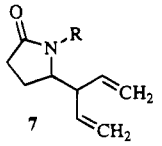
observed.[28] (2) The geometric purity of the newly formed dienyl side chain double bond is also quite good (>95% *E*).



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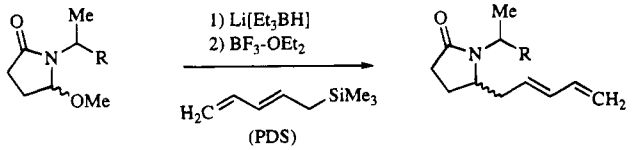
Recent studies by Polniaszek[23] show that a chiral substituent on nitrogen can exert a stereochemical bias on the addition of allylsilane to the diastereomeric faces of the intermediate acyliminium ion. Succinimides derived from (*S*)-1-phenylethylamine and (*R*)-1-(1-naphthyl)ethylamine were prepared, half-reduced with Li[Et_3BH] and converted to the α-methoxy lactams **8a,b** by treatment with acidic methanol. Treatment of the phenethylamine derived α-methoxy lactam **8a** with PDS (BF_3–OEt_2, CH_2Cl_2, −78 to 25 °C, 12 h) affords a 3:1 mixture of diastereomeric lactams **9** in 76% yield. For comparison, allyltrimethylsilane is reported to give a 4:1 mixture of diastereomeric addition products under similar conditions (3 equiv, 1.5 equiv of $SnCl_4$, CH_2Cl_2, −22 °C, 12 h).[23] The naphthyl derivative **8b** affords an 89% yield of dienylated product **9b** as a 4:1 mixture of diastereomers.

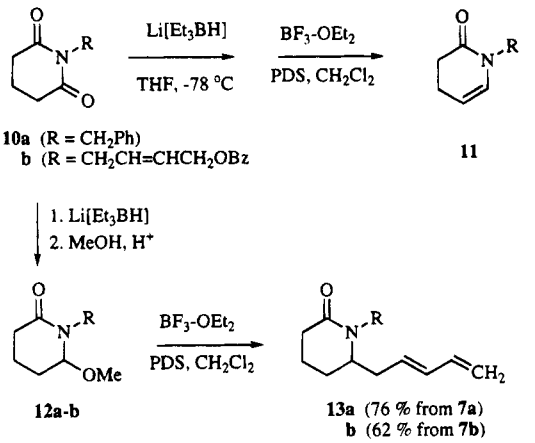


8a (R = Ph)
b (R = 1-naphthyl)

9a (76 %, 3:1 ratio)
b (89 %, 4:1 ratio)

While α-hydroxy lactams in the succinimide series are generally good substrates, the corresponding six-membered ring glutarimide derivatives more readily dehydrate to the corresponding enamide,[22] and this elimination competes with PDS addition under BF_3-catalysis. Thus, treatment of the crude α-hydroxy lactam obtained from Li[Et_3BH] half-reduction of **10b** with PDS and BF_3–OEt_2 affords predominantly the enamide **11**. To circumvent this problem, the α-hydroxylactams **10a,b** are first converted to the corresponding α-methoxy lactams **12a,b** and then treated with BF_3–OEt_2 and PDS. By this route piperidones **13a,b** are obtained in overall 76 and 62% yields from the corresponding imides.

The dienylation procedure described above is not restricted to α-hydroxy and α-alkoxy lactam substrates.



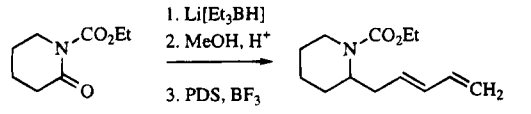
10a (R = CH_2Ph)
b (R = $CH_2CH{=}CHCH_2OBz$

11

12a-b

13a (76 % from **7a**)
b (62 % from **7b**)

For example, using the three-step procedure the *N*-acylpiperidone **14** is converted to the piperidine derivative **15** in 63% overall yield.



14

15 (63 %)

Experimental Section

General Procedures. ^1H NMR spectral data are reported in ppm from an internal standard tetramethylsilane or residual chloroform. ^{13}C spectra are reported in ppm from an internal standard deuterochloroform. In some cases, ^{13}C NMR resonances are assigned by DEPT, HETCOR, and/or APT experiments. Infrared spectra were obtained from thin films using the attenuated total reflectance (ATR) technique. IR wavelengths are reported in cm^{-1}, and in some cases, peak intensities reported in parentheses as percent absorbance. Combustion analyses were performed by M-H-W Analytical Labs, Phoenix, AZ. High resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, Lincoln, NE. THF was distilled under nitrogen from sodium benzophenone ketyl prior to use. Hexanes were purified by distillation. Dichloromethane was passed through a column of neutral activity I alumina. *n*-Butyllithium (Aldrich Chemicals) was used as a 2.5 M solution in hexanes. Lithium triethylborohydride (Aldrich Chemicals, Super-Hydride) was used as a 1.0 M solution in THF. All other reagents received from commercial sources were used without further purification. All temperatures are reported in degrees Celsius and unless otherwise noted are externally measured. Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen. Rotary evaporators were used to concentrate reaction mixtures *in vacuo* at aspirator pressure.

General Procedures for the BF_3-Promoted Addition of Pentadienylsilane (PDS). Procedure A. via the α-Hydroxy Lactam. Using the method of Polniaszek,[23] a THF solution of lithium triethylborohydride (1.7 equiv) was added in one portion to a cooled (−78 °C) solution of imide in dry THF (0.2–0.4 M). The resulting solution was stirred (20 min, −78 °C) and then warmed to 0 °C and quenched by the addition of saturated aqueous $NaHCO_3$ (5–10 mL) and 30% hydrogen peroxide (1–2 mL). The resulting mixture was stirred (20 min, 0 °C), and then the THF was removed *in vacuo* and the aqueous residue extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with saturated aqueous NaCl (10 mL), dried (Na_2SO_4), and concentrated to a volume of ca. 50 mL affording a solution of crude α-hydroxy lactam, which was used without further purification.

Procedure B. via the α-Methoxy Lactam. To a cooled (−78 °C) THF solution of imide (0.2–0.4 M) was added in one portion a standard THF solution of lithium triethylborohydride (1.7 equiv). The resulting solution was stirred (20 min, −78 °C) and then quenched by the addition of methanol (1–2 mL, −78 °C). The resulting mixture was warmed to 0 °C, and then

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(28) It is of interest that the Speckamp reaction (ref 21) was carried out at 0 °C).

saturated aqueous $NaHCO_3$ (5–10 mL) and 30% hydrogen peroxide (1–2 mL) were added. The resulting mixture was stirred (20 min, 0 °C), the THF was removed *in vacuo*, and the aqueous residue was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with saturated aqueous NaCl (10 mL), dried (Na_2SO_4), and concentrated via rotoevaporation. The residue was taken up in methanol (50 mL), cooled (−10 °C), and then acidified to ca pH 1 with *p*-TsOH. The resulting mixture was stirred (10 min, −10 °C) and then quenched by the addition of saturated aqueous $NaHCO_3$ until *ca.* pH 7. The methanol was removed *in vacuo* and the aqueous residue extracted with CH_2Cl_2 (2 × 50 mL). The combined organics were washed with saturated aqueous $NaHCO_3$ (2 × 10 mL) and saturated aqueous NaCl (10 mL) and then dried (Na_2SO_4) and concentrated to a volume of ca. 50 mL affording a solution of crude α-methoxy lactam, which was used without further purification.

Procedure C. PDS Addition Reaction. The CH_2Cl_2 solution of crude α-hydroxy lactam (or α-methoxy lactam) was cooled to −78 °C and BF_3–OEt_2 (1.4 equiv) added. After 15 min, PDS (1.5 equiv) was added. The resulting mixture was allowed to slowly warm from −78 °C to rt over 6–12 h. The reaction mixture was partitioned with saturated aqueous $NaHCO_3$ (2 × 10 mL) and saturated aqueous NaCl (10 mL). The organic phase was dried (Na_2SO_4) and concentrated and the residue chromatographed on silica (Fisher Scientific 60–200 mesh silica gel, EtOAc) to yield the pentadienylated product.

Preparation of 1-Benzyl-5-((2*E*)-2,4-pentadienyl)-2-pyrrolidinone (6a). Using procedure A, 1-benzylsuccinimide[25] (**4a**, 0.51 g, 2.70 mmol) was half-reduced with Li[Et_3BH] (4.6 mL, 4.6 mmol). A cooled solution of crude α-hydroxy lactam **5a** in 30 mL of CH_2Cl_2 at −78 °C was treated with BF_3–OEt_2 (0.50 mL, 3.8 mmol) and PDS (565 mg, 4.04 mmol) according to procedure C to afford **6a** (440 mg, 68%) as a pale yellow oil: TLC analysis (Kieselgel 60 F254 precoated 0.25 mm analytical plates, EtOAc) R_f 0.7; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3–7.2 (m, 5 H), 6.25 (ddd, 1 H, J = 16.7, 10.3, 6.4), 6.06 (dd, 1 H, J = 15.0, 10.3), 5.52–5.42 (m, 1 H), 5.11 (d, 1 H, J = 16.4), 5.02 (s, 1 H), 4.97 (d, 1 H, J = 6.9), 3.97 (d, 1 H, J = 15.0), 3.54–3.46 (m, 1 H), 2.45–2.29 (m, 3 H), 2.24–2.17 (m, 1 H), 2.09–1.96 (m, 1 H), 1.78–1.68 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 136.4, 136.3, 134.4, 128.4, 128.0, 127.7, 127.2, 116.2, 56.1, 43.9, 35.7, 29.8, 23.1; IR (neat, ATR) 1684 (100%); HRMS calcd for ($C_{16}H_{19}NO$ 241.14677, found *m/z* 241.14561.

Preparation of 1-((2*Z*)-4-(Benzyloxy)-2-butenyl)-5-((2*E*)-2,4-pentadienyl)-2-pyrrolidinone (6b). Using method A, 1-((2*Z*)-4-(benzyloxy)-2-butenyl)succinimide (**4b**, 2.00 g , 7.70 mmol) was half-reduced with Li[Et_3BH] (13.0 mL, 13.0 mmol). A −78 °C solution of crude α-hydroxy lactam **5b** in 50 mL of CH_2Cl_2 was treated with BF_3–OEt_2 (1.30 mL, 10.8 mmol) and PDS (1.60 g, 0.5 mmol) according to procedure C to afford **6b** (1.80 g, 75%) as a pale yellow oil: TLC analysis (EtOAc) R_f 0.4; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.26 (m, 5 H), 6.27 (ddd, 1 H, J = 16.9, 10.5, 6.4), 6.09 (dd, 1 H, J = 10.5, 4.4), 5.79 (ddd, 1 H, J = 10.9, 6.4, 4.8), 5.53–5.47 (m, 2 H), 5.12 (d, 1 H, J = 16.9), 5.03 (d, 1 H, J = 10.1), 4.52 (s, 2 H), 4.28 (dd, 1 H, J = 15.3, 5.6), 4.18–4.06 (m, 2 H), 3.68–3.61 (m, 2 H), 2.41–2.25 (overlapping m's, 3 H), 2.20–2.14 (m, 1 H), 2.10–2.02 (m, 1 H), 1.75–1.68 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 137.8, 136.3, 134.4, 129.6, 128.2(d), 128.0, 127.5, 127.45, 127.4, 116.2 , 72.3, 65.3, 56.6, 37.4, 36.0, 29.7, 23.1; IR (neat, ATR) 3026 (36%, Csp^2-H), 1683 (100%), 1602 (42%); HRMS calcd for ($C_{20}H_{25}NO_2$ 311.18792, found *m/z* 311.19146.

Preparation of 5-Methoxy-1-((1*S*)-1-phenylethyl)-2-pyrrolidinone (8a). Using procedure B, 1-((1*S*)-1-phenylethyl)-succinimide[26] (300 mg, 1.48 mmol) was half-reduced with Li[Et_3BH] (2.5 mL, 2.5 mmol) and treated with acidic methanol to afford after chromatography on silica (EtOAc) **8a** (231 mg, 71% overall) as a pale yellow oil. ^{1}H NMR integration indicated a 3:1 mixture of diastereomers: TLC analysis (EtOAc) R_f 0.54; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.17 (overlapping m's, 5 H), 5.31 (q, 0.75 H, J = 7.2), 5.12 (q, 0.25 H, J = 7.2), 5.03–5.01 (m, 0.25 H), 4.45–4.43 (m, 0.75 H,), 3.12 (s, 2.25 H,), 2.92 (s, 0.75 H), 2.64–2.50 (overlapping m's, 1 H), 2.35–2.25 (overlapping m's, 1 H), 1.98–1.82 (overlapping m's, 2 H), 1.64 (d, 0.75 H, J = 7.2), 1.59 (d, 2.25 H, J = 7.0); ^{13}C NMR (75 MHz, $CDCl_3$) major isomer: δ 174.5, 139.7, 128.4, 127.6, 127.5, 88.9, 52.4, 50.3, 29.1, 23.8, 18.0; minor isomer: δ 174.8, 141.6, 127.9, 127.3, 127.0, 88.7, 51.8, 51.1, 29.4, 24.1, 17.5; IR (neat, ATR) 1691 (97%), 1602 (31%); HRMS calcd for ($C_{13}H_{17}NO_2$ 219.12601, found *m/z* 219.12608.

Preparation of 1-((1*S*)-1-Phenylethyl)-5-((2*E*)-2,4-pentadienyl)-2-pyrrolidinone (9a). Using procedure C, a cooled (−78 °C) solution of **8a** (250 mg, 1.14 mmol) in 30 mL of CH_2Cl_2 was treated with BF_3–OEt_2 (0.20 mL, 1.6 mmol) and PDS (239 mg, 1.71 mmol) to afford **9a** (221 mg, 76%) as a pale yellow oil. ^{1}H NMR integration indicated a 3:1 mixture of diastereomers: TLC analysis (EtOAc) R_f 0.4; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.21 (overlapping m's, 5 H), 6.26–6.11 (overlapping m's, 1 H), 6.01 (dd, 0.25 H, J =15.3, 10.5), 5.83 (dd, 0.75 H, J = 15.3, 10.3), 5.50–5.38 (m, 1 H), 5.34–5.24 (m, 1 H), 5.13–4.95 (overlapping m's, 2 H), 3.80–3.72 (m, 0.75 H), 3.33–3.28 (m, 0.25 H), 2.53–1.86 (overlapping m's, 4 H), 1.77–1.66 (m, 2 H), 1.64 (d, 2.25 H, J = 7.2), 1.63 (d, 0.75 H, J = 7.4); ^{13}C NMR (75 MHz, $CDCl_3$) major isomer δ 175.2, 141.7, 136.4, 134.0, 128.8, 128.2, 127.3, 127.3, 127.1, 116.0, 56.2, 49.3, 37.4, 30.1, 24.0, 16.1; minor isomer δ 175.2, 139.6, 136.5, 134.3, 128.6, 128.4, 127.4, 116.3, 56.6, 53.3, 50.6, 38.2, 30.1, 23.8, 18.2; IR (neat, ATR) 1676 (93%). Anal. Calcd for $C_{17}H_{21}NO$: 79.96% C, 8.29% H. Found: 79.81% C, 8.39% H.

Preparation of 5-Methoxy-1-((1*R*)-1-(1-naphthyl)ethyl)-2-pyrrolidinone (8b). Using procedure B, 1-((1*R*)-1-(1-naphthyl)ethyl)succinimide (400 mg, 1.58 mmol) was half-reduced with Li[Et_3BH] (2.7 mL 2.7 mmol) and then treated with acidic methanol to afford after chromatography on silica (EtOAc) **8b** (364 mg, 85% overall yield for the two steps) as a white crystalline solid. ^{1}H NMR analysis indicated essentially a single diastereomer: TLC analysis (EtOAc) R_f 0.5; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88–7.46 (m, 7 H), 6.04 (q, 1 H, J = 6.9), 3.99 (d, 1 H, J = 5.7), 3.03 (s, 3 H), 2.65–2.56 (m, 1 H), 2.38–2.28 (m, 1 H), 1.82–1.64 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 134.6, 133.8, 131.7, 128.8, 128.7, 126.8, 125.9, 125.0, 124.9, 123.1, 89.2, 52.7, 46.4, 29.2, 24.0, 18.3; IR (neat, ATR) 1688 (83%). Anal. Calcd for $C_{17}H_{19}NO_2$: 75.81% C, 7.11% H. Found: 75.93% C, 6.94% H.

Preparation of 1-((1*R*)-1-(1-naphthyl)ethyl)-5-((2*E*)-2,4-pentadienyl)-2-pyrrolidinone (9b). Using procedure C, a solution of **8b** (317 mg, 1.18 mmol) in 30 mL of CH_2Cl_2 was treated with BF_3–OEt_2 (0.2 mL, 1.6 mmol) and PDS (248 mg, 1.77 mmol). Chromatography on silica (EtOAc) to afford **9b** (321 mg, 1.05 mmol, 89% yield) as a pale yellow oil. ^{1}H NMR integration indicated an approximate 4:1 mixture of diastereomers: TLC analysis (EtOAc) R_f 0.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24–7.43 (m, 7 H), 6.26 (q, 0.8 H, J = 7.3), 6.18 (ddd, 0.2 H, J = 16.9, 10.1, 6.5), 6.05 (q, 0.2 H, J = 7.3), 5.97 (overlapping ddd's, 1 H, J = 16.9, 10.5, 6.4), 5.41–5.34 (overlapping m's, 1 H,), 5.07 (d, 0.2 H, J = 16.5), 5.00–4.95 (overlapping m's, 1.2 H), 4.89 and 4.86 (overlapping d's, 1.6 H, J = 16.9, 10.1), 3.71–3.67 (m, 0.8 H), 2.77–2.74 (m, 0.2 H), 2.49–2.40 (m, 1 H), 2.34–2.16 (overlapping m's, 2 H), 2.04–1.95 (m, 1 H), 1.77 (d, 0.6 H, J = 6.85), 1.69 (d, 2.4 H, J = 6.85), 1.58–1.53 (m, 1 H), 1.15 (overlapping dd's, 2 H, J = 6.9, 6.0); ^{13}C NMR (125 MHz, $CDCl_3$) major isomer δ 174.8, 136.3, 134.2, 133.6, 132.0, 128.8, 128.6, 128.4, 126.6, 125.8, 124.7, 123.8, 123.7, 115.6, 55.0, 45.7, 36.4, 29.8, 24.4, 16.4; minor isomer δ 174.8, 136.2, 133.5, 133.4, 131.7, 128.7, 126.7, 125.8, 124.3, 122.8, 116.1, 56.3, 47.0, 38.3, 29.9, 23.2, 18.4; IR (neat, ATR) 1671 (89%). Anal. Calcd for $C_{21}H_{23}NO$ 82.58% C, 7.59% H. Found: 82.54% C, 7.51% H.

Preparation of 1-Benzyl-6-((2*E*)-2,4-pentadienyl)-2-piperidinone (13a). Using procedure B, 1-benzylglutarimide[25] (**10a**, 0.50 g, 2.46 mmol) was half-reduced with Li[Et_3BH] (4.2 mL, 4.2 mmol). The resulting solution of crude α-methoxy lactam **12a** in 30 mL of CH_2Cl_2 was treated with BF_3–OEt_2 (0.5 mL, 3.6 mmol) and PDS (538 mg, 3.84 mmol) according to procedure C to give after chromatography on silica (EtOAc) **13a** (475 mg, 76% overall yield for the three steps) as a pale yellow oil: TLC analysis (EtOAc) R_f 0.6; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67–7.14 (m, 5 H), 6.25 (ddd, 1 H, J = 16.9, 10.2, 6.7), 6.06 (dd, 1 H, J = 15.0, 10.5), 5.54–5.44 (m, 1 H), 5.40 (d, 1 H, J = 15.3), 5.12 (d, 1 H, J = 16.9), 5.01 (d, 1 H, J = 10.2), 3.97 (d, 1 H, J = 15.3), 3.37–3.30 (m, 1 H), 2.49–2.42 (m, 3 H),2.29–2.28 (m, 1 H,), 2.00–1.60 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 137.4, 136.4, 134.0, 129.5, 128.4, 127.6, 127.1, 116.2, 54.9, 47.3, 35.4, 31.8, 26.2, 17.0; IR (neat, ATR) 1633 (97%); HRMS calcd for $C_{17}H_{21}NO$ 255.16243, found *m/z* 255.16237.

Preparation of 1-((2*Z*)-4-(benzyloxy)-2-butenyl)-6-((2*E*)-2,4-pentadienyl)-2-piperidone (13b). Using procedure B, 1-((2*Z*)-4-(benzyloxy)-2-butenyl)glutarimide (**10b**, 2.98 g, 10.9 mmol) was half-reduced with Li[Et_3BH] (18.5 mL, 18.5 mmol). The resulting solution of crude α-methoxy lactam **12b** was treated with BF_3-OEt_2 (1.9 mL, 15.3 mmol).and PDS (2.29 g, 16.4 mmol) according to procedure C to give after chromatography on silica (EtOAc) **13b** (2.2 g, 62% yield for the three steps) as a pale yellow oil: TLC analysis (EtOAc) R_f 0.33; ^1H NMR (500 MHz, $CDCl_3$) δ 7.35–7.27 (m, 5 H), 6.27 (ddd, 1 H, J =16.9, 10.5, 6.4), 6.08 (dd, 1 H, J = 15.3, 10.5), 5.78 (ddd, 1 H, J = 11.3, 6.4, 4.8), 5.57–5.53 (m, 1 H), 5.52–5.51 (m, 1 H), 5.12 (d, 1 H, J = 16.5), 5.02 (d, 1 H, J = 10.5) , 4.54 (s, 2 H), 4.51–4.47 (m, 1 H), 4.17–4.07 (m, 2 H), 3.72 (dd, 1 H, J = 15.3, 7.7), 3.43–3.40 (m, 1 H), 2.45–2.35 (m, 3 H), 2.23 (ddd, 1 H, J = 14.1, 8.9, 5.2), 1.85–1.68 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 136.5, 134.1, 129.6, 129.1, 129.0, 128.4, 127.8, 127.7, 116.4, 72.5, 65.6, 55.7, 42.0, 35.8, 32.0, 26.3, 17.1; IR (neat, ATR) 1632 (98%), 1602 (56%); HRMS calcd for $C_{21}H_{27}NO_2$ 325.20431, found *m/z* 325.20431.

Preparation of 1-(Ethoxycarbonyl)-2-((2*E*)-2,4-pentadienyl)-1-piperidine (15). Using procedure B, 1-(ethoxycarbonyl)-2-piperidone[27] (**14**, 0.50 g, 2.92 mmol) was half-reduced with Li[Et_3BH] (5.0 mL, 5.0 mmol). The resulting solution of crude α-methoxy amide in 30 mL of CH_2Cl_2 was treated according to procedure C with BF_3-OEt_2 (0.50 mL, 4.1 mmol) and PDS (613 mg, 4.38 mmol) to afford after chromatography on silica (EtOAc) **15** (407 mg, 63% overall yield for the three steps) as a pale yellow oil: TLC analysis (EtOAc) R_f 0.7; ^1H NMR (300 MHz, $CDCl_3$) δ 6.24 (ddd, 1 H, J = 16.9, 10.3, 6.7), 6.02 (dd, 1 H, J = 15.3, 10.2), 5.62–5.52 (m, 1 H), 5.05 (d, 1 H, J = 16.7), 4.93 (d, 1 H, J = 10.5) , 4.3–3.9 (m, 4 H), 2.77 (dt, 1 H, J = 10.7, 2.1), 2.43–2.19 (m, 2 H), 1.60–1.40 (m, 4 H), 1.21–1.17 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.7, 136.8, 132.9, 131.2, 115.3, 60.9, 50.3, 39.0, 32.9, 27.4, 25.3, 18.6, 14.6; IR (neat, ATR) 1695 (45%); HRMS calcd for $C_{13}H_{21}NO_2$ 223.1573, found *m/z* 223.1562.

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Supplementary Material Available: Experimental procedures and spectral data for **4b**, **10b**, and 1-((1*R*)-1-(1-naphthyl)ethyl)succinimide, as well as full spectral assignments for all compounds described above (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.