128.5, 128.4, 128.2, 128, 126.2, 124.4, 124.3 (C aromat + CF_3), 91 and 89.3 (C_1 + C_1'), 78.3 and 76.8 (C benz + C′ benz), 74.5 and 74 (C benz + C′ benz), 43.5, 43.2, 41.9, 40.7 (2 N-CH_3 and 2 N′-CH_3), 35.6–33.7 (C_2), 17.2, 15.3 (C_3).

(*E*,*E*)-2,4-Nonadienal iron tricarbonyl complex[11] (10): ^{1}H NMR (C_6D_6) δ 7.8–6.8 (m, 8 H, H aromat), 4.7 and 4.55 (2 m, 2 H, C_4-H and C_3-H), 3.6–3.05 (m, 3 H, C_1-H + C-H benz), 2.5, 2.4, 2, 1.9 (4 s, 6 H, N-CH_3 + N′-CH_3), 1.6–0.7 (m, 11 H, C_4H_9 + C_5-H and C_2-H); ^{13}C NMR ($CDCl_3$) δ 210 ($FeCO_3$), 140.5, 131.6, 131.2, 131, 128.8, 128.5, 124.9, 124.5 (C aromat + CF_3), 88.1, 87, 86.2, 84.1, 82.2, 82 (C_1 + C_3 + C_4), 78.6 (C benz), 76.5 (C benz), 65.8 and 65.7–62.6 (C_2 + C_5), 40, 39.3, 37.4, 34.4, 34.3, 34.2, 33.9, 22.4, 13.9 (N-CH_3 + C_4H_9).

Methyl 6-Oxo-(*E*,*E*)-2,4-hexadienoate iron tricarbonyl complex[11] (11): ^{1}H NMR (C_6D_6) δ 7.9–6.8 (m, 8 H, H aromat), 5.7 (dd, J_{4-5} = 8.7 Hz, J_{4-3} = 5.2 Hz, 0.5 H, C_4-H), 5.6 (dd, J_{4-5} = 8.7 Hz, J_{4-3} = 5.2 Hz, 0.5 H, C_4-H), 4.7 (dd, J_{3-2} = 8.7 Hz, J_{3-4} = 5.2 Hz, 0.5 H, C_3-H), 4.5 (dd, J_{3-2} = 8.7 Hz, J_{3-4} = 5.2 Hz, 0.5 H, C_3-H), 3.65–3.05 (m, 6 H, C_1-H, CO_2CH_3, C-H benz), 2.32 (s, 1.5 H, N-CH_3), 2.22 (s, 1.5 H, N-CH_3), 1.98 (1, 1.5 H, N-CH_3), 1.8 (s, 1.5 H, N-CH_3), 1.3–0.9 (m, 2 H, C_2-H and C_5-H); ^{13}C NMR ($CDCl_3$) δ 210 ($FeCO_3$), 172 (CO), 140.7, 140.2, 140.1, 131.9, 131.5, 131.2, 131, 129.1, 129, 124.8 (C aromat + CF_3), 87.2, 87, 85.5, 84.5, 83.3 (C_1 + C_3 and C_4), 79–78.8 (C benz + C′ benz), 75.9–74.8 (C benz + C′ benz), 65 and 61.7 (C_5), 51.9 (OCH_3), 47.4 and 46.6 (C_2 + C_2'), 40.5, 40.2, 37.2, 34.4 (N-CH_3).

4-Acetoxy-2(*E*)-nonenal[8] (12): ^{1}H NMR (C_6D_6) δ 7.6–6.8 (m, 8 H, H aromat), 5.6 (m, 2 H, C_2-H and C_3-H), 5.5 (m, 1 H, C_4-H), 4.1 (d, J_{1-2} = 8.7 Hz, 1 H, C_1-H), 3.5 (2 d, J_{A-B} = 7 Hz, 1 H, C-H benz), 3.24 (2 d, J_{A-B} = 7 Hz, 1 H, CH benz), 2.13, 2.1, 2, 1.99 (4 s, 6 H, N-CH_3 + N′-CH_3), 1.77–1.76 (2 s, $OCOCH_3$ + $OCOCH_3$), 1.7–0.8 (m, 11 H, C_5H_{11}); ^{13}C NMR ($CDCl_3$) δ 140.5, 131.6, 131.2, 131, 128.8, 128.5, 124.9, 124.5 (C aromat + C_2 + C_3 + CF_3), 86.7 and 86.6 (C_1 + C_1'), 77.5 and 77.7 (C benz), 77 and 76.7 (C′ benz), 74 and 73.9 (C_4 + C_4'), 37.45 and 37.4 (N-CH_3), 35.15 and 35.2 (N′-CH_3), 34.5, 31.5, 24.9, 22.5, 13.9 (C_5H_{11}).

3-Phenylbutanal[13] (13): ^{1}H NMR (C_6D_6) δ 7.7–6.7 (m, 13 H, H aromat), 3.63, 3.28, 3.1 (3 m, 4 H, C_1-H + C_1'-H + C_3-H + C_3'-H, C-H benz + C′-H benz), 2.2–1.5 (m, + 4s (2.11 + 1.97 + 1.9 + 1.5), 8 H, C_2-H_2 + C_2'-H_2 + N-CH_3 + N′-CH_3), 1.36 (d, J = 6.4 Hz, 1.8 H, C_4-H_3), 1.26 (d, J= 6.4, 1, 2 H, C_4'-H_3); ^{13}C NMR ($CDCl_3$) δ 147.9, 147.3, 141.9, 141.6, 141.2, 140, 131.5, 131.4, 131.2, 131, 129, 128.7, 128.6, 127.3, 127.2, 127, 126.5, 126.1, 124.8, 124.7, 124.6, 124.5, 124.4, 124.3, 124 (C aromat + CF_3), 83.3 and 83 (C_1 + C_1'), 79.7 and 79.35 (C benz + C′ benz), 75.9 and 75.8 (C benz + C′ benz), 41.6 and 40.4, 39.8 and 38.3 (N-CH_3 + N′-CH_3), 36.3 and 36.24 (C_2 + C_2'), 35 and 34.5 (C_3 + C_3'), 24.5 and 22 (C_4 + C_4').

(*R*)-2,3-Isopropylideneglyceraldehyde[12] (14 with (+)-2b): ^{1}H NMR (C_6D_6) δ 7.9–6.7 (m, 8 H, H aromat), 4.1 (td, J_{2-3} = 7.3 Hz, J_{1-2} = 3 Hz, 1 H, C_2-H), 3.89 (d, J_{A-B} = 8.7 Hz, 1 H, C-H benz), 3.8 (d, J_{2-3} = 7.3 Hz, 2 H, C_3-H_2), 3.66 (d, J_{1-2} = 3 Hz, 1 H, C_1-H), 3.4 (d, J_{A-B} = 8.7 Hz, 1 H, C-H benz), 2.12 (2 s, 6 H, N-CH_3), 1.63 (s, 3 H, C_5-H), 1.4 (s, 3 H, C_6-H); ^{13}C NMR ($CDCl_3$) δ 140.8, 140.2, 138.5, 138, 132, 128.2, 128.6, 124.1, 124, 123.5 (C aromat + CF_3), 109 (C_4), 83.5 (C_1), 78.7–77.6 (C benz), 75.4 (C_2), 66.2 (C_3), 40.2–33.9 (N-CH_3), 26.6–25.6 (C_5 and C_6).

(*R*)-2,3-Isopropylideneglyceraldehyde (14 with (−)-2b): ^{1}H NMR (C_6D_6) δ 7.5–6.7 (m, 8 H, H aromat), 4.18 (m, 2 H, C_2-H and C-H benz), 4 (m, 2 H, C_3-H_2), 3.25 (m, 2 H, C_1-H, C-H benz), 2.17 (s, 6 H, N-CH_3), 1.48–1.4 (2 s, 6 H, C_5-H and C_6-H); ^{13}C NMR ($CDCl_3$) δ 140.8, 140, 131.8, 131.4, 131.3, 128.8, 128.4, 125, 124.9, 124.8, 124.7, 124.6, 124.5 (C aromat + CF_3), 110 (C_4), 85.3 (C_1), 78.7–76.9 (C benz), 75.1 (C_2), 66.6 (C_3), 42.5–34 (N-CH_3), 26.6–25 (C_5 and C_6).

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(11) We thank Dr. Gree for gift of iron tricarbonyl complex.
(12) Orgeat, B.; Samuelsson, B. *Proc. Natl. Acad. Sci.* **1979**, *76*, 3213.
(13) Mangeney, P.; Alexakis, A.; Normant, J. F. *Tetrahedron* **1984**, *40*, 1803.

The Urea Connection. Intramolecular Diels–Alder Reactions of Ureas

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Intramolecular Diels–Alder reactions with a urea tether afford adducts in good yields, yet the analogous carbamates fail to cyclize.

The intramolecular Diels–Alder reaction has become a powerful tool for constructing complex natural products.[1] As its potential continues to be probed, researchers have become increasingly aware that the atomic makeup of the tether can significantly affect the success of the reaction. In a classic set of experiments Boeckman and co-workers reported that while the ether **1** (X = H, H) cyclized to form **2**, the corresponding ester **1** (X = O) could not be induced to cyclize.[2] Babayan discovered that the ammonium salt **3** cyclized at 100 °C, whereas the tertiary amine **4** did not cyclize[3] (Scheme I). Many functional groups have been empolyed as part of the tether. Herein we report the first use of the urea moiety as part of a tether.

In connection with our studies on the intramolecular Diels–Alder reactions of indoles,[4] we required a tether that was sturdy enough to withstand thermolysis, oxidation, and mild reduction conditions and also amenable to selective cleavage at a later stage in the synthesis. The carbamate **5** was initially examined. Carbamate **5** was prepared in 50% yield by treating the sodium salt of indole-3-carboxaldehyde (**6**) with carbon dioxide gas followed by

(1) Desimoni, G.; Tacconi, G.; Barco, A.; Pollini, G. P. Natural product Synthesis Through Pericyclic Reactions; ACS Monograph 180, 1983.
(2) Boeckman, R. K., Jr.; Demko, D. M. *J. Org. Chem.* **1982**, *47*, 1789.
(3) Tagmazyan, K. T.; Mkrtchyan, R. S.; Babayan, A. T. *Zh. Org. Khim.* **1974**, *10*, 1642.
(4) Kraus, G. A.; Raggon, J. R.; Thomas, P. J.; Bougie, D. B. *Tetrahedron Lett.*, in press.

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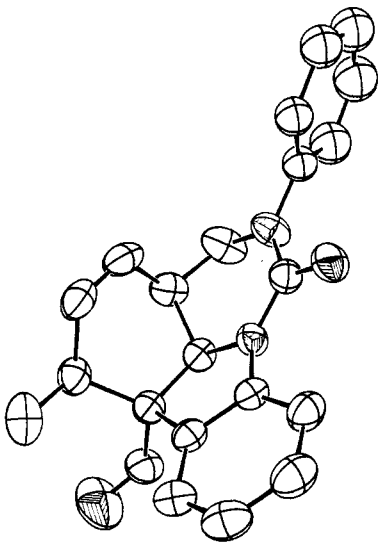
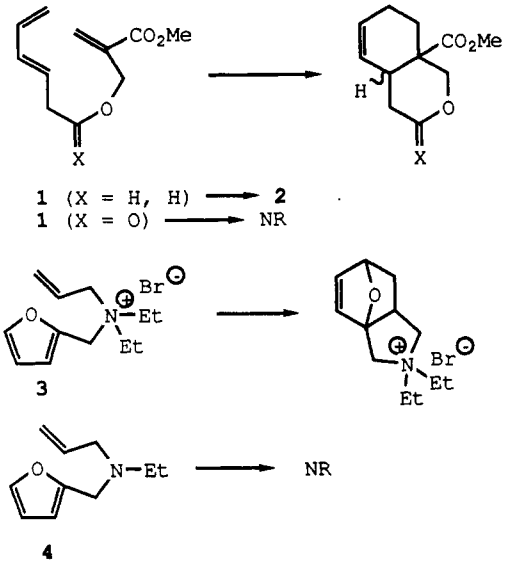


Figure 1. X-ray structure of adduct 9.

Scheme I



1-bromo-2,4-hexadiene, 7 (Scheme II). Surprisingly, carbamate 5 did not cyclize at temperatures as high as 290 °C. At higher temperatures, decomposition occurred. The urea 8 was next synthesized in 80% yield by treating the sodium salt of indole-3-carboxaldehyde with phenyl isocyanate and then alkylating the resulting urea anion with bromide 7. Fortunately, urea 8 cyclized to 9 in 93% yield at 240 °C. The product was a mixture of isomers in a 6:1 ratio. The major isomer was highly crystalline. Its structure was determined to be the exo isomer by X-ray crystallography (Figure 1). Several other ureas were then examined. The results are depicted in Table II. It is clear from the table that while an activating group on the indole is not required, it certainly accelerates the cyclization. Surprisingly, the indole bearing the propenoic acid moiety (entry 4) does not afford an adduct. This may be due to unfavorable nonbonded interactions as the transition state for cyclization develops. The sulfoxide (entry 2) afforded a mixture of the dihydro product and some completely aromatized product. In this case 1 equiv of trimethyl phosphite had to be present during the thermolysis in order to destroy the phenylsulfenic acid which was produced by sulfoxide elimination. Oxidation with DDQ in

Table I. Crystal Data

formula	$C_{22}H_{20}O_2N_2$
formual weight	344.42
space group	$P2_1/C$
a, Å	9.939 (2)
b, Å	11.106 (1)
c, Å	15.667 (2)
β, deg	90.97
V, Å^3	1729.1 (7)
Z	4
d_{calcd}, g/cm^3	1.323
crystal size, mm	0.31 × 0.42 × 0.20
μ (Mo Kα), cm^{-1}	0.798
data collection instrument	Enraf-Nonuis CAD4
radn. (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
orientation reflctns. number, range (2θ)	25, 14° < 2θ < 36°
temperature, °C	22 ± 1
scan method	$\theta - 2\theta$
data collection range, 2θ, deg	0–45
number, unique data, total:	2251
with $F_o^2 > 3\sigma(F_o^2)$:	1570
number of parameters refined	196
R^a	0.0562
R_w^b	0.0713
quality-of-fit indicator^c	1.44
largest shift/esd, final cycle	<0.01
largest peak, e/Å^3	0.55

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

Scheme II

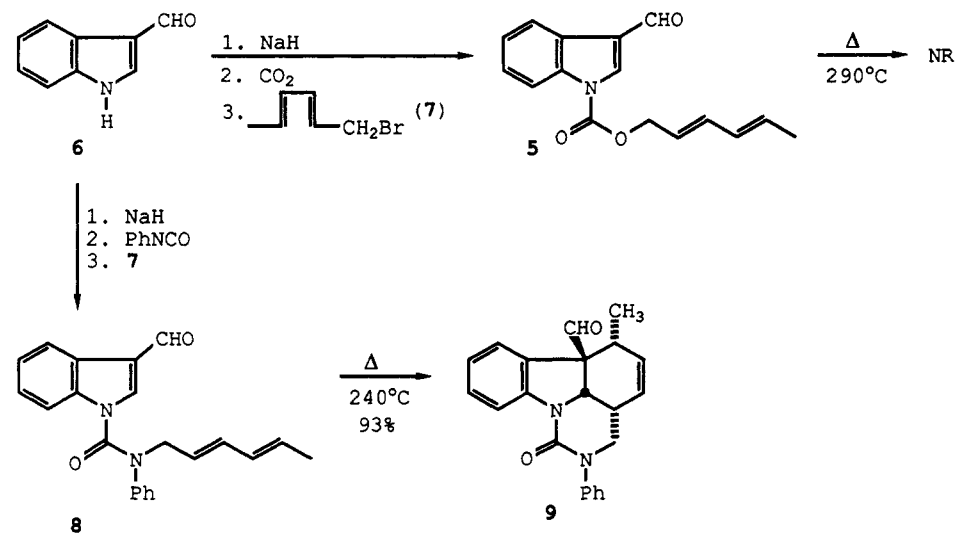
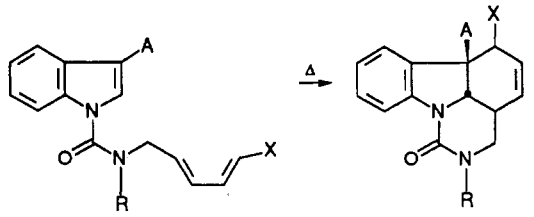
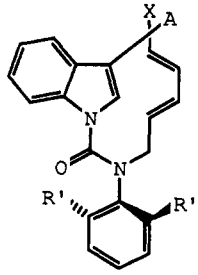


Table II. Diels–Alder Reactions of Ureas



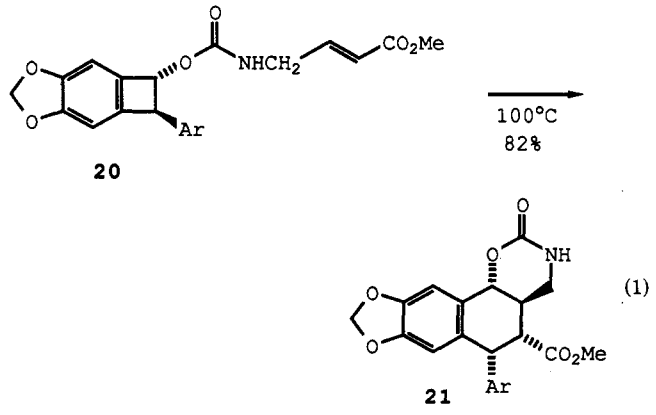
entry	R	X	A	compd no.	temp, °C	time, h	yield, %	compd no.
1	Ph	CH_3	CHO	8	240	12	93	9
2	Ph	CH_3	SOPh	10	240	6	68	11
3	Ph	CH_3	H	12	250	18	52	13
4	Ph	CH_3	$CH{=}CHCO_2Et$	14	270	12	–	
5	Ph	CO_2Et	CHO	15	240	12	20	16
6	tBu	CH_3	CHO	17	240	12	–	
7	2,6-$(Me)_2C_6H_3$	CH_3	CHO	18	170	18	67	19

Chart I



benzene at ambient temperature converted the mixture to the aromatized product in almost quantitative yield. The diene portion can contain both electron-withdrawing groups and electron-donating groups. Interestingly, the group R on the urea seems to exert the most pronounced effect on the rate of cyclization. When 2,6-dimethylphenyl isocyanate was employed, urea **18** was obtained in 35% yield. This compound cyclized under much milder conditions (170 °C vs 240 °C) than other ureas. When R is a smaller alkyl group, higher temperatures are necessary for cyclization. Unexpectedly, the thermolysis of **17**, which was prepared from *tert*-butyl isocyanate, afforded only decomposition products.

Boeckman ascribed the failure of ester **1** to cyclize to the loss of ester resonance in the transition state. Alternatively, the ester should have a preference for the transoid form and there may be a relatively high barrier for the interconversion of the two rotamers.[5] These very plausible arguments apparently do not apply to carbamate **5**, since Durst has recently demonstrated that carbamate **20** cyclizes to **21** at 100 °C in high yield[6] (eq 1). The interconversion of urea rotamers should be more facile than the interconversion of amide rotamers.[7] A possible transition state for cyclization based on the data from Table II is shown in Chart I.



(1)

The reactions described above demonstrate the utility of the urea connection. The ease by which diene and dienophile units can be linked together plus the stability of the tether to relatively high reaction temperatures make the urea tether worth considering for additional applications.

Experimental Section

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. H:EA refers to hexanes:ethyl acetate solvent mixtures for TLC and chromatography. The purity of all title compounds was determined to be ≥90% by ^1H NMR and/or elemental analysis.

General Procedure for the Reaction of Indoles, Isocyanates, and Dienes. To a suspension of hexanes-washed NaH (1.1 equiv in dry DMF (5 mL/mmol of indole) at 0 °C was added the requisite indole (1 equiv, 1 M in DMF). The reaction was stirred at 0 °C for 15 min. The isocyanate (1.1 equiv) was added, and the reaction was stirred at 0 °C for 15 min. The diene[9] (1.1 equiv) was then added and the reaction was stirred for 2 additional h. The reaction was diluted with ether and washed with brine. The organic layer was dried and concentrated. The crude product was then chromatographed by silica gel flash chromatography using 3:1 to 3:2 H:EA. All reactions were run on 2–4-mmol scales.

***N*-(2,4-Hexadienyl)-*N*-phenyl-1-(3-formylindolyl)urea (8)**: tan oil, 80% yield; 300-MHz NMR ($CDCl_3$) δ 1.73 (d, J = 7 Hz, 3 H), 4.54 (d, J = 6 Hz, 2 H), 5.63–5.82 (m, 2 H), 5.94–6.28 (m, 2 H), 7.00–7.10 (m, 2 H), 7.13–7.42 (m, 6 H), 7.97 (d, J = 8 Hz, 1 H), 8.19 (d, J = 8 Hz, 1 H), 9.70 (s, 1 H); IR (CH_2Cl_2) 3030, 1687, 1662, 1387, 1375 cm^{-1}; MS m/e 81, 119, 145, 167, 180, 315, 344; HRMS m/e for $C_{22}H_{20}N_2O_2$ calcd 344.15248, measured 344.15285; R_f (3:2 H:EA) 0.42.

***N*-(2,4-Hexadienyl)-*N*-phenyl-1-(3-(phenylsulfinyl)-indolyl)urea (10)**: tan oil, 62% yield; 300-MHz NMR ($CDCl_3$) δ 1.72 (d, J = 7 Hz, 3 H), 4.49 (d, J = 6.5 Hz, 2 H), 5.60–5.75 (m, 2 H) 5.97–6.25 (m, 2 H) 6.93–7.02 (m, 1 H), 7.08–7.48 (m, 13 H), 8.00 (d, J = 8 Hz, 1 H); IR ($CDCl_3$) 3055, 3020, 1700, 1685, 1592, 1490, 1445 cm^{-1}; MS m/e 81, 119, 193, 225, 241, 261, 315, 370, 424, 440; HRMS m/e for $C_{27}H_{24}H_2O_2S$ calcd 440.15586, measured 440.15527; R_f (3:2 H:EA) = 0.25.

***N*-(2,4-Hexadienyl)-*N*-phenyl-1-indolylurea (12)**: tan oil, 79% yield; 300-MHz NMR ($CDCl_3$) δ 1.73 (d, J = 7 Hz, 3 H), 4.51

(5) Parker, K. A.; Adamchuk, M. R. *Tetrahedron Lett.* **1978**, 1689.

(6) Macdonald, D. I.; Durst, T. *J. Org. Chem.* **1988**, *53*, 3663.

(7) Woodbrey, J. C.; Rogers, M. T. *J. Am. Chem. Soc.* **1962**, *84*, 13. They showed that $ClCO_2NMe_2$ had a lower barrier of rotation than $EtCONMe_2$. Our arguments parallel the arguments set forth in this paper.

(8) The X-ray structure of adduct **9** may be found in Figure 1.

(9) For the synthesis of 1-bromo-2,4-hexadiene from the alcohol, see: Jacobson, M. *J. Am. Chem. Soc.* **1955**, *77*, 2461. For the synthesis of 6-bromo-2,4-hexadienoic acid, ethyl ester, see: De Koning, H.; Subramanian-Erhart, K. E. C. *Synth. Commun.* **1973**, *3*, 25.

(d, J = 6 hz, 2 H), 5.58-5.86 (m, 2 H), 5.90-6.27 (m, 2 H), 6.24 (d, J = 3 Hz, 1 H), 6.77 (d, J = 3 Hz, 1 H), 6.98-7.06 (br d, J = 8 Hz, 2 H), 7.10-7.35 (m, 5 H), 7.47 (d, J = 8 Hz, 1 H), 8.07 (d, J = 8 Hz, 1 H); IR (film) 3020, 1685, 1592, 1450, 1383, 985 cm^{-1}; MS m/e 81, 117, 182, 197, 292, 316; HRMS for $C_{21}H_{20}N_2O$ calcd 316.15757, measured 316.15727; R_f (3:1 H:EA) = 0.42.

***N*-(2,4-Hexadienyl)-*N*-phenyl-1-(3-(3-ethoxy-3-oxo-1-propenyl)indolyl)urea (14)**: tan oil, 76% yield; NMR ($CDCl_3$) δ 1.32 (t, J = 7 Hz, 3 H), 1.72 (d, J = 7 Hz, 3 H), 4.22 (q, J = 7 Hz, 2 H), 4.51 (d, J = 4 Hz, 2 H), 5.60-6.27 (m, 4 H), 6.32 (d, J = 15 Hz, 1 H), 7.00-7.42 (m, 8 H), 7.49 (d, J = 15 Hz, 1 H), 7.26 (d, J = 8 Hz, 1 H), 8.07 (d, J = 8 Hz, 1 H); IR ($CDCl_3$) 1695, 1680, 1520, 1295 cm^{-1}; R_f (3:1 H:EA) = 0.48.

***N*-(6-Ethoxy-6-oxo-2,4-hexadienyl)-*N*-phenyl-1-(3-formylindolyl)urea (15)**: oil, 76% yield; NMR ($CDCl_3$) δ 1.27 (t, J = 7 Hz, 3 H), 4.19 (q, J = 7 Hz, 2 H), 4.63 (d, J = 4 Hz, 2 H), 5.34-6.40 (m, 3 H), 7.05-7.60 (m, 8 H), 7.99 (d, J = 8 Hz, 1 H), 8.18 (d, J = 8 Hz, 1 H), 9.70 (s, 1 H); IR ($CDCl_3$) 1700, 1668, 1392, 1262, 1239 cm^{-1}; MS m/e 119, 167, 180, 194, 299, 373, 402; HRMS calcd 402.15796, measured 402.15766.

***N*-(2,4-Hexadienyl)-*N*-*tert*-butyl-1-(3-formylindolyl)urea (17)**: solid; mp 68-70 °C; 64% yield; NMR ($CDCl_3$) δ 1.32 (s, 9 H), 1.76 (d, J = 7 Hz, 3 H), 4.78 (d, J = 6 H, 2 H), 5.64-6.26 (m, 4 H), 7.30-7.42 (m, 3 H), 7.73 (s, 1 H), 8.29-8.33 (m, 1 H), 10.00 (s, 1 H); IR (CH_2Cl_2) 1650, 1645, 1520, 1373, 1155 cm^{-1}.

***N*-(2,4-Hexadienyl)-*N*-(2,6-dimethylphenyl)-1-(3-formylindolyl)urea (18)**: solid; mp 123 °C; 35% yield; 300-MHz NMR ($CDCl_3$) δ 1.74 (d, J = 7 Hz, 3 H), 2.21 (s, 6 H), 4.35 (d, J = 7 Hz, 2 H), 5.62-5.76 (m, 1 H), 5.78-5.92 (m, 1 H), 5.95-6.18 (m, 2 H), 6.96-7.43 (m, 6 H), 8.10 (d, J = 8 Hz, 1 H), 8.16 (d, J = 8 Hz, 1 H), 9.57 (s, 1 H); IR ($CDCl_3$) 1685, 1667, 1392, 1232 cm^{-1}; MS m/e 81, 343, 372; R_f (3:2 H:EA) = 0.40.

General Procedure for the Diels-Alder Reactions. A 0.1 M solution of urea in dry degassed toluene was heated in a sealed glass tube at the temperature specified in Table II for the time specified in Table II. The reaction was allowed to cool to ambient temperature and purified by silica gel flash chromatography using 1:1 to 5:1 H:EA. Isomers were separated by chromatography. Main isomer spectral data are given. All reactions were run on a 2-3-mmol scale.

(3aβ,6aβ,11aβ)-2,3,3a,6,6a,11a-Hexahydro-6a-formyl-6-methyl-2-phenyl-1*H*-pyrimidino[3,2,1-*jk*]carbazol-1-one (9): solid; mp 171 °C (from ethyl acetate); 93% yield; 6:1 exo:endo ratio; 300-MHz NMR ($CDCl_3$) δ 1.12 (d, J = 7 Hz, 3 H), 2.80-2.97 (m, 2 H), 3.79 (dd, J = 2.8, 12 Hz, 1 H), 4.12 (dd, J = 3.6, 12 Hz, 1 H), 4.98 (d, J = 4.4 Hz, 1 H), 5.72-5.88 (m, 2 H), 6.97-7.18 (m, 2 H), 7.23-7.55 (m, 6 H), 7.99 (d, J = 8 Hz, 1 H), 9.85 (s, 1 H); IR (film) 2715, 1722, 1650, 1480, 1430 cm^{-1}; MS m/e 81, 145, 193, 289, 315, 344; HRMS m/e for $C_{22}H_{20}N_2O_2$ calcd 344.15248, measured 344.15277. The X-ray data are summarized in ref 8. Anal. Calcd: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.63; H, 5.87; N, 8.16.

(3aβ,6aα,6aβ,11aβ)-2,3,3a,6,6a,11a-Hexahydro-6a-formyl-6-(ethoxycarbonyl)-2-phenyl-1*H*-pyrimidino[3,2,1-*jk*]carbazol-1-one (16): solid; mp 157-158 °C (from ethyl acetate); one isomer; 300-MHz NMR ($CDCl_3$) δ 1.19 (t, J = 7 Hz, 3 H), 2.84-3.92 (m, 1 H), 3.85 (dd, J = 3.2, 12 Hz, 1 H), 4.03-4.16 (m, 2 H), 4.91 (d, J = 4.5 Hz, 1 H), 5.91 (br d, J = 10 Hz, 1 H), 6.30 (dt, J = 10, 3 Hz, 1 H), 6.97 (t, J = 8 Hz, 1 H), 7.14 (d, J = 8 Hz, 1 H), 7.24-7.54 (m, 6 H), 7.96 (d, J = 8 Hz, 1 H), 10.04 (s, 1 H); IR (film) 1724, 1670, 1475, 1417 cm^{-1}; MS m/e 119, 139, 180, 299, 373, 402; HRMS m/e for $C_{24}H_{22}N_2O_4$ calcd 402.15796, measured 402.15790. Anal. Calcd: C, 71.63; H, 5.51; N, 6.85. Found: C, 71.03; H, 5.56; N, 6.96.

(3aβ,6aα,6aβ,11aβ)-2,3,3a,6,6a,11a-Hexahydro-6-methyl-2-phenyl-1*H*-pyrimidino[3,2,1-*jk*]carbazol-1-one (13): tan oil; 52% yield; one isomer; 300-MHz NMR ($CDCl_3$) δ 1.53 (d, J = 7 Hz, 3 H), 2.35-2.58 (m, 2 H), 3.23-3.33 (m, 1 H), 3.52-3.62 (m, 1 H), 3.96-4.10 (m, 2 H), 5.76 (dt, J = 7, 3 Hz, 1 H), 5.92 (dt, J = 7, 3 Hz, 1 H), 6.97 (t, J = 8 Hz, 1 H), 7.14-7.55 (m, 7 H), 7.94 (d, J = 8 Hz, 1 H); IR (film) 3030, 2920, 1650, 1590, 1475, 1280 cm^{-1}; MS m/e 81, 117, 182, 162, 316; HRMS m/e for $C_{21}H_{20}N_2O$ calcd 316.15757, measured 316.15785; R_f (4:1 H:EA) = 0.37.

(3aβ,6aα,6aβ,11aβ)-2,3,3a,6,6a,11a-Hexahydro-6-methyl-2-phenyl-6a-(phenylsulfinyl)-1*H*-pyrimidino[3,21-*jk*]carbazol-1-one (11): tan oil; 68% yield; 300-MHz NMR ($CDCl_3$) δ 1.53 (d, J = 7 Hz, 3 H), 3.56-3.76 (m, 1 H), 3.80-4.08 (m, 3 H), 5.75 (dt, J = 10, 3 Hz, 1 H), 5.98 (dt, J = 10, 3 Hz, 1 H), 7.18-7.53 (m, 7 H), 7.62 (br d, J = 8 Hz, 1 H), 8.33 (br d, J = 8 Hz, 1 H); IR (film) 2970, 1685, 1467, 1406, 1318, 1292 cm^{-1}; MS m/e 106, 180, 193, 299, 314; HRMS m/e for $C_{21}H_{18}N_2O$ calcd 314.14192, measured 314.14176; R_f (3:2 H:EA) = 0.59.

(3aβ,6aα,6aβ,11aβ)-2,3,3a,6,6a,11a-Hexahydro-6-formyl-6-methyl-2-(2,6-dimethylphenyl)-1*H*-pyrimidino[3,2,1-*jk*]-carbazol-1-one (19): oil; 67% yield; 5:1 ratio of isomers; 300-MHz NMR ($CDCl_3$) δ 1.64 (d, J = 7 Hz, 3 H), 2.20 (s, 3 H), 2.32 (s, 3 H), 2.56-2.69 (m, 1 H), 2.80-2.92 (m, 1 H), 3.42-3.73 (m, 2 H), 4.42 (d, J = 10 Hz, 1 H), 5.72-5.94 (m, 2 H), 6.95-7.40 (m, 5 H), 7.56 (d, J = 8 Hz, 1 H), 7.98 (d, J = 8 Hz, 1 H), 9.80 (s, 1 H); R_f (1:1 H:EA) = 0.33.

Supplementary Material Available: Crystal data, methods of data collection and structure solution and refinement, ORTEP drawings, tables of bond distances, bond angles, positional parameters, general displacement parameter expressions, and root-mean-square amplitudes of thermal variation for **9** (19 pages); table of observed and calculated structure factors for **9** (1 page). Ordering information is given on any current masthead page.

Diels-Alder Reactions of Chiral Acrylylurea Derivatives and Resolution of the Adducts. Convenient Synthesis of Optically Pure Methyl (3*R*,4*R*,6*R*)-Bicyclo[2.2.1]heptene-4-carboxylate

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A new method to obtain optically pure methyl *endo*-bicyclo[2.2.1]heptene-4-carboxylates has been developed by using Diels-Alder reactions of chiral acrylylurea **3a** with cyclopentadiene and other dienes. The Diels-Alder adducts are easily separated by conventional column chromatography, and the chiral auxiliary is removed by methanolysis to give the methyl ester and the chiral urea **1**. The recovered urea can be converted to the acrylylurea **3** in two steps. Accordingly, the commercially available chiral source (both ((*S*)-1-phenylethyl)- and ((*R*)-1-phenylethyl)amine) can be recycled efficiently. The reaction has been investigated in the presence of various Lewis acids. Also studied were the reactions of acrylylurea **3a** with other dienes (1,3-cyclohexadiene and isoprene) and crotonylurea **3b** with cyclopentadiene. The excellent separability of the diastereomers is discussed based on conformational differences studied by ^1H NMR spectroscopy.

The asymmetric Diels-Alder reaction is becoming one of the most important synthetic tools in natural product synthesis,[1] and a spate of reports have appeared in recent years underlining its importance and presenting further

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