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Exocyclic Substituent Effects in the Unsymmetrically Cycloadditions of Electron-Deficient Heptafulvenes with Electron-Rich Fulvenes : Stereoselectivity, Periselectivity, and Regioselectivity

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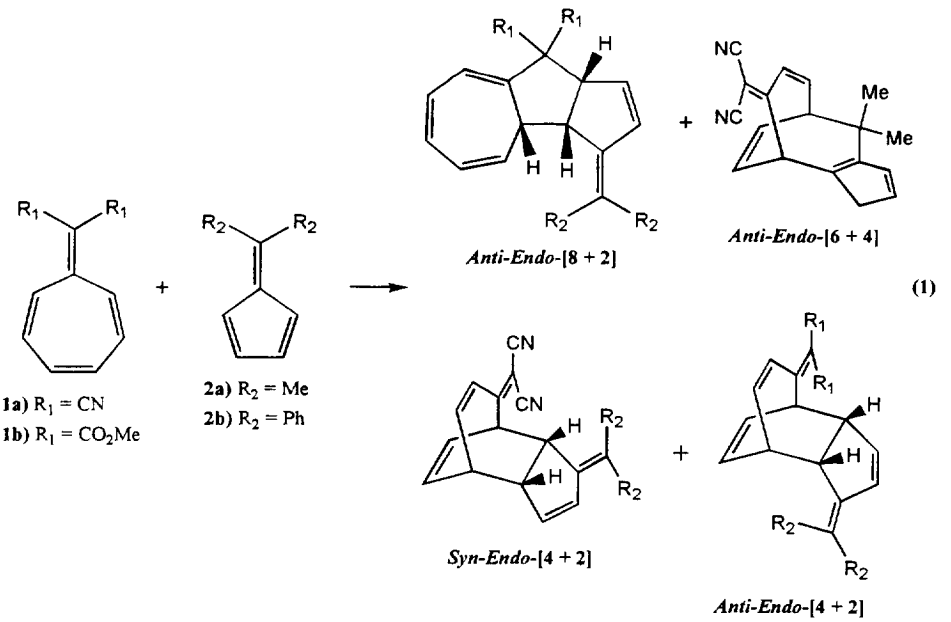
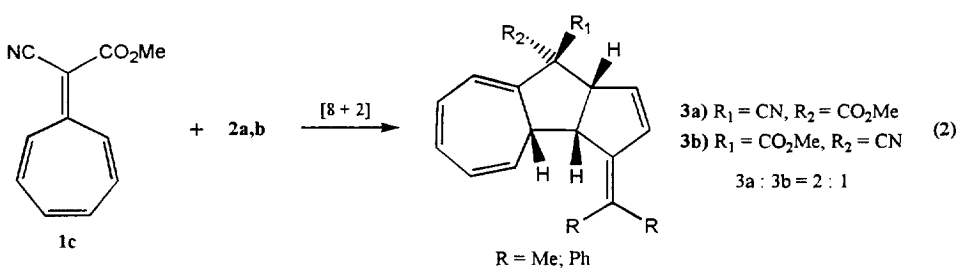
Abstract: The exocyclic substituent control of stereoselectivity, periselectivity, and regioselectivity in the unsymmetrical cycloaddition reactions of electron-deficient heptafulvenes with electron-rich fulvenes are discussed. © 1997 Elsevier Science Ltd.

INTRODUCTION

The competition among thermally allowed [4 + 2], [6 + 4], [8 + 2], and [8 + 6] cycloaddition reactions has prompted much investigation. We recently reported that the cycloaddition reactions of electron-deficient 8,8-dicyanoheptafulvene (**1a**) and 8,8-bis(methoxycarbonyl)heptafulvene (**1b**) with electron-rich 6,6-dimethylfulvene (**2a**) and 6,6-diphenylfulvene (**2b**) give endocyclic [8 + 2], endocyclic [4 + 2], and/or [6 + 4] cycloadducts, eq 1.[1] We proposed that the *endo* stereochemistry of these reactions is controlled by secondary orbital interactions, and the preferred *anti* regioselectivity (R_1 vs R_2) could be attributed to the steric repulsion between the exocyclic substituents on the heptafulvenes and fulvenes. We had also found that the exocyclic substituents on the heptafulvene exert some influence on the stereoselectivity and periselectivity only in the [8 + 2] cycloaddition reactions of unsymmetrically 8,8-disubstituted 8-cyano-8-methoxycarbonylheptafulvene (**1c**) and fulvenes **2a,b**, eq 2.[2] The fulvene exocyclic substituent control of periselectivity and regioselectivity in the [4 + 2] cycloadditions involving the endocycllic double bonds of fulvenes with mesoionic oxazolones and dithiolones has been reported.[3,4] The behaviors of these cycloaddition reactions seem to indicate sensitivity to steric requirements of exocyclic substitutents on the heptafulvenes and fulvenes, albeit, the structural, steric, and electronic factors that control the manner of these cycloadditions are not yet fully understood.





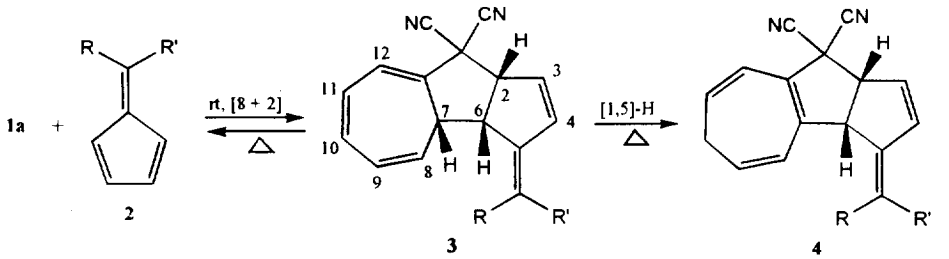
In this paper, we report the unsymetrically cycloaddition reactions of electron-deficient heptafulvenes **1a-d** with electron-rich fulvenes **2c-i** (Schemes 1-4). It has been found that the exocyclic substituent effects exerts a significant controlling influence upon the stereoselectivity, periselectivity, and regioselectivity of these cycloadditions.

RESULTS AND DISCUSSION

Reactions of Heptafulvene 1a with Unsymmetrically 6,6-Disubstituted Fulvenes 2c-i.

The reaction of 8,8-dicyanoheptafulvene (**1a**) with 6-isopropyl-6-methylfulvene (**2c**) in chloroform at room temperature for 1 day gave a single cycloadduct **3c** in 65% isolated yield (Scheme 1 and Table 1). The IR spectrum of cycloadduct **3c** showed a characteristic α,β-saturated cyano absorption at 2240 cm^{-1}. The structure was eventually proved by a complete analysis of the PMR spectra and double-resonance

Scheme 1



c) R = Me, R' = *i*-Pr; d) R = Me, R' = Ph;
e) R = Me, R' = $CHPh_2$; f) R = Me, R' = *t*-Bu;
g) R = *i*-Pr, R' = Ph; h) R = *c*-Hex, R' = Ph

Table 1. Cycloaddition Reactions of Heptafulvene **1a** with Fulvenes **2c-i**.

1a + 2x X	solvent	temp	time, days	product distribution, % [a] 3x	4x	5x	5x'	6x	6x'	Yield, %
c	chloroform	rt	1	100						65
	xylene	reflux	1/8		2.5	36	24	24	12	85
d	chloroform	rt	3	100						55
	xylene	reflux	2		6	42[b]	8	21	12	68
e	chloroform	rt	1	100						45
	xylene	reflux	1/8		7	76		17		51
f	chloroform	rt	1	100						60
	xylene	reflux	1/8		4	72		24		62
g	chloroform	rt	1	100						52
	xylene	reflux	1/8		5	38[c]	7	18[d]	21	55
h	chloroform	rt	1	100						35
	xylene	reflux	1/8		7	25	8	41	19	50
i	chloroform	rt	1					100		7
	xylene	reflux	1/8			14		77	9	61

[a] These value are normalized to reflect the relative amounts of the adducts in the individual mixtures.

[b] Exo isomer **7** was also obtained in 11% yield.

[c] Exo isomer **8** was also obtained in 7% yield.

[d] Exo isomer **9** was also obtained in 4% yield.

experiments. The PMR showed sharp doublets at δ 1.05 and 1.09 for the two methyl groups on the saturated carbon, a sharp singlet at δ 1.61 for the methyl group on the unsaturated carbon, a broad doublet of doublets for H-7 at δ 2.52 ($J_{6,7}$ = 9.8 Hz, $J_{7,8}$ = 4.9 Hz), a multiplet at δ 3.01 for the isopropyl proton, a doublet of doublets for H-6 at δ 3.89 ($J_{2,6}$ = 7.9 Hz, $J_{6,7}$ = 9.8 Hz), and a broad doublet for H-2 at δ 4.19 ($J_{2,3}$ = 2.4 Hz, $J_{2,4}$ = 1.5 Hz, $J_{2,6}$ = 7.9 Hz). The appropriate cycloheptatriene and cyclopentene resonances were also observed. The coupling constant of 9.8 Hz between H-6 and H-7 indicated an *endo* structure for this cycloadduct.[1,2,5-7] Furthermore, H-2 was coupled to H-3, H-4, and H-6, and no coupling was observed to the rest of the cycloheptatriene ring system. These results are compatible only with an *anti* relationship between the cyano and isopropylmethylmethylene groups. A series of NOE experiments further confirmed these structural assignments.

Upon irradiation at δ 1.61 (the methyl group on the unsaturated carbon), a large enhancement at δ 3.89 (H-6) and small enhancements at both δ 2.52 (H-7) and 5.03 (H-8) were observed. No enhancements were observed at δ 4.19 (H-2), 5.99 (H-3), 6.69 (H-4) or for the rest of cycloheptatriene ring system. Upon irradition at δ 3.01 (isopropyl proton), large enhancements at δ 1.07 (the two methyl groups on the saturated carbon), 1.61, and 6.69 (H-4) were observed. No enhancements were observed at δ 4.19 (H-2), 5.99 (H-3), 3.89 (H-6), 2.52 (H-7), 5.03 (H-8) or for the rest of cycloheptatriene ring system. All these results are consistent with the regiochemistry of the fulvene and cycloheptatriene moieties shown in structure **3c**. Irradiation at δ 3.89 (H-6), produced large enhancements at δ 1.61, 2.52 (H-7), and 4.19 (H-2), confirming the results stated above. These NOES not only confirmed the *endo* stereochemistry for this cycloadduct but also indicated that the smaller substituent, Me, on the exocyclic carbon of fulvene is *anti* to H-4.

Similarly, the reactions of heptafulvene **1a** with fulvenes **2d-h** in chloroform at room temperature afforded only the [8 + 2] cycloadducts **3d-h**, in 55, 45, 60, 52, and 35% yields, respectively (Scheme 1 and Table 1). The stereochemistry and regiochemistry of these cycloadducts were assigned on the basis of a careful analysis of their PMR spectra, double-resonance experiments, NOE experiments, and comparison of their spectra with those of related compounds.[1,2,5-7]

Like observations made in earlier studies,[1] these [8 + 2] cycloaddition reactions took place with exclusive *endo* diastereoselectivity and *anti* regioselectivity. The most important result of the present work is the fact that the exocyclic substituents of the fulvenes exert marked influence on the periselectivity between the two endocyclic double bonds. In all cases with the unsymmetrically 6,6-disubstituted fulvenes **2e-h**, these [8 + 2] cycloaddition reactions took place *exclusively* on the double bond which is *anti* to the larger exocyclic substituents of the fulvenes.

Since the steric repulsion between the exocyclic substituents on the heptafulvenes and fulvenes destabilizes the *syn* transition states relative to the *anti* transition states of the [8 + 2] cycloaddition reactions, as has been found in earlier examples.[1] The only possible transition-state geometry (*anti-endo*) for these cycloaddition reactions is sketched in Figure 1. Carefully examination of this transition state suggests that the possible steric repulsion mainly results from the proximity of the R_2 group of the fulvene to the C-4 and C-5

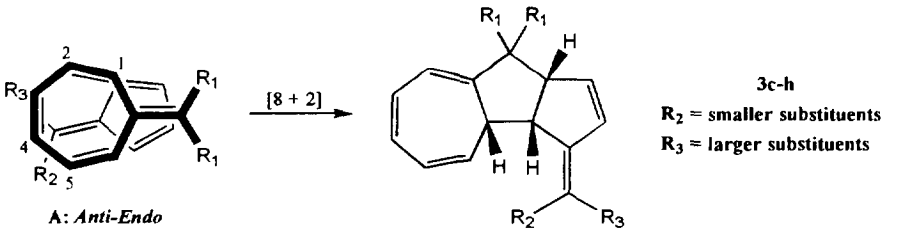
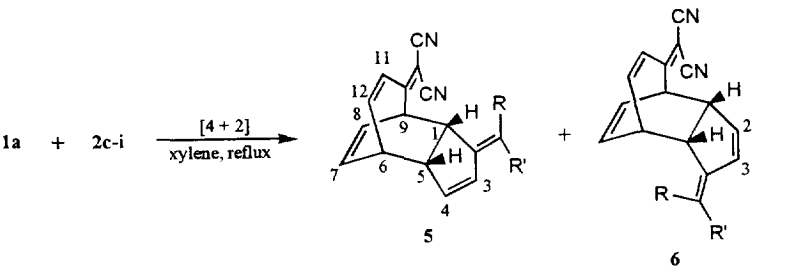


Figure 1. Anti-endo transition state, A, of the [8 + 2] cycloaddition reactions.

methine groups of the heptafulvene. Thus, transition state **A**, with the smaller R_2 substituent is more favorable and leads to the formation of cycloadducts **3c-h**.

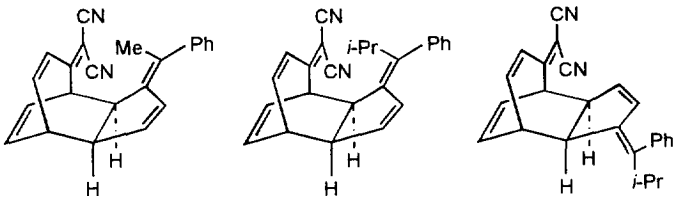
With a secondary steric repulsion results from the proximity of the R_3 group of the fulvene to the C-3 methine group of the heptafulvene, the 6-*t*-butyl-6-phenylfulvene (**2i**), with two bulky exocyclic substituents, destabilizes the *anti* transition state **A**, reacted sluggishly with **1a** in chloroform at room temperature afforded only traces of the [4 + 2] cycloadduct **6i** (Scheme 2 and Figure 2, see discussion below), no [8 + 2] cyclo-adduct was observed.

Scheme 2



c) R = Me, R' = *i*-Pr; **d**) R = Me, R' = Ph; **e**) R = Me, R' = $CHPh_2$; **f**) R = Me, R' = *t*-Bu;
c') R = *i*-Pr, R' = Me; **d'**) R = Ph, R' = Me; **e'**) R = $CHPh_2$, R' = Me; **f'**) R = *t*-Bu, R' = Me;

g) R = *i*-Pr, R' = Ph; **h**) R = *c*-Hex, R' = Ph; **i**) R = Ph, R' = *t*-Bu;
g') R = Ph, R' = *i*-Pr; **h'**) R = Ph, R' = *c*-Hex; **i'**) R = *t*-Bu, R' = Ph



When these reactions were carried out in refluxing xylene, mainly the [4 + 2] cycloadducts **5-6** were obtained (Scheme 2 and Table 1). Heptafulvene **1a** reacted smoothly with fulvene **2c** in refluxing xylene

for 3 h to give the *syn*-[4 + 2] cycloadducts **5c,c'** (1.5:1 ratio) and the *anti*-[4 + 2] cycloadducts **6c,c'** (2:1 ratio) in a ratio of about 1.6:1, along with minor amounts of the [8 + 2] cycloadduct **4c**. The IR spectra of cycloadducts **5c,c'** and **6c,c'** showed a characteristic α,β-unsaturated cyano absorption at 2215 cm^{-1}. The structures of these cyclodducts were eventually proved by a complete analysis of the PMR spectra and double-resonance experiments. The PMR spectra showed four downfield aliphatic protons at about δ 3.0-4.5 and six olefinic protons. The appropriate exocyclic substituents, methyl and isopropyl resonances, were also observed. The small couplings between H-1 and H-9 and between H-5 and H-6 in **5c,c'** and **6c,c'** are compatible only with an *endo* stereochemistry for these cycloadducts.[1,2,8-10] In cycloadducts **5c,c'**, H-5 was coupled to H-1, H-3, H-4, and H-6, respectively, indicating a *syn* regiochemistry of the cyano and isopropylmethylmethylene groups, whereas in cycloadducts **6c,c'**, H-1 was coupled to H-2, H-3, H-5, and H-9, respectively, indicating an *anti* regiochemistry. A series of NOE experiments further confirmed these structural assignments.

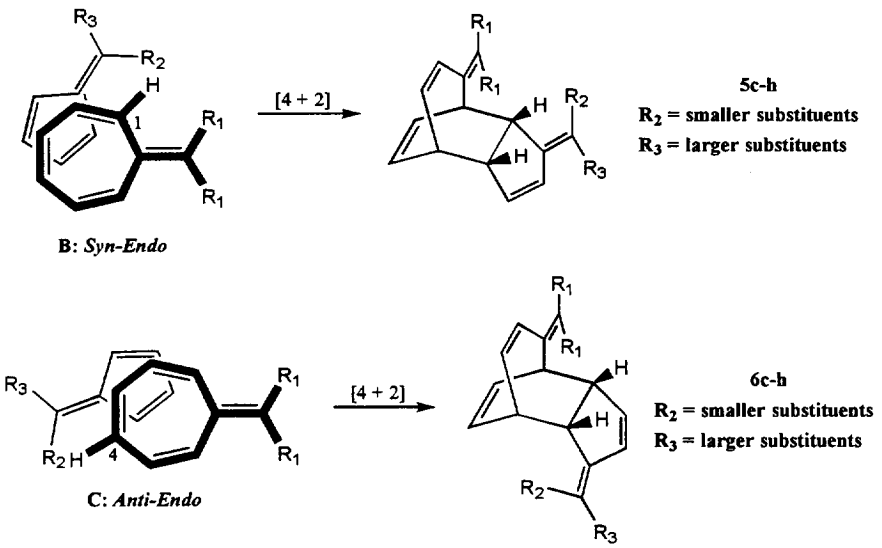


Figure 2. Endo transition states of the *syn*-[4 + 2] (B) and *anti*-[4 + 2] (C) cycloaddition reactions.

The present results show that the [4 + 2] cycloaddition reaction of **1a** and **2c** took place *preferentially* on the double bond that is *anti* to the larger exocyclic substituents of the fulvene. This periselectivity can be explained by comparing the various transition states involved in the cycloadditions. The possible transition state geometries (*endo*) for these cycloaddition reactions are sketched in Figure 2. Examination of these transition states indicates that steric repulsion results from the proximity of the R_2 group of the heptafulvene to the C-1 and C-4 methine groups of the fulvene in transition states **B** and **C**, respectively. Thus, transition states **B** and **C**, with the smaller R_2 substituents are more favorable and lead to the formation of cycloadducts **5c** and **6c**, respectively. Similarly, cycloadducts **5d** and **6d** are obtained preferentially. Increasing steric bulk of the larger one of the two exocyclic substituents on the fulvenes should cause a higher periselectivity, and

thus the reactions of fulvenes **2e,f** with **1a** took place *exclusively* on the double bond that is *anti* to the larger exocyclic substituents of the fulvene. As Table 1 indicates, the reactions of fulvenes **2c-g** with heptafulvene **1a**, proceed with predominant *syn* regioselectivity. With a secondary steric repulsion results from the proximity of the R_2 group of the fulvene to the R_1 group of the heptafulvene in transition state **B**, an nonbonded interaction which is absent in **C**, the fulvenes **2h,i**, with two bulky exocyclic substituents, destabilizes the *syn* transition state **B**, reacted with **1a** *predominantly* to give the *anti*-[4 + 2] cycloadducts **6h,i**, respectively.[1,2]

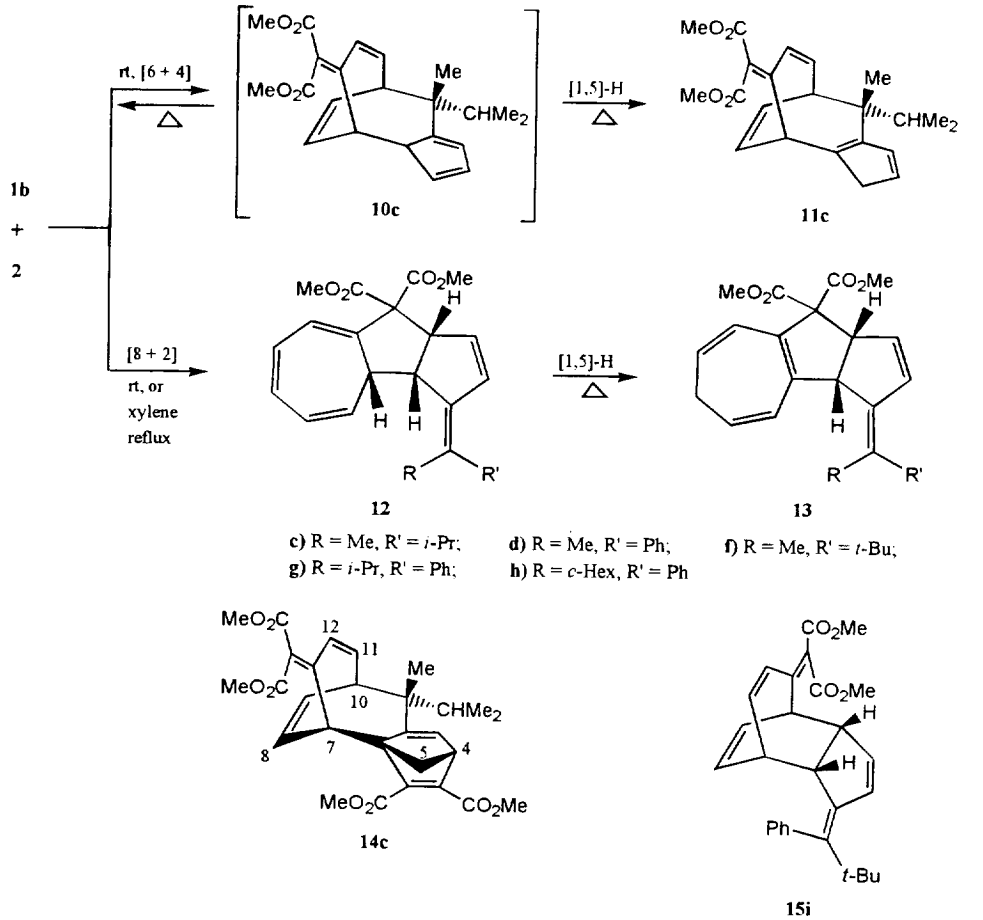
At this point the question arises whether formation of compounds **5-6** involves intermolecular [4 + 2] cycloaddition reactions of **1a** and **2** or intramolecular rearrangement of the [8 + 2] cycloadducts **3**. Heating a dilute solution of **3** in refluxing xylene mainly led to *retro*-[8 + 2] cycloaddition reactions of **3** to **1a** and **2**, along with minor amounts of the [8 + 2] cycloadducts **4**. Thus, the cycloadducts **4** arise from the intermolecular [8 + 2] cycloaddition reactions to form **3**, followed by 1,5-sigmatropic hydrogen shifts. As expected,[1,11,12] these [8 + 2] cycloadducts **3**, with two strongly electron-deficient cyano groups, although formed under milder conditions, mainly reverted back to starting matertals **1a** and **2** at higher temperatures and in turn recombined to form the thermodynamically more stable [4 + 2] cycloadducts **5-6**.

Reactions of Heptafulvene 1b with Unsymmetrically 6,6-Disubstituted Fulvenes 2c-i.

The more weakly electron-deficient and more hindered 8,8-bis(methoxycarbonyl)heptafulvene (**1b**) reacted sluggishly with 6-isopropyl-6-methylfulvene (**2c**) in chloroform at room temperature for 15 days to give mainly [6 + 4] cycloadduct **11c** in about 16% yield, along with traces of [8 + 2] cycloadduct **12c** (Scheme 3). Cycloadduct **11c** must arise from an initial [6 + 4] cycloaddition that forms **10c** followed by a 1,5-sigmatropic hydrogen shift in the cyclopentadiene moiety. Although cycloadduct **11c** could not be isolated in pure form because they underwent *retro*-[6 + 4] cycloaddition to starting materials **1b** and **2c**, samples suitable for spectral analysis were obtained by flash column chromatography. Its structure was assigned on the basis of a careful analysis of its PMR spectra, double-resonance experiments, and comparison of its spectrum with those of related compounds.[1,2,13-17] Additional structural evidence for **11c** is the [4 + 2] cycloaddition reaction of **11c** with DMAD, which gave **14c**. However, the reactions of heptafulvene **1b** with fulvenes **2d** and **2f-h** in chloroform at room temperature afforded only the [8 + 2] cycloadducts **12d**, and **12f-h**, respectively, in low yields (Scheme 3). No [6 + 4] cycloadduct was observed. Unfortunately, the attempted reactions of heptafulvene **1b** with fulvenes **2e,i** in chloroform at room temperature gave small amounts of complex reaction mixtures. No products of these reactions have been identified.

When heptafulvene **1b** was reacted with fulvenes **2c-d** and **2f-h** in refluxing xylene, the [8 + 2] cyclodducts **13c-d** and **13f-h** were obtained, respectively, in moderate yields (Scheme 3). Because **12c-d** and **12f-h** were converted to **13c-d** and **13f-h**, respectively, when heated at 190 °C for 7 h, cycloadducts **13c-d** and **13f-h** were believed to come from [8 + 2] cycloadditions followed by 1,5-sigmatropic hydrogen shifts. When the two bulky exocyclic substituted 6-*t*-butyl-6-phenylfulvene (**2i**) was reacted with heptafulvene **1b**, the [4 + 2] cycloadduct **15i** was the sole isolated reaction product, no [8 + 2] cycloadduct was observed.

Scheme 3



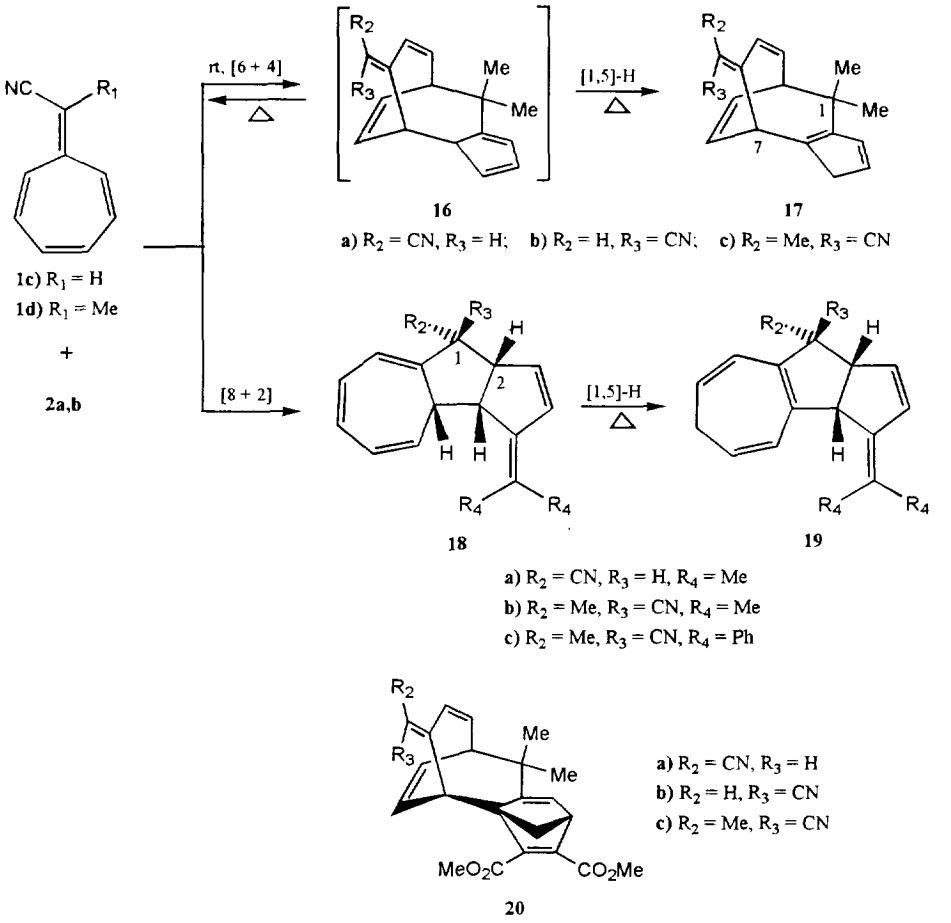
All these results show that these [8 + 2] and [4 + 2] cycloaddition reactions took place with exclusive *endo* diastereoselectivity and *anti* regioselectivity, and that the exocyclic substituents of the fulvenes exert marked influence on the periselectivity between the two endocyclic double bonds. In all cases with the unsymmetrically 6,6-disubstituted fulvenes, these cycloaddition reactions took place *exclusively* on the double bond which is *anti* to the larger exocyclic substituents of the fulvenes.

In order to obtain more information about the effects of the exocyclic substituent on the heptafulvene, we have now investigated the cycloaddition reactions of electron-deficient unsymmetrically substituted heptafulvenes **1c,d** with fulvenes **2a,b** (Scheme 4).

Reactions of Unsymmetrically Substituted Heptafulvenes 1c,d with Fulvenes 2a,b.

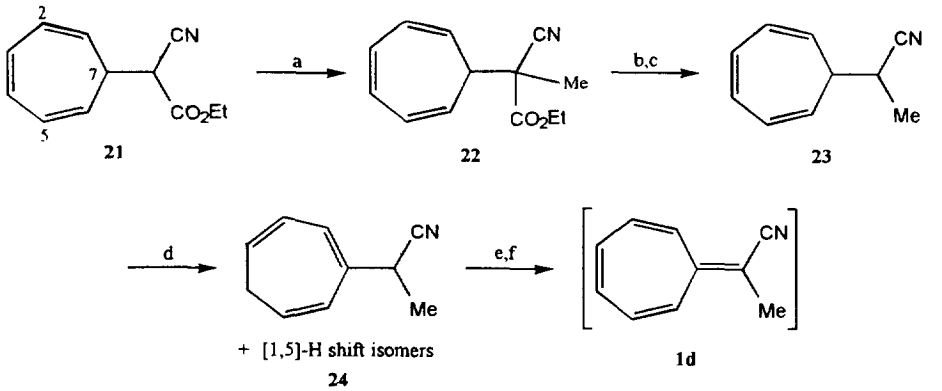
The reaction of 8-cyanoheptafulvene (**1c**) with 6,6-dimethylfulvene (**2a**) in chloroform at room

Scheme 4



temperature for 7 days afforded the [6 + 4] cycloadducts **17a,b** (1:1 mixture of inseparable regioisomers) and [8 + 2] cycloadduct **18a** in a 4:1 ratio (Scheme 4). When the reaction was carried out in refluxing xylene, only the [8 + 2] cycloadduct **19a** was obtained. Because **18a** was converted to **19a**, when heated at 190 °C for 7 h, cycloadduct **19a** was believed to come from an [8 + 2] cycloaddition followed by a 1,5-sigmatropic hydrogen shift. The [6 + 4] cycloadducts **17a,b**, although formed under milder conditions, mainly reverted back to starting materials **1c** and **2a** at higher temperatures and in turn recombined to form the thermodynamically more stable [8 + 2] cycloadduct **19a**. The stereochemistry and regiochemistry of these adducts were assigned on the basis of a careful analysis of their PMR spectra, double-resonance experiments, NOE experiments, and comparison of their spectra with those of related compounds. Additional structural evidence for **17a,b** are the [4 + 2] cycloaddition reactions of **17a,b** with DMAD, which gave **20a,b**, respectively. Unfortunately, the attempted reaction of **1c** with **2b** in chloroform at room temperature or in refluxing xylene gave complex reaction mixtures.

Scheme 5



(a) NaOEt, EtOH, $(CH_3O)_2SO_2$, reflux, 24h, (42%); **(b)** KOH, aq. EtOH (100%); **(c)** Cu, xylene, reflux, 19h (89%); **(d)** 205 °C, 7h (95%); **(e)** $(C_6H_5)_3C^+BF_4^-$, $CHCl_3$, 2h; **(f)** Et_3N, CH_2Cl_2, 1h (46% from 24).

The more hindered 8-cyano-8-methylheptafulvene (**1d**) was prepared from ethyl tropylcyanoacetate (**21**)[18] shown in Scheme 5. Alkylation of **21** with sodium ethoxide and dimethyl sulfate in dry ethanol gave **22** in 42% yield. Hydrolysis and decarboxylation of **22** gave **23** in 89% yield after careful flash chromatography. Thermal rearrangement of **23** gave a mixture of 1- and 3-substituted cycloheptatrienes **24** (95%), which provides a satisfactory starting material for hydride abstraction.[6,19,20] The mixture of nitrile **24** was dehydrogenated with trityl fluoroborate followed by triethylamine[6,19,20] to give a deep red oil. The red oil is is presumed to be **1d**, although it underwent decomposition upon attempted purification by silica gel chromatography or upon removal of solvent.

The reactions of 8-cyano-8-methylheptafulvene (**1d**) with fulvenes **2a,b**, respectively, in refluxing xylene gave only the [8 + 2] cycloadducts **19b** and **19c**, respectively (Scheme 4). When the reaction of **1d** with **2a** was carried out in refluxing chloroform, only the [6 + 4] cycloadduct **17c** was obtained. Adducts **19b** and **19c** were believed to come from [8 + 2] cycloadditions to form **18b** and **18c**, respectively, followed by 1,5-sigmatropic hydrogen shifts. The [6 + 4] cycloadduct **17c** although formed under milder conditions, mainly reverted back to starting materials **1d** and **2a** at higher temperatures and in turn recombined to form the thermodynamically more stable [8 + 2] cycloadduct **19b**. The stereochemistry and regiochemistry of these adducts were assigned on the basis of a careful analysis of their NMR spectra, double-resonance experiments, NOE experiments, and comparison of their spectra with those of related compounds. Additional structural evidence for **17c** is the [4 + 2] cycloaddition reaction of **17c** with DMAD, which gave **20c**.

Interestingly, the cycloaddition reactions of 8-cyanoheptafulvene (**1c**) with 6,6-dimethylfulvene (**2a**) gave [6 + 4] cycloadducts **17a,b** in an approximately 1:1 ratio. However, in the [8 + 2] cycloaddition reactions, cycloadduct **18a**, with the cyano substituent *trans* to H-2, was the sole cycloadduct observed. All these results can be explained by comparing the various transition states involved in the cycloadditions. The possible transition state geometries (*anti-endo*) for these cycloaddition reactions are sketched in Figure 3.

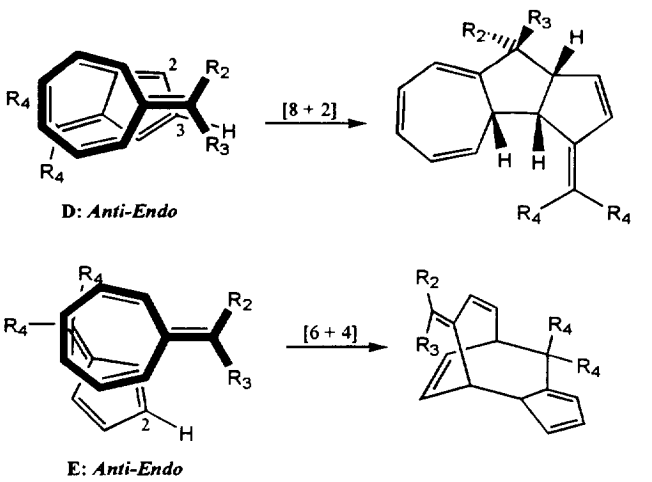


Figure 3. Anti-endo transition states of the [8 + 2] (D) and [6 + 4] (E) cycloaddition reactions.

Examination of these transition states indicates that secondary orbital interactions results from the proximity of the R_2 group of the heptafulvene to the C-2 methine group of the fulvene in the [8 + 2] transition state **D**, an interaction which is absent in the [6 + 4] transition state **E**. Thus, transition state **D**, with the cyano substituent (R_2) to be *endo* relative to the fulvene, is more favorable and leads to the formation of cycloadduct **8a**.

In contrast to the stereoselectivity and periselectivity observed in the cycloaddition reaction of **1c** and **2a**, the [8 + 2] cycloaddition reactions of more hindered 8-cyano-8-methylheptafulvene (**1d**) with **2a,b** gave cycloadducts **18b,c**, respectively, both with the cyano substituent *cis* to H-2 (*exo* relative to the fulvene). And, in the [6 + 4] cycloaddition reactions, cycloadduct **17c**, with the cyano substituent *syn* to H-7, was the sole cycloadduct observed. Examination of the various transition states involved in the cycloadditions (Figure 3) indicates that steric repulsion results from the proximity of the R_3 groups of the heptafulvene to the C-3 and C-2 methine groups of the fulvene in transition states **D** and **E**, respectively. Thus, transition states **D** and **E**, with the smaller R_3 substituents (CN < Me), respectively, are more favorable and lead to the formation of cycloadducts **18b,c** and **17c**, respectively.

All these results show that the exocyclic substituent effects exerts a significant controlling influence upon the stereoselectivity, periselectivity, and regioselectivity of these cycloadditions.

EXPERIMENTAL SECTION

General Methods. Infrared (IR) spectra were determined on a JASCO IR Report-100 infrared spectrometer. ^{1}H-NMR spectra were determined on a Varian Jemini-200L (200 MHz) spectrometer with tetramethylsilane

(δ = 0) as the internal standard and $CDCl_3$ as the solvent. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad signal. Mass spectra were determined on a JEOL JMS-D-100 mass spectrometer. High resolution mass spectra (HRMS) were determined on a JEOL JMS-HX-110 mass spectrometer. All reagents were of reagent grade and were purified prior to use. All reactions were performed under an inert atmosphere of nitrogen. The preparations of heptafulvenes **1a,b**,[18] and **1c**[19] and fulvenes **2c-i**[21,22] were by literature procedures.

General Procedure for Cycloaddition Reactions of Heptafulvenes 1a,b with Fulvenes 2c-i. A solution containing 1.0 mmol of heptafulvenes **1a,b** and 1.1 mmol of fulvenes **2c-i** in 8 mL of solvent was stirred for a certain period of time (the solvents and the reaction conditions are all indicated in Table 1). After evaporation of the excess solvent under reduced pressure, the crude mixture was subjected to silica gel flash column chromatography with 0-10% EtOAc in n-hexane as the eluant to give the pure products. IR spectra data for cycloadducts (cm^{-1}): **3**,**4**,**18**,**19** 2240-2245 (CN); **5-9**, **20** 2215-2220 (CN); **12**,**13** 1740-1745 (C=O); **15** 1720-1725 (C=O). Other data, PMR, MS, HRMS, for:

3c: ^{1}H NMR δ 1.05 (d, 3 H, J = 7.3 Hz, -CH***Me***Me), 1.09 (d, 3 H, J = 7.3 Hz, -CHMe***Me***), 1.61 (s, 3 H, Me), 2.52 (dd, 1 H, $J_{6,7}$ = 9.8 Hz, $J_{7,8}$ = 4.9 Hz, H-7), 3.01 (m, 1 H, J = 7.3 Hz, -C***H***Me_2), 3.89 (dd, 1 H, $J_{2,6}$ = 7.9 Hz, $J_{6,7}$ = 9.8 Hz, H-6), 4.19 (m, 1 H, H-2), 5.03 (dd, 1 H, $J_{7,8}$ = 4.9 Hz, $J_{8,9}$ = 8.4 Hz, H-8), 5.99 (dd, 1 H, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 6.09 (m, 1 H, H-9), 6.69 (m, 4 H, H-4, H-10-12); MS *m/z* 288 (M^+); exact mass calcd for $C_{20}H_{20}N_2$ 288.1628, found 288.1622.

5c: ^{1}H NMR δ 0.98 (d, 3 H, J = 7.0 Hz, -CH***Me***Me), 1.02 (d, 3 H, J = 7.0 Hz, -CHMe***Me***), 1.75 (s, 3 H, Me), 2.86 (m, 1 H, J = 7.0 Hz, -C***H***Me_2), 3.06 (d, 1 H, $J_{1,5}$ = 7.7 Hz, H-1), 3.47 (m, 1 H, H-6), 3.59 (m, 1 H, H-5), 4.04 (m, 1 H, H-9), 5.55 (dd, 1 H, $J_{3,4}$ = 5.8 Hz, $J_{4,5}$ = 2.2 Hz, H-4), 5.99 (dd, 1 H, $J_{7,8}$ = 7.9 Hz, $J_{8,9}$ = 7.3 Hz, H-8), 6.26 (bt, 1 H, $J_{6,7}$ = 7.4 Hz, $J_{7,8}$ = 7.9 Hz, H-7), 6.51 (dd, 1 H, $J_{3,4}$ = 5.8 Hz, $J_{3,5}$ = 2.1 Hz, H-3), 6.56 (dd, 1 H, $J_{9,11}$ = 1.5 Hz, $J_{11,12}$ = 10.9 Hz, H-11), 6.99 (dd, 1 H, $J_{6,12}$ = 8.6 Hz, $J_{11,12}$ = 10.9 Hz, H-12); MS *m/z* 288 (M^+); exact mass calcd for $C_{20}H_{20}N_2$ 288.1628, found 288.1637.

5c': ^{1}H NMR δ 1.02 (d, 3 H, J = 7.0 Hz, -CH***Me***Me), 1.18 (d, 3 H, J = 7.0 Hz, -CHMe***Me***), 1.68 (s, 3 H, Me), 2.71 (m, 1 H, J = 7.0 Hz, -C***H***Me_2), 3.28 (d, 1 H, $J_{1,5}$ = 7.7 Hz, H-1), 3.47 (m, 1 H, H-6), 3.59 (m, 1 H, H-5), 4.04 (m, 1 H, H-9), 5.55 (dd, 1 H, $J_{3,4}$ = 5.8 Hz, $J_{4,5}$ = 2.2 Hz, H-4), 5.99 (dd, 1 H, $J_{7,8}$ = 7.9 Hz, $J_{8,9}$ = 7.3 Hz, H-8), 6.26 (bt, 1 H, $J_{6,7}$ = 7.3 Hz, $J_{7,8}$ = 7.9 Hz, H-7), 6.41 (dd, 1 H, $J_{3,4}$ = 5.8 Hz, $J_{3,5}$ = 2.1 Hz, H-3), 6.56 (dd, 1 H, $J_{9,11}$ = 1.5 Hz, $J_{11,12}$ = 10.9 Hz, H-11), 6.99 (dd, 1 H, $J_{6,12}$ = 8.6 Hz, $J_{11,12}$ = 10.9 Hz, H-12); MS *m/z* 288 (M^+); exact mass calcd for $C_{20}H_{20}N_2$ 288.1628, found 288.1637.

6c: ^{1}H NMR δ 0.95 (d, 3 H, J = 7.1 Hz, -CH***Me***Me), 0.98 (d, 3 H, J = 7.1 Hz, -CHMe***Me***), 1.70 (s, 3 H, Me), 2.81 (m, 1 H, J = 7.0 Hz, -C***H***Me_2), 3.32 (m, 2 H, H-1, H-5), 3.55 (bt, 1 H, $J_{6,7}$ = 8.1 Hz, $J_{6,12}$ = 8.8 Hz, H-6), 4.07 (bd, 1 H, $J_{8,9}$ = 7.4 Hz, H-9), 5.68 (m, 1 H, H-2), 5.89 (dd, 1 H, $J_{7,8}$ = 8.8 Hz, $J_{8,9}$ = 7.4 Hz, H-8), 6.33 (bt, 1 H, $J_{6,7}$ = 8.1 Hz, $J_{7,8}$ = 8.8 Hz, H-7), 6.49 (dd, 1 H, $J_{1,3}$ = 1.5 Hz, $J_{2,3}$ = 5.7 Hz, H-3), 6.57 (dd, 1 H, $J_{9,11}$ = 1.8 Hz, $J_{11,12}$ = 10.9 Hz, H-11), 7.01 (dd, 1 H, $J_{6,12}$ = 8.8 Hz, $J_{11,12}$ = 10.9 Hz, H-12); MS *m/z* 288 (M^+); exact mass calcd for $C_{20}H_{20}N_2$ 288.1628, found 288.1626.

6c': ^{1}H NMR δ 0.97 (d, 3 H, J = 7.1 Hz, -CH*Me*Me), 1.10 (d, 3 H, J = 7.1 Hz, -CHMe*Me*), 1.60 (s, 3 H, Me), 2.70 (m, 1 H, J = 7.1 Hz, -C*H*Me$_2$), 3.32 (m, 2 H, H-1, H-5), 3.55 (bt, 1 H, $J_{6,7}$ = 8.1 Hz, $J_{6,12}$ = 8.8 Hz, H-6), 4.07 (bd, 1 H, $J_{8,9}$ = 7.4 Hz, H-9), 5.68 (m, 1 H, H-2), 5.89 (dd, 1 H, $J_{7,8}$ = 8.8 Hz, $J_{8,9}$ = 7.4 Hz, H-8), 6.33 (bt, 1 H, $J_{6,7}$ = 8.1 Hz, $J_{7,8}$ = 8.8 Hz, H-7), 6.40 (dd, 1 H, $J_{1,3}$ = 1.5 Hz, $J_{2,3}$ = 5.7 Hz, H-3), 6.57 (dd, 1 H, $J_{9,11}$ = 1.8 Hz, $J_{11,12}$ = 10.9 Hz, H-11), 7.06 (dd, 1 H, $J_{6,12}$ = 8.8 Hz, $J_{11,12}$ = 10.9 Hz, H-12); MS *m/z* 288 (M^+); exact mass calcd for $C_{20}H_{20}N_2$ 288.1628, found 288.1626.

3d: ^{1}H NMR δ 2.10 (s, 3 H, Me), 2.66 (dd, 1 H, $J_{6,7}$ = 9.7 Hz, $J_{7,8}$ = 5.0 Hz, H-7), 4.10 (dd, 1 H, $J_{2,6}$ = 7.4 Hz, $J_{6,7}$ = 9.7 Hz, H-6), 4.35 (m, 1 H, H-2), 5.16 (dd, 1 H, $J_{7,8}$ = 5.0 Hz, $J_{8,9}$ = 9.5 Hz, H-8), 6.08 (dd, 1 H, $J_{2,3}$ = 2.2 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 6.18 (m, 1 H, H-9), 6.54 (dd, 1 H, $J_{2,4}$ = 2.6 Hz, $J_{3,4}$ = 6.0 Hz, H-4), 6.75 (m, 3 H, H-10-12), 7.35 (m, 5 H, Phenyl); MS *m/z* 322 (M^+); exact mass calcd for $C_{23}H_{18}N_2$ 322.1471, found 322.1468.

4d: ^{1}H NMR δ 2.20 (s, 3 H, Me), 2.20 (m, 1 H, H-10), 2.51 (m, 1 H, H-10), 4.05 (m, 1 H, H-2), 4.52 (d, 1 H, $J_{2,6}$ = 7.9 Hz, H-6), 5.45 (m, 1 H, H-9), 5.56 (m, 1 H, H-11), 5.92 (dd, 1 H, $J_{2,3}$ = 2.7 Hz, $J_{3,4}$ = 6.0 Hz, H-3), 6.28 (m, 2 H, H-8, H-12), 6.35 (m, 1 H, H-4), 7.20 (m, 5 H, Phenyl); MS *m/z* 322 (M^+); exact mass calcd for $C_{23}H_{18}N_2$ 322.1471, found 322.1466.

5d: ^{1}H NMR δ 2.22 (s, 3 H, Me), 3.25 (d, 1 H, $J_{1,5}$ = 7.3 Hz, H-1), 3.51 (bt, 1 H, $J_{6,7}$ = 6.9 Hz, $J_{6,12}$ = 8.6 Hz, H-6), 3.67 (m, 1 H, H-5), 4.22 (bd, 1 H, $J_{8,9}$ = 7.1 Hz, H-9), 5.60 (dd, 1 H, $J_{3,4}$ = 5.7 Hz, $J_{4,5}$ = 2.2 Hz, H-4), 6.07 (bt, 1 H, $J_{7,8}$ = 7.8 Hz, $J_{8,9}$ = 7.1 Hz, H-8), 6.29 (m, 2 H, H-3, H-7), 6.62 (dd, 1 H, $J_{9,11}$ = 1.9 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 7.02 (dd, 1 H, $J_{6,12}$ = 8.6 Hz, $J_{11,12}$ = 10.8 Hz, H-12), 7.25 (m, 5 H, Phenyl); MS *m/z* 322 (M^+); exact mass calcd for $C_{23}H_{18}N_2$ 322.1471, found 322.1467.

5d': ^{1}H NMR δ 2.10 (s, 3 H, Me), 3.40 (bt, 1 H, $J_{6,7}$ = 6.8 Hz, $J_{6,12}$ = 8.6 Hz, H-6), 3.67 (m, 3 H, H-1, H-5, H-9), 5.75 (bd, 1 H, $J_{3,4}$ = 5.7 Hz, H-4), 5.97 (bt, 1 H, $J_{7,8}$ = 8.0 Hz, $J_{8,9}$ = 7.5 Hz, H-8), 6.21 (bt, 1 H, $J_{6,7}$ = 6.8 Hz, $J_{7,8}$ = 8.0 Hz, H-7), 6.41 (dd, 1 H, $J_{9,11}$ = 1.8 Hz, $J_{11,12}$ = 10.6 Hz, H-11), 6.59 (m, 1 H, H-3), 6.87 (dd, 1 H, $J_{6,12}$ = 8.6 Hz, $J_{11,12}$ = 10.6 Hz, H-12), 7.25 (m, 5 H, Phenyl); MS *m/z* 322 (M^+); exact mass calcd for $C_{23}H_{18}N_2$ 322.1471, found 322.1471.

6d: ^{1}H NMR δ 2.16 (s, 3 H, Me), 3.39 (m, 1 H, H-1), 3.54 (bd, 1 H, $J_{1,5}$ = 7.3 Hz, H-5), 3.71 (bt, 1 H, $J_{6,7}$ = 7,6 Hz, $J_{6,12}$ = 8.6 Hz, H-6), 4.08 (bd, 1 H, $J_{8,9}$ = 7.2 Hz, H-9), 5.72 (dd, 1 H, $J_{1,3}$ = 1.8 Hz, $J_{2,3}$ = 5.8 Hz, H-3), 5.94 (bt, 1 H, $J_{7,8}$ = 8.3 Hz, $J_{8,9}$ = 7.2 Hz, H-8), 6.28 (dd, 1 H, $J_{1,2}$ = 2.0 Hz, $J_{2,3}$ = 5.8 Hz, H-2), 6.45 (bt, 1 H, $J_{7,8}$ = 8.3 Hz, $J_{6,7}$ = 7.6 Hz, H-7), 6.61 (dd, 1 H, $J_{9,11}$ = 1.7 Hz, $J_{11,12}$ = 10.7 Hz, H-11), 7.09 (dd, 1 H, $J_{6,12}$ = 8.6 Hz, $J_{11,12}$ = 10.7 Hz, H-12), 7.20 (m, 5 H, Phenyl); MS *m/z* 322 (M^+); exact mass calcd for $C_{23}H_{18}N_2$ 322.1471, found 322.1463.

6d': ^{1}H NMR δ 2.10 (s, 3 H, Me), 2.87 (bt, 1 H, $J_{6,7}$ = 7,6 Hz, $J_{6,12}$ = 7.2 Hz, H-6), 3.31 (m, 1 H, H-1), 3.70 (bd, 1 H, $J_{1,5}$ = 7.7 Hz, H-5), 3.98 (bd, 1 H, $J_{8,9}$ = 7.3 Hz, H-9), 5.89 (bt, 1 H, $J_{7,8}$ = 7.8 Hz, $J_{8,9}$ = 7.3 Hz, H-8), 5.93 (m, 1 H, H-2), 6.19 (bt, 1 H, $J_{7,8}$ = 7.8 Hz, $J_{6,7}$ = 7.6 Hz, H-7), 6.41 (m, 1 H, H-11), 6.57 (dd, 1 H, $J_{1,3}$ = 1.9 Hz, $J_{2,3}$ = 5.9 Hz, H-3), 7.10 (dd, 1 H, $J_{6,12}$ = 7.2 Hz, $J_{11,12}$ = 10.8 Hz, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 322 (M^+); exact mass calcd for $C_{23}H_{18}N_2$ 322.1471, found 322.1477.

7: ^{1}H NMR δ 2.28 (s, 3 H, Me), 3.60 (m, 1 H, H-1), 3.72 (m, 2 H, H-5-6), 4.41 (bt, 1 H, $J_{1,5}$ = 5.9 Hz, $J_{1,9}$ = 5.6 Hz, H-9), 5.49 (bd, 1 H, $J_{3,4}$ = 5.8 Hz, H-4), 6.20 (bd, 1 H, $J_{3,4}$ = 5.8 Hz, H-3), 6.25 (bt, 1 H, $J_{7,8}$ = 8.0 Hz, $J_{8,9}$ = 7.2 Hz, H-8), 6.65 (m, 3 H, H-7, H-11-12), 7.25 (m, 5 H, Phenyl); MS *m/z* 322 (M^+); exact mass calcd for $C_{23}H_{18}N_2$ 322.1471, found 322.1474.

3e: ^{1}H NMR δ 1.65 (s, 3 H, Me), 2.55 (dd, 1 H, $J_{6,7}$ = 9.6 Hz, $J_{7,8}$ = 4.5 Hz, H-7), 4.00 (dd, 1 H, $J_{2,6}$ = 7.9 Hz, $J_{6,7}$ = 9.6 Hz, H-6), 4.27 (m, 1 H, H-2), 5.01 (dd, 1 H, $J_{7,8}$ = 4.5 Hz, $J_{8,9}$ = 9.3 Hz, H-8), 5.49 (s, 1 H, -C*H*Ph_2), 6.05 (m, 1 H, H-9), 6.10 (m, 1 H, H-3), 6.70 (m, 3 H, H-10-12), 6.78 (dd, 1 H, $J_{2,4}$ = 1.6 Hz, $J_{3,4}$ = 6.1 Hz, H-4), 7.25 (m, 10 H, Phenyl); MS *m/z* 412 (M^+); exact mass calcd for $C_{30}H_{24}N_2$ 412.1941, found 412.1935.

5e: ^{1}H NMR δ 1.79 (s, 3 H, Me), 3.20 (bd, 1 H, $J_{1,5}$ = 7.5 Hz, H-1), 3.48 (bt, 1 H, $J_{6,7}$ = 6.7 Hz, $J_{6,12}$ = 8.2 Hz, H-6), 3.61 (m, 1 H, H-5), 4.16 (bd, 1 H, $J_{8,9}$ = 7.5 Hz, H-9), 5.31 (s, 1 H, -C*H*Ph_2), 5.61 (dd, 1 H, $J_{3,4}$ = 6.0 Hz, $J_{4,5}$ = 2.0 Hz, H-4), 6.00 (bt, 1 H, $J_{7,8}$ = 7.8 Hz, $J_{8,9}$ = 7.5 Hz, H-8), 6.28 (bt, 1 H, $J_{6,7}$ = 6.7 Hz, $J_{7,8}$ = 7.8 Hz, H-7), 6.49 (dd, 1 H, $J_{3,4}$ = 6.0 Hz, $J_{3,5}$ = 2.1 Hz, H-3), 6.58 (dd, 1 H, $J_{9,11}$ = 1.8 Hz, $J_{11,12}$ = 10.6 Hz, H-11), 6.99 (dd, 1 H, $J_{6,12}$ = 8.2 Hz, $J_{11,12}$ = 10.6 Hz, H-12), 7.20 (m, 10 H, Phenyl); MS *m/z* 412 (M^+); exact mass calcd for for $C_{30}H_{24}N_2$ 412.1941, found 412.1939.

5e': ^{1}H NMR δ 1.60 (s, 3 H, Me), 3.36 (m, 2 H, H-1, H-6), 3.65 (bd, 1 H, $J_{1,5}$ = 7.5 Hz, H-5), 4.06 (bd, 1 H, $J_{8,9}$ = 7.5 Hz, H-9), 5.21 (s, 1 H, -C*H*Ph_2), 5.85 (m, 1 H, H-4), 5.89 (bt, 1 H, $J_{7,8}$ = 8.1 Hz, $J_{8,9}$ = 7.5 Hz, H-8), 6.20 (bt, 1 H, $J_{6,7}$ = 7.7 Hz, $J_{7,8}$ = 8.1 Hz, H-7), 6.49 (m, 1 H, H-3), 6.52 (m, 1 H, H-11), 6.85 (dd, 1 H, $J_{6,12}$ = 8.2 Hz, $J_{11,12}$ = 10.6 Hz, H-12), 7.20 (m, 10 H, Phenyl); MS *m/z* 412 (M^+); exact mass calcd for for $C_{30}H_{24}N_2$ 412.1941, found 412.1949.

6e: ^{1}H NMR δ 1.65 (s, 3 H, Me), 3.35 (m, 1 H, H-1), 3.47 (bd, 1 H, $J_{1,5}$ = 7.6 Hz, H-5), 3.60 (bt, 1 H, $J_{6,7}$ = 7,5 Hz, $J_{6,12}$ = 7.7 Hz, H-6), 4.06 (bd, 1 H, $J_{8,9}$ = 7.2 Hz, H-9), 5.30 (s, 1 H, -C*H*Ph_2), 5.75 (dd, 1 H, $J_{1,3}$ = 1.6 Hz, $J_{2,3}$ = 5.6 Hz, H-3), 5.90 (bt, 1 H, $J_{7,8}$ = 8.1 Hz, $J_{8,9}$ = 7.2 Hz, H-8), 6.37 (bt, 1 H, $J_{6,7}$ = 7.5 Hz, $J_{7,8}$ = 8.1 Hz, H-7), 6.49 (dd, 1 H, $J_{1,2}$ = 1.2 Hz, $J_{2,3}$ = 5.6 Hz, H-2), 6.55 (dd, 1 H, $J_{9,11}$ = 1.5 Hz, $J_{11,12}$ = 11.5 Hz, H-11), 7.10 (dd, 1 H, $J_{6,12}$ = 7.7 Hz, $J_{11,12}$ = 11.5 Hz, H-12), 7.25 (m, 10 H, Phenyl); MS *m/z* 412 (M^+); exact mass calcd for for $C_{30}H_{24}N_2$ 412.1941, found 412.1937.

3f: ^{1}H NMR δ 1.28 (s, 9 H, *t*-Butyl), 1.72 (s, 3 H, Me), 2.57 (dd, 1 H, $J_{6,7}$ = 9.7 Hz, $J_{7,8}$ = 5.2 Hz, H-7), 3.92 (dd, 1 H, $J_{2,6}$ = 7.5 Hz, $J_{6,7}$ = 9.7 Hz, H-6), 4.08 (m, 1 H, H-2), 5.02 (dd, 1 H, $J_{7,8}$ = 5.2 Hz, $J_{8,9}$ = 10.1 Hz, H-8), 6.02 (dd, 1 H, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 6.10 (m, 1 H, H-9), 6.68 (m, 3 H, H-10-12), 6.95 (dd, 1 H, $J_{2,4}$ = 2.6 Hz, $J_{3,4}$ = 5.7 Hz, H-4); MS *m/z* 302 (M^+); exact mass calcd for $C_{21}H_{22}N_2$ 302.1785, found 302.1787.

4f: ^{1}H NMR δ 1.20 (s, 9 H, *t*-Butyl), 1.94 (s, 3 H, Me), 2.02 (m, 1 H, H-10), 2.71 (m, 1 H, H-10), 3.92 (m, 1 H, H-2), 4.48 (d, 1 H, $J_{2,6}$ = 5.9 Hz, H-6), 5.45 (m, 1 H, H-9), 5.60 (m, 1 H, H-11), 6.00 (dd, 1 H, $J_{2,3}$ = 2.7 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 6.18 (d, 1 H, $J_{8,9}$ = 9.5 Hz, H-8), 6.38 (d, 1 H, $J_{11,12}$ = 9.5 Hz, H-12), 6.35 (dd, 1 H, $J_{2,4}$ = 2.2 Hz, $J_{3,4}$ = 5.9 Hz, H-4); MS *m/z* 302 (M^+); exact mass calcd for $C_{21}H_{22}N_2$ 302.1785, found 302.1784.

5f: ^{1}H NMR δ 1.19 (s, 9 H, *t*-Butyl), 1.88 (s, 3 H, Me), 3.11 (bd, 1 H, $J_{1,5}$ = 7.3 Hz, H-1), 3.50 (m, 2 H, H-5, H-6), 3.97 (bd, 1 H, $J_{8,9}$ = 6.7, H-9), 5.56 (dd, 1 H, $J_{3,4}$ = 5.9 Hz, $J_{4,5}$ = 1.6 Hz, H-4), 5.97 (bt, 1 H, $J_{7,8}$ = 7.9 Hz, $J_{8,9}$ = 6.7 Hz, H-8), 6.23 (bt, 1 H, $J_{6,7}$ = 6.9 Hz, $J_{7,8}$ = 7.9 Hz, H-7), 6.58 (dd, 1 H, $J_{9,11}$ = 1.9 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 6.75 (dd, 1 H, $J_{3,4}$ = 5.9 Hz, $J_{3,5}$ = 1.9 Hz, H-3), 6.99 (dd, 1 H, $J_{6,12}$ = 8.4 Hz, $J_{11,12}$ = 10.8 Hz, H-12); MS *m/z* 302 (M^+); exact mass calcd for $C_{21}H_{22}N_2$ 302.1785, found 302.1787.

6f: ^{1}H NMR δ 1.12 (s, 9 H, *t*-Butyl), 1.80 (s, 3 H, Me), 3.22 (bd, 1 H, $J_{1,5}$ = 7.6 Hz, H-1), 3.39 (bd, 1 H, $J_{1,5}$ = 7.6 Hz, H-5), 3.49 (bt, 1 H, $J_{6,7}$ = 8.1 Hz, $J_{6,12}$ = 8.1 Hz, H-6), 4.06 (bd, 1 H, $J_{8,9}$ = 7.3 Hz, H-9), 5.69 (dd, 1 H, $J_{1,2}$ = 2.4 Hz, $J_{2,3}$ = 5.9 Hz, H-2), 5.89 (bt, 1 H, $J_{7,8}$ = 8.1 Hz, $J_{8,9}$ = 7.3 Hz, H-8), 6.33 (bt, 1 H, $J_{6,7}$ = 8.1 Hz, $J_{7,8}$ = 8.1 Hz, H-7), 6.57 (dd, 1 H, $J_{9,11}$ = 2.0 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 6.72 (dd, 1 H, $J_{1,3}$ = 2.0 Hz, $J_{2,3}$ = 5.9 Hz, H-3), 7.02 (dd, 1 H, $J_{6,12}$ = 8.1 Hz, $J_{11,12}$ = 10.8 Hz, H-12); MS *m/z* 302 (M^+); exact mass calcd for $C_{21}H_{22}N_2$ 302.1785, found 302.1787.

3g: ^{1}H NMR δ 0.98 (d, 3 H, J = 7.2 Hz, -CH***Me***Me), 1.02 (d, 3 H, J = 7.2 Hz, -CHMe***Me***), 2.60 (dd, 1 H, $J_{6,7}$ = 9.7 Hz, $J_{7,8}$ = 5.0 Hz, H-7), 2.76 (m, 1 H, J = 7.2 Hz, -C***H***Me_2), 4.12 (dd, 1 H, $J_{2,6}$ = 7.4 Hz, $J_{6,7}$ = 9.7 Hz, H-6), 4.28 (m, 1 H, H-2), 5.22 (dd, 1 H, $J_{7,8}$ = 5.0 Hz, $J_{8,9}$ = 9.6 Hz, H-8), 5.97 (m, 2 H, H-3-4), 6.20 (m, 1 H, H-9), 6.75 (m, 3 H, H-10-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1776.

4g: ^{1}H NMR δ 1.05 (d, 3 H, J = 7.2 Hz, -CH***Me***Me), 1.14 (d, 3 H, J = 7.2 Hz, -CHMe***Me***), 2.32 (m, 1 H, H-10), 2.59 (m, 1 H, H-10), 3.08 (m, 1 H, J = 7.2 Hz, -C***H***Me_2), 4.12 (m, 1 H, H-2), 4.62 (d, 1 H, $J_{2,6}$ = 6.1 Hz, H-6), 5.60 (m, 2 H, H-9, H-11), 5.84 (dd, 1 H, $J_{2,3}$ = 2.1 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 5.91 (dd, 1 H, $J_{2,4}$ = 2.0 Hz, $J_{3,4}$ = 5.7 Hz, H-4), 6.41 (d, 2 H, $J_{8,9,}$ = $J_{11,12}$ = 10.0 Hz, H-8, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1778.

5g: ^{1}H NMR δ 1.05 (m, 6 H, -CH***Me***$_2$), 3.00 (m, 1 H, -C***H***Me_2), 3.33 (bd, 1 H, $J_{1,5}$ = 7.0 Hz, H-1), 3.44 (m, 1 H, H-6), 3.65 (m, 1 H, H-5), 4.22 (bd, 1 H, $J_{8,9}$ = 7.3 Hz, H-9), 5.48 (dd, 1 H, $J_{3,4}$ = 5.7 Hz, $J_{4,5}$ = 2.1 Hz, H-4), 5.69 (m, 1 H, H-3), 6.05 (bt, 1 H, $J_{7,8}$ = 7.9 Hz, $J_{8,9}$ = 7.3 Hz, H-8), 6.20 (bt, 1 H, $J_{6,7}$ = 6.7 Hz, $J_{7,8}$ = 7.9 Hz, H-7), 6.60 (dd, 1 H, $J_{9,11}$ = 1.5 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 6.99 (m, 1 H, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1783.

5g': ^{1}H NMR δ 1.55 (m, 6 H, -CH***Me***$_2$), 2.55 (m, 1 H, -C***H***Me_2), 2.60 (m, 1 H, H-1), 3.30 (m, 1 H, H-6), 3.36 (m, 1 H, H-5), 3.79 (bd, 1 H, $J_{8,9}$ = 7.0 Hz, H-9), 5.15 (m, 1 H, H-4), 5.94 (bt, 1 H, $J_{7,8}$ = 7.7 Hz, $J_{8,9}$ = 7.0 Hz, H-8), 6.31 (m, 1 H, H-3), 6.40 (m, 1 H, H-7), 6.48 (m, 1 H, H-11), 6.78 (m, 1 H, H-12), 7.20 (m, 5 H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1786.

6g: ^{1}H NMR δ 0.81 (d, 3 H, J = 7.1 Hz, -CH***Me***Me), 1.06 (d, 3 H, J = 7.1 Hz, -CH***Me***Me), 2.95 (m, 1 H, H-6), 3.05 (m, 1 H, -C***H***Me_2), 3.26 (m, 2 H, H-1, H-5), 3.98 (bd, 1 H, $J_{8,9}$ = 6.9 Hz, H-9), 5.86 (m, 2 H, H-2, H-8), 6.28 (bt, 1 H, $J_{6,7}$ = 7.5 Hz, $J_{7,8}$ = 8.1 Hz, H-7), 6.38 (m, 1 H, H-11), 6.64 (dd, 1 H, $J_{1,3}$ = 1.8 Hz, $J_{2,3}$ = 5.7 Hz, H-3), 7.12 (dd, 1 H, $J_{6,12}$ = 8.7 Hz, $J_{11,12}$ = 10.6 Hz, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1784.

6g': ^{1}H NMR δ 0.98 (d, 3 H, J = 7.1 Hz, -CH***Me***Me), 1.06 (d, 3 H, J = 7.1 Hz, -CHMe***Me***), 2.91 (m, 1 H, -C***H***Me$_2$), 3.38 (m, 1 H, H-1), 3.55 (bd, 1 H, $J_{1,5}$ = 7.4 Hz, H-5), 3.49 (bt, 1 H, $J_{6,7}$ = 7,5 Hz, $J_{6,12}$ = 7.7 Hz, H-6), 4.05 (bd, 1 H, $J_{8,9}$ = 7.1 Hz, H-9), 5.60 (dd, 1 H, $J_{1,2}$ = 2.2 Hz, $J_{2,3}$ = 5.9 Hz, H-2), 5.69 (dd, 1 H, $J_{1,3}$ = 1.5 Hz, $J_{2,3}$ = 5.9 Hz, H-3), 5.91 (bt, 1 H, $J_{7,8}$ = 8.1 Hz, $J_{8,9}$ = 7.1 Hz, H-8), 6.48 (bt, 1 H, $J_{6,7}$ = 7.5 Hz, $J_{7,8}$ = 8.1 Hz, H-7), 6.60 (dd, 1 H, $J_{9,11}$ = 1.7 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 7.11 (dd, 1 H, $J_{6,12}$ = 7.7 Hz, $J_{11,12}$ = 10.8 Hz, H-12), 7.30 (m, 5H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1786.

8: ^{1}H NMR δ 0.81 (m, 3 H, -CH***Me***Me), 1.05 (m, 3 H, -CHMe***Me)***, 3.00 (m, 2 H, H-1, -C***H***Me$_2$), 3.44 (m, 1 H, H-6), 3.56 (m, 1 H, H-5), 3.65 (m, 1 H, H-9), 5.69 (m, 1 H, H-4), 6.05 (bt, 1 H, $J_{7,8}$ = 7.9 Hz, $J_{8,9}$ = 7.3 Hz, H-8), 6.20 (bt, 1 H, $J_{6,7}$ = 6.7 Hz, $J_{7,8}$ = 7.9 Hz, H-7), 6.35 (dd, 1 H, $J_{9,11}$ = 1.8 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 6.88 (dd, 1 H, $J_{3,4}$ = 1.5 Hz, $J_{3,5}$ = 5.8 Hz, H-3), 6.79 (dd, 1 H, $J_{6,12}$ = 7.5 Hz, $J_{11,12}$ = 10.8 Hz, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1783.

9: ^{1}H NMR δ 1.80 (m, 6 H, -CH***Me***$_2$), 2.30 (m, 2 H, H-1, -C***H***Me$_2$), 2.90 (m, 1 H, H-5), 3.15 (m, 1 H, H-6), 3.90 (bd, 1 H, $J_{8,9}$ = 7.2 Hz, H-9), 5.30 (m, 1 H, H-2), 6.07 (m, 1 H, H-8), 6.40 (m, 2 H, H-3, H-7), 6.48 (m, 1 H, H-11), 6.88 (m, 1 H, H-12), 7.20 (m, 5 H, Phenyl); MS *m/z* 350 (M^+); exact mass calcd for $C_{25}H_{22}N_2$ 350.1785, found 350.1786.

3h: ^{1}H NMR δ 1.60 (m, 10 H, -$(CH_2)_5$), 2.28 (m, 1 H, -C***H***CH$_2$-), 2.52 (dd, 1 H, $J_{6,7}$ = 9.7 Hz, $J_{7,8}$ = 4.9 Hz, H-7), 4.07 (dd, 1 H, $J_{2,6}$ = 7.3 Hz, $J_{6,7}$ = 9.7 Hz, H-6), 4.19 (m, 1 H, H-2), 5.12 (dd, 1 H, $J_{7,8}$ = 4.9 Hz, $J_{8,9}$ = 9.6 Hz, H-8), 5.86 (m, 2 H, H-3-4), 6.11 (m, 1 H, H-9), 6.65 (m, 3 H, H-10-12), 7.20 (m, 5 H, Phenyl); MS *m/z* 390 (M^+); exact mass calcd for $C_{28}H_{26}N_2$ 390.2098, found 390.2091.

5h: ^{1}H NMR δ 1.60 (m, 10 H, -$(CH_2)_5$), 2.49 (m, 1 H, -C***H***CH$_2$-), 3.31 (bd, 1 H, $J_{1,5}$ = 7.6 Hz, H-1), 3.45 (bt, 1 H, $J_{6,7}$ = 7,1 Hz, $J_{6,12}$ = 8.6 Hz,, H-6), 3.65 (m, 1 H, H-5), 4.12 (bd, 1 H, $J_{8,9}$ = 6.5 Hz, H-9), 5.41 (dd, 1 H, $J_{3,4}$ = 5.7 Hz, $J_{4,5}$ = 2.2 Hz, H-4), 5.68 (dd, 1 H, $J_{3,4}$ = 5.7 Hz, $J_{3,5}$ = 2.0 Hz, H-3), 6.14 (bt, 1 H, $J_{7,8}$ = 8.0 Hz, $J_{8,9}$ = 6.5 Hz, H-8), 6.26 (bt, 1 H, $J_{6,7}$ = 7.1 Hz, $J_{7,8}$ = 8.0 Hz, H-7), 6.61 (dd, 1 H, $J_{9,11}$ = 1.5 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 6.99 (m, 1 H, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 390 (M^+); exact mass calcd for $C_{28}H_{26}N_2$ 390.2098, found 390.2095.

5h': ^{1}H NMR δ 1.60 (m, 10 H, -$(CH_2)_5$), 2.61 (m, 1 H, -C***H***CH$_2$-), 3.00 (bd, 1 H, $J_{1,5}$ = 7.3 Hz, H-1), 3.45 (bt, 1 H, $J_{6,7}$ = 7,1 Hz, $J_{6,12}$ = 8.5 Hz,, H-6), 3.55 (m, 1 H, H-5), 3.66 (bd, 1 H, $J_{8,9}$ = 7.2 Hz, H-9), 5.68 (dd, 1 H, $J_{3,4}$ = 5.8 Hz, $J_{3,5}$ = 2.0 Hz, H-3), 6.04 (bt, 1 H, $J_{7,8}$ = 7.7 Hz, $J_{8,9}$ = 7.2 Hz, H-8), 6.16 (bt, 1 H, $J_{6,7}$ = 7.1 Hz, $J_{7,8}$ = 7.7 Hz, H-7), 6.31 (dd, 1 H, $J_{9,11}$ = 1.6 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 6.68 (dd, 1 H, $J_{3,4}$ = 5.8 Hz, $J_{4,5}$ = 2.1 Hz, H-4), 6.79 (dd, 1 H, $J_{6,12}$ = 8.5 Hz, $J_{11,12}$ = 10.8 Hz, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 390 (M^+); exact mass calcd for $C_{28}H_{26}N_2$ 390.2098, found 390.2095.

6h: ^{1}H NMR δ 1.60 (m, 10 H, -$(CH_2)_5$), 2.45 (m, 1 H, -C***H***CH$_2$-), 3.38 (bd, 1 H, $J_{1,5}$ = 7.5 Hz, H-1), 3.56 (bd, 1 H, $J_{1,5}$ = 7.5 Hz, H-5), 3.60 (bt, 1 H, $J_{6,7}$ = 7,3 Hz, $J_{6,12}$ = 8.6 Hz,, H-6), 4.03 (bd, 1 H, $J_{8,9}$ = 8.1 Hz, H-9), 5.57 (dd, 1 H, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 5.7 Hz, H-2), 5.66 (dd, 1 H, $J_{1,3}$ = 2.2 Hz, $J_{2,3}$ = 5.7 Hz, H-3), 5.85 (m, 1 H, H-8), 6.45 (bt, 1 H, $J_{6,7}$ = 7.3 Hz, $J_{7,8}$ = 7.7 Hz, H-7), 6.60 (dd, 1 H, $J_{9,11}$ = 1.5 Hz,

$J_{11,12}$ = 10.8 Hz, H-11), 6.95 (m, 1 H, H-12), 7.25 (m, 5 H, Phenyl); MS *m/z* 390 (M^+); exact mass calcd for $C_{28}H_{26}N_2$ 390.2098, found 390.2094.

6h': ^{1}H NMR δ 1.60 (m, 10 H, -$(CH_2)_5$), 2.60 (m, 1 H, -C*H*CH_2-), 2.95 (m, 1 H, H-6), 3.21 (m, 2 H, H-1, H-5), 3.98 (bd, 1 H, $J_{8,9}$ = 7.5 Hz, H-9), 5.88 (m, 2 H, H-2, H-8), 6.24 (bt, 1 H, $J_{6,7}$ = 8.0 Hz, $J_{7,8}$ = 7.7 Hz, H-7), 6.35 (m, 1 H, H-11), 6.67 (m, 1 H, H-3), 7.10 (m, 1 H, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 390 (M^+); exact mass calcd for $C_{28}H_{26}N_2$ 390.2098, found 390.2094.

5i: ^{1}H NMR δ 1.11 (s, 9 H, *t*-Butyl), 2.80 (bd, 1 H, $J_{1,5}$ = 6.6 Hz, H-1), 3.45 (m, 2 H, H-5, H-6), 3.70 (bd, 1 H, $J_{8,9}$ = 7.5 Hz, H-9), 5.65 (dd, 1 H, $J_{3,4}$ = 6.0 Hz, $J_{4,5}$ = 1.8 Hz, H-4), 6.10 (m, 2 H, H-7-8), 6.29 (dd, 1 H, $J_{9,11}$ = 2.0 Hz, $J_{11,12}$ = 10.8 Hz, H-11), 6.75 (dd, 1 H, $J_{6,12}$ = 8.1 Hz, $J_{11,12}$ = 10.8 Hz, H-12); 6.89 (dd, 1 H, $J_{3,4}$ = 6.0 Hz, $J_{3,5}$ = 2.0 Hz, H-3), 7.30 (m, 5 H, Phenyl); MS *m/z* 364 (M^+); exact mass calcd for $C_{26}H_{24}N_2$ 364.1941, found 364.1933.

6i: ^{1}H NMR δ 1.15 (s, 9 H, *t*-Butyl), 3.04 (bt, 1 H, $J_{6,7}$ = 7,4 Hz, $J_{6,12}$ = 8.0 Hz,, H-6), 3.15 (bs, 2 H, H-1, H-5), 3.99 (bd, 1 H, $J_{8,9}$ = 7.3 Hz, H-9), 5.85 (m, 2 H, H-2, H-8), 6.28 (m, 2 H, H-7, H-11), 6.85 (dd, 1 H, $J_{1,3}$ = 1.4 Hz, $J_{2,3}$ = 5.8 Hz, H-3); 7.02 (m, 1 H, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 364 (M^+); exact mass calcd for $C_{26}H_{24}N_2$ 364.1941, found 364.1950.

6i': ^{1}H NMR δ 1.22 (s, 9 H, *t*-Butyl), 3.41 (m, 1 H, H-1), 3.80 (m, 2 H, H-5-6), 4.09 (bd, 1 H, $J_{8,9}$ = 7.3 Hz, H-9), 5.48 (m, 2 H, H-2, H-3), 6.28 (m, 1 H, H-8), 6.49 (bt, 1 H, $J_{6,7}$ = 6.8 Hz, $J_{7,8}$ = 7.8 Hz, H-7), 6.62 (dd, 1 H, $J_{9,11}$ = 1.7 Hz, $J_{11,12}$ = 10.2 Hz, H-11), 7.12 (dd, 1 H, $J_{6,12}$ = 8.2 Hz, $J_{11,12}$ = 10.2 Hz, H-12), 7.30 (m, 5 H, Phenyl); MS *m/z* 364 (M^+); exact mass calcd for $C_{26}H_{24}N_2$ 364.1941, found 364.1932.

12d: ^{1}H NMR δ 2.01 (s, 3 H, Me), 2.33 (dd, 1 H, $J_{6,7}$ = 10.8 Hz, $J_{7,8}$ = 5.0 Hz, H-7), 3.75 (m, 6 H, -CO_2Me), 3.90 (dd, 1 H, $J_{2,6}$ = 7.3 Hz, $J_{6,7}$ = 10.8 Hz, H-6), 4.34 (m, 1 H, H-2), 4.96 (dd, 1 H, $J_{7,8}$ = 5.0 Hz, $J_{8,9}$ = 9.4 Hz, H-8), 5.59 (dd, 1 H, $J_{2,3}$ = 1.2 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 6.04 (m, 1 H, H-9), 6.27 (dd, 1 H, $J_{2,4}$ = 2.7 Hz, $J_{3,4}$ = 5.7 Hz, H-4), 6.45 (m, 1 H, H-12), 6.59 (m, 2 H, H-10-11), 7.20 (m, 5 H, Phenyl); MS *m/z* 388 (M^+); exact mass calcd for $C_{25}H_{24}O_4$ 388.1675, found 388.1671.

12f: ^{1}H NMR δ 1.20 (s, 9 H, *t*-Butyl), 1.70 (s, 3 H, Me), 2.31 (dd, 1 H, $J_{6,7}$ = 6.1 Hz, $J_{7,8}$ = 5.3 Hz, H-7), 3.20 (dd, 1 H, $J_{2,6}$ = 6.8 Hz, $J_{6,7}$ = 6.1 Hz, H-6), 3.78 (m, 6 H, -CO_2Me), 4.16 (m, 1 H, H-2), 4.95 (dd, 1 H, $J_{7,8}$ = 5.3 Hz, $J_{8,9}$ = 9.9 Hz, H-8), 5.58 (dd, 1 H, $J_{2,3}$ = 2.1 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 6.05 (m, 1 H, H-9), 6.60 (m, 3 H, H-10-12), 6.77 (dd, 1 H, $J_{2,4}$ = 2.8 Hz, $J_{3,4}$ = 5.9 Hz, H-4); MS *m/z* 368 (M^+); exact mass calcd for $C_{23}H_{28}O_4$ 368.1988, found 368.1993.

12g: ^{1}H NMR δ 0.95 (d, 6 H, -CH*Me*$_2$), 2.32 (dd, 1 H, $J_{6,7}$ = 9.7 Hz, $J_{7,8}$ = 5.1 Hz, H-7), 2.80 (m, 1 H, -C*H*Me_2), 3.78 (m, 6 H, -CO_2Me), 4.00 (dd, 1 H, $J_{2,6}$ = 7.0 Hz, $J_{6,7}$ = 9.9 Hz, H-6), 4.35 (m, 1 H, H-2), 5.12 (dd, 1 H, $J_{7,8}$ = 5.1 Hz, $J_{8,9}$ = 9.9 Hz, H-8), 5.51 (dd, 1 H, $J_{2,3}$ = 2.2 Hz, $J_{3,4}$ = 5.8 Hz, H-3), 5.79 (dd, 1 H, $J_{2,4}$ = 2.5 Hz, $J_{3,4}$ = 5.8 Hz, H-4), 6.15 (m, 1 H, H-9), 6.50 (m, 1 H, H-12), 6.59 (m, 1 H, H-11), 6.68 (m, 1 H, H-10), 7.30 (m, 5 H, Phenyl); MS *m/z* 416 (M^+); exact mass calcd for $C_{27}H_{28}O_4$ 416.1988, found 416.1984.

13c: ^{1}H NMR δ 0.98 (d, 3 H, J = 6.8 Hz, -CH***Me***Me), 1.02 (d, 3 H, J = 6.8 Hz, -CHMe***Me***), 1.82 (s, 3 H, Me), 2.14 (m, 1 H, H-10), 2.32 (m, 1 H, H-10), 3.01 (m, 1 H, J = 6.8 Hz, -C***H***Me$_2$), 3.78 (m, 6 H, -CO$_2$Me), 4.15 (m, 1 H, H-2), 4.29 (d, 1 H, $J_{2,6}$ = 7.1 Hz, H-6), 5.40 (m, 3 H, H-3, H-9, H-11), 6.18 (d, 1 H, $J_{8,9}$ = 9.6 Hz, H-8), 6.45 (m, 2 H, H-4, H-12); MS *m/z* 354 (M^+); exact mass calcd for $C_{22}H_{26}O_4$ 354.1831, found 354.1831.

13d: ^{1}H NMR δ 2.29 (s, 3 H, Me), 2.30 (m, 2 H, H-10), 3.76 (s, 3 H, -CO$_2$Me), 3.82 (s, 3 H, -CO$_2$Me), 4.23 (m, 1 H, H-2), 4.50 (d, 1 H, $J_{2,6}$ = 5.6 Hz, H-6), 5.46 (m, 3 H, H-3, H-9, H-11), 6.20 (dd, 1 H, $J_{2,4}$ = 2.2 Hz, $J_{3,4}$ = 5.7 Hz, H-4), 6.35 (d, 1 H, $J_{8,9}$ = 9.7 Hz, H-8), 6.50 (d, 1 H, $J_{11,12}$ = 10.0 Hz), 7.25 (m, 5 H, Phenyl); MS *m/z* 388 (M^+); exact mass calcd for $C_{25}H_{24}O_4$ 388.1675, found 388.1669.

13f: ^{1}H NMR δ 1.21 (s, 9 H, *t*-Butyl), 1.92 (s, 3 H, Me), 2.01 (m, 1 H, H-10), 2.43 (m, 1 H, H-10), 3.72 (s, 3 H, -CO$_2$Me), 3.80 (s, 3 H, -CO$_2$Me), 4.04 (m, 1 H, H-2), 4.38 (d, 1 H, $J_{2,6}$ = 5.5 Hz, H-6), 5.37 (m, 2 H, H-9, H-11), 5.48 (m, 1 H, H-3), 6.16 (d, 1 H, $J_{8,9}$ = 9.6 Hz, H-8), 6.49 (d, 1 H, $J_{11,12}$ = 9.5 Hz), 6.69 (dd, 1 H, $J_{2,4}$ = 2.4 Hz, $J_{3,4}$ = 5.9 Hz, H-4); MS *m/z* 368 (M^+); exact mass calcd for $C_{23}H_{28}O_4$ 368.1988, found 368.1989.

13g: ^{1}H NMR δ 1.01 (d, 3 H, J = 7.1 Hz, -CH***Me***Me), 1.09 (d, 3 H, J = 7.1 Hz, -CHMe***Me***), 2.29 (dd, 2 H, $J_{9,10}$ = $J_{10,11}$ = 6.8 Hz, H-10), 3.11 (m, 1 H, J = 7.1 Hz, -C***H***Me$_2$), 3.75 (m, 6 H, -CO$_2$Me), 4.20 (m, 1 H, H-2), 4.50 (d, 1 H, $J_{2,6}$ = 5.9 Hz, H-6), 5.38 (dd, 1 H, $J_{2,3}$ = 2.1 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 5.45 (m, 2 H, H-9, H-11), 5.65 (dd, 1 H, $J_{2,4}$ = 2.3 Hz, $J_{3,4}$ = 5.9 Hz, H-4), 6.45 (d, 1 H, $J_{8,9}$ = 9.6 Hz, H-8), 6.49 (m, 2 H, H-4, H-12); 7.20 (m, 5 H, Phenyl); MS *m/z* 416 (M^+); exact mass calcd for $C_{27}H_{28}O_4$ 416.1988, found 416.1984.

13h: ^{1}H NMR δ 1.60 (m, 10 H, -(CH$_2$)$_5$), 2.30 (dd, 2 H, $J_{9,10}$ = $J_{10,11}$ = 6.8 Hz, H-10), 2.70 (m, 1 H, -C***H***CH$_2$-), 3.75 (m, 6 H, -CO$_2$Me), 4.21 (m, 1 H, H-2), 4.50 (d, 1 H, $J_{2,6}$ = 5.9 Hz, H-6), 5.38 (dd, 1 H, $J_{2,3}$ = 2.1 Hz, $J_{3,4}$ = 5.9 Hz, H-3), 5.45 (m, 2 H, H-9, H-11), 5.62 (dd, 1 H, $J_{2,4}$ = 2.3 Hz, $J_{3,4}$ = 5.9 Hz, H-4), 6.34 (d, 1 H, $J_{8,9}$ = 9.6 Hz, H-8), 6.49 (m, 2 H, H-4, H-12); 7.20 (m, 5 H, Phenyl); MS *m/z* 456 (M^+); exact mass calcd for $C_{30}H_{32}O_4$ 456.2301, found 456.2295.

15i: ^{1}H NMR δ 1.14 (s, 9 H, *t*-Butyl), 2.75 (bt, 1 H, $J_{6,7}$ = 6.6 Hz, $J_{6,12}$ = 8.6 Hz,, H-6), 3.19 (bs, 2 H, H-1, H-5), 3.74 (s, 3 H, -CO$_2$Me), 3.82 (s, 3 H, -CO$_2$Me), 4.13 (bd, 1 H, $J_{8,9}$ = 7.9 Hz, H-9), 5.82 (m, 2 H, H-2, H-8), 5.90 (dd, 1 H, $J_{6,12}$ = 8.6 Hz, $J_{11,12}$ = 11.1 Hz, H-12), 6.21 (bt, 1 H, $J_{6,7}$ = 6.6 Hz, $J_{7,8}$ = 8.0 Hz, H-7), 6.29 (dd, 1 H, $J_{9,11}$ = 1.8 Hz, $J_{11,12}$ = 11.1 Hz, H-11), 6.80 (dd, 1 H, $J_{1,3}$ = 1.8 Hz, $J_{2,3}$ = 5.7 Hz, H-3), 7.25 (m, 5 H, Phenyl); MS *m/z* 430 (M^+); exact mass calcd for $C_{28}H_{30}O_4$ 430.2145, found 430.2146.

Thermolysis of [8 + 2] Cycloadducts 3. Thermolysis of **3** (10 mg) in 50 mL of xylene at 150 °C for 1 day in a sealed tube afforded a reddish yellow oil. Column chromatography, using 0-10% EtOAc in n-hexane as eluant, gave mainly starting materials **1a** and **2** and trace amounts of cycloadducts **4** were also observed.

Isomerization of [8 + 2] Cycloadducts 12d,f,g-h to 13d,f,g-h. Thermal isomerization of **12d** (10 mg), or **12f** (10 mg) or **12g** (10 mg) or **12h** (10 mg) in 20 mL of xylene at 190 °C for 7 h in a sealed tube in the presence of BHT afforded a yllow oil. Column chromatography, using 10% EtOAc in n-hexane as eluant, gave **13d**, **13f**, **13g**, **13h**, respectively, in about 85-90 % yield.

Diels-Alder Cycloaddition Reaction of 11c with DMAD. A solution of **11c** (0.05 mmol) and DMAD (0.07 mmol) in chloroform (20 mL) was stirring at room temperature for 3 days afforded a yellowish oil. Column chromatography, using 20% EtOAc in n-hexane as eluant, gave **14c** in 75% yield: ^{1}H NMR δ 0.51 (d, 3 H, J = 7.3 Hz, -CH*Me*Me), 0.85 (d, 3 H, J = 7.3 Hz, -CHMe*Me*), 1.10 (s, 3 H, Me), 1.85 (m, 1 H, -C*H*Me$_2$), 1.91 (bd, 1 H, J_{gem} = 6.8 Hz, H-5), 2.25 (bd, 1 H, J_{gem} = 6.8 Hz, H-5), 3.10 (bt, 1 H, $J_{9,10}$ = 8.1 Hz, $J_{10,11}$ = 8.1 Hz, H-10), 3.70 (m, 1 H, H-4), 3.75 (m, 6 H, -CO$_2$Me), 4.45 (d, 1 H, $J_{7,8}$ = 8.5 Hz, H-7), 5.89 (dd, 1 H, $J_{7,8}$ = 8.5 Hz, $J_{8,9}$ = 9.5 Hz, H-8), 6.18 (bt, 1 H, $J_{8,9}$ = 9.5 Hz, $J_{9,10}$ = 8.1 Hz, H-9), 6.35 (dd, 1 H, $J_{10,11}$ = 8.1 Hz, $J_{11,12}$ = 12.1 Hz, H-11), 6.45 (dd, 1 H, $J_{3,4}$ = 3.3 Hz, H-3), 6.79 (dd, 1 H, $J_{11,12}$ = 12.1 Hz, $J_{10,12}$ = 0.7 Hz, H-12); IR 1720-1725 (C=O) cm^{-1}; MS *m/z* 496 (M$^+$); exact mass calcd for $C_{28}H_{32}O_8$ 496.2098, found 496.2096.

Cycloaddition Reactions of Heptafulvene 1c with Fulvenes 2a,b and Diels-Alder Cycloaddition Reactions of [6 + 4] Adduct 17a,b with DMAD. A solution of heptafulvene **1c** (350 mg, 2.71 mmol) and fulvene **2a** (287 mg, 2.71 mmol) in chloroform (8 mL) was stirred at room temperature for 7 days afforded a yellow oil. Column chromatography, using 5% EtOAc in n-hexane as eluant, gave the [6 + 4] cycloadducts **17a,b** (1:1 mixture of inseparable regioisomers) and [8 + 2] cycloadduct **18a** in a 4:1 ratio (59%). Then, a solution of cycloadducts **17a,b** and excess of DMAD in 10 mL of chloroform was stirred at room temperature for 3 days afforded a yellowish oil. Purification by silica gel flash chromatography, using 10% EtOAc in n-hexane as eluant, gave **20a,b** (85%). When the reaction was carried out in refluxing xylene for 2h, [8 + 2] cycloadduct **19a** was formed in 71% yield.

18a: ^{1}H NMR δ 1.65 (s, 1 H, Me), 1.85 (s, 1 H, Me), 2.23 (m, 1 H, H-7), 3.61 (dd, 1 H, $J_{2,6}$ = 7.5 Hz, $J_{6,7}$ = 9.9 Hz, H-6), 3.81 (bt, 1 H, $J_{1,2}$ = 8.8 Hz, $J_{2,3}$ = 2.3 Hz, $J_{2,6}$ = 7.5 Hz, H-2), 4.12 (d, 1 H, $J_{1,2}$ = 8.8 Hz, H-1), 4.90 (m, 1 H, H-8), 6.00 (m, 2 H, H-4, H-9), 6.30 (m, 1 H, H-12), 6.46 (dd, 1 H, $J_{2,3}$ = 2.3 Hz, $J_{3,4}$ = 5.7 Hz, H-3), 6.53 (m, 2 H, H-10-11); IR 2240 (CN) cm^{-1}; MS *m/z* 235 (M$^+$); exact mass calcd for $C_{17}H_{17}N$ 235.1362, found 235.1352.

19a: ^{1}H NMR δ 1.75 (s, 1 H, Me), 1.85 (s, 1 H, Me), 2.05 (m, 1 H, H-10), 2.41 (m, 1 H, H-10), 3.63 (m, 1 H, H-2), 4.10 (d, 2 H, $J_{1,2}$ = $J_{2,6}$ = 7.6 Hz, H-1, H-6), 6.10 (m, 2 H, H-9, H-11), 5.97 (m, 1 H, H-3), 6.14 (d, 1 H, $J_{11,12}$ = 9.5 Hz, H-12), 6.24 (d, 1 H, $J_{8,9}$ = 9.5 Hz, H-8), 6.40 (dd, 1 H, $J_{2,4}$ = 2.2 Hz, $J_{3,4}$ = 5.5 Hz, H-4); IR 2245 (CN)cm^{-1}; MS *m/z* 235 (M$^+$); exact mass calcd for $C_{17}H_{17}N$ 235.1362, found 235.1362.

20a: ^{1}H NMR δ1.01 (s, 3 H, Me), 1.22 (s, 3 H, Me), 1.78 (db, 1 H, J_{gem} = 6.7 Hz, H-5), 2.02 (db, 1 H, J_{gem} = 6.7 Hz, H-5), 2.80 (bt, 1 H, $J_{9,10}$ = 7.7 Hz, $J_{10,11}$ = 7.1 Hz, H-10), 3.53 (d, 1 H, $J_{7,8}$ = 7.4 Hz, H-7), 3.68 (m, 3 H, -CO$_2$Me), 3.70 (m, 1 H, H-4), 3.78 (m, 3 H, -CO$_2$Me), 5.06 (s, 1 H, NCC*H*), 5.81

(dd, 1 H, $J_{7,8}$ = 8.4 Hz, $J_{8,9}$ = 9.4 Hz, H-8), 6.09 (bt, 1 H, $J_{8,9}$ = 9.4 Hz, $J_{9,10}$ = 7.7 Hz, H-9), 6.32 (dd, 1 H, $J_{10,11}$ = 7.5 Hz, $J_{11,12}$ = 11.8 Hz, H-11), 6.52 (m, 2 H, H-3, H-12); IR 2220 (CN) cm^{-1}; MS *m/z* 377 (M^+); exact mass calcd for $C_{23}H_{23}NO_4$ 377.1628, found 377.1635.

20b: ^1H NMR δ1.01 (s, 3 H, Me), 1.22 (s, 3 H, Me), 1.78 (db, 1 H, J_{gem} = 6.6 Hz, H-5), 2.25 (m, 1 H, H-5), 2.79 (bt, 1 H, $J_{9,10}$ = 8.0 Hz, $J_{10,11}$ = 8.1 Hz, H-10), 3.68 (m, 3 H, $-CO_2Me$), 3.70 (m, 1 H, H-4), 3.81 (m, 3 H, $-CO_2Me$), 4.22 (d, 1 H, $J_{7,8}$ = 7.2 Hz, H-7), 5.04 (s, 1 H, NCC*H*), 5.88 (dd, 1 H, $J_{7,8}$ = 8.4 Hz, $J_{8,9}$ = 8.9 Hz, H-8), 6.01-6.35 (m, 3 H, H-9, H-11, H-12), 6.52 (m, 1 H, H-3); IR 2225 (CN) cm^{-1}; MS *m/z* 377 (M^+); exact mass calcd for $C_{23}H_{23}NO_4$ 377.1628, found 377.1638.

Preparation of Ethyl Methyltropylcyanoacetate (22). To a solution of 8.12 g (0.04 mol) of ethyl tropylcyanoacetate (**21**)[18] in 30 mL of anhydrous ethanol was added 18.0 mL (0.048 mol, 21 wt. % solution in denatured ethanol) of NaOEt. After being stirred at room temperature for 1 h, 7.56 g (0.06 mol) of dimethyl sulfate was added, and the mixture was refluxed for 20 h. Ten milliliters of water was then added. The mixture was concentrated in vacuo and extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with 20 mL of brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. Purification by silica gel flash chromatography, using 7.5% EtOAc in n-hexane as eluant, gave 3.68 g (42%) of **22** as a yellowish oil: ^1H NMR δ 1.34 (t, 3 H, J = 7.2 Hz, $-CO_2CH_2CH_3$), 1.72 (s, 3 H, Me), 1.92 (bt, 1 H, $J_{1,7} = J_{6,7}$ = 5.7 Hz), 4.31 (q, 2 H, J = 7.2 Hz, $-CO_2CH_2CH_3$), 5.35 (m, 2 H, H-1, H-6), 6.31 (m, 2 H, H-2, H-5), 6.74 (m, 2 H, H-3-4); IR 1742 (C=O), 2244 (CN) cm^{-1}; MS *m/z* 217 (M^+); exact mass calcd for $C_{13}H_{15}N0_2$ 217.1104, found 217.1102.

Preparation of 7-(1-Cyanoethyl)cycloheptatriene (23). To a solution of 3.68 g (16.9 mmol) of Ethyl Methyltropylcyanoacetate (**22**) in 50 mL of ethanol at 0 °C was added a solution of 5.00 g (87.7 mmol) of potassium hydroxide in 20 mL of water. After stirring overnight at room temperature, the solution was neutralized and further acidified with 6N HCl. The mixture was concentrated in vacuo and extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with 30 mL of water, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to give quantitatively the acid. A mixture of the crude acid and 1.0 g of copper in 15 mL of xylene was refluxed for 19 h. The mixture was filtered, concentrated in vacuo, and extracted with Et_2O (3 × 30 mL). The combined organic extracts were concentrated in vacuo and purified by silica gel flash chromatography, using 10% EtOAc in n-hexane as eluant, gave 2.2 g (89%) of **23** as a yellow oil: ^1H NMR δ 1.35 (d, 3 H, J = 7.2 Hz, Me), 1.94 (m, 1 H, H-7), 2.85 (m, 1 H, H-8), 5.22 (m, 1 H, H-6), 5.39 (m, 1 H, H-1), 6.25 (m, 2 H, H-2, H-5), 6.65 (m, 2 H, H-3-4); IR 2239 (CN) cm^{-1}; MS *m/z* 145 (M^+); exact mass calcd for $C_{10}H_{11}N$ 145.0892, found 145.0885.

Preparation of A Mixture of 1- and 3-(1-Cyanoethyl)cycloheptatriene (24). Thermal isomerization of **23** (2.2 g) in 30 mL of xylene at 205 °C for 7 h in a sealed tube in the presence of BHT afforded a yellow oil. Purification by silica gel flash chromatography, using 10% EtOAc in n-hexane as eluant, gave 2.1 g (95%) of **24** as a yellowish oil: ^1H NMR δ 1.30-1.50 (m, 3 H), 2.05-2.45 (m), 3.43 (m), 5.30-5.54 (m), 6.02-6.18 (m),

6.40-6.71 (m); IR 2239 (CN) cm^{-1}; MS *m/z* 145 (M^+); exact mass calcd for $C_{10}H_{11}N$ 145.0892, found 145.0886.

Cycloaddition Reactions of 6,6-Dimethylfulvene (2a) and 6,6-Diphenylfulvene (2b), Respectively, with 8-Cyano-8-methylheptafulvene (1d) and Diels-Alder Cycloaddition Reaction of [6 + 4] Adduct 17c with DMAD. A mixture of 1- and 3-(1-Cyanoethyl)cycloheptatriene (**24**) (2.1 g, 14.5 mmol) was dissolved in 70 mL of chloroform, and this solution was added to a solution of triphenylmethyl fluoroborate (5.7 g, 17.4 mmol) in 150 mL of chloroform. After being stirred at room temperature for 2 h, excess triethylamine was added. Purification by silica gel flash chromatography, using 10% EtOAc in n-hexane as eluant, gave 0.95 g (46%) as a red oil. The red oil is presumed to be 8-cyano-8-methylheptafulvene (**1d**), although it underwent decomposition upon removal of solvent. A solution of the crude heptafulvene **1d** (680 mg, 4.76 mmol) and **2a** (504 mg, 4.76 mmol) in chloroform (10 mL) was heated under reflux for 8 days afforded a yellow oil. Purification by silica gel flash chromatography, using 10% EtOAc in n-hexane as eluant, gave 0.38 g of a complex mixture, in 75% yield based upon recovered heptafulvene **1d**. Then, a solution of this mixture (380 mg) and DMAD (440 mg, 3.10 mmol) in 10 mL of chloroform was stirred at room temperature for 3 days afforded a yellowish oil. Purification by silica gel flash chromatography, using 10% EtOAc in n-hexane as eluant, gave **20c** (35%). The similar reaction (21 days) of **1d** with **2b**, then with DMAD gave complex reaction mixtures. No products of these reactions have been identified. **20c**: ^1H NMR δ 1.01 (s, 3 H, Me), 1.22 (s, 3 H, Me), 1.70 (bd, 1 H, J_{gem} = 6.6 Hz, H-5), 1.89 (s, 3 H, NC-C-Me), 2.17 (bd, 1 H, J_{gem} = 6.3 Hz, H-5), 2.76 (bt, 1 H, $J_{9,10}$ = 6.7 Hz, H-10), 3.62 (m, 1 H, H-4), 3.65 (s, 3 H, $-CO_2Me$), 3.79 (s, 3 H, $-CO_2Me$), 4.28 (d, 1 H, $J_{7,8}$ = 8.1 Hz, H-7), 5.86 (bt, 1 H, $J_{7,8}$ = $J_{8,9}$ = 8.1 Hz, H-8), 6.06 (bt, 1 H, $J_{8,9}$ = $J_{9,10}$ = 8.1 Hz, H-9), 6.21 (m, 2 H, H-11-12), 6.48 (bd, 1 H, $J_{3,4}$ = 3.2 Hz, H-3); IR 2220 (CN) cm^{-1}; MS *m/z* 391 (M^+); exact mass calcd for $C_{24}H_{25}NO_4$ 391.1784, found 391.1776.

A solution of the crude heptafulvene **1d** (0.50 g, 3.50 mmol) and **2a** (0.37 g, 3.50 mmol) in xylene (10 mL) was heated under reflux for 3 days afforded a yellow oil. Purification by silica gel flash chromatography, using 5% EtOAc in n-hexane as eluant, gave **19b** (55%). The similar reaction of **1d** with **2b** gave **19c** (50%).

19b: ^1H NMR δ 1.61 (s, 3 H, Me), 1.82 (s, 3 H, Me), 1.95 (s, 3 H, Me), 2.20 (m, 1 H, H-10), 2.37 (m, 1 H, H-10), 3.81 (m, 1 H, H-2), 4.36 (bd, 1 H, $J_{2,6}$ = 5.9 Hz, H-6), 5.42 (m, 2 H, H-9, H-11), 5.75 (m, 1 H, H-3), 6.17 (d, 1 H, $J_{11,12}$ = 9.5 Hz, H-12), 6.23 (d, 1 H, $J_{8,9}$ = 9.5 Hz, H-8), 6.38 (dd, 1 H, $J_{2,4}$ = 2.2 Hz, $J_{3,4}$ = 5.6 Hz, H-4); IR 2243 (CN) cm^{-1}; MS *m/z* 249 (M^+); exact mass calcd for $C_{18}H_{19}N$ 249.1518, found 249.1512.

19c: ^1H NMR δ 2.10-2.35 (m, 1 H, H-10), 2.55 (m, 1 H, H-10), 3.90 (m, 1 H, H-2), 4.90 (d, 1 H, $J_{2,6}$ = 6.6 Hz, H-6), 5.10 (m, 1 H, H-9), 5.47 (m, 2 H, H-8, H-11), 5.90 (dd, 1 H, $J_{2,3}$ = 2.3 Hz, $J_{3,4}$ = 5.6 Hz, H-3), 6.18 (d, 1 H, $J_{11,12}$ = 9.6 Hz, H-12), 6.35 (m, 1 H, H-4), 7.10-7.50 (m, 10 H, Ph); IR 2245 (CN) cm^{-1}; MS m/z 373 (M^+); exact mass calcd for $C_{28}H_{23}N$ 373.1832, found 373.1841.

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