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Substituent Effects on the Stereochemistry of 1,3-Dipolar Cycloadditions to 7-Substituted Norbornadienes

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SUBSTITUENT EFFECTS ON THE STEREOCHEMISTRY OF 1,3-DIPOLAR CYCLOADDITIONS TO 7-SUBSTITUTED NORBORNADIENES

by

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DEDICATION

Dedicated to the memory of Professor James W. Wilt

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VITA

The author, Ramakrishnan Subramanian, is the son of Nirmala Subramanian and Rajagopalan Subramanian. He was born on July 18, 1964, in Madras, India.

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In August 1986, he joined the Chemistry Department, Loyola University of Chicago, to pursue the degree of Doctor of Philosophy in Chemistry. He was awarded a graduate assistantship from August 1986 to July 1987, and from June 1988 to August 1989. From August 1987 to May 1988, he was supported by a grant awarded by the Petroleum Research Foundation to Dr. James W. Wilt. In September 1989, he was awarded the Arthur J. Schmitt Fellowship, enabling him to complete the Degree of Doctor of Philosophy in 1990, under the supervision of Dr. David S. Crumrine.

List of Publications

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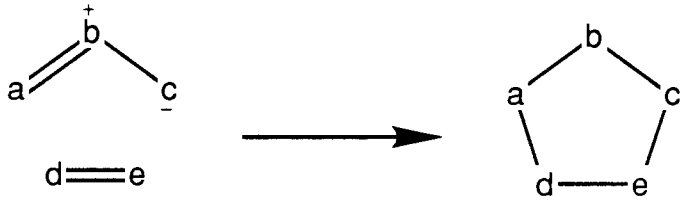
STATEMENT OF THE PROBLEM

1,3-Dipolar cycloadditions, along with Diels Alder reactions, are an important class of organic reactions. Cycloadditions are employed in the synthesis of a variety of heterocycles, an integral part of naturally occurring compounds. 1,3-Dipolar cycloadditions are defined as reactions in which a 1,3-dipole adds to a multiple bond to give a five membered ring,[1] as shown in Fig. 1.

Figure 1

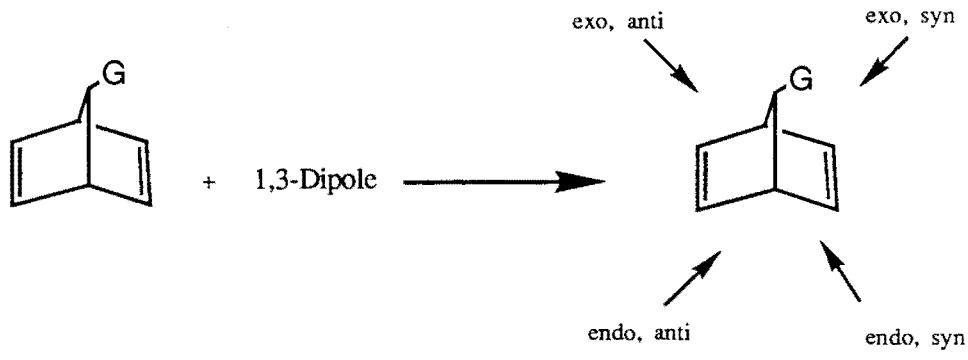


The transition state has 6 π electrons, a Huckel transition state, and is by symmetry an allowed reaction.[2]

Norbornenes and norbornadienes are good models to study steric effects in 1,3-dipolar cycloaddition chemistry due to their ring strain.[3] Phenylazide adds to norbornene about 5600 times faster than to cyclohexene.[4] This can be explained by the fact that there is a reduction in the potential angle from 120^{o} to 109^{o} and hence there is a release of ring strain. Alder and Stein evaluated ring strain of various norbornenes from the rates of cycloadditions with phenylazides.[5]

1,3-Dipoles give exclusively exo addition products (adducts) with norbornene.[1] But the addition to norbornadienes is less specific because, in some cases, endo adducts are also formed.[6] The introduction of a group at the 7-position makes the addition even less specific as the adducts could either be syn or anti, as shown in Fig. 2.

Figure 2



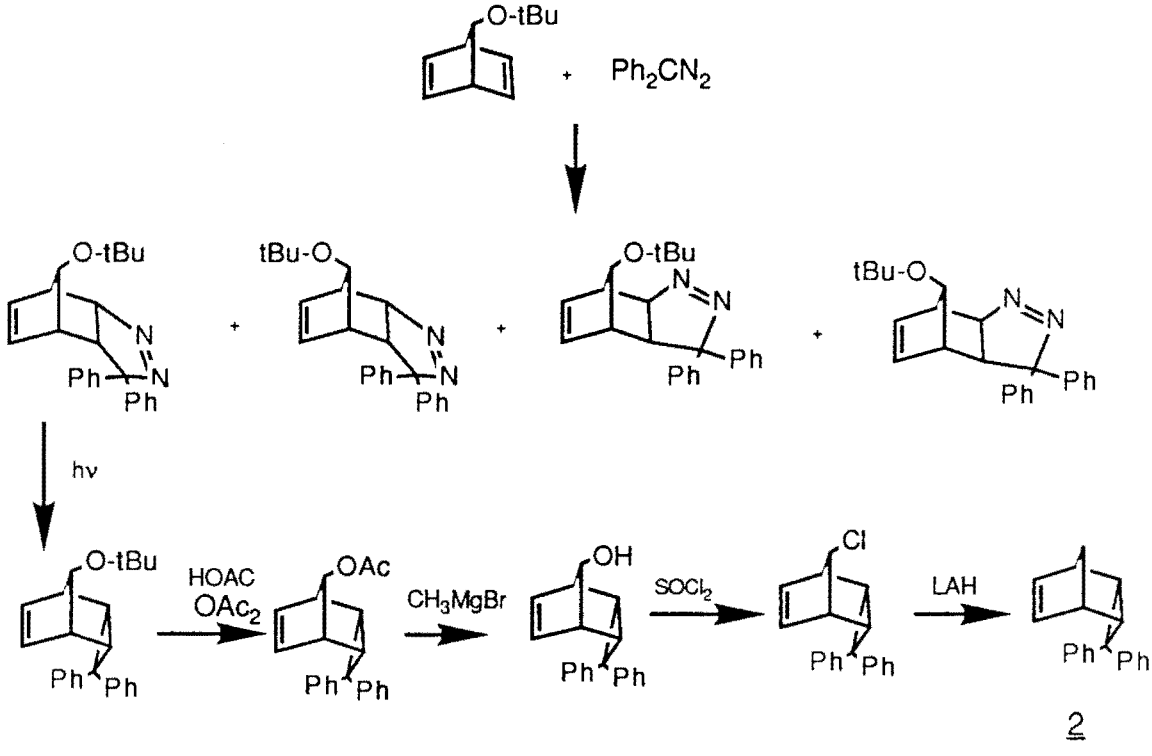
Fukui's Frontier Molecular Orbital (FMO) theory can be used to predict the relative orientations of the dipoles and the dipolarophiles but it does not deal with the question of exo and endo addition in the case of norbornadienes.[7,8] A systematic study is thus needed to better understand the electronic and steric demands on reactions of these norbornadienes.

A series of 7-substituted norbornadienes will be reacted with several 1,3-dipoles. The substituents will be classified as either electron withdrawing, donating or conjugating. Theoretical calculations will be done to correlate the computed energies of the adducts with the experimental results. The coefficients of the HOMO and LUMO orbitals of the reactants will be computed in an effort to rationalize the stereochemical outcome of these reactions.

HISTORICAL BACKGROUND

Wilt and Malloy synthesized hydrocarbon 1 through the addition of diphenyldiazomethane to norbornadiene.[9] The more complicated route to hydrocarbon 2 started with a similar addition of diphenyldiazomethane to 7-tert.butoxynorbornadiene (Scheme 1).[10]

Scheme 1b



2

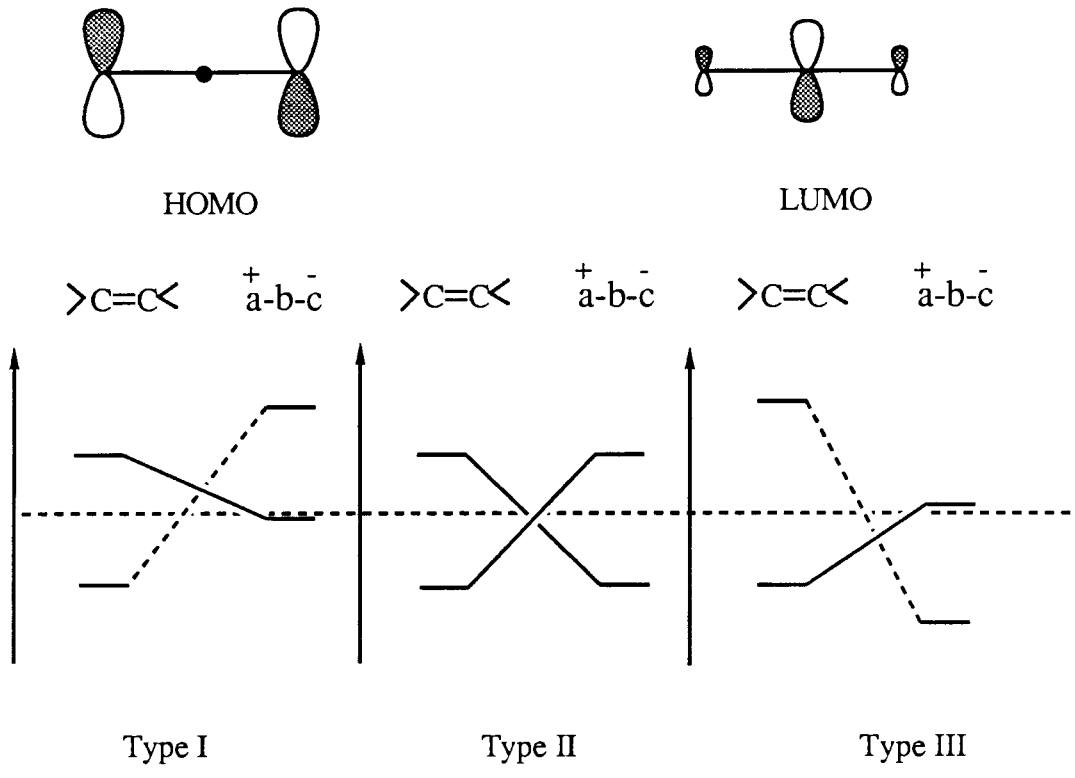
It is obvious that the reactions differed. The former gave only exo addition while the latter gave all 4 possible adducts. Table 1 lists the additions of various 1,3-dipoles to some 7-substituted norbornadienes.

Table 1 The stereochemistry of 1,3-dipolar cycloaddition of some 1,3-dipoles to some 7-substituted norbornadienes (Fig 2).

Entry	G	Dipole	% Adduct				Ref.
		-diazomethane	e, a	n, a	n, s	e, s	
1	H	Dimethyl	100				11
2	H	Diphenyl	100				9
3	OH	Methyl	70	--	30	--	12
4	O-t-Bu	Methyl	--	--	--	100	12
5	O-t-Bu	Diphenyl	36.5	25	36	2.5	10
6	Cl	Parent	--	100	--	--	12
7	Cl	Methyl	--	100	--	--	12
8	Cl	Diphenyl	26	58	16	--	13
		-azide					
9	H	Phenyl	92	8			14
10	O-t-Bu	Phenyl	30	--	55	15	15

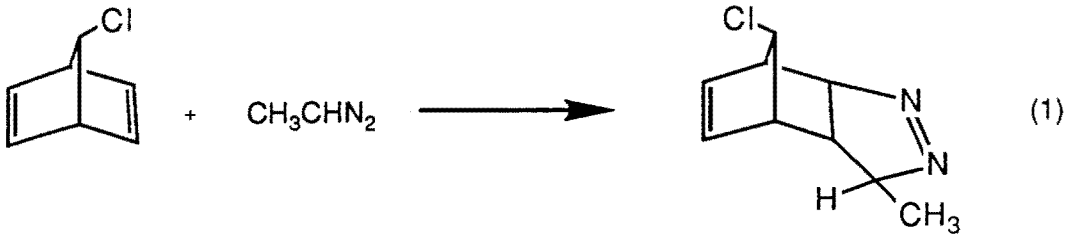
Three basic mechanisms have been proposed for 1,3-dipolar cycloadditions. They are the zwitterionic, biradical and concerted mechanisms.[16] Several theories have been used to explain reactivity and orientation in these reactions. The most commonly used theory is the perturbation theory based on Frontier Molecular Orbitals.[17-20] Sustmann used FMO theory to classify 1,3-dipolar cycloadditions as Type I, Type II and Type III reactions,[21] as shown in Fig. 3.

Figure 3



Type I reactions are those that are controlled by the HOMO of the dipole while Type III reactions are those in which the HOMO of the dipolarophile is the dominating factor. Type II reactions are those in which the HOMOs of both the dipole and the dipolarophile affect the reaction.

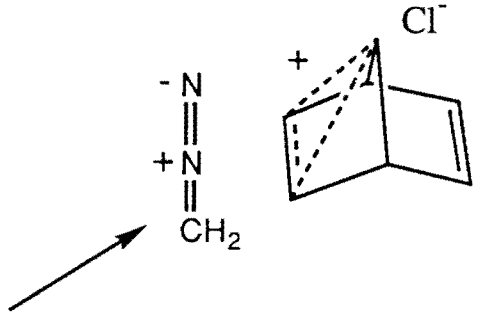
Symmetrical diazoalkanes add to norbornene and norbornadiene to give only exo addition as stated by the Alder-Stein Rule.[22,23] But substituents at the 7-position cause the addition to be less selective and 4 possible monoadducts can now form. Frank-Neumann and Sedrati reported a regiospecific addition (conditions unspecified) of diazoethane to 7-chloro-norbornadiene.[12] They claimed that the endo, anti isomer was the only product formed as shown below in Eq. 1.



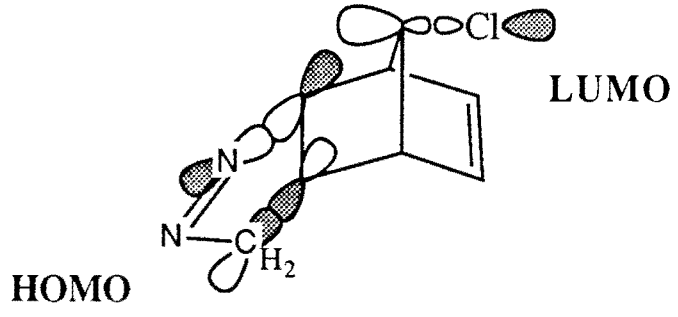
(1)

The reaction is a typical HOMO dipole controlled process. They explained their result by arguing that the FMO energy gap is lessened as the LUMO of the 7-halonorbornadiene is decreased in energy. This, they claimed, is best achieved by an endo, anti attack, as shown below, in Fig. 4.

Figure 4



or

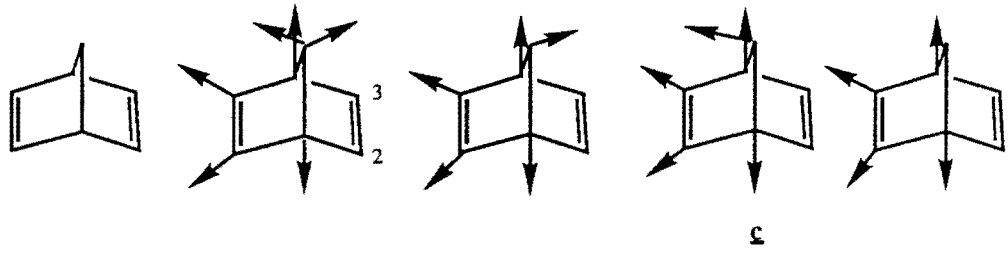


Wilt and Roberts studied the reaction between diphenyldiazomethane and 7-chloro-norbornadiene and found that all of the monoadducts except the exo, syn isomer were

formed.[13] It was surprising that the addition of two phenyl groups to the dipole could result in such a drastic change. Later, Wilt and Peeran repeated the work of Frank-Neumann and Sedrati and found not one, but two monoadducts.[24] It is interesting to note that the endo, anti isomer was still the major isomer but by no means the only isomer.

While diazomethane and diphenyldiazomethane showed a preference for endo attack, 2-diazopropane showed predominantly exo attack. DeMicheli and coworkers studied the relative rates (exo vs endo) of cycloaddition for 2-diazopropane to various polychloronorbornadienes and their results are shown in Table 2.[11] Note first that only the 2,3-double bond was attacked, and second, that compound C was preferentially attacked from the exo direction.

Table 2 Exo/ endo selectivity in the addition (a) of 2-Diazopropane to Polychloronorbornadienes (⟶-Cl)



k(rel) exo	(1)	<0.01	<0.01	4.2	8.4
k(rel) endo	<0.01	11.8	1.9	2.6	0.1

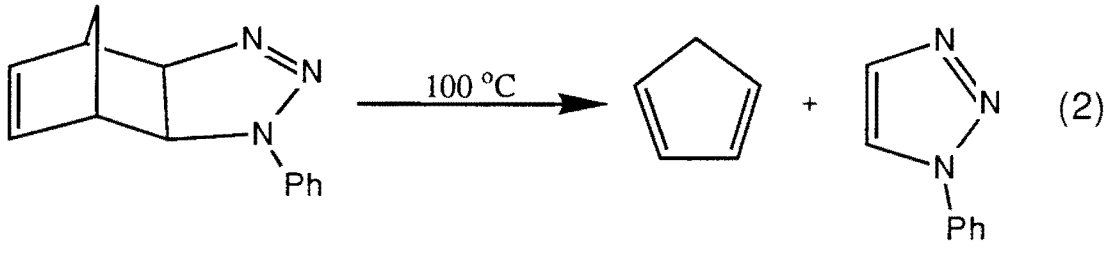
(a) All additions occurred at the C-2,3 double bond.

DeMicheli reported that C varied in a "strange manner" toward exo/endo addition with different dipoles. This ratio equalled 0.68 for nitrile oxide, 0.19 for nitrilimine and 1.6 for diazoalkane additions. Based on HOMO energies and their relation to nucleophilicities DeMicheli arranged the dipoles in decreasing order of nucleophilicities as diazoalkanes, nitrilimines and nitrile

oxides. This explains the varying ratios for the addition of these dipoles to C, but this fails to explain why only the unsubstituted 2,3-double bond was attacked. Surely the more nucleophilic diazoalkane should have attacked the more electron poor 5,6-double bond to some extent.

Steric hindrance in the 7-position seems to play an important role in phenyl azide addition, a Type II process. Spiro[cyclopentane-1,1-7H-norbornadiene] does not react with phenyl azide at all.[15] The reaction between phenylazide and norbornadiene gives both exo and endo products. Halton and Woodhouse studied the additions of azides to 7-substituted norbornadienes.[25] 7-*t*-Butoxynorbornadiene gave 56% of the endo, syn adduct, while 7-benzoyloxynorbornadiene gave 4% each of the endo, syn and the endo, anti adducts. The high yield of the endo, syn adduct is surprising because, the endo, anti face of the norbornadiene seems unencumbered and available for addition. One might assume that the coefficient of the HOMO for the syn double bond is particularly high on the endo side, or that secondary orbital interactions of the approaching azide are either attractive on the endo side or particularly repulsive on the exo, anti face.[26]

The monoadduct from phenyl azide and norbornadiene undergoes a retro Diels-Alder reaction at 100 °C to give cyclopentadiene and 1-phenyl-1,2,3-triazole (Eq. 2).[27]



(2)

Nitrile oxides and nitrile imines add exclusively on the exo face of norbornenes.[28] Norbornadiene gives 90% exo and 10% endo addition with benzonitrile oxide, and 87% exo and 13% endo addition with nitrilimine.[29] The exo/endo selectivity changes were very large

with substituents at the 7-position. It was also noticed that the rates and, to some extent, the stereochemistry varied as a function of solvent polarity and temperature.[1] Another potential dipole studied was ethyl diazoacetate but this turned out to be a poor choice because it did not give any stable adduct with norbornadiene.[30]

The FMO theory has been successfully used to explain reactivity and regiochemistry in many cases. Albert Padwa and co workers observed that electron deficient dienes add to C-phenyl-N-alkylnitrones to yield regiospecific 5-methylene substitutued isoxazolines.[31] These reactions follow Frontier Orbital predictions.

A number of reports have cited computational data that the HOMOs of 7-chloronorbornadiene and 7-*t*-butoxynorbornadiene are localized at the π bond syn to the substituent.[10,32,33] Astin and Mackenzie use this point to rationalize the preference for endo, syn product from the Diels-Alder reaction of these alkenes with electron deficient dienes.[33]

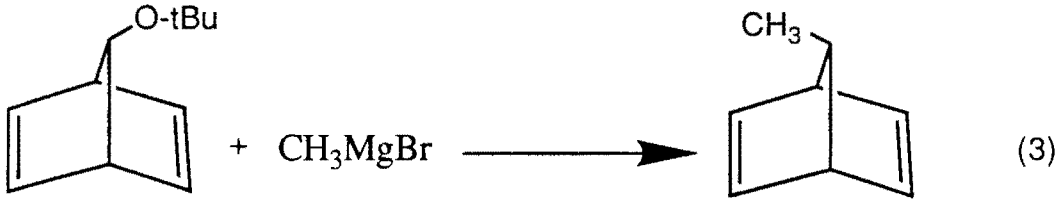
Computational chemistry is a rapidly developing science. Molecular mechanics, a semi empirical method, is now being increasingly used to do the energy calculations. This method treats the molecule as a collection of particles held together by simple harmonic forces.[34,35] Allinger and co-workers have developed the MM2 program which modifies a trial set of three dimensional atom coordinates to minimize its steric energy.[36] It thus predicts a conformation for the molecule that has the least steric energy and assumes that it would be the most favorable conformation for the isolated molecule. Hopfinger and others have also developed software packages to do MNDO and MINDO calculations.[37] Pioneers like Houk, Sustmann, Alston and Ottenbrite have used orbital calculations to explain concepts like regioselectivity in 1,3-dipolar cycloadditions.[17,32,33,38,39] But curiously enough the question of exo/endo selectivity has not been looked into in much detail. Also Houk has stated that all the earlier computational studies done on the norbornadiene system are deficient in one way or the other.[40] For example, Alston and Ottenbrite performed CNDO/2 calculations on several 7-substituted norbornadienes and found that the attack of reagents was affected by the polarization of the

isolated norbornadiene orbitals by the 7-susbstituent.[52] Houk argues that the model used to explain this polarization involves mixing of donor orbitals of the substituents with the norbornadiene orbital, an effect which should raise the HOMO energy.[40] But the photoelectron spectra and calculations done by Houk and co-workers indicate that these types of substituents lower the HOMO energies.[40]

RESULTS

1. The synthesis of 7-methylnorbornadiene

The synthesis of 7-methylnorbornadiene has been reported earlier,[41] and was attempted using methylmagnesium bromide instead of the iodide (Eq. 3).

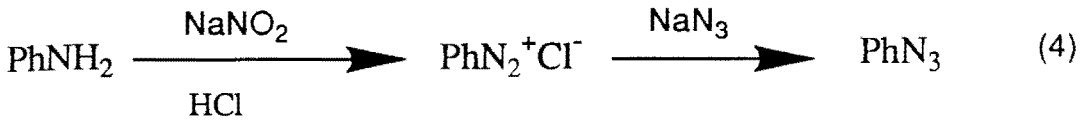


(3)

This was not very successful and the maximum yields obtained were around 5%. The synthesis was repeated by making the methylmagnesium iodide in situ and the yields improved to around 25%. The major reason for the poor yields was the decomposition of 7-methylnorbornadiene during the distillation to give benzene and ethylene. This was confirmed by the fact that during the distillation above 80 ^{o}C, more benzene distilled over along with the desired product. This could be reduced to some extent by distilling the mixture at lower temperatures and reduced pressures.

2. The synthesis of phenylazide

The synthesis of phenylazide has been reported earlier.[42] The synthesis was attempted using the Clayfen method[43,44] but no phenyl azide could be recovered though TLC indicated the formation of the product. Phenylazide was successfully prepared using the "aniline" method,[42] where aniline was diazotized using hydrochloric acid and sodium nitrite and sodium azide solution added to this diazonium salt (Eq. 4).



(4)

p-Nitrophenylazide and p-methoxyphenylazide were prepared using the same procedure with p-nitroaniline and p-methoxyaniline respectively.[45,46]

3. Isolation of the adducts

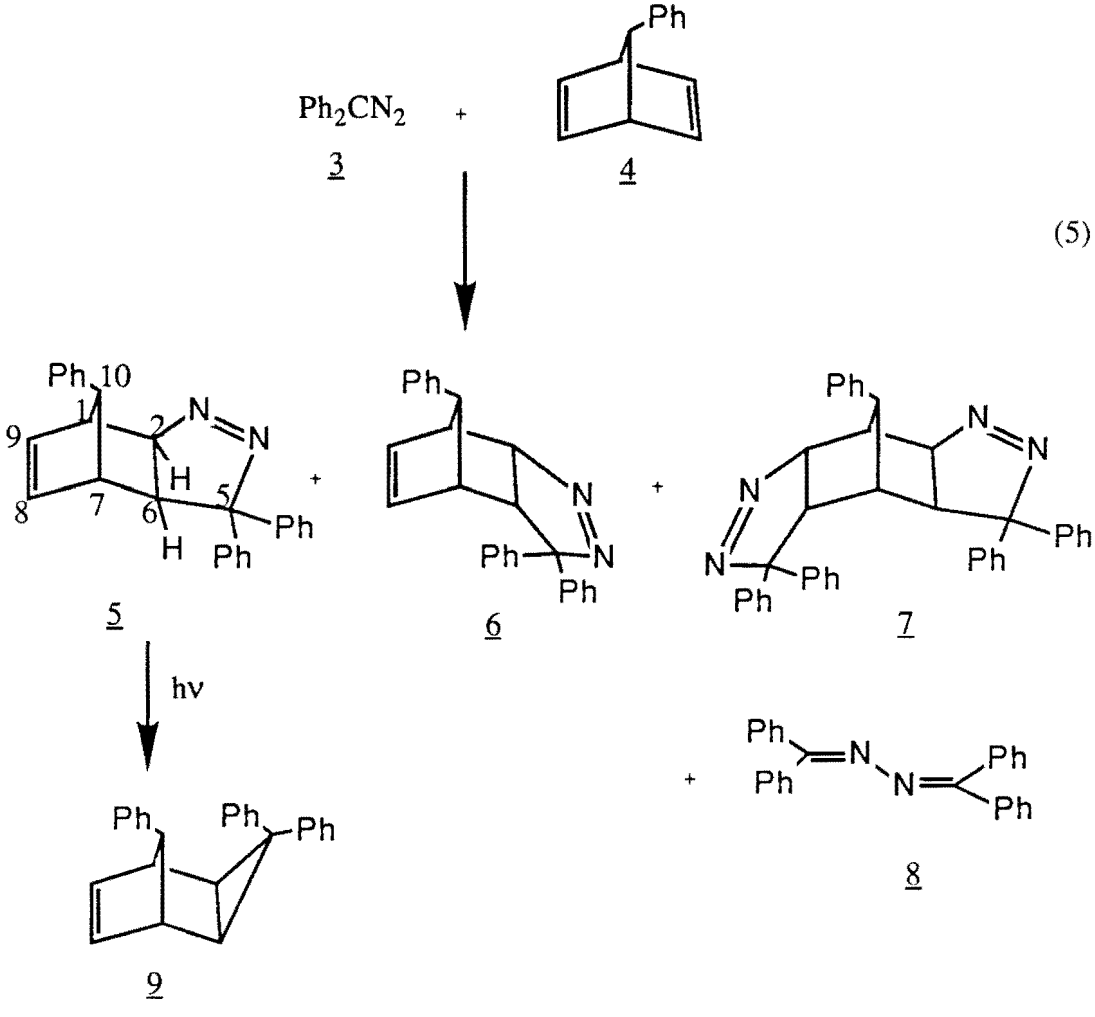
The adducts were isolated from the reaction mixtures using rotational TLC on a Chromatotron. In all cases a mixture of either pentane and ether or petroleum ether and ether was used as the eluent. The chromatography was started using 100% pentane (or pet. ether) and the amount of ether was increased gradually until 100% ether was used.

4. The reaction of diphenyldiazomethane with 7-phenylnorbornadiene

The addition of diphenyldiazomethane (3) to 7-phenylnorbornadiene (4) gave two mono adducts and a bis adduct, as shown in Eq. 5. The exo, anti mono adduct (5) was the first one to elute and was formed in 56.1% yield. The endo, anti isomer (6) was the next to elute and was obtained in 3.1% yield. The exo, anti-endo, syn bis adduct (7) eluted last and was obtained in 5.5% yield. The stereochemistry of the adducts was assigned by comparison of the ^{1}H multiplicities and the ^{1}H and ^{13}C NMR chemical shifts, to those of similar structures of known stereochemistry.[10,13,24,47-49] The exo adducts are easily distinguished from the endo isomers by examining the multiplicity of the pyrazolinic protons,[50] H_2 and H_6,[51] which appear as doublets in the exo adducts and as doublets of doublets in the endo isomers. The coupling between the pyrazolinic Hs and the bridge head Hs is small in the exo adducts because the dihedral angle between them is close to 90^{0}, so H_2 and H_6 appear as simple doublets. In the endo isomers, however, the coupling constant between the pyrazolinic Hs and the bridge head Hs

is larger because the dihedral angle between them is close to 0^{o}, so the signals appear as doublets of doublets.

The syn and anti assignments were made by comparing the chemical shifts of the vinylic protons, vinylic carbons and bridge top proton of the adducts and the parent dienes.[10] The stereochemical assignment of the monoadduct **5** formed from the diene **4** is discussed below and the assignment of the stereochemistry of the other adducts was done in a similar manner.



Both the elemental analysis and the presence of vinylic protons in the ^{1}H NMR indicates that **5** is a monoadduct. The pyrazolinic protons, H_2 and H_6, in monoadduct 5 appear as two doublets, at 3.05 and 5.37 ppm, hence **5** is exo (vide supra). The bridge top proton, H_7, appears

at 3.75 ppm in **4** and at 2.60 ppm in **5** (here designated H_{10}). If the adduct were syn, then H_{10} would experience little change in environment from the parent diene **4** and would appear close to the 3.75 ppm value of **4**.[41] The signal observed at 2.60 ppm, assigned to H_{10}, could be explained by shielding when pushed into the face of the -N=N double bond. When **5** was photolyzed to produce **9**, the bridgetop proton (H_8) appears at 2.90 ppm as it is near the diphenyl cyclopropyl group, so **5** has been assigned an anti configuration.

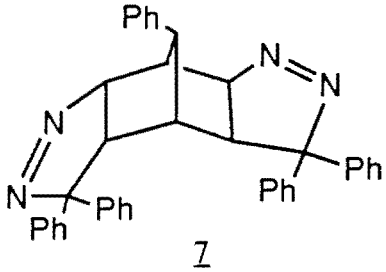
The pyrazolinic protons in the exo adduct from the reaction of **3** with norbornadiene appear at 5.30 and 2.87 ppm which are close to the values for the pyrazolinic protons in **5**.[9] This suggests again that the stereochemistry of **5** is exo, anti. The long range "W" coupling between the bridgetop proton and the vinylic protons was observed in the ^1H-^1H COSY spectrum of the photolyzed cyclopropyl compound **9**. These cyclopropyl compounds,used in previous cases to assign stereochemistry, helped to confirm the stereochemistry of the pyrazolinic compounds. The chemical shifts for C_3 and C_8 (both appear at 54.0 ppm) compared well with the predicted chemical shifts (57.7 ppm for C_3 and 49.9 ppm for C_8) based on the substituent effects for tricyclo[3.2.1.$0^{2,4}$]octane systems.[49]

The vinylic proton and carbon chemical shifts can also be used to strengthen the argument for the anti assignment. In **4** the vinylic protons appear at 6.85 and 6.50 ppm as the anti and the syn protons respectively. The syn vinylic carbons appearing at 139.95 ppm are shielded when compared to their anti counterparts which appear at 144.42 ppm. In **5**, the vinylic protons (H_8 and H_9) appear at 6.00 and 6.20 ppm, respectively, while the vinylic carbons appear at 138.61 and 138.64 ppm. This suggests that, since the NMR signals of the syn vinylic protons and carbons are little changed while those of the anti vinylic protons and carbons disappeared, the dipole necessarily added anti. The pyrazolinic protons in **6** appeared as doublets of doublets at 4.62 and 3.59 ppm, so the adduct was endo. The vinylic carbons and protons appeared at 130.23, 132.34 and 6.00, 5.60 ppm respectively, so the adduct was anti. The relative stereochemistry of all the other adducts were assigned in a similar fashion.

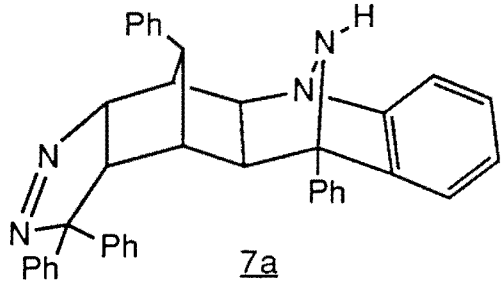
The absence of vinylic protons and carbons in the NMR and the elemental analysis indicated that compound 7 is a bis adduct. The presence of one pair of doublets and a pair of doublets of doublets suggests that one side of the bis adduct is exo and the other side is endo. The chemical shift of the bridge top proton which appears at 2.49 ppm, suggests that the bis adduct has an exo, anti - endo, syn configuration. If the adduct were syn on the exo side then the proton should appear near 3.75 ppm, as in the parent 4.

Assigning the structure of 7 is further complicated by the presence of an IR band at 3300 cm-1 which indicates the presence of an N-H. This is supported by the appearance of a broad signal at 7.85 ppm in the ^{1}H NMR spectrum integrating for 1 proton which did not exchange with D_2O but exchanged with DCl/D_2O. Three possible structures and the usual bis pyrazolinic structure are shown below in Fig. 5, and we have tentatively assigned structure 7b to the bis adduct.

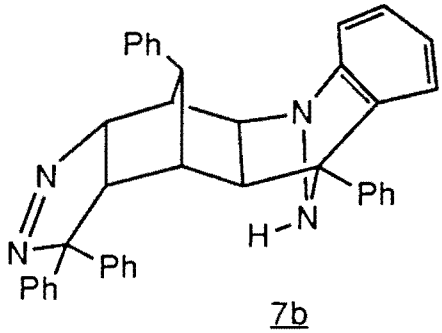
Figure 5



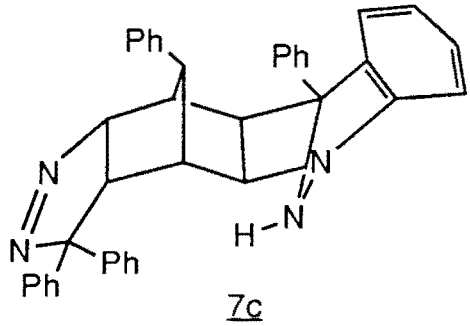
7



7a



7b



7c

The usual bis pyrazolinic structure 7 can be ruled out due to the absence of an N-H. Although 7a has an N-H proton, it was rejected because one would expect the N-H proton in this position to exchange fairly readily with D_2O. The N-H in 7b is pushed into the endo phenyl ring of the endo, syn monoadduct leading to intramolecular hydrogen bonding to the π system which would explain the lack of exchange with D_2O. The bridge top proton (H_{10}) which appears at 2.60 ppm in 4, is now further shielded by the phenyl ring and appears at 2.49 ppm. Furthermore, the calculated steric energy is greater by about 20 Kcal mol^{-1} when the N-H is exo (as in 7a) than when it is endo (as in 7b).[52a] This is also true for a carbon analogue where the steric energy of the exo compound is greater than that of the endo compound by about 10 Kcal mol^{-1}.[53]

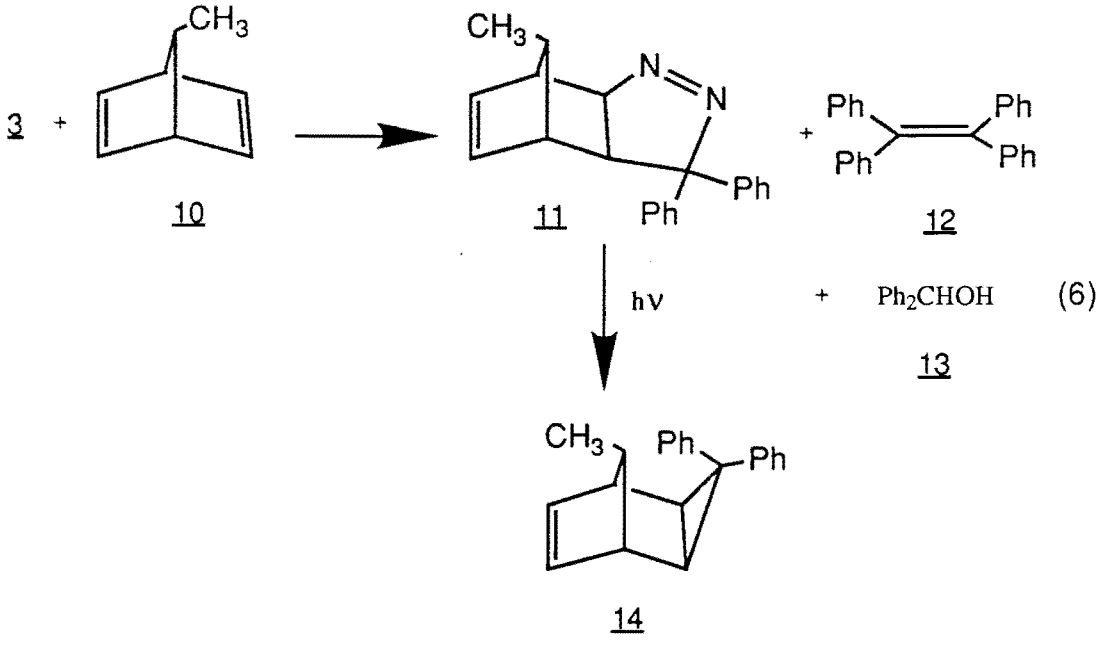
The chemical shift of the bridgetop proton (H_{14}) NMR signal observed at 2.49 ppm can be explained by shielding from the benzo ring of either 7b or 7c, but structure 7c was eliminated because the bridgehead protons H_1 and H_8 should have similar chemical shifts as each would be β to a nitrogen and β to a phenyl. Although one N is exo and the other is endo that should not make a major difference in the chemical shifts. Examination of a model of 7c suggests that the proximity of the β phenyls to the protons of interest are quite similar, so the ^1H chemical shifts should be closer in value than was observed.

Although we cannot conclusively rule it out, structure 7a appears to be less probable for three reasons. First, the 2.49 ppm chemical shift of the bridgetop proton is too high as there are no shielding groups nearby. It should be nearer to the 3.75 ppm of the parent diene. Second, the 7.85 ppm ^1H absorption for the NH is very low for such a nonacidic NH. Inspection of a model of 7b shows that the NH is very close to the endo-10-phenyl. The proximity of the edge of the phenyl ring could deshield the NH to its extraordinarily low chemical shift. No such interaction is available for structure 7a.

5. The reaction of diphenyldiazomethane with 7-methylnorbornadiene

The addition of **3** to 7-methylnorbornadiene (**10**) gave only the exo, anti mono adduct (**11**), as shown in Eqn. 6. The pyrazolinic protons appeared as doublets at 2.81 and 5.20 ppm and the vinylic protons and carbons appeared at 6.10 and 133.23, 138.40 ppm respectively, so the adduct was exo, anti. It was interesting to note that in addition to tetraphenylketazine (8.9%), two other decomposition products of diphenyldiazomethane, tetraphenylethylene (**12**) (23.4%) and benzhydrol (**13**) (3.1%), were also formed.[54]

The adduct was photolyzed to give the symmetrical tricyclic compound **14**. The proton COSY spectrum of this photolyzed adduct showed the long range "W" coupling between the bridgetop proton and the vinylic protons, as in the case of the tricyclic octene **9**.



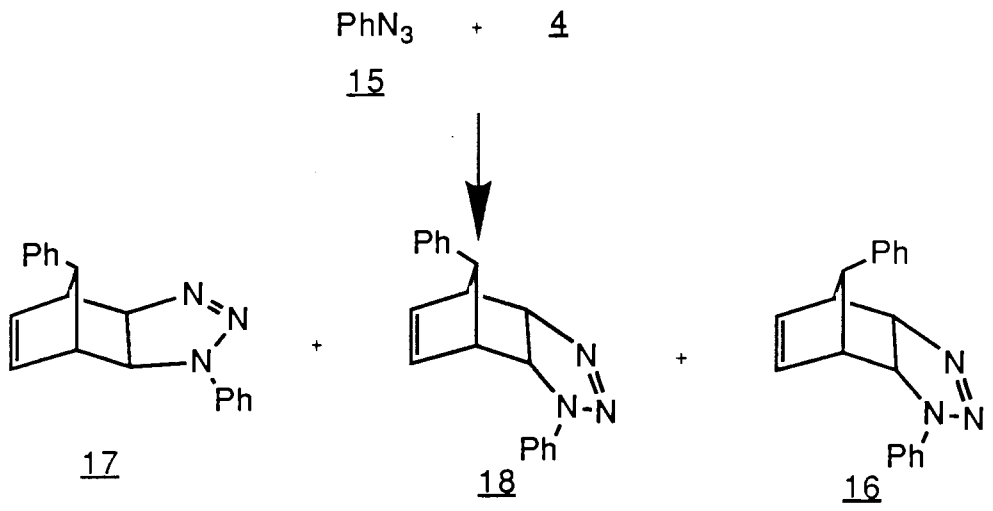
6. Calculation of percent yields

The calculation of the percent yields in the reaction with 7-phenylnorbornadiene were based on mmoles of diphenyldiazomethane reacted. This was calculated using the mass of recovered **3**, which agreed well with the mass as estimated by UV analysis of the reaction mixture. The calculation of percent yields in the reaction with **10** was complicated by the

presence of three decomposition products of diphenyldiazomethane, **8**, **12** and **13**, formed during chromatography of the reaction mixture. Also the mass of **3** as estimated by UV analysis of the reaction mixture did not correspond to the masses of the decomposition products of **3**. So the yields were based on mmoles of diphenyldiazomethane used for the reaction (10 mmoles). The yield of the exo, anti adduct **11** was 100%, based on mmoles of adduct formed.

7. The reaction of phenylazide with 7-phenylnorbornadiene

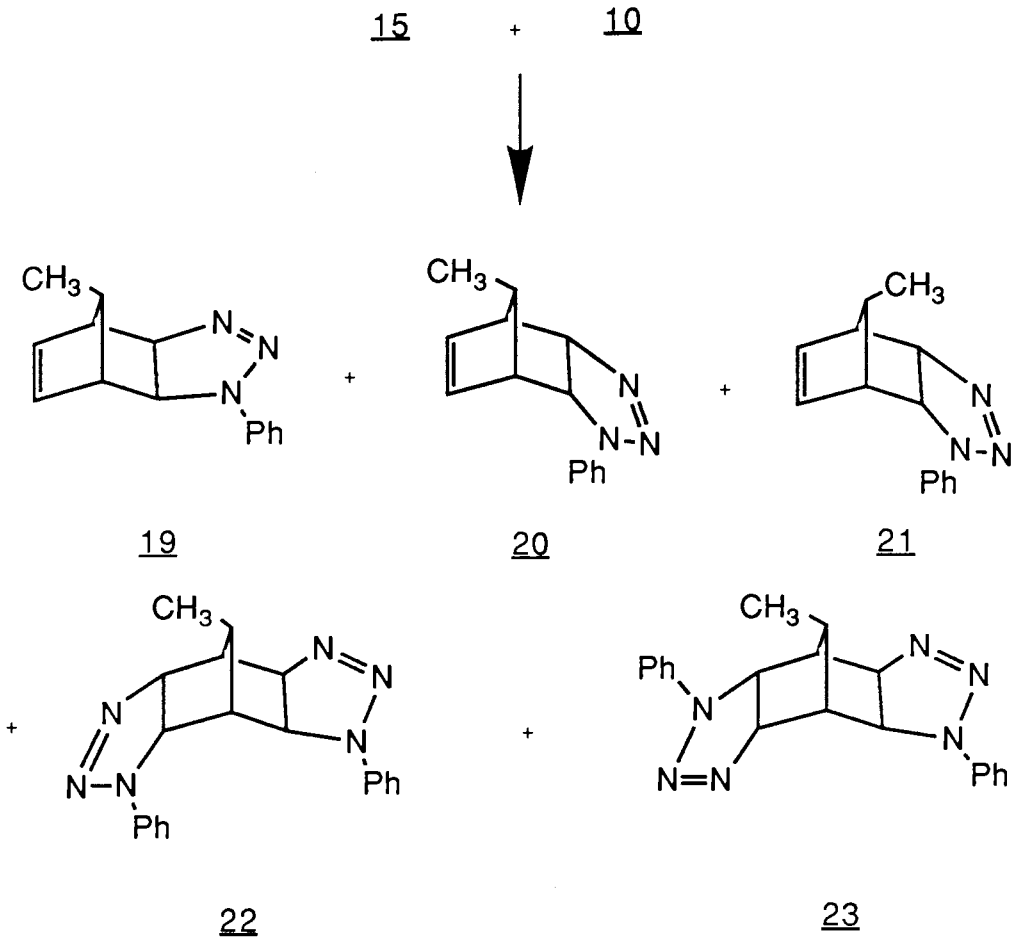
The addition of phenylazide (**15**) to **4** gave three mono adducts, all except the exo, syn mono isomer, as shown in Eq. 7. The endo, syn isomer (**16**) was the first adduct to elute and was obtained in 7.3% yield. The triazolinic protons appeared as doublets of doublets at 4.19 and 5.14 while the vinylic protons and carbons appeared at 5.85, 6.07 and 134.05, 136.49 ppm respectively, so the adduct was endo, syn. The major isomer (**17**), the exo, anti adduct, eluted next and was obtained in 42.2% yield. The triazolinic protons appeared as doublets at 4.15 and 5.00 ppm while the vinylic protons and carbons appeared at 6.10 and 134.79, 135.35 ppm respectively, so the adduct was exo, anti. This was followed by the endo, anti adduct (**18**) which was obtained in 23.8% yield. The triazolinic protons appeared as doublets of doublets at 4.44 and 5.40 ppm while the vinylic protons and carbons appeared at 5.63, 5.74 and 131.10 and 133.57 respectively, so the adduct was endo, anti. The vinylic carbons in the endo, anti isomer appear upfield compared to the ones in the endo, syn isomer. In the endo, anti isomer, the triazoline ring and the C-10 phenyl ring shield the vinylic carbons- the γ *gauche* effect.[52b] The vinylic carbons in the endo, syn adduct experience the γ effect from the triazoline ring alone, and so they appear downfield compared to the vinylic carbons in the endo, anti adduct. The corresponding γ effect in the exo adducts (γ-*trans*) is smaller than the effect in the endo compounds.



(7)

8. The reaction of phenylazide with 7-methylnorbornadiene

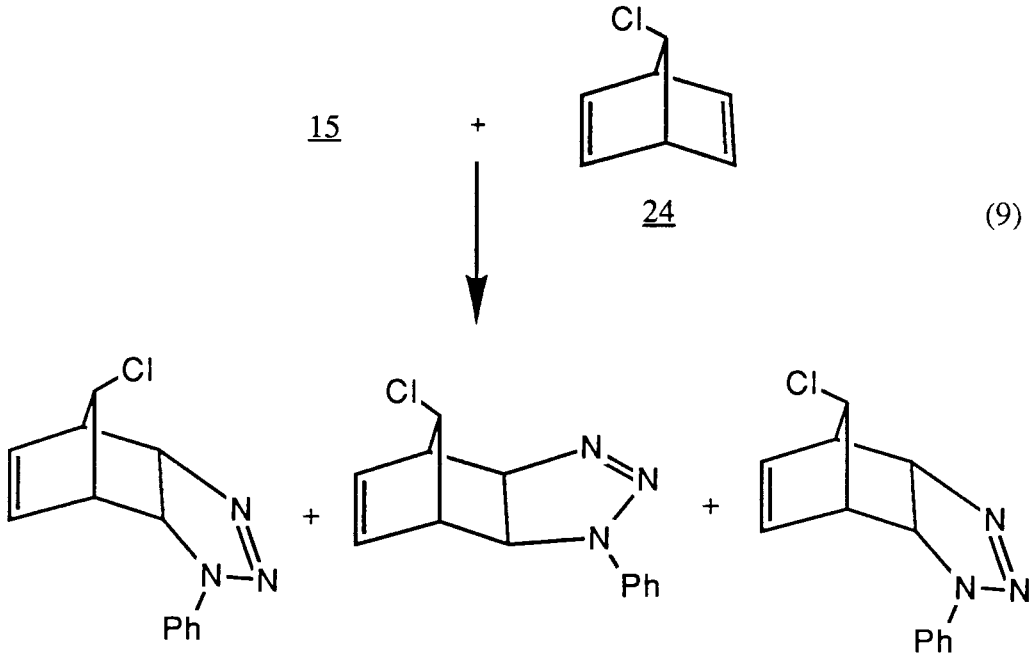
The addition of **15** to **10** gave three mono adducts and two bis adducts, as shown in Eq. 8. The exo, anti isomer (**19**) was the first adduct to elute and was obtained in 62.2% yield. The triazolinic protons appeared as doublets at 3.95 and 4.85 ppm while the vinylic protons and carbons appeared at 6.05, 6.15 and 134.50, 136.00 respectively, so the adduct was exo, anti. This was followed by the endo, anti mono adduct (**20**) (14.2%). The triazolinic protons appeared as doublets of doublets at 4.22 and 5.40 ppm while the vinylic protons and carbons appeared at 5.80, 6.00 and 134.60, 137.90 ppm respectively, so the adduct was endo, anti. The endo, syn isomer (**21**) eluted next and was obtained in 18.7% yield. The triazolinic protons appeared as doublets of doublets at 4.35 and 5.40 ppm while the vinylic protons and carbons appeared at 5.68, 5.89 and 130.44, 132.90 ppm respectively, so the adduct was endo, syn. The two bis adducts (**22** and **23**) eluted next-the exo, anti-endo, syn cis (2.9%) and trans (2%). The ^{1}H NMR of both these adducts showed no vinylic protons and carbons. The first bis adduct showed doublets of doublets at 4.49 and 5.38 ppm and doublets at 3.85 and 4.42 ppm.



The bridge top proton appeared at 2.05 ppm (where the bridge top proton appeared in the endo, syn mono adduct), so the bis adduct was exo, anti-endo, syn. The other bis adduct **23** also had similar chemical shift and multiplicity data and was established to be exo, anti-endo, syn. The bridgehead protons in the first bis adduct appeared at 3.30 and 2.90 ppm while in the second bis adduct they appeared at 3.05 ppm. This could be possible only if the dipoles added cis in the first case but trans in the second case. In the trans compound both the bridgehead protons would be β to the -N=N and the -N-Ph systems thus making the chemical shifts of the two identical. If both the dipoles added cis, then one bridgehead proton would be β to both the -N=N systems while the other would be β to both the -N-Ph systems, thus making the chemical shifts different.

9. The reaction of phenylazide with 7-chloronorbornadiene

The reaction of **15** with 7-chloronorbornadiene (**24**) also gave three mono adducts, all except the exo, syn isomer, but did not give any bis adduct (Eq. 9).

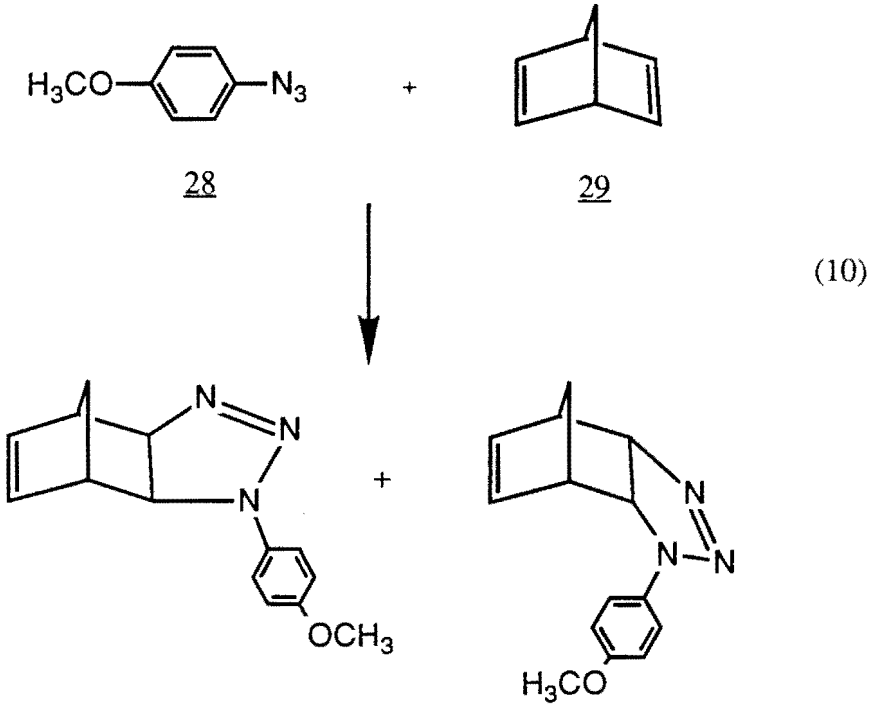


25 26 27

The endo, syn isomer (**25**) eluted first and was obtained in 29.5% yield. The triazolinic protons appeared as doublets of doublets at 4.71 and 5.65 ppm while the vinylic protons and carbons appeared at 5.82, 6.02 and 133.09, 135.91 ppm respectively, so the adduct was endo, syn. This was followed by the exo, anti isomer (**26**) which was obtained in 31.4% yield. The triazolinic protons appeared as doublets at 4.20 and 5.05 ppm while the vinylic protons and carbons appeared at 6.25, 6.38 and 134.16, 135.04 ppm respectively, so the adduct was exo, anti. The endo, anti adduct (**27**) was the last to elute and was obtained in 39.1% yield. The triazolinic protons appeared as doublets of doublets at 4.40 and 5.34 ppm while the vinylic protons and carbons appeared at 5.87, 6.06 and 130.23, 132.55 ppm respectively, so the adduct was endo, anti.

10. The reaction of p-methoxyphenylazide with norbornadiene

The addition of p-methoxyphenylazide (**28**) to norbornadiene (**29**) yielded both the exo and endo adducts, as shown in Eq. 10.



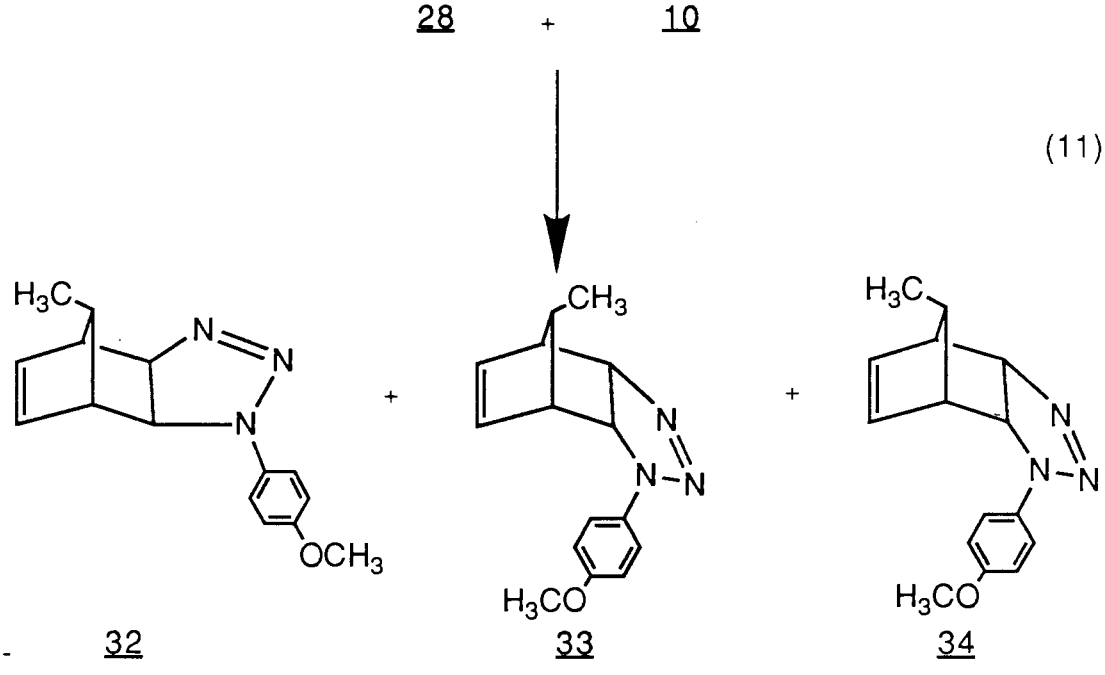
(10)

The exo isomer (**30**) eluted first and was obtained in 95% yield. The triazolinic protons appeared as doublets at 4.09 and 4.93 ppm, so the adduct was exo. The endo isomer (**31**) eluted next and was obtained in 5% yield. The triazolinic protons appeared as doublets of doublets at 4.40 and 5.35 ppm, so the adduct was endo. It has to be mentioned that the recovery of the unreacted azide was very difficult due to the decomposition of the azides as they were loaded on to the plate. The nature of the decomposition product (pink in color) was difficult to establish; the ^{1}H NMR had resonances only in the aromatic region which seemed to indicate a

para pattern while the IR spectrum did not show any characteristic absorptions. It could be the bis-paramethoxyphenylhydrazine with weak NH stretching in the IR and broadening of the NH proton in the NMR.

11. The reaction of p-methoxyphenylazide with 7-methylnorbornadiene

The addition of **28** to **10** gave three mono adducts, all except the exo, syn isomer, as shown in Eq. 11.



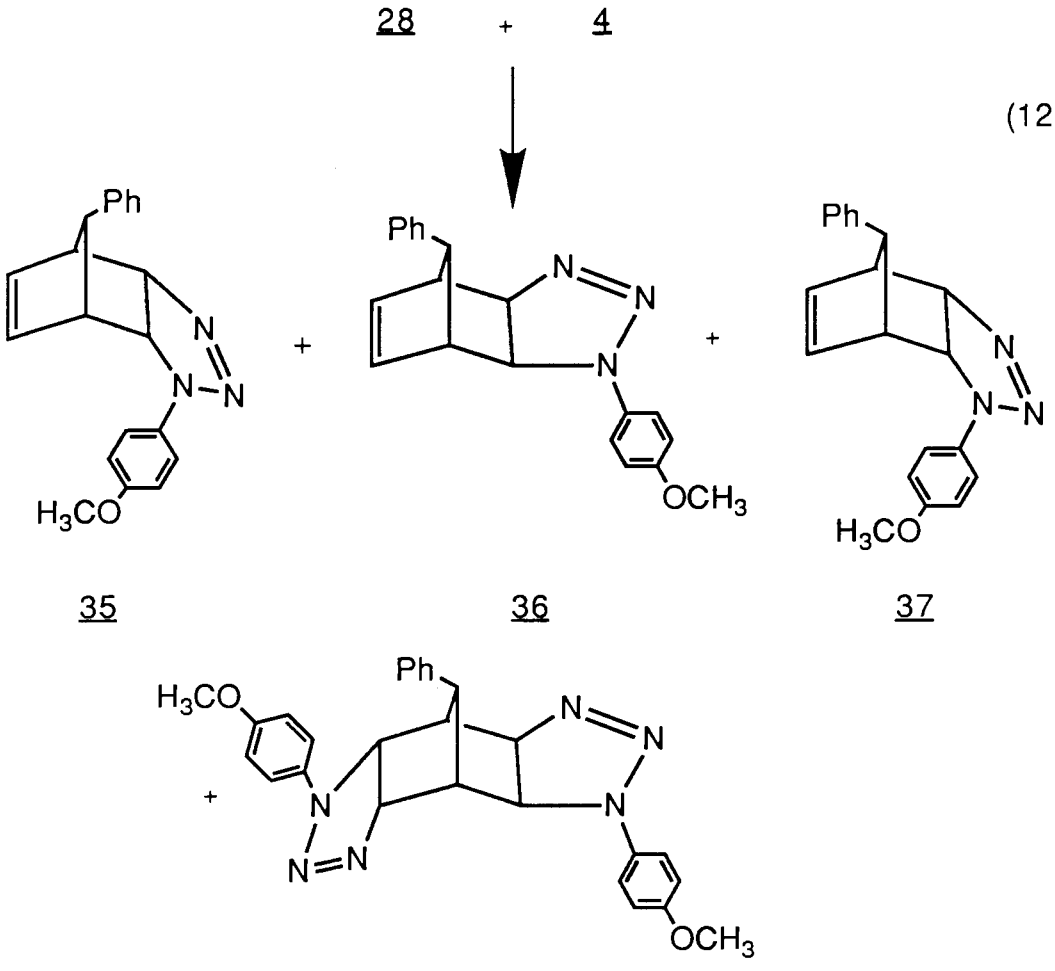
32 33 34

The exo, anti isomer (**32**) was the major product (56.6%) and eluted first. The triazolinic protons appeared as doublets at 4.90 and 4.03 ppm while the vinylic protons and carbons appeared at 6.12, 6.08 and 136.18, 135.15 ppm respectively, so the adduct was exo, anti. The endo, syn adduct (**33**) was the next to elute and was obtained in 19.1% yield. The triazolinic protons appeared as doublets of doublets at 5.32 and 4.40 ppm while the vinylic protons and carbons appeared at 5.96, 5.78 and 137.91, 135.50 ppm respectively, so the adduct was endo,

syn. This was followed by the endo, anti isomer (**34**) which was obtained in 24.3%. The triazolinic protons appeared as doublets of doublets at 5.29 and 4.32 ppm while the vinylic protons and carbons appeared at 5.85, 5.66 and 133.78, 131.18 ppm respectively, so the adduct was endo, anti. Again the vinylic carbons in the endo, anti adduct appear upfield due to the γ effect from both the triazoline ring and the C-10 substituent,. The vinylic carbons in the endo, syn isomer appear downfield because of reduced γ interaction.

12. The reaction of p-methoxyphenylazide with 7-phenylnorbornadiene

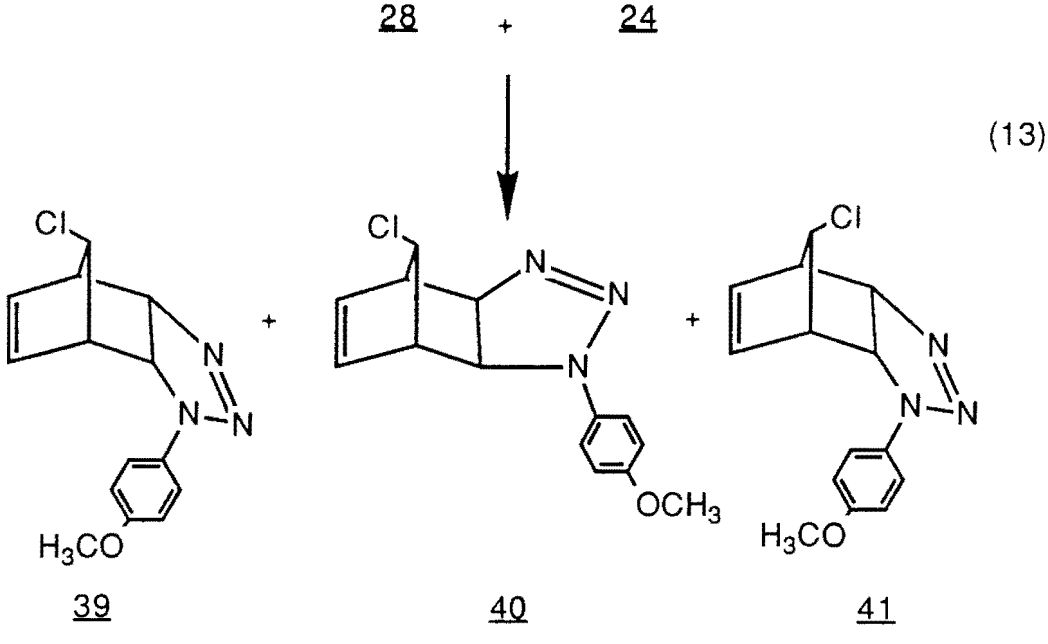
The addition of **28** to **4** gave three mono adducts, all except the exo, syn isomer, and one bis adduct, as shown in Eq. 12. The endo, syn adduct (**35**) was the first to elute and was obtained in 12.6% yield. The triazolinic protons appeared as doublets of doublets at 5.17 and 4.02 ppm while the vinylic protons and carbons appeared at 6.12, 5.93 and 137.01, 134.02 ppm respectively, so the adduct was endo, syn. The major product was the exo, anti isomer (**36**) and was obtained in 61.5% yield. The triazolinic protons appeared as doublets at 5.05 and 4.20 ppm while the vinylic protons and carbons appeared at 6.12and 135.3, 134.6 ppm respectively, so the adduct was exo, anti. The endo, anti isomer (**37**) was the next to elute and was obtained in 13.7% yield. The triazolinic protons appeared as doublets of doublets at 5.49 and 4.54 ppm while the vinylic protons and carbons appeared at 5.88, 5.69 and 133.88, 130.10 ppm respectively, so the adduct was endo, anti. Again the vinylic carbons in the endo, anti adduct appear upfield due to the γ effect from both the triazoline ring and the C-10 substituent,. The vinylic carbons in the endo, syn isomer appear downfield because of reduced γ interaction.



The exo, anti-endo, syn bis adduct (**38**) eluted last and was obtained in 12.3% yield. The ^{1}H NMR showed no vinylic protons and carbons but had doublets of doublets at 5.68 and 4.21 ppm, and doublets at 4.55 and 4.02 ppm. The bridge top proton appeared at 3.26 ppm. So the bis adduct was exo, anti-endo, syn. There was only one bridgehead signal, so the dipole added trans.

13. The reaction of p-methoxyphenylazide with 7-chloronorbornadiene

The reaction between **28** and **24** resulted in three mono adducts and, once again, the exo, syn isomer was not formed, as shown in Eq. 13. The major isomer, as in the reaction with phenylazide, was the endo, anti adduct (**39**) which eluted first in 60.7% yield. The triazolinic protons appeared as doublets of doublets at 5.25 and 4.30 ppm while the vinylic protons and carbons appeared at 5.99, 5.79 and 133.13, 130.72 ppm respectively, so the adduct was endo, anti. This was followed by the exo, anti isomer (**40**) which was obtained in 26.2% yield. The triazolinic protons appeared as doublets at 4.95 and 4.11 ppm while the vinylic protons and carbons appeared at 6.27, 6.16 and 135.56, 134.60 ppm respectively, so the adduct was exo, anti. The endo, syn compound (**41**) eluted last and was obtained in 13.1% yield. The triazolinic protons appeared as doublets of doublets at 5.58 and 4.65 ppm while the vinylic protons appeared at 5.98,and 5.88 ppm, so the adduct was endo, syn.



39 40 41

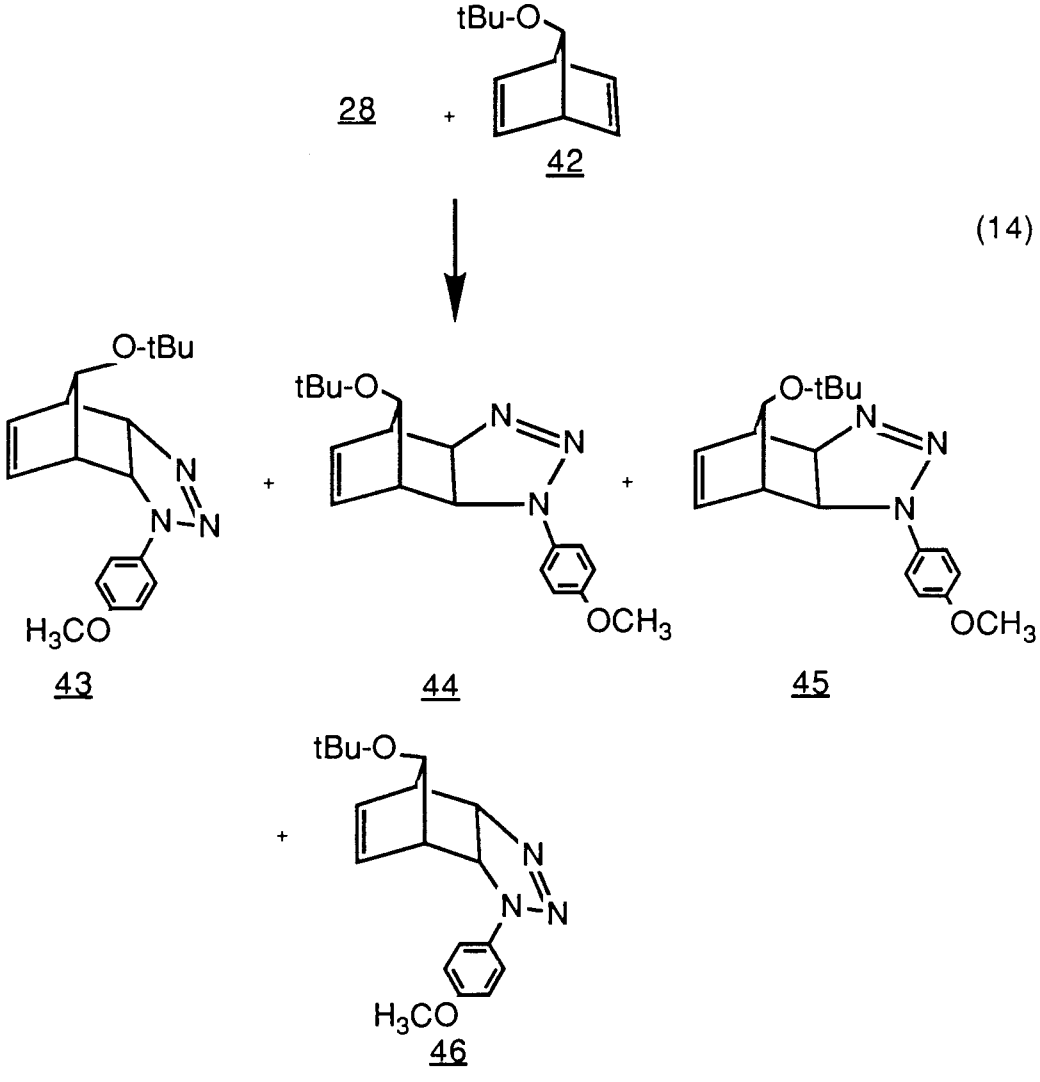
(13)

The total recovery in this reaction was very poor because of decomposition of both the arylazide and the 7-chloronorbornadiene. The decomposition caused the plate to turn black and visualization of the bands as they eluted was severely hampered. It should be mentioned that 7-

chloronorbornadiene is not very stable under these chromatographic conditions.[52c] The chromatography of the adducts of **24**, both the pyrazolines and the triazolines, has always been difficult as the tricyclic ring systems open very easily on silica gel media. Even the use of triethylamine, which was helpful in the case of the phenylazide reactions, did not reduce the decomposition of the adducts and the starting materials.

14. The reaction of p-methoxyphenylazide with 7-*t*-butoxynorbornadiene

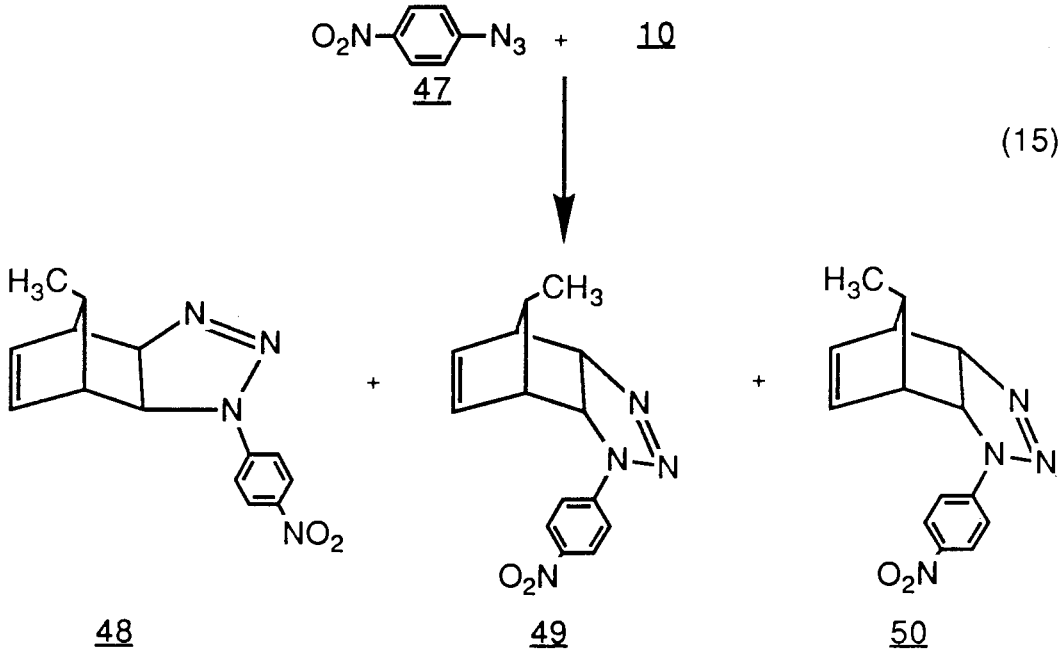
The reaction of **28** with 7-*t*-butoxynorbornadiene (**42**) gave all the four mono adducts, as shown in Eq. 14. The endo, syn compound (**43**) was the major product and was obtained in 49.3%. The triazolinic protons appeared as doublets of doublets at 5.48 and 4.59 ppm while the vinylic protons and carbons appeared at 5.90, 5.72 and 134.12, 131.96 ppm respectively, so the adduct was endo, syn. This was in comparison to the chemical shifts of the vinylic carbons of norbornene, norbornadiene and 7-*t*-butoxynorbornadiene which appear at 136.02, 136.75 and 137.27 (syn), 139.83 (anti) respectively. The exo, anti isomer (**44**) was the next to elute and was obtained in 21.2% yield. The triazolinic protons appeared as doublets at 4.82 and 3.98 ppm while the vinylic protons and carbons appeared at 6.28, 6.19 and 135.00, 134.05 ppm respectively, so the adduct was exo, anti. The exo, syn adduct (**45**) eluted next and was obtained in 7.8% yield. The triazolinic protons appeared as doublets at 4.94 and 4.23 ppm while the vinylic protons and carbons appeared at 6.22, 6.18 and 137.88, 136.83 ppm respectively, so the adduct was exo, syn. The endo, anti isomer (**46**) eluted last and was obtained in 20.5% yield. The triazolinic protons appeared as doublets of doublets at 5.21 and 4.29 ppm while the vinylic protons and carbons appeared at 6.02, 5.82 and 132.32, 130.03 ppm respectively, so the adduct was endo, anti. The vinylic carbons of **46** are upfield compared to those of **43** where the γ effect is from the triazoline ring alone. The oxygen of the *t*-butoxy group can contribute to the shielding of the vinylic carbons in **46**.



15. The reaction of p-nitrophenylazide with 7-methylnorbornadiene

The reaction of p-nitrophenylazide (47) with **10** gave three mono adducts and once again the exo, syn isomer was not formed (Eq. 15). The first product to elute was the exo, anti isomer (**48**), the major product, which was obtained in 67.2% yield. The triazolinic protons appeared as doublets at 4.94 and 3.92 ppm while the vinylic protons and carbons appeared at 6.15, 6.02 and 135.94, 134.80 ppm respectively, so the adduct was exo, anti. The next compound to elute was the endo, syn mono adduct (**49**) which was obtained in 14.6% yield. The triazolinic protons appeared as doublets of doublets at 5.58 and 4.48 ppm while the vinylic

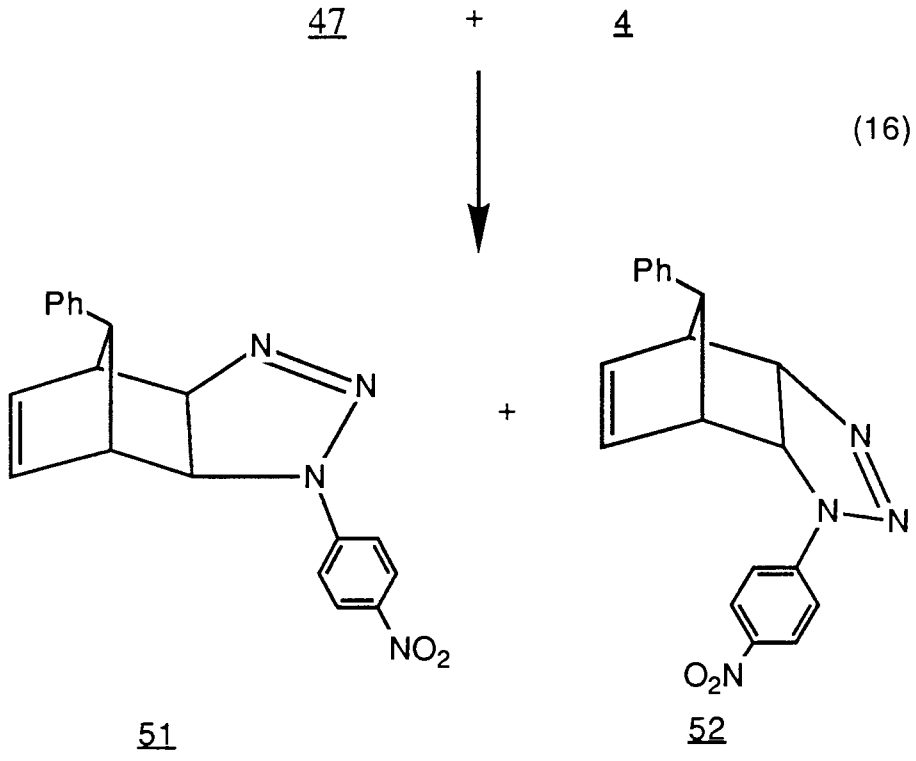
protons appeared at 6.05 and 5.82 ppm, so the adduct was endo, syn. The last adduct to elute was the endo, anti isomer (**50**) and was obtained in 18.2% yield. The triazolinic protons appeared as doublets of doublets at 5.49 and 4.38 ppm while the vinylic protons and carbons appeared at 5.91, 5.70 and 134.02, 130.82 ppm respectively, so the adduct was endo, anti.



16. The reaction of p-nitrophenylazide with 7-phenylnorbornadiene

The reaction of 47 with 4 gave only two mono adducts, the exo, anti and the endo, anti isomers (Eq. 16). The exo, anti isomer (**51**) was the first to elute and was obtained in 33% yield. The triazolinic protons appeared as doublets at 5.25 and 4.26 ppm while the vinylic protons and carbons appeared at 6.22 and 135.9, 134.9 ppm respectively, indicating that the adduct was exo, anti. The major isomer, the endo anti adduct (**52**), eluted next and was obtained in 67% yield. The triazolinic protons appeared as doublets of doublets at 5.39 and 4.26

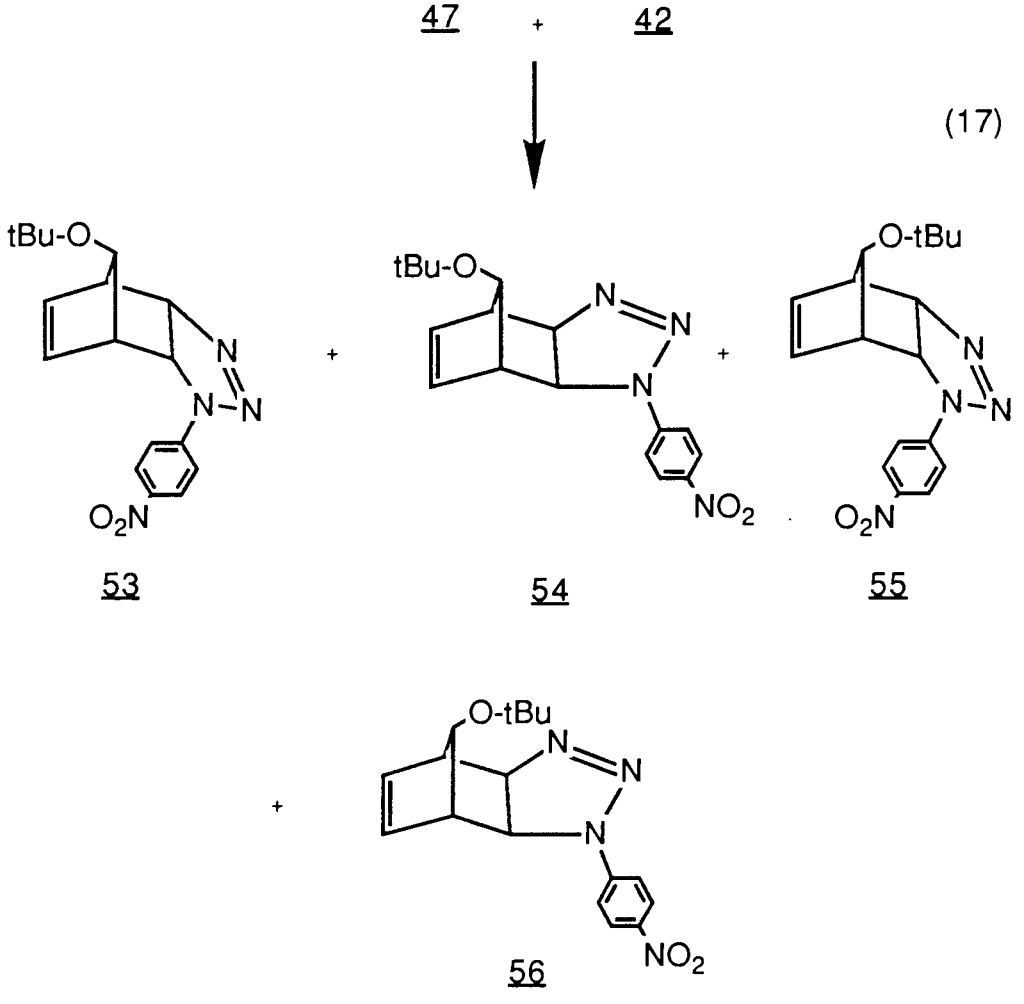
ppm while the vinylic protons and carbons appeared at 6.19, 5.95 and 137.5, 134.5 ppm respectively, indicating that the adduct was endo, anti.



17. The reaction of p-nitrophenylazide with 7-*t*-butoxynorbornadiene

The reaction of **47** with **42** gave all four mono adducts (Eq. 17). The endo, anti mono adduct (**53**) was the first to elute and was obtained in 38.7% yield. The triazolinic protons appeared as doublets of doublets at 5.64 and 4.60 ppm while the vinylic protons and carbons appeared at 5.91, 5.70 and 133.98, 130.86 ppm respectively, so the adduct was endo, anti. The exo, anti adduct (**54**) eluted next and was obtained in 38.4% yield. The triazolinic protons appeared as doublets at 5.08 and 4.24 ppm while the vinylic protons and carbons appeared at 6.32, 6.24 and 137.80, 136.42 ppm respectively, so the adduct was exo, anti. The next isomer to elute was the endo, syn adduct (**55**) which was obtained in 18.7% yield. The triazolinic protons appeared as doublets of doublets at 5.40 and 4.25 ppm while the vinylic protons and

carbons appeared at 5.98, 5.78 and 132.85, 129.98 ppm respectively, so the adduct was endo, syn. The exo, syn adduct (**56**) eluted last and was obtained in 4.2% yield. The triazolinic protons appeared as doublets at 5.08 and 4.21 ppm while the vinylic protons appeared at 6.26 and 6.16 and ppm, so the adduct was exo, syn.



18. The reaction of p-nitrophenylazide with 7-chloronorbornadiene

None of the adducts formed in this reaction could be isolated because the reaction mixture decomposed as soon as it was loaded on the plate. Even the addition of some triethylamine to the eluent system did not prevent the decomposition which turned the plate black. This decomposition product, presumably some polymeric material, eluted only with

methanol and NMR and IR analysis of this fraction did not show any characteristic peaks and it was not further characterized.

19. Theoretical Calculations

Table 3 lists the computed heats of formation and the HOMO-LUMO energy levels of five 7-substituted norbornadienes. Table 4 lists the calculated heats of formation and strain energies of the mono adducts in the reaction between diphenyldiazomethane and five 7-substituted norbornadienes and their experimental yields. Calculations were performed on an AT&T 6300 PC with MNDO and MMX (including π SCF calculations) programs purchased from Serena Software. The structures were drawn and files written with PCMODEL.

Table 3. Heats of formation and HOMO-LUMO energies (MNDO) of some norbornadienes.

G	ΔH_f (k cal/mole)	Coefficients							
		HOMO				LUMO			
		C_2	C_3	C_5	C_6	C_2	C_3	C_5	C_6
H	63.193	.3627	.3627	-.3589	-.3580	.4347	-.4324	-.4255	.4264
			(-9.4669)				(.8024)		
CH_3	60.572	.3554	.3594	-.3585	-.3550	.4275	-.4263	-.4257	.4244
			(-9.4523)				(.7784)		
Ph	96.714	.2955	.3001	-.3380	-.3377	-.4310	.4341	.4138	-.4130
			(-9.4285)				(.7863)		
Cl	56.047	.2279	.2801	-.4264	-.4252	-.4817	.4808	.3601	-.3596
			(-9.7674)				(.4850)		
O-t.Bu	31.373	.2218	.2101	-.4490	-.4690	.4969	-.4746	-.3364	.3504
			(-9.3450)				(.7983)		

Numbers in parentheses indicate HOMO and LUMO energies; C_2 and C_3 form the <u>syn</u> double bond while C_5 and C_6 form the <u>anti</u> double bond.

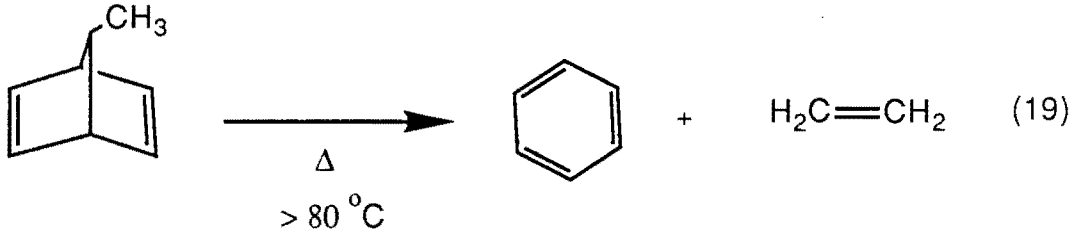
Table 4. Strain energies, heats of formation (MMX with π atoms) and actual yields of the mono adducts in the reaction between diphenyldiazomethane and some 7-substituted norbornadienes.

Group	Stereochemistry	ΔH_f (k cal/mole)	Strain Energy	% Yield
H	Exo	140.5	60.3	100
	Endo	141.3	60.7	0
CH_3	Exo, syn	138.2	65.4	0
	Exo, anti	134.2	61.3	100
	Endo, syn	136.0	62.6	0
	Endo, anti	135.1	61.7	0
Ph	Exo, syn	168.3	73.9	0
	Exo, anti	170.5	75.6	86.8
	Endo, syn	166.7	71.4	8.5
	Endo, anti	171.7	76.3	4.7
Cl	Exo, syn	135.3	65.0	0
	Exo, anti	132.0	61.8	26.0
	Endo, syn	133.3	63.0	16.0
	Endo, anti	133.5	63.2	58.0
O-*t*-Bu	Exo, syn	79.8	63.8	2.5
	Exo, anti	81.1	64.7	36.5
	Endo, syn	80.6	63.9	36.0
	Endo, anti	81.1	64.3	25.0

DISCUSSION OF RESULTS

1. Preparation of 7-methylnorbornadiene

The preparation of 7-methylnorbornadiene was attempted using a modification of the procedure of Story and Fahrenholtz.[41] The Grignard displacement of the 7-*t*-butoxy group using commercially available methylmagnesium bromide solution gave yields below 10%. The yields improved to around 30% when methylmagnesium iodide, prepared in situ, was used as the Grignard reagent. The low yield in this reaction was coupled with problems in distilling the product from the reaction mixture using a spinning band column. The 7-methylnorbornadiene was probably undergoing a cheletropic extrusion reaction to give ethylene and benzene,[2,55] as shown below in Eq. 19.



(19)

This was supported by the fact that more benzene was obtained along with the product after the solvent, benzene, had been distilled away prior to distillation using the spinning band distillation column. The 7-methylnorbornadiene was used as a solution in benzene because it was felt that benzene would not greatly alter the steric course of the reaction.

2. Preparation of the Aryl Azides

The synthesis of phenyl azide was attempted using the "Clayfen" method, but yields were very poor and recovery of the azide was problematic. The diazotization of aniline followed by

displacement using sodium azide worked very well and gave good yields of pure phenyl azide. The p-nitro and p-methoxy analogues were prepared by the same method starting from p-nitro and p-methoxyaniline respectively.

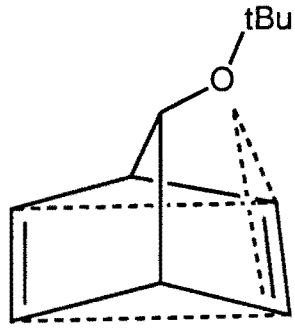
3. The Addition of Diphenyldiazomethane

1,3-Dipolar cycloadditions to norbornene follow the Alder Stein "exo rule".[22,23] Fukui suggested that orbital mixing of the syn 7 C-H bond with the double bond produces asymmetric electron distributions that explain the preference for exo attack on norbornene,[56] and Taniguchi et al. invoked homoconjugation to explain the reduced selectivity for norbornadienes.[57,58] Klumpp et al. suggested that electron rich 7-substituents could enhance the electron density on the syn double bond of a substituted norbornadiene.[15]

The addition of diazoalkanes is a Type I (HOMO dipole controlled) reaction in which the LUMO of the dipolarophile is the other governing factor. Semi-empirical MO calculations support the idea that the syn/anti selectivity is related to the size of these HOMO and LUMO coefficients. The addition of diphenyldiazomethane (3) to 7-methyl norbornadiene (10) is again exo, and MO calculations show that the presence of a methyl group at the 7-position does not alter the HOMO-LUMO coefficients on the double bond carbons. So 10 behaves like norbornadiene and the exo, anti adduct is kinetically preferred. With 7-phenylnorbornadiene, 3 gives two monoadducts and a bis adduct. The exo, anti stereochemistry in the major adduct 5 reflects the favorable stereoelectronic factors just discussed.

The predominance of endo addition in the case of 7-*t*-butoxy norbornadiene was attributed to favorable electronic effects involving the *t*-butoxy group. A lone pair of electrons on the t-butoxy group (or the chloro group) could donate electron density to the syn double bond and, via homoconjugation on the endo face of the diene, to the anti double bond (Fig. 6).[59a]

Figure 6



This increased electron density would steer some of the incoming dipole to the endo side. The delocalization of the π electrons in the 7-phenyl ring of **4** would be less effective at increasing the electron density on the endo face than would a lone pair of electrons, and thus only small amounts of endo adducts were formed in the addition of **3** with **4**. MO calculations confirm that the HOMO coefficients are larger for the syn double bond whereas the LUMO coefficients are larger for the anti double bond. Hence anti addition is the preferred mode of attack. Steric factors would also favor exo addition.

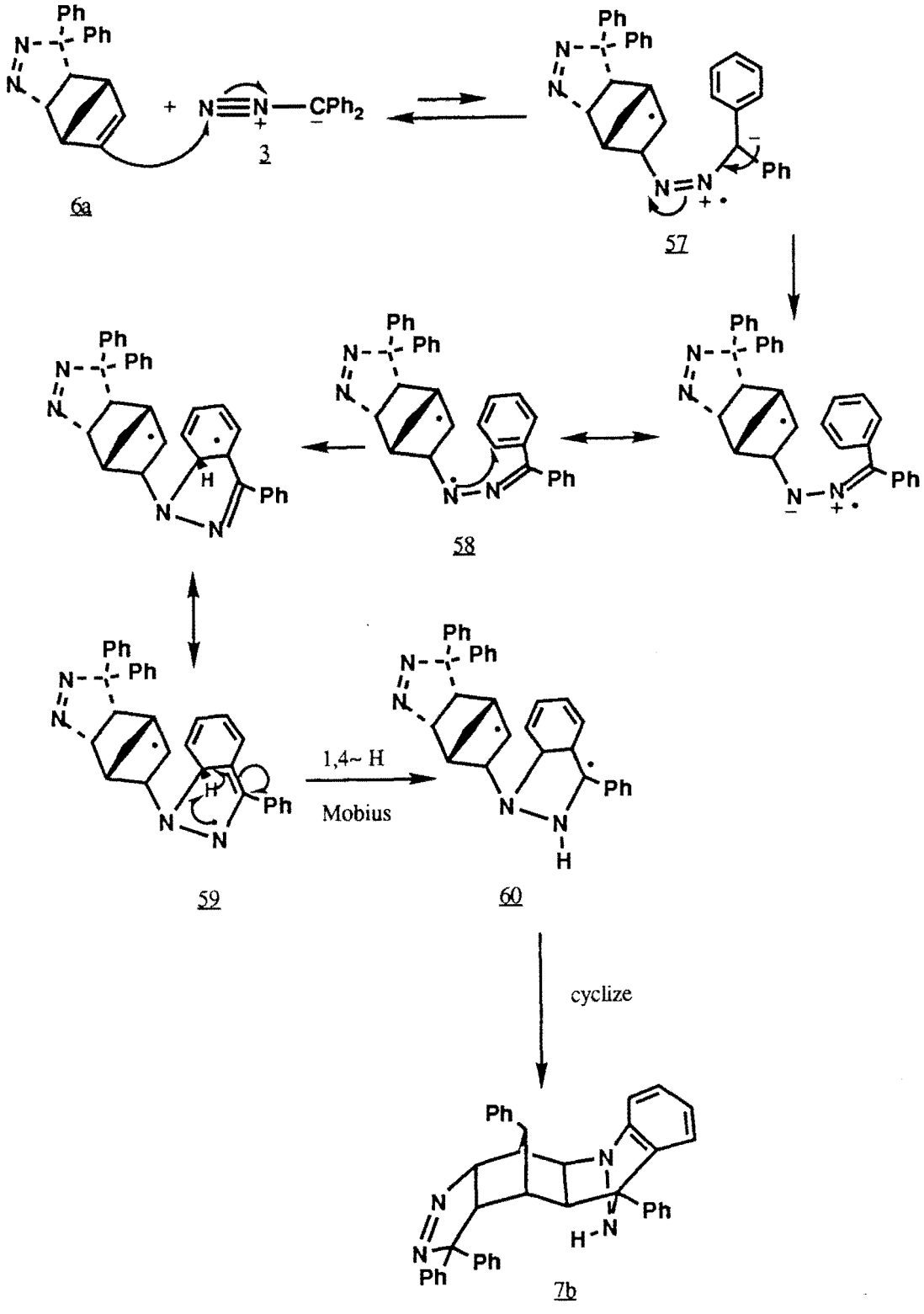
The assignment of an exo, anti-endo, syn stereochemistry to the bis adduct **7** is very significant. The bis adduct could be formed in one of two ways, i.e. either by cycloaddition of **3** on the exo, anti monoadduct **5** or cycloaddition of **3** on the endo, syn monoadduct **6a**. It is unlikely that the second equivalent of the dipole added endo to **5**, because the "exo rule" is very general for norbornenes and because there is no energetic rationale for the subsequent rearrangement of the previously formed exo pyrazoline.

If the endo, syn monoadduct were formed first, then exo addition would be followed during bis adduct formation, but cycloaddition to the endo, syn compound must be very fast to explain the absence of any isolated monoadduct of this stereochemistry. This is supported by the fact that no **7** is formed when **3** is added to the exo, anti mono adduct. The formation of **7b** is probably best explained by the nonconcerted cycloaddition of **3** on the endo, syn

monoadduct. The endo phenyl ring makes the anti double bond more electron deficient and thus enhances the rate of cycloaddition.[59] If the reaction is not concerted and the nitrogen end of the dipole adds first, the product determining transition state for the diradical intermediate **57** occurs late in the reaction pathway.[60-62] Closure to give a normal bis adduct **7a** would be sterically unfavorable, but a nitrogen centered radical **58** could initiate an electrophilic addition on the syn benzene ring. That intermediate, **59**, could then rearomatize via an allowed antarafacial 1,4 H migration to give biradical **60**. which would cyclize to the observed **7b** (Scheme 2).

Photolysis of the exo, anti adducts, **5** and **11**, gave the corresponding symmetrical exo 3,3-diphenyltricyclooctanes **9** and **14**, respectively. The spectroscopic data confirmed the assignment of the exo, anti stereochemistry of these adducts and the 2D NMR showed the long range "W" coupling between the bridge top and vinylic protons.

Scheme 2



4. Reactions with Phenylazide

The addition of phenylazide with norbornadiene gave both the exo and the endo adducts, and that with 7-*t*-butoxynorbornadiene gave three mono adducts, all except the endo, anti isomer. According to Reiner Sustmann's classification, phenylazide is a Type II dipole.[21] This means that the HOMO of both dipole and dipolarophile would influence the addition.

Calculations done by Alston and Ottenbrite[32] and in this laboratory reveal that when there is a substituent on the 7-position, the LUMOs are concentrated on the anti double bond while the HOMOs are concentrated on the syn double bond. Thus in a reaction controlled by both the HOMO and LUMO of the dipolarophile, one would expect both syn and anti additions. The case of exo vs endo addition involves more steric than electronic factors, and the exo addition is less hindered. In the reaction with 7-*t*-butoxy norbornadiene the endo, syn adduct was the major isomer. The explanation given was that the coefficient of the HOMO of the syn double bond is particularly high on the endo side, or that secondary orbital effects of the approaching azide are either attractive on the endo side or particularly repulsive on the exo, anti side.

The distribution of adducts in additions of phenylazide is shown in Table 5.

Table 5. Distribution of adducts in the addition of phenylazide

G	% Adduct					% Recovery
	Exo, syn	Exo, anti	Endo, syn	Endo, anti	Bis	
H	-	92	8	-	-	a
CH_3	-	62.2	18.7	14.2	2.9, 2.0	67
Ph	-	57.6	10.2	32.2	-	82
Cl	-	31.4	29.5	39.1	-	58
O-t.Bu	15	30	55	-	-	b

a: Ref. 14, b: Ref. 15

The reaction of phenylazide with 7-phenylnorbornadiene gave three mono adducts, all except the exo, syn isomer. The exo, anti isomer was the major product. The fact that no exo, syn adduct was formed could be explained by the steric hindrance that the bulky phenyl ring would pose for the incoming azide. The anti addition (both exo and endo) accounted for about 90% of the total addition. Since the coefficients of the LUMO are higher on the anti double bond of the norbornadiene, one could assume that this reaction involved the HOMO of the phenylazide. The excess of exo attack suggests that it is still the sterically less hindered side.

The reaction with 7-methylnorbornadiene also gave three mono adducts, and again the exo, anti adduct was the major isomer. The presence of a methyl group at the 7-position of norbornadiene does not appreciably alter the HOMO/LUMO energies of the double bonds and that may be why the endo, syn and endo, anti modes of addition were comparable. Favorable steric factors involving the pi lobes promote exo addition from the anti face while steric hindrance by the methyl group precludes the same addition from the syn face. Two bis adducts, the cis and trans exo, anti-endo, syn, were also formed along with the mono adducts.

The reaction with 7-chloronorbornadiene gave the same three mono adducts as the previous two norbornadienes. The predominance of anti addition (70%) suggests that the reaction is controlled more by the LUMO of the norbornadiene than by its HOMO. The predominance of endo addition (69%) is due more to electronic factors than steric factors (in the case of the parent and 7-methylnorbornadiene). Endo addition predominated in the dipolar additions to 7-*t*-butoxy and 7-chloronorbornadiene. This could probably be due to a favorable secondary orbital interaction initiated by the lone pair of electrons on the 7-substituent which steers the incoming dipole to the endo side, even though the steric factors favor exo addition. It must be mentioned that all these adducts were so unstable during chromatography that they turned black as soon as they were loaded on the silica gel plate. They were, however, more stable if some triethylamine was used along with the eluent system. Apparently addition of a small amount of base

neutralized the acidic effect of the silica gel on these sensitive triazolines. The photolytic conversion of the triazolines to the symmetrical azirines was attempted but only a black residue was obtained in these cases. Probably the triazolines first ring opened and generated the nitrenes (along with loss of nitrogen) which underwent some further reaction to give the black residue.

5. Reactions with p-methoxyphenylazide

The distribution of adducts in the addition of p-methoxyphenylazide to some 7-substituted norbornadienes is shown below in Table 6.

Table 6. Distribution of adducts in the addition of p-methoxyphenylazide

G	% Adduct					% Recovery
	Exo, syn	Exo, anti	Endo, syn	Endo, anti	Bis	
H	95	-	5	-	-	80
CH_3	-	56.6	19.1	24.3	-	47
Ph	-	61.5	12.6	13.7	12.3	93
Cl	-	26.2	13.1	60.7	-	28
O-t-Bu	7.8	21.2	49.3	21.8	-	20

The reaction of p-methoxyphenylazide with norbornadiene gave both the exo (95%) and the endo (5%) adducts. The reaction with 7-methylnorbornadiene gave three adducts, all except the exo, syn isomer. The exo, anti isomer was formed as the major product and was isolated in 57% yield. As in the reaction with phenylazide the two endo adducts were formed in comparable amounts, 19% for the syn and 24% for the anti. 7-Phenylnorbornadiene gave four adducts with p-methoxyphenylazide, three mono and one bis. Again due to steric reasons the

exo, syn isomer was not formed. The other exo adduct was the major product (62%), and the two endo isomers were formed in equal amounts (12.5% each). The bis adduct had an exo, anti-endo, syn stereochemistry, and was presumably formed by the addition of the second equivalent of phenylazide to the endo, syn mono adduct.

Based on previous knowledge of the reactions of 7-chloro and 7-*t*-butoxynorbornadiene with diphenyldiazomethane and phenylazide, one would expect that the addition of p-methoxyphenylazide to these two dienes would also give predominantly endo addition, and that was indeed the case. 7-Chloronorbornadiene reacted with p-methoxyphenylazide to give all the mono adducts except the exo, syn isomer. The endo, anti adduct (49%) was formed in slight excess of its other endo isomer (36%), and the exo adduct accounted for the remaining 15%. The reaction with 7-*t*-butoxy norbornadiene gave all the four mono adducts, and once again endo addition (71%) predominated (exo addition was 29%). The endo, syn isomer was the major product (49%) followed by nearly equal amounts of the endo, anti and exo, anti adducts (22% and 21% respectively). An inspection of the model reveals that the *t*-butoxy group at the 7-position is far removed from the syn double bond and would not hinder an approaching dipole. Accordingly, a small amount (8%) of the exo, syn isomer was formed in this reaction.

The predominance of anti addition suggests that the HOMO of the dipole (and thus the LUMO of the norbornadiene) plays a greater part in the addition than its LUMO. The lone pair of electrons in the case of the 7-chloro and the 7-*t*-butoxynorbornadiene again promotes more of endo addition through a secondary orbital interaction. The same trend was observed during the addition of hexachlorocyclopentadiene to various 7-substituted norbornadienes. When there are no lone pairs of electrons present at the 7-position, exo addition predominates because of favorable steric effects and overlap between the pi orbitals of the reactants.

6. Reactions with p-nitrophenylazide

The distribution of adducts in the addition of p-nitrophenylazide to some 7-substituted norbornadienes is shown below in Table 7.

Table 7. Distribution of adducts in the addition of p-nitrophenylazide

G	% Adduct					% Recovery
	Exo, syn	Exo, anti	Endo, syn	Endo, anti	Bis	
H	-	100	-	-	-	a
CH_3	-	67.2	14.6	18.2	-	57
Ph	-	33.1	-	66.9	-	59
O-t.Bu	4.2	38.4	18.7	38.7	-	69

a: Ref. 27

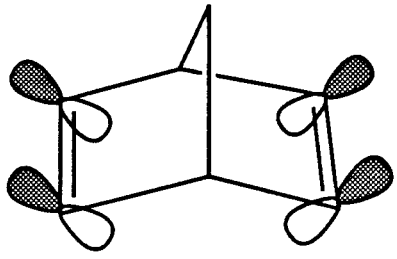
The reaction of p-nitrophenylazide with 7-methylnorbornadiene gave three mono adducts, again all except the exo, syn isomer. The other exo isomer was the major product (67%) while the two endo isomers were formed in comparable amounts (15% and 18% for the syn and anti isomers respectively). The addition followed the same trend as in the additions to the other two azides. The surprising result was in the addition of p-nitrophenylazide to 7-phenylnorbornadiene. The major adduct was the endo, anti isomer (67%) while the exo, anti adduct accounted for the rest. None of the syn isomers were formed. This is surprising because the other additions of this diene all resulted in predominantly exo addition, similar to that of the 7-methyl analog. The reaction with 7-*t*-butoxynorbornadiene gave all four adducts, as in the reaction with the p-methoxyphenylazide. The endo adducts (57%) predominated over the exo isomers (43%) but not by much. The amounts of the exo-anti and endo, anti adducts

were about the same (38% each). None of the adducts formed in the reaction with 7-chloronorbornadiene could be isolated because they decomposed as soon as they were loaded on the plate. Even the addition of triethylamine did not help in the chromatography. It has been observed before that the adducts of 7-chloronorbornadiene are quite unstable and the triazoline adducts are perhaps the least stable of them all.

7. Theoretical Considerations

Fukui's Molecular Orbital Theory involving the HOMO and the LUMO of the reactants are applicable if the transition state (TS) of the reaction is closer to the reactant side than the product side. Studies have revealed that these cycloadditions do indeed have early (and hence more reactant like) TS,[1,63-65] and so it is felt that the frontier orbitals do influence the course of the reaction. The results suggest that for the additions to Type I dipoles, such as diphenyl-diazomethane, the HOMO of the dipole is the controlling factor and hence anti addition is preferred (because the coefficient of the LUMO of the norbornadiene is greater on the anti double bond). For reactions with Type II dipoles, such as phenyl azides, the HOMOs and LUMOs of both the reactants may be important. The predominance of anti addition in the additions to the three different phenylazides suggests that the LUMO of the diene may be more involved than its HOMO. Overall, norbornadienes prefer exo addition because of steric reasons, the π overlap between the incoming dipole and the diene is better on the exo face than on the endo face, as shown in Fig. 7.

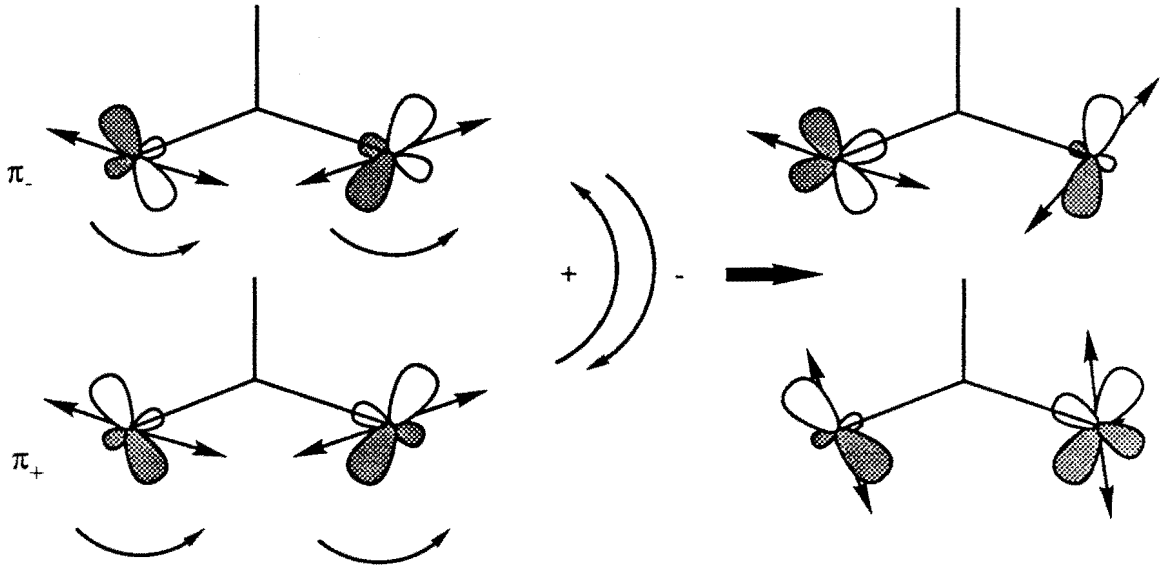
Figure 7



This is observed in the additions to the parent, 7-methyl and 7-phenylnorbornadiene, the only exception being the addition of the 7-phenyl compound to p-nitrophenylazide where the endo isomer was the major product. With substituents that have a lone pair of electrons on the atom bonded at the 7-position endo addition predominates.

Frank-Neumann and Sedrati claimed that the preference of endo, anti addition in the addition of diazoalkanes to 7-halonorbornadienes arises from the interaction of the anti pi bond with the $\sigma^*_{C\text{-}X}$ bond which lowers the LUMO of the anti orbital.[12] But Houk argues that the STO-3G calculations done on the norbornadienes did not reveal any such interaction between the anti π bond and the $\sigma^*_{C\text{-}X}$ bond, although a lowering of the LUMO on the anti double bond is indeed observed.[40] He also suggests that the orbitals are "tilted" in such a way to make endo addition more feasible (Fig. 8).

Figure 8



The polarization of the norbornadiene orbitals by substituents at the 7-position is accompanied by a change in the "tilt" of these orbitals. Fig. 8 shows how this occurs. A donor, or negative charge, on the "right hand side" and/or acceptor, or positive charge, on the "left hand side" of norbornadiene causes π_+ to mix into π_- in a plus fashion on the right hand side and π_- into π_+ in a negative fashion on the right side. The arrows indicate the orientation of the resultant p orbitals. Houk points out that the presence of an electronegative substituent actually decreases the rate of the reaction and that the polarization of the HOMO away from the anti double bond diminishes the rate of endo, anti attack. The predominance of endo addition, he claims, is more because the exo, anti pathway is deactivated (exo, syn is sterically unfavorable) than due to an activation of endo addition.

Gajewski points out that the preference of the endo mode of Diels-Alder addition of cyclopentadiene to itself is due to a favorable volume of activation (ΔV^{act}) in the transition state.[66] The ΔV^{act} is lower for the endo transition state than for the exo transition state, and he claims that this is influenced by the internal pressure of the solvent. One feels that such an

argument might not be too relevant here as the internal pressure of hexane is not high enough to cause significant changes in the volumes of activation of the transition states of the various adduct stereochemistries.[67,68] Another possible explanation is that a lone pair of electrons on the 7-substituent interacts with the syn double bond which in turn increases the electron density on the anti double bond.[59a] This increased electron density which favors exo addition in similar cases, helps explain the increased formation of endo adducts.

The calculation of the strain energies of the adducts in the reactions with diphenyldiazomethane does not show any correlation with the actual distribution of the adducts. The adduct with the lowest computed strain energy and heat of formation was not necessarily the one that was the major adduct in the reaction. Also the relative strain energies and heats of formation do not correspond to relative amounts of the adducts in the experiment. This suggests that these cycloaddition product yields are kinetically determined. Heats of formation for the dienes calculated by MMX and MNDO are similar. Therefore we feel that the numbers are reliable. Although the differences in the Molecular Mechanics heats of formation are small, a comparison of results feom MMX with and without π and PCMODEL with π show similar trends. Entropic factors were not considered in these calculations.

8. The effect of the 7-substituents

The presence of a group at the 7-position of norbornadiene creates a difference in the energy levels of the double bonds that is expressed in the lack of regioselectivity in 1,3-dipolar cycloadditions. The groups that were chosen represented electron donating (methyl and *t*-butoxy), electron conjugating (phenyl), and net withdrawing (chloro) substituents. Molecular orbital calculations show that these substituents cause the LUMOs to be concentrated on the anti double bonds while the HOMOs are concentrated on the syn double bonds.[32,40,52] The distribution of adducts formed during the addition of the dipoles to the five 7-substituted

norbornadienes are shown in Tables 8-12. The percentages of the endo, syn mono adducts have been corrected to include the bis adducts, as it has been shown that the bis adducts have an exo, anti-endo, syn stereochemistry and are formed by the addition of the second equivalent of the dipole to the endo, syn mono adduct.

Table 8. Distribution of mono adducts in the addition to norbornadiene

Dipole	% Adduct		Ref.
	Exo	Endo	
Diphenyldiazomethane	100	-	9
Phenylazide	92	8	4
p-Methoxyphenylazide	95	5	
p-Nitrophenylazide	97	3	27

Table 9. Distribution of mono adducts in the addition to 7-methylnorbornadiene

Dipole	% Adduct				Ref.
	Exo, syn	Exo, anti	Endo, syn	Endo, anti	
Diphenyldiazomethane	-	100	-	-	
Phenylazide	-	62.2	23.6	14.2	
p-Methoxyphenylazide	-	56.6	19.1	24.3	
p-Nitrophenylazide	-	67.2	14.6	18.2	

Table 10. Distribution of mono adducts in the addition to 7-phenylnorbornadiene

Dipole	% Adduct				Ref.
	Exo, syn	Exo, anti	Endo, syn	Endo, anti	
Diphenyldiazomethane	-	86.8	8.5	4.7	
Phenylazide	-	57.6	10.2	32.2	
p-Methoxyphenylazide	-	61.5	26	12.6	
p-Nitrophenylazide	-	33.1	-	66.9	

Table 11. Distribution of mono adducts in the addition to 7-chloronorbornadiene

Dipole	% Adduct				Ref.
	Exo, syn	Exo, anti	Endo, syn	Endo, anti	
Diphenyldiazomethane	-	26	16	58	13
Phenylazide	-	31.4	29.5	39.1	
p-Methoxyphenylazide	-	26.2	13.1	60.7	
p-Nitrophenylazide	-	-	-	-	a

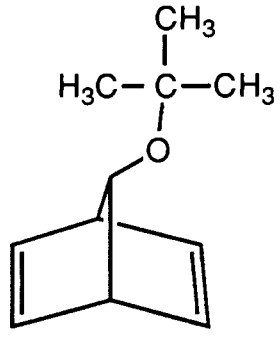
a: No adduct could be isolated.

Table 12. Distribution of mono adducts in the addition to 7-*t*-butoxynorbornadiene

Dipole	% Adduct				Ref.
	Exo, syn	Exo, anti	Endo, syn	Endo, anti	
Diphenyldiazomethane	2.5	36.5	36	25	10
Phenylazide	15	30	55	-	15
p-Methoxyphenylazide	7.8	21.2	21.8	49.3	
p-Nitrophenylazide	4.2	38.4	18.7	38.7	

For reactions with Type I dipoles the LUMO of the norbornadiene would be the determining factor, and hence anti addition predominates. This is what is observed for all the substituents. This electronic demand is complemented by steric factors involving the substituent and norbornadiene itself. The tilting of the π lobes of the norbornadiene cause the exo side to be more accessible to the dipole than the endo face. The bulk of a substituent at the 7-position precludes the addition of a dipole on the exo, syn face of the diene. Accordingly no exo, syn adduct is observed for the reactions with the methyl, phenyl and chloro substituents. The exception is the *t*-butoxy group which gives a small amount of the exo, syn isomer with the dipoles. At first this seemed rather surprising because the *t*-butoxy group appeared to be the bulkiest of all the substituents considered and should therefore form the least amount of the exo, syn isomer. This is easily explained by looking at the energy minimized structure of the 7-*t*-butoxynorbornadiene in which the *t*-butyl group is positioned away from the syn double bond,[52] as shown in Fig. 9. The effective size of the *t*-butoxy is more comparable to that of an n-propyl group than to that of a *t*-butyl group.

Figure 9



Another interesting feature is the predominance of endo addition in the case of 7-chloro amd 7-*t*-butoxynorbornadiene. This has been explained to be a consequence of the secondary orbital interactions[69] induced by the lone pair of electrons on the chlorine and the oxygen respectively. It is interesting to note that in studies carried out by Houk and others, endo addition predominates if the substituent at the 7-position has a lone pair of electrons.[12,29,40,70-72] In all other additions exo addition predominated. Thus it is clear that in the absence of favorable electronic effects, steric factors will promote exo addition. The question syn vs. anti addition on the other hand depends on the energy state of the dipoles, though anti addition seems to predominate. The balance between syn and anti addition is quite delicate and subtle variations could cause a shift to either side.

EXPERIMENTAL

1. General information.

Chemicals used were from Aldrich Chemical Company except where mentioned. All solvents were purchased from Fisher Scientific Inc. and used as such except where mentioned, and the norbornadienes, except 7-methylnorbornadiene, were purchased from Frinton Labs. All melting points were determined on a calibrated Fisher-Johns melting point block. Thin layer chromatography (TLC) was performed using plastic backed silica gel coated plates (EM Science and Eastman Kodak Company). All chromatographic separations were performed by rotational TLC using a Chromatotron (Harrison Research Model 7294) with 1 mm, 2 mm and 4 mm plates coated with silica gel 60 PF_{254}, containing calcium sulfate as binder (EM Science). The force field calculations were done using the MMX molecular mechanics program with π SCF calculations on an AT&T 6300 PC. The MNDO calculations were done on the same machine using the program purchased from Serena Software. Structures were drawn and files were written to disk using PCMODEL. Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded using chloroform-d as the solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane as the internal standard. Low field ^{1}H NMR spectra were recorded using a 60 MHz, Varian 360A spectrometer. High field ^{1}H NMR, ^{13}C NMR and two dimensional NMR spectra were recorded using a Varian VXR 300 Spectrometer. Infrared spectra were recorded on a Perkin Elmer 1310 Instrument with sodium chloride cells with a fixed path length of 0.1 mm. Ultra violet spectra were recorded using a Hewlet Packard diode array spectrophotometer. Photolysis of the cycloadducts were done at 366 nm done using a Bradford Scientific Inc. photolysis chamber. Combustion analyses were performed by Microtech Laboratories, Skokie, Illinois, and by Midwest Microlab Ltd., Indianapolis, Indiana. High resolution mass spectra were recorded on a Varian -MAT 731

spectrometer with Electron Ionization (EI) on a solids probe at 10, 000/1 resolution with per fluorokerosene (PFK) as the internal standard.

2. Synthesis of 7-methylnorbornadiene

The synthesis of this hydrocarbon has been reported earlier.[41] However it must be mentioned that the yields for this reaction are rather poor. It must also be mentioned that in this Grignard reaction, the methylmagnesium iodide is a better reagent than the methylmagnesium bromide as it gives much better yields. The 7-methylnorbornadiene was used as a solution in benzene.

In a 3 necked, 500 mL flask, fitted with a mechanical stirrer, flame dried and purged with argon, was placed 14.0 g of magnesium turnings and 82 g methyl iodide (0.56 mmoles) in 350 mL of anh. ether. To this was added 300 mL benzene, 35 g of 7-*t*-butoxynorbornadiene (0.22 mmoles) and the mixture was refluxed for 4 days. After this time the excess Grignard reagent was destroyed with about 100 mL of water and the benzene solution decanted. The solvent was removed by distillation at atmospheric pressure, and upon distillation at a pressure of 0.05 atm, 4.4 g (.04 mmoles) of 7-methylnorbornadiene was obtained in 19.1% yield (determined by mass and NMR).

3. Synthesis of the aryl azides

The synthesis of phenyl azide has been reported earlier.[42] Two different methods were tried in this study: the clayfen method[43,44] and the aniline method.[42] Though the authors claim a high percent yield for the clayfen method, it failed to work under our laboratory conditions. The aniline method on the other hand worked smoothly and gave a high yield (62.5%, determined by mass and NMR).

To 9.3 g of aniline (0.1 mmole) in a 500 mL, 2 necked flask equipped with a stirrer, was added 22.5 mL conc. hydrochloric acid and 40 mL water. To this mixture, kept in a dry ice

bath, was added a solution of sodium nitrite (7.4 g in 25 mL water) and the mixture stirred for an hour. To the solution, which was transferred to a 2 L beaker, was added a solution of sodium azide (6.5 g in 25 mL water). The organic layer was then extracted with ether, dried over anh. potassium sulfate and the solvent removed by rotary evaporation to give 7.4 g (0.06 mmoles) of phenylazide (verified by TLC and NMR) in 62.5% yield.

To 12.3 g of p-methoxyaniline (0.1 mmole) in a 500 mL, 2 necked flask equipped with a stirrer, was added 22.5 mL conc. hydrochloric acid and 40 mL water. To this mixture, kept in a dry ice bath, was added a solution of sodium nitrite (7.4 g in 25 mL water) and the mixture stirred for an hour. To the solution, which was transferred to a 2 L beaker, was added a solution of sodium azide (6.5 g in 25 mL water). The organic layer was then extracted with ether, dried over anh. potassium sulfate and the solvent removed by rotary evaporation to give 8.9 g (0.06 mmoles) of p-methoxyphenylazide (verified by TLC and NMR) in 60% yield.

To 13.8 g of p-nitroaniline (0.1 mmole) in a 500 mL, 2 necked flask equipped with a stirrer, was added 22.5 mL conc. hydrochloric acid and 40 mL water. To this mixture, kept in a dry ice bath, was added a solution of sodium nitrite (7.4 g in 25 mL water) and the mixture stirred for an hour. To the solution, which was transferred to a 2 L beaker, was added a solution of sodium azide (6.5 g in 25 mL water). The organic layer was then extracted with ether, dried over anh. potassium sulfate and the solvent removed by rotary evaporation to give 8.7 g (0.05 mmoles) of p-nitrophenylazide (mp 70.1 ^{o}) in 52% yield.

4. Reaction of diphenyldiazomethane with 7-phenylnorbornadiene

To 7-phenylnorbornadiene (**4**) (2.0 g, 12.0 mmoles, Frinton Labs) was added diphenyldiazomethane[73] (**3**) (1.9 g, 10.0 mmoles). The mixture was dissolved in 10.0 mL of hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. At the end of one month, the mixture was subjected to rotational TLC using a 2 mm plate and petroleum ether-ether gradient elution. The unreacted **3** eluted first as a dark red band (588 mg, 3.0 mmoles) and was followed

by the unreacted diene. Among the adducts, the exo, anti adduct (**5**) eluted first, followed by the endo, anti mono adduct (**6**) and the exo, anti-endo, syn bis adduct (**7**) in that order. Upon evaporation of the solvent from the product fractions and recrystallization from ether, 1856 mg (5.1 mmoles, 56.1%) of colorless crystals **5** were obtained. From the next fraction 100 mg (0.3 mmoles, 3.1%) of colorless crystals of **6** were obtained in a similar fashion. The bis adduct, 140 mg (0.5 mmoles, 5.5%), was obtained as a colorless solid. Besides the adducts, 38 mg (0.2 mmoles, 2.3%) of yellow crystals of tetraphenylketazine (**8**) were also obtained. The overall recovery was about 92%. All calculations were based on the number of moles of diphenyldiazomethane that reacted. The mono adduct was photolyzed at 366 nm, in acetone until evolution of nitrogen ceased, to yield colorless crystals of the cyclopropyl compound (**9**).[59]

5,5,Anti-10-triphenyl exo-3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**5**)

mp 197-198 ^{o}C; ^{1}H NMR 7.1-7.6 (13H m, Ar), 6.68 (2H d, ortho Hs on C_{10} phenyl ring), 6.24 (1H m, H_9), 6.03 (1H m, H_8), 5.37 (1H d, J=6.5 Hz, H_2), 3.95 (1H s, H_1), 3.05 (1H d, J=6.5 Hz, H_6), 2.6 (1H s, H_{10}), 2.5 (1H s, H_7); IR (CCl4) 3000, 1600, 1550, 1500, 1450, 1320 cm^{-1}; ^{13}C NMR 143.25, 141.29, 141.26 (Ar ipso), 138.64 (C_9), 133.82 (C_8), 128.54, 128.37, 128.19, 127.68, 127.55, 127.40, 127.18, 125.63 (Ar), 101.13 (C_2), 96.83 (C_5), 56.12 (C_{10}), 49.66 (C_6), 49.23 (C_1), 47.46 (C_7). Anal. Calcd. for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12. Found: C, 85.73; H, 6.04.

5,5,Anti-10-triphenyl endo-3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**6**)

mp 173-174.5 ^{o}C; ^{1}H NMR 7.0-7.73 (15H m, Ar), 6.0 (1H m, H_9), 5.6 (1H m, H_8), 4.62 (1H m, H_2), 4.02 (1H s, H_1) 3.59 (1H m, H_6), 3.37 (1H s, H_{10}), 3.2 (1H s, H_7) ; IR (CCl4) 3600, 3060, 3000, 1950, 1875, 1825, 1600, 1550, 1490, 1445 cm^{-1}; ^{13}C NMR 144.53, 142.49, 138.63 (Ar ipso), 132.34 (C_9), 130.23 (C_8), 128.77, 128.74, 128.39, 128.35, 127.96, 127.64, 127.21, 126.75 (Ar), 100.74 (C_2), 98.41 (C_5), 64.15 (C_{10}), 51.50 (C_1), 50.35 (C_6), 51.01 (C_7). Anal. Calcd. for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12. Found: C, 85.86; H, 6.08.

4,5-Benzo-6,10,10,anti-14-tetraphenyl-exo-2,7-endo-9,13-tetraza-3,11,12,15-tetracyclo-[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]pentadeca-4,11-diene (**7**) mp 168-171 ^{o}C; ^{1}H NMR 6.70-7.85 (15H m, Ar) 5.45 (1H m, H_{12}), 5.01 (1H d, J=7.0 Hz, H_2), 4.40 (1H m, H_1), 2.75 (1H m, H_8), 2.49 (1H s, H_{13}), 2.16 (1H s, H_6), 1.93 (1H s, H_7); IR (CCl4) 3300, 3000, 1600, 1490, 1445 cm^{-1}; ^{13}C NMR 143.12, 142.79, 142.06, 141.20, 137.65 (Ar ipso), 129.01, 128.77, 128.13, 127.93, 127.53, 127.47, 127.12, 126.90, 126.76, 126.52, 125.88 (Ar), 103.62 (C_9), 97.10 (C_5), 94.52 (C_{12}), 93.34 (C_2), 49.98 (C_{13}), 46.42 (C_8), 46.24 (C_6), 43.49 (C_1), 40.51 (C_7). Anal. Calcd. for $C_{39}H_{32}N_4$: C, 84.17; H, 5.79. Found: C, 84.20; H, 5.81.

3,3,Anti-8-triphenyl exo tricyclo[3.2.1.0^{2,4}]oct-6-ene (**9**) mp 151-152 ^{o}C; ^{1}H NMR 6.75-7.49 (15H m, Ar) 6.32 (2H s, $H_{6,7}$), 3.40 (2H s, $H_{1,5}$), 2.90 (1H s, H_8), 1.90 (2H s, $H_{2,4}$); IR (CCl4) 3000, 1600, 1500, 1445,1375 cm^{-1}; ^{13}C NMR 141.1, 142.7 (Ar ipso), 129.30, 128.50, 128.30, 127.60, 127.55 (Ar), 138.4 ($C_{6,7}$), 54.0 ($C_{3,8}$), 48.7 ($C_{1,5}$), 39.8 ($C_{2,4}$). Anal. Calcd. for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.16; H, 6.66.

5. Reaction of diphenyldiazomethane with 7-methylnorbornadiene

To 7-methylnorbornadiene (**10**) (1.3 g, 12.0 mmoles) was added **3** (1.9 g, 10.0 mmoles) the mixture dissolved in 10.0 mL of hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After a month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The unreacted **3** lost its color as soon as it was loaded on to the plate. This band nevertheless eluted out first to give 50 mg (0.3 mmoles, 3.0%) of colorless crystals of tetraphenylethylene (**12**). The unreacted diene eluted next but could not be visualized as it does not have any chromophores. The next compound to elute was **8**, of which 160 mg (0.9 mmoles, 8.9%) were obtained as colorless crystals. The exo, anti isomer (**11**) eluted next, and recrystallization yielded 710 mg (2.4 mmoles, 23.7%) of colorless crystals. The last fraction was benzhydrol (**13**) of which 430 mg (2.3 mmoles, 23.3%) were obtained as white crystals. The total recovery was about 59%. The mono adduct was

photolyzed at 366 nm, in acetone in an NMR tube till evolution of nitrogen ceased, to yield colorless crystals of the cyclopropyl compound (**14**).

Anti-10-methyl-5,5-diphenyl exo-3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**11**) mp 135-136 ^{o}C; ^{1}H NMR 7.2-7.4 (10H m, Ar), 6.10 (2H s, $H_{8,9}$), 5.20 (1H d, J=6.4 Hz, H_2), 3.33 (1H s, H_1), 2.81 (1H d, J=6.4 Hz, H_6), 1.91 (1H s, H_7), 1.33 (1H q, J=6.0 Hz, H_{10}), 0.54 (3H d, J=6.0 Hz, CH_3); IR (CCl4) 3000, 1600, 1490, 1445 cm^{-1}; ^{13}C NMR 143.61, 141.61 (Ar ipso), 128.45, 128.09, 127.96, 127.52, 127.40, 126.91 (Ar), 138.40 (C_9), 133.23 (C_8), 103.21 (C_2), 101.60 (C_5), 49.85 (C_1), 49.58 (C_{10}), 49.40 (C_7), 47.02 (C_6), 10.91 (CH_3). Anal. Calcd. for $C_{21}H_{20}N_2$: C, 83.96; H, 6.71. Found: C, 84.25; H, 6.80.

Anti-8-methyl-3,3-diphenyl exo tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**14**) mp 129.5-130.5 ^{o}C; ^{1}H NMR 7.03-7.60 (Ar), 6.48 (2H s, $H_{6,7}$), 2.85 (2H s, $H_{1,5}$), 1.79 (2H s, $H_{2,4}$), 1.69 (1H q, J=6.0 Hz, H_8), 0.45 (3H d, J=6.0 Hz, CH_3); IR (CHCl3) 3000, 2980, 1600, 1490, 1445, 1375, 1305 cm^{-1}; ^{13}C NMR 148.70, 143.43 (Ar ipso), 126.04, 125.76, (Ar para), 129.15, 128.52, 128.30, 127.63 (Ar), 138.55 ($C_{6,7}$), 58.80 (C_3), 48.64 ($C_{1,5}$), 43.94 (C_8), 39.65 ($C_{2,4}$), 12.34 (CH_3). Anal. Calcl. for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.75; H, 7.55.

6. Reaction of phenylazide with 7-phenylnorbornadiene

To **4** (2.0 g, 12.0 mmoles) was added phenylazide (**15**) (1.2 g, 10.0 mmoles). The mixture was dissolved in 10.0 mL of hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After a month the mixture was subjected to rotational TLC using a 2mm plate, impregnated with triethylamine, and a hexane-ether gradient (containing 1% by volume of triethylamine) elution. Phenylazide and the 7-phenylnorbornadiene have very similar R_f values and hence elute at almost the same rate with the azide eluting first. When the solvent was removed 260 mg (2.2 mmoles) of **15** and 870 mg (52 mmoles) of the diene were recovered.

The endo, syn adduct (**16**) eluted next and recrystallization from ether yielded 170 mg (0.6 mmoles, 7.3%) of colorless crystals. The next fraction to elute out was the exo, anti isomer (**17**) which on recrystallization from ether afforded 983 mg (3.4 mmoles, 42.2%) of colorless crystals. The endo, anti adduct (**18**) was the next fraction which when recrystallized afforded 558 mg (1.9 mmoles, 23.8%) of a white fluffy powder. The total recovery in this reaction was about 82%. The separations were not possible without triethylamine in the eluting solvent system.

5,Syn-10-diphenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**16**)

mp 141-141.5 ^{o}C; ^{1}H NMR 6.95-7.39 (10H m, Ar), 6.07 (1H m, H_9), 5.85 (1H m, H_8), 5.14 (1H d of d, J=9.0 Hz, J=3.0 Hz, H_2), 4.19 (1H d of d, J=9.0 Hz, J=3.0 Hz, H_6), 4.01 (1H s, H_1), 3.84 (1H s, H_7), 3.20 (1H s, H_{10}); IR (CCl4) 3000, 1600, 1495, 1470, 1450, 1355 cm^{-1}; ^{13}C NMR 138.07 (Ar ipso), 136.49 (C_9), 134.05 (C_8), 129.40, 128.85, 126.93, 126.80, 122.07, 113.88 (Ar), 85.57 (C_2), 62.08 (C_6), 58.86 (C_{10}), 49.48 (C_1), 48.51 (C_7). Anal. Calcd. for $C_{19}H_{17}N_3$: C, 79.42; H, 5.96. Found: C, 79.39; H, 5.99.

5,Anti-10-diphenyl exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**17**)

mp 130.5-131.5 ^{o}C; ^{1}H NMR 7.00-7.48 (10H m, Ar), 6.10 (2H s, $H_{8,9}$), 5.00 (1H d, J=10.0 Hz, H_2), 4.15 (1H d, J=10.0 Hz, H_6), 3.72 (1H s, H_1), 3.60 (1H s, H_7), 3.10 (1H s, H_{10}); IR (CCl4) 3000, 1600, 1500, 1470, 1450, 1355 cm^{-1}; ^{13}C NMR 140.39, 138.21 (Ar ipso), 135.35 (C_9), 134.79 (C_8), 129.85, 129.10, 128.13, 126.37, 122.69, 114.44 (Ar),.88.86 (C_2), 62.14 (C_6), 57.15 (C_{10}), 52.47 (C_1), 51.13 (C_7). Anal. Calcd. for $C_{19}H_{17}N_3$: C, 79.42; H, 5.96. Found: C, 79.69; H, 6.00.

5,Anti-10-diphenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**18**)

mp 192.5-194.5 ^{o}C; ^{1}H NMR 6.70-7.41 (10H m, Ar), 5.74 (1H m, H_9), 5.63 (1H m, H_8), 5.40 (1H d of d, J=10.9 Hz, J=3.7 Hz, H_2), 4.44 (1H d of d, J=10.9 Hz, J=3.7 Hz, H_6), 3.85 (1H s, H_1), 3.70 (1H s, H_{10}), 3.15 (1H s, H_7); IR (CCl4) 3000, 1600, 1495, 1470, 1450, 1355 cm^{-1}; ^{13}C NMR 140.74, 138.26 (Ar ipso), 133.57 (C_9), 131.10 (C_8), 130.19, 129.34,

128.65, 120.13, 116.38, 115.05, 114.87, 114.74 (Ar), 86.58 (C_2), 61.76 (C_6), 60.75 (C_{10}), 52.37 (C_1), 51.53 (C_7). Anal. Calcd. for $C_{19}H_{17}N_3$: C, 79.42; H, 5.96. Found: C, 79.03; H, 5.55.

7. The reaction of phenylazide with 7-methylnorbornadiene

To a solution of **10** (1.3 g, 12.0 mmoles) was added **15** (1.2 g, 10.0 mmoles), the mixture dissolved in 10 mL hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After 30 days the mixture was subjected to rotational TLC on a 2 mm plate with a pet. ether-ether (containing 1% by volume triethylamine) elution. The unreacted azide was the first to elute and upon evaporation of the solvent 260 mg (2.2 mmoles) of the same was recovered. The exo, anti monoadduct (**19**) eluted next and was obtained as white needles (630 mg, 2.8 mmoles) in 62.2% yield. This was followed by the endo, anti monoadduct (**20**) of which 143 mg (0.6 mmoles, 14.2%) were obtained as white crystals after recrystallization. The endo, syn monoadduct (**21**) followed and was obtained as a white powder (190 mg, 0.8 mmoles) in 18.7% yield. The two bis adducts, exo,anti-endo,syn-cis (**22**) and exo,anti-endo,syn-trans (**23**) eluted next in that order. The cis adduct **23** was obtained as a white powder (45 mg, 0.1 mmoles) in 2.9% yield, while the trans compound was obtained in 2.0% yield (30 mg, 0.1 mmoles). The total recovery was around 67%.

Anti-10-methyl-5-phenyl exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**19**)

mp 75-76 ^{o}C; ^{1}H NMR 7.25-7.35 (3H m, Ar), 7.00 (2H t, Ar orhto), 6.15 (1H m, H_9), 6.05 (1H m, H_8), 4.85 (1H d, J=9.0 Hz, H_2), 3.95 (1H d, J=9.0 Hz, H_6), 3.19 (1H bs, H_1), 3.05 (1H bs, H_7), 1.9 (1H q, J=6.0 Hz, H_{10}), 0.80 (3H d, J=6.0 Hz, CH_3); IR 3060, 2980, 2960, 1600, 1500, 1480, 1360, 1115, 910 cm^{-1}; ^{13}C NMR 140.00 (Ar ipso), 136.00 (C_9), 134.5 (C_8), 129.25 (Ar meta), 122.00 (Ar para), 114.00 (Ar ortho), 88.75 (C_2), 62.00 (C_1), 53.00 (C_7), 52.00 (C_6), 48.00 (C_{10}), 10.75 (CH_3). Anal. Calcd. for $C_{14}H_{15}N_3$: C; 74.64, H; 6.71. Found: C; 74.84, H; 6.66.

Syn-10-methyl-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**20**)

mp 133-134 ^{o}C; ^{1}H NMR 7.29-7.40 (3H m, Ar), 7.05 (2H t, Ar ortho), 6.0 (1H m, H_9), 5.8 (1H m, H_8), 5.4 (1H d of d, J=12.0 Hz, J=3.0 Hz, H_2), 4.42 (1H d of d, J=12.0 Hz, H_6), 3.0 (1H bs, H_1), 3.21 (1H bs, H_7), 2.11 (1H q, J=6.1 Hz, H_{10}), 1.0 (3H d, J=6.1 Hz, CH_3); IR 2980, 2940, 1600, 1500, 1480, 1450, 1360, 1120 cm^{-1}; ^{13}C NMR 144.20 (Ar ipso), 137.90 (C_9), 134.60 (C_8), 130.00 (Ar para), 122.00 (Ar meta), 114.00 (Ar ortho), 84.00 (C_2), 59.60 (C_1), 51.60 (C_7), 50.20 (C_6), 55.50 (C_{10}), 13.9 (CH_3). Mass Calcd. for $C_{14}H_{15}N$: 197.1204. Found: 197.1191.

Anti-10-methyl-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**21**)

mp 102-103 ^{o}C; ^{1}H NMR 7.20-7.40(3H m, Ar), 7.00 (2H t, Ar ortho), 5.89 (1H m, H_9), 5.68 (1H m, H_8), 5.40 (1H d of d, J=12.2 Hz, J=3.0 Hz, H_2), 4.35 (1H d of d, J=12.2 Hz, J=3.0 Hz, H_6), 3.40 (1H bs, H_1), 3.25 (1H bs, H_7), 2.05 (1H q, J=6.1 Hz, H_{10}), 0.90 (3H d, J=6.1 Hz, CH_3); IR 2980, 1600, 1500, 1480, 1450, 1365, 1120 cm^{-1}; ^{13}C NMR 140.40 (Ar ipso), 132.90 (C_9), 130.44 (C_8), 129.35 (Ar para), 121.91 (Ar meta), 113.80 (Ar ortho), 87.22 (C_2), 59.92 (C_1), 52.94 (C_7), 52.18 (C_6), 52.76 (C_{10}), 11.39 (CH_3). Anal. Calcd. for $C_{14}H_{15}N_3$: C; 74.64, H; 6.71. Found: C; 74.69, H; 6.66.

Anti-13-methyl-3,9-diphenyl exo-3,4,5-endo-9,10,11-bis(triaza) tetracyclo[5.5.1.$0^{2,6}0^{8,12}$] tridecan-4,10-diene (**22**) mp 209-210 ^{o}C; ^{1}H NMR 7.25-7.55 (6H m, Ar), 7.00-7.13 (4H m, Ar ortho), 5.38 (1H d of d, J=12.2 Hz, J=6.1 Hz, H_{12}), 4.49 (1H d of d, J=12.2 Hz, J=6.1 Hz, H_8), 3.85 (1H d, J=9.2 Hz, H_2), 4.42 (1H d, J=9.2 Hz, H_6), 3.05-3.10 (2H bs, $H_{1,7}$), 2.05 (1H q, J=6.1 Hz, H_{13}), 1.10 (3H d, J=6.1 Hz, CH_3); IR 3010, 2980, 1600, 1500, 1480, 1450, 1210 cm^{-1}; ^{13}C NMR 140.05, 139.68 (Ar ipso), 129.76, 129.54 (Ar para), 123.17, 122.49 (Ar meta), 114.18, 114.09 (Ar ortho), 83.95 (C_{12}), 80.88 (C_6), 57.40 (C_8), 55.64 (C_2), 48.52, 49.40 ($C_{1,7}$), 40.23 (C_{13}), 10.76 (CH_3). Anal. Calcd. for $C_{20}H_{20}N_6$: C; 69.75, H; 5.85. Found: C; 69.32, H; 5.94.

Anti-13-methyl-5,9-diphenyl exo-3,4,5-endo-9,10,11-bis(triaza) tetracyclo[5.5.1.$0^{2,6}0^{8,12}$] trideca-3,10-diene (**23**) mp 202.5 204 ^{o}C; ^{1}H NMr 7.25-7.55 (6H m, Ar), 7.00-7.15 (4H m, Ar ortho), 5.42 (1H d of d, J=12.2 Hz, J=6.1 Hz, H_{12}), 4.48 (1H d of d, J=12.2 Hz, J=6.1 Hz, H_8), 4.62 (1H d, J=9.2 Hz, H_2), 3.55 (1H d, J=9.2 Hz, H_6), 3.30 (1H d, H_1), 2.90 (1H d, H_7), 2.00 (1H q, J=6.1 Hz, H_{13}), 1.10 (3H d, J=6.1 Hz, CH_3); IR 2990, 2880, 1705, 1600, 1500, 1480, 1450, 1110 cm^{-1}; ^{13}C NMR 140.34, 139.64 (Ar ipso), 129.86, 129.39 (Ar para), 123.13, 122.20 (Ar meta), 114.07, 113.71 (Ar ortho), 87.32 (C_{12}), 83.41 (C_2), 57.27 (C_8), 55.33 (C_6), 49.58 (C_1), 40.10 (C_7), 46.77 (C_{13}), 10.74 (CH_3). Anal. Calcd. for $C_{20}H_{20}N_6$: C; 69.75, H; 5.85. Found: C; 69.81, H; 5.76.

8. The reaction of phenylazide with 7-chloronorbornadiene

To a solution of 7-chloronorbornadiene (**24**) (1.0 g, 7.7 mmoles) was added **15** (0.8 g, 6.4 mmoles), the mixture dissolved in 8 mL hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After 30 days the mixture was subjected to rotational TLC on a 2mm plate using a pet. ether-ether (containing 1% by volume of triethylamine) gradient elution. The unreacted **15** eluted first and upon evaporation of solvent 130 mg (1.1 mmoles) of the same was recovered. The endo, syn monoadduct (**25**) eluted next. Evaporation of the solvent afforded 190 mg (0.8 mmoles, 29.5%) of beautiful needle-like crystals of **25**. The exo, anti monoadduct (**26**) eluted next and upon recrystallization 200 mg were obtained as white crystals (0.8 mmoles, 31.4%). The endo, syn (**27**) isomer was the last to elute and recrystallization afforded 250 mg (1.0 mmoles, 39.1%) of white crystals. The total recovery was around 58%.

Syn-10-chloro-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**25**)
mp 117 ^{o}C; ^{1}H NMR 7.22-7.40 (4H m, Ar), 7.05 (1H t, J=9.9 Hz, Ar para), 6.02 (1Hm, H_9), 5.82 (1H m, H_8), 5.65 (1H d of d, J=11.0 Hz, J=3.0 Hz, H_2), 4.71 (1H d of d, J=11.0 Hz, J=3.1 Hz, H_6), 3.98 (1H s, H_{10}), 3.73 (1H bs, H_1), 3. 58 (1H bs, H_7); IR 3000, 2950, 1600, 1500, 1480, 1450, 1360, 1120 cm^{-1}; ^{13}C NMR 139.30 (Ar ipso), 135.91 (C_9), 133.09 (C_8),

129.48 (Ar para), 122.40 (Ar meta), 113.93 (Ar ortho), 85.37 (C_2), 66.76 (C_1), 58.67 (C_7), 52.49 (C_{10}), 51.52 (C_6). Anal. Calcd. for $C_{13}H_1N_3Cl$: C; 63.54, H; 4.93. Found: C; 63.62, H, 4.83.

Anti-10-chloro-5-phenyl exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**26**)

mp 104 °C; ^{1}H NMR 7.30-7.50 (4H m, Ar), 7.13 (1H t, J=6.0 Hz, Ar para), 6.38 (1H m, H_9), 6.25 (1H m, H_8), 5.05 (1H d, J=12.0 Hz, H_2), 4.20 (1H d, J=12.0 Hz, H_6), 3.98 (1H s, H_{10}), 3.70 (1H bs, H_1), 3.58 (1H bs, H_7); IR 2960, 2900, 1690, 1590, 1490, 1300, 1250 cm^{-1}; ^{13}C NMR 139.30 (Ar ipso), 135.04 (C_9), 134.16 (C_8), 129.62 (Ar para), 122.86 (Ar meta), 114.11 (Ar ortho), 86.48 (C_2), 69.06 (C_1), 60.22 (C_7), 54.25 (C_{10}), 53.77 (C_6). Anal. Calcd. for $C_{13}H_{12}N_3Cl$: C; 63.54, H; 4.93. Found: C; 63.71, H; 5.01.

Anti-10-chloro-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**27**)

mp 109-112 °C; ^{1}H NMR 7.28-7.46 (4H m, Ar), 7.10 (1H t, J=6.1 Hz, Ar para), 6.06 (1H m, H_9), 5.87 (1H m, H_8), 5.34 (1H d of d, J=10.6 Hz, J=3.1 Hz, H_2), 4.40 (1H d of d, J=10.6 Hz, J=3.1 Hz, H_6), 4.00 (1H s, H_{10}), 3.85 (1H bs, H_1), 3.71 (1H bs, H_7); IR 3000, 1600, 1500, 1450, 1360, 1270, 1120 cm^{-1}; ^{13}C NMR 139.92 (Ar ipso), 132.55 (C_9), 130.23 (C_8), 129.54 (Ar para), 122.64 (Ar meta), 113.93 (Ar ortho), 82.76 (C_2), 68.58 (C_1), 56.82 (C_7), 53.86 (C_{10}), 53.50 (C_6). Anal. Calcd. for $C_{13}H_{12}N_3Cl$: C; 63.54, H; 4.93. Found: C; 63.50, H; 4.95.

9. The reaction of p-methoxyphenylazide with norbornadiene

To a solution of norbornadiene (**29**) (1.1 g, 12.0 mmoles) was added p-methoxyphenylazide (**28**) (1.5 g, 10.0 mmoles), the mixture dissolved in 10 mL hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 °C. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The unreacted norbornadiene and the azide (240 mg, 1.6 mmoles) were the first to elute followed by the exo mono adduct (**30**). Evaporation of the solvent and recrystallization with ether yielded

beautiful white crystals of **30** (1465mg, 6.1 mmoles) in 95% yield. The endo adduct (**31**)was the next to elute and was obtained as white crystals (77 mg, 0.3 mmoles) in 5% yield. The total recovery was around 80%.

5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**30**)

mp 106-108 ^{o}C; ^{1}H NMR 7.30 (2H d, J=8.7 Hz, Ar ortho to OCH_3), 6.95 (2H d, J=8.7 Hz, Ar meta to OCH_3), 6.32 (1H m, H_9), 6.20 (1H m, H_8), 4.93 (1H d, J=8.7 Hz, H_2), 4.09 (1H d, J=8.7 Hz, H_6), 3.84 (3H s, OCH_3), 3.49 (1H bs, H_1), 3.33 (1H bs, H_7), 1.58 (1H d, J=11.3 Hz, H_{10}syn), 1.32 (1H d, H=11.3 Hz, H_{10}anti); IR 2980, 1510, 1455, 1240 cm^{-1}; ^{13}C NMR 155.25 (Ar ipso to OCH_3), 138.18 (Ar meta to OCH_3), 137.18 (Ar ortho to OCH_3), 134.04 (Ar ipso to triazoline), 115.51 (C_9), 114.79 (C_8), 87.39 (C_2), 61.69 (OCH_3), 55.65 (C_6), 47.85 (C_1), 46.69 (C_{10}), 42.52 (C_7). Anal. Calcd. for $C_{14}H_{15}N_3O$: C; 69.69, H; 6.27. Found: C; 69.64, H; 6.26.

5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**31**)

mp 120-122 ^{o}C; ^{1}H NMR 7.28 (2H d, J=9.3 Hz, Ar ortho to OCH_3), 6.95 (2H d, J=9.3 Hz, Ar meta to OCH_3), 6.02 (1H m, H_9), 5.83 (1H m, H_8), 5.35 (1H d of d, J=10.8 Hz, J=4.6 Hz, H_2), 4.40 (1H d of d, J=10.8 Hz, J=4.6 Hz, H_6), 3.86 (3H s, OCH_3), 3.69 (1H bs, H_1), 3.50 (1H bs, H_7), 1.58 (1H d, J=9.2 Hz, H_{10}syn), 1.40 (1H d, J=9.2 Hz, H_{10}anti); IR 2980, 2830, 1510, 1455, 1240, 1120 cm^{-1}; ^{13}C NMR 138.18 (Ar ipso to OCH_3), 135.85 (Ar meta to OCH_3), 135.27 (Ar ortho to OCH_3), 128.55 (Ar ipso to triazoline), 115.17 (C_9), 114.76 (C_8), 86.46 (C_2), 60.31 (C_6), 55.61 (OCH_3), 47.65 (C_1), 46.53 (C_{10}), 45.94 (C_7). Anal. Calcd. for $C_{14}H_{15}N_3O$: C; 69.69, H. 6.27. Found: C; 69.53, H; 6.15.

10. The reaction of p-methoxyphenylazide with 7-methylnorbornadiene

To a solution of **10** (636 mg, 6.0 mmoles) was added **28** (745 mg, 5.0 mmoles), the mixture dissolved in 5 mL hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a

petroleum ether-ether gradient elution. The unreacted **10** and **28** were the first to elute followed by the exo, anti mono adduct (**32**). Evaporation of the solvent and recrystallization with ether yielded beautiful white crystals of **32** (340 mg, 1.3 mmoles) in 56.6% yield. The endo, syn adduct (**33**) was the next to elute and was obtained as white crystals (115 mg, 0.5 mmoles) in 19.1% yield. The endo, anti mono adduct (**34**) eluted next and was obtained as white crystals (145 mg, 0.6 mmoles) in 24.3% yield. It should be mentioned that the quantity of the unreacted p-methoxy phenylazide was difficult to establish due to its decomposition on the plate, the structure of the decomposition product being difficult to elucidate. The total recovery was around 47%.

Anti-10-methyl-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**32**) mp 90-91 ^{o}C; ^{1}H NMR 7.30 (2H d, J=7.7 Hz, Ar meta to OCH_3), 6.95 (2H d,J=7.7 Hz, Ar ortho to OCH_3), 6.12 (1H m, H_9), 6.08 (1H m, H_8), 4.90 (1H d, J=10.2 Hz, H_2), 4.03 (1H d, J=10.2 Hz, H_6), 3.85 (3H s, OCH_3), 3.22 (1H bs, H_1), 3.10 (1H bs, H_7), 2.00 (1H q, J=6.0 Hz, H_{10}), 0.89 (3H d, J=6.0 Hz, CH_3); IR 3000, 1500, 1450 cm^{-1}; ^{13}C NMR 155.67, 134.57 (Ar ipso), 136.18 (C_9), 135.15 (C_8), 116.13, 115.57 (Ar), 89.16 (C_2), 63.31 (C_6), 56.44 (OCH_3), 53.94 (C_1), 53.09 (C_7), 48.37 (C_{10}), 11.50 (CH_3). Mass Calcd. for $C_{15}H_{17}NO$: 227.1310. Found: 227.1312.

Syn-10-methyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**33**) mp 80-83 ^{o}C; ^{1}H NMR 7.21 (2H d, J=7.7 Hz, Ar meta to OCH_3), 6.89 (2H d, J=7.7 Hz, Ar ortho to OCH_3), 5.96 (1H m, H_9), 5.78 (1H m, H_8), 5.32 (1H d of d, J=10.2 Hz, J=5.1 Hz, H_2), 4.40 (1H d of d, J=10.2 Hz, J=5.1 Hz, H_6), 3.78 (3H s, OCH_3), 3.36 (1H bs, H_1), 3.16 (1H bs, H_7), 2.07 (1H q, J=6.0 Hz, H_{10}), 0.95 (3H d, J=6.0 Hz, CH_3); IR 3000, 1500, 1450 cm^{-1}; ^{13}C NMR 155.85 (Ar ipso), 137.91 (C_9), 135.50 (C_8), 115.95, 115.52 (Ar), 86.35 (C_2), 60.33 (C_6), 56.40 (OCH_3), 55.18 (C_1), 52.09 (C_7), 50.90 (C_{10}), 14.23 (CH_3). Mass Calcd. for $C_{15}H_{17}NO$: 227.1310. Found: 227.1307.

Anti-10-methyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (34) mp 90-92 ^{o}C; ^{1}H NMR 7.20 (2H d, J=10.2 Hz, Ar meta to OCH_3), 6.89 (2H d, J=10.2 Hz, Ar ortho to OCH_3), 5.85 (1H m, H_9), 5.66 (1H m, H_8), 5.29 (1H d of d, J=10.2 Hz, J=5.1 Hz, H_2), 4.32 (1H d of d, J=10.2 Hz, J=5.1 Hz, H_6), 3.79 (3H s, OCH_3), 3.38 (1H bs, H_1), 3.19 (1H bs, H_7), 2.01 (1H q, J=5.8 Hz, H_{10}), 0.89 (3H d, J=5.8 Hz, CH_3); IR 3000, 1500, 1450 cm^{-1}; ^{13}C NMR 155.80 (Ar ipso), 133.78 (C_9), 131.18 (C_8), 115.85, 115.51 (Ar), 87.36 (C_2), 61.24 (C_6), 56.40 (OCH_3), 53.78 (C_1), 53.44 (C_7), 52.97 (C_{10}), 12.18 (CH_3).

11. The reaction of p-methoxyphenylazide with 7-phenylnorbornadiene

To a solution of 4 (2.0 g, 12.0 mmoles) was added 28 (1.5 g, 10.0 mmoles), the mixture dissolved in 10 mL hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The unreacted 4 was the first to elute as a blue band followed by the unreacted azide (670 mg, 4.5 mmoles) and the endo, syn mono adduct (35). Evaporation of the solvent and recrystallization with ether yielded white crystals of 35 (197 mg, 0.6 mmoles) in 12.6% yield. The exo, anti adduct (36) was the next to elute and was obtained as white crystals (964 mg, 3.0 mmoles) in 61.5% yield. The endo, anti mono adduct (37) eluted next and was obtained as white crystals (214 mg, 0.7 mmoles) in 13.7% yield, which was followed by the exo, anti-endo, syn bis adduct (38) obtained in 12.3 % yield (142 mg, 0.5). The total recovery was around 92.9%.

Syn-10-phenyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (35) mp 192.5-195 ^{o}C; ^{1}H NMR 7.2-7.41 (7H m, Ar), 6.92 (2H d, Ar ortho to OCH_3), 6.12 (1H m, H_9), 5.93 (1H m, H_8), 5.17 (1H d of d, J=10.8 Hz, J=4.8 Hz, H_2), 4.02 (1H d of d, J=10.8 Hz, J=4.8 Hz, H_6), 4.07 (1H bs, H_1), 3.78 (1H bs, H_7), 3.70 (3H s, OCH_3), 3.38 (1H s, H_{10}); IR 2980, 1510, 1460, 1240 cm^{-1}; ^{13}C NMR 137.01 (C_9), 134.02 (C_8), 129.2,

127.3, 116.3, 115.8 (Ar), 85.7 (C_2), 62.2 (OCH_3), 59.8 (C_6), 55.9 (C_1), 49.9 (C_{10}), 49.0 (C_7). Mass Calcd. for $C_{20}H_{19}NO$: 289.1466. Found: 289.1466.

Anti-10-phenyl-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**36**) mp 103-106 ^oC; ^1H NMR 6.92-7.38 (9H m, Ar), 6.12 (2H m, $H_{8,9}$), 5.05 (1H d, J=9.6 Hz, H_2), 4.20 (1H d, J=9.6, H_6), 3.82 (3H s, OCH_3), 3.75 (1H bs, H_1), 3.60 (1H bs, H_7), 3.27 (1H s, H_{10}); IR 2980, 1510, 1460, 1240 cm^{-1}; ^{13}C NMR 139.0 (Ar ipso), 135.3 (C_9), 134.6 (C_8), 129.0, 128.0, 126.2, 117.6, 116.8 (Ar), 88.1 (C_2), 61.6 (OCH_3), 56.7 (C_6), 55.8 (C_1), 52.3 (C_{10}), 51.0 (C_7). Anal. Calcd, for $C_{20}H_{19}N_3O$: C; 75.69, H; 6.03. Found: C; 76.47, H; 6.28.

Syn-10-phenyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**37**) mp 128-130 ^oC; ^1H NMR 7.07-7.08 (7H m, Ar), 6.90 (2H d, J=9.3 Hz, Ar), 5.88 (1H m, H_9) 5.69 (1H m, H_8), 5.49 (1H d of d, J=10.0 Hz, J=3.9 Hz, H_2), 4.54 (1H d of d, J=10.0 Hz, J=3.9 Hz, H_6), 3.92 (1H bs, H_1), 3.80 (3H s, OCH_3), 3.73 (1H bs, H_7), 3.22 (1H s, H_{10}); IR 2980, 2890, 1500, 1450, 1240 cm^{-1}; ^{13}C NMR.135.41 (Ar ipso), 133.88 (C_9), 131.10 (C_8), 129.50, 128.80, 127.12, 116.05, 115.75 (Ar), 87.00 (C_2), 61.96 (OCH_3), 61.21 (C_6), 57.45 (C_1), 52.52 (C_{10}), 51.73 (C_7). Mass Calcd. for $C_{20}H_{19}NO$: 289.1466. Found: 289.1439.

Anti-13-phenyl-5,11-bis (4'-methoxyphenyl) exo-3,4,5-endo-9,10,11-bis(triaza) tetracyclo [5.5.1.$0^{2,6}0^{8,12}$]trideca-3,9-diene (**38**) ^1H NMR 6.92-7.38 (13H m, Ar), 5.68 (1H d of d, J=13.3 Hz, J=5.0 Hz, H_8), 4.55 (1H d, J=10.0 Hz, H_2), 4.21 (1H d of d, J=13.3 Hz, J=5.0 Hz, H_{12}), 4.02 (1H d, J=10.0 Hz, H_6), 3.80-3.85 (6H pseudo d, OCH_3s), 3.71 (2H m, $H_{1,7}$), 3.26 (1H s, H_{13}); 13C NMR 136.59 (Ar ipso), 129.75, 128.22, 127.94, 116.57, 116.24, 115.90, 115.68 (Ar), 87.52 ($C_{2,8}$), 62.23 (OCH_3s), 61.82 (C_{12}), 57.00 (C_6), 53.01 ($C_{1,7}$), 52.17 (C_{13}). Anal. Calcd. for $C_{27}H_{26}N_6O_2$: C; 69.51, H; 5.62. Found: C; 69.55, H; 5.70.

12. The reaction of p-methoxyphenylazide with 7-chloronorbornadiene

To a solution of **24** (1.3 g, 10.0 mmoles) was added **28** (1.2 g, 8.0 mmoles), the mixture dissolved in 8 mL hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The unreacted **28** was the first to elute (202 mg, 1.4 mmoles) followed by the endo, anti mono adduct (**39**). Evaporation of the solvent and recrystallization with ether yielded white crystals of **39** (140 mg, 0.5 mmoles) in 60.7% yield. The exo, anti adduct (**40**) was the next to elute and was obtained as white crystals (61 mg, 0.2 mmoles) in 26.2% yield. The endo, syn mono adduct (**41**) eluted next and was obtained as white crystals (29 mg, 0.1 mmoles) in 13.1% yield. The total recovery was around 27.5%.

Anti-10-chloro-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**39**) mp 99-105 ^{o}C; ^{1}H NMR 7.18 (2H d of d, J=7.8 Hz, Ar meta to OCH_3), 6.89 (2H d of d, J=7.8 Hz, Ar ortho to OCH_3), 5.99 (1H m, H_9), 5.79 (1H m, H_8), 5.25 (1H d of d, J=9.8 Hz, J=3.9 Hz, H_2), 4.30 (1H d of d, J=9.8 Hz, J=3.9 Hz, H_6), 3.95 (1H s, H_{10}), 3.78 (3H s, OCH_3), 3.76 (1H bs, H_1), 3,58 (1H bs, H_7); IR 3000, 1510, 1460, 1240 cm^{-1}; ^{13}C NMR 133.13 (C_9), 130.72 (C_8), 115.85, 115.37 (Ar), 82.95 (C_2), 69.07 (OCH_3), 57.90 (C_6), 56.11 (C_1), 54.46 (C_{10}), 54.06 (C_7). Anal. Calcd. for $C_{14}H_{14}N_3OCl$: C; 60.98, H; 5.12. Found: C; 60.85, H; 4.94.

Anti-10-chloro-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**40**) mp 87-91 ^{o}C; ^{1}H NMR 7.21 (2H d, J=9.0 Hz, Ar meta to OCH_3), 6.91 (2H d of d, J=9.0 Hz, Ar ortho to OCH_3), 6.27 (1H m, H_9), 6.16 (1H m, H_8), 4.95 (1H d, J=10.5 Hz, H_2), 4.11 (1H d, J=10.5 Hz, H_6), 3.92 (1H s, H_{10}), 3.80 (3H s, OCH_3), 3.61 (1H bs, H_1), 3.49 (1H bs, H_7); IR 3000, 1510, 1460, 1240 cm^{-1}; ^{13}C NMR 135.56 (C_9), 134.60 (C_8), 116.18, 115.43 (Ar), 86.72 (C_2), 69.62 (OCH_3), 61.36 (C_6), 56.15 (C_1), 54.87 (C_{10}), 54.45 (C_7). Mass Calcd. for. $C_{14}H_{14}NOCl$: 247.0763. Found: 247.0774.

Syn-10-chloro-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (41) ^{1}H NMR 7.19 (2H d of d, J=8.8 Hz, Ar meta to OCH_3), 6.85 (2H d of d, J=8.8 Hz, Ar ortho to OCH_3), 5.98 (1H m, H_9), 5.88 (1H m, H_8), 5.58 (1H d of d, J=9.8 Hz, J=4.5 Hz, H_2), 4.65 (1H d of d, J=9.8 Hz, J=4.5 Hz, H_6), 3.95 (1H s, H_{10}), 3.75 (3H s, OCH_3), 3.65 (1H bs, H_1), 3.46 (1H bs, H_7); IR 3000, 1510, 1420, 1240 cm^{-1}. Mass Calcd. for $C_{14}H_{14}NOCl$: 247.0763. Found: 247.0770.

13. The reaction of p-methoxyphenylazide with 7-*t*-butoxynorbornadiene

To a solution of 7-*t*-butoxynorbornadiene (42) (1.3 g, 8.0 mmoles) was added 28 (1.0 g, 6.6 mmoles), the mixture dissolved in 7 mL hexane, purged with nitrogen, sealed and placed in the refrigerator at 4 ^oC. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The unreacted 42 and the azide were the first to elute. The endo, syn adduct (43) eluted next and was ontained in 49.3% yield (210 mg, 0.7 mmoles). The exo, anti adduct (44) was the next to elute and was obtained as a yellow solid (90 mg, 0.3 mmoles) in 21.2% yield. The exo, syn mono adduct (45) eluted next and was obtained as a yellow solid (33 mg, 0.1 mmoles) in 7.8% yield, which was followed by the endo, anti adduct (46) obtained in 21.8 % yield (92 mg, 0.3 mmoles). The total recovery was around 20.5%.

Syn-10-*t*-butoxy-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (43) ^{1}H NMR 7.29 (2H d, J=9.8 Hz, Ar meta to OCH_3), 6.95 (2H d of d,J=9.8 Hz, Ar ortho to OCH_3), 5.90 (1H m, H_9), 5.72 (1H m, H_8), 5.48 (1H d of d, J=9.8 Hz, J=4.9 Hz, H_2), 4.59 (1H d of d, J=9.8 Hz, J=4.9 Hz, H_6), 3.85 (3H s, OCH_3), 3.75 (1H s, H_{10}), 3.49 (1H bs, H_1), 3.28 (1H bs, H_7), 1,26 (9H s, *t*-bu); IR 3030, 2985, 1580, 1505, 1460, 1420, 1360, 1240 cm^{-1}; ^{13}C NMR 155.21 (Ar ipso), 134.12 (C_9), 131.96 (C_8), 117.92, 117.21 (Ar), 86.20 (C_2), 85.96 (C_{10}), 74.50 (quat. C in *t*-bu), 60.20 (C_6), 56.12 (C_{10}), 52.46 (C_1), 51.12 (C_7), 29.05 (CH_3's in *t*-bu). Mass Calcd. for $C_{18}H_{23}NO_2$: 285.1730. Found: 285.1737.

Anti-10-*t*-butoxy-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (44) ^{1}H NMR 7.30 (2H d, J=3.7 Hz, J=9.5 Hz, Ar meta to OCH_3), 6.95 (2H d, J=9.5 Hz, Ar ortho to OCH_3), 6.28 (1H m, H_9), 6.19 (1H m, H_8), 4.82 (1H d, J=9.6 Hz, H_2), 3.98 (1H d, J=9.6 Hz, H_6), 3.83 (3H s, OCH_3), 3.79 (1H s, H_{10}), 3.42 (1H bs, H_1), 3.24 (1H bs, H_7), 1.09 (9H s, *t*-bu); IR 2985, 1500, 1460, 1360, 1240 cm^{-1}; ^{13}C NMR 156.02, 134.86 (Ar ipso), 135.00 (C_9), 134.05 (C_8), 116.45, 115.86 (Ar), 86.38 (C_2), 84.22 (C_{10}), 74.60 (quat. C in *t*-bu), 60.86 (C_6), 56.18 (OCH_3), 53.03 (C_1), 52.76 (C_7), 28.87 (CH_3's in *t*-bu). Mass Calcd. for $C_{18}H_{23}NO_2$: 285.1730. Found: 285.1725.

Syn-10-*t*-butoxy-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (45) ^{1}H NMR 7.24 (2H d, J=9.8 Hz, Ar meta to OCH_3), 6.91 (2H d, J=9.8 Hz, Ar ortho to OCH_3), 6.22 (1H m, H_9), 6.18 (1H m, H_8), 4.94 (1H d, J=9.0 Hz, H_2), 4.23 (1H d, J=9.0 Hz, H_6), 3.80 (1H s, H_{10}), 3.79 (3H s, OCH_3), 3.42 (1H bs, H_1), 3.22 (1H bs, H_7), 1.18 (9H s, *t*-bu); IR cm^{-1}; ^{13}C NMR 137.88 (C_9), 136.83 (C_8), 115.97, 115.39 (Ar), 87.72 (C_2), 85.60 (C_{10}), 74.42 (quat. C in *t*-bu), 61.48 (C_6), 56.37 (OCH_3), 52.42 (C_1), 49.01 (C_7), 28.55 (CH_3's in tBu). Mass Calcd. for $C_{18}H_{23}NO_2$: 285.1730. Found: 285.1730.

Anti-10-*t*-butoxy-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (46) ^{1}H NMR 7.22 (2H d, J=9.8 Hz, Ar meta to OCH_3), 6.93 (2H d, J=9.8 Hz, Ar ortho to OCH_3), 6.02 (1H m, H_9), 5.82 (1H m, H_8), 5.21 (1H d of d, J=10.8 Hz, J=4.8 Hz, H_2), 4.29 (1H d of d, J=10.8 Hz, H=4.8 Hz, H_6), 3.86 (1H s, H_{10}), 3.79 (3H s, OCH_3), 3.60 (1H bs, H_1), 3.40 (1H bs, H_7), 1.25 (9H s, *t*-bu); IR 2980, 1500, 1460, 1240 cm^{-1}; ^{13}C NMR 155.72, 134.40 (Ar ipso), 132.32 (C_9), 130.03 (C_8), 115.96, 115.40 (Ar), 85.74 (C_2), 82.23 (C_{10}), 74.25 (quat. C in *t*-bu), 57.32 (C_6), 56.06 (OCH_3), 53.11 (C_1), 52.10 (C_7), 29.02 (CH_3's in *t*-bu). Mass Calcd. for $C_{18}H_{23}NO_2$: 285.1730. Found: 285.1703.

14. The reaction of p-nitrophenylazide with 7-methylnorbornadiene

To a solution of **10** (636 mg, 6.0 mmoles) was added p-nitrophenylazide (**47**) (820 mg, 5.0 mmoles), the mixture dissolved in 5 mL chloroform, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The unreacted **10** and the **47** were the first to elute followed by the exo, anti mono adduct (**48**) (mp 155-158 ^{o}C). Evaporation of the solvent yielded yellow crystals of **48** (519 mg, 1.9 mmoles) in 67.2% yield. The endo, syn adduct (**49**) was the next to elute and was obtained as yellow crystals (111 mg,0.4 mmoles) in 14.6% yield. The endo, anti mono adduct (**50**) was the next to elute and was obtained as a yellow powder (141 mg, 0.5 mmoles) in 18.2% yield. The total recovery was around 57%.

Anti-10-methyl-5-(4'-nitrophenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**48**) mp 155-157 ^{o}C; ^{1}H NMR 8.19 (2H d, J=6.6 Hz, Ar ortho to NO_2), 7.20 (2H d, J=6.6 Hz, Ar meta to NO_2), 6.15 (1H m, H_9), 6.02 (1H m, H_8), 4.94 (1H d, J=9.9 Hz, H_2), 3.92 (1H d, J=9.9 Hz, H_6), 3.20 (1H bs, H_1), 3.00 (1H bs, H_7), 1.80 (1H q, J=6.6 Hz, H_{10}), 0.82 (3H d, J=6.6 Hz, CH_3); IR 2995, 1595, 1510, 1500, 1370, 1330, 1190 cm^{-1}; ^{13}C NMR 145.46, 142.46 (Ar ipso), 135.94 (C_9), 134.80 (C_8), 126.40, 113.67 (Ar), 90.94 (C_2), 61.58 (C_6), 53.04 (C_1), 52.21 (C_{10}), 48.16 (C_7), 11.07 (CH_3). Anal. Calcd. for $C_{14}H_{14}N_4O_2$: C; 62.21, H; 5.22. Found: C; 62.15, H; 5.09.

Syn-10-methyl-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**49**) mp 145-148 ^{o}C; ^{1}H NMR 8.30 (2H d, J=6.5 Hz, Ar ortho to NO_2), 7.40 (2H d, J=6.5 Hz, Ar meta to NO_2), 6.05 (1H m, H_9), 5.82 (1H m, H_8), 5.58 (1H d of d, J=10.5 Hz, J=3.0 Hz, H_2), 4.48 (1H d of d, J=10.5 Hz, J=3.0 Hz, H_6), 3.49 (1H bs, H_1), 3.30 (1H bs, H_7), 2.24 (1H q, J=6.0 Hz, H_{10}), 1.08 (3H d, J=6.0 Hz, CH_3); ^{13}C NMR 137.8 (C_9), 134.8 (C_8), 126.4, 113.5 (Ar), 88.3 (C_2), 58.7 (C_6), 55.5 (C_1), 51.5 (C_{10}), 50.2 (C_7), 13.8 (CH_3). Mass Calcd. for $C_{14}H_{14}N_2O_2$: 242.1055. Found: 242.1067.

Anti-10-phenyl-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**52**) mp 167-170 ^{o}C; ^{1}H NMR 8.30 (2H d, J=9.5 Hz, Ar ortho to NO_2), 7.2-7.50 (7H m, Ar), 6.19 (1H m, H_9), 5.95 (1H m, H_8), 5.39 (1H d of d, J=9.6 Hz, J=3.0 Hz, H_2), 4.26 (1H d of d, J=9.6 Hz, J=3.0 Hz, H_6), 4.18 (1H bs, H_1), 3.99 (1H bs, H_7), 3.42 (1H s, H_{10}); IR 3000, 1600, 1500, 1490, 1410 cm^{-1}; ^{13}C NMR 138.3 (Ar ipso), 137.5 (C_9), 134.5 (C_8), 129.9, 128.0, 127.5, 126.8, 113.9 (Ar), 88.3 (C_2), 63.3 (C_6), 58.8 (C_1), 50.1 (C_{10}), 49.19 (C_7). Mass Calcd. for $C_{19}H_{16}N_2O_2$: 304.1211. Found: 304.1204.

16. The reaction of p-nitrophenylazide with 7-*t*-butoxynorbornadiene

To a solution of **42** (2.0 g, 12.0 mmoles) was added **47** (1.4 g, 10.0 mmoles), the mixture dissolved in 10 mL chloroform, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The unreacted **42** and the **47** were the first to elute followed by the endo, anti (**53**) exo, anti (**54**) endo, anti (**55**) and the endo, syn (**56**) mono adducts in that order. While **53** was obtained as a white powder (876 mg, 2.7 mmoles) in 38.7% yield, **54** was obtained as a yellow solid (868 mg, 2.7 mmoles) in 38.4% yield. The endo, syn adduct (**55**) eluted next and was obtained in 18.7% yield 4246 mg, 1.3 mmoles), which was followed by 4.2% of **56** (95 mg, 0.3 mmoles). The total recovery was around 69%. Anti-10-*t*-butoxy-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**53**) ^{1}H NMR 8.29 (2H d, J=11.3 Hz, Ar ortho to NO_2), 7.30 (2H d, J=11.3 Hz, Ar meta to NO_2), 5.91 (1H m, H_9), 5.70 (1H m, H_8), 5.64 (1H d of d, J=11.3 Hz, J=5.0 Hz, H_2), 4.60 (1H d of d, J=11.3 Hz, J=5.0 Hz, H_6), 3.84 (1H s, H_{10}), 3.52 (1H bs, H_1), 3.34 (1H bs, H_7), 1.28 (9H s, *t*-bu); IR 2985, 1590, 1500, 1360, 1330, 1100, 1090 cm^{-1}; ^{13}C NMR 145.62 (Ar ipso), 133.98 (C_9), 130.86 (C_8), 126.0, 112.99 (Ar), 88.00 (C_2), 85.98 (C_{10}), 74.62 (quat.C in *t*-bu), 58.26 (C_6), 51.86 (C_1), 50.18 (C_7), 28.22 (CH_3's in*t*-bu). Mass Calcd. for $C_{17}H_{20}N_2O_2$: 300.1474. Found: 300.1458.

Anti-10-*t*-butoxy-5-(4'-nitrophenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (54) ^{1}H NMR 8.29 (2H d, J=9.0 Hz, Ar ortho to NO_2), 7.30 (2H d, J=9.0 Hz, Ar meta to NO_2), 6.32 (1H m, H_9), 6.24 (1H m, H_8), 5.08 (1H d, J=9.5 Hz, H_2), 4.24 (1H d, J=9.5 Hz, H_6), 3.74 (1H s, H_{10}), 3.52 (1H bs, H_1), 3.32 (1H bs, H_7), 1.00 (9H s, *t*-bu); ^{13}C NMR 137.9 (C_9), 136.2 (C_8), 126.2, 115.6 (Ar), 89.8 (C_2), 85.7 (C_{10}), 74.3 (quat.C in *t*-bu), 60.0 (C_6), 51.9 (C_1), 48.2 (C_7), 28.2 (CH_3's in*t*-bu). Mass Calcd. for $C_{17}H_{20}N_2O_2$: 300.1474. Found: 300.1475.

Syn-10-*t*-butoxy-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (55) ^{1}H NMR 8.07 (2H d, J=9.5 Hz, Ar ortho to NO_2), 6.66 (2H d, J=9.5 Hz, Ar meta to NO_2), 5.98 (1H m, H_9), 5.78 (1H m, H_8), 5.40 (1H d of d, J=9.5 Hz, J=3.8 Hz, H_2), 4.25 (1H d of d, J=9.5 Hz, J=3.8 Hz, H_6), 3.90 (1H s, H_{10}), 3.62 (1H bs, H_1), 3.45 (1H bs, H_7), 1.14 (9H s, *t*-bu); IR cm^{-1}; ^{13}C NMR 145.38 (Ar ipso), 132.85 (C_9), 129.98 (C_8), 126.68, 113.76 (Ar), 85.80 (C_2), 84.58 (C_{10}), 74.82 (quat. C in *t*-bu), 55.62 (C_6), 52.52 (C_1), 51.80 (C_7), 28.94 (CH_3's in *t*-bu). Mass Calcd. for $C_{17}H_{20}N_2O_2$: 300.1474. Found: 300.1472.

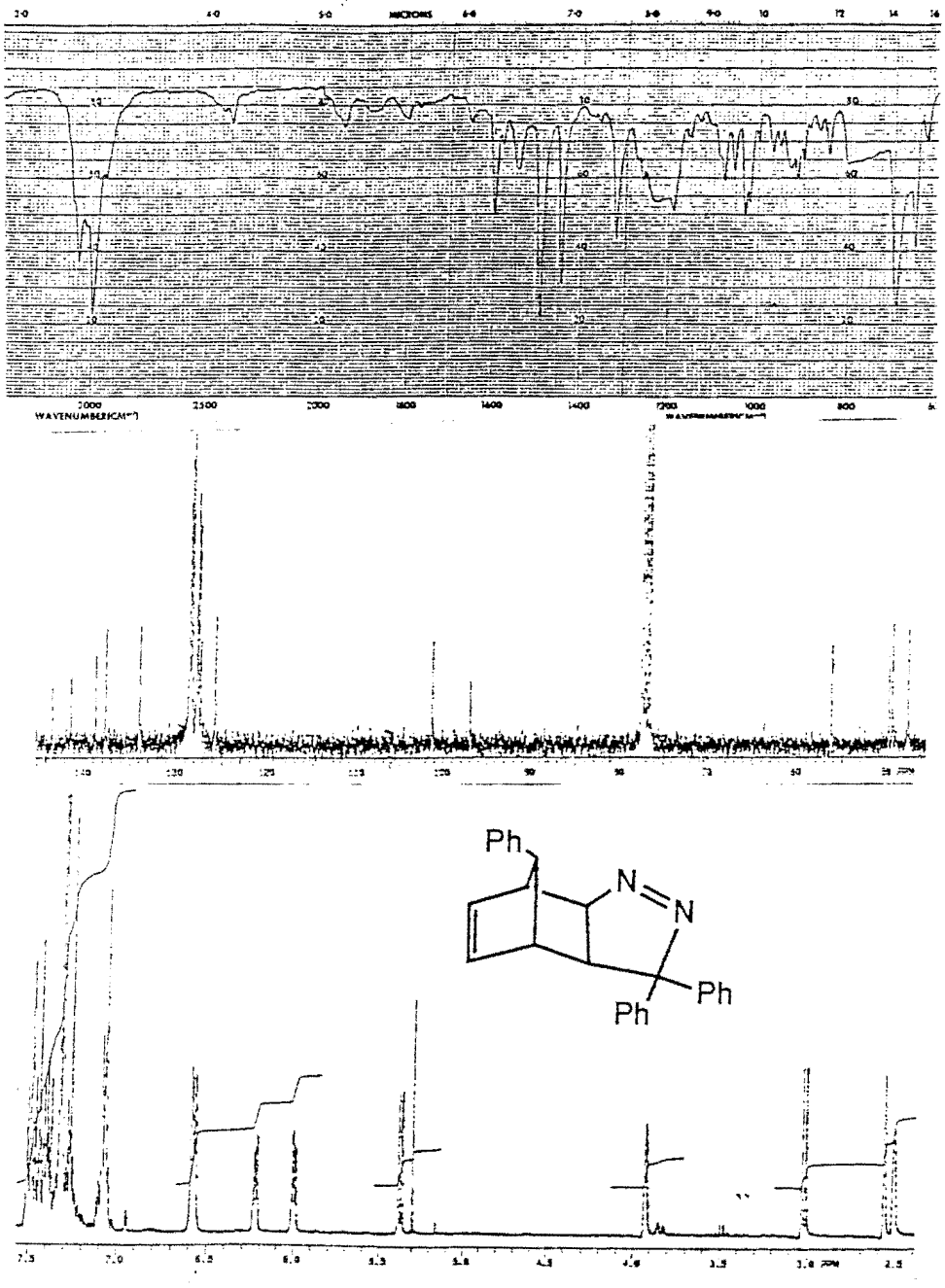
Syn-10-*t*-butoxy-5-(4'-nitrophenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (56) ^{1}H NMR 7.14 (2H d, J=9.0 Hz, Ar ortho to NO_2), 6.62 (2H d, J=9.0 Hz, Ar meta to NO_2), 6.26 (1H m, H_9), 6.16 (1H m, H_8), 5.08 (1H d, J=9.5 Hz, H_2), 4.21 (1H d, J=9.5 Hz, H_6), 3.08 (1H bs, H_1), 2.62 (1H s, H_{10}), 2.58 (1H bs, H_7), 1.21 (9H s, *t*-Bu); ^{13}C NMR 134.8 (C_9), 133.9 (C_8), 126.5, 114.8 (Ar), 85.2 (C_2), 84.0 (C_{10}), 59.2 (C_6), 51.1 (C_1), 28.6 (CH_3's in *t*-bu). Mass Calcd. for $C_{17}H_{20}N_2O_2$: 300.1474. Found: 300.1475.

17. The reaction of p-nitrophenylazide with 7-chloronorbornadiene

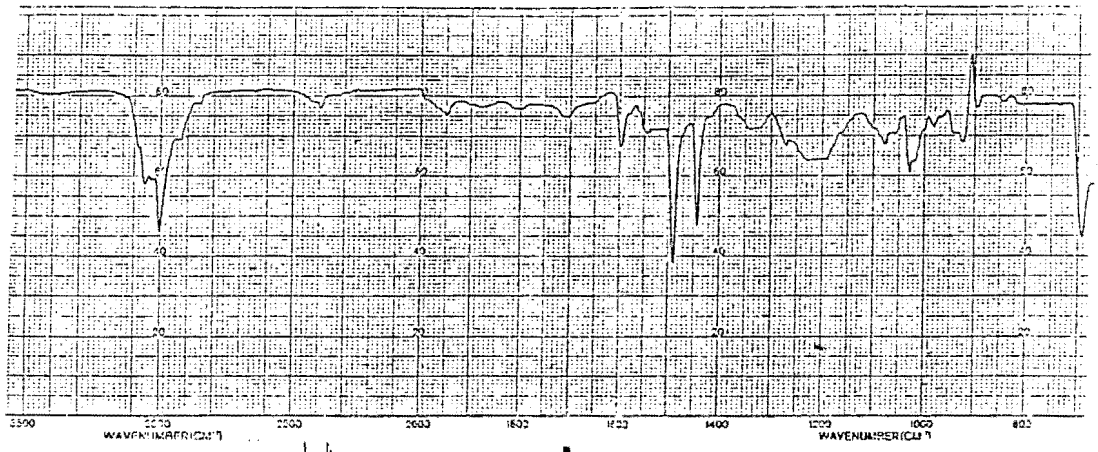
To a solution of 24 (759 mg, 6.0 mmoles) was added 47 (820 mg, 5.0 mmoles), the mixture dissolved in 5 mL chloroform, purged with nitrogen, sealed and placed in the refrigerator at 4 ^{o}C. After one month the mixture was subjected to rotational TLC using a 2 mm plate and a petroleum ether-ether gradient elution. The mixture turned black a soon as it was

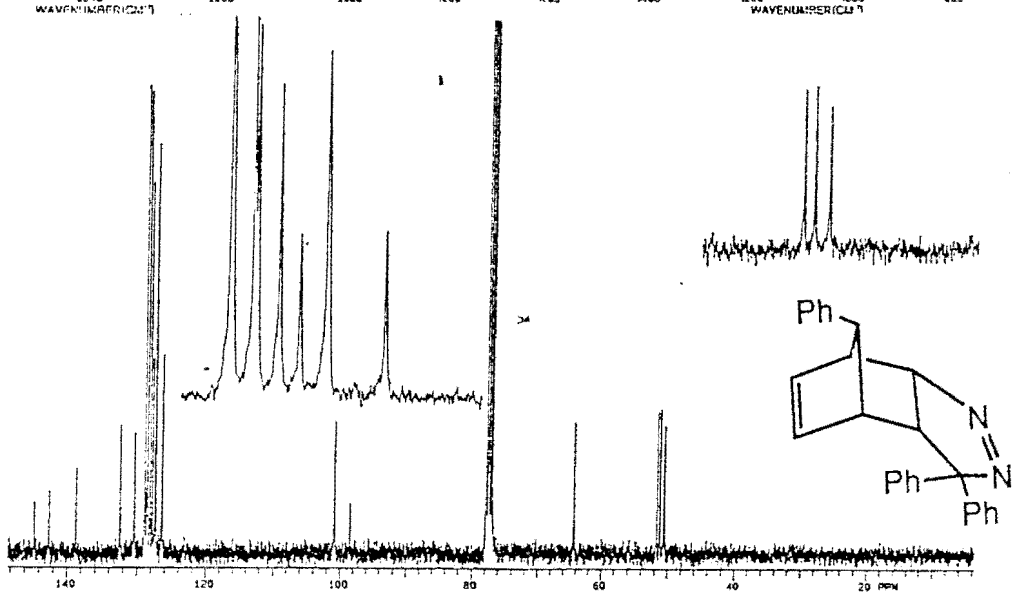
loaded on to the plate and separation of the adducts was impossible. Several fractions were collected but ^{1}H NMR did not indicate the presence of even one adduct. The nature of the decomposed material was difficult to ascertain because both the IR and the ^{1}H NMR did not show any characteristic peaks.

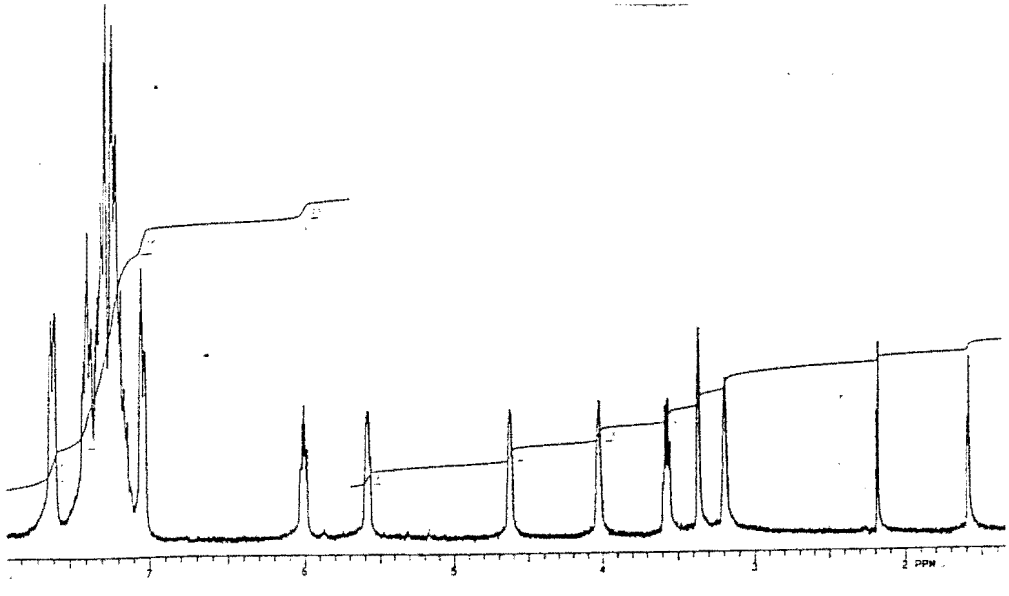
5,5,Anti-10-triphenyl exo-3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (5)



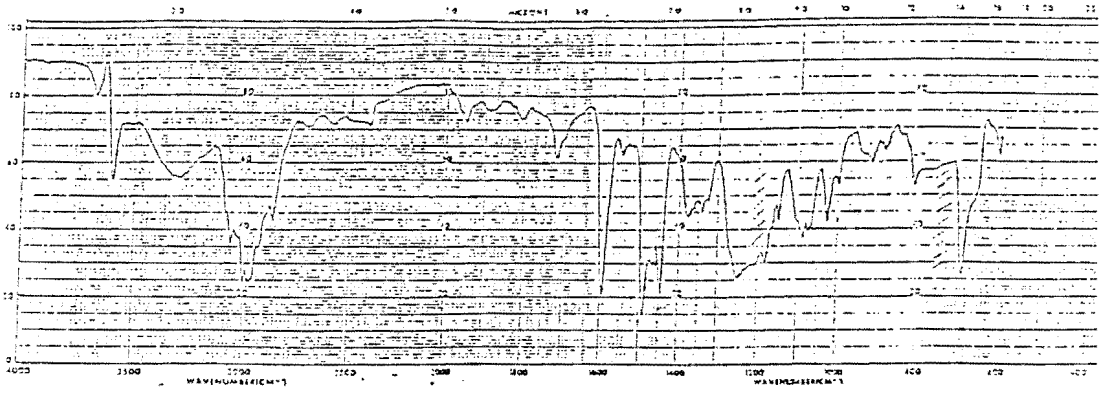
5,5,Anti-10-triphenyl endo-3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**6**)

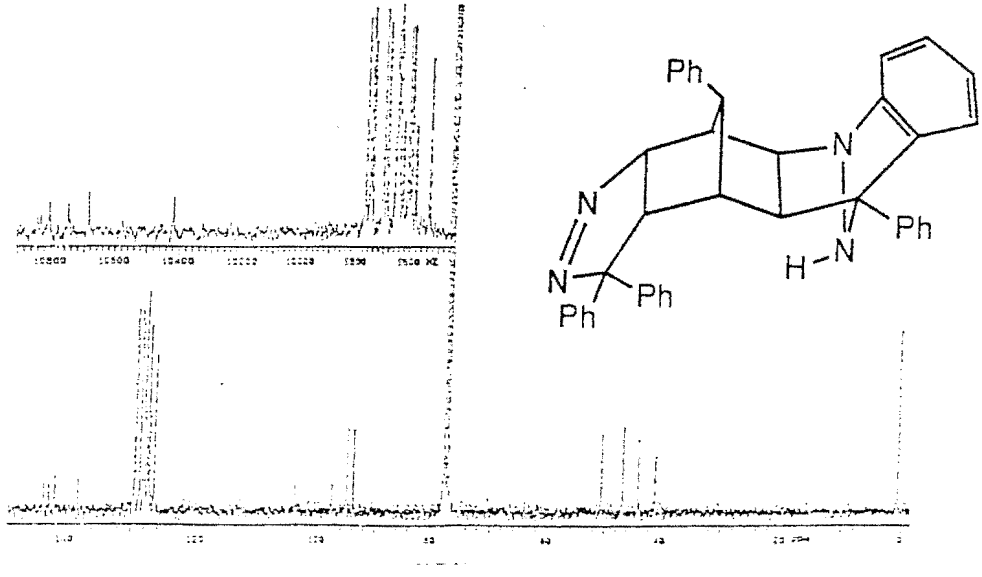


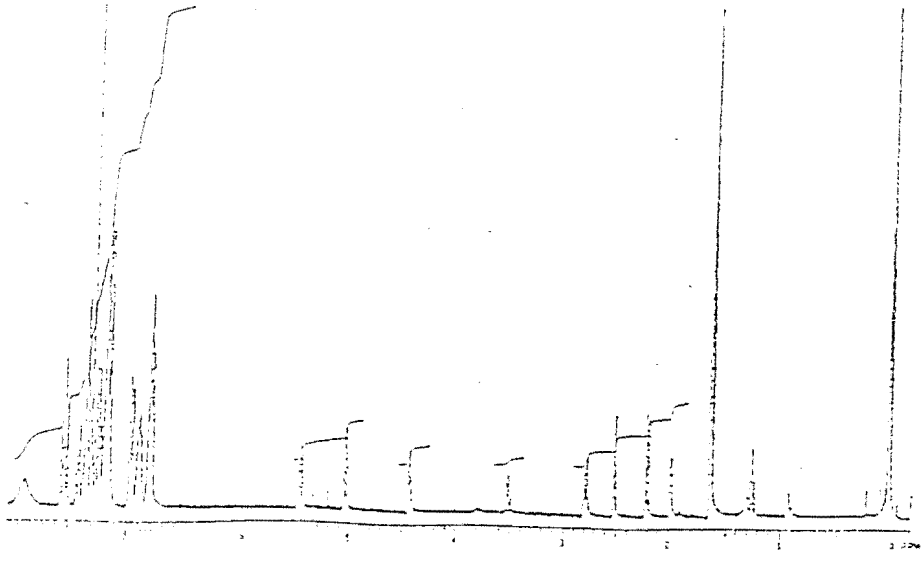




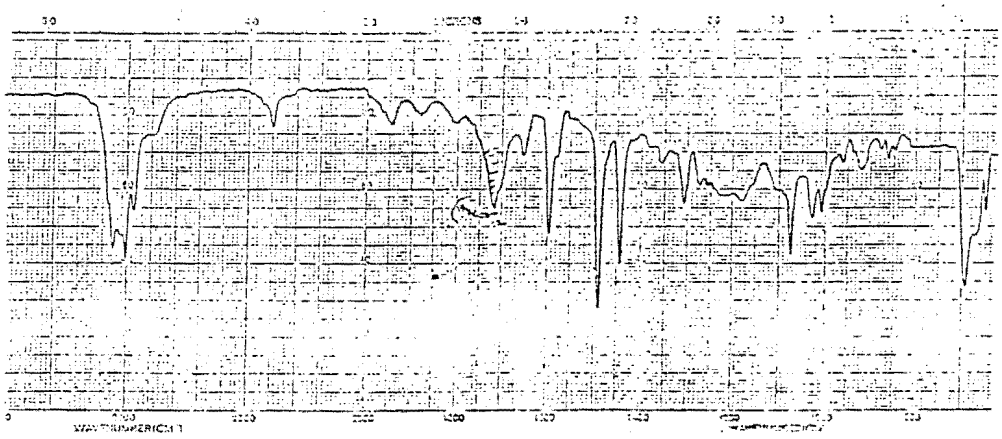
4,5-Benzo-6,10,10,anti-14-tetraphenyl-exo-2,7-endo-9,13-tetraza-3,11,12,15-tetracyclo-[6.5.1.1^{3,6}.0^{2,7}.0^{9,13}]pentadeca-4,11-diene (7)

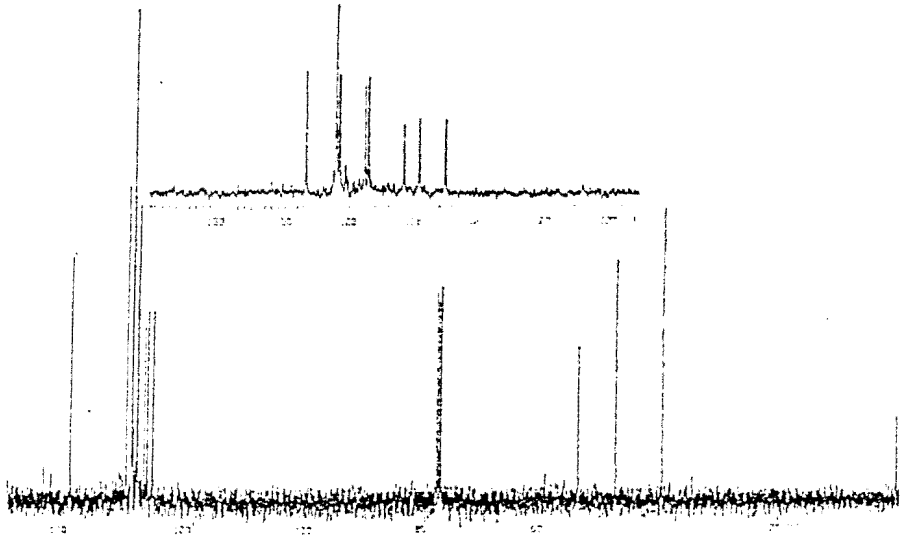


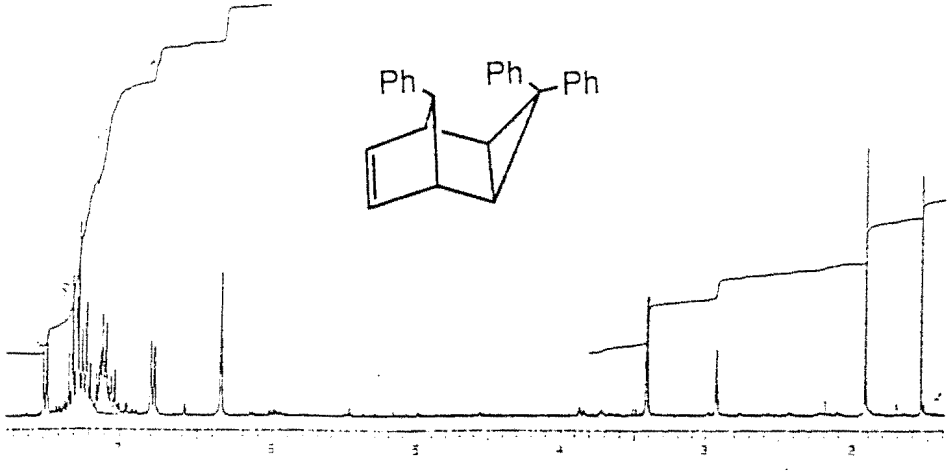




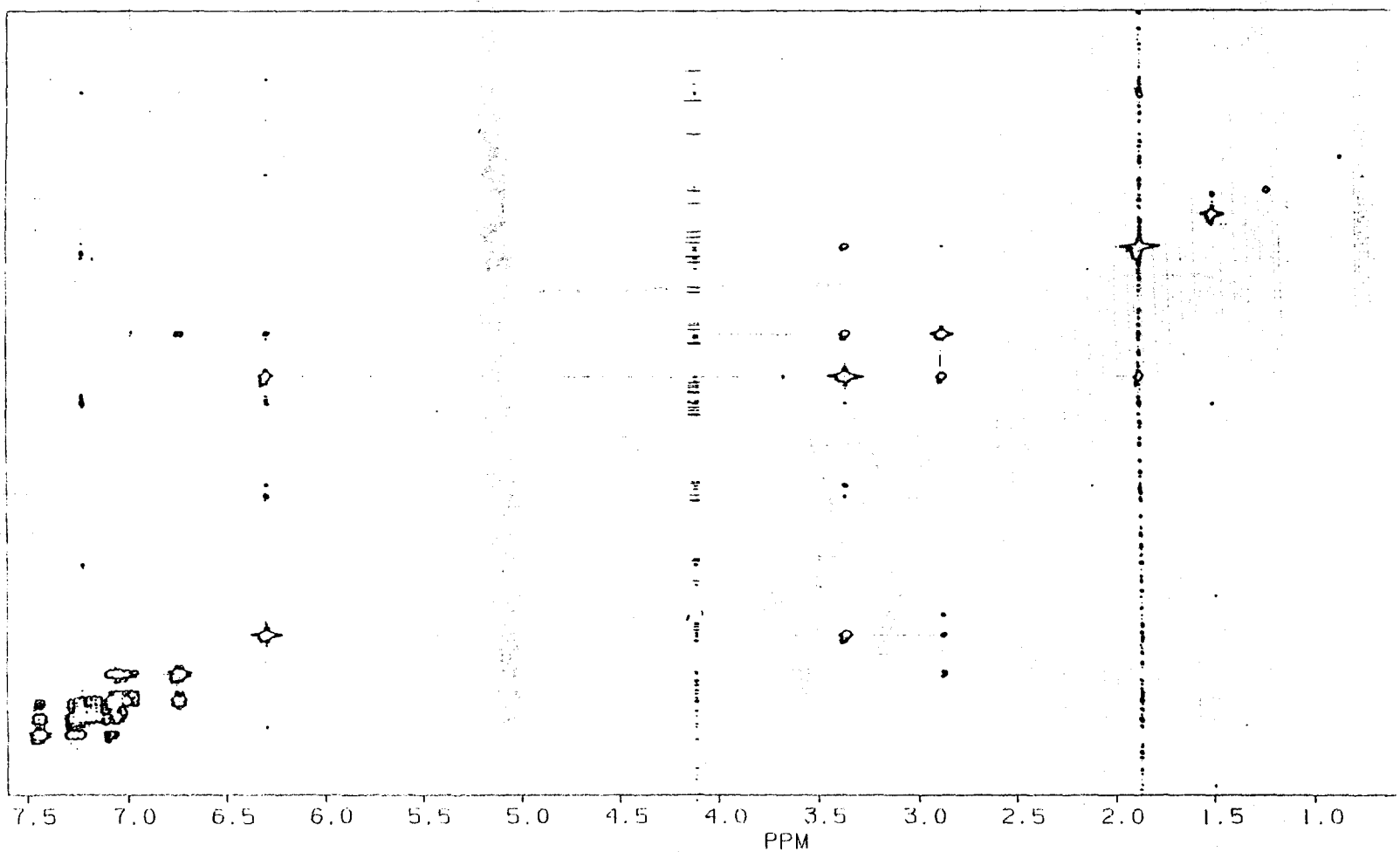
3,3,Anti-8-triphenyl exo tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**9**)



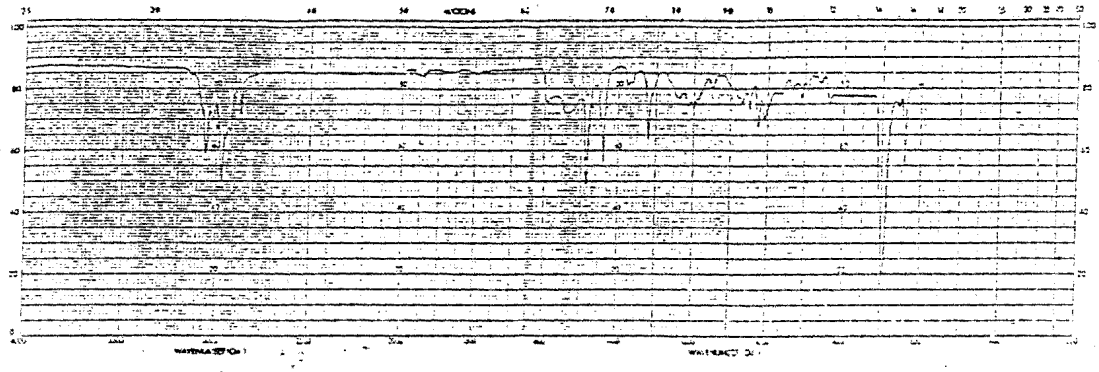


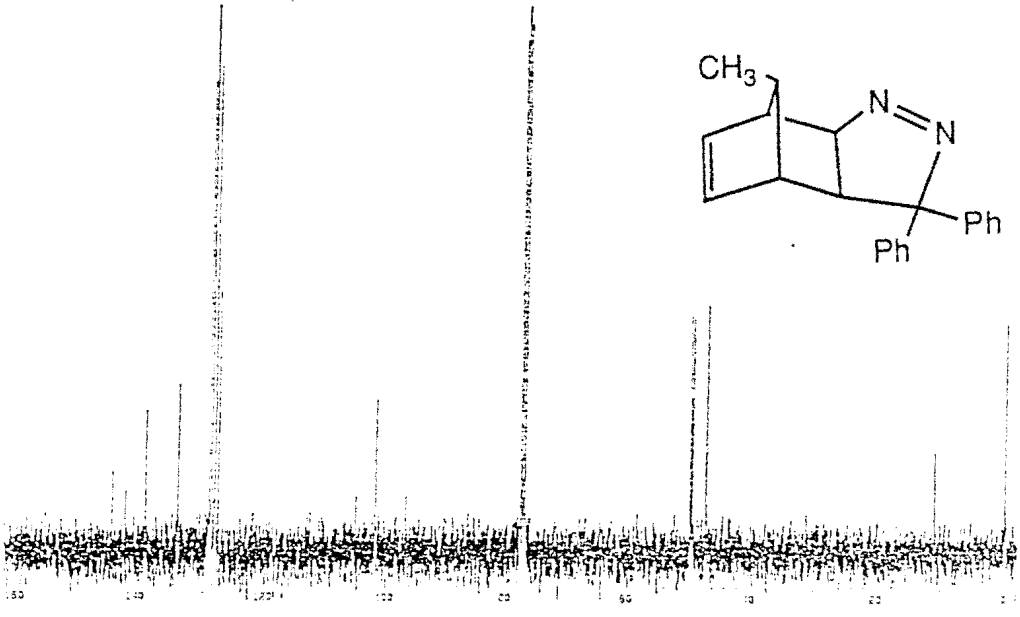


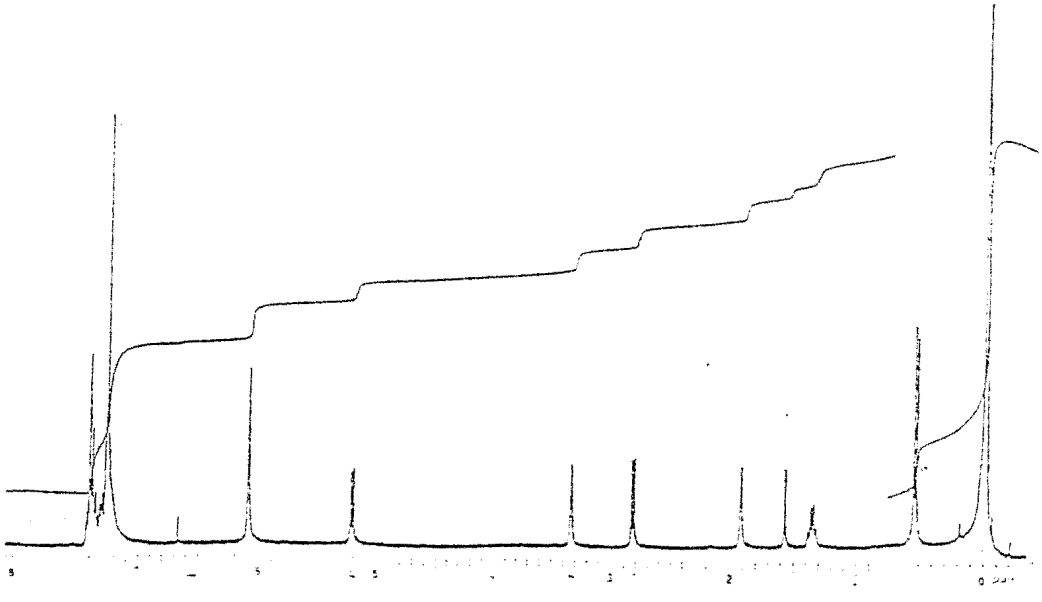
3,3,Anti-8-triphenyl exo tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**9**)



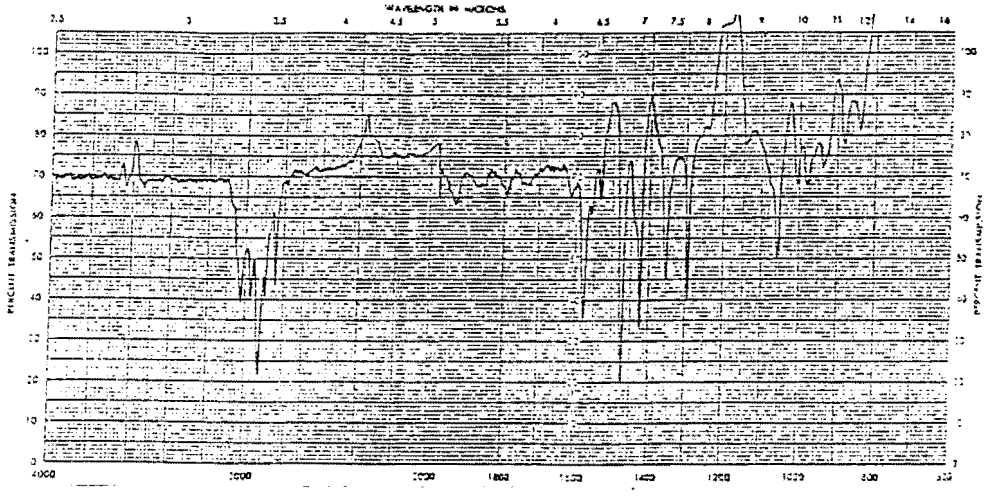
anti-10-methyl-5,5-diphenyl exo-3,4-diazatricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**11**)

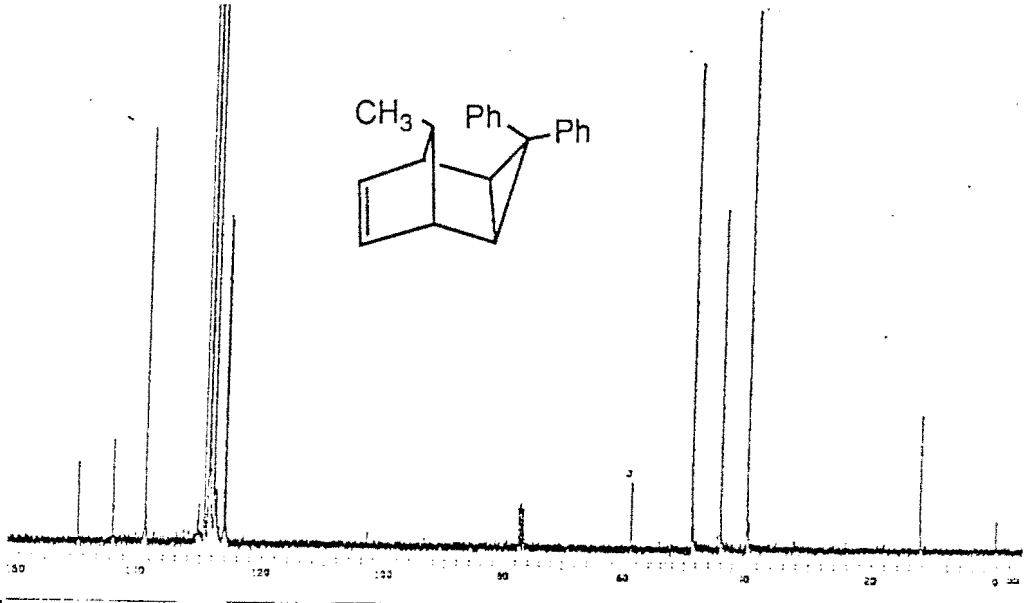


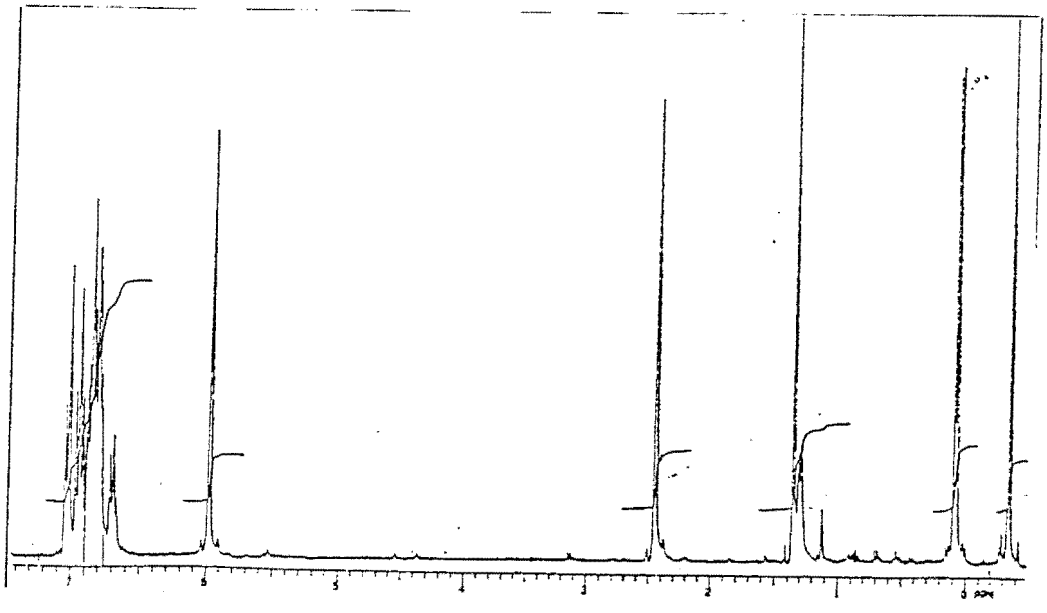




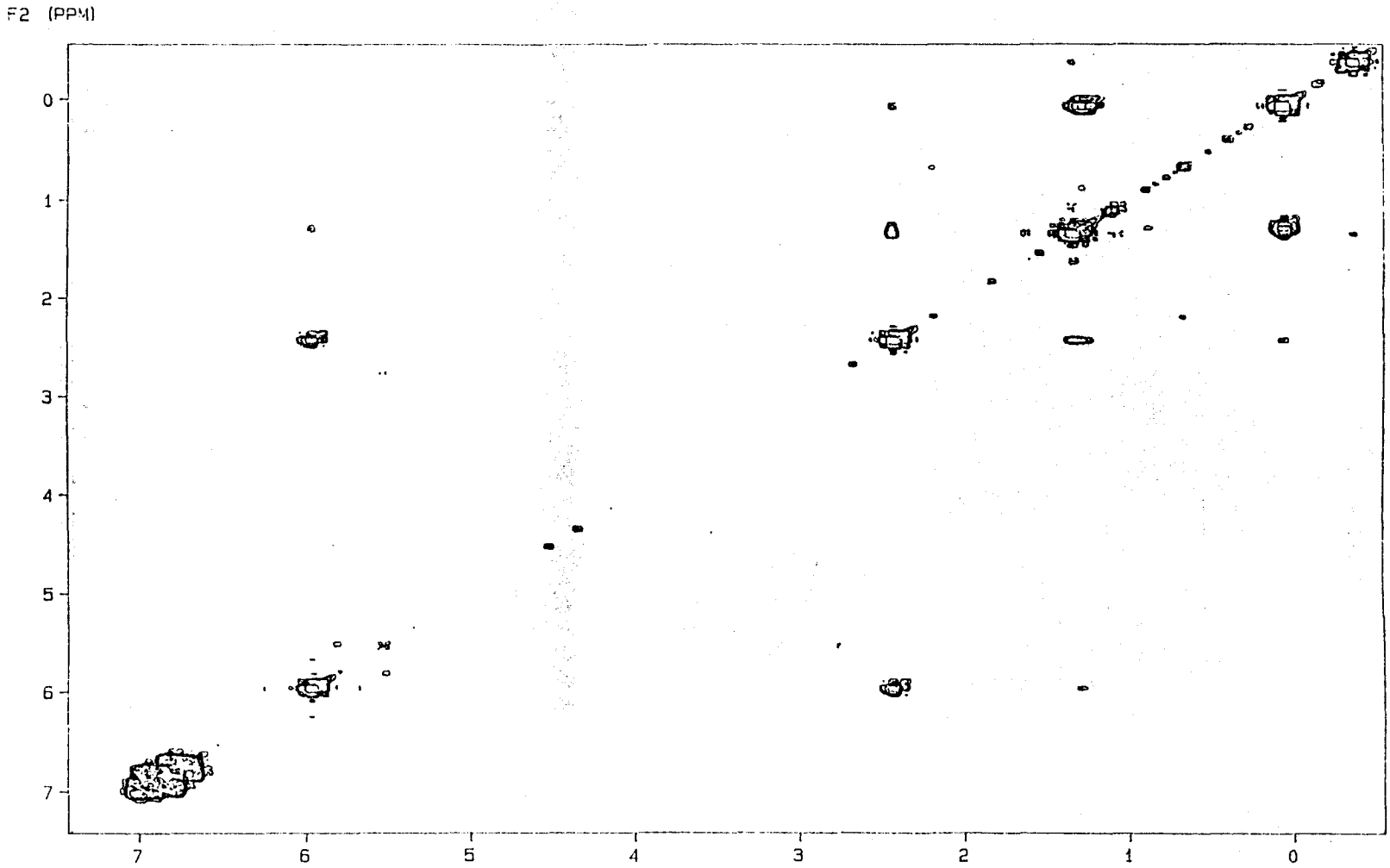
Anti-8-methyl-3,3-diphenyl exotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**14**)



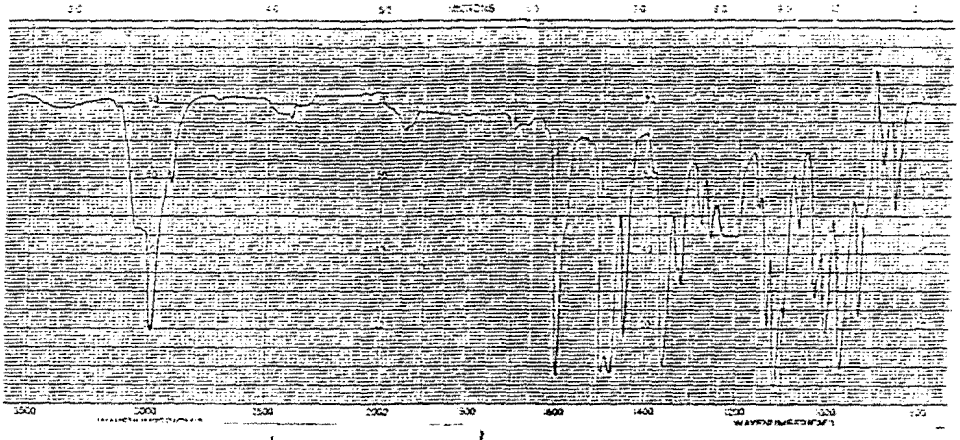


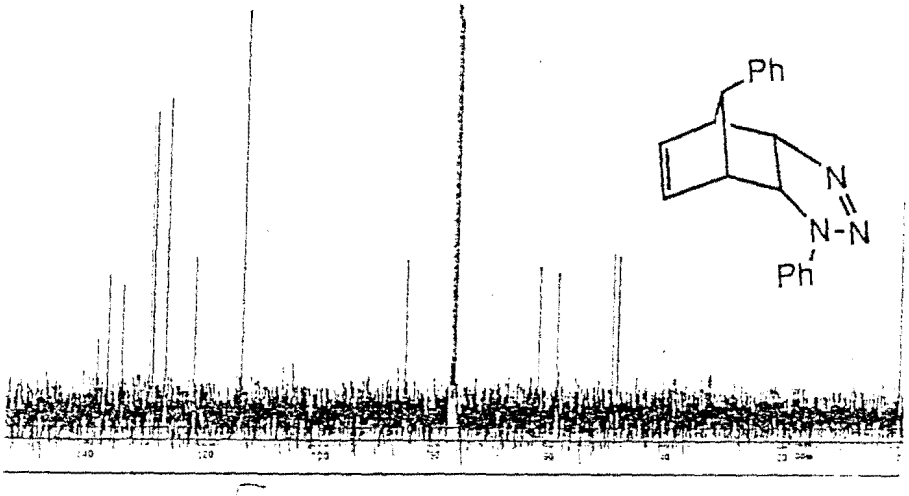


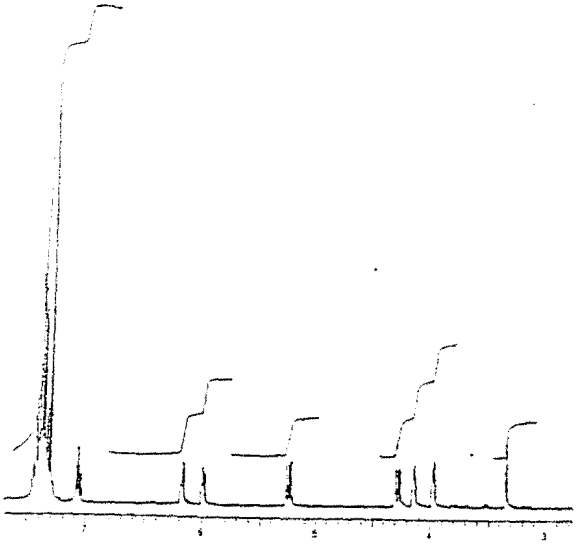
Anti-8-methyl-3,3-diphenyl exotricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**14**)



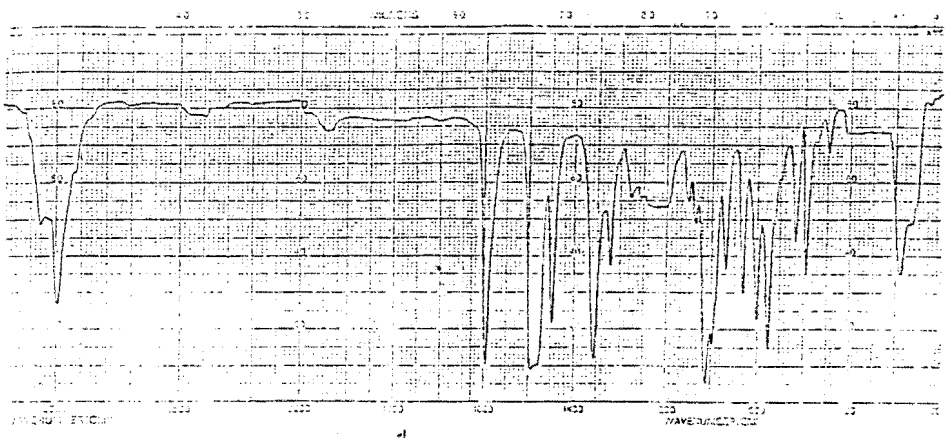
5,Syn-10-diphenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**16**)

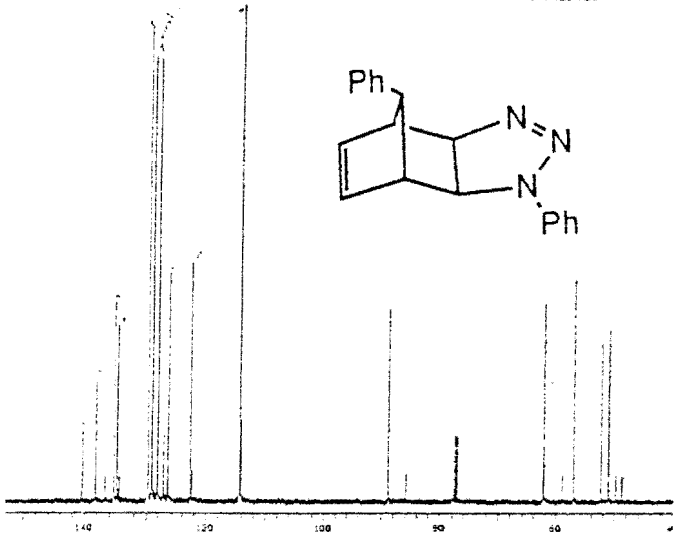


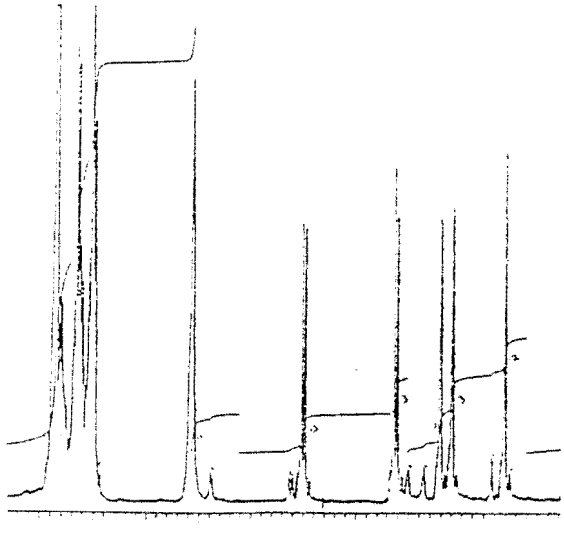




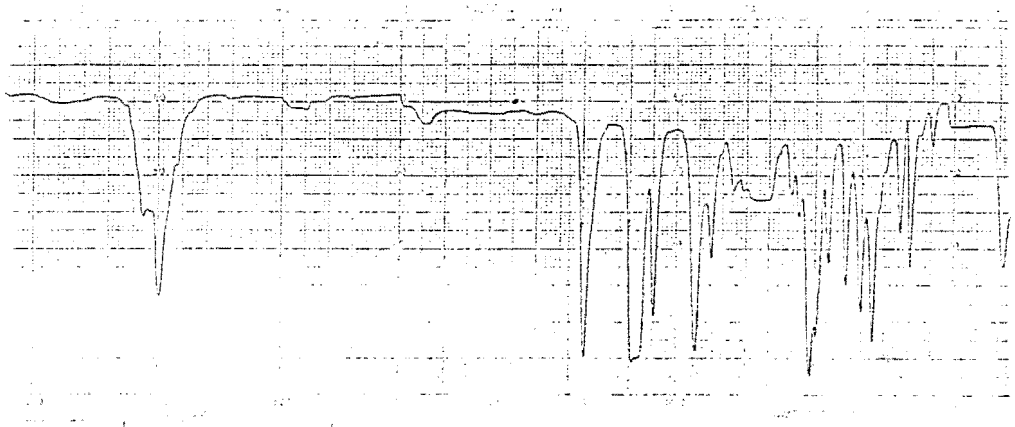
5,Anti-10-diphenyl exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (17)

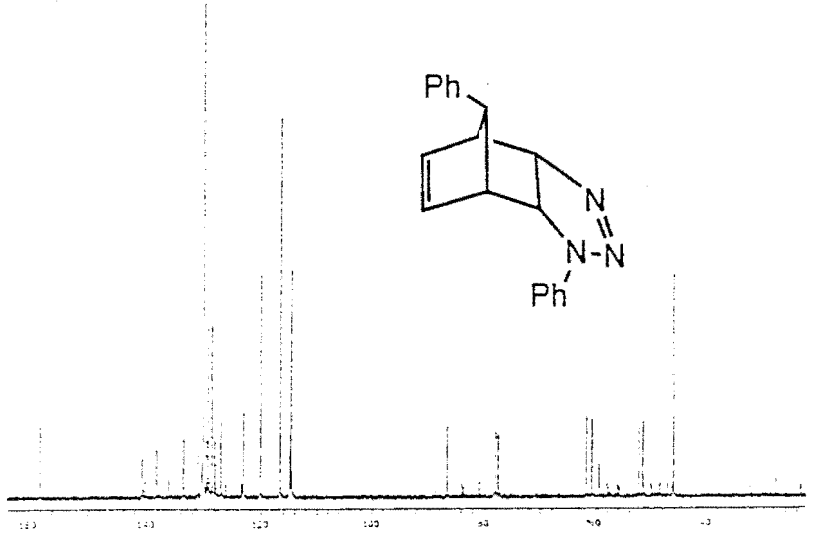


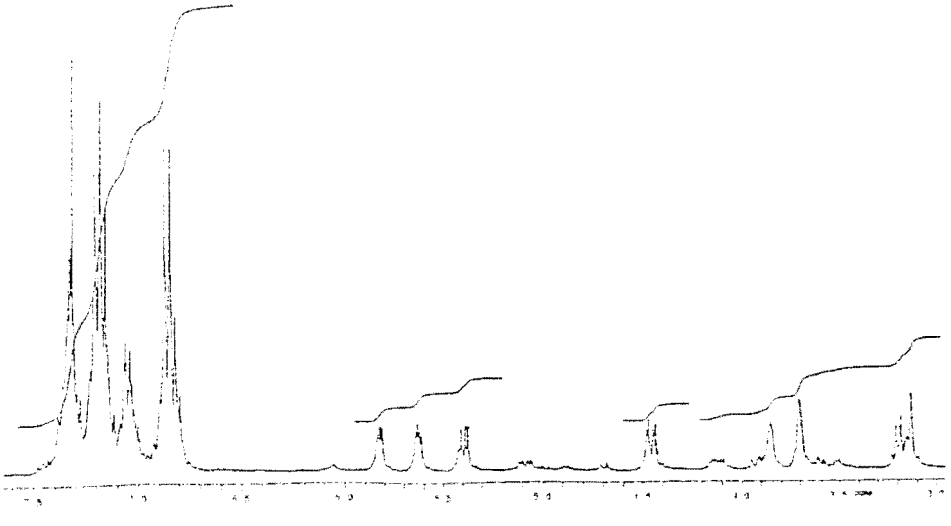




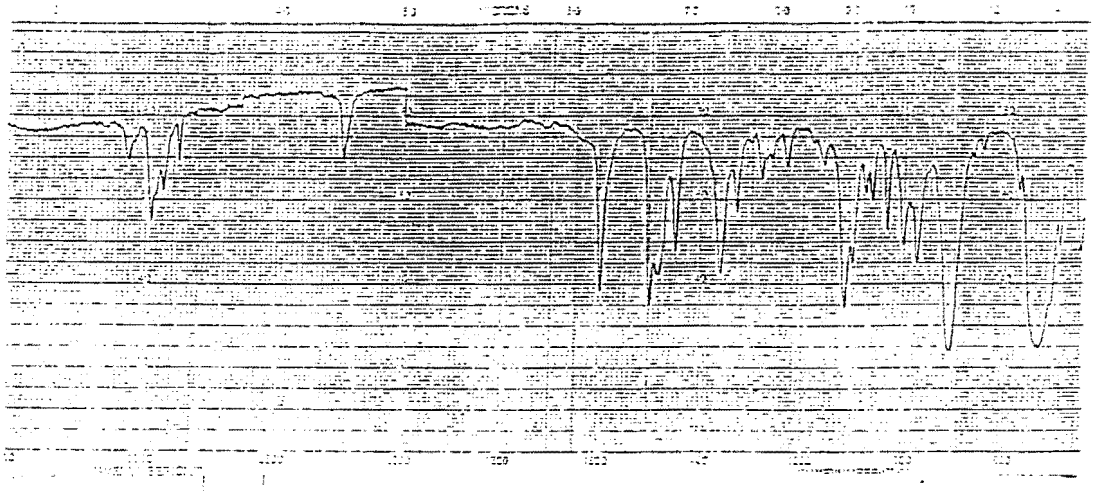
5.Anti-10-diphenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**18**)

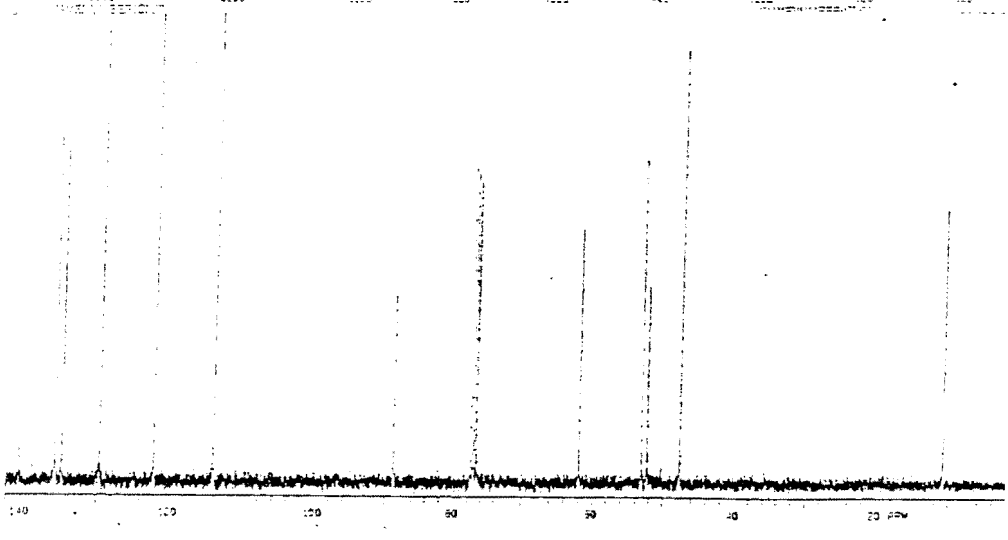


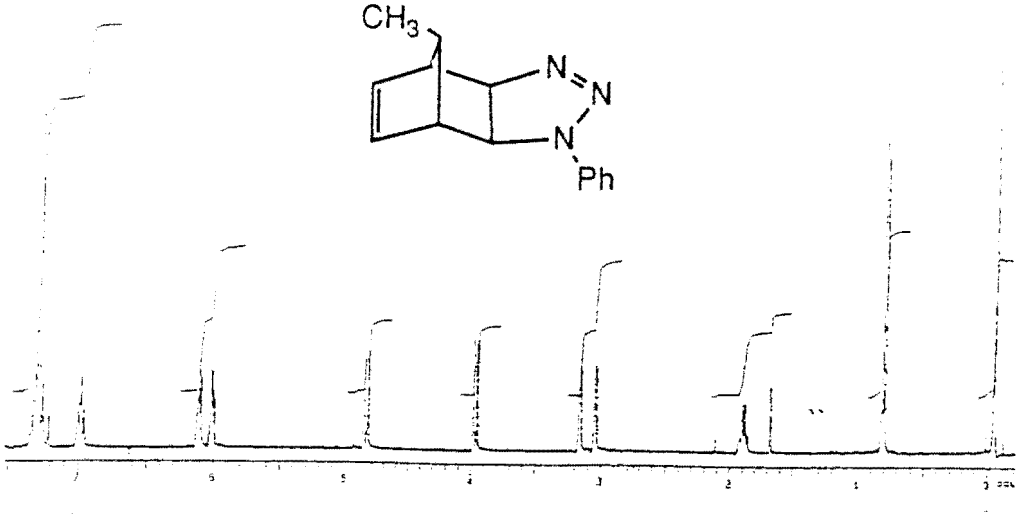




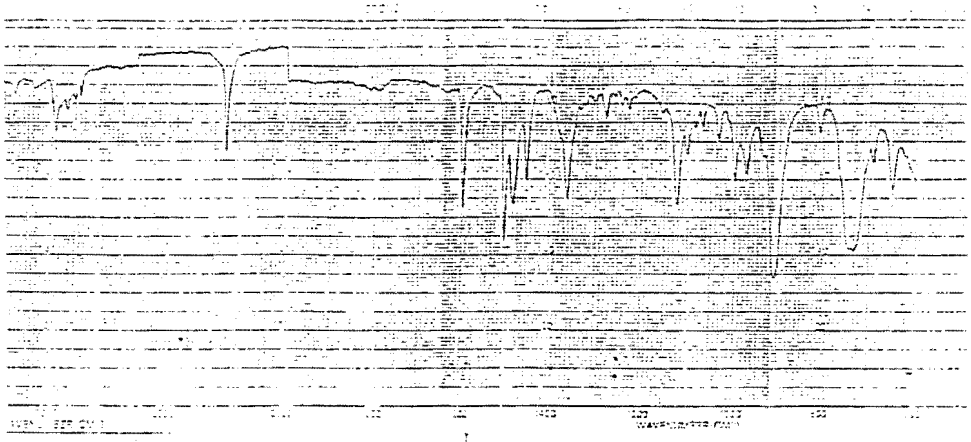
Anti-10-methyl-5-phenyl exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**19**)

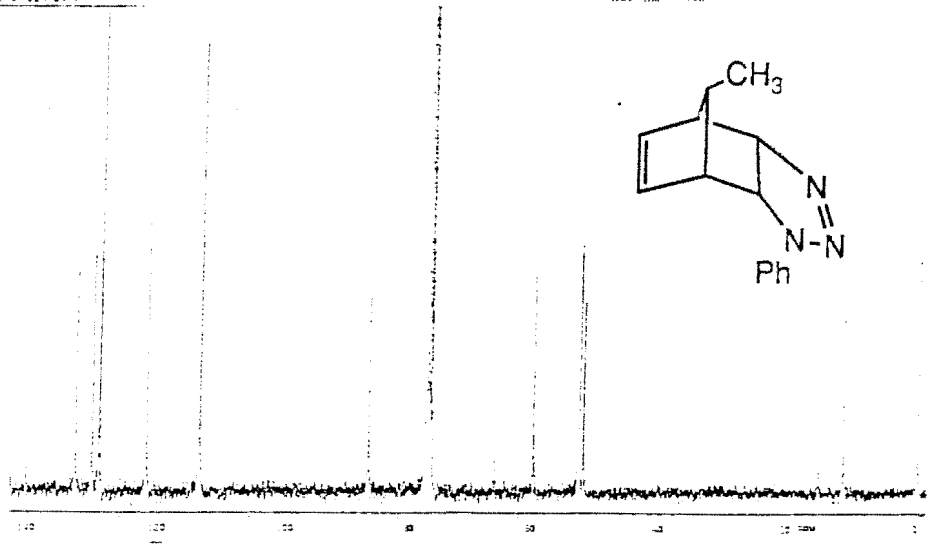


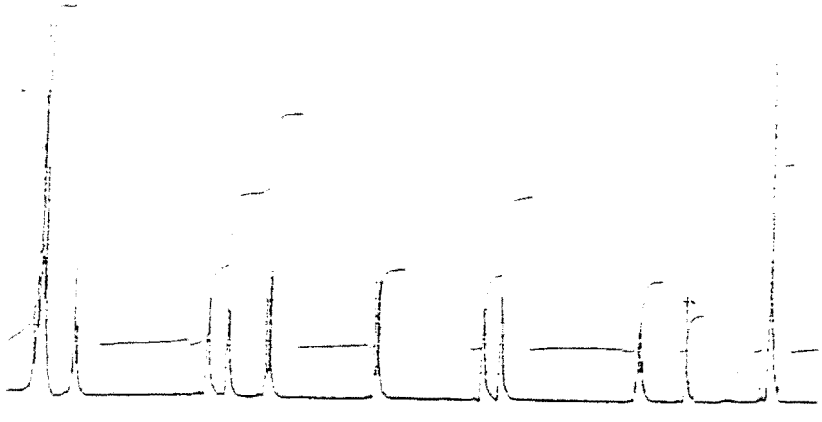




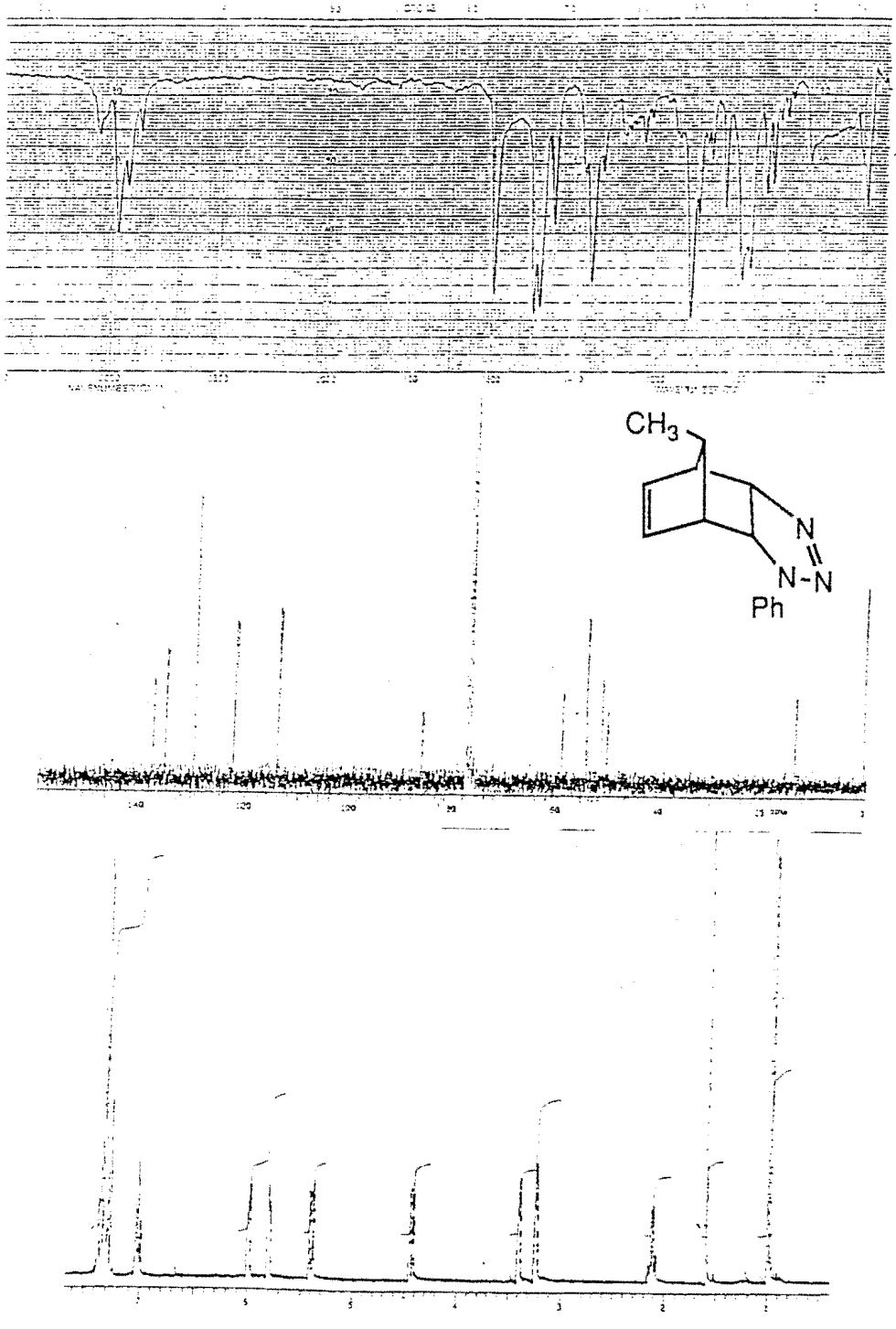
Syn-10-methyl-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**20**)





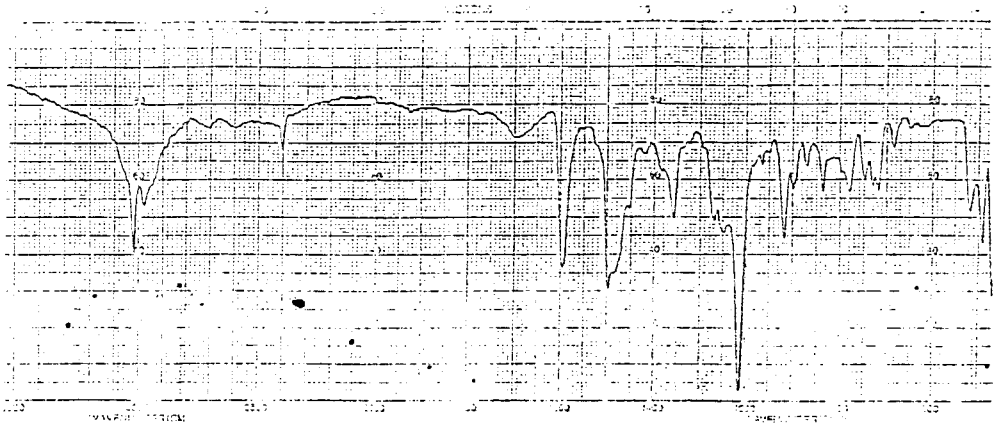


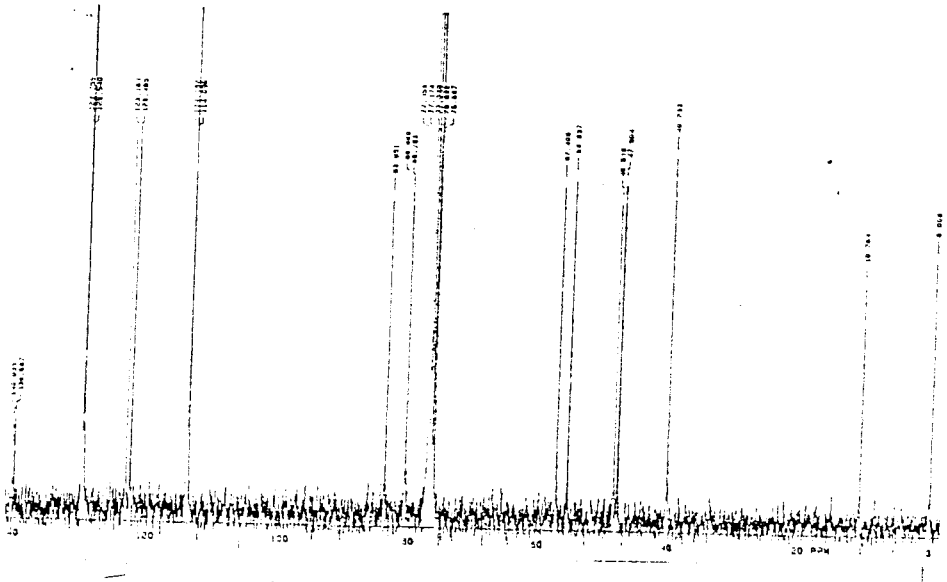
Anti-10-methyl-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (21)

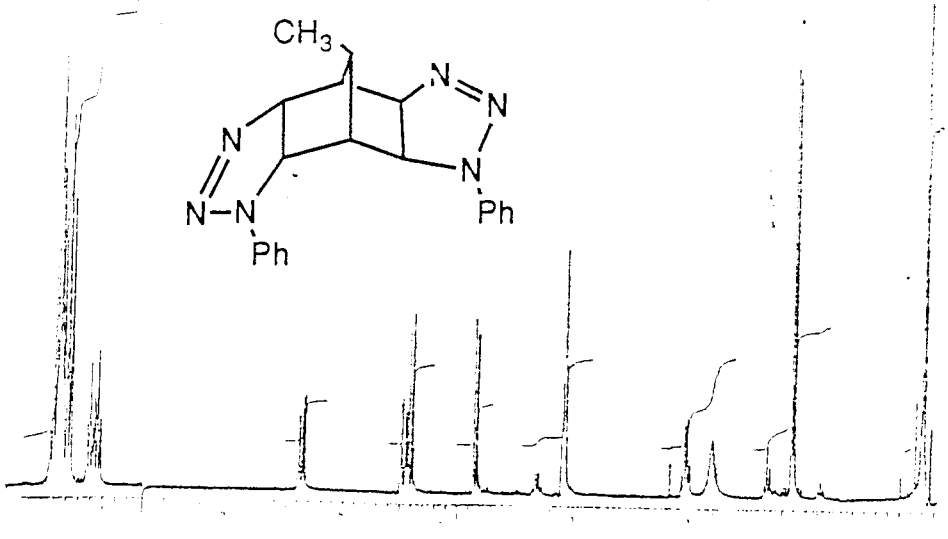


Anti-13-methyl-3,9-diphenyl exo-3,4,5-endo-9,10,11-bis(triaza) tetracyclo[5.5.1.$0^{2,6}0^{8,12}$]

tridecan-4,10-diene (**22**)

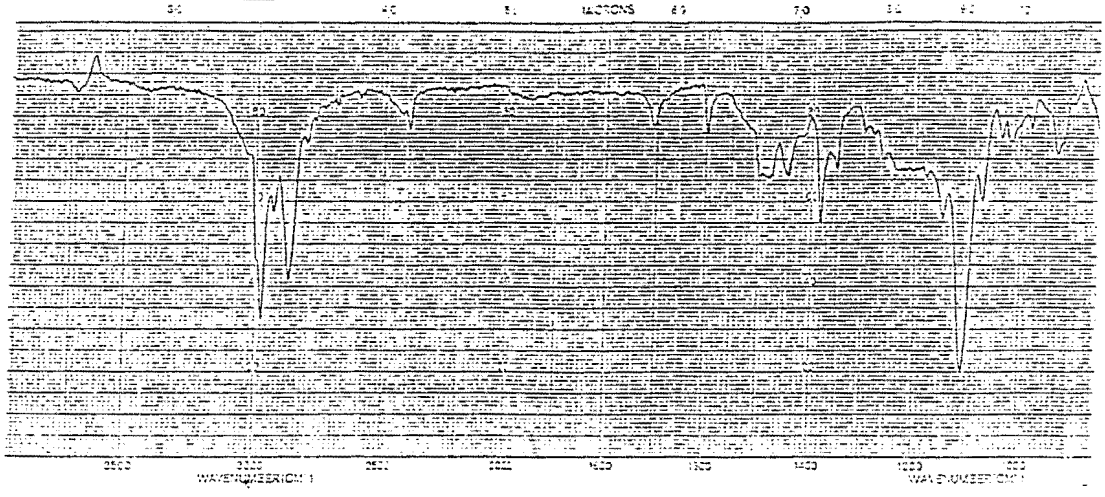


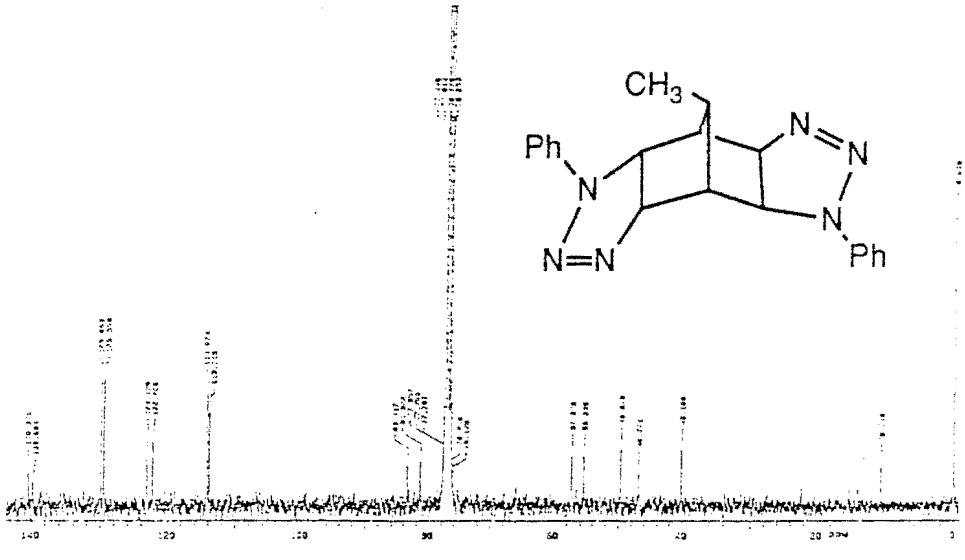


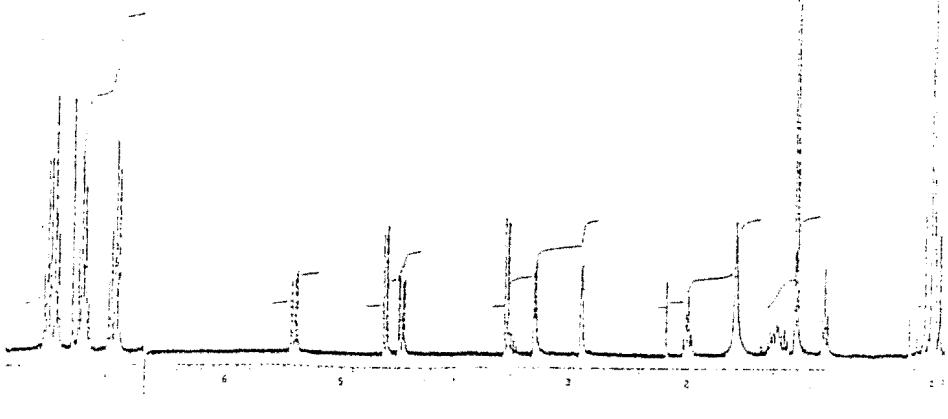


Anti-13-methyl-5,9-diphenyl exo-3,4,5-endo-9,10,11-bis(triaza) tetracyclo[5.5.1.$0^{2,6}0^{8,12}$]

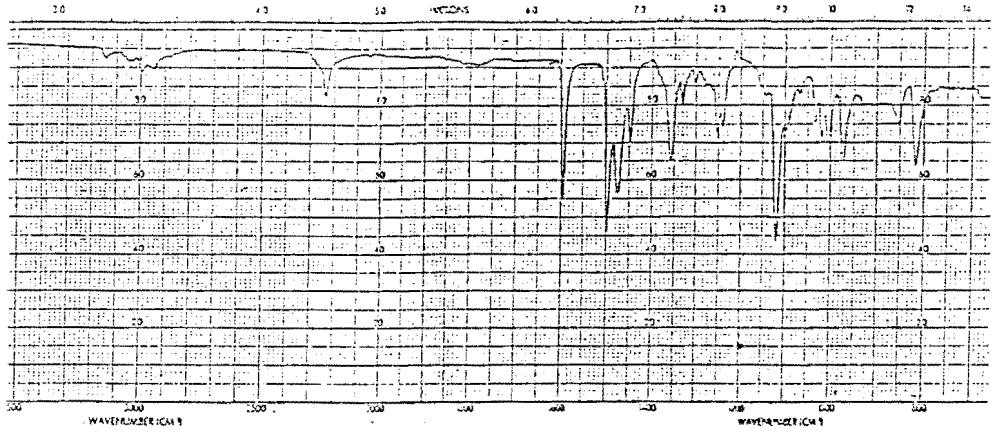
trideca-3,10-diene (**23**)

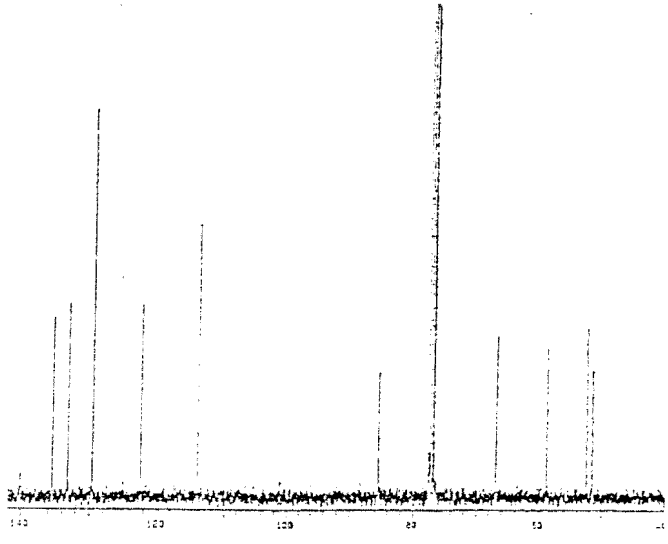


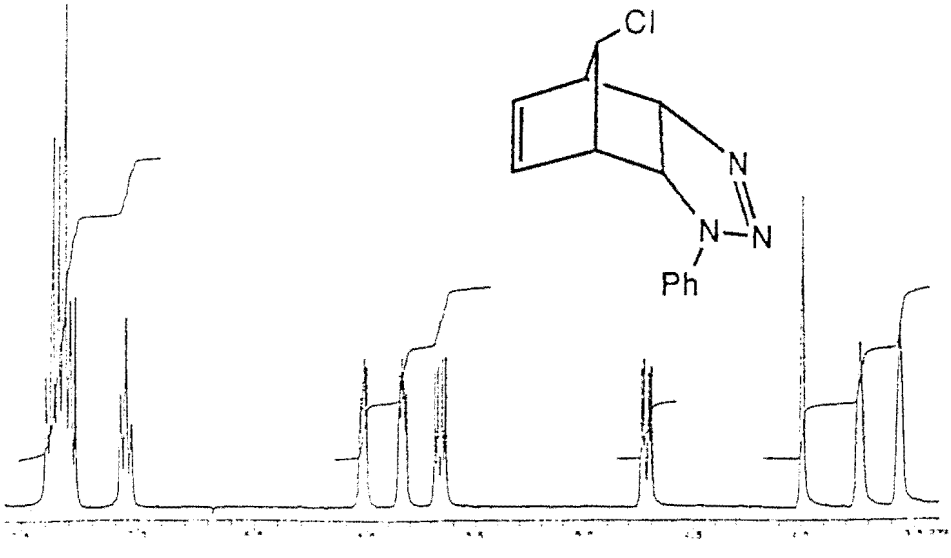




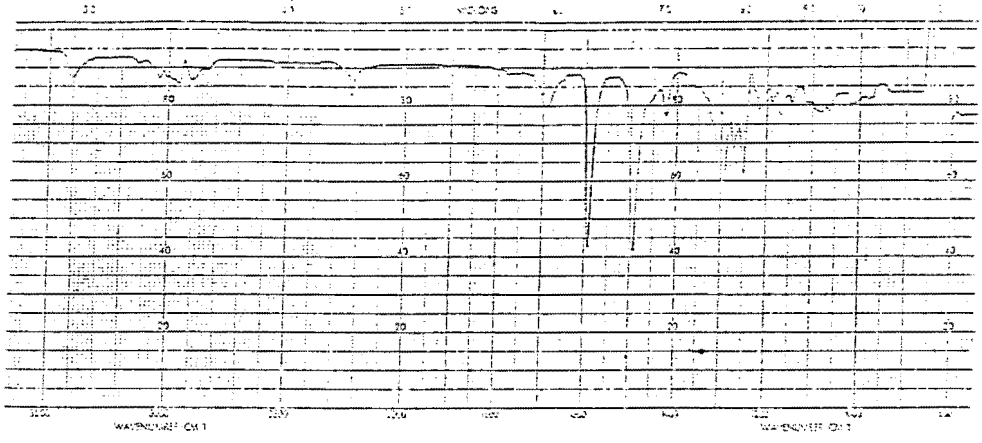
Syn-10-chloro-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**25**)

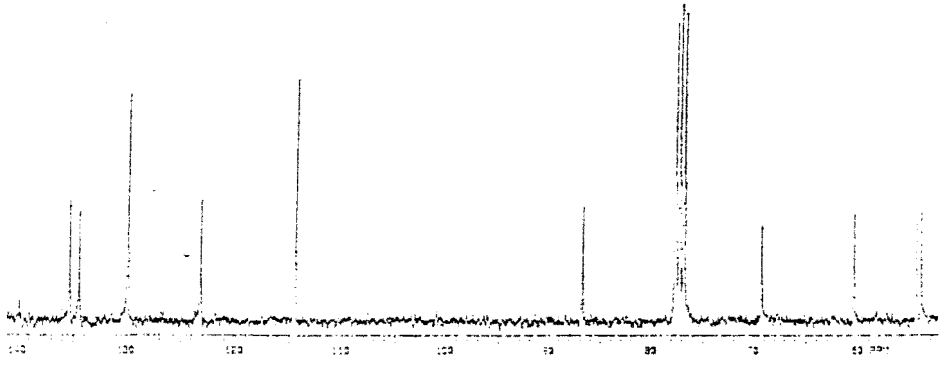


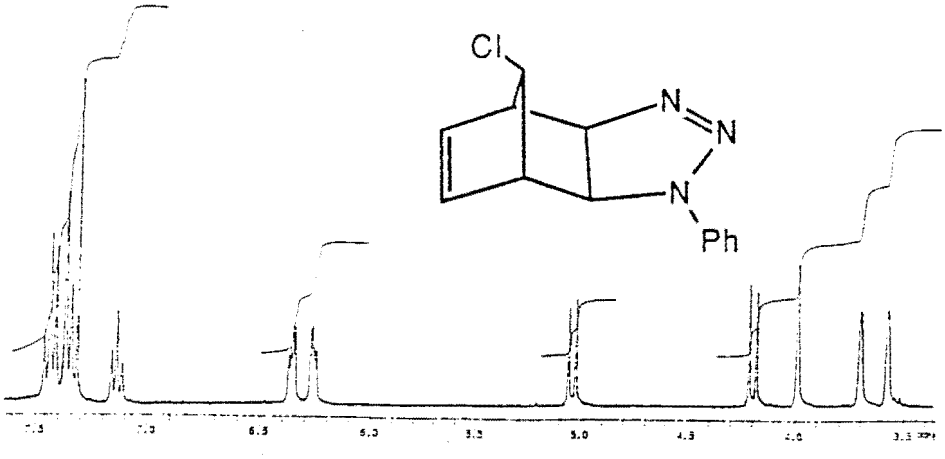




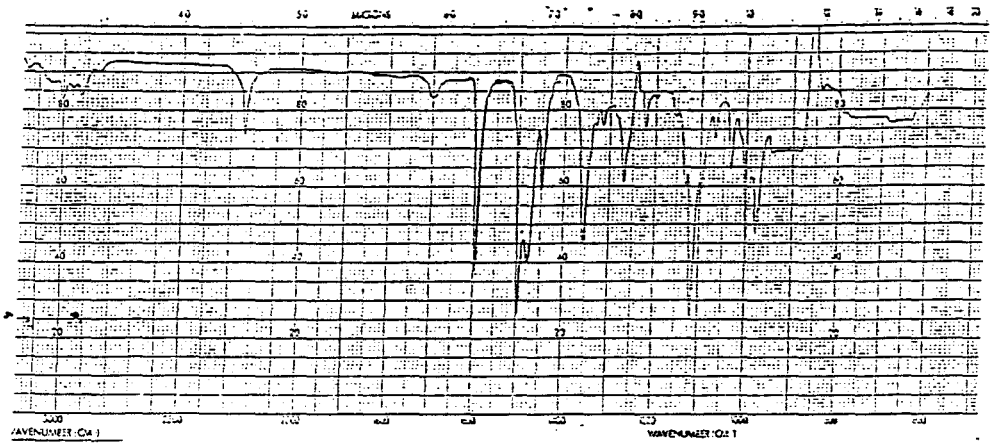
Anti-10-chloro-5-phenyl exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**26**)

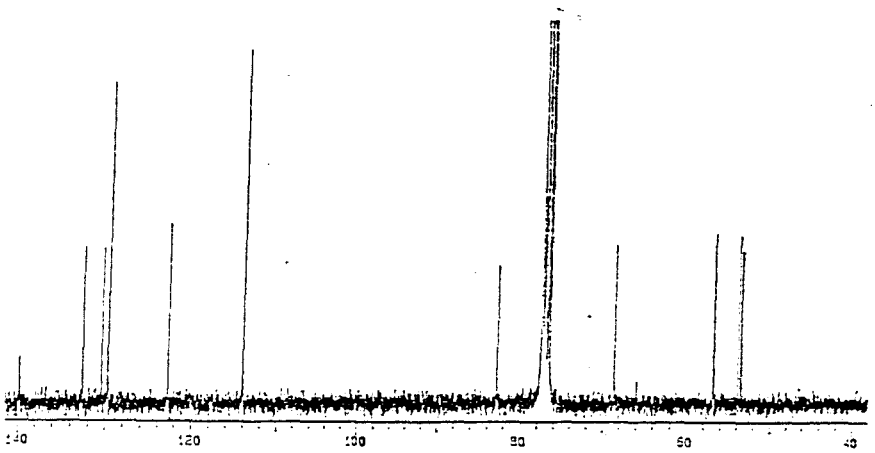


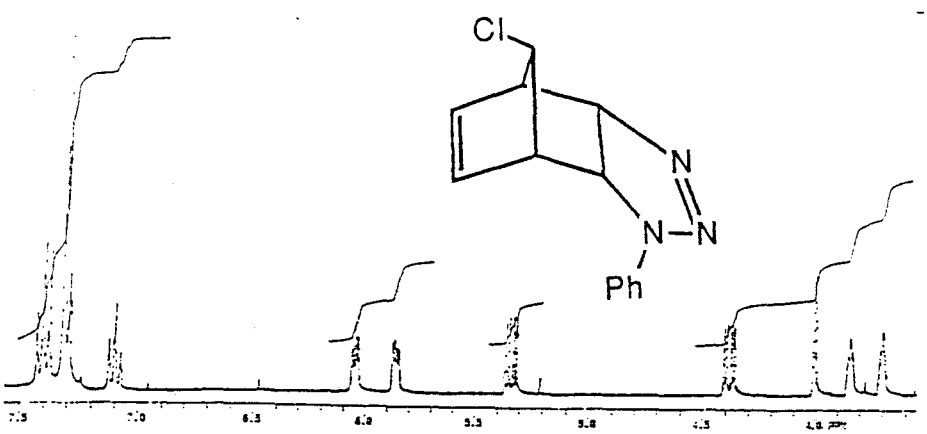




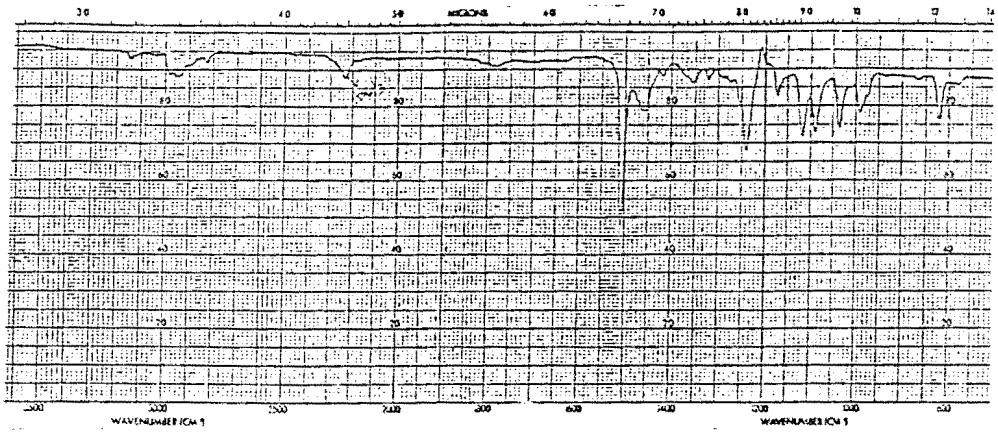
Anti-10-chloro-5-phenyl endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (27)

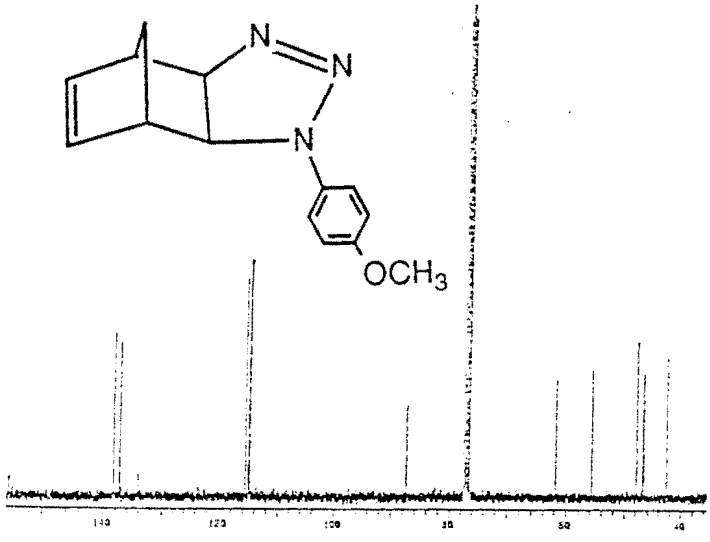


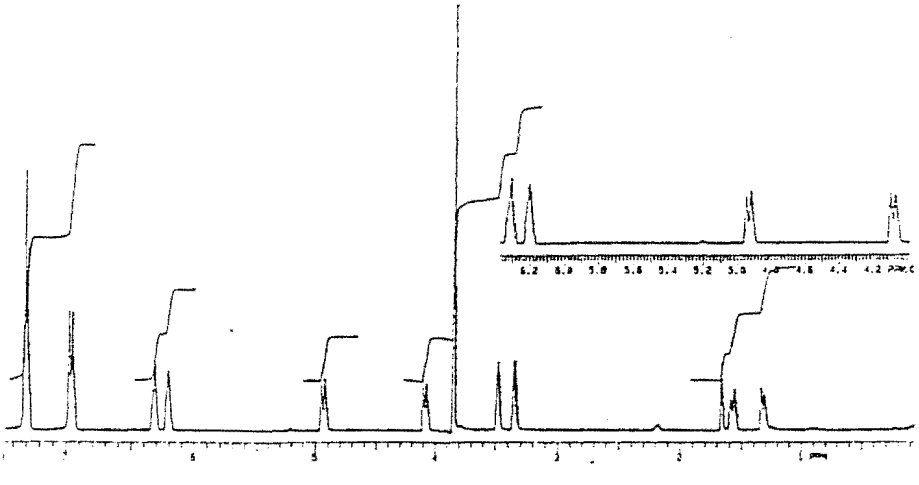




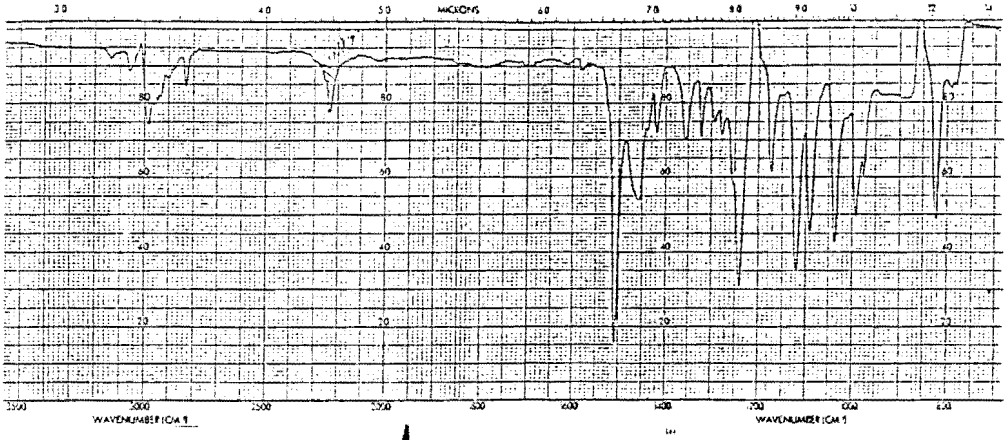
5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**30**)

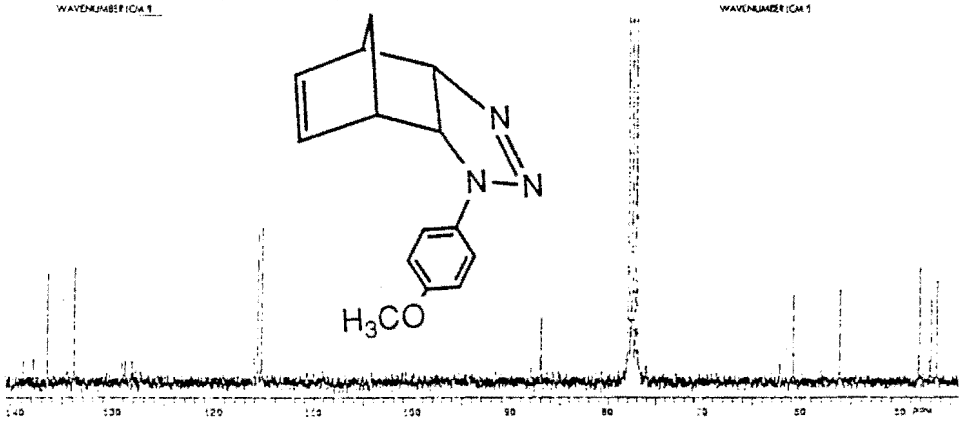


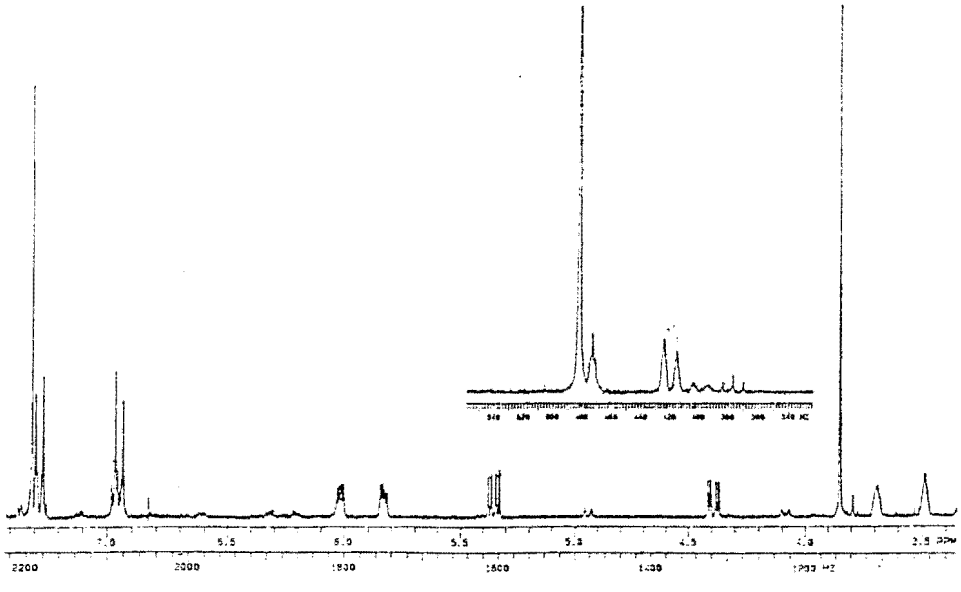




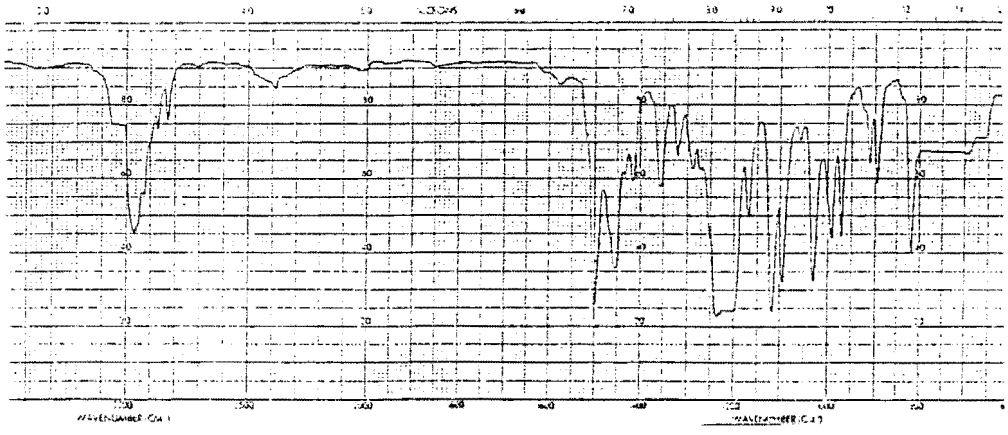
5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**31**)

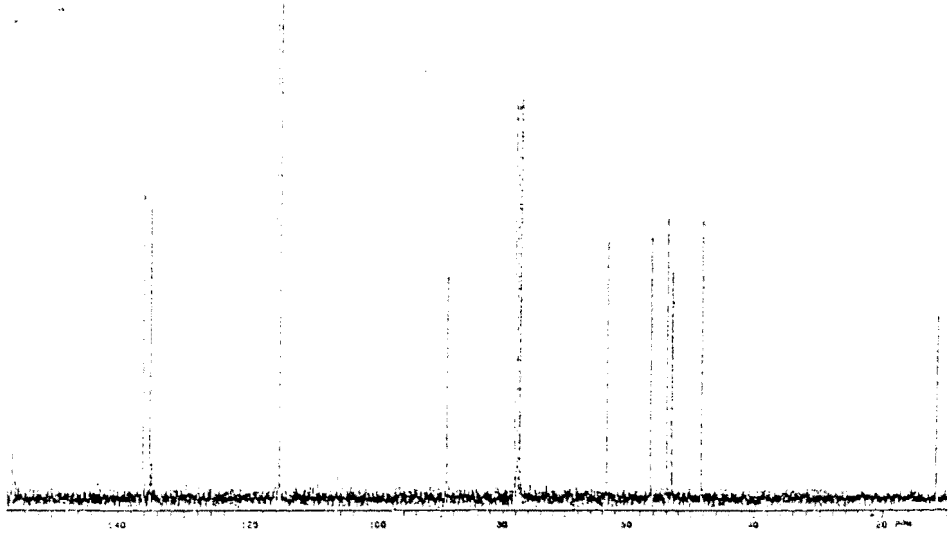


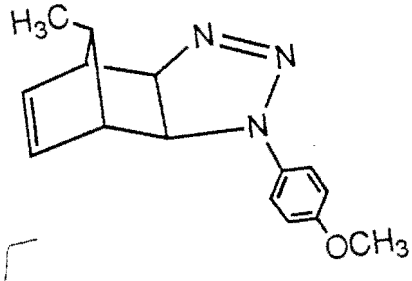


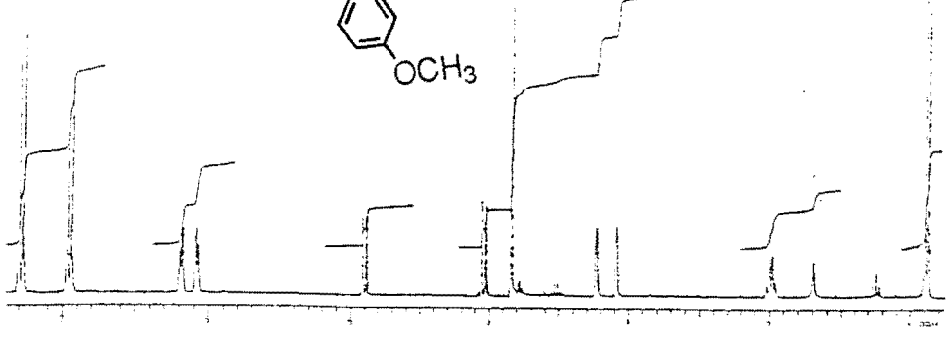


Anti-10-methyl-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (32)

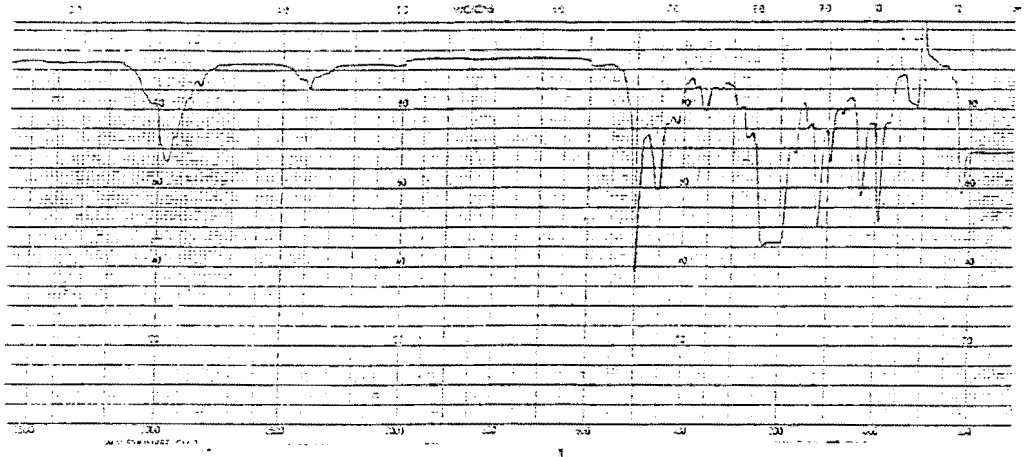


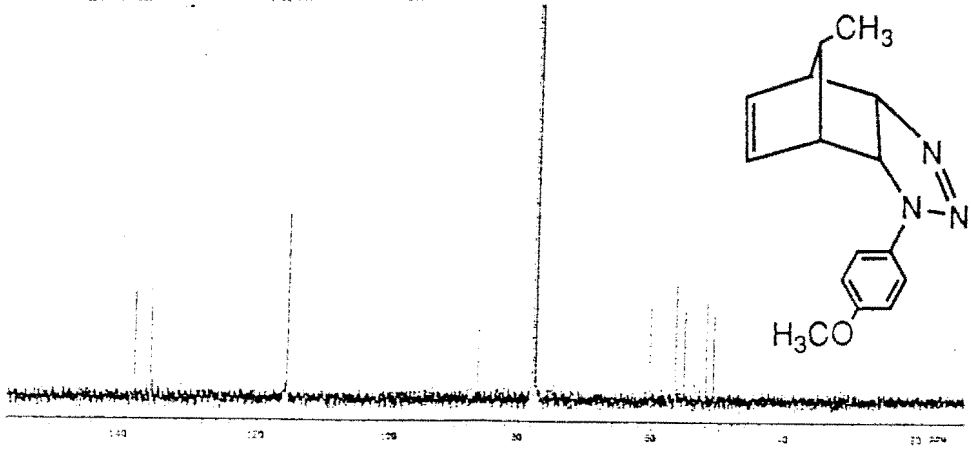


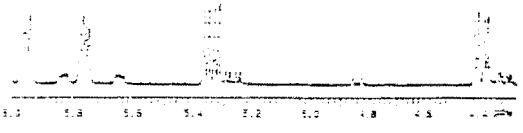


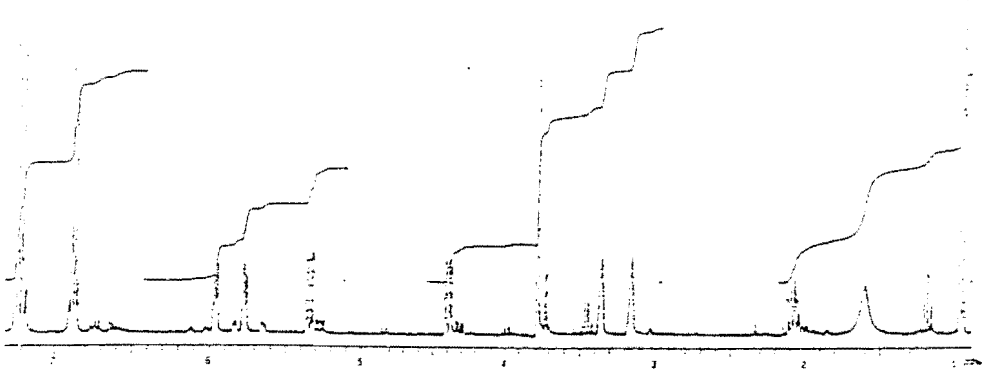


Syn-10-methyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (33)

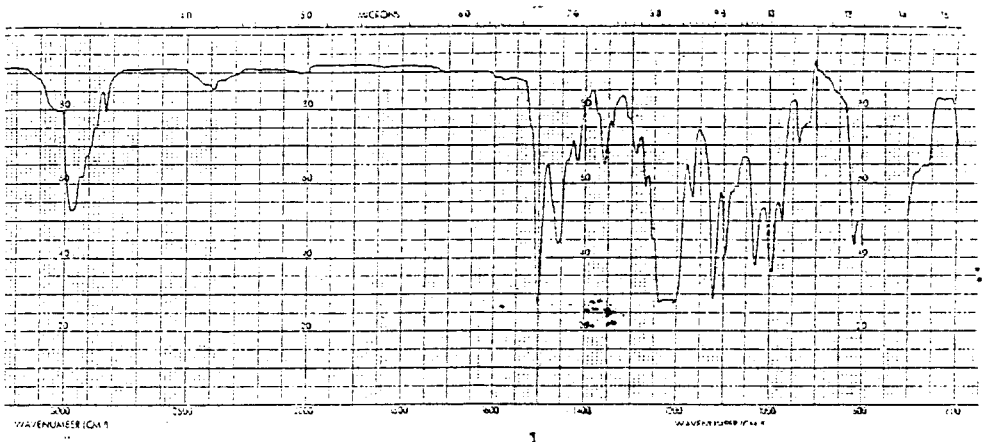


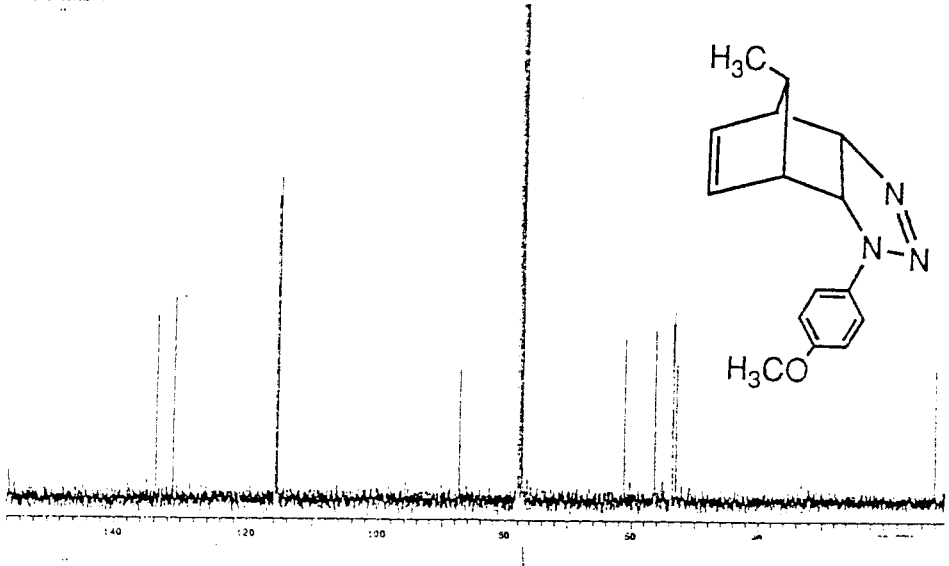


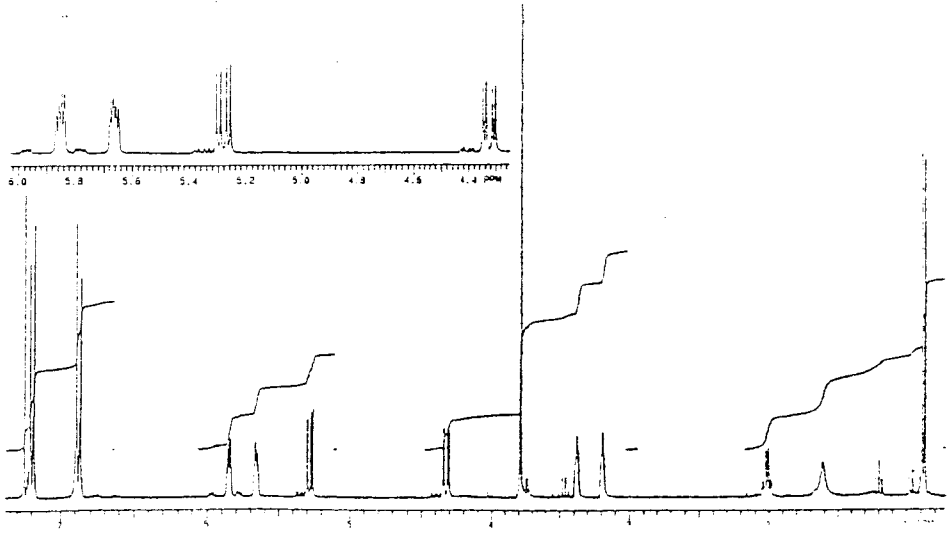




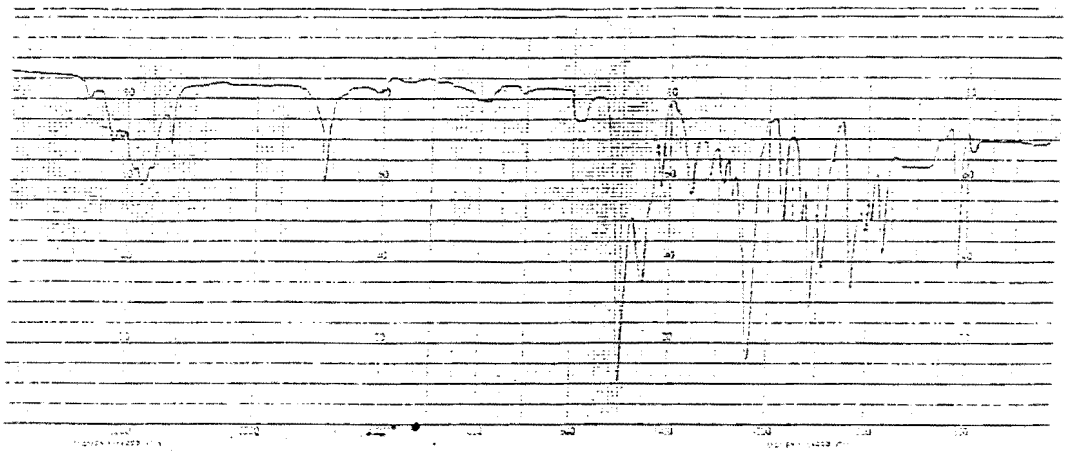
Anti-10-methyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (34)

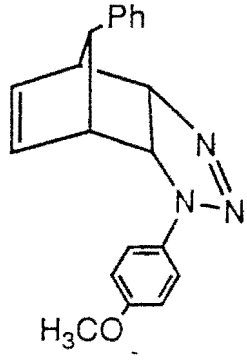


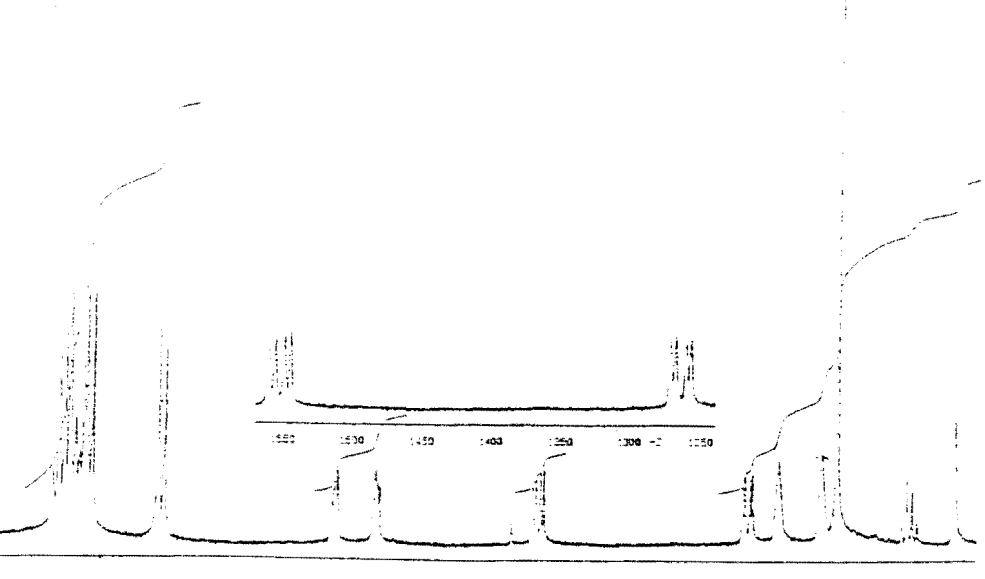




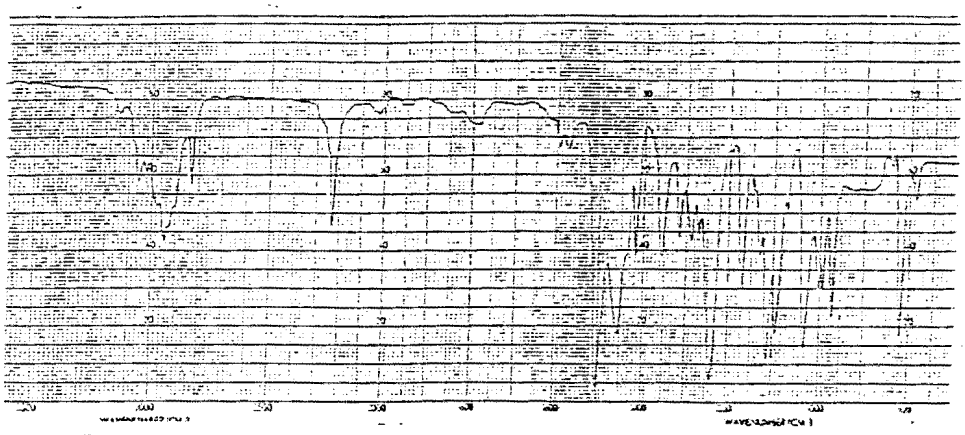
Syn-10-phenyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (35)

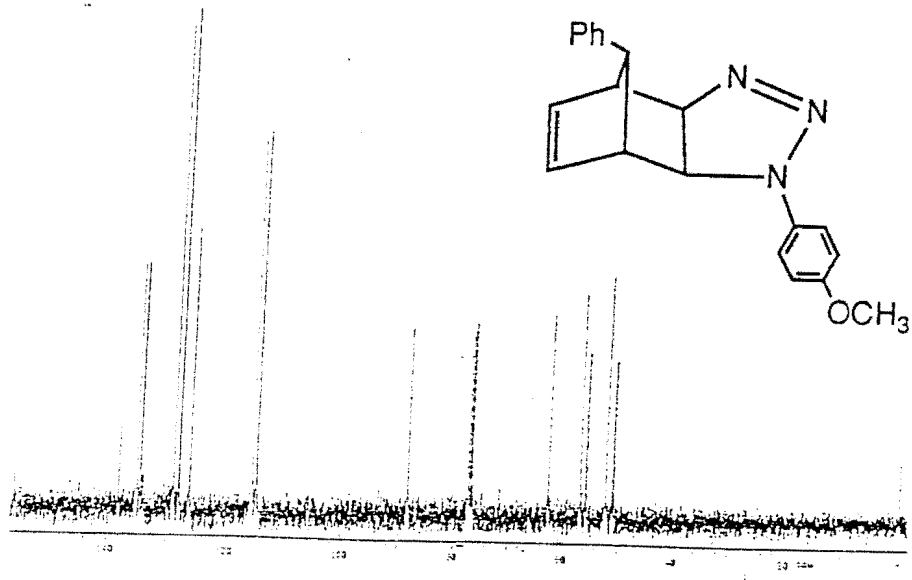


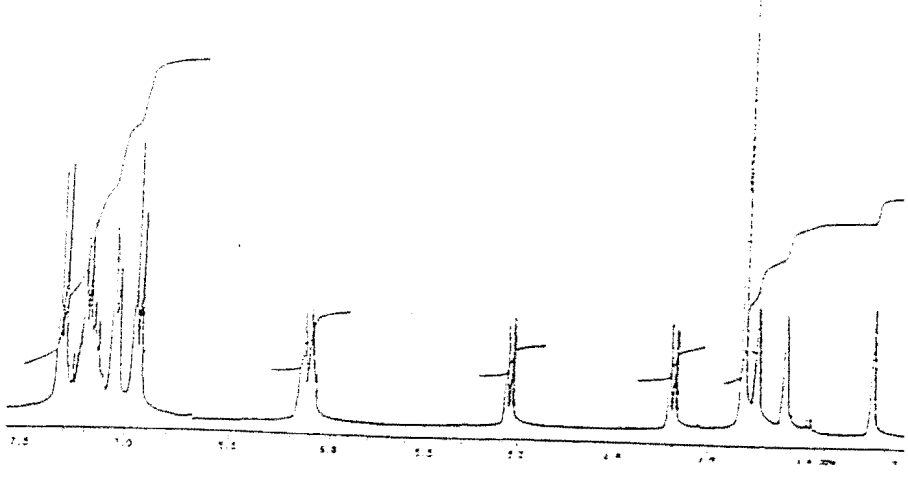




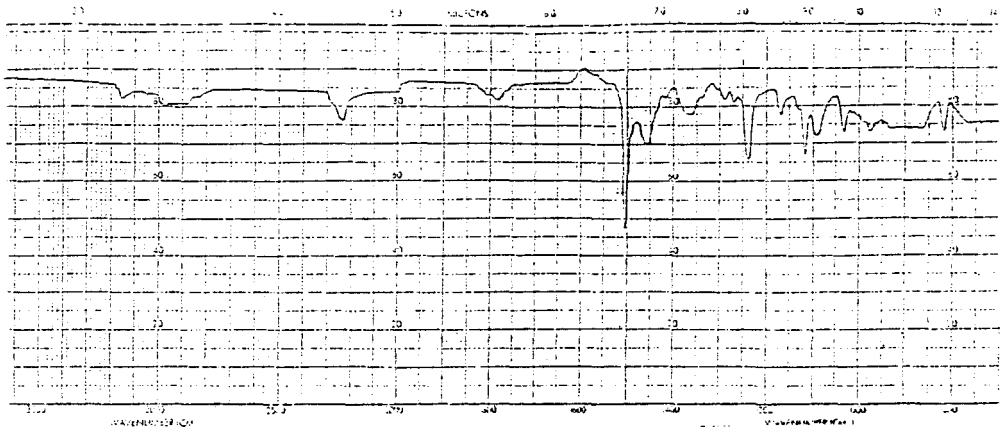
Anti-10-phenyl-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**36**)

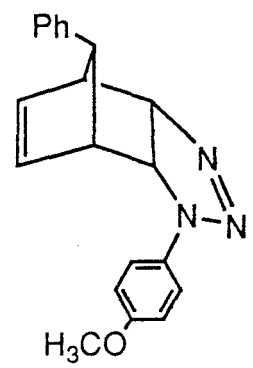


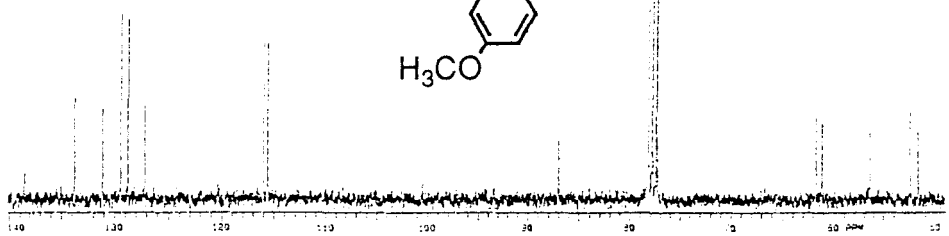


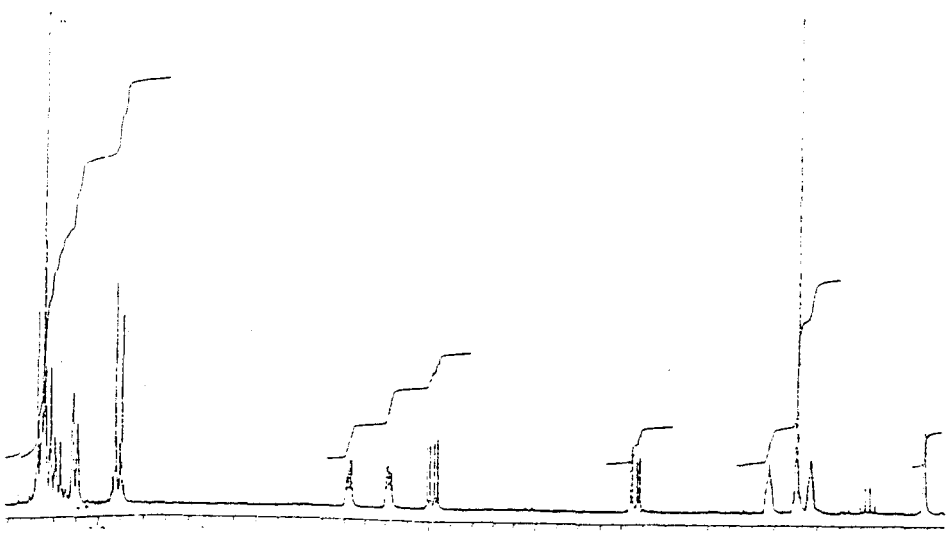


Syn-10-phenyl-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (37)

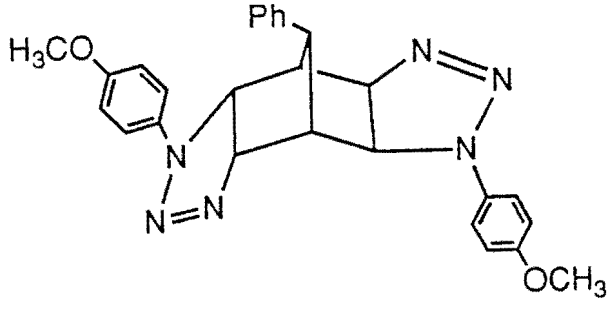


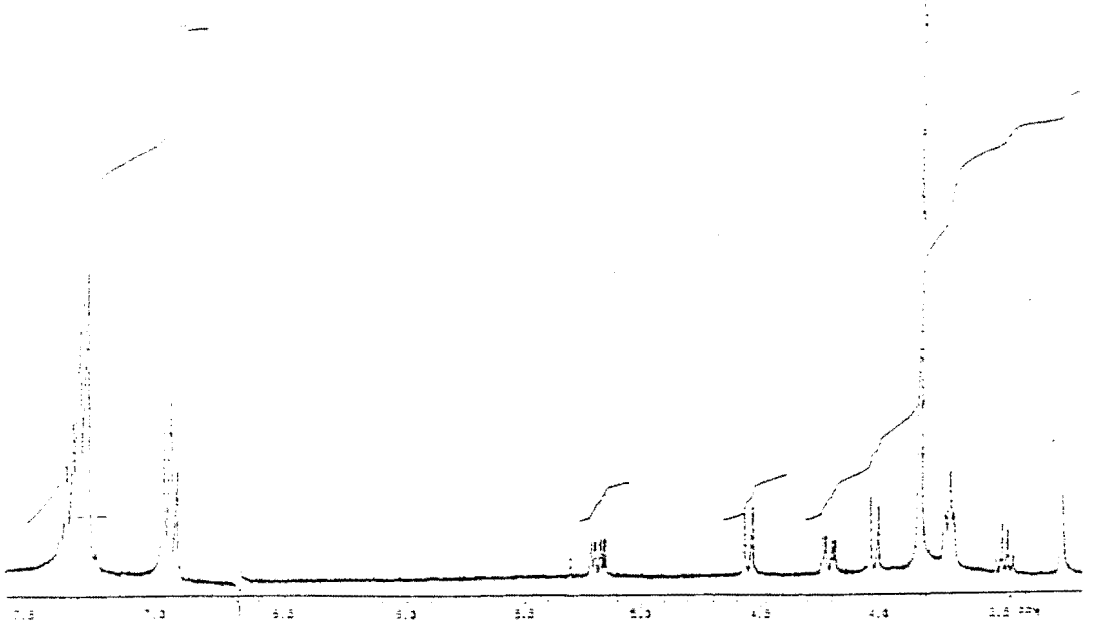




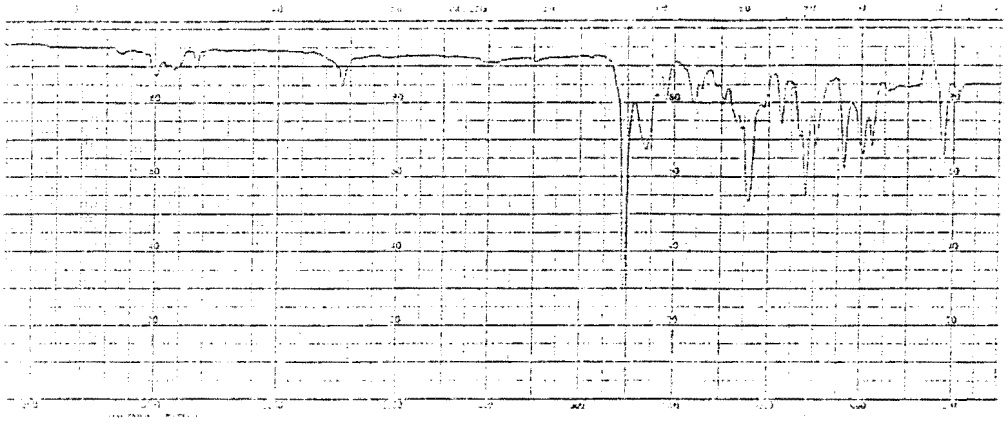


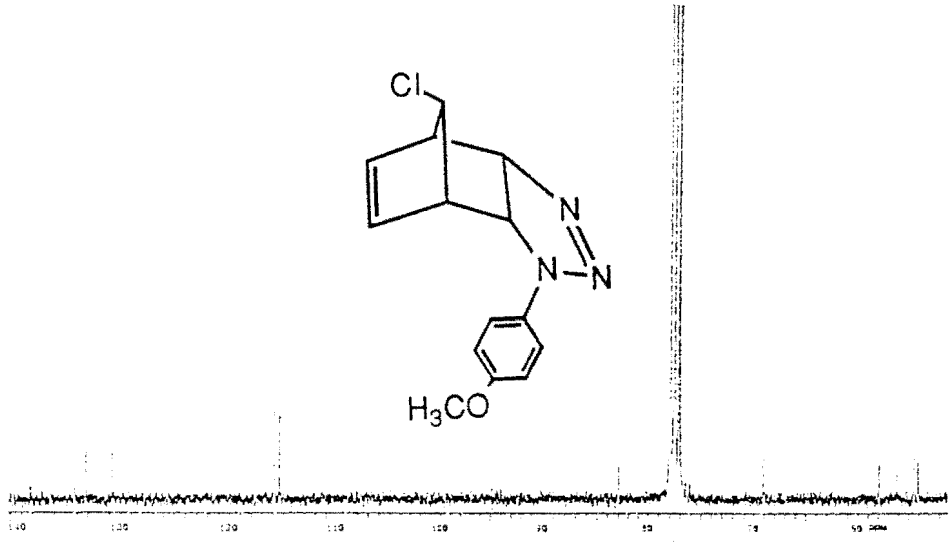
Anti-13-phenyl-5,11-bis (4'-methoxyphenyl) exo-3,4,5-endo-9,10,11-bis(triaza) tetracyclo [5.5.1.$0^{2,6}0^{8,12}$]trideca-3,9-diene (**38**)

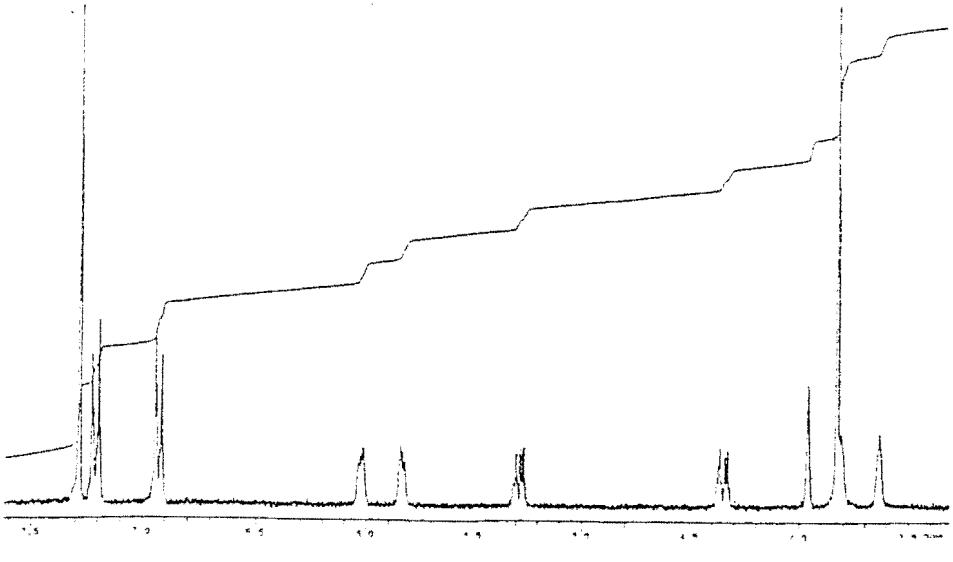




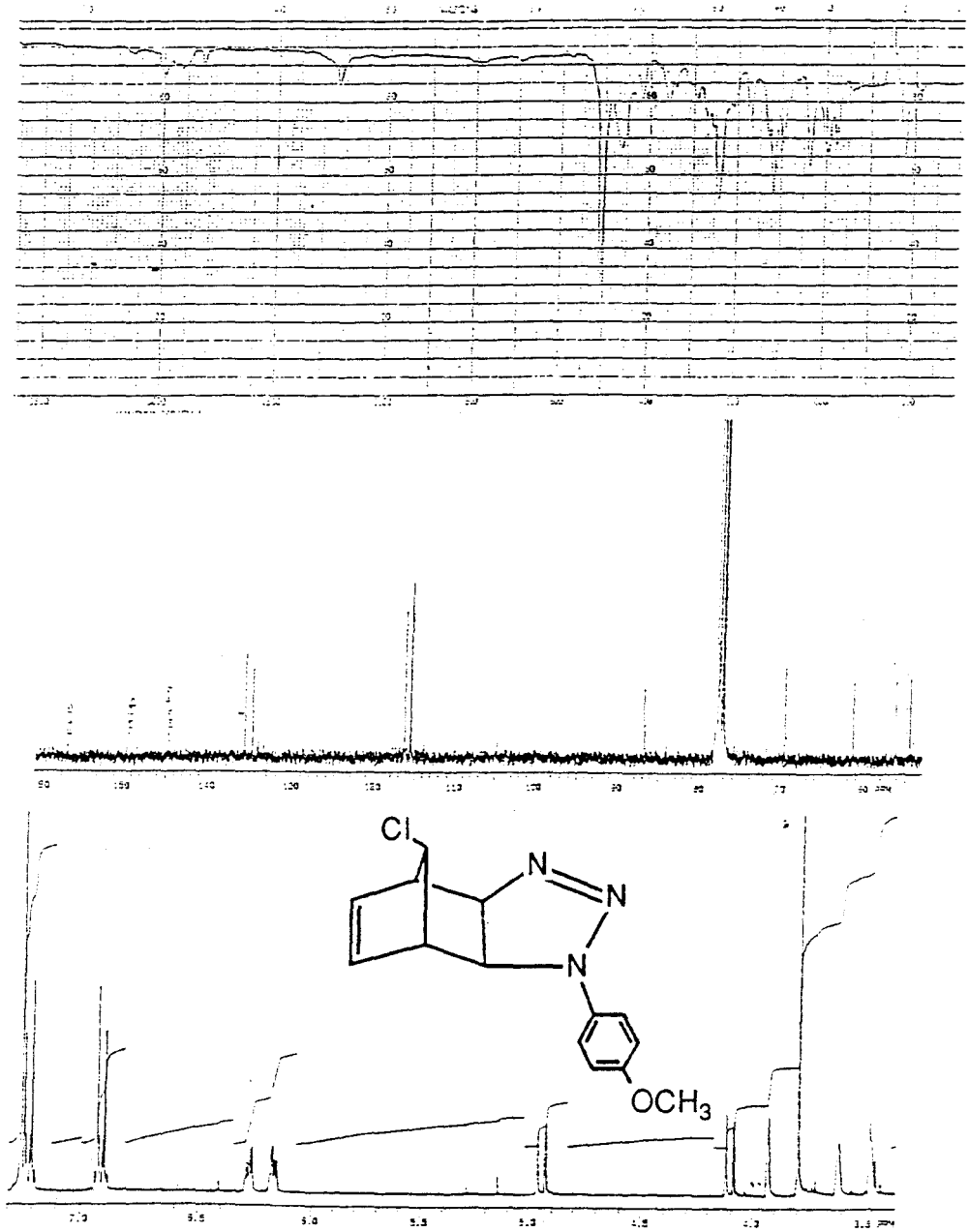
Anti-10-chloro-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**39**)



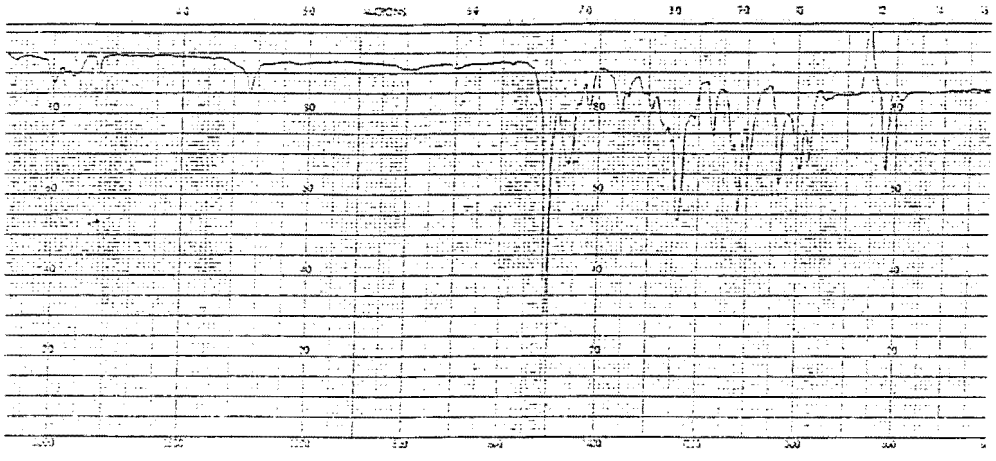


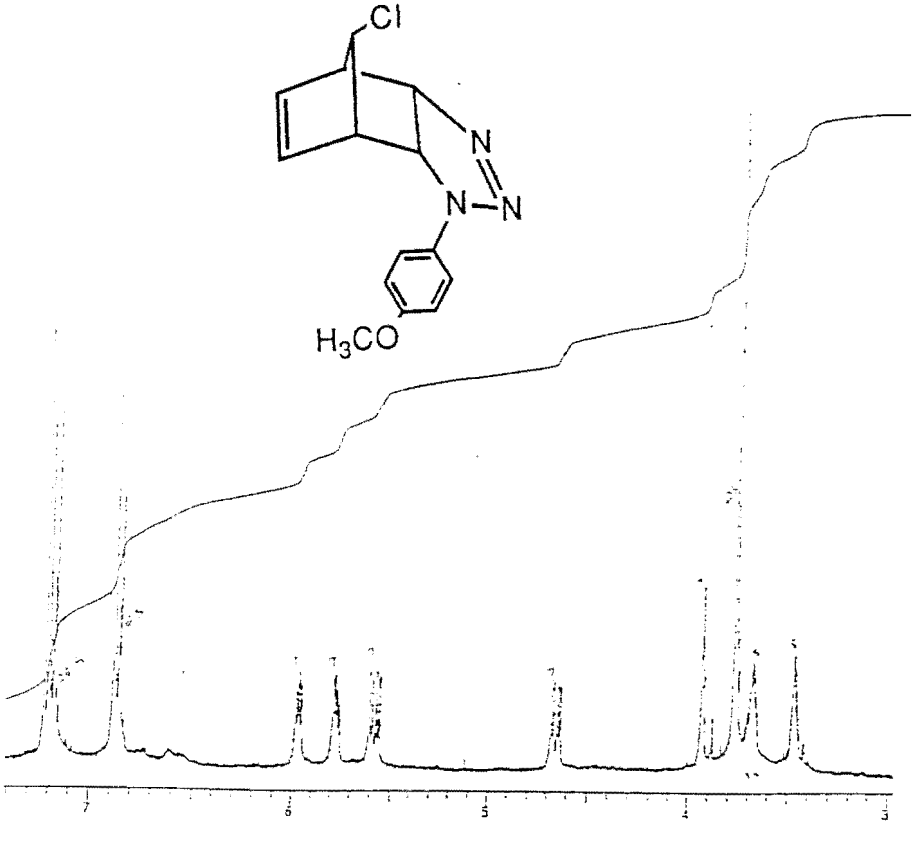


Anti-10-chloro-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**40**)



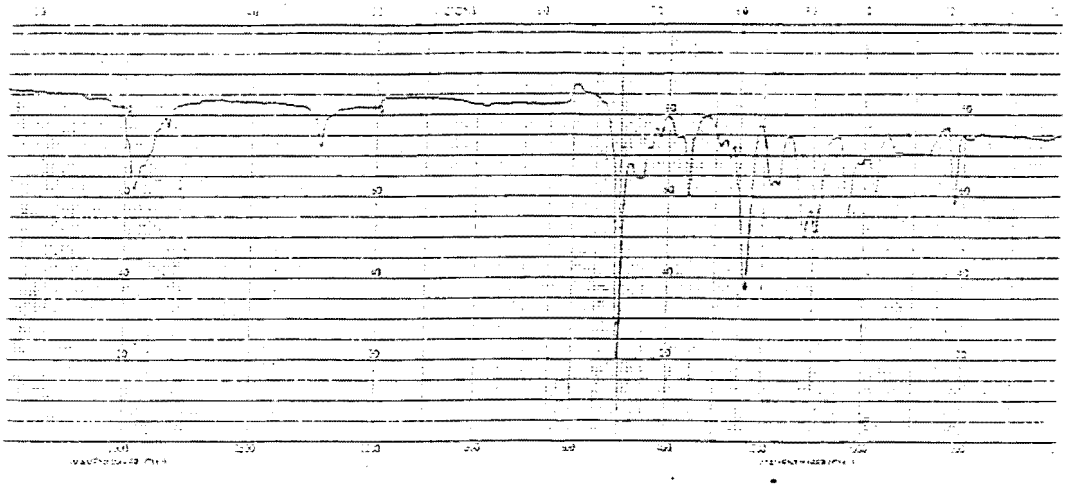
Syn-10-chloro-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (41)

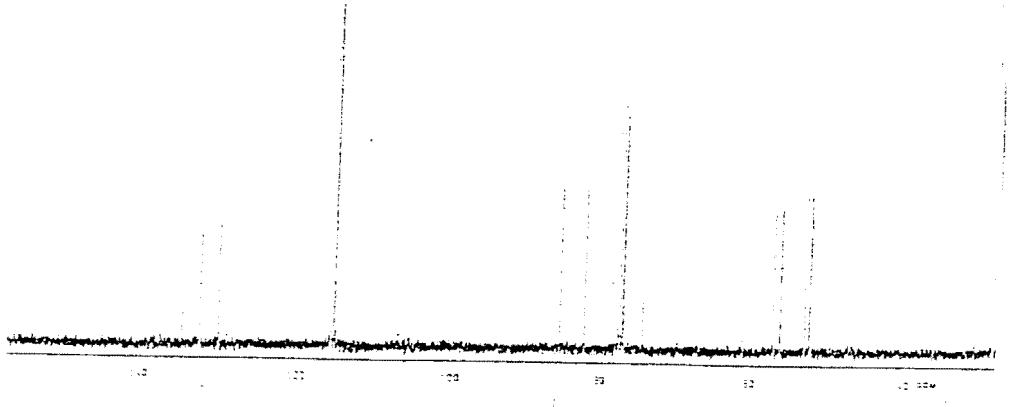


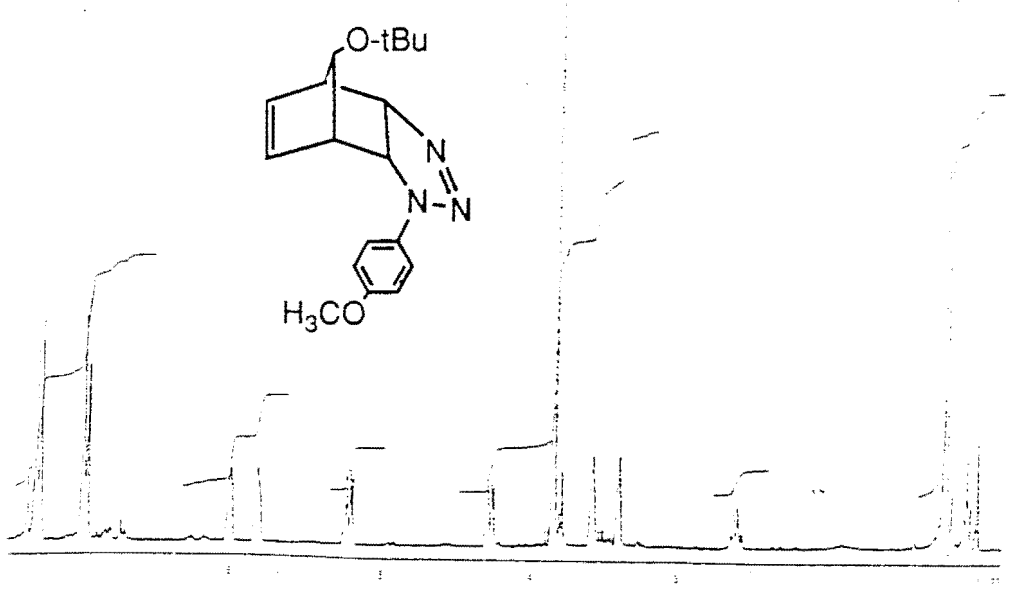


Syn-10-*t*-butoxy-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene

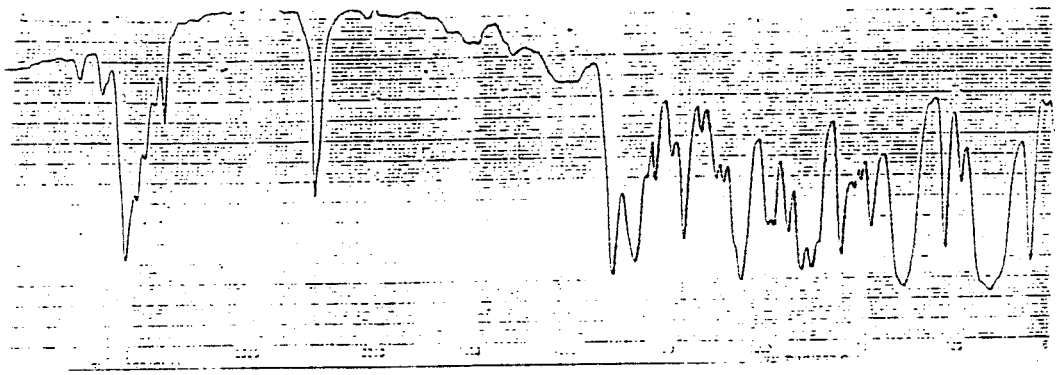
(43)

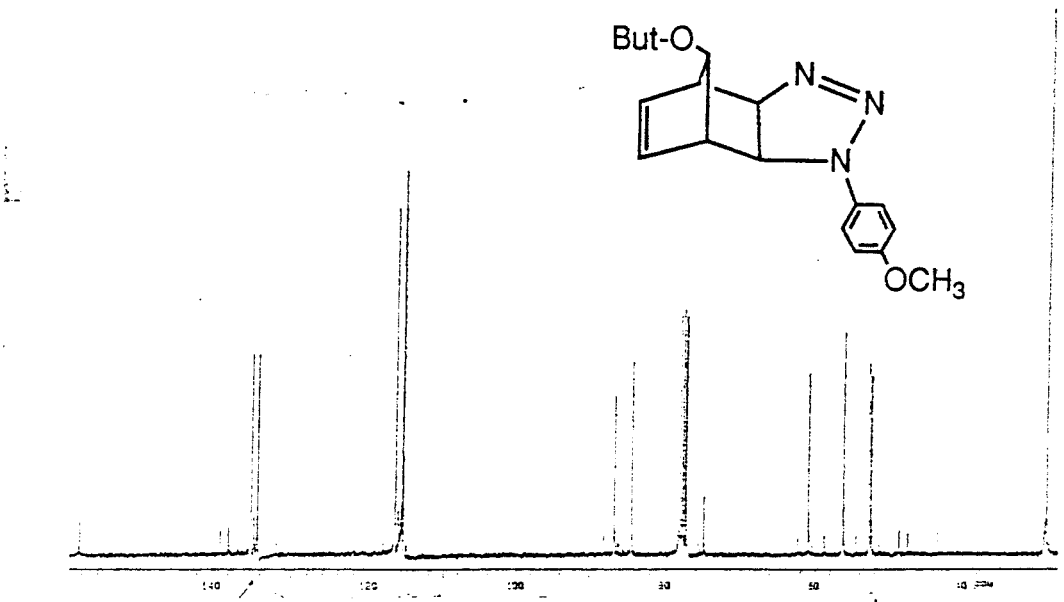


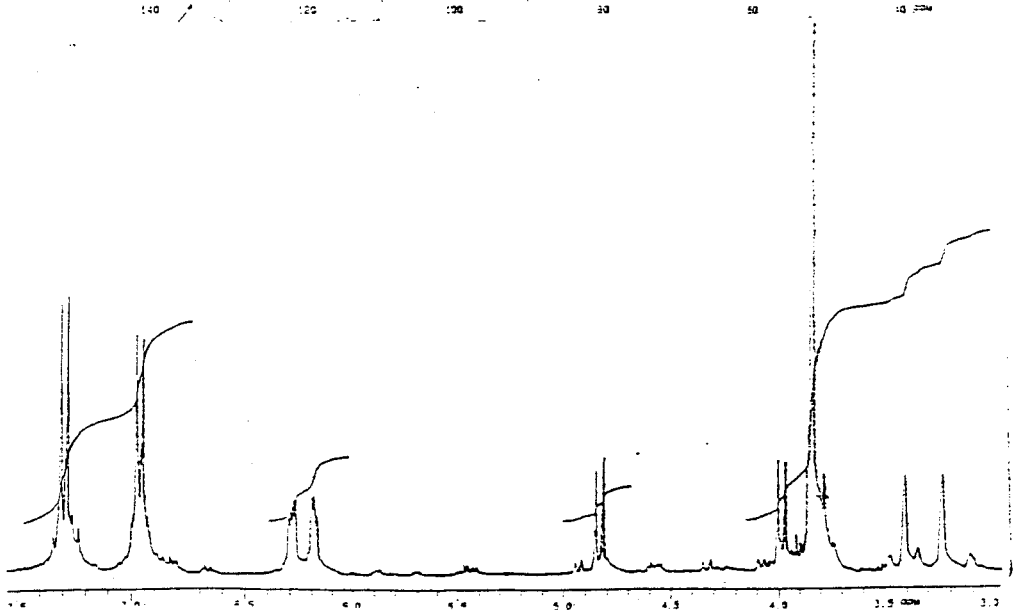




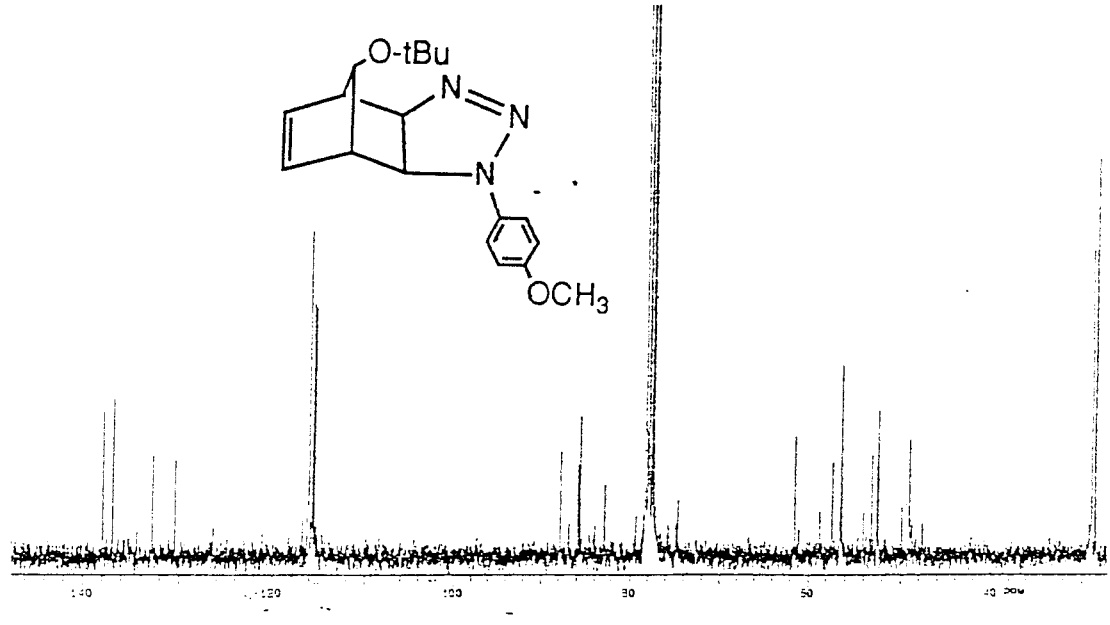
Anti-10-*t*-butoxy-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**44**)

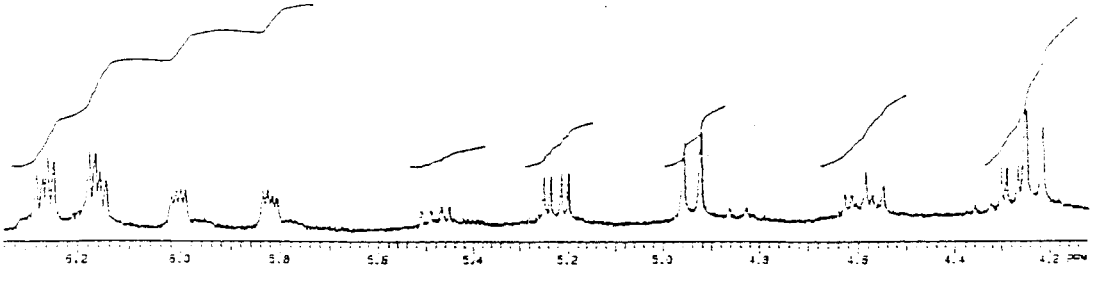






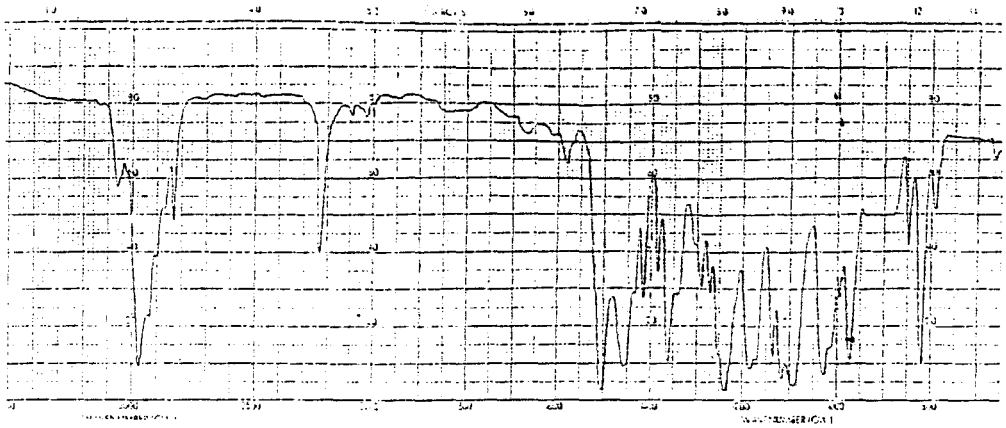
Syn-10-*t*-butoxy-5-(4'-methoxyphenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (45)

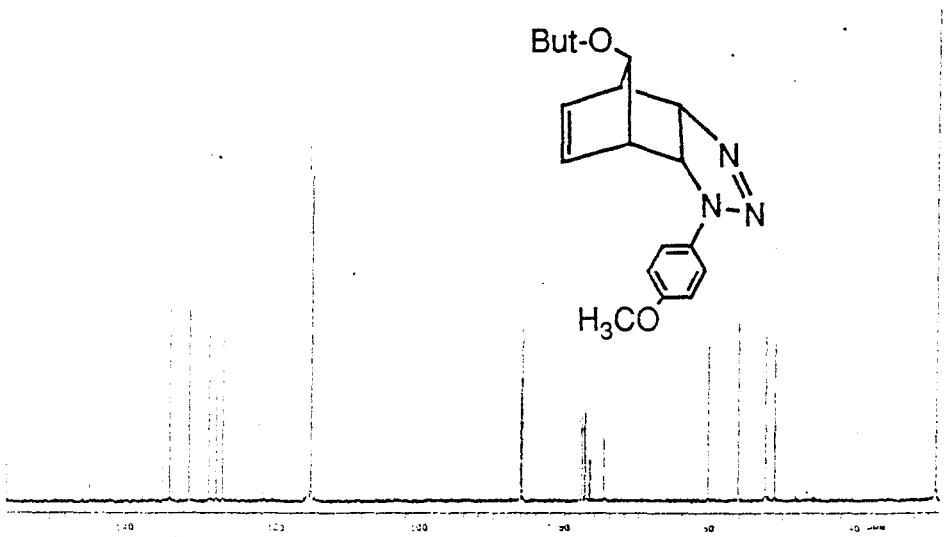


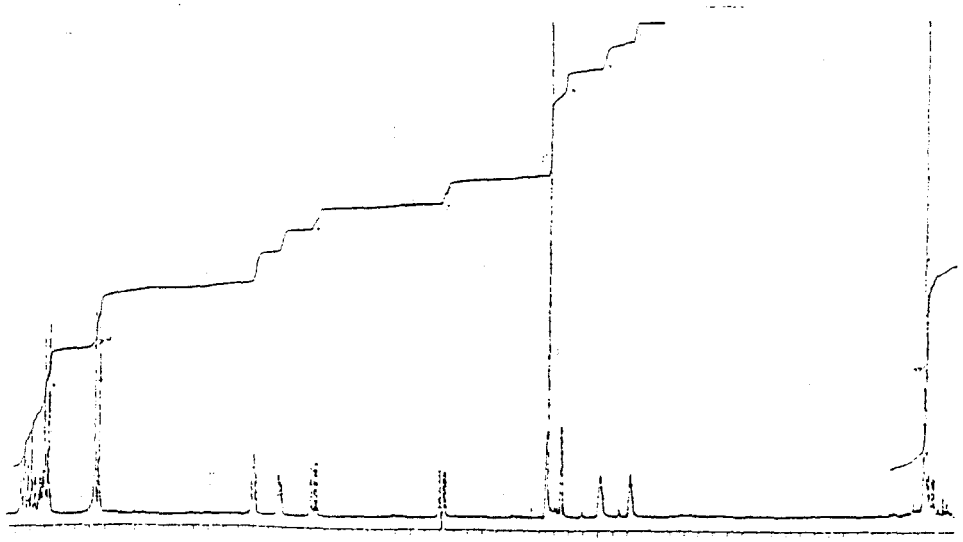


Anti-10-*t*-butoxy-5-(4'-methoxyphenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene

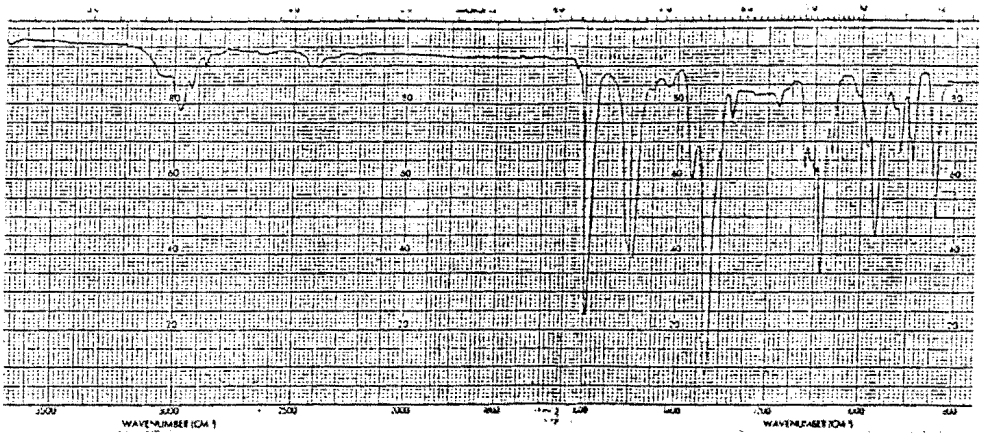
(46)

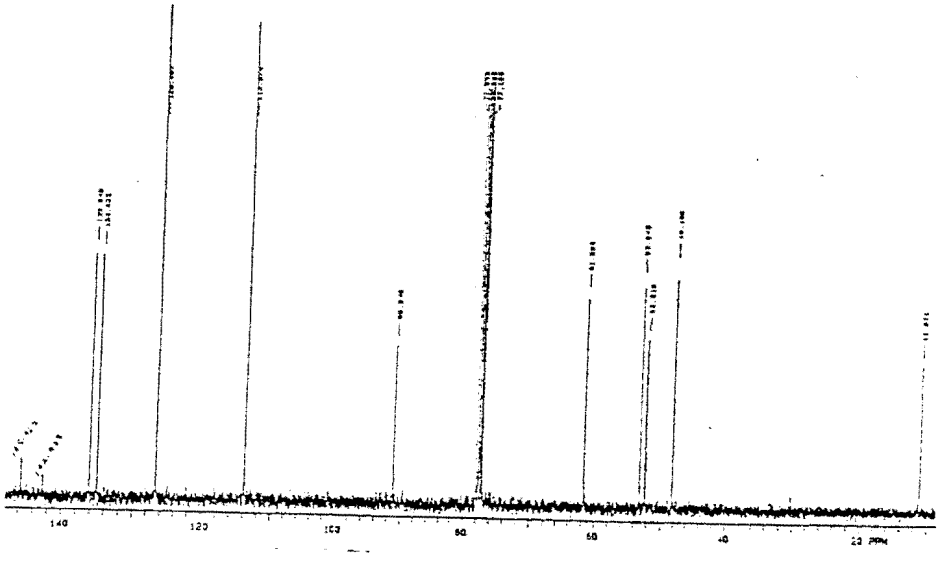


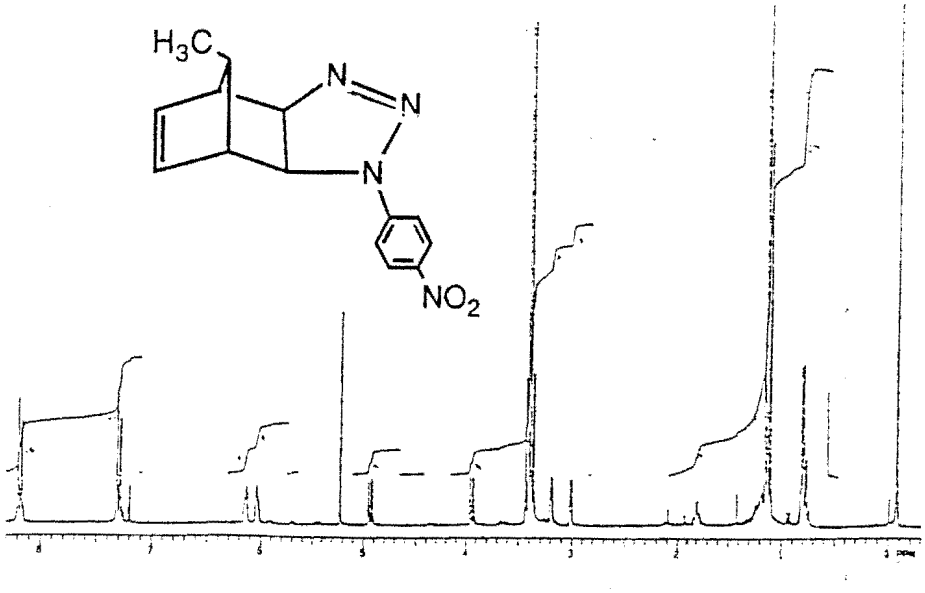




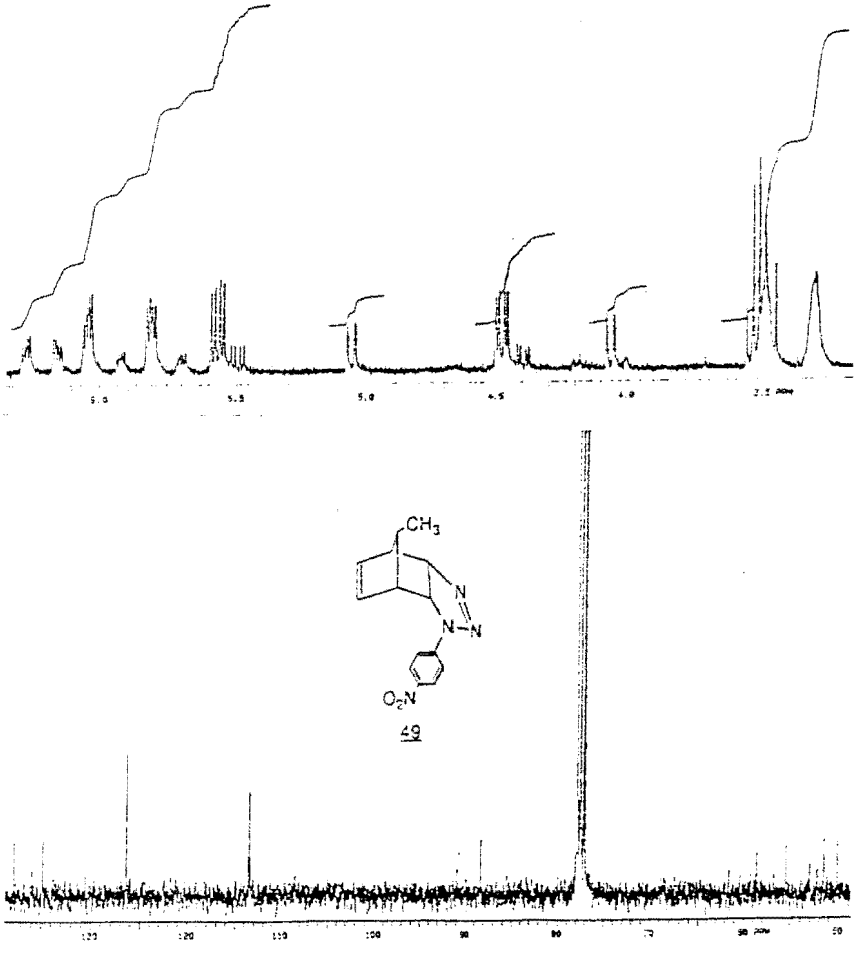
Anti-10-methyl-5-(4'-nitrophenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (48)





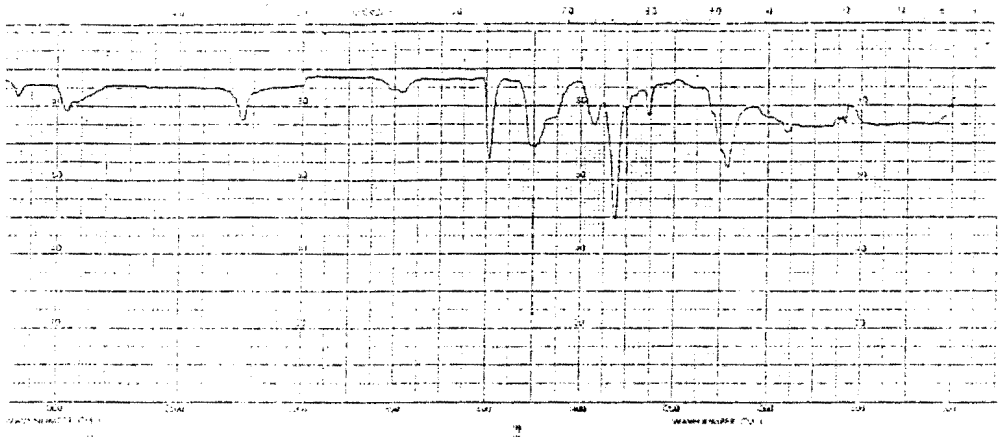


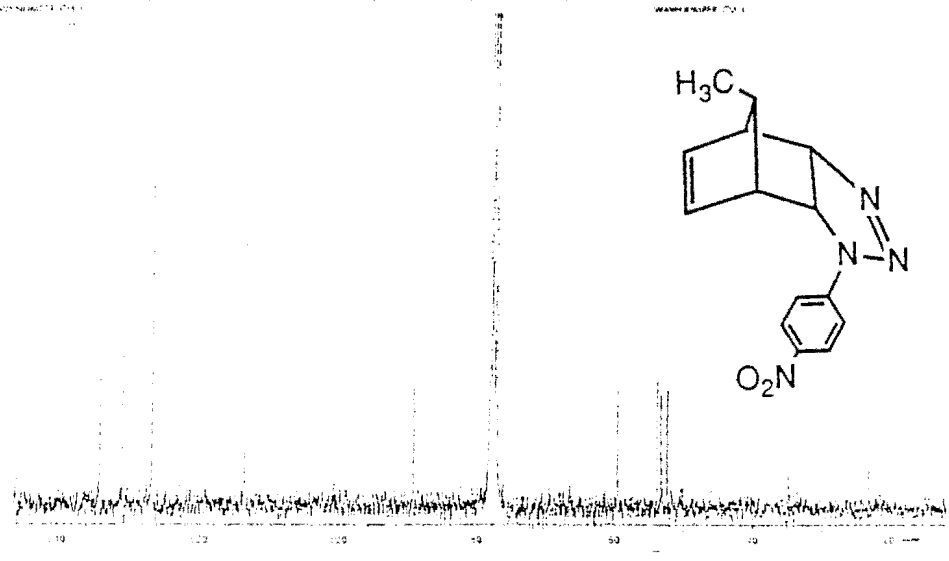
Syn-10-methyl-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (49)



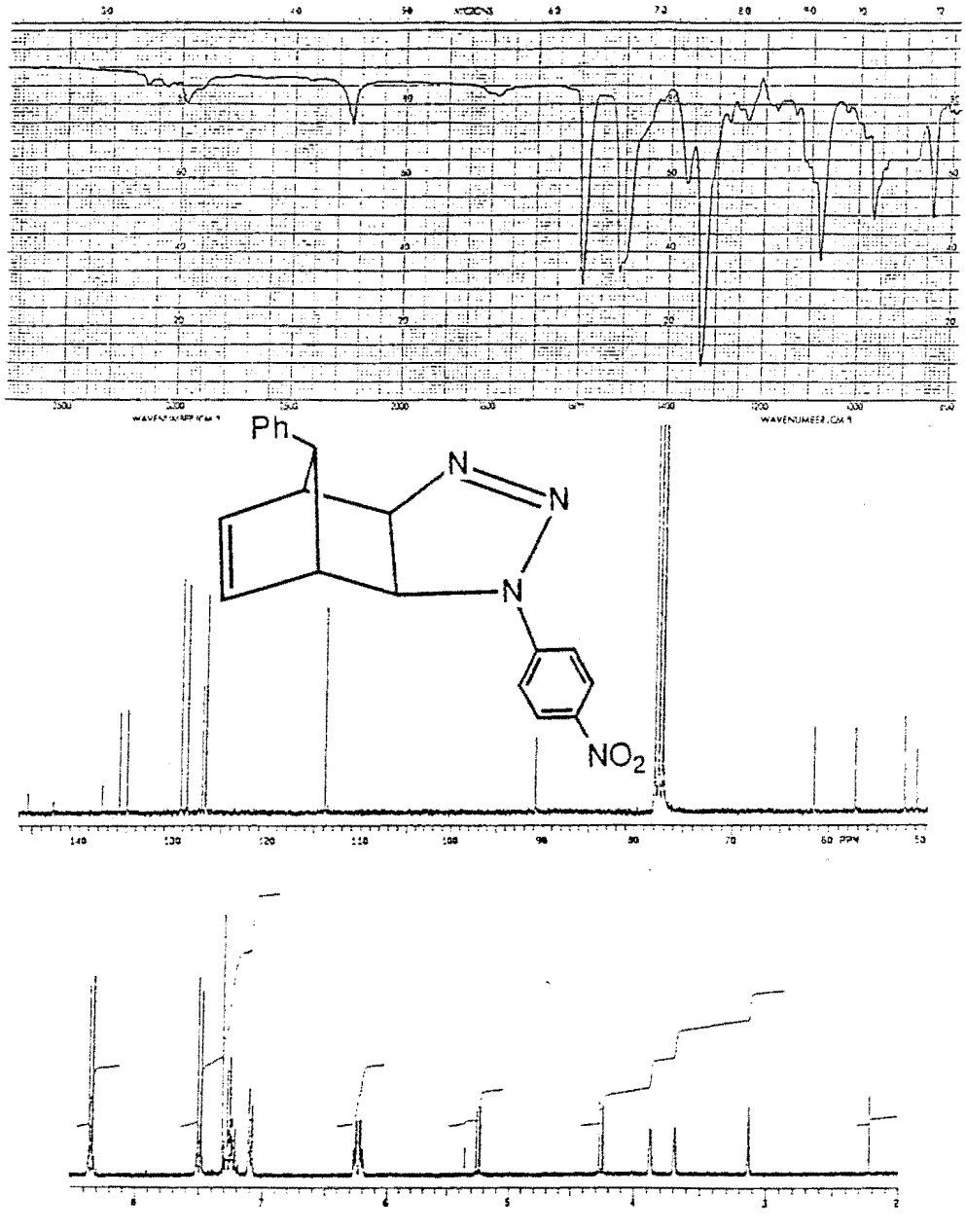
49

Anti-10-methyl-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3.8-diene (**50**)

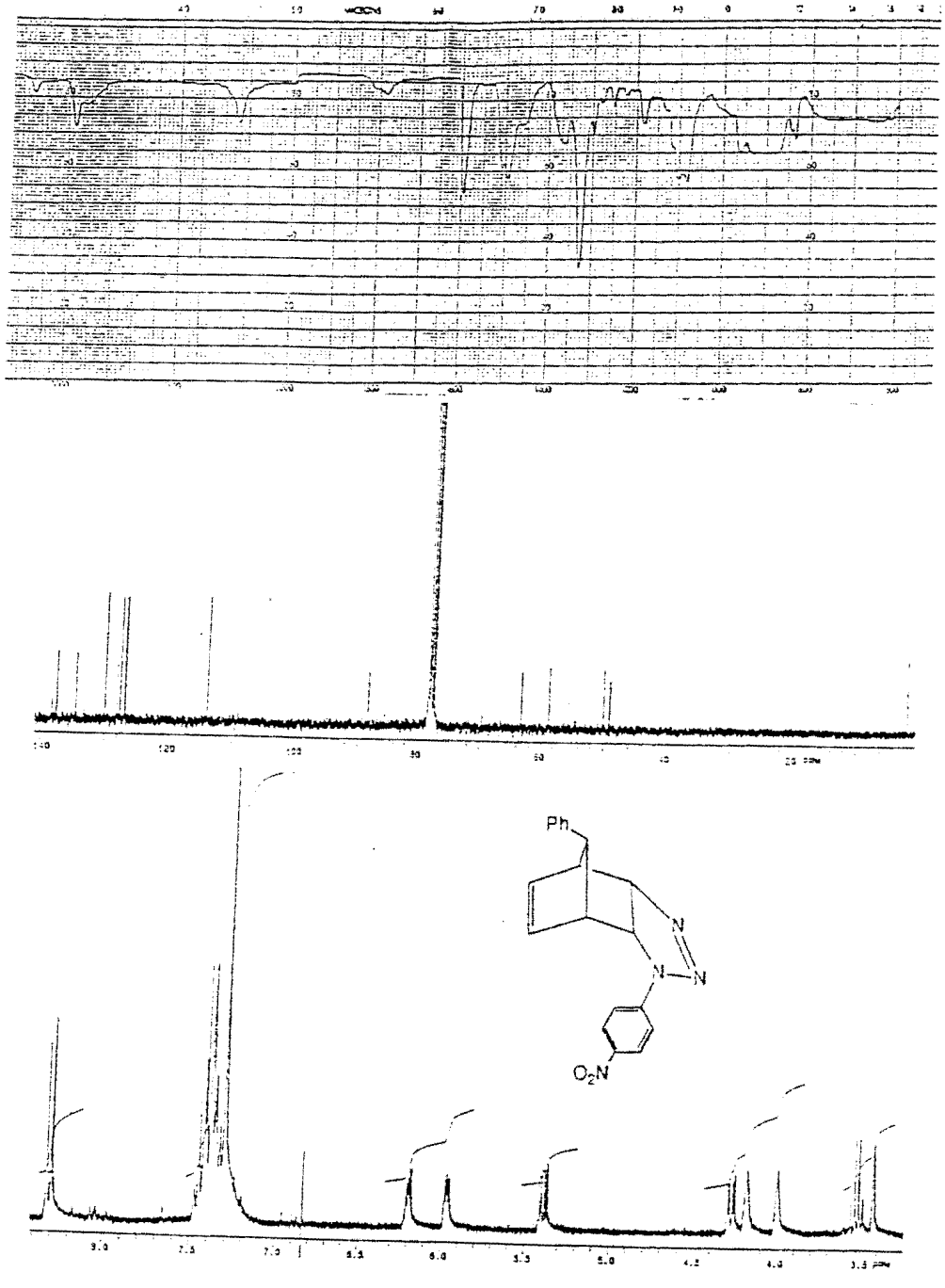




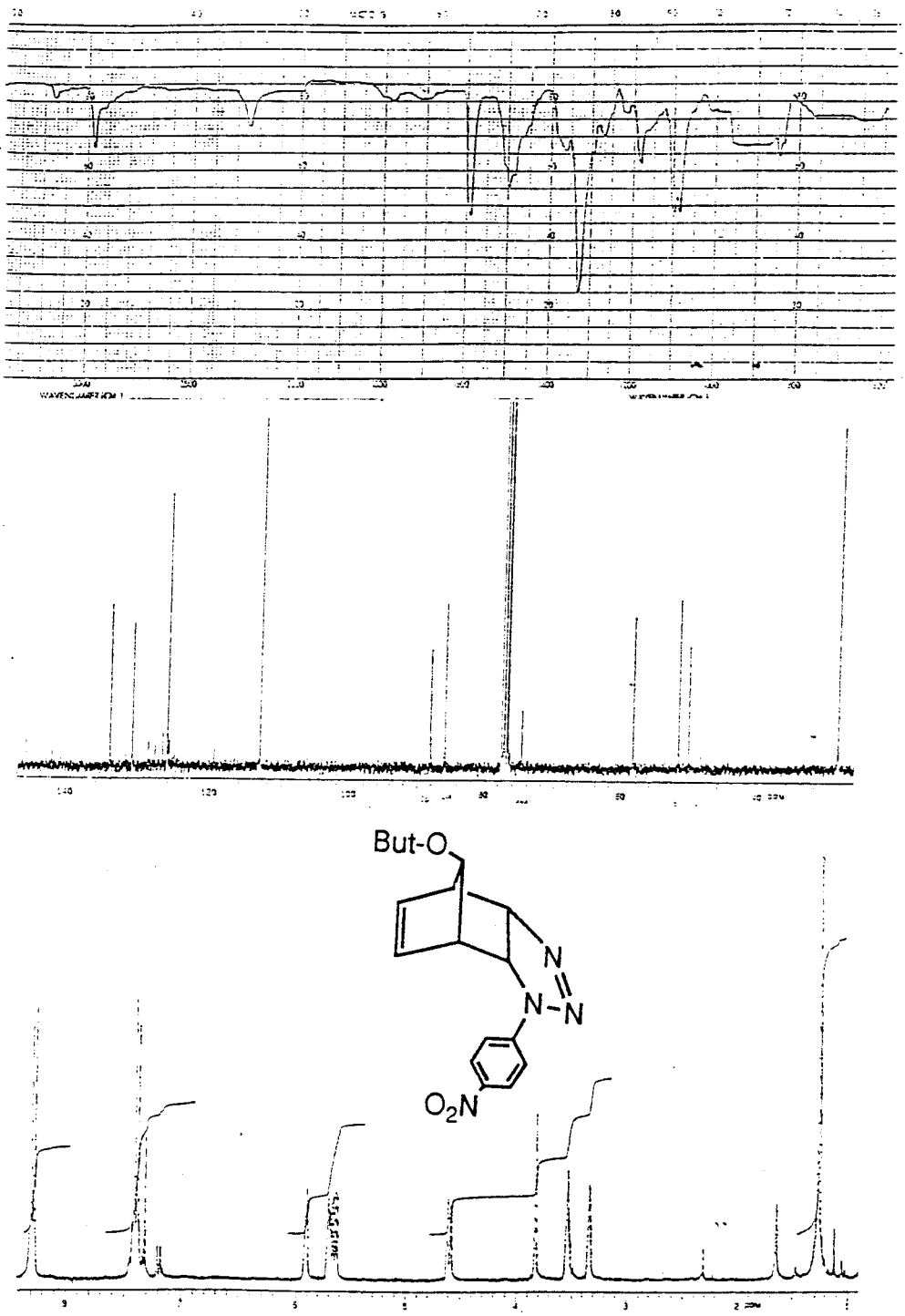
Anti-10-phenyl-5-(4'-nitrophenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**51**)



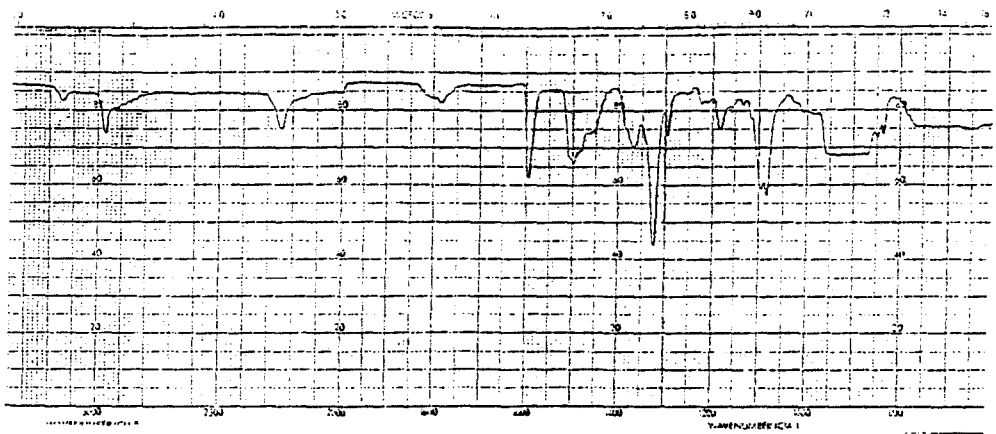
Anti-10-phenyl-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**52**)

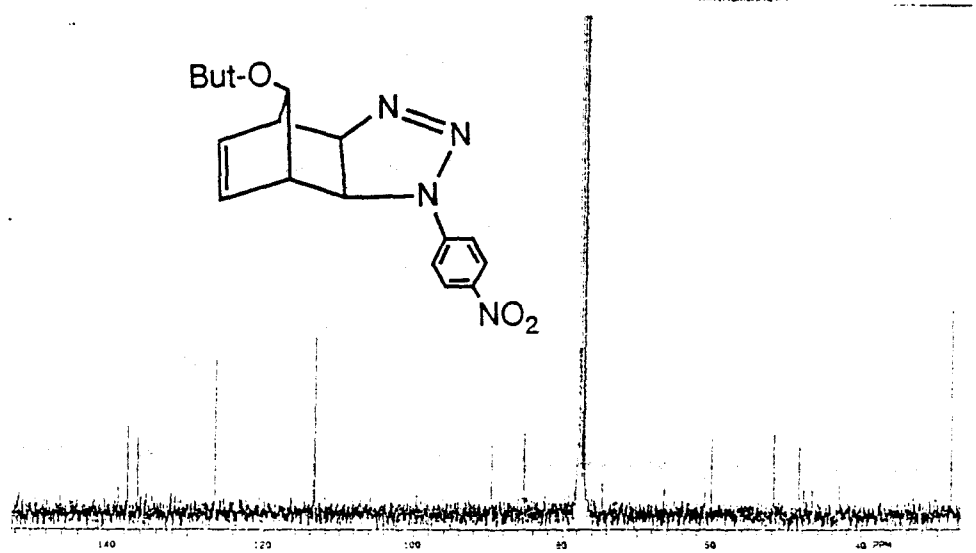


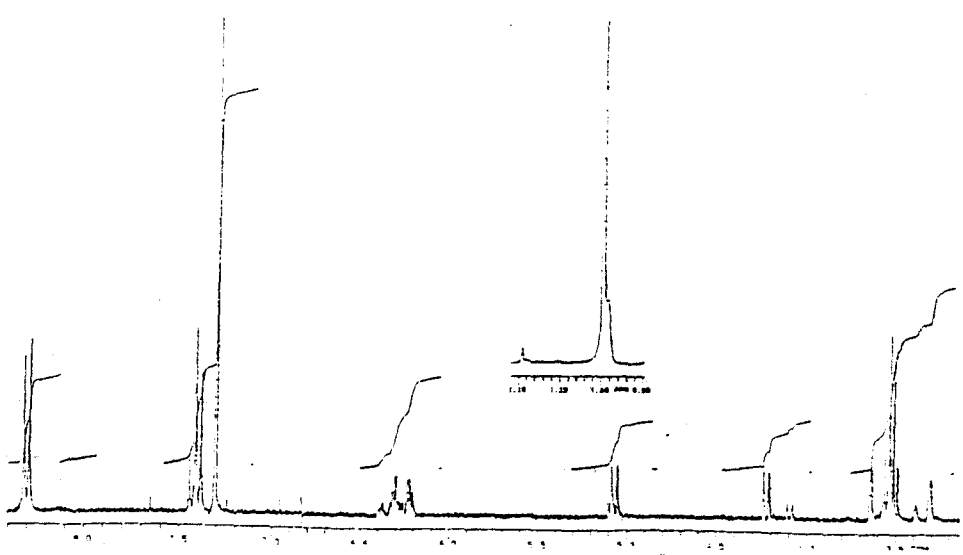
Anti-10-*t*-butoxy-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**53**)



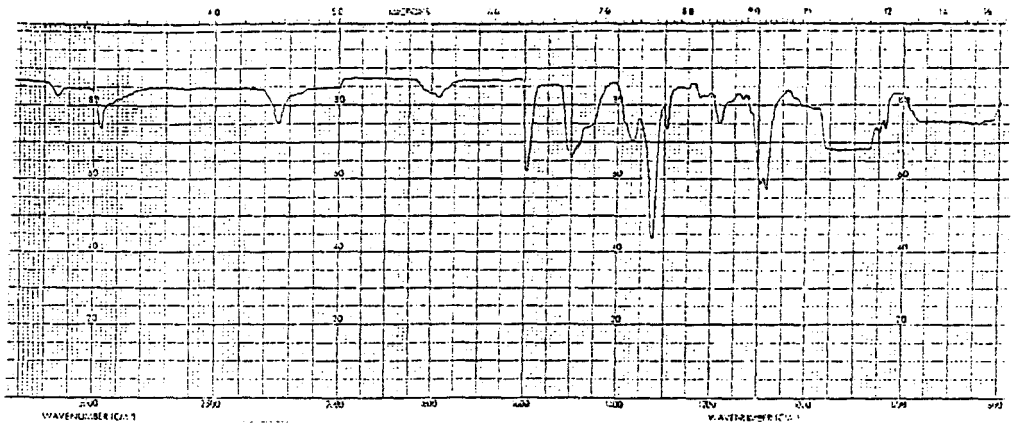
Anti-10-*t*-butoxy-5-(4'-nitrophenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (54)

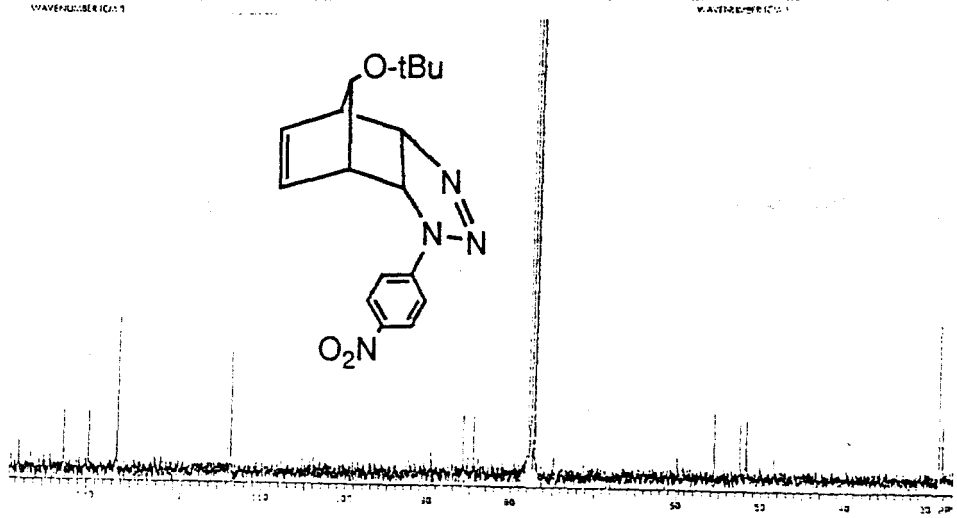


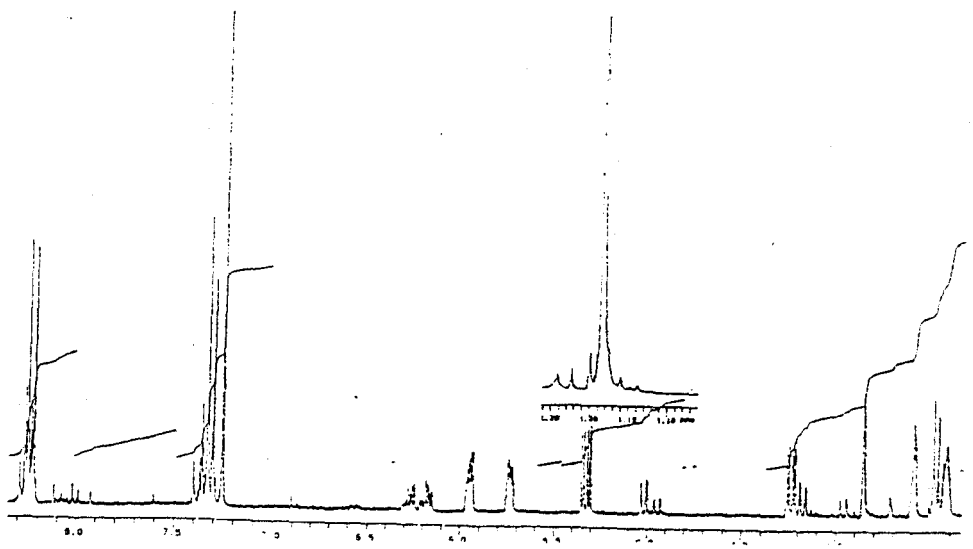




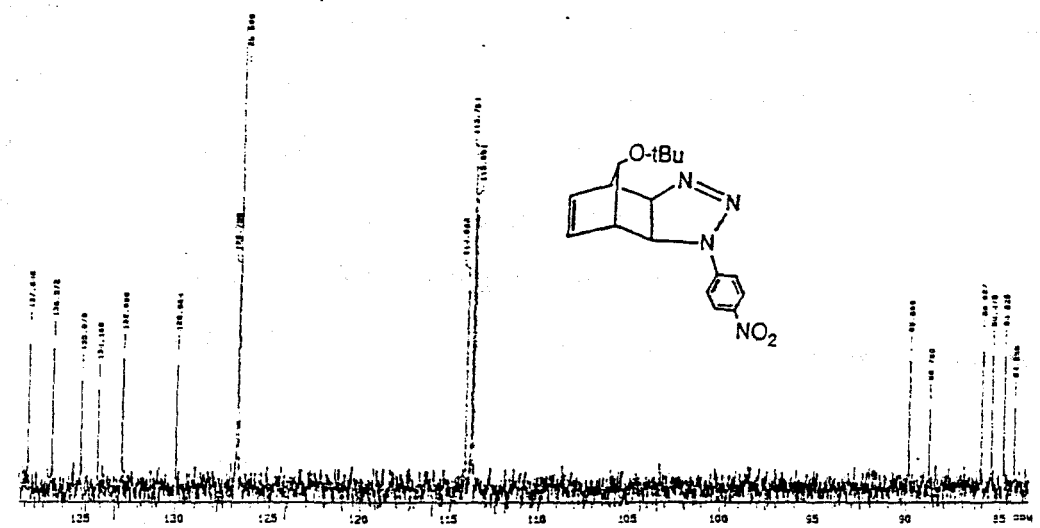
Syn-10-*t*-butoxy-5-(4'-nitrophenyl) endo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**55**)

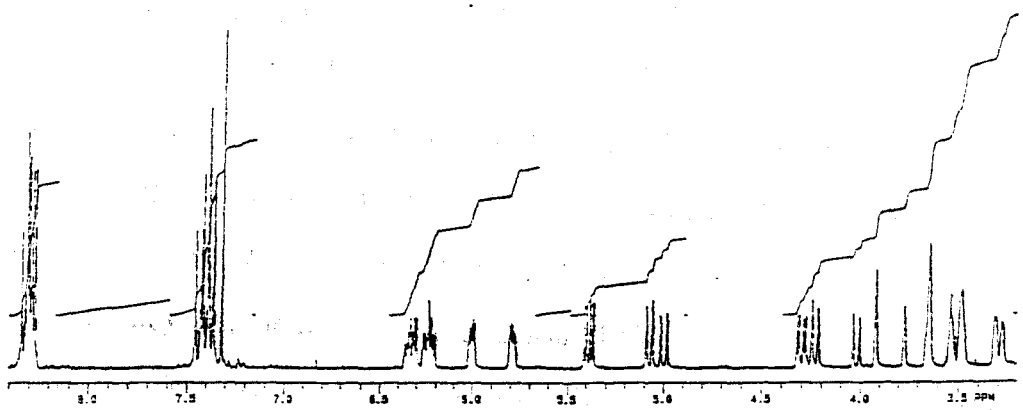






Syn-10-*t*-butoxy-5-(4'-nitrophenyl) exo-3,4,5-triaza tricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene (**56**)





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APPROVAL SHEET

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The final copies have been examined by the director of the dissertation and the signature which appears below verifies the fact that any necessary changes have been incorporated and that the dissertation is now given final approval by the committee with reference to content and form.

The dissertation is therefore accepted in partial fulfillment of the requirements for the degree of **Doctor of Philosophy**.

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