FINAL TECHNICAL REPORT

On

Design, Synthesis and Evaluation of Organic Non-linear Optical Chromophores With Configurationally And Conformationally Locked Polyene Bridges

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14. ABSTRACT
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ABSTRACT

A modular, synthetic scheme was developed for versatile variation of donors, acceptors and polyene bridge length of NLO-chromophores. Configurational and conformational rigidity of the polyene bridges were realized by making each set of adjacent double and single bond pair part of a fused cyclohexene ring. Substituent effects on the reactions leading to the establishment of the donor, elongation of the fused polyene bridge and the final introduction of the acceptor moiety were uncovered and used to control regioselectivity, chemoselectivity and reactivity in the overall synthetic scheme. A set of chromophores with 1:1, 1:2 and 1:3 ratio of donor:acceptor respectively per chromophore unit was prepared and partially characterized.

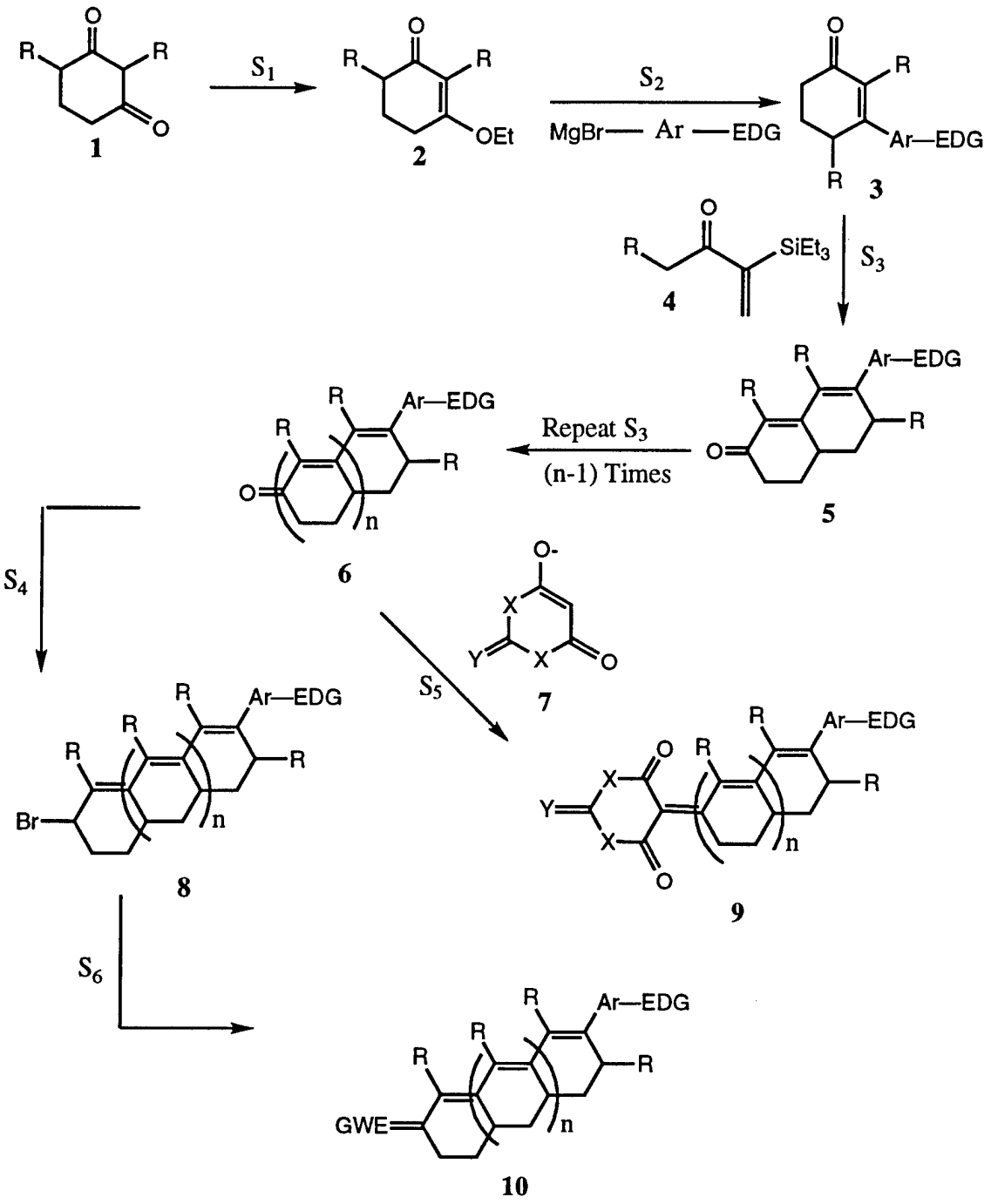
Introduction

The objective of this project was to develop a synthetic scheme for organic non-linear optical (NLO)chromophores in which the polyene bridge cannot undergo any configurational and conformational changes after the synthesis and under conditions of device fabrication and use. The scheme was also expected to allow for versatile introduction of diverse donors and acceptors and easy control of polyene bridge length from simple, available starting materials.

Cis-trans isomerization and s-trans/s-cis conformational changes in the open chain polyene bridge of non-linear optical chromophores reduce the optimal non-linearity that can be realized during use with a given chromophore structure and can also increase chemical instability of the chromophore. Chromophores in which the polyene bridge is enclosed in fused, cyclic subunits will maintain the optimal geometry designed into the structure during synthesis and thus ensure optimal non-linearity for the structure under all reasonable conditions of use.

We took a modular approach in which the typical chromophore was divided into three synthetic segments: (a) The anchor segment (S_1 - S_2, Scheme I) consisted of the donor group and the first C=C bond of the polyene bridge in conjugation. To assemble this segment, we exploited the versatile chemistry of 1,3- cyclohexanediones and easily prepared, reactive organometallic reagents to generate cyclohexenones bearing donor groups at C-3; (b) The body segment(S_3 iterated) consisted of the fused cyclohexene rings that constituted the locked polyene bridge. This segment was to be realized by iterative Robinson annulation through the kinetic enolate of the intermediate cyclohexenones. Some structure features of the cyclohexenones were designed to favor Robinson annelation rather than two sequential conjugate additions which lead to bicyclo[2.2.2]-octanones;[1] and (c) The cap segment(S_4 or S_5 route) consisted of the acceptor and the last C=C bond of the bridge. It was to be realized by condensation of the terminal cylohexenone ring with an activated methylene compound that would furnish the acceptor group to complete the chromophore structure. The proposed scheme incorporating the three segments is given in Scheme I.

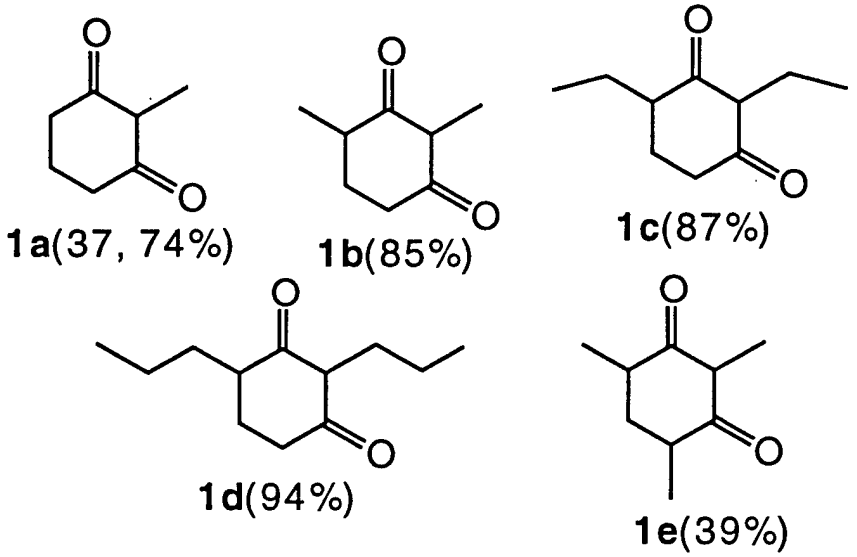
Scheme I


R
O
1
S1
2
OEt
S2
MgBr— Ar —EDG
Ar—EDG
3
4
SiEt3
S3
5
Repeat S3
(n-1) Times
6
n
S4
7
O-
X
Y
S5
8
Br
9
S6
GWE
10

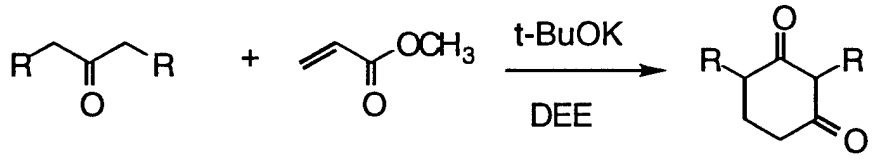
Results and Discussion

1. Synthesis of Substituted 1,3-Cyclohexanediones

The particular cyclohexanediones of interest are the structures **1a** - **1e**. 2-Methyl-1,3-cyclohexanedione is available commercially but we studied two routes for its preparation. Methylation of 1,3-cyclohexanedione under basic conditions using different solvent



mixtures and different bases was only achieved in a maximum yield of 37%. The best yield reported in the literature is 56%[2]. The other method that we used was a 4-step route starting from propionyl acetate ester which gave an overall yield of 74%. Cyclohexanediones **1b** - **1e** were prepared from the corresponding ketones according to Eq. 1.[3] 2,4,6-trimethy-1,3-cyclohexadione, **1e** was prepared using methyl methacrylate.



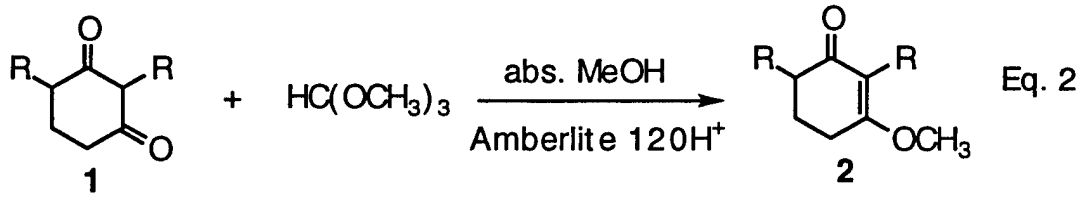
Eq. 1

DEE = Dimethoxyethyl Ether

2. Synthesis of Vinylogous Esters of Substituted 1,3-Cyclohexanediones

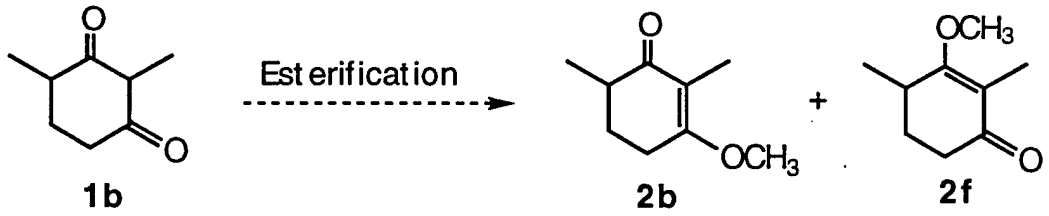
Conversion of the cyclohexanediones to their corresponding vinylogous esters allows regiospecific introduction of the donor groups in the next step, using the remaining carbonyl functionality.

Most of the methods described in the literature for preparation of enol ethers use sulfuric or sulfonic acids as catalysts.[2] These acids did not work well with our alkyl-substituted 1,3- cyclohexandiones. The method reported by Shepherd et al[4] , which uses orthoformates and amberlite as acid catalyst worked best(Eq. 2). For 2-methyl-1,3-



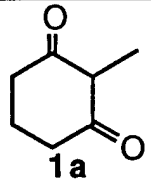
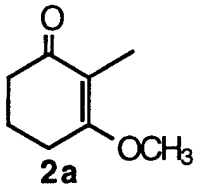
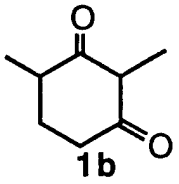
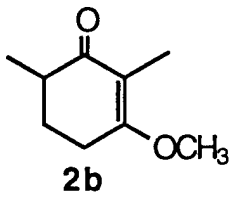
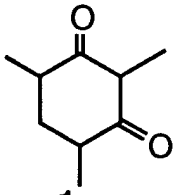
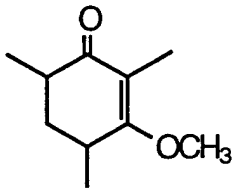
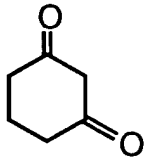
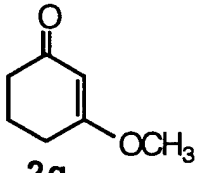
cyclohexanedione, 2,4-dimethyl- and the 2,4,6-trimethyl analogs, this method gave good yields of the corresponding esters **2a**, **2b** and **2c** even though the reaction could not be driven to 100% conversion for 2- methyl-1,3-cyclohexanedione. In each case however, the unreacted dione could be eliminated by extracting the vinylogous ester into hexane. After this, chromatographic separation on silica gel was used to remove any residual impurities. Most yields were above 80%(Table I).

The preparation of ester **2e** was used to resolve the question of regioselectivity in the esterification of **1b** for which the ester **2f** is also possible. The ester **2e** has all the ^1H NMR signals that would be expected from both regioisomers **2b** and **2f**. In



the ^1H NMR of the crude **2e**, there were no signals matching the —CH_3—CH—$C(OCH_3)$=$C(CH_3)$— pattern found in **2e** and expected in crude **2b** if **2f** were present. It follows therefore that the esterification of **1b** is highly regioselective and favors the less hindered carbonyl group.

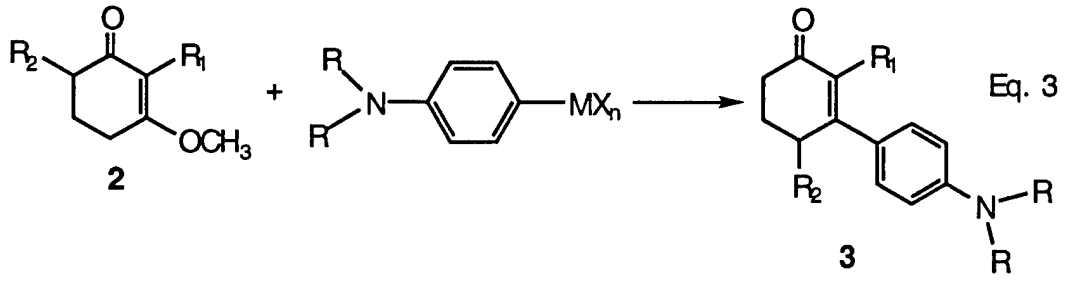
Table I: Conversions and Yields of Esters of Cyclohexanediones

Dione	Vinylogous Ester	% Conversion	% Yield
 1a	 2a	84	85
 1b	 2b	100	86
 1e	 2e	100	84
 1g	 2g	100	64

3. Preparation and Coupling of the Organometallic Derivatives of Donor Groups to the Vinylogous Esters

Organometallic compounds, through nucleophilic attack on the carbonyl of the vinylogous esters, provide a general route for the generation of C-3 substituted cyclohexenones. The two types of organometallic reagents we examined are the Grignard[5] and the organolithium[6] derivatives of electron-donating aryl halides.

Methods for the preparation of the Grignard of p-bromo-N,N-dimethylaniline have been reported.[7] We chose the method that activates the magnesium turnings before adding a solution of the aryl halide.[5] Eventually, we found organolithium derivatives to give better yields in simpler and faster reactions than Grignards. We have prepared the lithium derivative of p-bromo-N,N-dimethylaniline, the monolithium, dilithium and trilithium derivatives of tris(p-bromophenyl)amine and these have



been successfully coupled to different vinylogous esters. Adding vinylogous ester to the Grignard or organolithium reagents at low temperature, followed by acid work-up resulted in quite good yields of most of the cyclohexenones **3**(Eq. 3) shown in Table II. This step completed the assembly of the anchor segment.

Table II: Anchor Cyclohexenones **3** From Corresponding Organolithiums

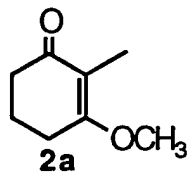
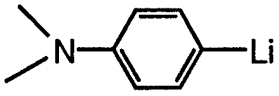
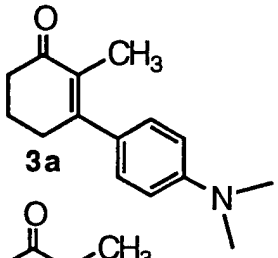
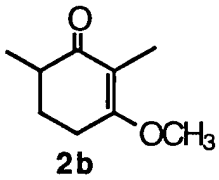
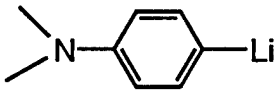
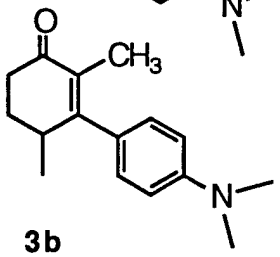
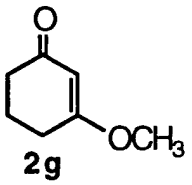
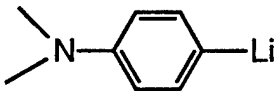
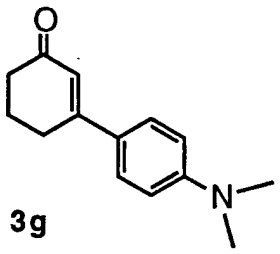
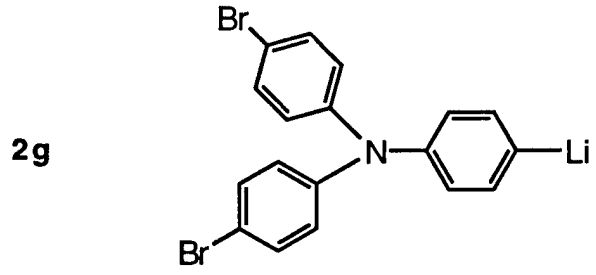
Ester	Organometallic	Product	% Yield
 **2a**		 **3a**	87
 **2b**		 **3b**	40
 **2g**		 **3g**	78

Table II Cont'd



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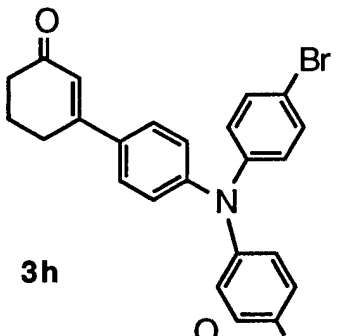

3h

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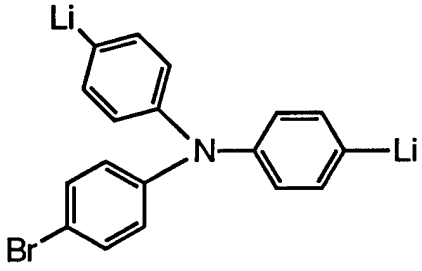

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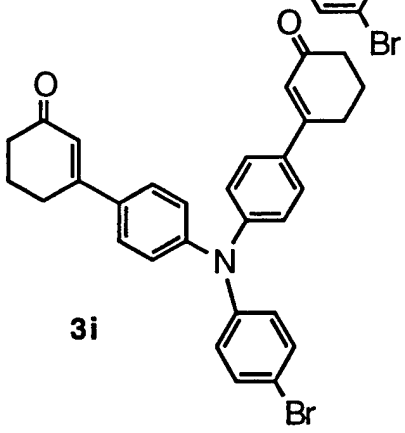

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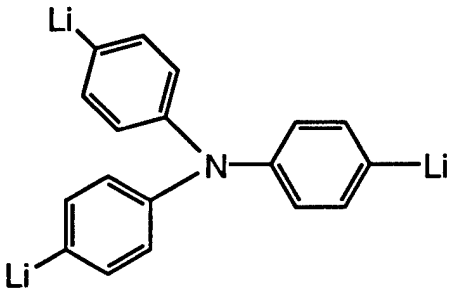

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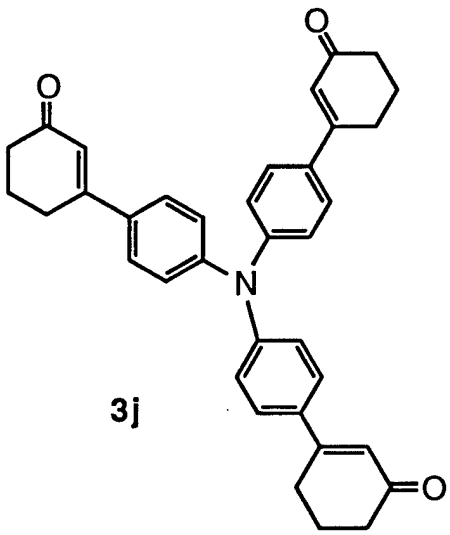
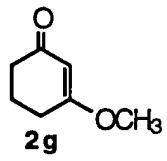
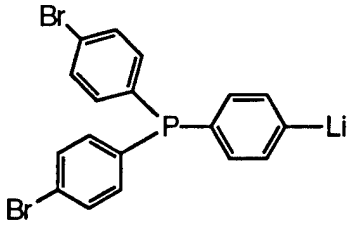
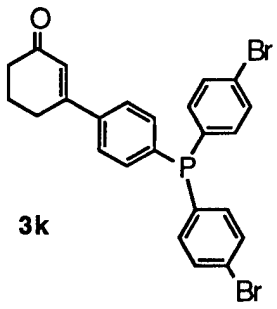
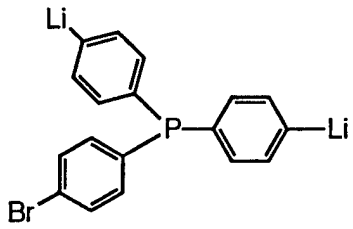
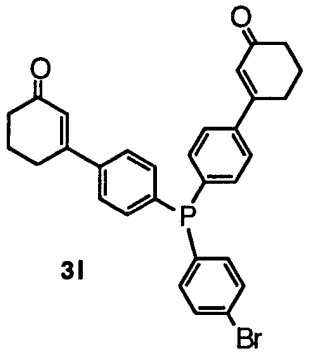
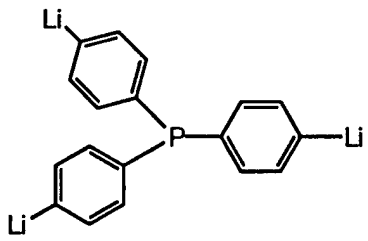
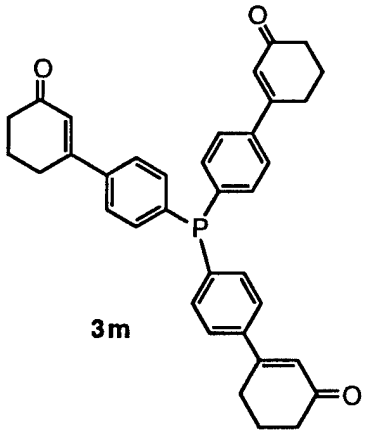


3j

26

The phosphorus centered 3-arylcyclohexenones **3k - m**(Table III) where similarly prepared from tris-(p-bromophenyl)phosphine in the yields indicated.

Table III: Triphenylphosphinocyclohexenone Anchor Enones

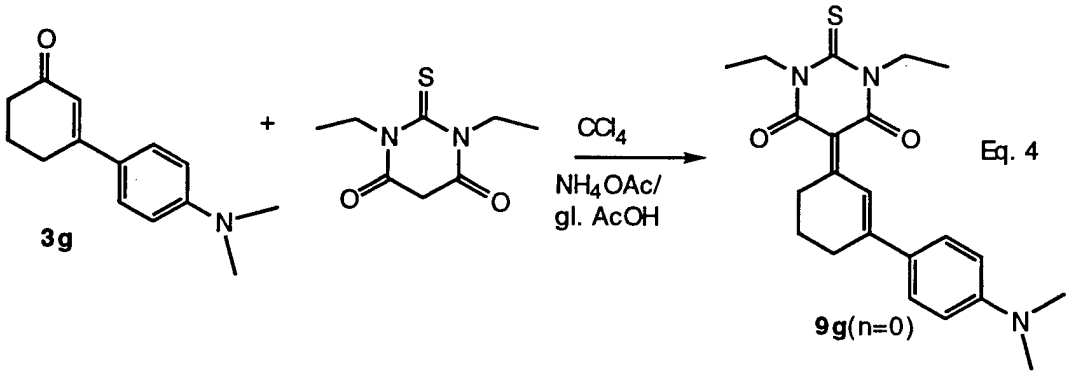
Ester	Organometallic	Product	% Yield
 2g		 3k	69
2g		 3l	41
2g		 3m	14

4. Capping of Donor-bearing Cyclohexenones - Completion of the Synthetic Scheme for the Simplest Class of the General Target Structure

The anchor segment has an electron-donor moiety in conjugation with a C=C and a C=O bonds. If the carbonyl of the aanchor enones is converted to an aacceptor ylidene, the resulting products would represent the simplest class of our target chromophore structure. We therefore decided that capping the donor-bearing

cyclohexenones **3** with electron-withdrawing groups would lead to the complete synthesis of the simplest analogs of **9** or **10,** i.e. structures with only one cyclohexene ring per donor/acceptor unit. These simple analogs provide material for early evaluation of the effect of combinations of donor/acceptor pairs on non-linearity as well as to test feasibility of the capping step before applying it to advanced anchor units.

The capping process would require a Knoevenagel condensation of an α,β–enone which is not as common and facile as the reaction with α,β–enals. Infact, the only α,β–enone reported in the literature up till the beginning of this project, as undergoing Knoevenagel condensation with thiobarbituric acid was isophorone.[8] Lack of success in effecting this condensation with the anchor enone **3a** under a variety of conditions, led us to suspect that the C-2 methyl substituent might be the cause. This was confirmed when we were able to effect the condensation with the enone **3g** which did not have a C-2 substituent(Eq. 4). Most of the α,β–enones reported to have been successfully used in Knoevenagel condensations with other activated methylene compounds have no C-2



Eq. 4

substituent.

Using thiobarbituric acid as the acceptor precursor, the anchor enones **3g - j**, which bear no C—2 methyl group, were capped in high yield(Table IV), whereas the C—2 methyl bearing anchor enones **3a,b** did not react under any condition even with malononitrile.

Table IV: Yield of Chromophores with Thiobarbituric Acid Acceptor

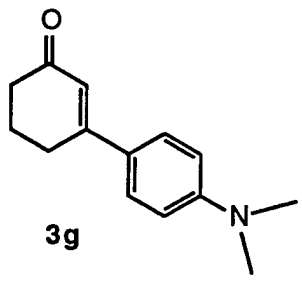
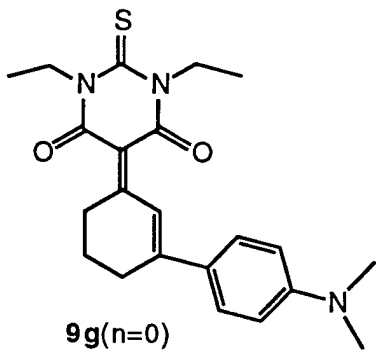
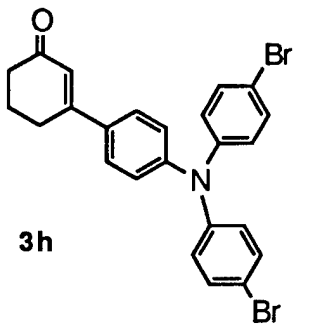
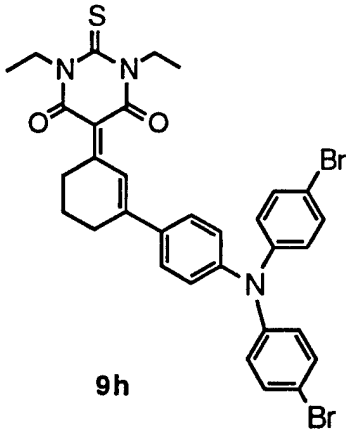
Enone	Product	% Yield
 **3g**	 **9g**(n=0)	100

Table IV Cont'd:

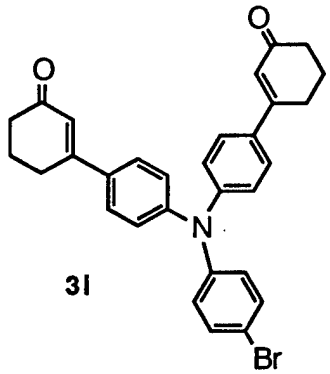


3h

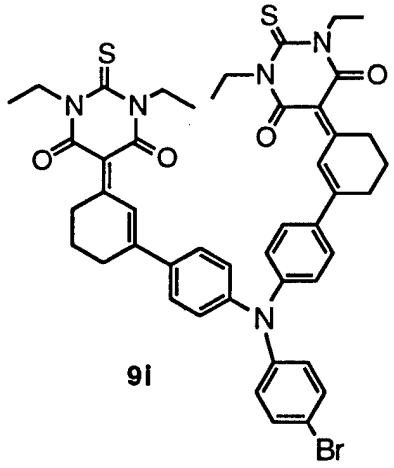


9h

80

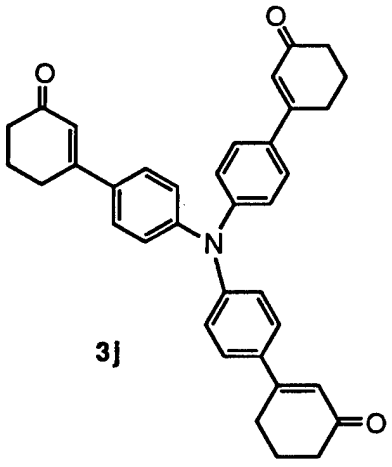


3l

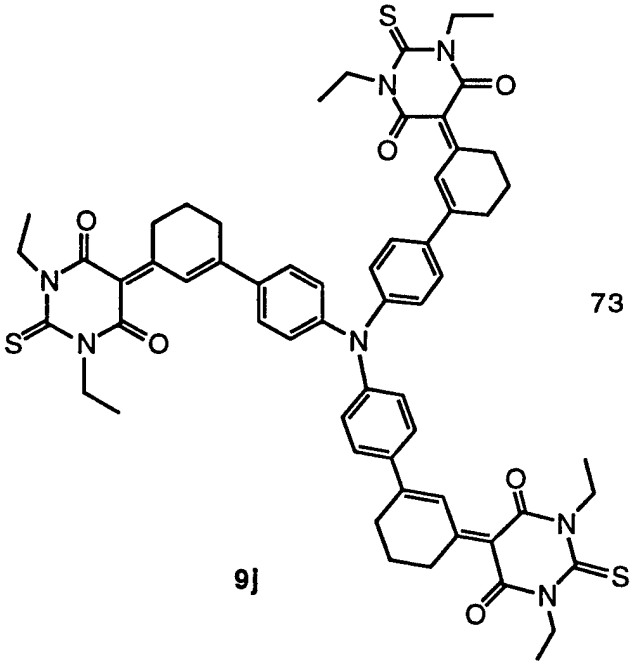


9l

89



3j



9j

73

Table V contains spectroscopic and thermal data for some of these nitrogen

Table V: Spectroscopic and Thermal Data for Some Nitrogen Donor Chromophores

Chromophore	Abs. Max	Solvent	Em. Max	Solvent	T_g	TGA
9g	557nm	$CHCl_3$	643nm	CH_3OH	174	330
9h	515nm	"	729nm	"	86	391
9i	544nm	"	675nm	"	92	395

donor chromophores.

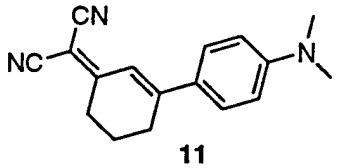
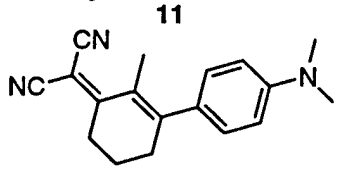
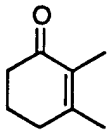
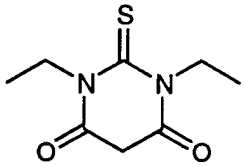
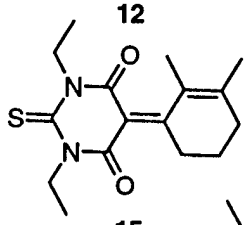
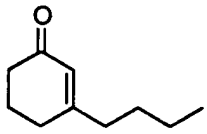
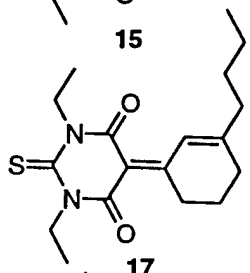
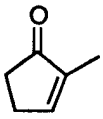
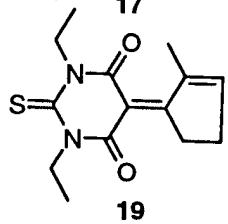
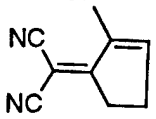
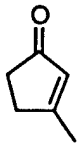
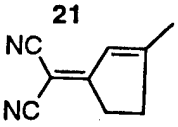
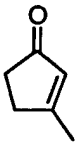
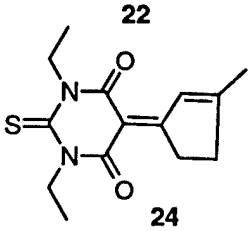
Attempts to prepare the analogous phosphorus chromophores from the triphenylphosphinocyclo-hexenones **3k** - **m** always resulted in mixtures containing other products that could not be separated for characterization.

The synthesis of the chromophores given in Table IV demonstrates that more complex enones than the often used isophorone can undergo this condensation. The complete failure of this condensation with the anchor enones bearing a C—2-methyl group led us to the important conclusion that C-2 substitution prevented Knoevenagel condensation of cyclohexenones. To confirm that this was a general effect, a number of simple cyclohexenones with and without C—2 methyl substituents were subjected to Knoevenagel condensarttion with various activated methylene compounds. The results in Table VI illustrate that the C—2 methyl effect is general. This finding has led to the following modification of our original scheme for the synthesis of analogs with elongated bridges: whereas earlier fused cyclohexenone rings could each have a C-2 substituent to direct the next Robinson annelation, the terminal cyclohexenone will have no C-2 substituent so as to allow for capping by Knoevenagel condensation!

5. Synthetic Elongation of the Fused Polyene Bridge:

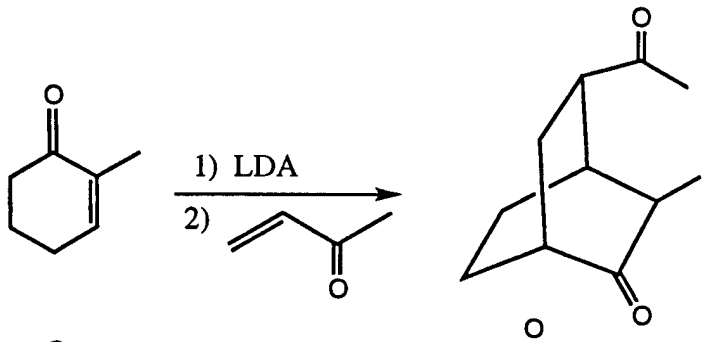
We originally proposed to have each cyclohexene unit of the fused polyene bridge bear a methyl group at C—2. This was due to the fact that having substituents at C—2 and C—3 of the intermediate cyclohexenones was expected to provide control in favor of intramolecular aldol condensation of the product of the initial conjugate addition. In the absence of C—2 and C—3 substituents, the product of the initial conjugate addition was known to undergo an intramolecular conjugate addition to form a bicyclo[2.2.2]octanone

Table VI: Knoevenagel Condensation of Methyl- and Non-methyl-Substituted Cyclohexenones

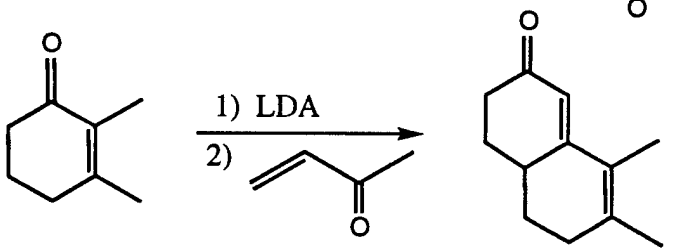
Cycloalkenone	Activated Methylene	Expected Product	Yield(%)
2g	 10	 11	53
2g	10	 12	0
 13	 14	 15	0
 16	14	 17	79
 18	14	 19	0
18	10	 21	0
 20	10	 22	71
 23	14	 24	80

(Compare Eq. 5 and 6). Eq. 5 represents a conjugate addition to the kinetic enolate of a C-2 only substituted cyclohexenone, followed by an intramolecular conjugate addition by the intermediate. On the other hand, Eq. 6 represents an initial conjugate addition to the kinetic enolate of a C-2/C-3 disubstituted cyclohexenone, followed by intramolecular aldol cyclization of the intermediate. This substituent directed selectivity in cyclization was first reported by Reusch and co-workers[1] in 1978.

It was this anticipated effect of C-2/C-3 substituents that led us to initially target



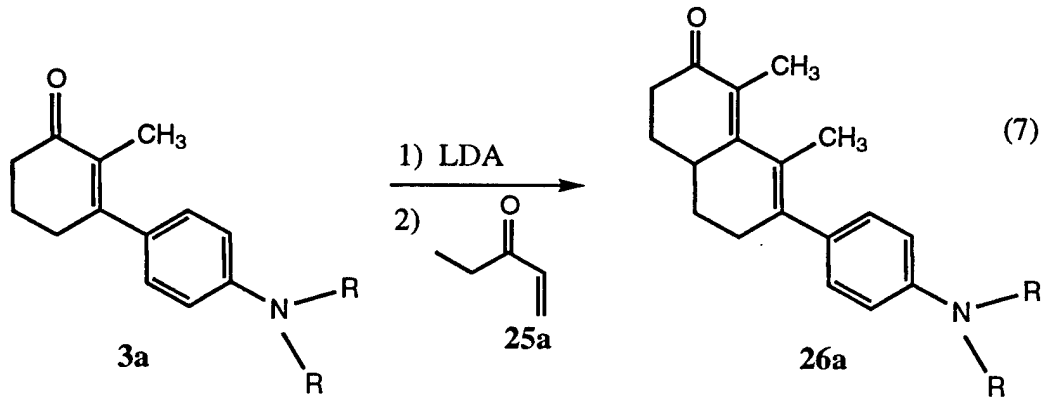
(5)



(6)

2-methyl-3-substituted cyclohexenones such as **3a**. Conjugate addition of **25a** to the kinetic enolate of **3a**, followed by intramolecular aldol condensation should lead to fused (polyen)ones such as **26a**(Eq. 7). Our decision to investigate first the attachment of acceptors to enones such as **3a** was a fortunate one because it led us to the early discovery that C-2 substituents blocked Knoevenagel condensation of cyclohexenones such as **3a** and **26a**.

We have already demonstrated that Knoevenagel condensations of C-2 unsubstituted cyclohexenones is facile and occured in high yields. These effects of C-2 substitution on the two stages of the synthetic scheme suggested the modified scheme for elongated bridges in which the terminal fused cyclohexenone of elongated

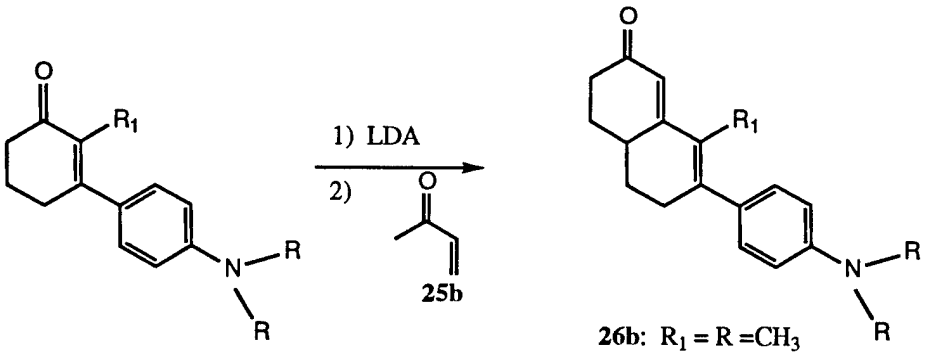


3a **25a** **26a** (7)

C-2/C-3-substituted π-bridges would not be substituted at C-2. This would allow the final synthetic step for capping the chromophore.

To demonstrate the feasibility of this strategy, we planned to effect the annulation of a C-2 unsubstituted ring on to **3a** which by itself, could not undergo Knoevenagel condensation. If the resulting bicyclic dienone could be capped, e.g with thiobarbituric acid, the resulting chromophore would represent formal proof of the strategy. Thereafter, the fused polyene bridge can be elongated to desired length by iterative annelation as in Eq 7, but ending with terminal C-2 unsubstituted cyclohexenone ring for capping with acceptors. Our result is illustrated in Scheme II. After generation of the kinetic enolate **3a**, the formed amine was removed by vacuum evaporation at room temperature. The residual solid was redissolved in anhydrous THF and the vinyl ketone **25b** was added. The intermediate Michael adduct was subjected to aldol condensation with minimal work-up. The bicyclic dienone **26b** was obtained in 95% yield. The dienone **26b** was capped with thiobarbituric acid quantitatively to give **9d**. Use of the C-3-only

Scheme II

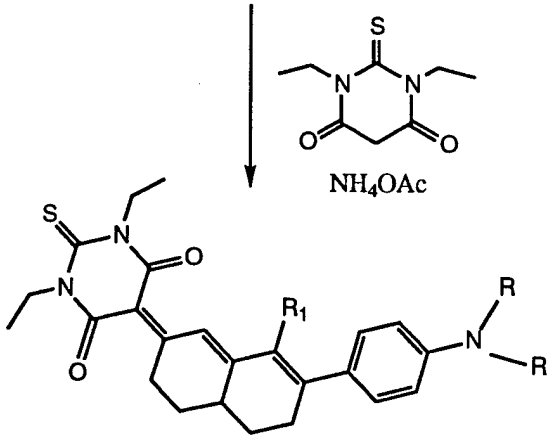


3a: $R_1 = R = CH_3$

3g: $R_1 = H; R = CH_3$

26b: $R_1 = R = CH_3$

26c: $R_1 = H; R = CH_3$



9d: $R_1 = R = CH_3$

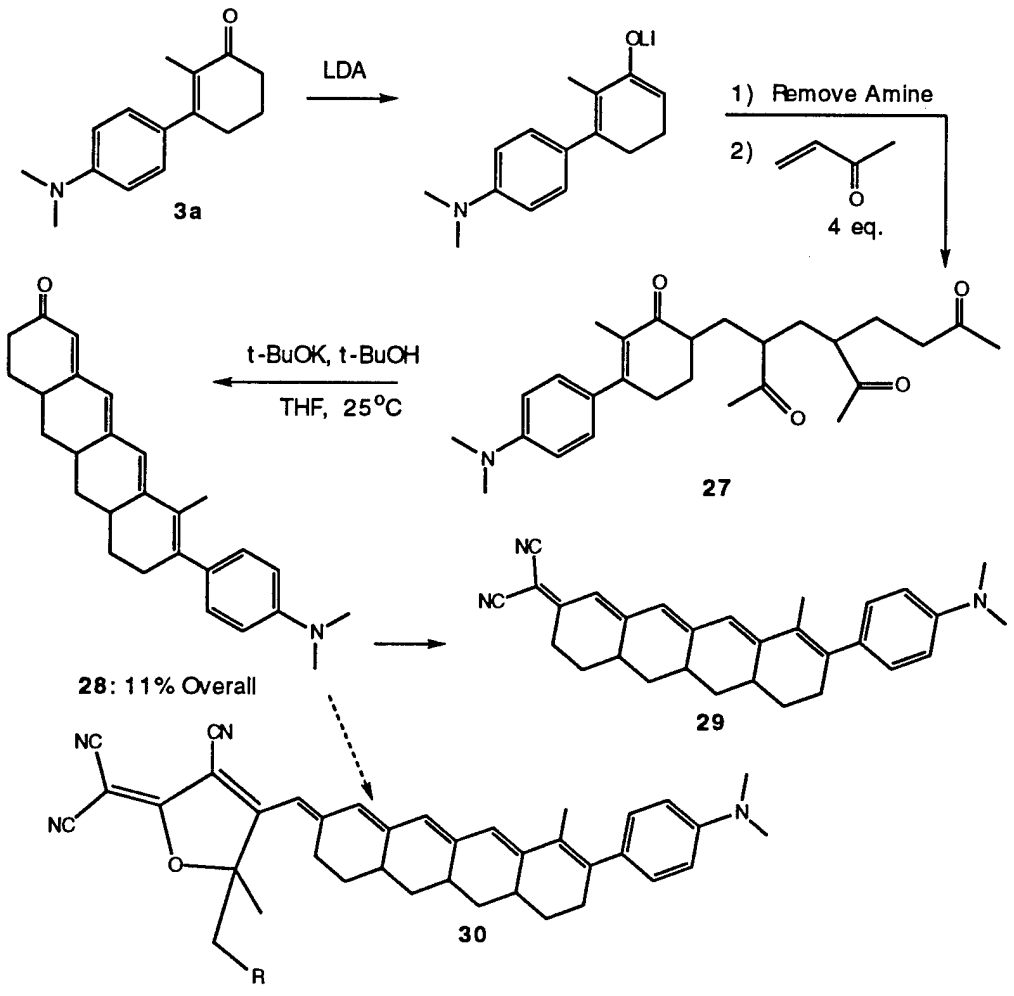
9e: $R_1 = H; R = CH_3$

substituted cyclohexenone **3g** gave the corresponding dienone **26c** in 36% yield which was also capped in quantitative yield to give **9e**. The successful annulation to **3g** is similar to results reported earlier by Dalton[9] and also Jen[10] with C-3 substituted-5,5-dimethylcyclohexenones.

When the above procedure, starting with **3a,** was carried out using excess methyl vinyl ketone **25b**, the tetracycle **28** (Scheme III)was isolated in 11% overall yield from **3a. This overall yield is still twice the overall yield reported for an analogous tricycle prepared from a C-3 substituted cyclohexenone by iterative annelation.**[10] The trimer **27** was presumed to have cyclized in an ordered sequence to give the tetracycle **28.** The tetracycle **28** was capped with malononitrile to give the chromophore **29** which represents the kongest fused ring chromophore reported yet!

In discussion with a prospective collaborator for determination of nonlinear properties of 29, it was suggested that the use of the strong acceptor, 2-dicyanomethylene- 3-cyano-4,5,5-trimethyl-2,5-dihydrofuran(TCF), 31(R_1 = H, Scheme

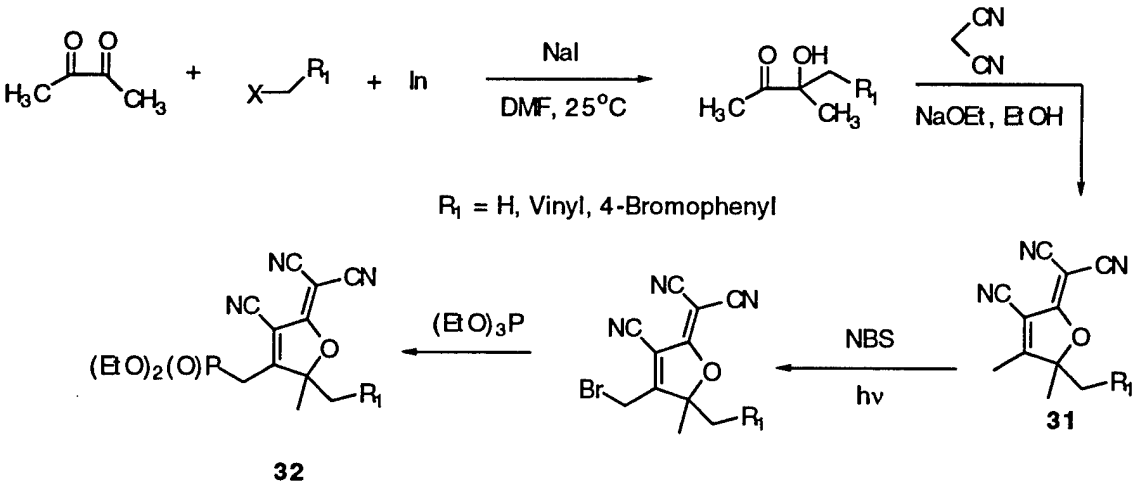
Scheme III



IV). We therefore embarked on the investigation of Scheme IV for the synthesis of derivatives of TCF such as the phosphonate **32**. The parent TCF is known to condense quite easily and efficiently with aldehydes and α.β–unsaturated aldehydes but there are no reports of its condensation with α.β–enones such as **28**. That was why we planned to use the more reactive phosphonate intermediate. Synthesis of these derivatives also offer the opportunity to incorporate a monomeric function at this end of the chromophore. This work, which would lead to chromophore such as **30**, is not yet concluded.

We also investigated the reproducibility of the polyannulation reaction shown in Scheme III that yielded the tetracyclic polyeneone **28** in a one pot reaction. It was found that the product could not be formed in isolable yields in reactions using less than 10g of the enone **3a**. It was concluded from this observation, the high yield and reproducibility of the single ring annelation, that iterative annulation was the better route to elongated fused ring polyene bridges.

Scheme IV: Syntheses of Derivatives of Tricyanodihydrofuran(TCF)

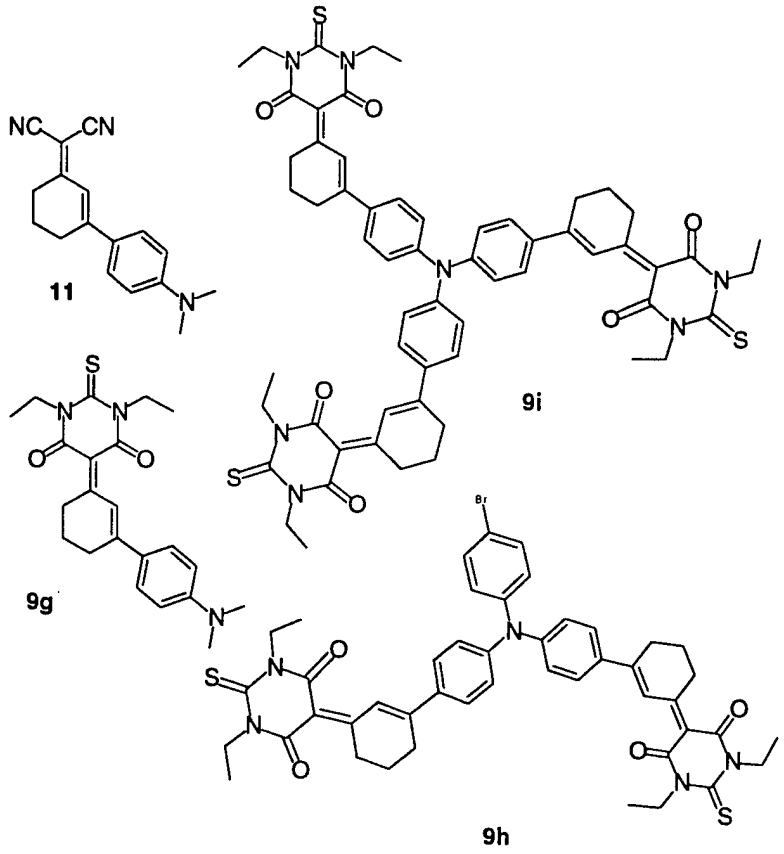


The following chromophores in Fig. 1 have been provided to a materials scientist at NASA Langley Reserach center in Hampton, VA for evaluation as active components in electrostrictive thin films. Their evaluation is still on-going.

Conclusion:

A modular, synthetic scheme was developed for versatile variation of donors, acceptors and fused ring polyene bridge length of NLO-chromophores. Configurational and conformational rigidity of the polyene bridges were realized by making each set of

Fig. 1: FUSED RING CHROMOPHORES BEING TESTED FOR ELECTROSTRICTIVE ACTIVITY



adjacent double and single bonds part of a fused cyclohexene ring. Substituent effects on the regioselective establishment of the donor, chemoselective elongation of the fused polyene bridge and reactivity in the final introduction of the acceptor moiety were uncovered and used, at appropriate stages in the overall synthetic scheme to control regioselectivity and chemoselectivity and reactivity. New chromophores with 1:1, 1:2 and 1:3 donor:acceptor ratios per chromophoric unit were prepared and characterized spectroscopically and thermally. It was concluded that iterative annelative ring fusion would be method of choice for realizing longer fused bridges. The only weak component of the demonstrated scheme is the sluggishness of the Knoevenagel condensation and the pausity of activated methylene compounds that can be utilized with good yields, especially when the carbonyl is an unsaturated ketone. It remains to be determined whether the phosphonate route which we are now considering would overcome this problem.

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