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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The class of laser dye known as 4PyMPO was given an expanded fluorophor by substitution of a biphenylene for the phenylene group. Neither the derived quaternary salt or zwitterion had a higher extinction coefficient, quantum yield, or bathochromic shift of absorption from that of the parent compound. Replacement of the methoxy "M" by julolidino was not achieved. In 2-(4'-methoxy-4-biphenyl)-1-propylbenzimidazole, the methanesulfonate acid salt was no higher in quantum yield than the methanesulfonate quat., indicating no steric hindrance to planarity in the excited state. Addition of a phenylene group, again, did not improve the fluorescence properties. A symmetrical version with benzimidazolium ions at both ends is being prepared. Synthesis of a bridged quaterphenyl with stilbenylmethyl groups as potential intramolecular triplet state quenchers is one step from the target molecule. Synthesis of a high-energy dye related to the most effective bridged sexiphenyls known by replacement of benzene rings B and E by furan rings is one step from the target molecule.				
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18. benzimidazole, benzimidazolium ion, quaternary salt, pyridinium salt, zwitterion, 4PyMPO, julolidine, auxofluor fluorescence, quantum yield, extinction coefficient ~~4-15~~



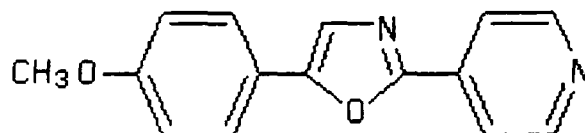
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I. Photostable dyes for repetitive use in solution

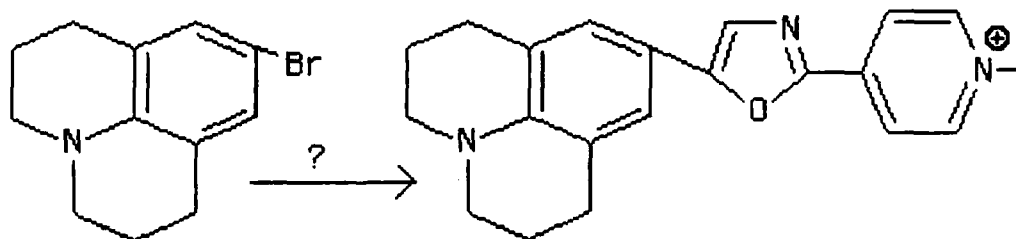
A. Dyes related to 4PyMPO:



1. Incorporation of additional phenylene groups – Quaternary salts of 4PyMPO are exceptionally photostable, but have low energy output (Fletcher,84). Since quaterphenyls have higher energy output than terphenyls, and the difference is thought to be related to the larger extinction coefficient of the larger fluorophor (Kauffman,88), we synthesized a homolog (21 in Scheme A) in order to raise the extinction coefficient. The entire synthesis in Scheme A was carried out successfully, with preparation of small amounts of quat 1 and of quat 1a, a zwitterion. The N-dodecyl p-toluenesulfonate quat of 21 was also prepared, containing the same fluorophor as quat 1a. Its extinction coefficient (28,000 at 362nm in abs. ethanol) was not higher than that of the smaller lead compound! Since it has been found that zwitterions in this series sometimes lase better than quaternary salts, 1a was prepared, with the same result ($\epsilon=25,000$ at 410nm in abs. ethanol). This was accompanied by a low fluorescence quantum yield and poor lasing (Avco-Everett).*

The longer fluorophor, in this case, did not have adequate coupling between its push-pull auxofluors. Bridging one or more pairs of rings, as was under investigation by the late Herbert Hall, might improve this class of dye. We plan no more work on this class of dye this year.

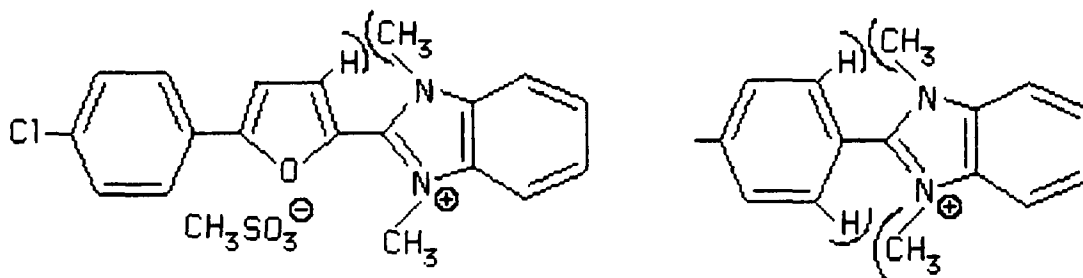
2. Analog with julolidino in place of methoxy:



Use of NBS in DMF gave 9-bromojulolidine hydrochloride (above) with some difficulty. We were never able to replace the bromine with a metal in order to couple it with another aromatic ring. This is still worth pursuing, perhaps by nitrosation of 9-acetyljulolidine; but we do not plan on doing it this year.

* Submitted 170 mg to MICOM on 22 Nov 89.

B. Evaluation of N,N'-dialkylbenzimidazolium ion as an auxofluor:



The lead compound for this series was a 2-(2-furyl)benzimidazolium ion (above left), which lased well when XeCl^* laser pumped (Rinke,84). The steric hindrance to attainment of planarity by the excited singlet state is minimal because of the 108° angles in the furan ring, and the existence of only a single hydrogen near one of the N-methyl groups. We wanted to make phenylene compounds, thinking they would be more stable (above right). In this case, the phenylene ring has 120° angles and two hydrogens potentially too close to the N-methyl groups. We had to make model compounds (8a and 8b in Scheme C) to verify retention of quantum yield (Φ).

To do this, the surprisingly difficult synthesis of the free base 35 was achieved (Scheme B). While the monomethylation of o-phenylenediamine (28) has been reported, we could not do a monopropylation to 30. Reduction of the monoallyl (31) to 30 was reported, but we could not duplicate it. While alkylation of 32 to make the nitroamine 33 went very well, and reduction to 30 was successful, 30 was extremely unstable to air oxidation, and gave a poor yield of benzimidazole 35. It was found that 36 could be made on a large scale, and the difficult alkylation to 35 accomplished with 1-iodopropane with sodium hydroxide in acetone.

Coupling the Grignard reagent 20a (Scheme C) with 35 gave the free base 38a, from which the acid salt 8a and the quat 8b were prepared. When Φ was determined against the standard quinine bisulfate in 1 N sulfuric acid ($\Phi = 0.55$) the acid salt (with N—H) did not have higher Φ than the quat (with N—Me), and was actually poorer in water (Table I):

Table I. Effect of N' Substitution on Φ of Benzimidazoles

Compound	Solvent	Φ
8a	ethanol	0.80
8b	"	0.77
8a	ethanol:water::1:1	0.78
8b	"	0.78
8a	water	0.56
8b	"	0.66

This result is in stark contrast to the effect of internal alkyl groups on oligophenylenes, where Φ plummets because of the steric hindrance. The model compounds 8a and 8b display fine violet fluorescence in solution. Naturally, we went ahead and prepared the next higher homolog, 39 in Scheme C, to red-shift the fluorescence into a more desirable range for this project and to raise ϵ . Again, just as in the case of "stretched" 4PyMPO quats, a red-shift was not obtained; λ_{max} fell to 312 nm ($\epsilon = 42,100$), and 39 displayed a weak green luminescence with a whitish overcast. This property in other compounds has indicated triplet state formation. We believe the compound is not even worth testing. It is another example of poor coupling between push-pull auxofluors.

Taking into account the fact that most powerful laser dyes are symmetrical along the long axis of the fluorophor, even when that axis is bent (rhodamines, and "JB2" as reported for Joe Boyer by Ted Pavlopoulos at LASERS '89), we have begun to prepare a symmetrical derivative by attempting to couple two moles of 35 to 2,7-dibromo-9,9-dipropylfluorene (48a in Scheme E).

II. Laser dyes incorporating an intramolecular triplet-state quencher

A. Bridged quaterphenyls (10b in Scheme D and 55 in Scheme E) – Fluorenes dialkylated at the 9-position by 4-(chloromethyl)stilbene (47 in Scheme D) were prepared by following the synthetic scheme in the Proposal: 2,7-dibromofluorene was dialkylated with 4-(chloromethyl)stilbene (47), which recently became available from Aldrich, to give 48b. The attempt to couple the Grignard reagent from 4-bromoanisole (20a) caused polymerization of 10b. This was surprising in view of the reactivity of the catalysts reported to be required to polymerize phenyl-terminated alkenes. (In earlier work rapid polymerization of the 9,9-diallyl analog of 10b occurred.)

Since the original work cited in the Proposal indicated that a methylene link between the stilbene and the aromatic fluorophor was superior to an ethylene link, and a renewed literature search turned up a useful procedure for coupling aryl Grignard reagents with benzyl halides, the process in Scheme E was largely completed. The Grignard reagent from 3-bromotoluene was coupled with 48a to give the new quaterphenyl 53. Reaction of 53 with two moles of N-bromosuccinimide has given the benzyl halide 54, according to PMR spectra. Since no catalyst of any kind is needed for coupling 4-bromostilbene with 54, no polymerization is anticipated in the preparation of target molecule 55. (We think the 4-bromostilbene would be prepared most easily by means of a Wittig-Hörner reaction between 4-bromobenzaldehyde and diethyl benzylphosphonate.)

B. Furan-containing oligophenylenes (Scheme F) – Laser dyes which are bridged sexiphenyls were superior to bridged quaterphenyls in every way (Kauffman, LASERS '89). Since the wavelengths are limited to about 420 nm in sexiphenyls, and probably to 440 nm in octiphenyls, too short for this project, the judicious substitution of furan rings for rings B and E in a bridged sexiphenyl should give a reasonably soluble

compound with a lasing peak near 460 nm. With the reactive 2- and 5-positions of the furan ring blocked by phenyls, stability should be adequate. These furans are also amenable to stilbene substitution to provide intramolecular triplet-state quenching.

All of the furan syntheses in the proposal were dependent on the success of the Gomberg-Bachmann coupling of diazotized p-anisidine (50 in Scheme F) with furan to form 2-(p-anisyl)furan (51, Ayres,68). We were unable to duplicate this work. Luckily, a recent report from workers who could not duplicate it either presented a direct lithiation of furan, followed by interchange to the 2-furylzinc chloride, and coupling with a number of aryl halides in the presence of a Pd(0) catalyst. We have coupled 2-furylzinc chloride with aid of a Pd(II) catalyst with 48a to give the previously unreported 56. Another lithiation and coupling should give the target molecule 12a. This route will allow a wide variety of "ends" and auxofluors to be joined with a common "middle".

Acknowledgment

Extensive discussions were held with John Ehrlich and Wayne Davenport (Army Missile Command) at the LASERS '89 meeting in New Orleans (December). Many contacts by telephone were made before and since. The encouragement provided by Dr. Ehrlich is greatly appreciated.

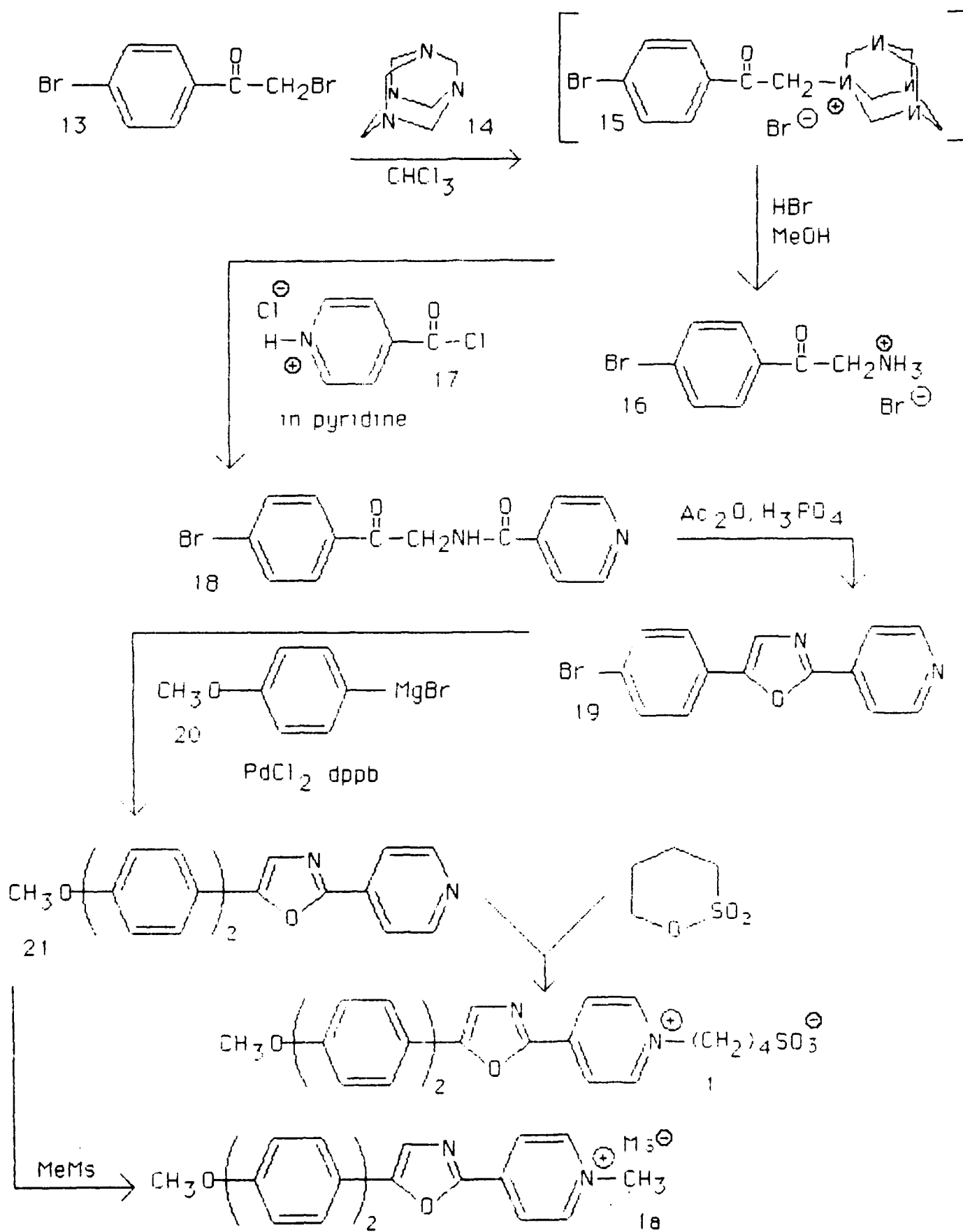
John Novinski was contracted to work on this Project as a Postdoctoral Fellow. He has carried out some of the benzimidazole, some of the stilbene, and all of the furan synthesis.

The extensive technical assistance of Ali Khalaj was very valuable. Discussions with Charles J. Kelley, Walter Boyko, Ted Pavlopoulos, and James H. Bentley were greatly appreciated. Determination of spectra by Damien T. Cole and Walter Boyko was highly professional.

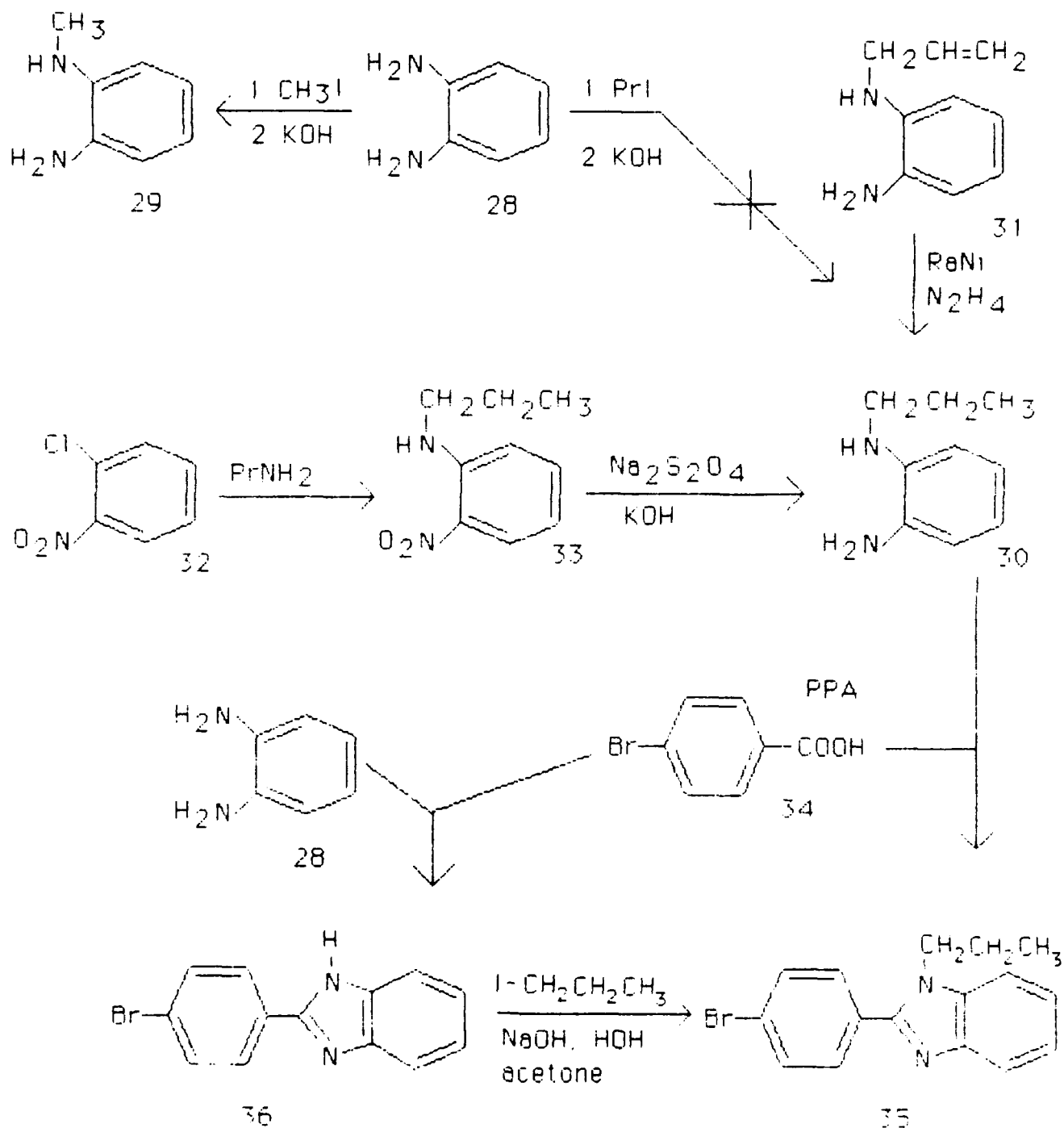
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2. Fletcher,84: A. N. Fletcher, R. A. Henry, R. F. Kubin, R. A. Hollins, Optics Communs. 47, 57.
3. Kauffman,88: J. M. Kauffman, C. J. Kelley, A. Giorghis, E. Neister, L. Armstrong, Laser Chem. 7, 343.
4. Rinke,84: M. Rinke, Doctoral Dissertation, Universität Karlsruhe and Research Report KfK 3810, Kernforschungszentrum Karlsruhe.

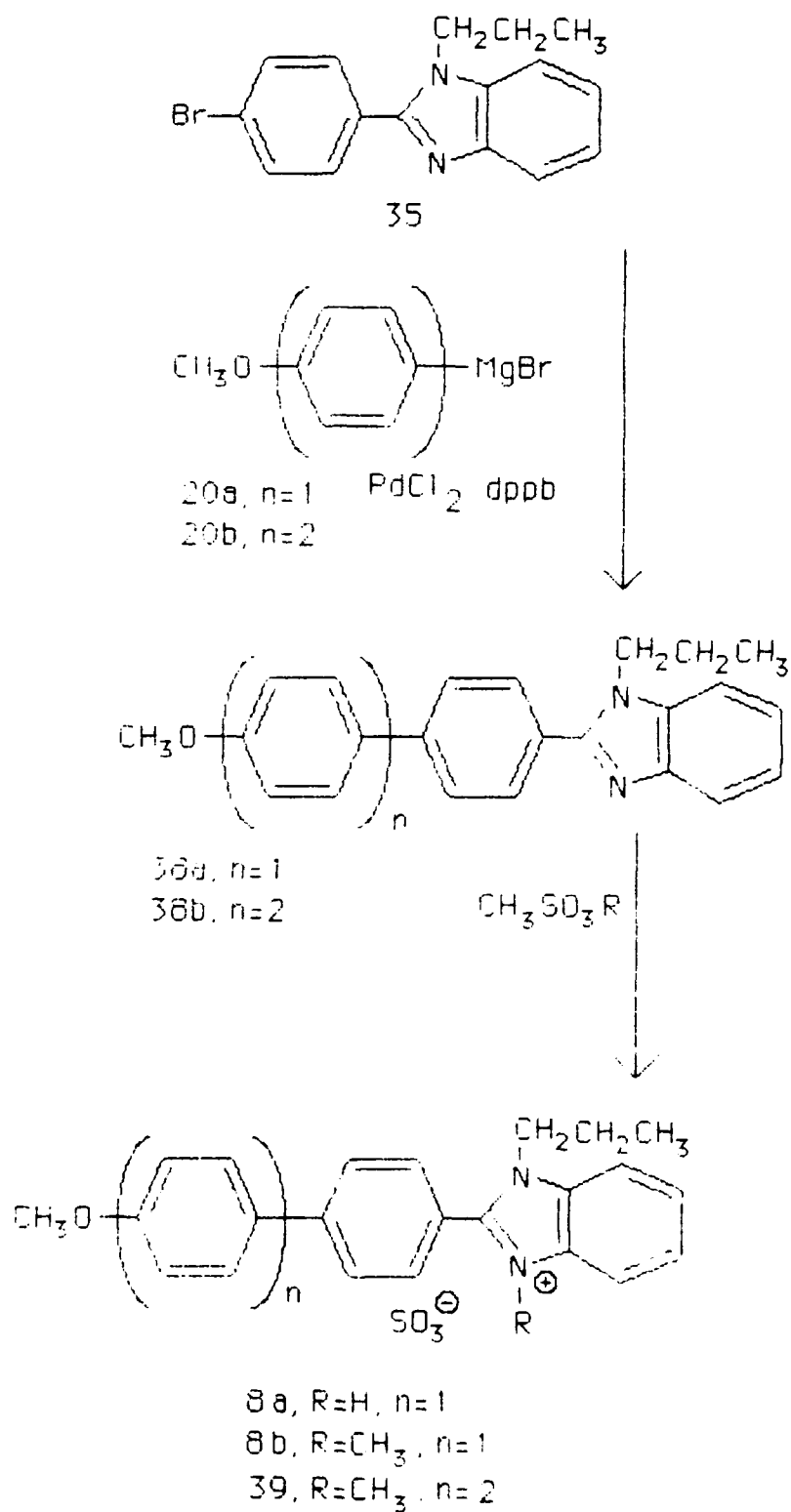
Scheme A. Synthesis of Oligomer of 4PyMPO



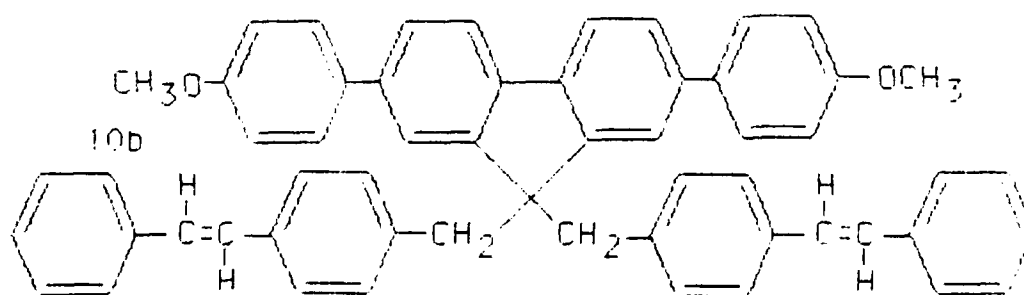
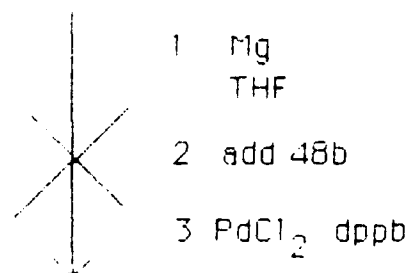
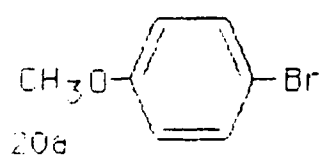
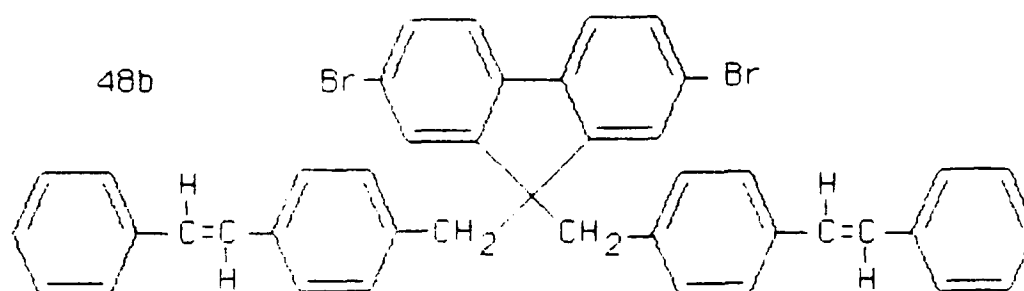
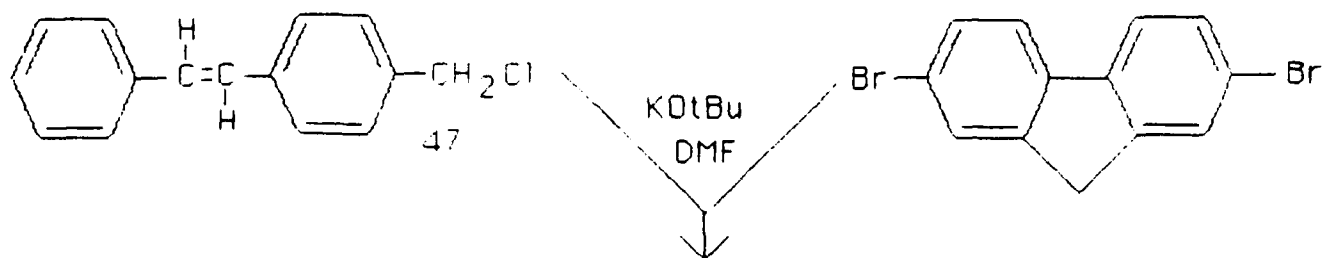
Scheme B Synthesis of N-Alkyl-2-arylbenzimidazoles



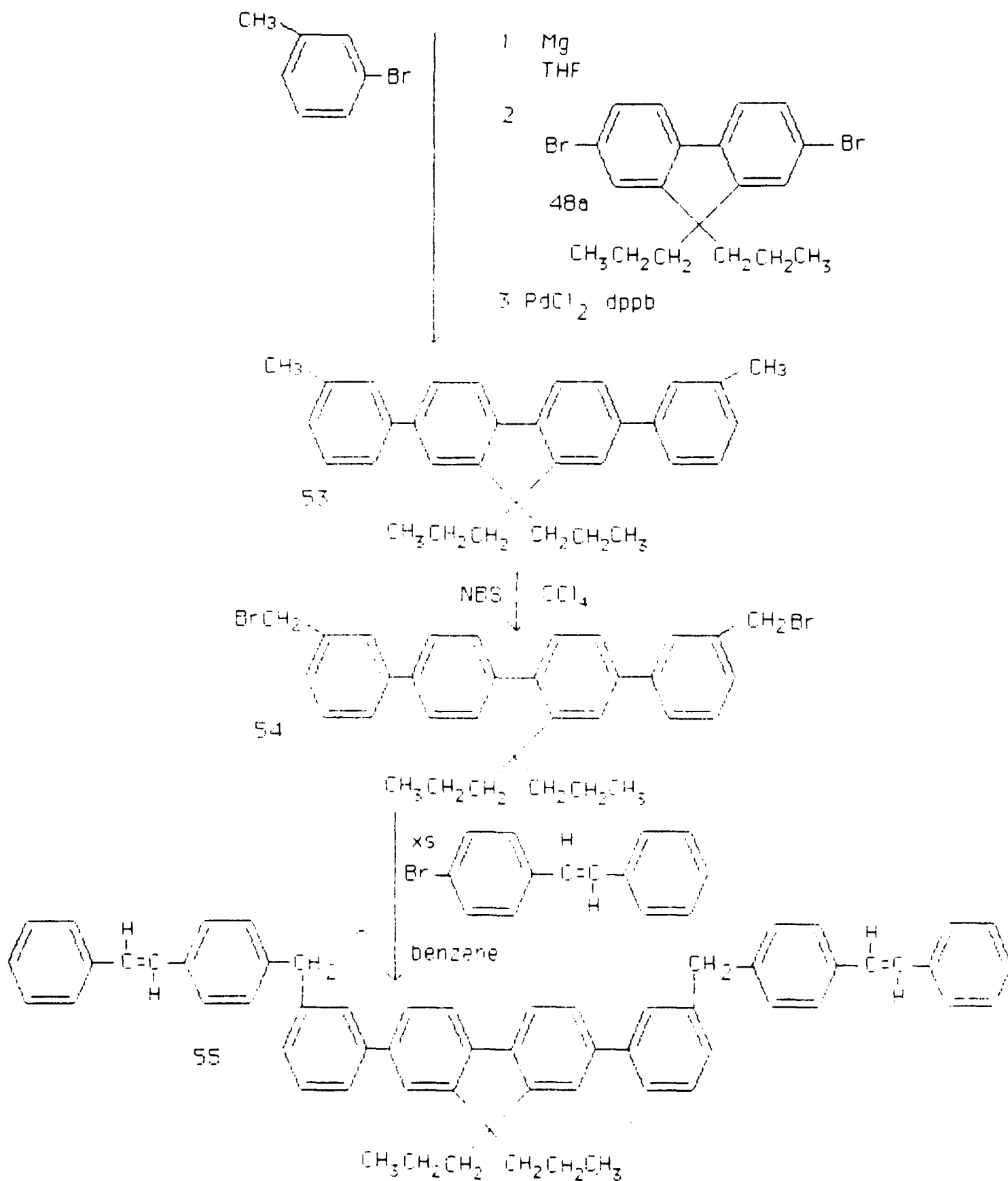
Scheme C Synthesis of Potential Laser Dyes
Containing the 1,3-Dialkylbenzimidazolium Ion



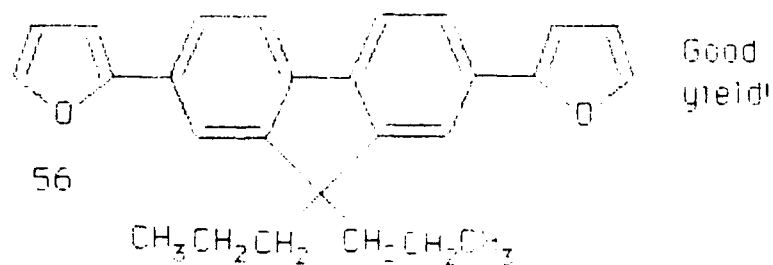
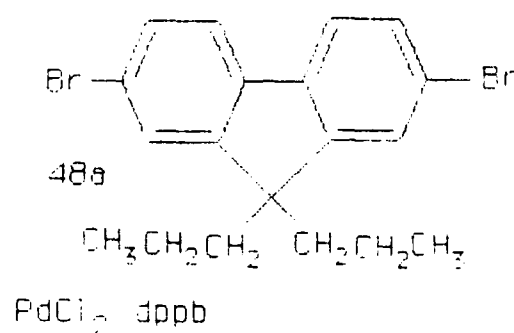
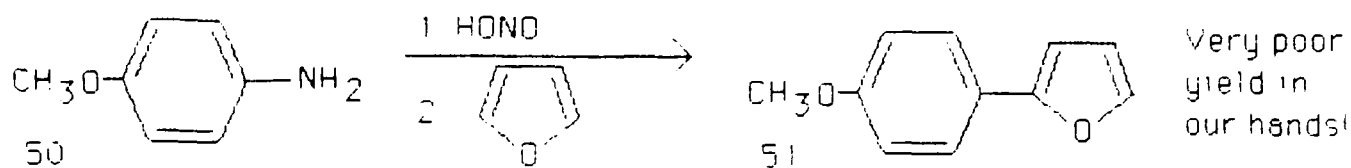
Scheme D. Syntheses of Oligophenylenes Bonded to Stilbene



Scheme E Alternate Synthesis of Oligophenylenes Bonded to Stilbene



Scheme F Synthesis of Furan-Containing Oligophenylenes



1. $t\text{-BuLi}$
2. ZnCl_2
3. 4-bromoanisole
4. PdCl_2 dppb

