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New Photolabile Protecting Groups of the 2-(2-Nitrophenyl)ethoxycarbonyl- and the 2-(2-Nitrophenyl)ethylsulfonyl-Type for the Oligonucleotide Synthesis

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**NEW PHOTOLABILE PROTECTING GROUPS
OF THE 2-(2-NITROPHENYL)ETHOXYCARBONYL- AND THE
2-(2-NITROPHENYL)ETHYLSULFONYL-TYPE FOR THE
OLIGONUCLEOTIDE SYNTHESIS**

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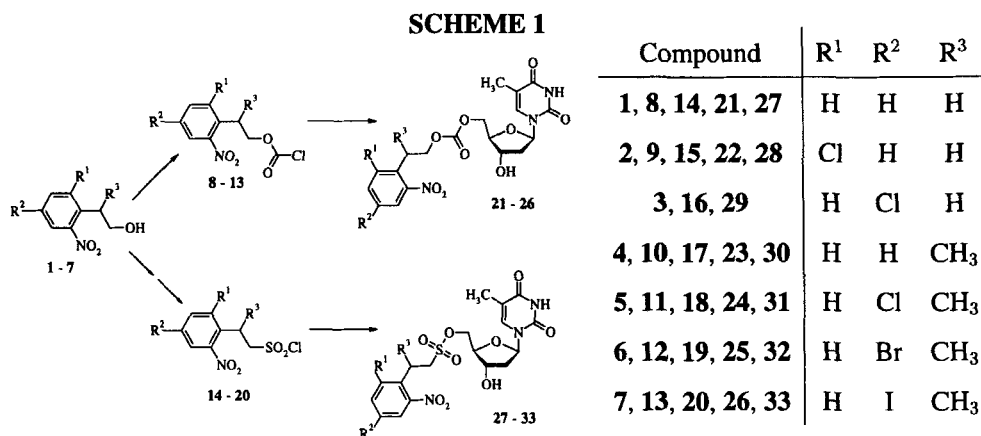
ABSTRACT: New photolabile blocking groups have been synthesized and introduced into the 5'-OH position of thymidine. The 5'-O-protected thymidines were irradiated at 365 nm under identical conditions and the half-lives and thymidine yields were determined to investigate the influence of different substituents in the two corresponding series.

Light-directed synthesis of oligonucleotides permits the preparation of thousands of different sequences at small location. These DNA chips are a rapid and inexpensive tool in sequencing of DNA. Therefore, a great need of very efficient photoremovable protecting groups exists, however, the photochemical deprotection still results in lower yields compared to acid deprotection.

The preparation of the protecting group reagents could be achieved in one (carbonyl series)¹ or two (sulfonyl series)²⁻⁵ steps starting from the corresponding alcohols⁶⁻⁷ (Scheme 1).

The introduction of the new blocking groups into the 5'-OH position of thymidine was carried out in pyridine/CH₂Cl₂ 1:1 at low temperature.

The photochemical half-lives t_H and thymidine yields (table 1) of the 5'-O-protected thymidine derivatives were determined by irradiation with a 200 W mercury lamp (365 nm, methanol/water 1:1), followed by HPLC analysis. The half-lives were calculated

**TABLE 1:** Photolysis data of 5'-O-protected thymidines

Substituents			Carbonate-Series			Sulfonate-Series		
R ¹	R ²	R ³		<i>t_H</i>	Yield thymidine		<i>t_H</i>	Yield thymidine
H	H	H	21	7.5 min	80 % (60 min)	27	10.9 min	43 % (90 min)
Cl	H	H	22	82 min	80 % (60 min)	28	16.3 min	18 % (2 h)
H	Cl	H	—			29	10.9 min	36 % (2 h)
H	H	CH ₃	23	56 s	76 % (10 min)	30	82 s	43 % (10 min)
H	Cl	CH ₃	24	62 s	85 % (10 min)	31	66 s	60 % (10 min)
H	Br	CH ₃	25	60 s	85 % (10 min)	32	70 s	63 % (10 min)
H	I	CH ₃	26	53 s	81 % (10 min)	33	60 s	64 % (10 min)

from the plot of concentration (peak area at time *t* (*A_t*) divided by peak area at time zero (*A₀*) multiplied with 100 %) versus the irradiation time.

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