



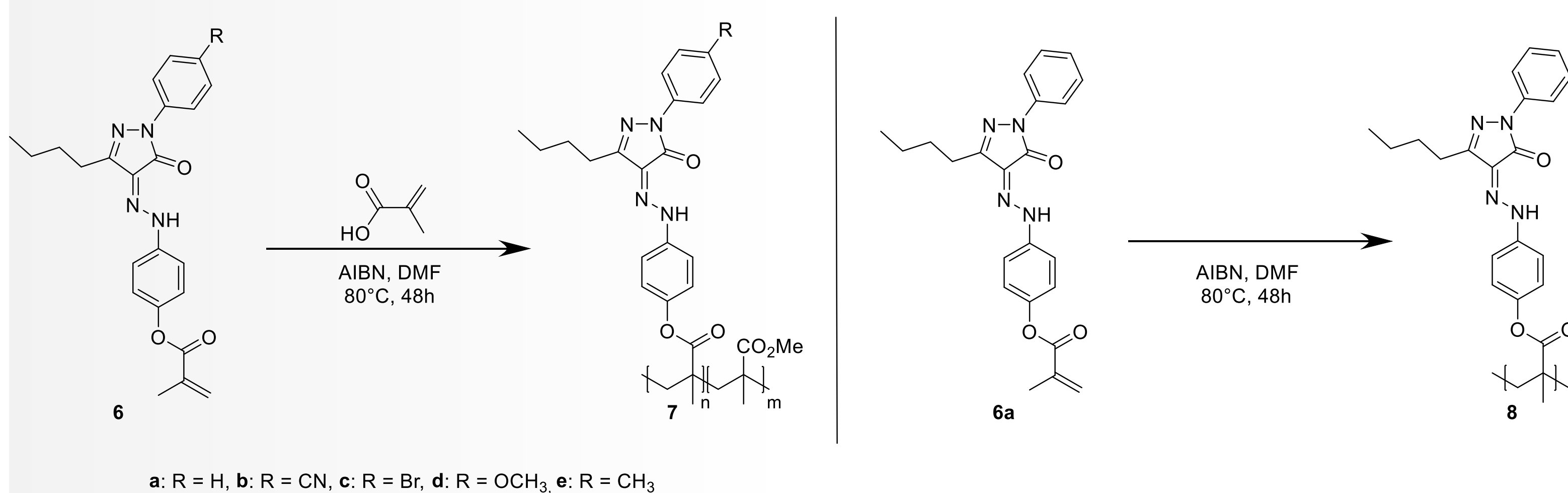
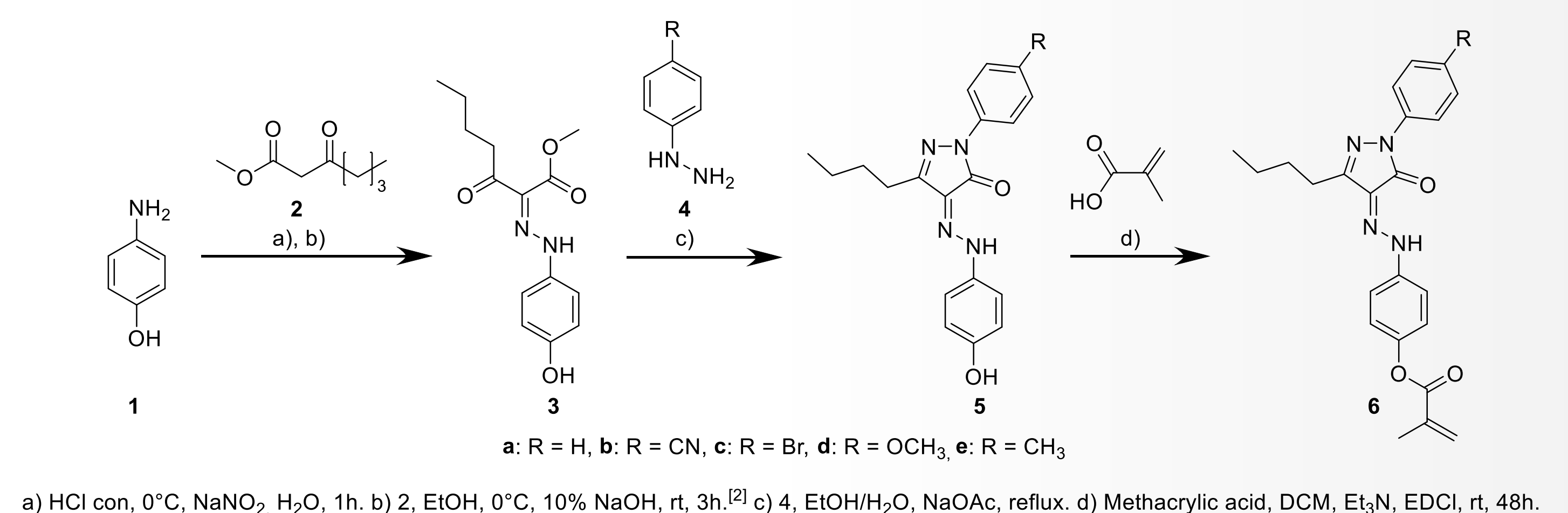
Polymeric Dyes with Hydrazone-Pyrazolones Units: Design, Synthesis, and Optical Properties

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Summary

In this work, we present the synthesis and seminal results obtained for novel methacrylic polymeric dyes incorporating hydrazone-pyrazolones moieties.^[1] Hydrazone-pyrazolone homopolymer and copolymers with structural variations have been systematically studied. It was shown that polymeric dyes with hydrazone-pyrazolone fragments can detect a number of inorganic and organic anions as well as the impact of the side-chain chromophore on chromogenic detection properties of polymers was discussed. We also present the optical properties of this novel class of methacrylic polymers containing dyes in side chain.

Polymer synthesis



➤ $M_n = 47\ 800 - 100\ 600$ g/mol

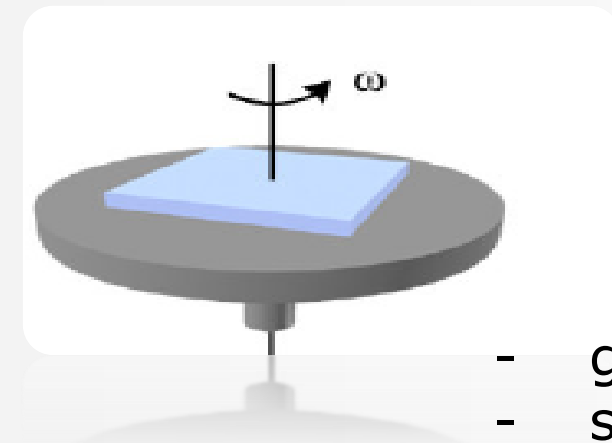
➤ $M_w / M_n = 1.2 - 1.7$

➤ $T_g = 120-146$ °C

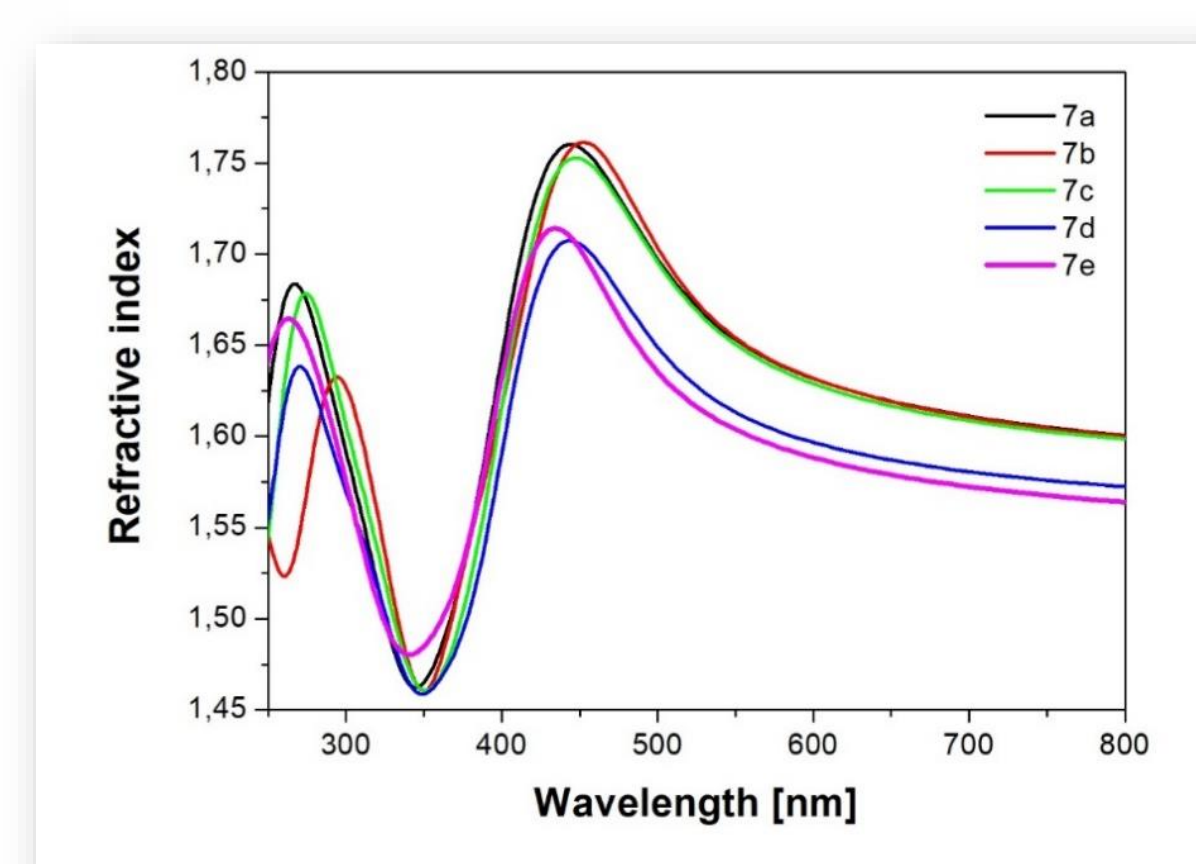
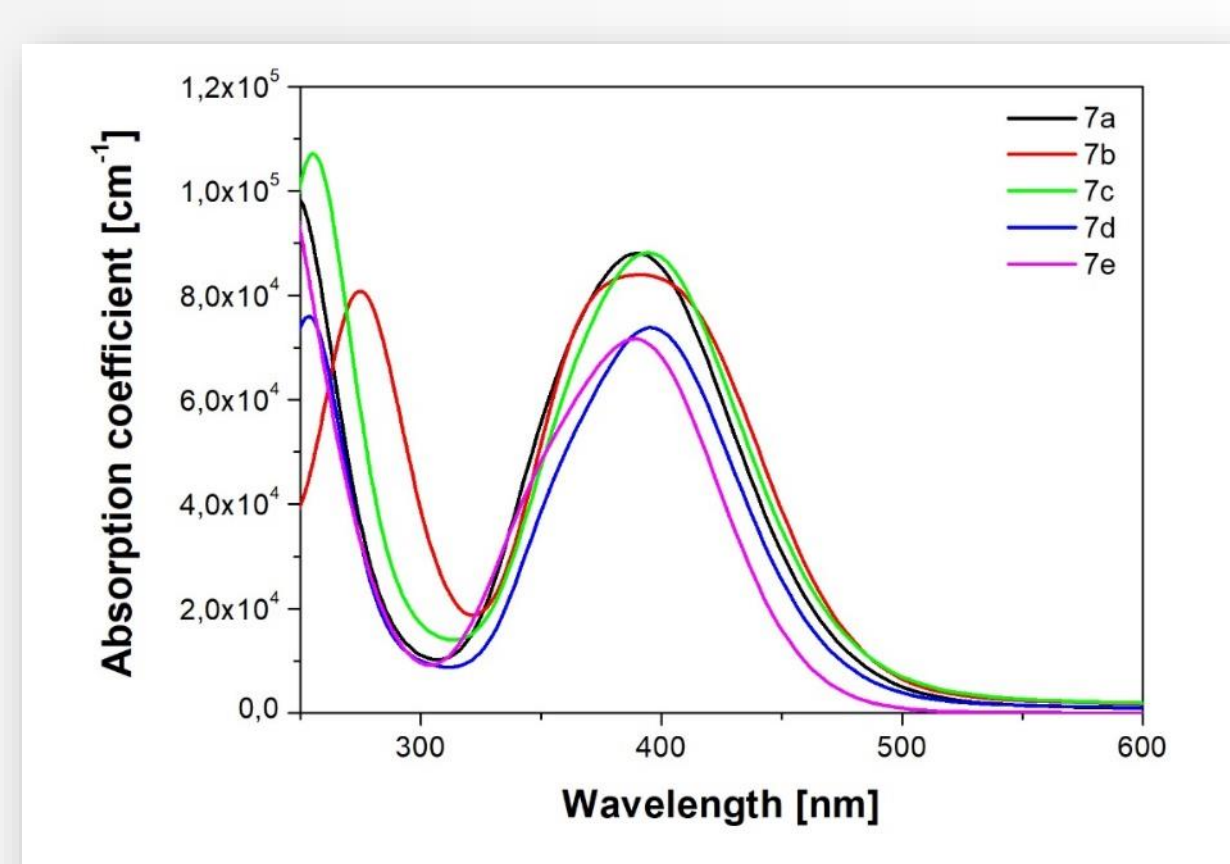
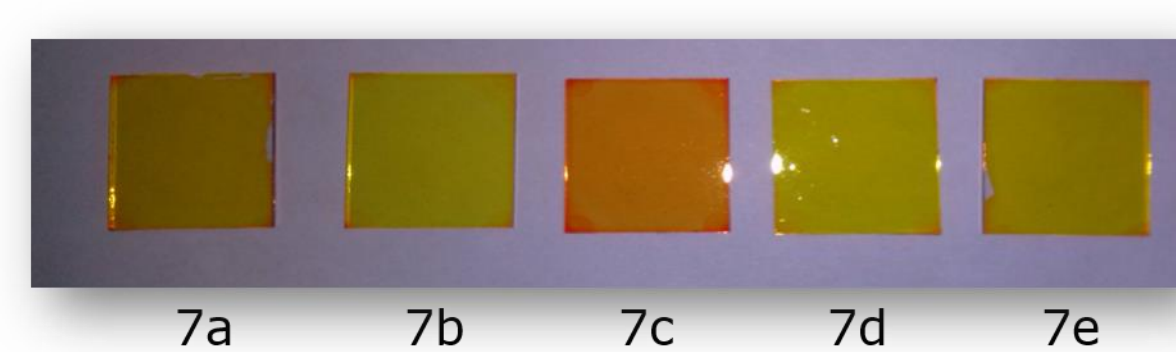
➤ $T_m = 249-263$ °C



Optical properties



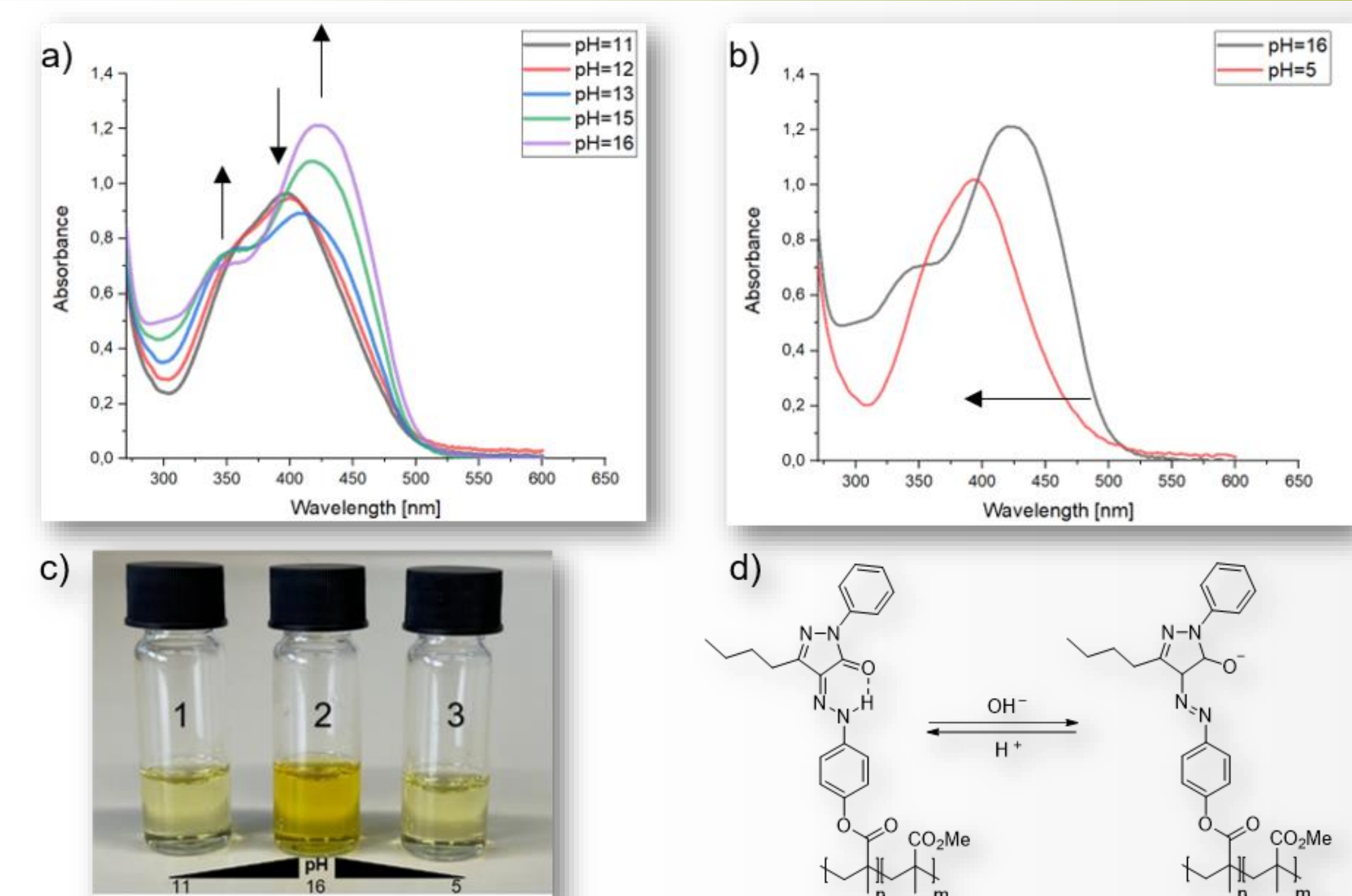
- glass slides BK7
- spin-coat at 1000 rpm/ 60s
- 10 wt % 1,1,2- trichloroethane solution



Absorption coefficient of the thin films of the methacrylic polymeric dyes incorporating hydrazone-pyrazolones moiety as a function of wavelength.

Refractive index of the studied polymeric dyes with hydrazone-pyrazolones fragment.

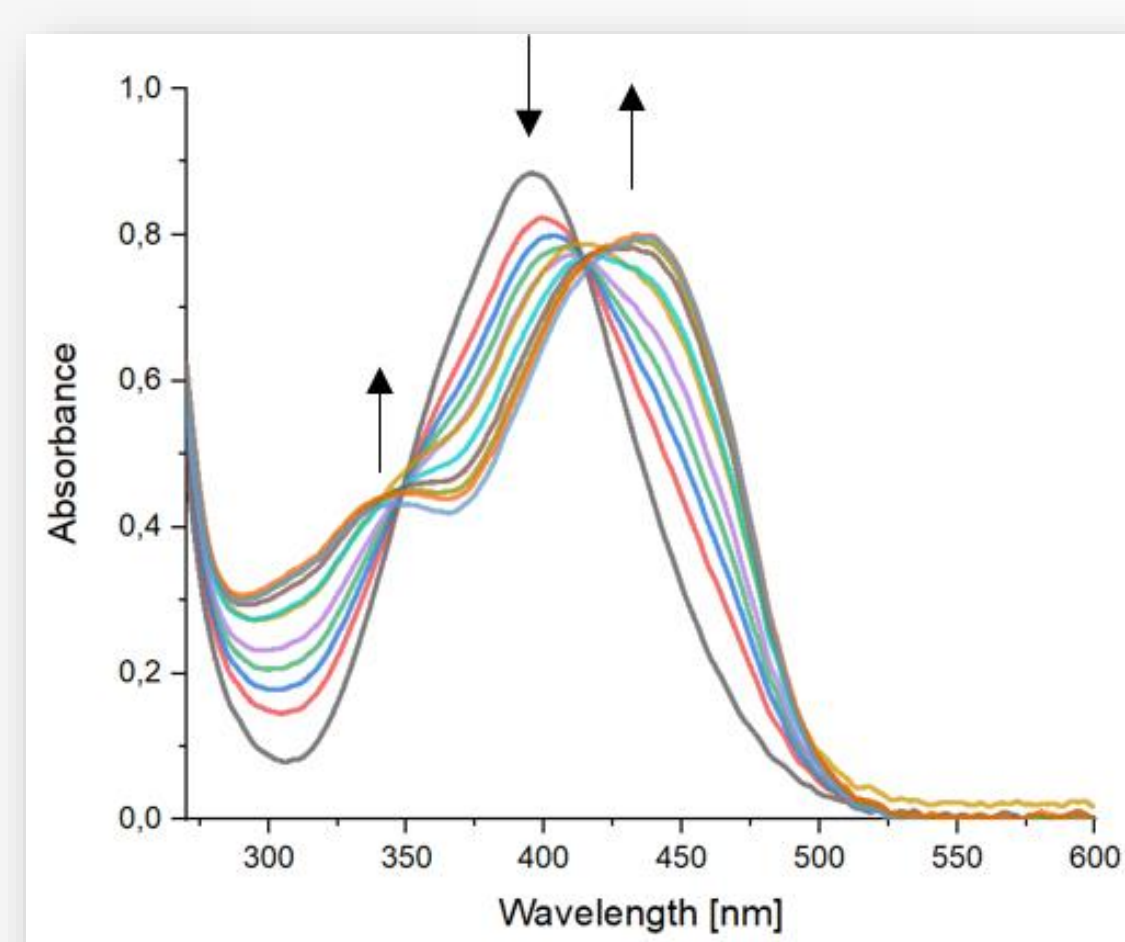
UV-Vis studies



Changes in the UV-Vis spectra and pH value of **7a** (1×10^{-5} M) a) during titration by CsOH in DMSO; b) after adding HCl in DMSO; c) color changes of **7a** in DMSO (1) after adding CsOH, pH=11; (2) pH=16; (3) reverse color change after adding HCl, pH=5. d) two tautomeric forms hydrazone at pH=11 and azo in basic media (pH=16).

Anion detection

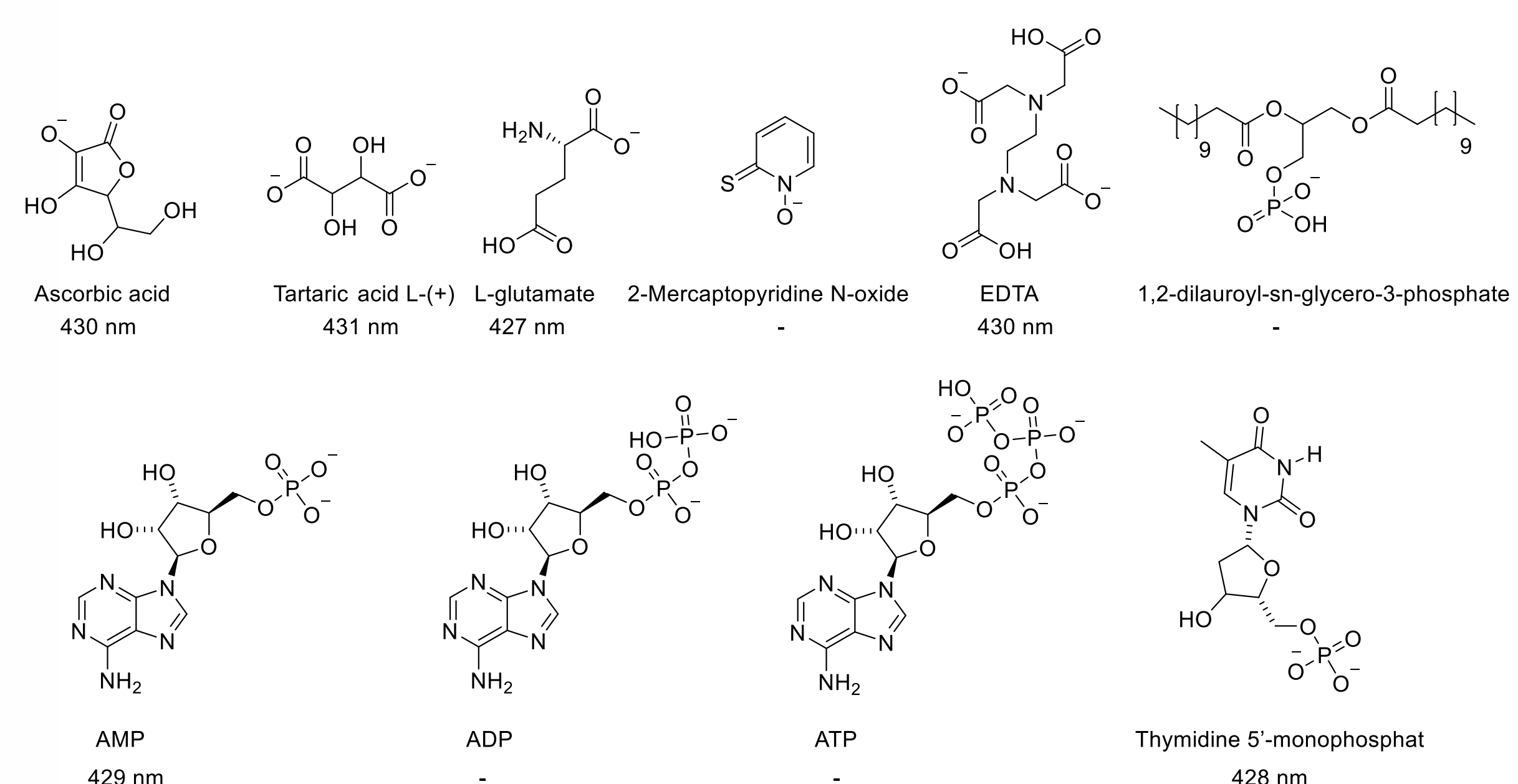
The polymers **7a-e** were tested for chromogenic detection of anions by UV-Vis titrations in DMSO solution. The investigated polymers could form a hydrogen bond to an inorganic and organic anions.



Changes in the UV-Vis spectra for the **7a** (1×10^{-5} M) in the absence and presence of fluoride anion in DMSO solution.

Table 1: Absorption maxima of the polymers **7a-e** in DMSO before and after titration by inorganic anions.

	F ⁻	AcO ⁻	H ₂ PO ₄ ⁻	CrO ₄ ⁻	WO ₄ ⁻	Br ⁻	I ⁻
	λ_{max} [nm]	λ_{max} [nm]	λ_{max} [nm]	λ_{max} [nm]	λ_{max} [nm]	λ_{max} [nm]	λ_{max} [nm]
7a	400	436	432	428	430	-	-
7b	402	429	425	427	-	-	-
7c	405	427	428	435	-	-	-
7d	401	435	424	433	-	-	-
7e	400	432	431	420	-	-	-



Changes the maxima of the polymers **7a** in DMSO after titration by organic anions.

[1] Inukai, Y. Syntheses of Polymeric Azo Dyes of Pyrazolone Series. Contemporary Topics in Polymer Science, pp 183-199.
[2] Singh, U.P.; Bhat, H.R.; Verma, A.; Kumawat, M.K.; Kaur, R.; Guptac S.K.; Singh R.K. Phenyl hydrazone bearing pyrazole and pyrimidine scaffolds: design and discovery of a novel class of non-nucleoside reverse transcriptase inhibitors (NNRTIs) against HIV-1 and their antibacterial properties. RSC Adv., 2013, 3, 17335-17348.



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