

Supplementary material

The applicability of 2-amino-4,6-diphenyl-pyridine-3-carbonitrile sensors for monitoring different types of photopolymerization processes and acceleration of cationic and free-radical photopolymerization under near UV light

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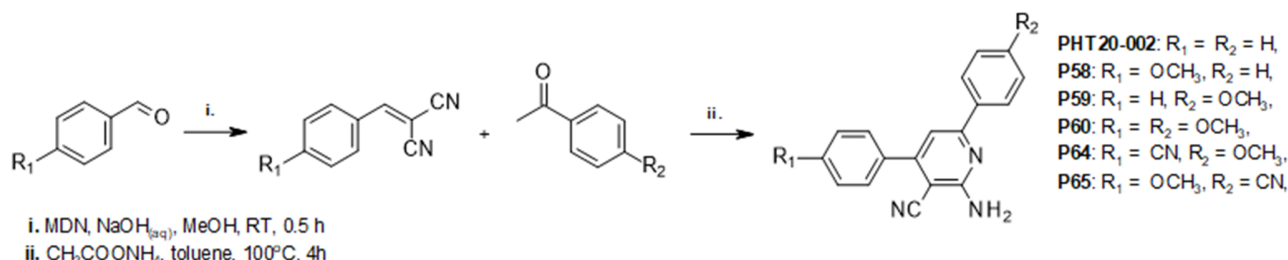
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1. Preparation and characterization of 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives

Derivatives of 2-amino-4,6-diphenylpyridine-3-carbonitrile were synthesized by modified protocol by Kambe et al. [48]. This procedure involved condensation reaction between earlier synthesized 2-benzylidenepropanedinitrile derivative and commercially available acetophenone.

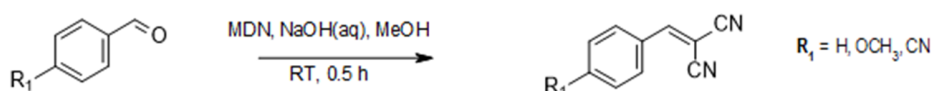


1.1. Materials and methods

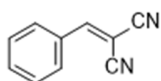
Reagents for synthesis were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification.

Structure and purity of obtained products were confirmed by NMR and LC-MS analysis. ¹H NMR spectra were recorded in DMSO-D₆ on Avance III HD 400 MHz (Bruker) spectrometer. Chemical shifts are reported in parts per million (δ) and referenced to residual protonated solvent peak (δ = 2.50 ppm). LC-MS analyses were obtained on Shimadzu LCMS-2020 with ESI ionization method. Acetonitrile was used as eluent.

1.2. Synthesis of 2-benzylidenepropanedinitrile derivatives



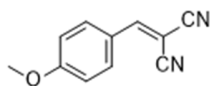
The solution of sodium hydroxide (0.5 mmol, 20 mg) in water (5.0 cm³) was added dropwise to mixed solution of appropriate benzaldehyde derivative (10.0 mmol) and malononitrile (12.0 mmol, 793 mg) in methanol (30.0 cm³). After 30 minutes of stirring the resulting crystal-like precipitate was filtered under reduced pressure and dried under vacuum.



2-benzylidenepropanedinitrile,

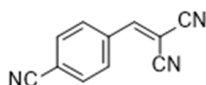
10.00 g, yield: 65%,

¹H NMR (400 MHz, DMSO) δ 8.56 (s, 1H), 7.99 – 7.92 (m, 2H),
7.73 – 7.66 (m, 1H), 7.66 – 7.59 (m, 2H).



2-[(4-methoxyphenyl)methylene]propanedinitrile,

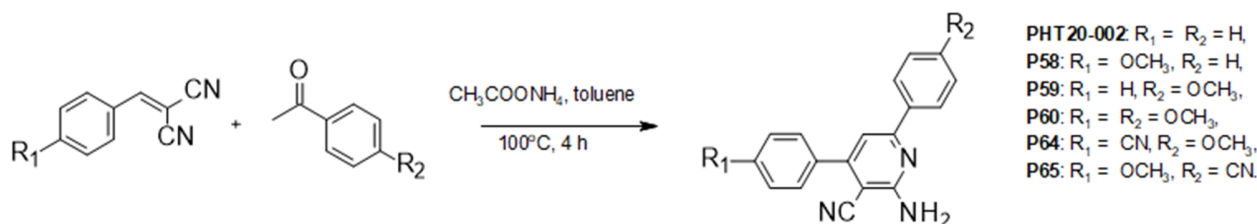
15.76 g, yield: 86%,
¹H NMR (400 MHz, DMSO) δ 8.39 (s, 1H), 8.00 – 7.94 (m, 2H),
 7.22 – 7.15 (m, 2H), 3.88 (s, 3H).



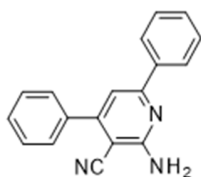
2-[(4-cyanophenyl)methylene]propanedinitrile,

16.10 g, yield: 90%,
¹H NMR (400 MHz, DMSO) δ 8.65 (s, 1H), 8.12 – 8.07 (m, 2H),
 8.07 – 8.02 (m, 2H).

1.3. Synthesis of 2-amino-4,6-diphenylpyridine-3-carbonitrile derivatives

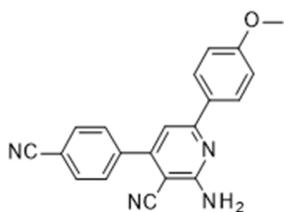


Ammonium acetate (7.10 mmol, 547 mg) was added to mixed solution of appropriate derivatives of acetophenone (6.50 mmol) and 2-benzylidenepropanedinitrile (6.50 mmol) in toluene (10.0 cm³). Resulting mixture was heated for 4 hours in temperature 100°C. Obtained solution was washed with water and saline, dried over anhydrous magnesium sulphate and concentrated under reduced pressure. Product with satisfying purity was obtained after crystallization from methanol.



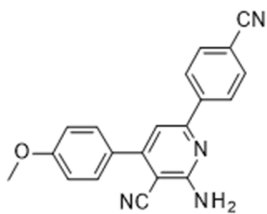
2-amino-4,6-diphenylpyridine-3-carbonitrile (PHT20-002);

0.698 g Yield: 33%;
 purity (LC): >99%;
¹H NMR (400 MHz, DMSO) δ 8.17 – 8.10 (m, 2H), 7.72 – 7.65 (m,
 2H), 7.60 – 7.53 (m, 3H), 7.52 – 7.46 (m, 3H), 7.28 (s, 1H), 7.02
 (brs, 2H);
 MS (ESI) m/z(%): 272 ([M+H]⁺, 28%), 313 ([M+CH₃CN]⁺, 100%).



2-amino-4-(4-cyanophenyl)-6-(4-methoxyphenyl)pyridine-3-carbonitrile (P64);

0.730 g, yield: 30%;
 purity (LC): 95%;
¹H NMR (400 MHz, DMSO) δ 8.15 – 8.09 (m, 2H), 8.07 – 8.01 (m,
 2H), 7.90 – 7.84 (m, 2H), 7.27 (s, 1H), 7.09 – 7.01 (m, 4H), 3.82
 (s, 3H);
 MS (ESI) m/z(%): 327 ([M+H]⁺, 19%), 368 ([M+CH₃CN]⁺, 100%).



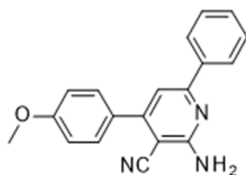
2-amino-6-(4-cyanophenyl)-4-(4-methoxyphenyl)pyridine-3-carbonitrile (P65);

0.370 g, yield: 15%;

purity (LC): 94%;

¹H NMR (400 MHz, DMSO) δ 8.34 – 8.28 (m, 2H), 8.00 – 7.93 (m, 2H), 7.71 – 7.65 (m, 2H), 7.38 (s, 1H), 7.14 – 7.10 (m, 2H), 7.08 (brs, 2H), 3.84 (s, 3H);

MS (ESI) m/z(%): 327 ([M+H]⁺, 10%), 368 ([M+CH₃CN]⁺, 100%)



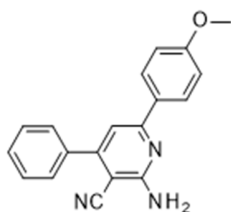
2-amino-4-(4-methoxyphenyl)-6-phenylpyridine-3-carbonitrile (P58);

0.630 g, yield: 27%;

purity (LC): >99%;

¹H NMR (400 MHz, DMSO) δ 8.15 – 8.09 (m, 2H), 7.70 – 7.63 (m, 2H), 7.53 – 7.44 (m, 3H), 7.25 (s, 1H), 7.14 – 7.08 (m, 2H), 6.95 (brs, 2H), 3.84 (s, 3H);

MS (ESI) m/z(%): 302 ([M+H]⁺, 64%), 343 ([M+CH₃CN]⁺, 100%).



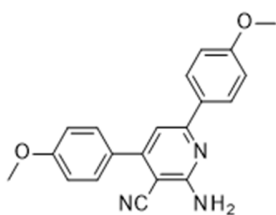
2-amino-6-(4-methoxyphenyl)-4-phenylpyridine-3-carbonitrile (P59);

0.790 g, yield: 34%;

purity (LC): >99%;

¹H NMR (400 MHz, DMSO) δ 8.15 – 8.08 (m, 2H), 7.70 – 7.63 (m, 2H), 7.58 – 7.50 (m, 3H), 7.22 (s, 1H), 7.07 – 7.00 (m, 2H), 6.94 (brs, 2H), 3.82 (s, 3H);

MS (ESI) m/z(%): 302 ([M+H]⁺, 62%), 343 ([M+CH₃CN]⁺, 100%).



2-amino-4,6-bis(4-methoxyphenyl)pyridine-3-carbonitrile (P60);

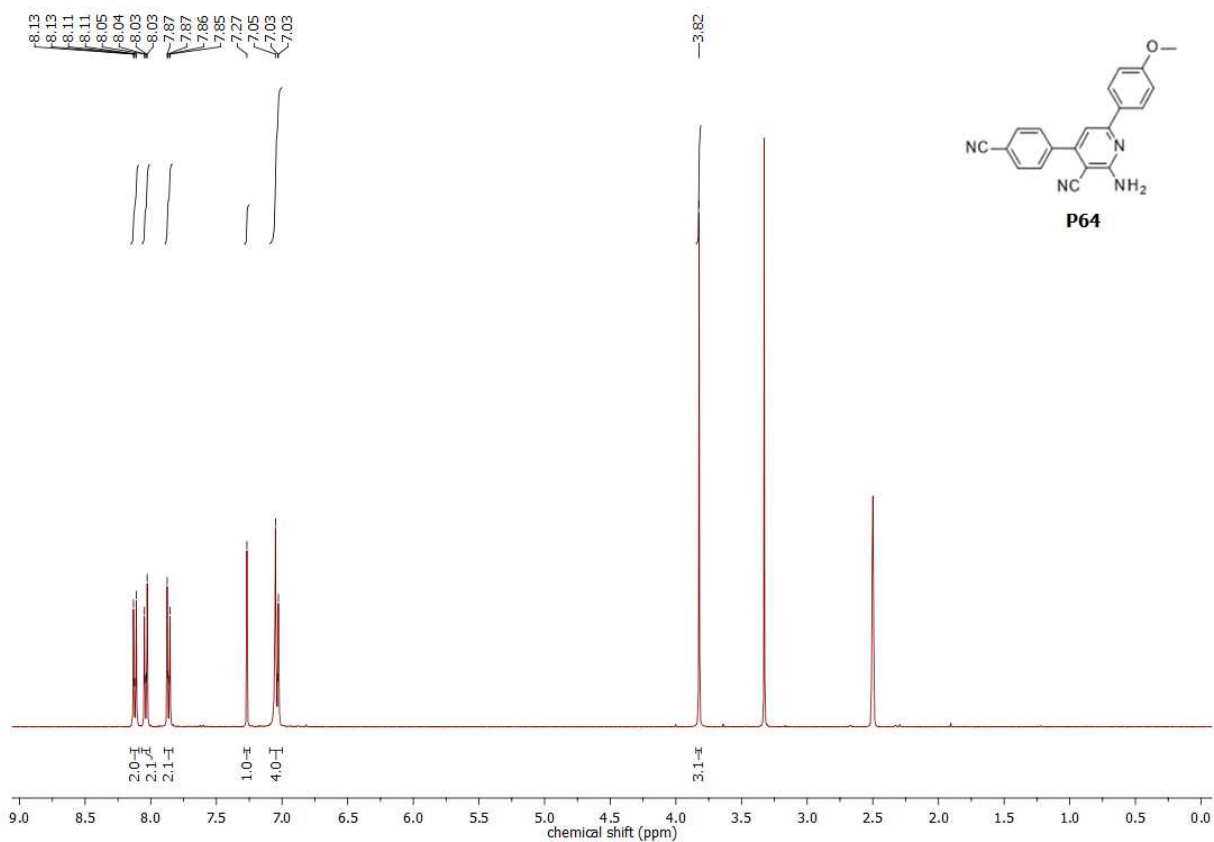
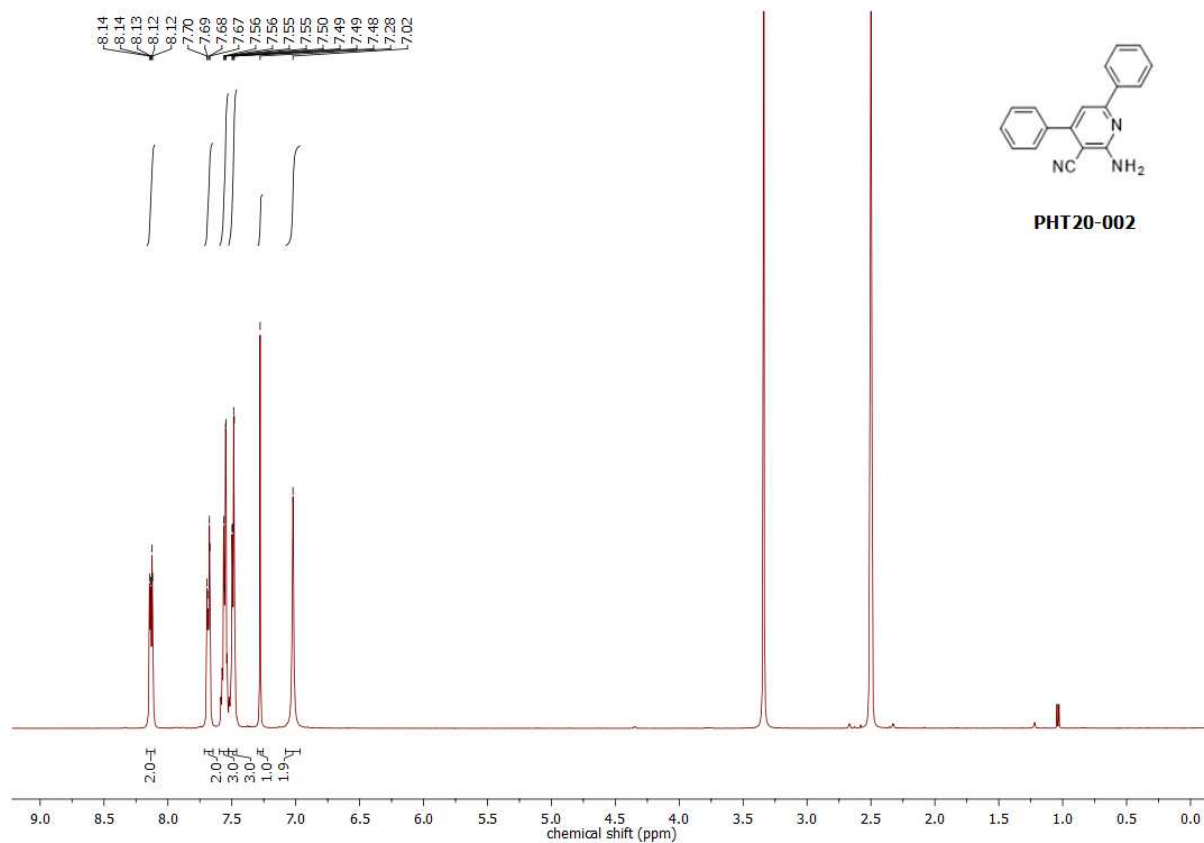
0.800 g, yield: 32%;

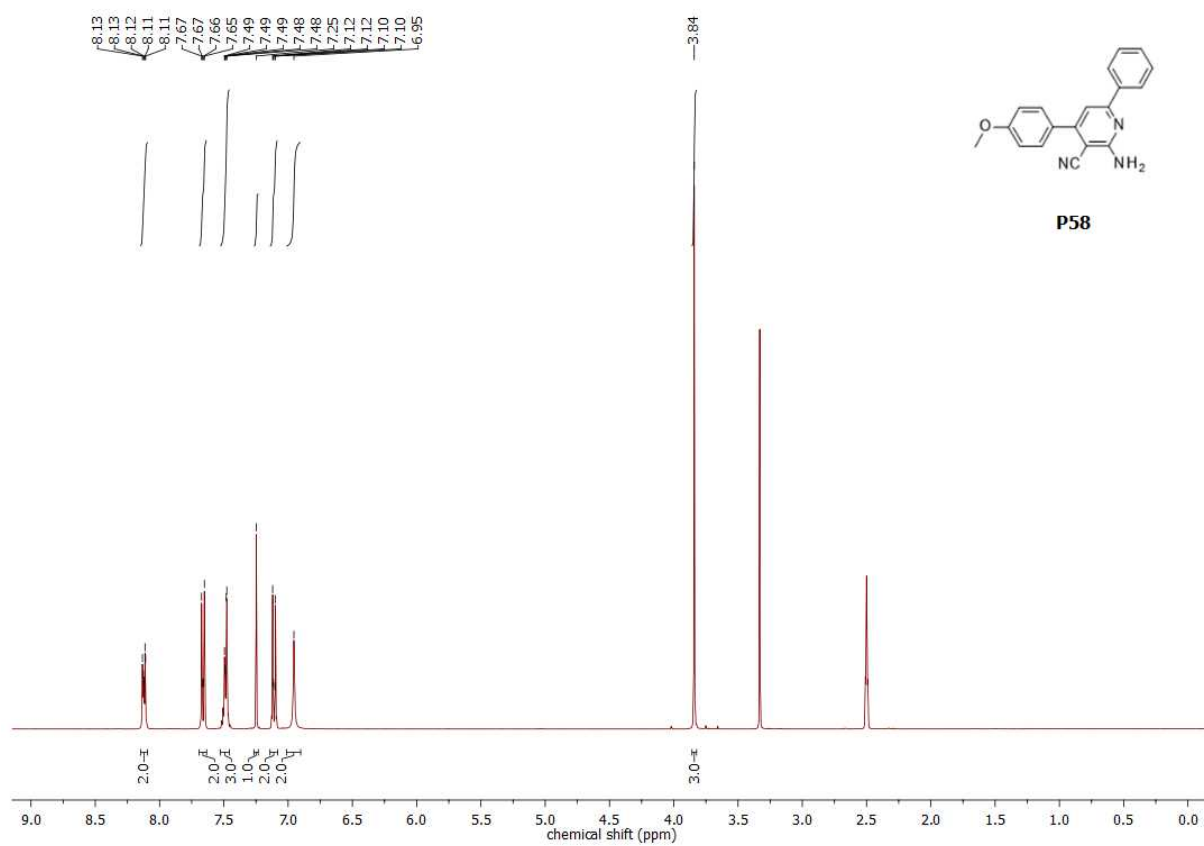
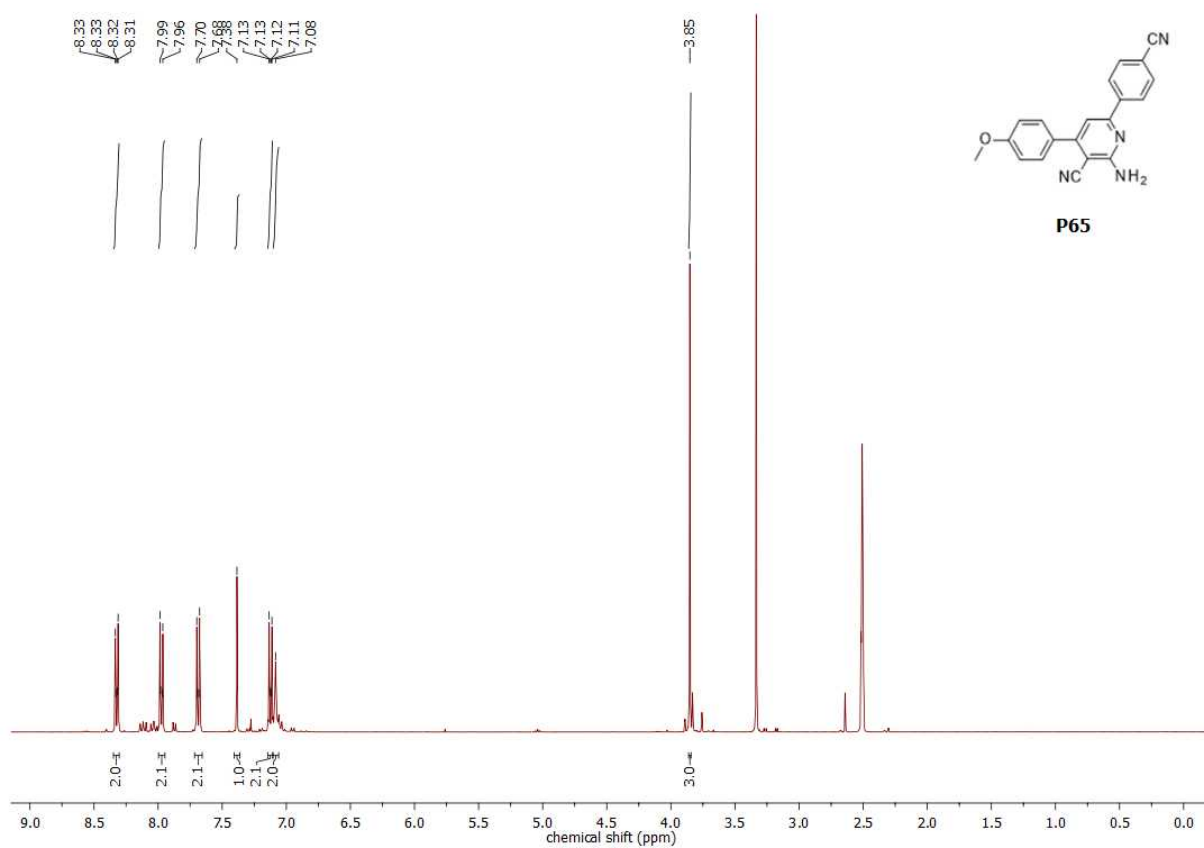
purity (LC): >99%;

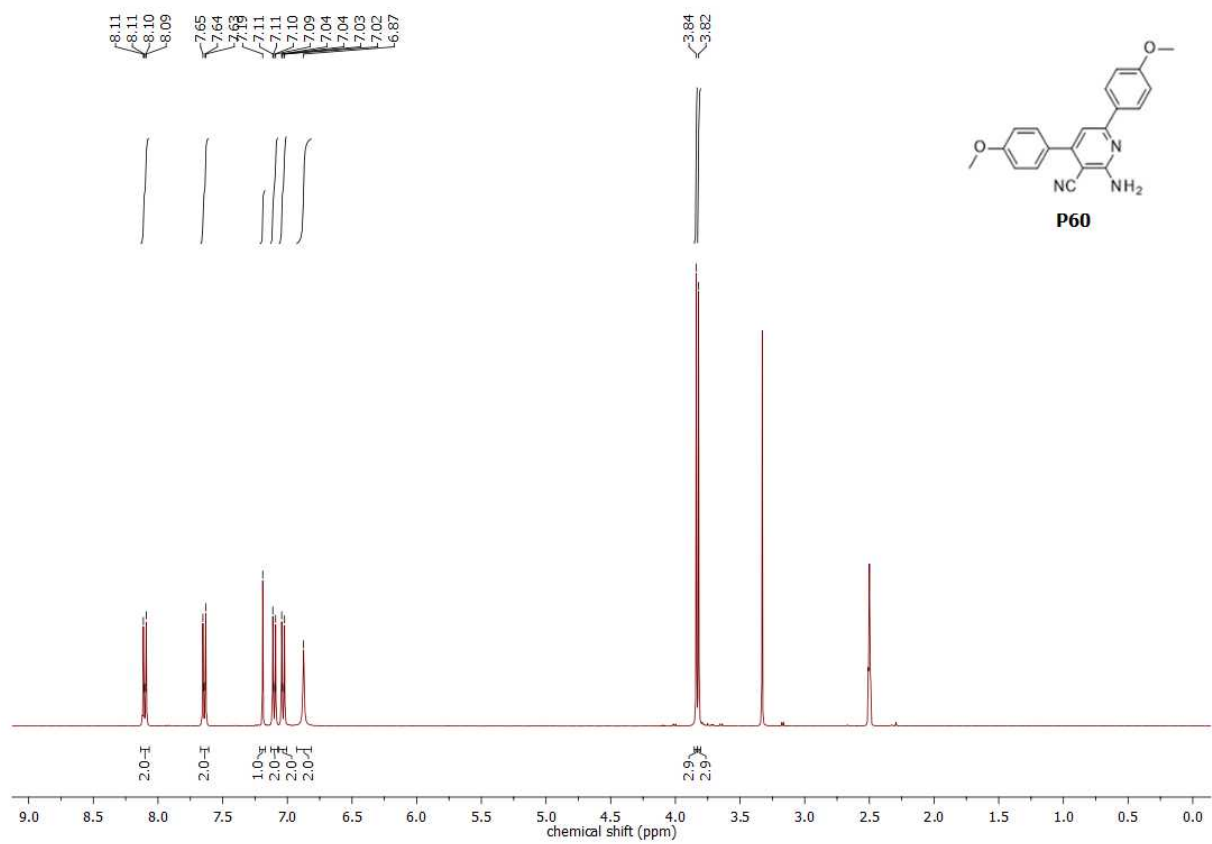
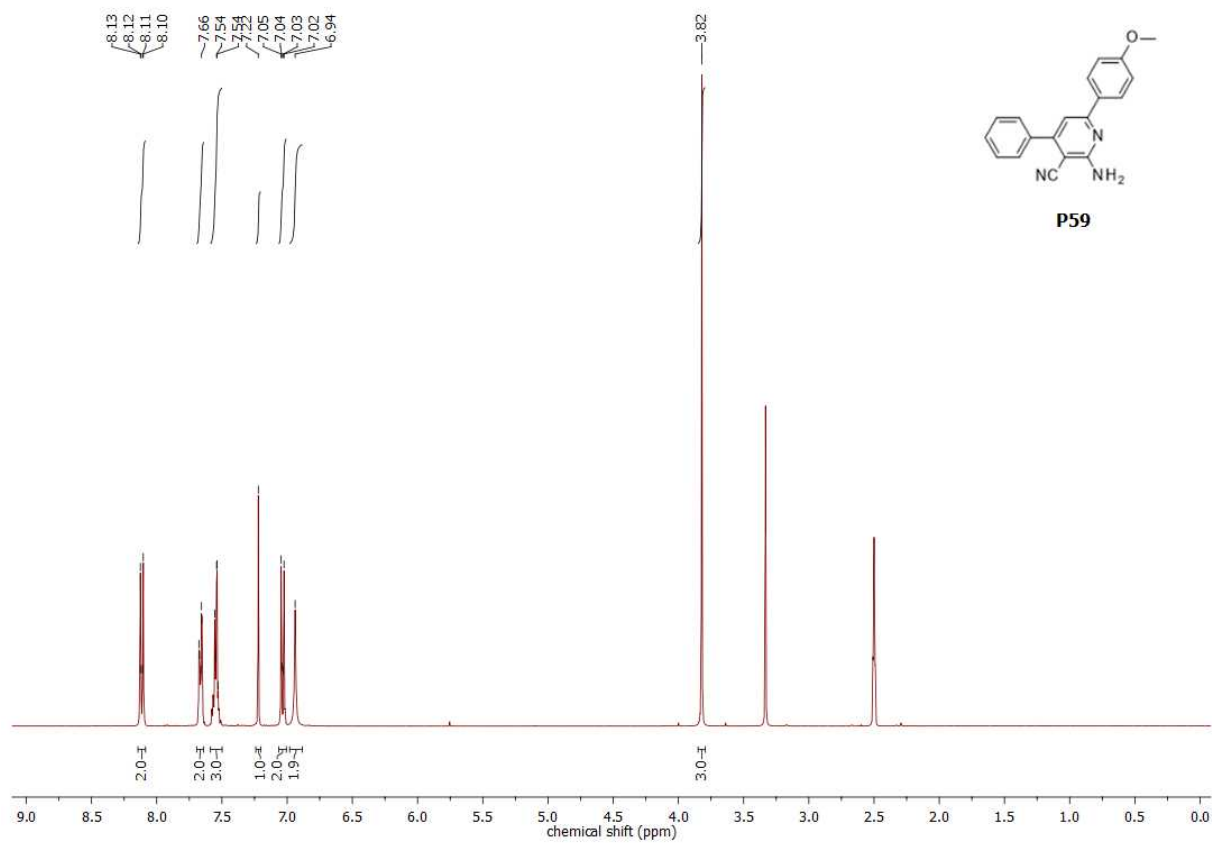
¹H NMR (400 MHz, DMSO) δ 8.14 – 8.06 (m, 2H), 7.68 – 7.61 (m, 2H), 7.19 (s, 1H), 7.14 – 7.07 (m, 2H), 7.06 – 7.00 (m, 2H), 6.87 (brs, 2H), 3.84 (s, 3H), 3.82 (s, 3H);

MS (ESI) m/z(%): 332 ([M+H]⁺, 74%), 373 ([M+CH₃CN]⁺, 100%).

2. ¹H NMR spectra of 2-amino-4,6-diphenylpyridine-3-carbonitrile derivatives







3. Materials for photopolymerization processes

3.1. Cationic photopolymerization under UV light with λ_{\max} =320 nm and under λ_{\max} =365 nm respectively.

3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (CADE, from Allnex) as a cycloaliphatic epoxide monomer was used for the compositions cured by ring opening cationic photopolymerization. Triethylene glycol divinyl ether (TEGDVE, from Sigma Aldrich) was applied as a model vinyl ether monomer for cationic chain photopolymerization. For the role of cationic photoinitiator the diphenyliodonium hexafluorophosphate (HIP, from Alfa Aesar) was used under UV light with λ_{\max} =320 nm. The bimolecular photoinitiating systems based on diphenyliodonium hexafluorophosphate (HIP) and 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives were used during the photopolymerization processes under UV light with λ_{\max} =365 nm.

3.2. Free-radical photopolymerization under UV light with λ_{\max} =320 nm.

Trimethylopropane triacrylate (TMPTA, from Sigma Aldrich) and 2,2-dimethoxy-2-phenylacetophenone (DMPA, from Sigma Aldrich), were employed as an methacrylate monomer and a free-radical photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, from Sigma Aldrich) for the compositions polymerized by a free-radical mechanism for FPT experiments under UV light with λ_{\max} =320 nm.

3.3. Free-radical photopolymerization under UV light with λ_{\max} =365 nm.

For the compositions polymerized by a free-radical mechanism under UV light with λ_{\max} =365 nm were used trimethylopropane triacrylate (TMPTA, from Sigma Aldrich) as a model acrylate monomer and the bimolecular systems based on diphenyliodonium hexafluorophosphate (HIP) and 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives as photoinitiators.

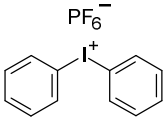
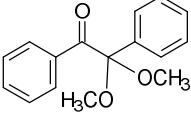
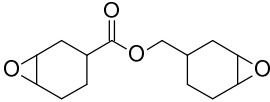
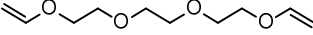
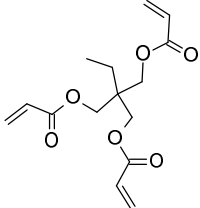
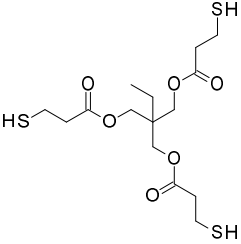
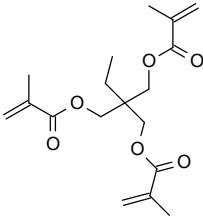
3.4. Thiol-ene photopolymerization under UV light with λ_{\max} =320 nm.

Moreover, trimethylopropane trimethacrylate (TMPTMA, from Sigma Aldrich) and trimethylopropane tris(3-mercaptopropionate) (MERCAPTO, from Sigma Aldrich) were utilized as a methacrylate and thiol monomers for the compositions polymerized by the thiol-ene mechanism. 2,2-dimethoxy-2-phenylacetophenone (DMPA, from Sigma Aldrich) was applied as the photoinitiator in the thiol-ene polymerization process for FPT experiments under UV light with λ_{\max} =320 nm.

3.5. Thiol-ene photopolymerization under UV light with λ_{\max} =365 nm.

Respectively, trimethylopropane trimethacrylate (TMPTMA, from Sigma Aldrich) and trimethylopropane tris(3-mercaptopropionate) (MERCAPTO, from Sigma Aldrich) were applied as the monomers for thiol-ene process of photopolymerization. For the role of UV -long wavelength photoinitiators were used diphenyliodonium hexafluorophosphate (HIP) and 2-amino-4,6-diphenyl-pyridine-3-carbonitrile derivatives. Structures of the monomers are shown in Table 1.

Table 1. Chemical structures of the monomers and iodonium salt.

One component photoinitiators		
		
HIP – one component cationic photoinitiator		DMPA – one component free-radical photoinitiator
Monomers		
		
CADE	TEGDVE	TMPTA
		
MERCAPTO	TMPTMA	

4. References:

[48] Kambe, S., Saito, K., Sakurai, A., Midorikawa, H., A simple method for the preparation of 2-amino-4-aryl-3-cyanopyridines by condensation of malononitrile with aromatic aldehydes and alkyl ketones in the presence of ammonium acetate, *Synthesis* 1980, 366-368