Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Material

New highly versatile bimolecular photoinitiating systems for free-radical, cationic and thiol-ene photopolymerization processes under low light intensity UV and visible LEDs for 3D-VAT printing application

Emilia Hola[1], Monika Topa[1], Anna Chachaj-Brekiesz[2], Maciej Pilch[1], Paweł Fideor[1], Mariusz Galek[3], Joanna Ortyl[1,3*]

[1] Cracow University of Technology, Faculty of Chemical Engineering and Technology, Warszawska 24, 31-155 Cracow, Poland

[2] Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Cracow, Poland

[3] Photo Hitech Ltd., Bobrzyńskiego 14, 30-348 Cracow, Poland

Corresponding author: E-mail: jortyl@chemia.pk.edu.pl (Joanna Ortyl)

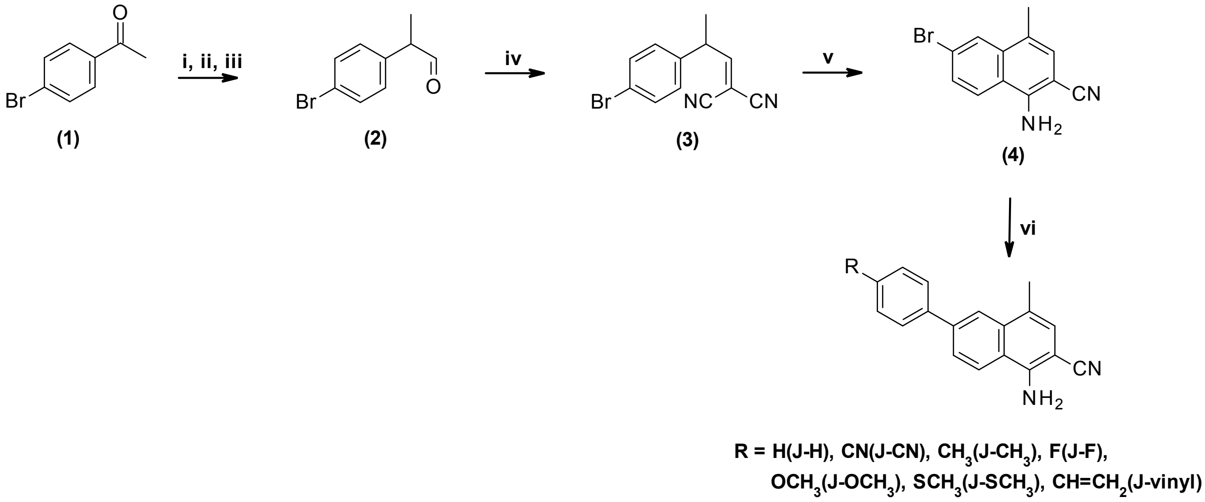
1. Materials and experimental techniques

Reagents for synthesis were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification. High purity solvents were provided by Chempur and used directly, with exception of acetronitrile (which was dried with calcium hydride prior use).

Structure and purity of obtained products were confirmed by high field NMR, ESI mass spectrometry and liquid chromatography. ^{1}H and ^{13}CNMR spectra were recorded in $CDCl_3$ or DMSO-D_6 on Advance III 600 MHz (Bruker) or Advance III HD 400 MHz (Bruker) spectrometers. Chemical shifts were reported in parts per million (δ) and referenced to residual protonated solvent peak (δ=7.26 ppm for $CDCl_3$ or δ=2.50 ppm for DMSO-D_6 in ^{1}HNMR spectra and δ=77.16 ppm for $CDCl_3$ or δ=39.52 in ppm for DMSO-D_6 ^{13}CNMR spectra). LC and MS(ESI) analyses were obtained on LCMS-2020 (Shimadzu). Melting points were determined with capillary melting-point apparatus and were uncorrected.

2. Methods of synthesis

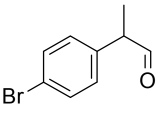
Synthetic pathway to 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives (J-H, J-CN, J-CH_3, J-F, J-OCH_3, J-SCH_3, J-vinyl) was outlined in Scheme S.1 [1]. The key stage of this synthetic approach was based on Suzuki coupling reaction of 1-amino-6-bromo-4-methyl-naphthalene-2-carbonitrile with appropriate derivative of phenylboronic acid. Substrate for this reaction was synthesized starting from 4-bromoacetophenone in multistep linear synthesis according to modified synthetic protocols [2]-[4].



Scheme S.1. Synthesis of 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives. Experimental conditions: **i**. $CH_2ClCOOH$, NaH, acetonitrile, reflux, 4h; **ii**. NaOH, ethanol/water, reflux, 4h; **iii**. HCl, reflux, 1h; **iv**. MDN, CH_3COONH_4, CH_3COOH, benzene, reflux, 4h; **v**. conc. H_2SO_4, r.t., 1.5 h; **vi**. R-C_6H_4-$B(OH)_2$, $Pd(PPh_3)_4$, Cs_2CO_3, dioxane/water, 110°C, 4h.

3. Synthesis of 1-amino-6-bromo-4-methyl-naphthalene-2-carbonitrile (4)

2-(4-bromophenyl)propanal (2)

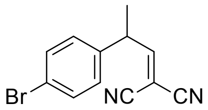


To a solution of p-bromoacetophenone (20.00 g, 0.100 mol) and ethyl chloroacetate (13.53 g, 0.110 mol) in acetonitrile (60 cm^3) stirred at 50˚C under nitrogen sodium hydride (60%

suspension in mineral oil, 4.40 g, 0.110 mol) was added portion wise during 30 minutes. Resulting suspension was refluxed for 4 hours and after cooling the solvent was evaporated under vacuum. Oily residue was treated with water (20 cm^3) and extracted with chloroform (3x30 cm^3). Organic phases were combined and concentrated under vacuum. Next, the crude oily byproduct was refluxed during 4 hours in the mixture of ethanol (60 cm^3) and 10% aqueous sodium hydroxide solution (80 cm^3). After cooling ethanol was evaporated and reaction mixture was treated with water (100 cm^3) and extracted with diethyl ether (3x20 cm^3). Then the inorganic phase was acidified with concentrated hydrochloric acid and the solution was heated under reflux for an hour. The mixture was cooled, and extracted with chloroform (3x40 cm^3). Combined organic phases were dried over anhydrous magnesium sulphate and concentrated under reduced pressure. 2-(4-bromophenyl)propanal in form of colourless oil (10.00 g, 47% yield) was obtained after purification by column chromatography (silica gel/chloroform).

^{1}HNMR (600 MHz, $CDCl_3$) δ [ppm] 9.65 (d, *J* = 1.4 Hz, 1H), 7.51 – 7.48 (m, 2H), 7.10 – 7.07 (m, 2H), 3.60 (m, 1H), 1.43 (d, *J* = 7.1 Hz, 3H).
^{13}CNMR (151 MHz, $CDCl_3$) δ [ppm] 200.43, 136.82, 132.28, 130.08, 121.68, 52.46, 14.67

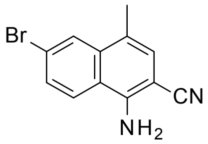
2-[2-(4-bromophenyl)propylidene]propanedinitrile (3)



Suspension of 2-(4-bromophenyl)propanal (9.00 g, 0.040 mol), malononitrile MDN (3.00 g, 0.045 mol), ammonium acetate (0.38 g, 0.005 mol), acetic acid (1.0 cm^3) in benzene (40 cm^3) was refluxed using Dean-Stark apparatus for 4 hours. Then reaction mixture was cooled and organic layer was washed with water (20 cm^3). Organic phase was dried over anhydrous magnesium sulphate and concentrated under vacuum yielding 2-[2-(4-bromophenyl) propylidene]propanedinitrile as brown oil (8.40 g, 80% yield).

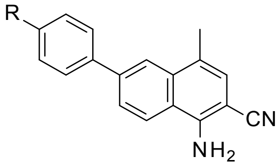
^{1}HNMR (600 MHz, $CDCl_3$) δ [ppm] 7.54 – 7.50 (m, 2H), 7.26 (d, *J* = 10.7 Hz, 1H), 7.14 – 7.10 (m, 2H), 4.10 (m, 1H), 1.54 (d, *J* = 6.9 Hz, 3H).
^{13}CNMR (151 MHz, $CDCl_3$) δ [ppm] 170.63, 138.36, 132.73, 128.79, 122.40, 111.89, 110.53, 88.56, 42.42, 19.70.

1-amino-6-bromo-4-methyl-naphthalene-2-carbonitrile (4)



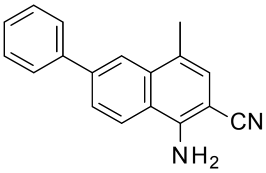
2-[2-(4-bromophenyl)propylidene]propanedinitrile (2.84 g, 0.011 mol) was added dropwise to concentrated sulphuric acid (12 cm^3) and stirred at room temperature for 90 minutes. Then the reaction was quenched with crushed ice (ca. 30 cm^3) and inorganic phase was extracted with chloroform (3 x 30 cm^3). Organic phases were combined, dried over anhydrous magnesium sulphate and concentrated under vacuum. 2-[2-(4-bromophenyl) propylidene]propanedinitrile in form of bright yellow crystals (1.56 g, 55% yield) was obtained after purification by column chromatography (silica gel/chloroform).
m.p. 160-162˚C.
^{1}HNMR (600 MHz, $CDCl_3$) δ [ppm] 8.07 (d, *J* = 1.9 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.62 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.17 (m, 1H), 4.94 (s, 2H).

4. General procedure for synthesis of 1-amino-6-bromo-4-methyl-naphthalene-2-carbonitrile derivatives J-H, J-CN, J-CH$_3$, J-F, J-OCH$_3$, J-SCH$_3$, J-vinyl

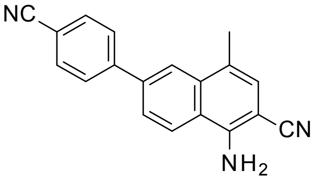


To a solution of 1-amino-6-bromo-4-methyl-naphthalene-2-carbonitrile (100 mg, 0,38 mmol) in 1,4-dioxane/water mixture (4.0 cm^3/1.2 cm^3) appropriate derivative of phenylboronic acid (0.42 mmol), tetrakis(triphenylphosphine)palladium(0) (10 mg) and caesium carbonate (375 mg, 1.15 mmol) were added. The mixture was heated in pressure vial at 110˚C under nitrogen for 4 hours. Reaction mixture was cooled, water (15 cm^3) was added and inorganic phase was extracted with chloroform (3x15 cm^3). Organic extracts were combined, dried over anhydrous magnesium sulphate and concentrated under reduced pressure. 1-amino-6-bromo-4-methyl-naphthalene-2-carbonitrile derivatives were obtained after purification by column chromatography (silica gel/chloroform) followed by crystallization (chloroform/*n*-hexane).

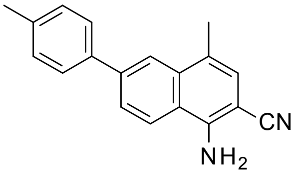
5. Physical and spectroscopic data of synthesized compounds J-H, J-CN, J-CH$_3$, J-F, J-OCH$_3$, J-SCH$_3$, J-vinyl



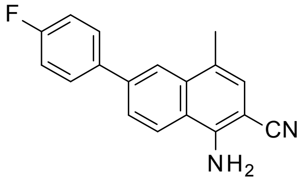
1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile **J-H**; 70 mg, 82% yield;
m.p. 149-155˚C;
^{1}H NMR (600 MHz, DMSO) δ 8.44 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 1.8 Hz, 1H), 7.87 – 7.83 (m, 3H), 7.55 – 7.50 (m, 2H), 7.45 – 7.41 (m, 1H), 7.19 (d, *J* = 0.8 Hz, 1H), 6.70 (s, 2H), 2.52 (d, *J* = 0.8 Hz, 3H);
^{13}C NMR (101 MHz, DMSO) δ 148.92, 140.26, 139.64, 135.15, 129.04, 128.00, 127.26, 126.77, 124.52, 124.26, 122.17, 121.82, 121.30, 119.28, 85.71, 18.14;
MS (ESI) m/z(%): 259 ([M+H]$^+$, 100%);
purity (LC): >96%.



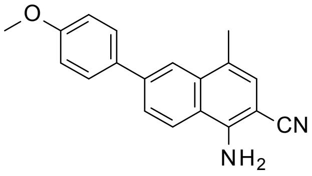
1-amino-6-(4-cyanophenyl)-4-methyl-naphthalene-2-carbonitrile **J-CN**; 133 mg, 81% yield; m.p. >260˚C;
^{1}H NMR (600 MHz, DMSO) δ 8.48 (d, *J* = 8.8 Hz, 1H), 8.16 (d, *J* = 1.8 Hz, 1H), 8.12 – 8.07 (m, 2H), 8.01 – 7.97 (m, 2H), 7.91 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.22 (d, *J* = 0.9 Hz, 1H), 6.75 (s, 2H), 2.53 (d, *J* = 0.8 Hz, 3H);
^{13}C NMR (101 MHz, DMSO) δ 148.83, 144.10, 138.24, 135.03, 132.88, 128.18, 127.05, 124.78, 124.07, 123.15, 122.06, 121.91, 119.13, 118.83, 110.51, 86.25, 18.09;
MS (ESI) m/z(%): 284 ([M+H]$^+$, 100%);
purity (LC): >95%.



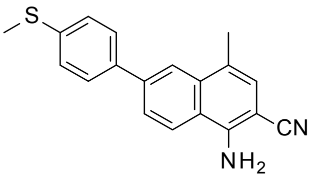
1-amino-4-methyl-6-(4-methylphenyl)-naphthalene-2-carbonitrile **J-CH$_3$**; 154 mg, 98% yield; m.p. 170-173˚C;
^{1}H NMR (600 MHz, DMSO) δ 8.42 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 1.8 Hz, 1H), 7.83 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.34 – 7.32 (m, 2H), 7.18 (d, *J* = 0.9 Hz, 1H), 6.68 (s, 2H), 2.51 (d, *J* = 0.8 Hz, 3H), 2.37 (s, 3H);
^{13}C NMR (101 MHz, DMSO) δ 148.92, 140.17, 137.44, 136.70, 135.18, 129.63, 127.06, 126.70, 124.47, 124.11, 121.75, 121.69, 121.13, 119.31, 85.59, 20.72, 18.15;
MS (ESI) m/z(%): 273 ([M+H]$^+$, 100%);
purity (LC): >98%.



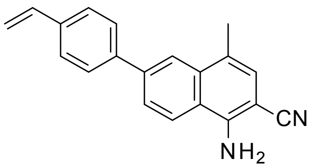
1-amino-6-(4-fluorophenyl)-4-methyl-naphthalene-2-carbonitrile **J-F**; 132 mg, 83% yield;
m.p. 190-192˚C;
^{1}H NMR (600 MHz, DMSO) δ 8.43 (d, *J* = 8.8 Hz, 1H), 8.05 (d, *J* = 1.8 Hz, 1H), 7.94 – 7.88 (m, 2H), 7.83 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.19 (d, *J* = 0.8 Hz, 1H), 6.70 (s, 2H), 2.51 (d, *J* = 0.8 Hz, 3H);
^{13}C NMR (101 MHz, DMSO) δ 162.24 (d, *J* = 245.2 Hz), 148.90, 139.19, 136.10 (d, *J* = 3.1 Hz), 135.13, 129.33 (d, *J* = 8.3 Hz), 126.82, 124.56, 124.18, 122.14, 121.82, 121.24, 119.26, 115.84 (d, *J* = 21.4 Hz), 85.74, 18.13;
MS (ESI) m/z(%): 277 ([M+H]$^+$, 100%);
purity (LC): >90%.



1-amino-6-(4-methoxyphenyl)-4-methyl-naphthalene-2-carbonitrile **J-OCH$_3$**; 85 mg, 78% yield;
m.p. 172-174˚C;
^{1}H NMR (600 MHz, DMSO) δ 8.40 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 1.9 Hz, 1H), 7.83 – 7.80 (m, 3H), 7.17 (d, *J* = 1.0 Hz, 1H), 7.10 – 7.07 (m, 2H), 6.66 (s, 2H), 3.83 (s, 3H), 2.51 (d, *J* = 0.8 Hz, 3H);
^{13}C NMR (101 MHz, DMSO) δ 159.39, 148.93, 139.92, 135.22, 131.88, 128.40, 126.67, 124.43, 123.98, 121.70, 121.26, 120.86, 119.34, 114.49, 85.44, 55.24, 18.16;
MS (ESI) m/z(%): 289 ([M+H]$^+$, 100%);
purity (LC): >98%.



1-amino-4-methyl-6-(4-methylsulfanylphenyl)naphthalene-2-carbonitrile **J-SCH_3**; 80 mg, 69% yield;
m.p. 212-214 ˚C;
^{1}H NMR (600 MHz, DMSO) δ 8.42 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 1.8 Hz, 1H), 7.85 – 7.80 (m, 3H), 7.41 – 7.39 (m, 2H), 7.18 (d, *J* = 0.8 Hz, 1H), 6.69 (s, 2H), 2.54 (s, 3H), 2.51 (d, *J* = 0.7 Hz, 3H);
MS (ESI) m/z(%): 305 ([M+H]$^+$, 100%);
purity (LC): >96%.



1-amino-4-methyl-6-(4-vinylphenyl)naphthalene-2-carbonitrile **J-vinyl**; 129 mg, 79% yield;
m.p. 174-178˚C;
^{1}H NMR (600 MHz, DMSO) δ 8.44 (d, *J* = 8.8 Hz, 1H), 8.09 (d, *J* = 1.8 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.64 – 7.60 (m, 2H), 7.19 (d, *J* = 0.9 Hz, 1H), 6.82 (dd, *J* = 17.7, 11.0 Hz, 1H), 6.70 (s, 2H), 5.92 (dd, *J* = 17.7, 0.8 Hz, 1H), 5.33 (dd, *J* = 10.9, 0.8 Hz, 1H), 2.52 (d, *J* = 0.9 Hz, 3H);
^{13}C NMR (101 MHz, DMSO) δ 148.90, 139.69, 138.95, 136.81, 136.13, 135.15, 127.42, 126.81, 126.79, 124.54, 124.06, 121.94, 121.84, 121.31, 119.28, 114.79, 85.73, 18.14;
MS (ESI) m/z(%): 285 ([M+H]$^+$, 100%);
purity (LC): >94%.

6. NMR spectra of 1-amino-6-bromo-4-methyl-naphthalene-2-carbonitrile derivatives

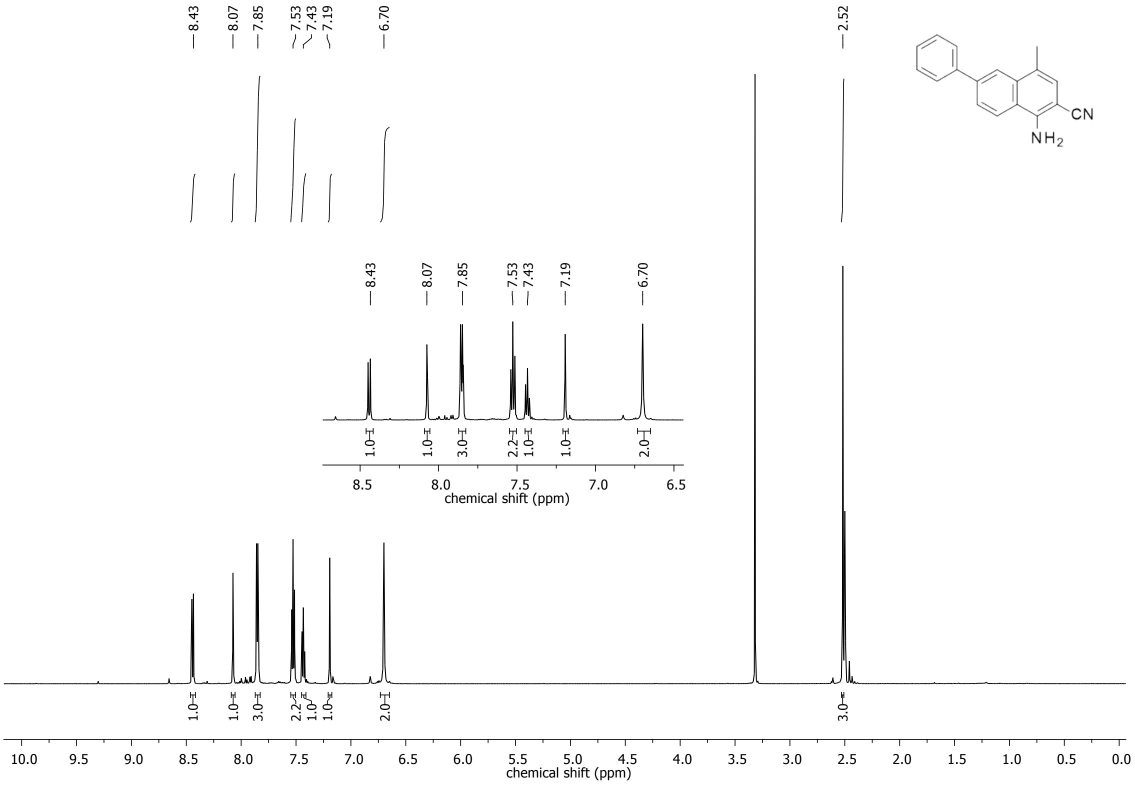


Figure S1: ^{1}HNMR spectrum of 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile **J-H**.

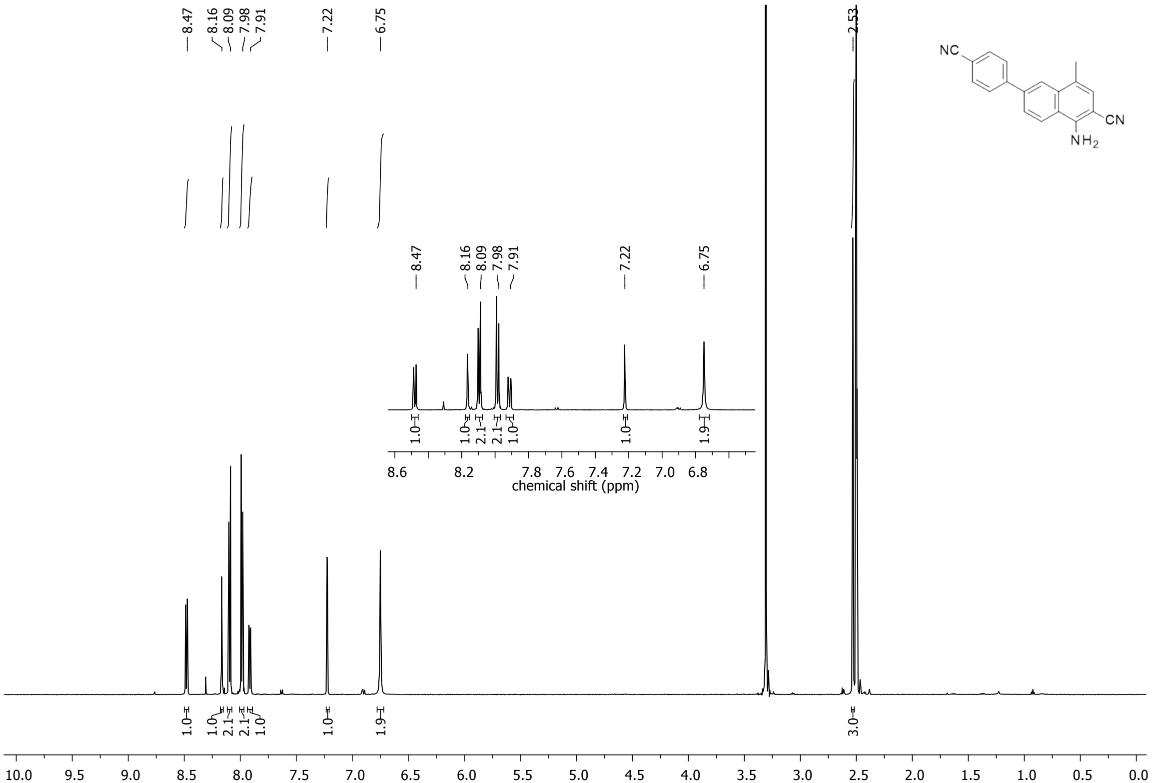


Figure S2: ^{1}HNMR spectrum of 1-amino-6-(4-cyanophenyl)-4-methyl-naphthalene-2-carbonitrile **J-CN**.

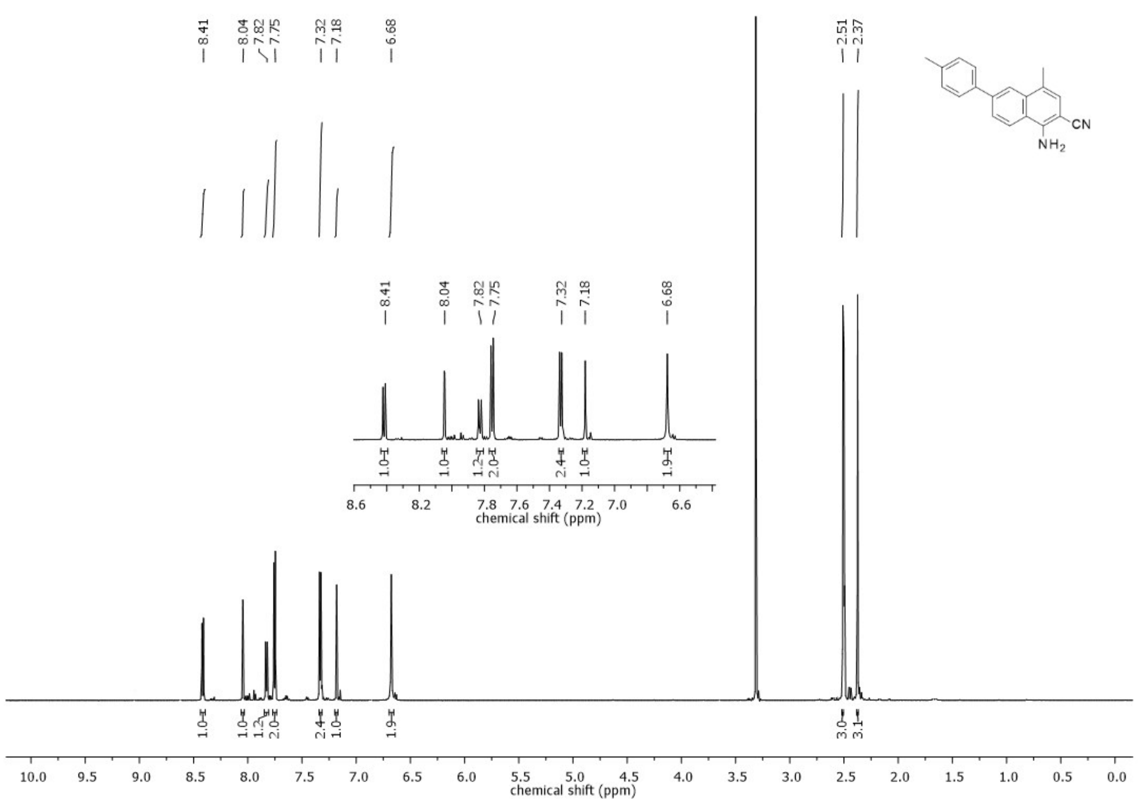


Figure S3: ^{1}HNMR spectrum of 1-amino-4-methyl-6-(4-methylphenyl)-naphthalene-2-carbonitrile **J-CH$_3$**.

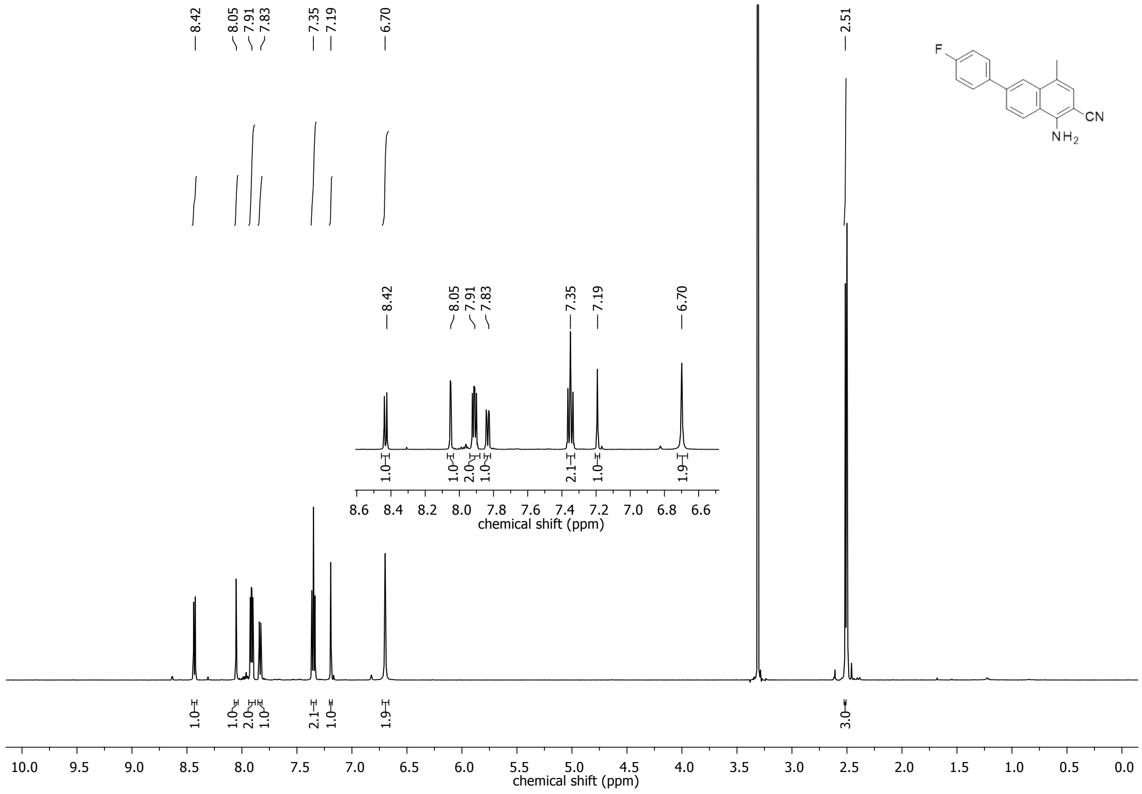


Figure S4: ^{1}HNMR spectrum of 1-amino-6-(4-fluorophenyl)-4-methyl-naphthalene-2-carbonitrile **J-F**.

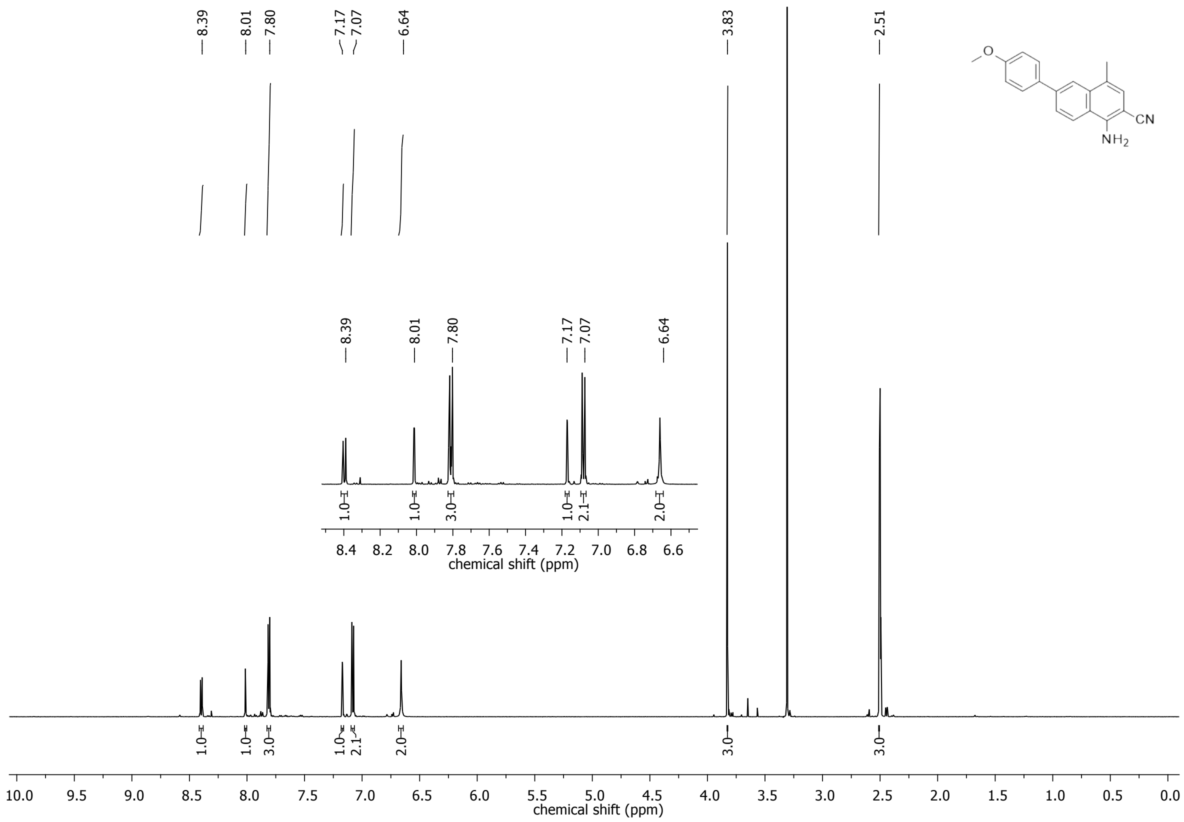


Figure S5: ^{1}HNMR spectrum of 1-amino-6-(4-methoxyphenyl)-4-methyl-naphthalene-2-carbonitrile **J-OCH$_3$**.

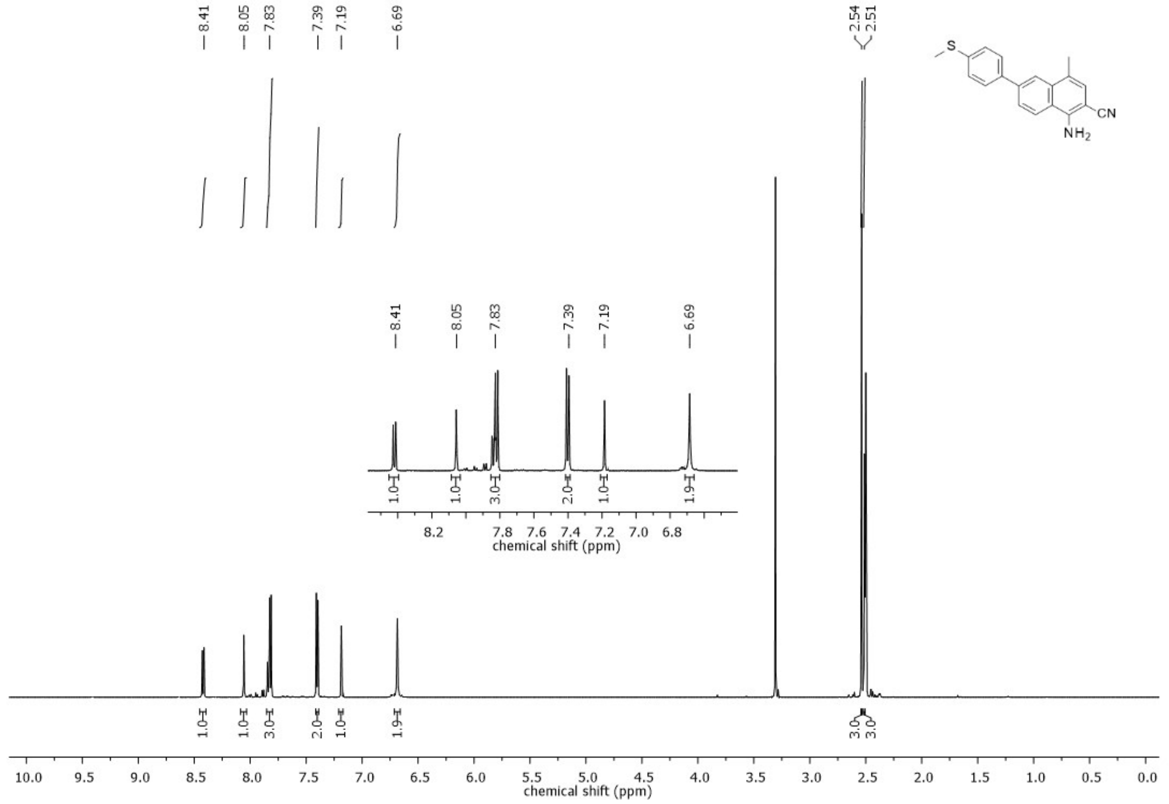


Figure S6: ^{1}HNMR spectrum of 1-amino-4-methyl-6-(4-methylsulfanylphenyl)naphthalene-2-carbonitrile **J-SCH$_3$**.

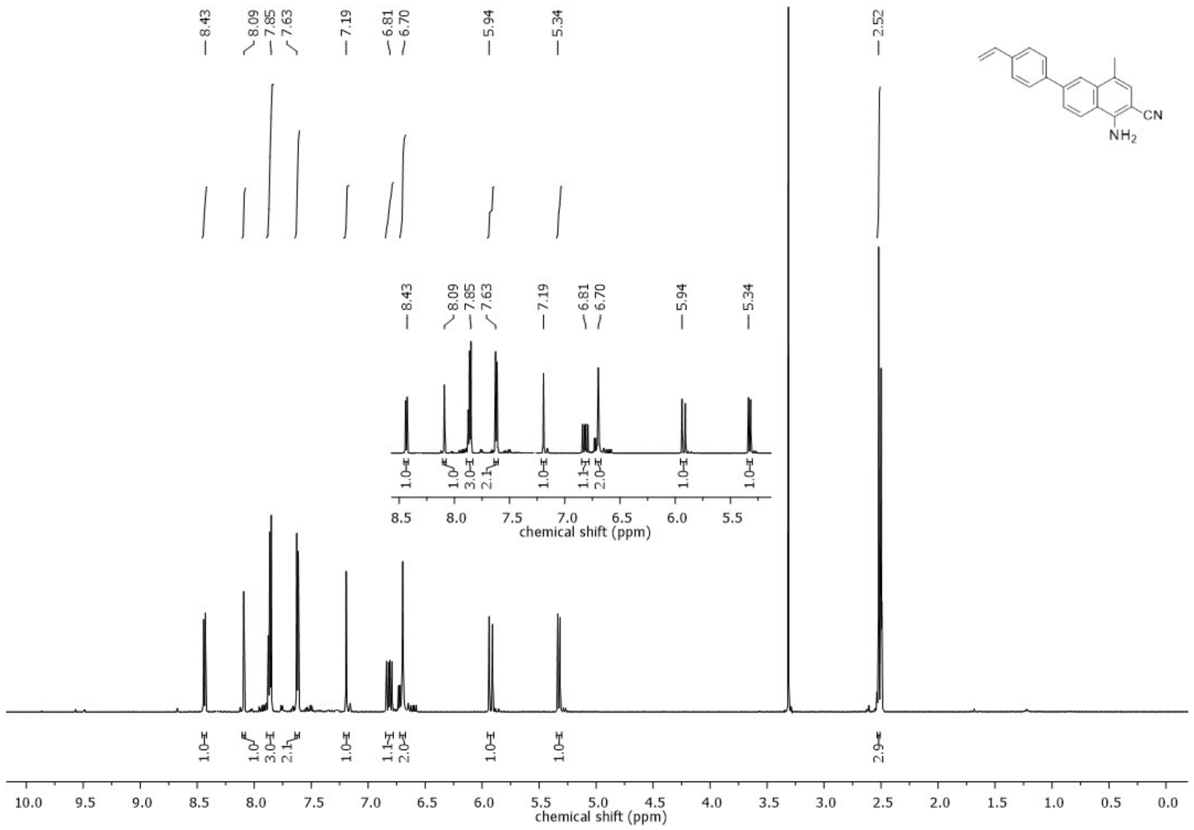


Figure S7: ^{1}HNMR spectrum of 1-amino-4-methyl-6-(4-vinylphenyl)naphthalene-2-carbonitrile **J-vinyl**.

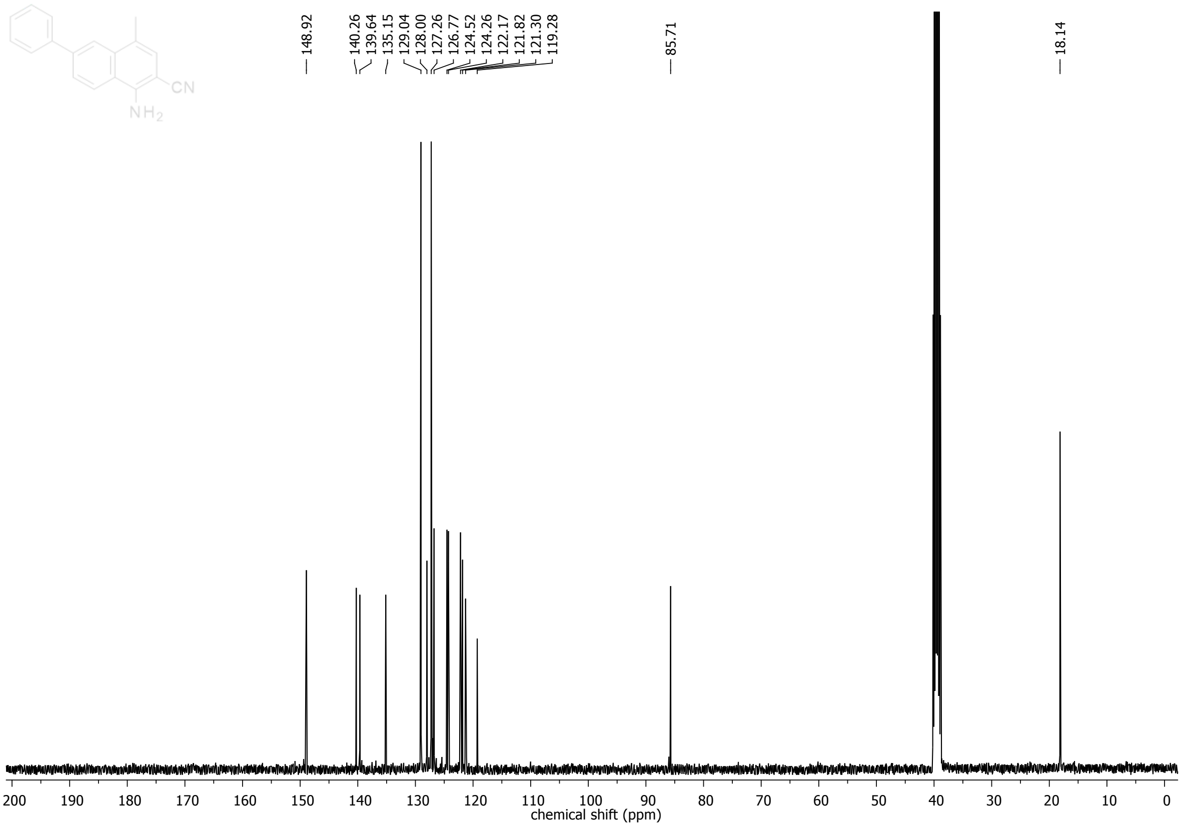


Figure S8: ^{13}C NMR spectrum of 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile **J-H**.

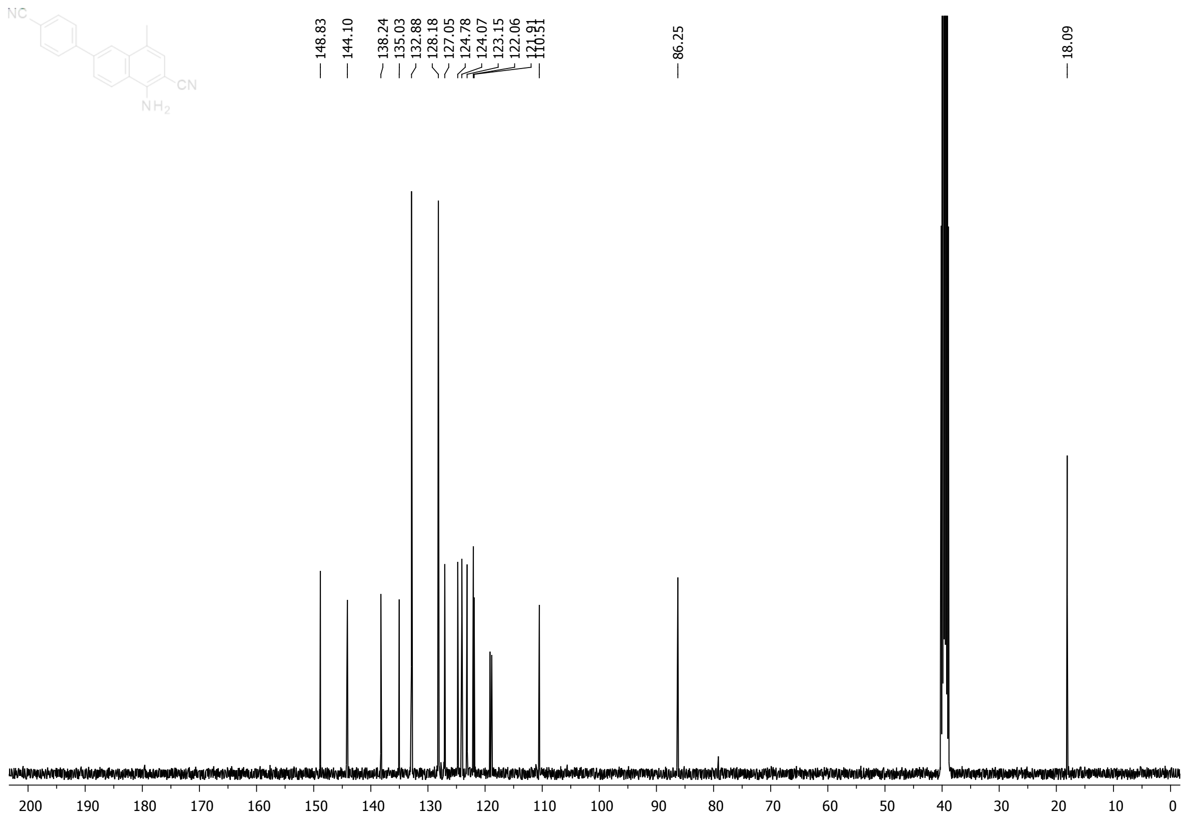


Figure S9: ^{13}C NMR spectrum of 1-amino-6-(4-cyanophenyl)-4-methyl-naphthalene-2-carbonitrile **J-CN**.

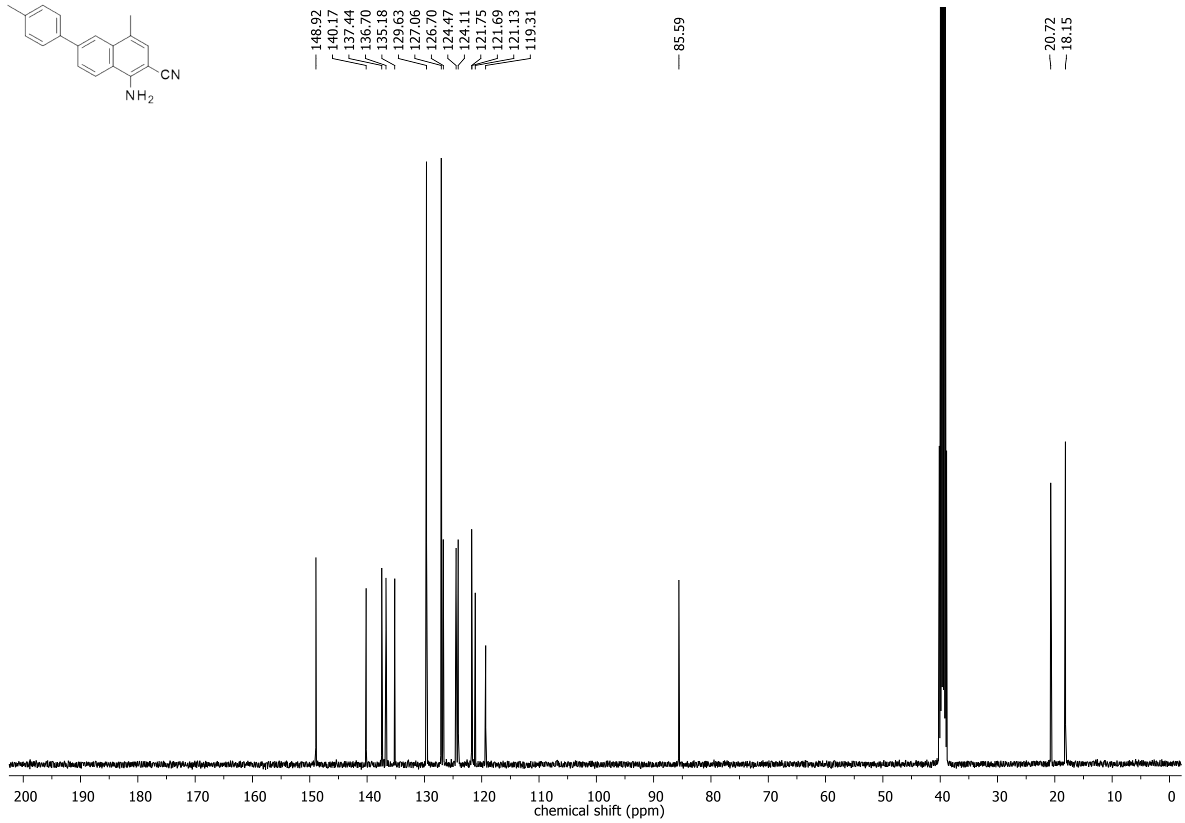


Figure S10: ^{13}C NMR spectrum of 1-amino-4-methyl-6-(4-methylphenyl)-naphthalene-2-carbonitrile **J-CH$_3$**.

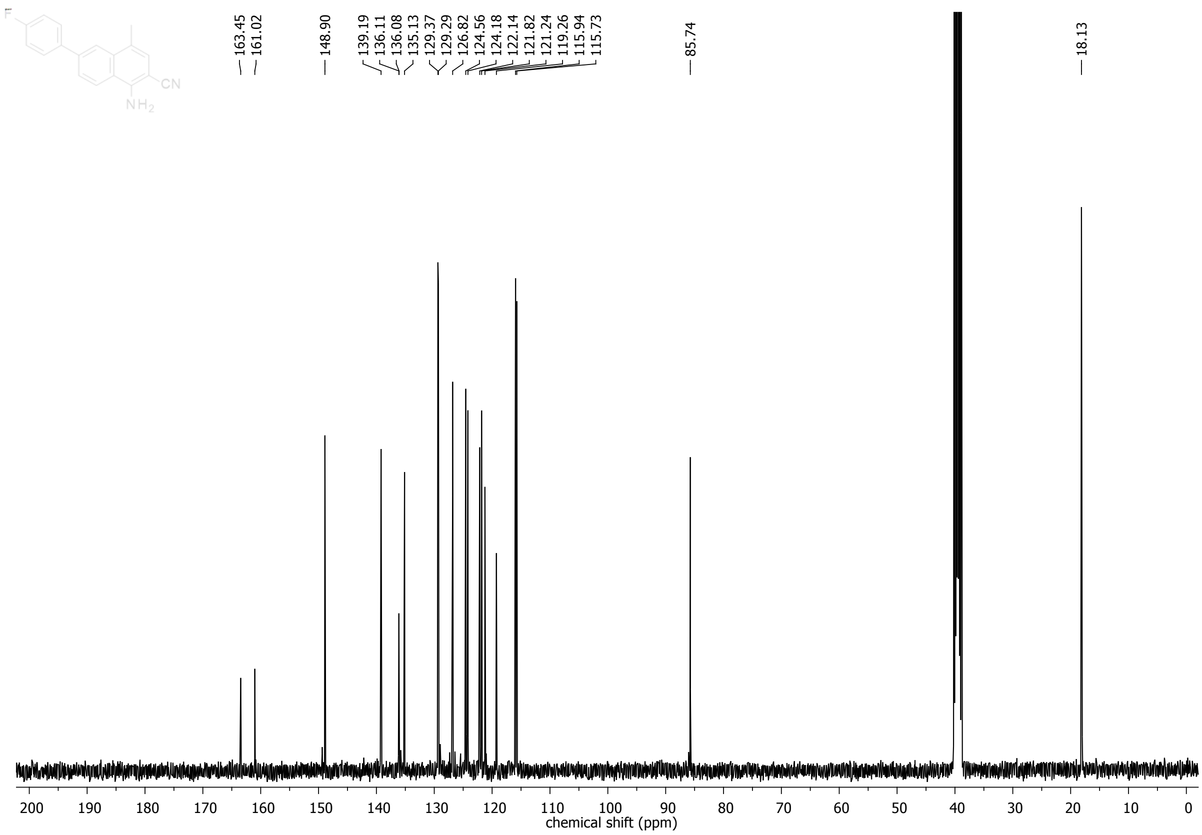


Figure S11: ^{13}C NMR spectrum of 1-amino-6-(4-fluorophenyl)-4-methyl-naphthalene-2-carbonitrile **J-F**.

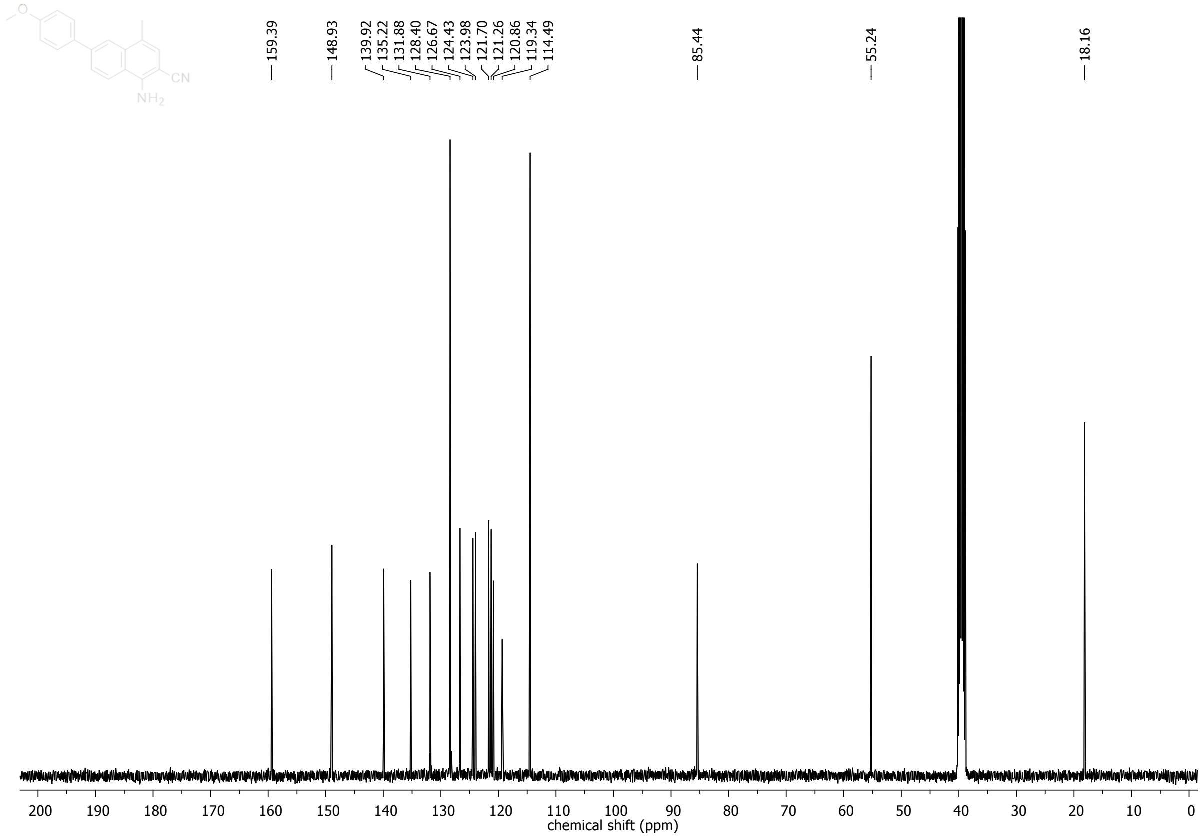


Figure S12: ^{13}C NMR spectrum of 1-amino-6-(4-methoxyphenyl)-4-methyl-naphthalene-2-carbonitrile **J-OCH$_3$**.

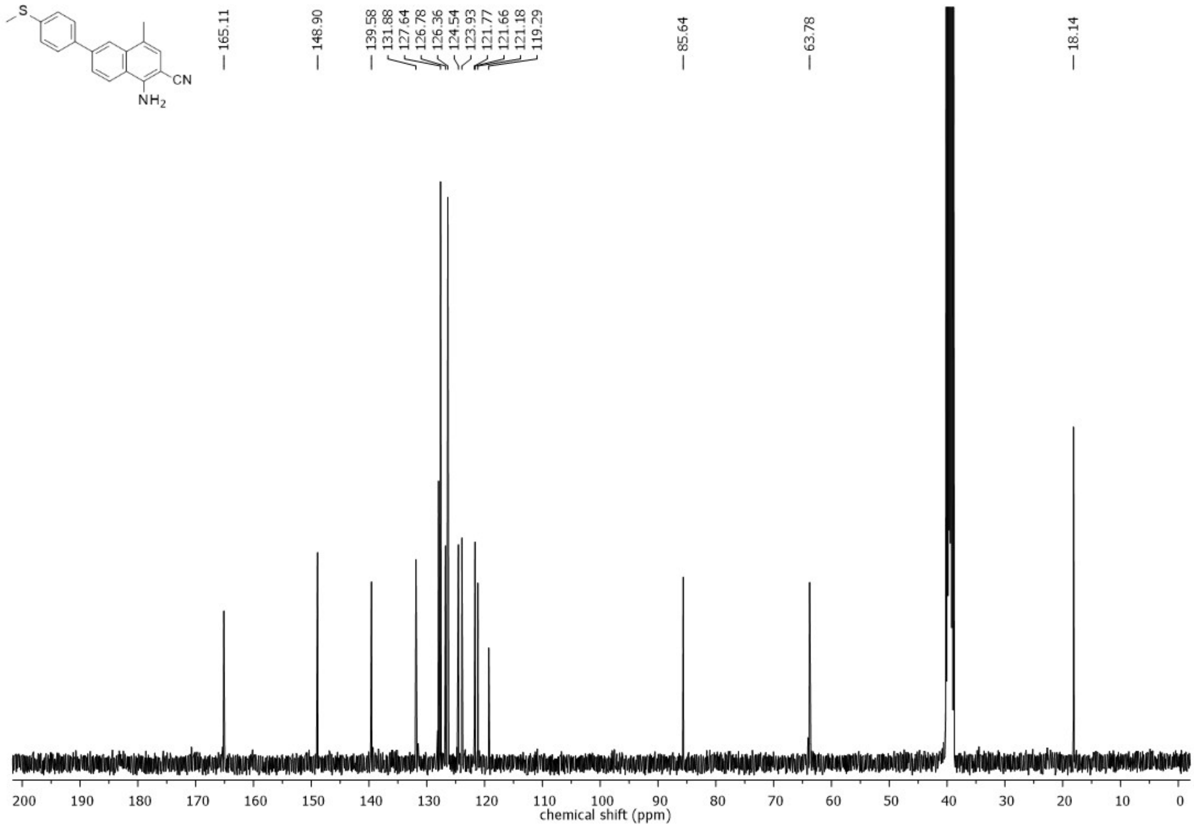


Figure S13: ^{13}C NMR spectrum of 1-amino-4-methyl-6-(4-methylsulfanylphenyl)naphthalene-2-carbonitrile **J-SCH$_3$**.

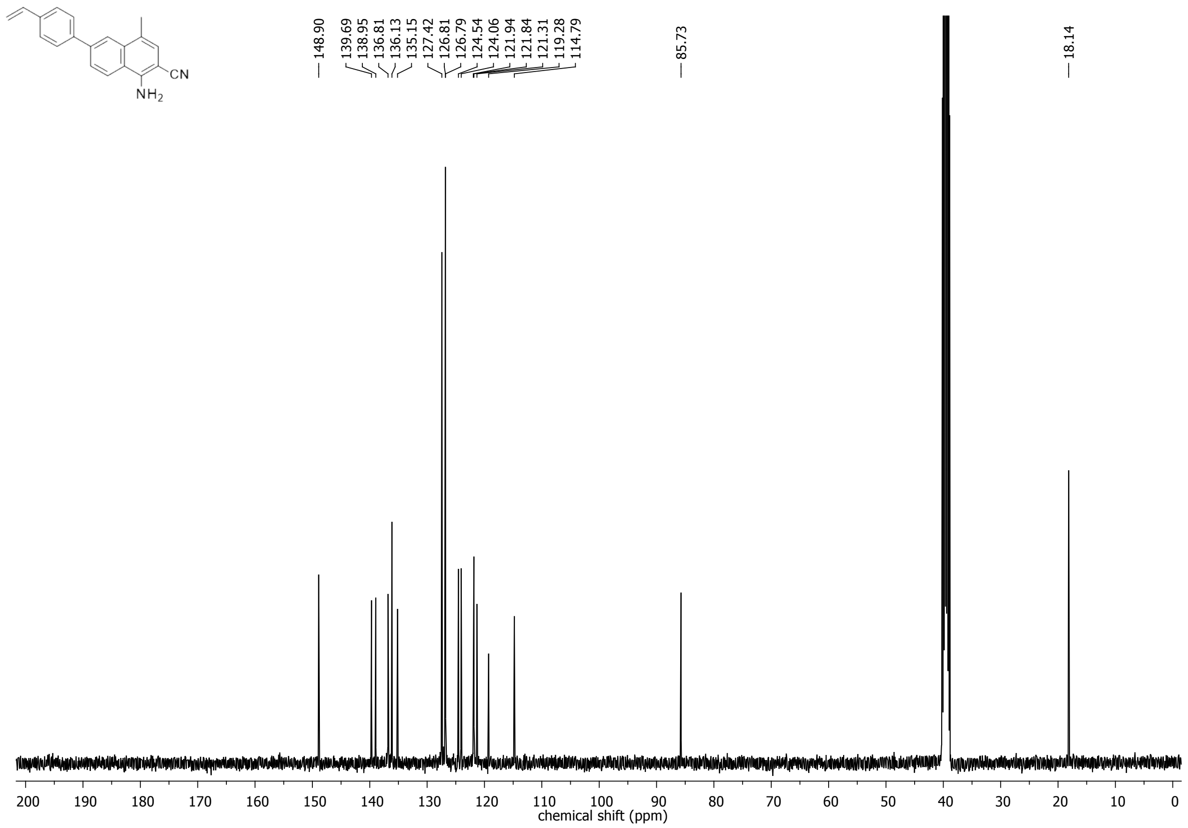


Figure S14: ^{13}C NMR spectrum of 1-amino-4-methyl-6-(4-vinylphenyl)naphthalene-2-carbonitrile **J-vinyl**.

7. Cyclic voltammetry curves showing oxidation processes the 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives in acetonitrile.

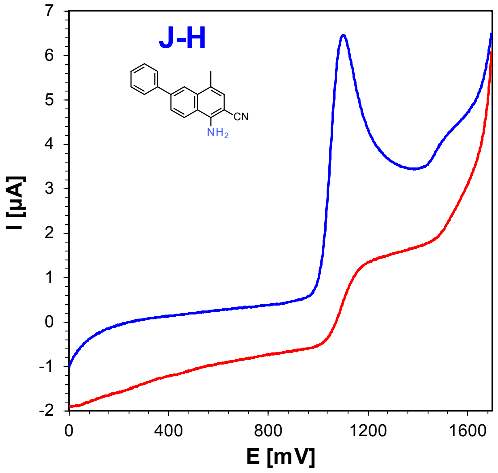


Figure S15: Cyclic voltammogram curves of the J-H oxidation in ACN.

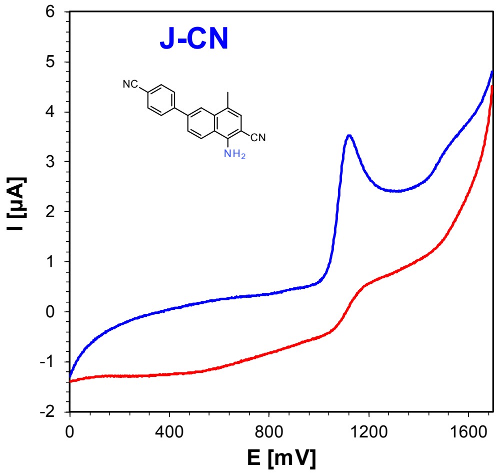


Figure S16: Cyclic voltammogram curves of the J-CN oxidation in ACN.

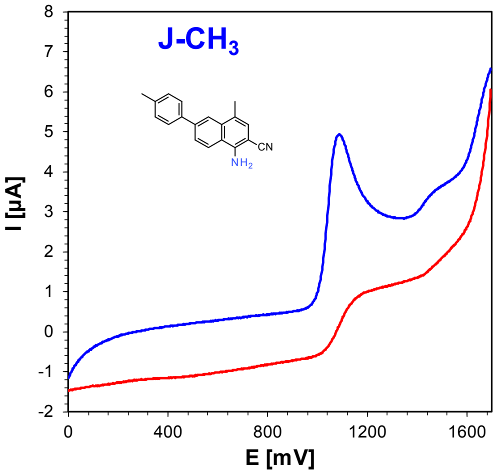


Figure S17: Cyclic voltammogram curves of the J-CH_3 oxidation in ACN.

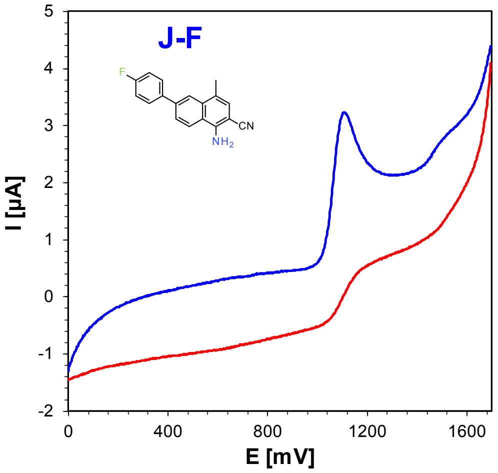


Figure S18: Cyclic voltammogram curves of the J-F oxidation in ACN.

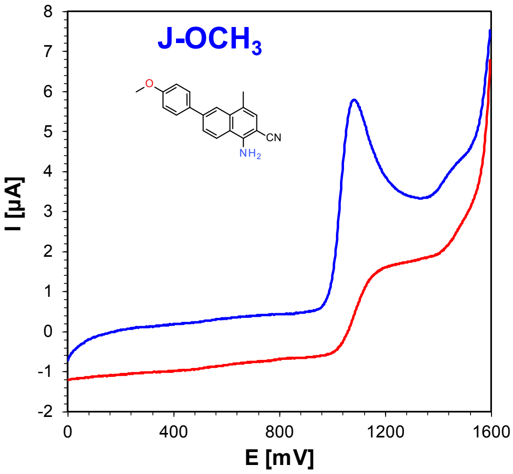


Figure S19: Cyclic voltammogram curves of the J-OCH_3 oxidation in ACN.

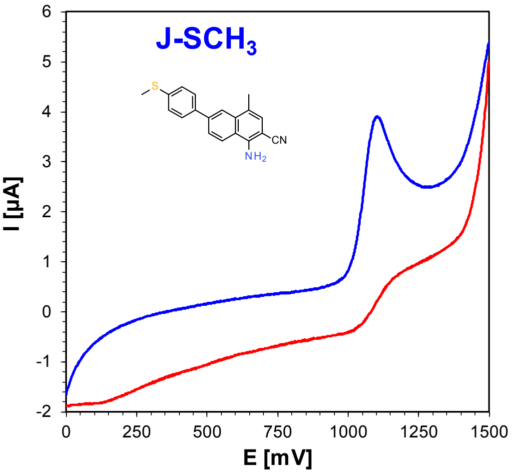


Figure S20: Cyclic voltammogram curves of the J-SCH_3 oxidation in ACN.

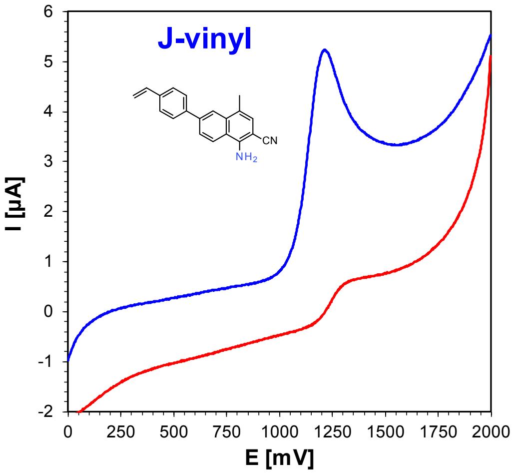


Figure S21: Cyclic voltammogram curves of the J-vinyl oxidation in ACN.

8. Emission and excitation spectra for the determination of the excited singlet state energy for investigated of 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives in acetonitrile

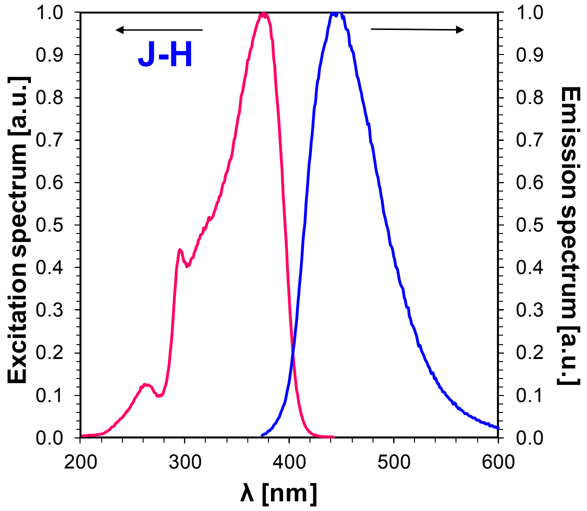


Figure S22: Emission and excitation spectra for the determination of the excited singlet state energy for J-H derivative.

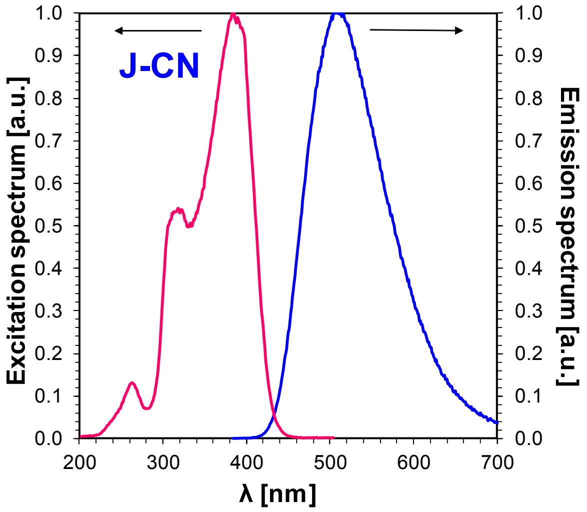


Figure S23: Emission and excitation spectra for the determination of the excited singlet state energy for J-CN derivative.

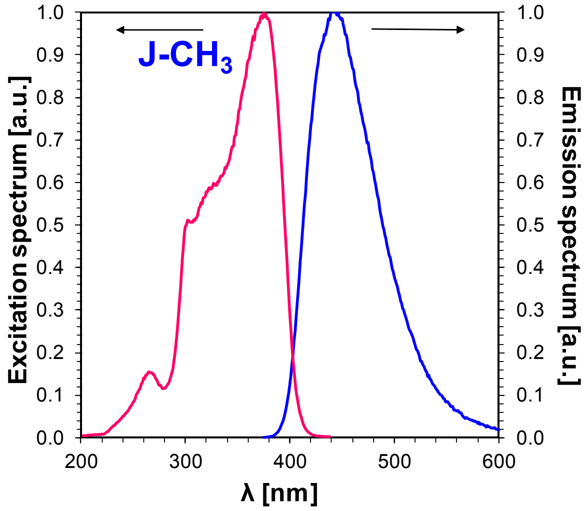


Figure S24: Emission and excitation spectra for the determination of the excited singlet state energy for J-CH_3 derivative.

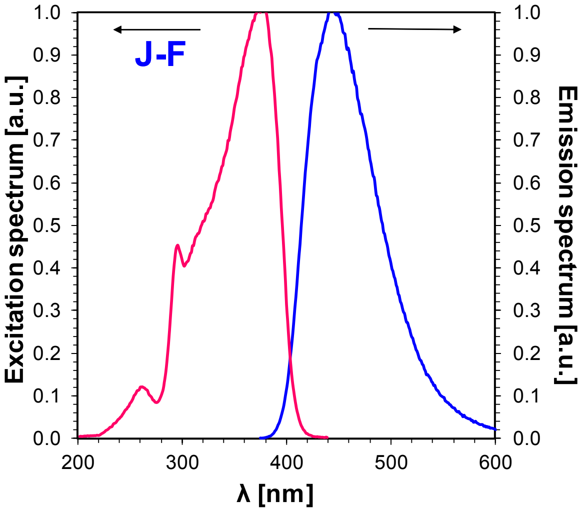


Figure S25: Emission and excitation spectra for the determination of the excited singlet state energy for J-F derivative.

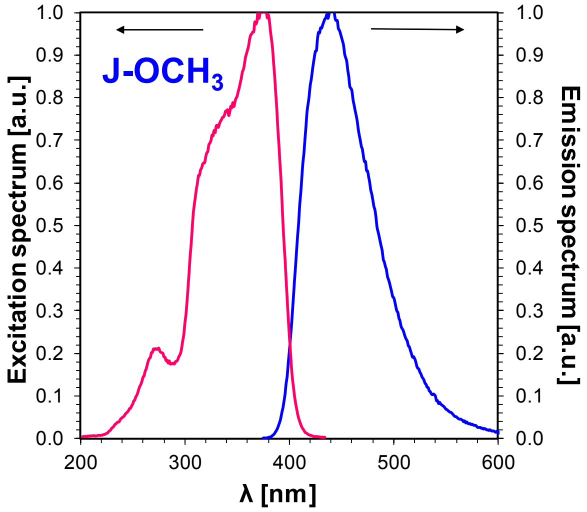


Figure S26: Emission and excitation spectra for the determination of the excited singlet state energy for J-OCH$_3$ derivative.

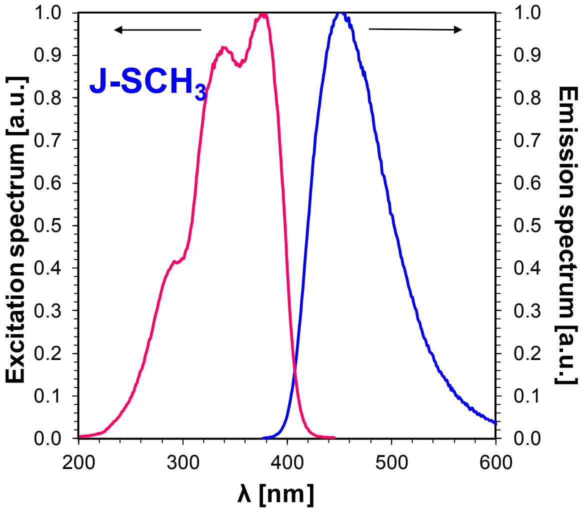


Figure S27: Emission and excitation spectra for the determination of the excited singlet state energy for J-SCH$_3$ derivative.

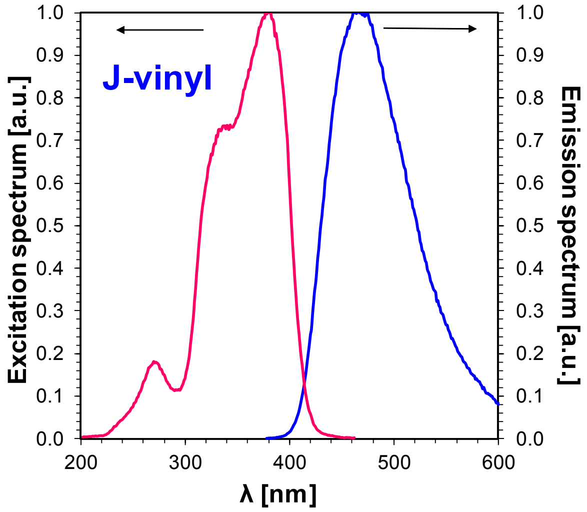
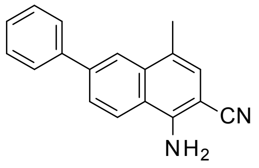
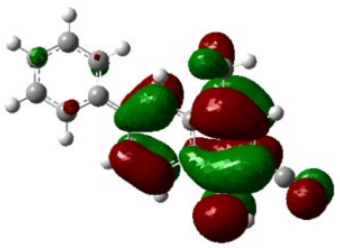
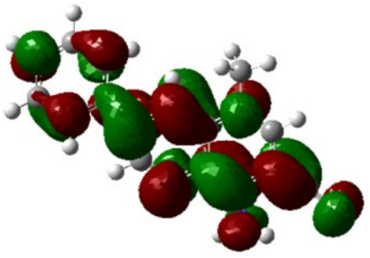
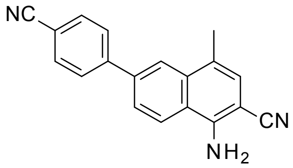
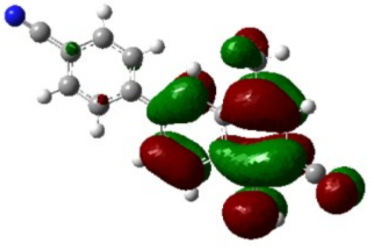
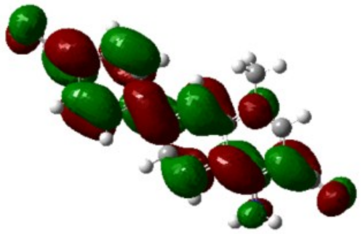
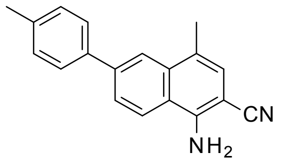
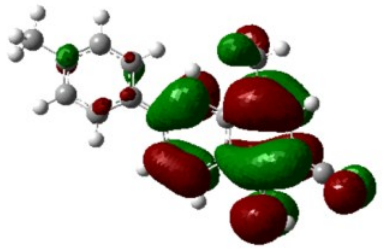
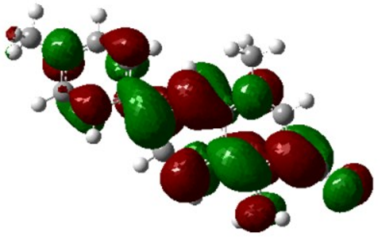
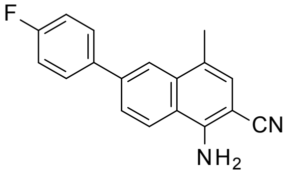
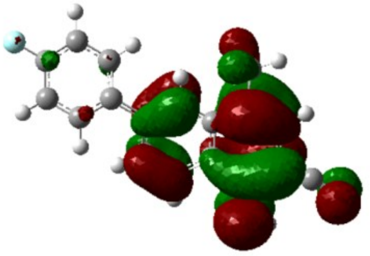
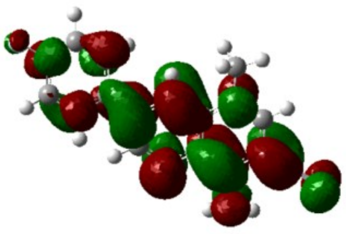
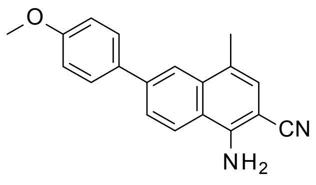
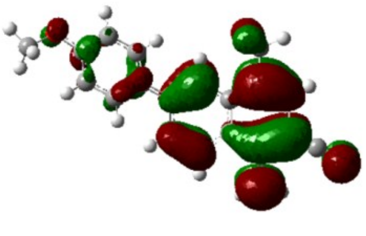
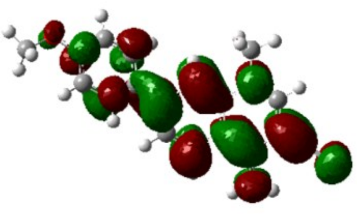
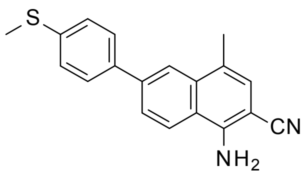
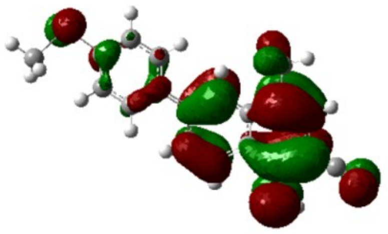
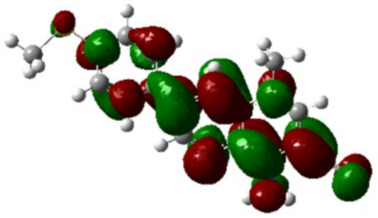
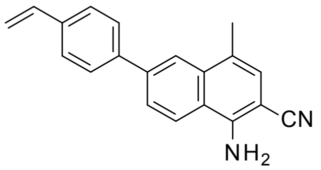
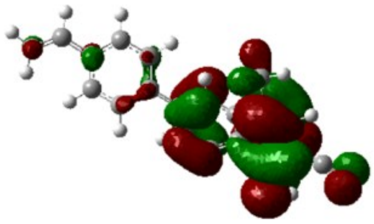
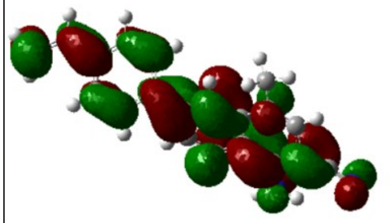


Figure S28: Emission and excitation spectra for the determination of the excited singlet state energy for J-vinyl derivative.

9. The optimized structures and HOMO and LUMO orbitals of investigated 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives free molecules determined with the use of uB3LYP/6-31G* level of theory

1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives	HOMO	LUMO
 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile **J-H**		
 1-amino-6-(4-cyanophenyl)-4-methyl-naphthalene-2-carbonitrile **J-CN**		
 1-amino-4-methyl-6-(4-methylphenyl)-naphthalene-2-carbonitrile **J-CH$_3$**		
 1-amino-6-(4-fluorophenyl)-4-methyl-naphthalene-2-carbonitrile **J-F**		
 1-amino-6-(4-methoxyphenyl)-4-methyl-naphthalene-2-carbonitrile **J-OCH$_3$**		

 1-amino-4-methyl-6-(4-methylsulfanylphenyl)naphthalene-2-carbonitrile **J-SCH$_3$**		
 1-amino-4-methyl-6-(4-vinylphenyl)naphthalene-2-carbonitrile **J-vinyl**		

10. Fluorescence quenching with Speedcure 938 of investigated 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives together with Stern-Volmer correlation

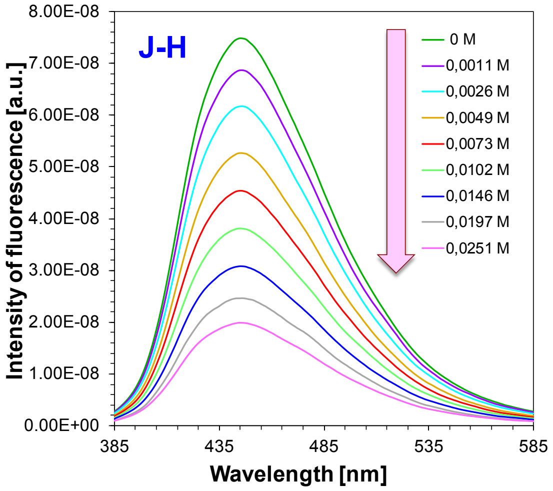


Figure S29: Fluorescence emission quenching of J-H by different concentration of Speedcure 938 in ACN; concentration [J-H] = 7.75·10^{-5} [mol/dm^3].

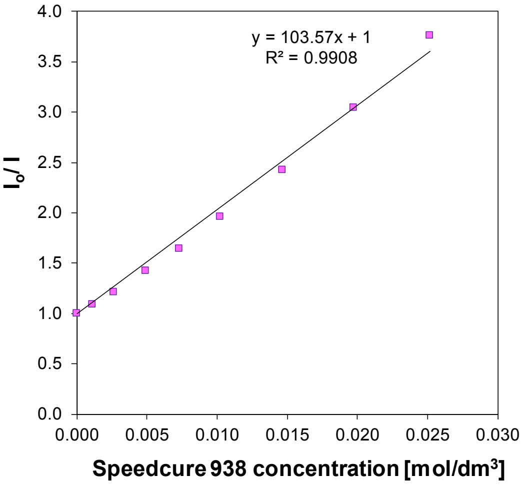
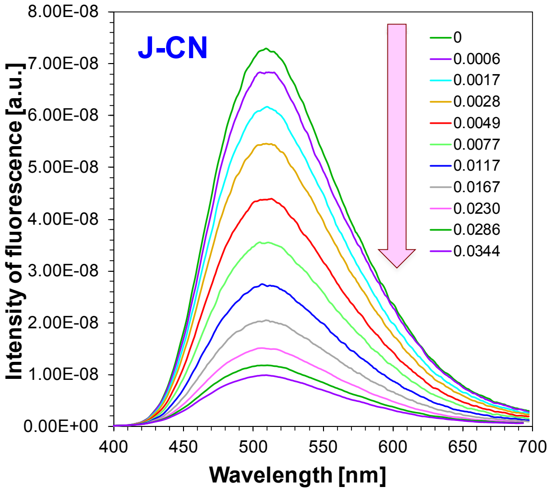


Figure S30: Stern-Volmer treatment for the J-H/Iod fluorescence quenching.



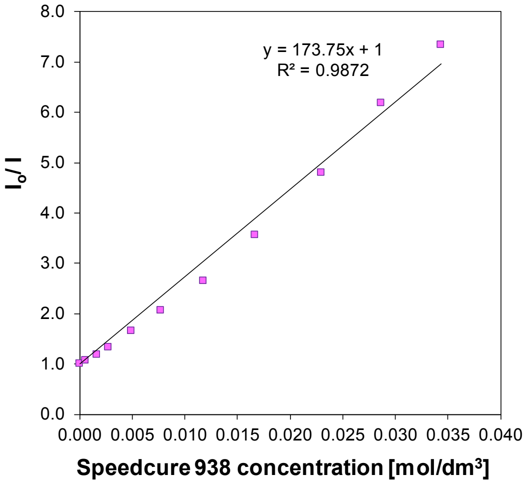
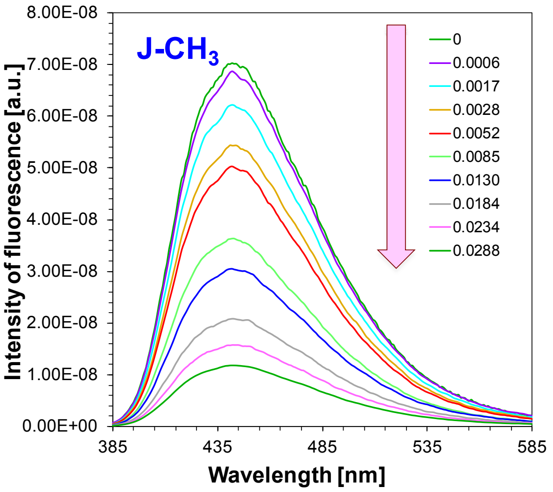


Figure S31: Fluorescence emission quenching of J-CN by different concentration of Speedcure 938 in ACN; concentration [J-CN] = $7.35 \cdot 10^{-5}$ [mol/dm^3].

Figure S32: Stern-Volmer treatment for the J-CN/Iod fluorescence quenching.



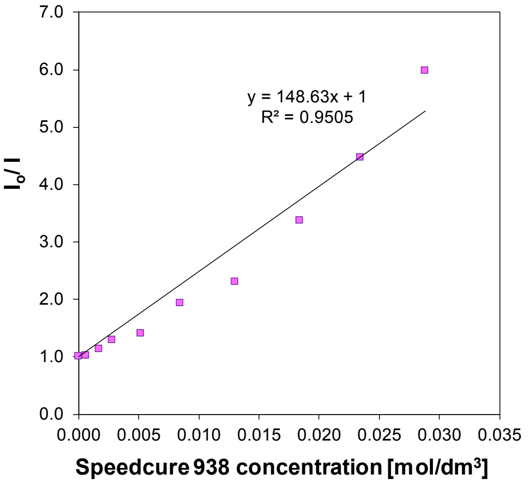
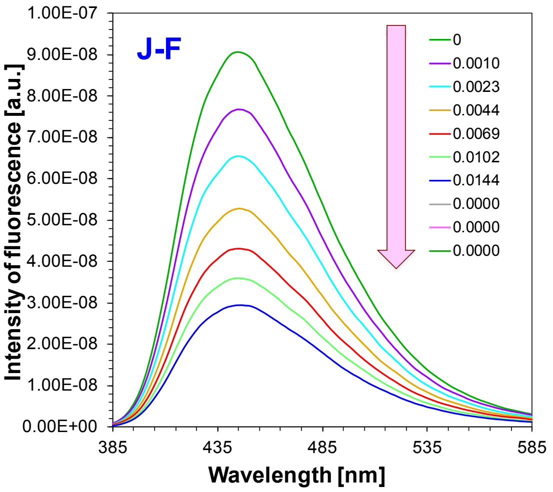


Figure S33: Fluorescence emission quenching of J-CH$_3$ by different concentration of Speedcure 938 in ACN; concentration [J-CH$_3$] = $7.20 \cdot 10^{-5}$ [mol/dm^3].

Figure S34: Stern-Volmer treatment for the J-CH$_3$/Iod fluorescence quenching.



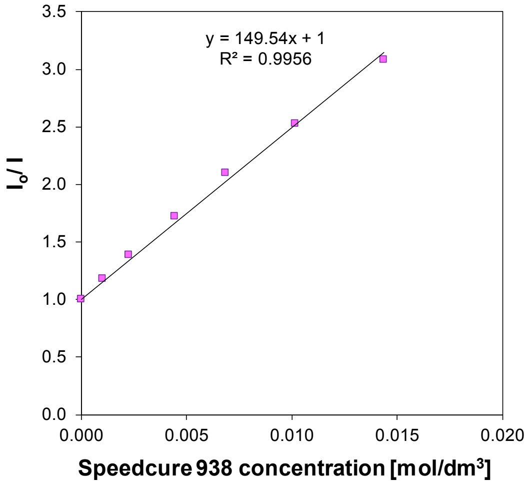
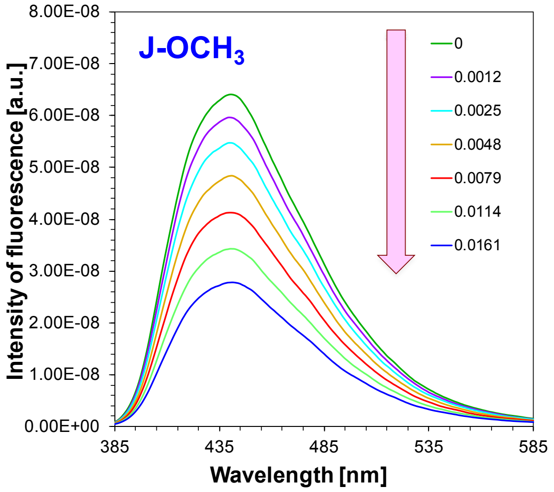


Figure S35: Fluorescence emission quenching of J-F by different concentration of Speedcure 938 in ACN; concentration [J-F] = $7.32 \cdot 10^{-5}$ [mol/dm^3].

Figure S36: Stern-Volmer treatment for the J-F/Iod fluorescence quenching.



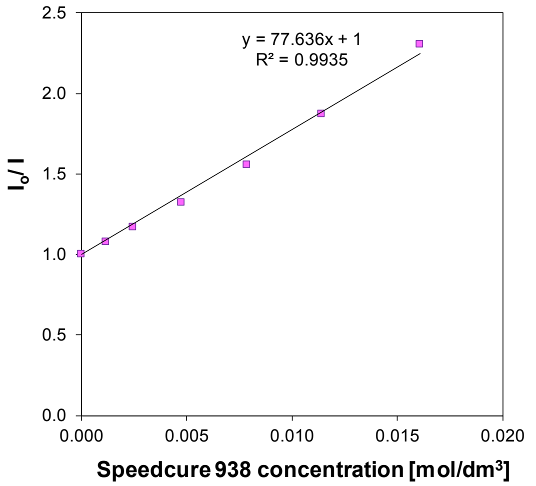
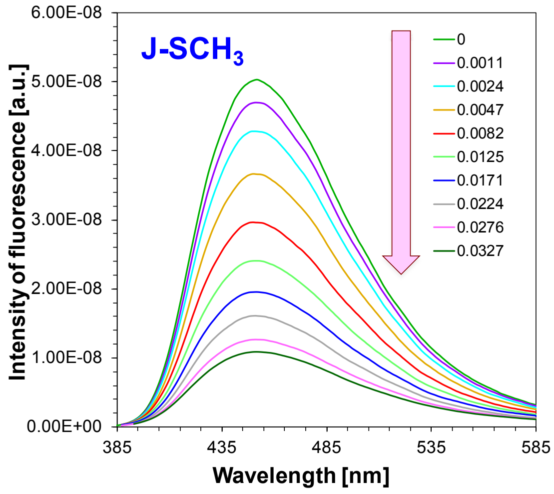


Figure S37: Fluorescence emission quenching of J-OCH_3 by different concentration of Speedcure 938 in ACN; concentration [J-OCH_3] = $7.15 \cdot 10^{-5}$ [mol/dm^3].

Figure S38: Stern-Volmer treatment for the J-OCH_3/Iod fluorescence quenching.



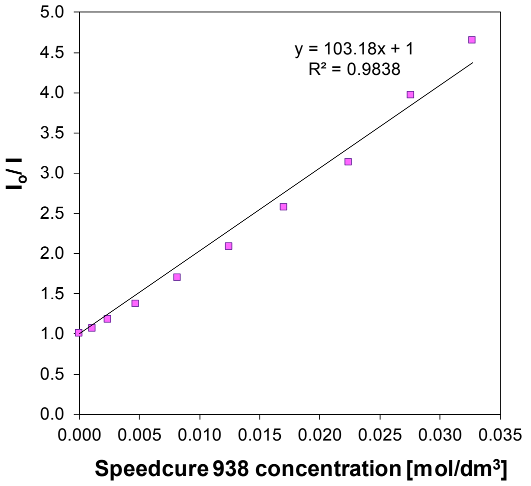
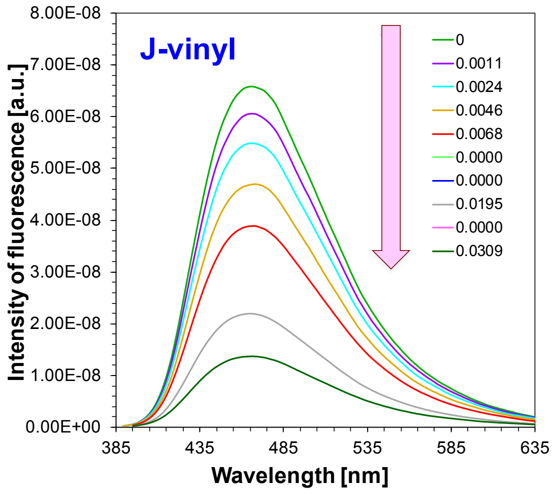


Figure S39: Fluorescence emission quenching of J-SCH_3 by different concentration of Speedcure 938 in ACN; concentration [J-SCH_3] = $6.71 \cdot 10^{-5}$ [mol/dm^3].

Figure S40: Stern-Volmer treatment for the J-SCH_3/Iod fluorescence quenching.



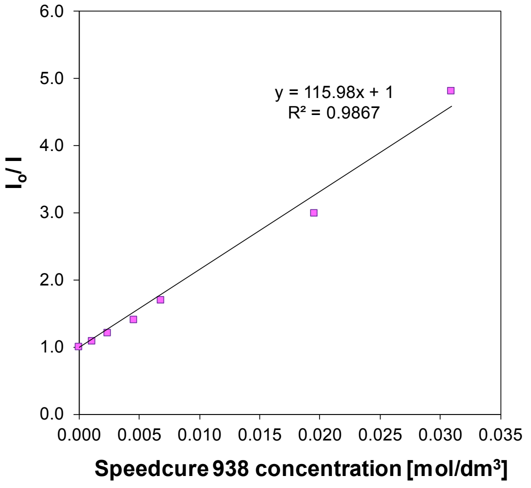
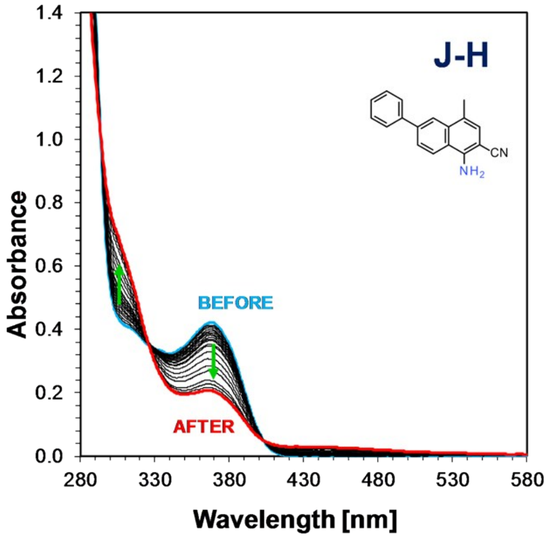


Figure S41: Fluorescence emission quenching of J-vinyl by different concentration of Speedcure 938 in ACN; concentration [J-vinyl] = $7.32 \cdot 10^{-5}$ [mol/dm^3].

Figure S42: Stern-Volmer treatment for the J-vinyl/Iod fluorescence quenching.

11. Steady state photolysis upon exposure with LED @365nm for 1-amino-4-methyl-6-phenyl-naphthalene-2-carbonitrile derivatives in acetonitrile



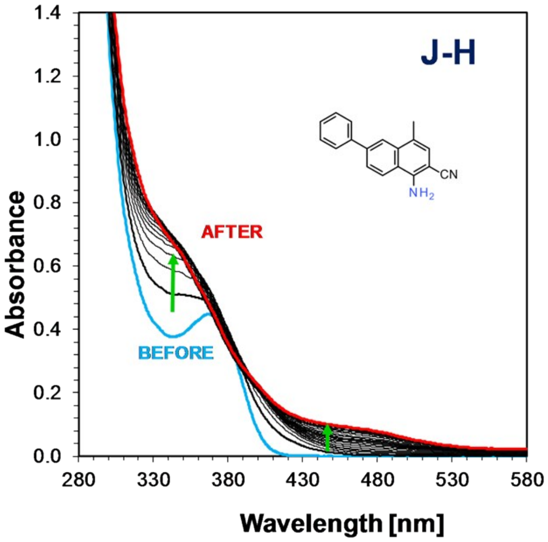
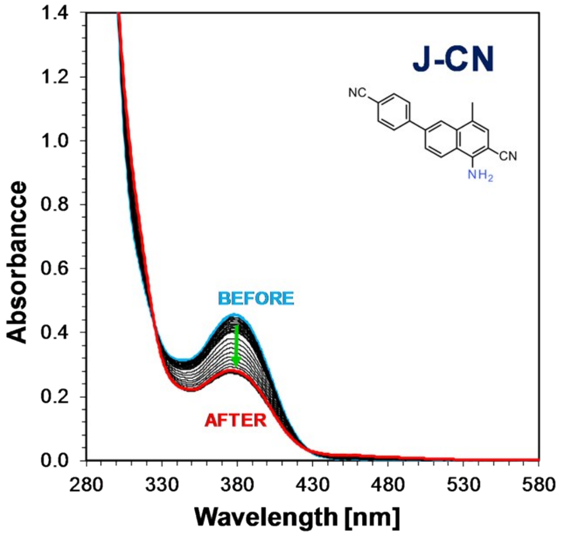


Figure S43: Photolysis of J-H (concentration: 7.75·10^{-5} [mol/dm^3]) in ACN under 365nm (13.6mW/cm^2).

Figure S44: Photolysis of J-H + Speedcure 938 (concentration: 1.59·10^{-3} [mol/dm^3]) in ACN under 365nm (13.6mW/cm^2).



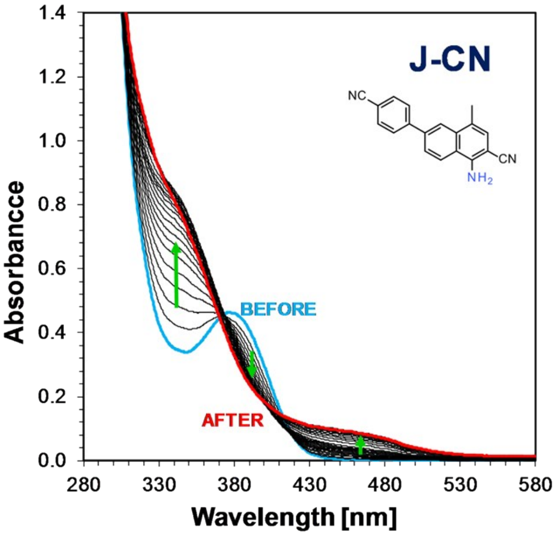
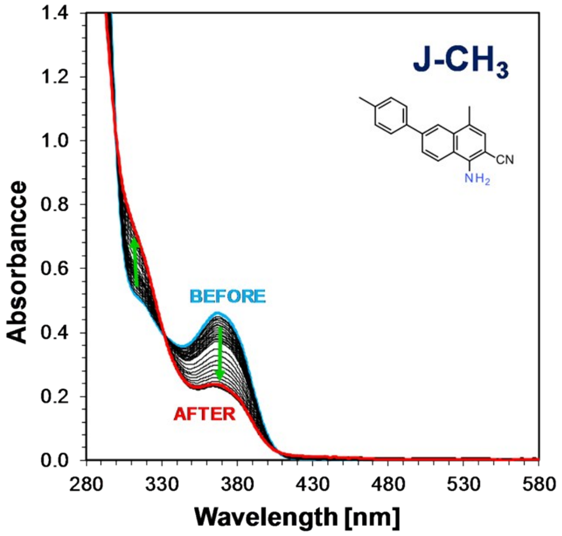


Figure S45: Photolysis of J-CN (concentration: 7.35·10^{-5} [mol/dm^3]) in ACN under 365nm (13.6mW/cm^2).

Figure S46: Photolysis of J-CN + Speedcure 938 (concentration: 1.59·10^{-3} [mol/dm^3]) in ACN under 365nm (13.6mW/cm^2).



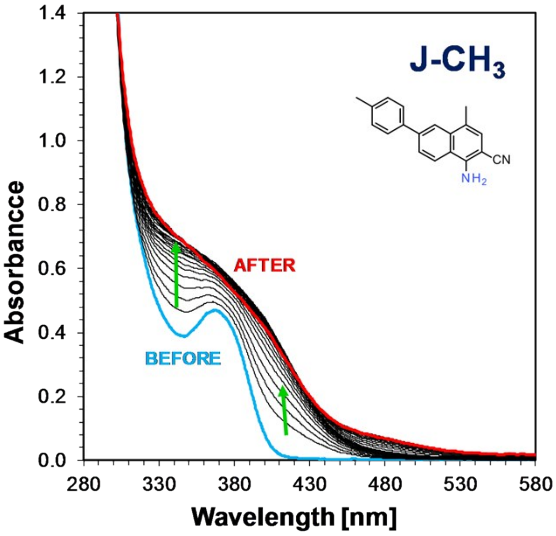


Figure S47: Photolysis of J-CH$_3$ (concentration: 7.20·10^{-5} [mol/dm^3]) in ACN under 365nm

Figure S48: Photolysis of J-CH$_3$ + Speedcure 938 (concentration: 1.59·10^{-3} [mol/dm^3]) in ACN under

($13.6 mW/cm^2$).

365nm ($13.6 mW/cm^2$).

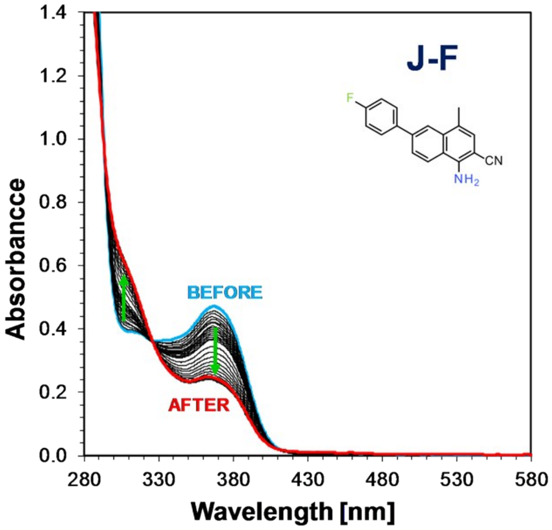


Figure S49: Photolysis of J-F (concentration: $7.32 \cdot 10^{-5}$ [mol/dm^3]) in ACN under 365nm ($13.6 mW/cm^2$).

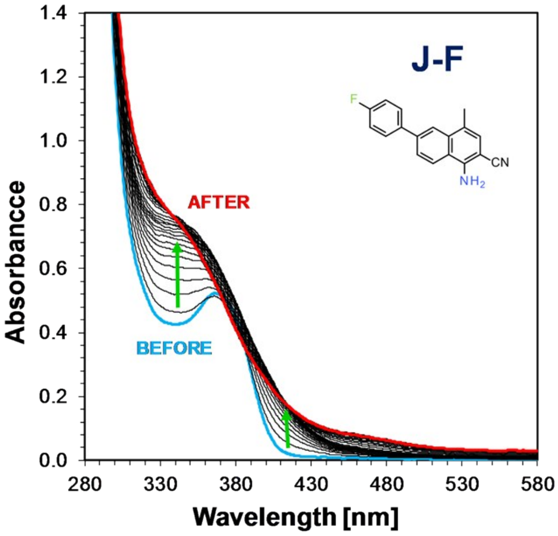


Figure S50: Photolysis of J-F + Speedcure 938 (concentration: $1.59 \cdot 10^{-3}$ [mol/dm^3]) in ACN under 365nm ($13.6 mW/cm^2$).

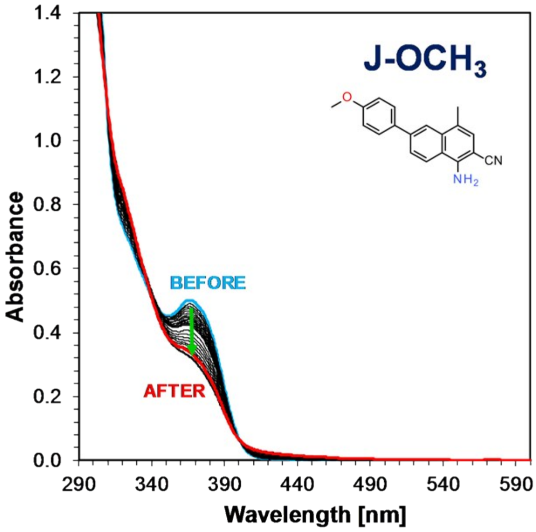


Figure S51: Photolysis of J-OCH_3 (concentration: $7.15 \cdot 10^{-5}$ [mol/dm^3]) in ACN under 365nm ($13.6 mW/cm^2$).

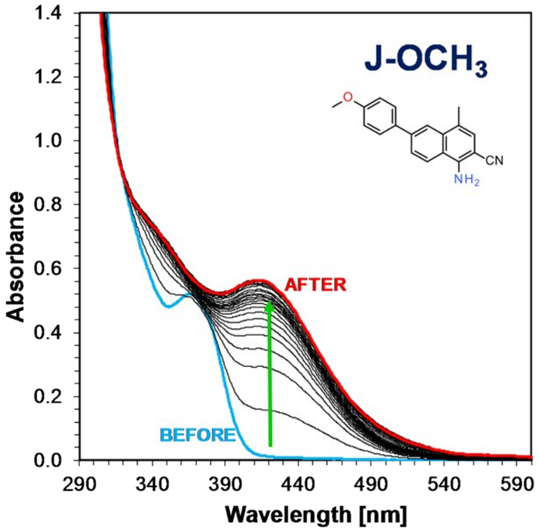


Figure S52: Photolysis of J-OCH_3 + Speedcure 938 (concentration: $1.59 \cdot 10^{-3}$ [mol/dm^3]) in ACN under 365nm ($13.6 mW/cm^2$).

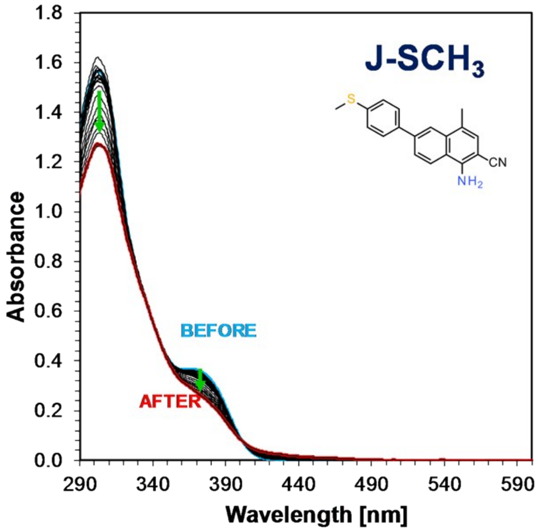


Figure S53: Photolysis of J-SCH_3 (concentration: $6.71 \cdot 10^{-5}$ [mol/dm^3]) in ACN under 365nm ($13.6 mW/cm^2$).

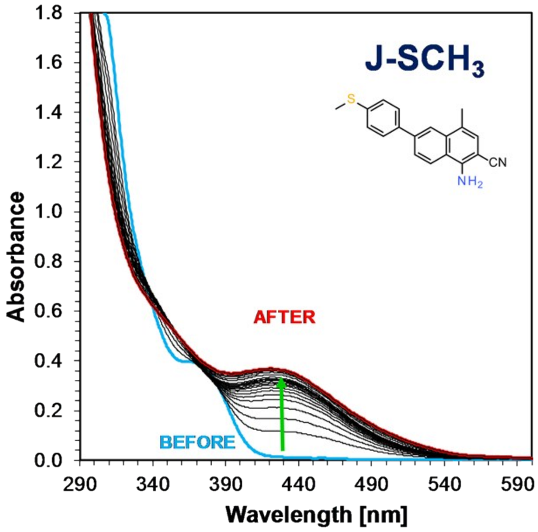


Figure S54: Photolysis of J-SCH_3 + Speedcure 938 (concentration: $1.59 \cdot 10^{-3}$ [mol/dm^3]) in ACN under 365nm ($13.6 mW/cm^2$).

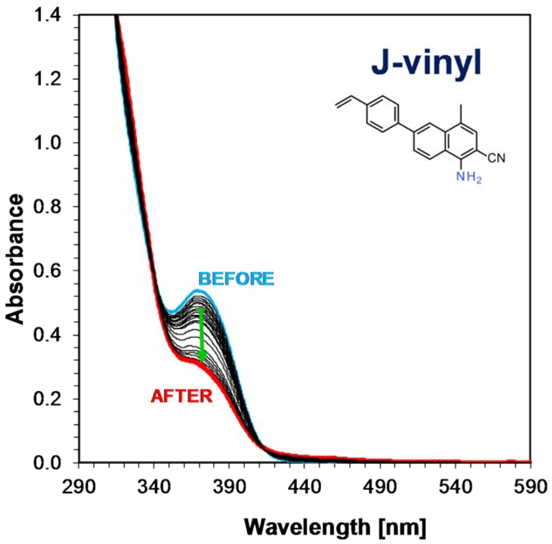


Figure S55: Photolysis of J-vinyl (concentration: $7.32 \cdot 10^{-5}$ [mol/dm^3]) in ACN under 365nm (13.6mW/cm^2).

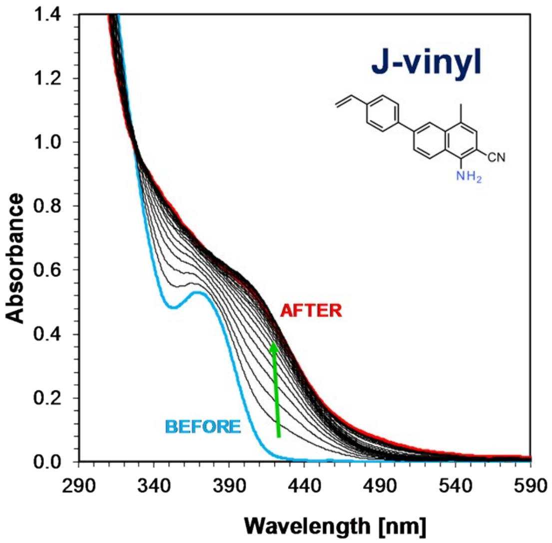


Figure S56: Photolysis of J-vinyl + Speedcure 938 (concentration: $1.59 \cdot 10^{-3}$ [mol/dm^3]) in ACN under 365nm (13.6mW/cm^2).

The pattern obtained after the 3D printing experiment based on bimolecular photoinitating systems, characterized by numerical optical microscopy.

The pattern obtained after the 3D printing experiment based on formulation J-SCH_3(0.05% w/w)/Speedcure 938 (1.0% w/w)/TMPTA/S105 (1:1 w/w), characterized by numerical optical microscope DSX1000 (Olympus).

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