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Supplementary Materials

Development of New High-Performance Biphenyl And Terphenyl Derivatives as Versatile Photoredox Photoinitiating Systems and their Applications in 3D printing Photopolymerization Processes

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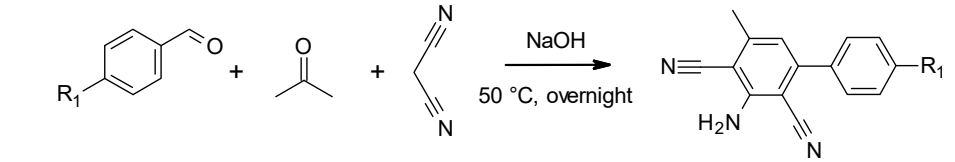
Synthesis - Chemicals and general synthetic procedures

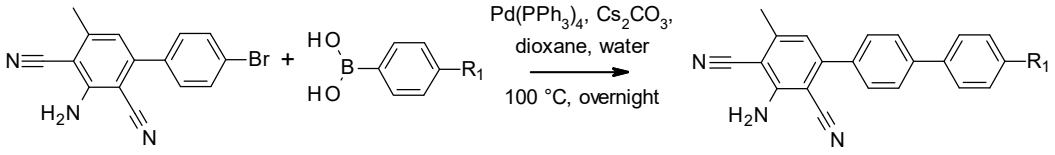


R_1 = H (**B1A**), CH_3 (**B2A**), OCH_3 (**B3A**), CN (**B4A**), SO_2CH_3 (**B5A**), SCH_3 (**B6A**), CF_3 (**B7A**) or Br (**B8A**)

R_1 = H (**B1A**), CH_3 (**B2A**), OCH_3 (**B3A**), CN (**B4A**), SO_2CH_3 (**B5A**), SCH_3 (**B6A**), CF_3 (**B7A**) or Br (**B8A**)

Scheme S1: Synthetic path to 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitriles.

Derivatives of 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile (**B1A**-**B8A**) were synthesized in multistage, cascade process catalyzed by sodium hydroxide. Straightforward application of literature protocol based on grinding method [1] did not lead to expected product, therefore some significant modifications of experimental conditions were implemented. Extended reaction times and heating the reagents in hermetic vial (to avoid evaporation of acetone) allowed to obtain pure products in moderate yields.



B8A

R_1 = H (**B1**), CH_3 (**B2**), OCH_3 (**B3**), CN (**B4**), SO_2CH_3 (**B5**), SCH_3 (**B6**) or CF_3 (**B7**)

Scheme S2: Synthetic path to 2-amino-4-methyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitriles.

Derivatives of 2-amino-4-methyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile (**B1-B7**) were prepared by Suzuki coupling of 2-amino-4-(4-bromophenyl)-6-methyl-benzene-1,3-dicarbonitrile **B8A** with an appropriate derivative of phenylboronic acid.

All reagents for synthesis were purchased from commercial sources and used without any further purification.

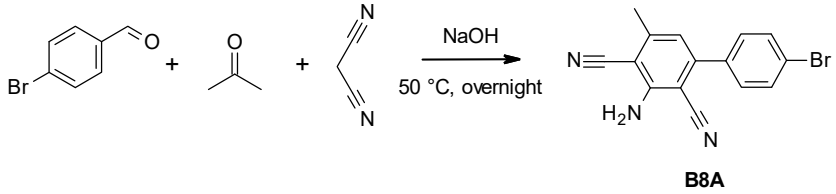
^{1}H and ^{13}C NMR spectra used in characterization of products were recorded in DMSO-D$_6$ on Advance III HD 400 MHz (Bruker) spectrometer. Chemical shifts are reported in parts per million (δ) and referenced to residual protonated solvent peak (δ = 2.50 ppm in ^{1}HNMR or δ = 39.52 ppm in ^{13}CNMR).

Elemental analyses of additionally purified samples were carried out using Vario El III CHNS Analyzer.

LC-MS analyses were obtained on LCMS-2020 (Shimadzu) with ESI ionization method. Acetonitrile was used as eluent.

Synthesis - Procedure for 2-amino-4-(4-bromophenyl)-6-methyl-benzene-1,3-dicarbonitrile (B8A)

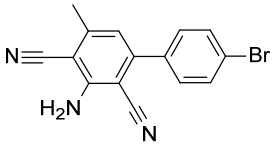
Synthetic route to compound **B8A** has been outlined in the scheme below:



B8A

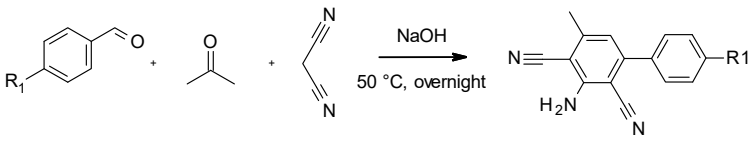
4-bromobenzaldehyde (740 mg, 4.0 mmol), malononitrile (661 mg, 10.0 mmol) and acetone (0.73 cm^3, 10.0 mmol) were placed in pressure vial. Powdered sodium hydroxide (240 mg, 6.0 mmol) was added and obtained viscous mixture was stirred overnight in temperature 50 °C. Then cool water was added and resulting precipitate was collected by filtration. Pure product in form of yellow powder was obtained after crystallization from ethanol.

Structure and purity of obtained product 2-amino-4-(4-bromophenyl)-6-methyl-benzene-1,3-dicarbonitrile

P08A  *2-amino-4-(4-bromophenyl)-6-methyl-benzene-1,3-dicarbonitrile*	Yield: 286 mg (23%). ^{1}H NMR (400 MHz, DMSO) δ 7.75 – 7.70 (m, 2H), 7.51 – 7.47 (m, 2H), 6.78 – 6.69 (m, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.43, 149.48, 148.15, 138.97, 134.74, 128.90, 127.97, 118.23, 116.20, 115.47, 95.41, 92.61, 20.92. Anal. Calcd for $C_{15}H_{10}BrN_3$: C, 57.7; H, 3.2; N, 13.5. Found: C, 57.6; H, 3.4; N, 13.2. MS (ESI), m/z (%): 313 (97%, $[M+H]^+$), 315 (100%, $[M+H+2]^+$). Purity (LC): 99%.

Synthesis - General procedure for derivatives of 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile

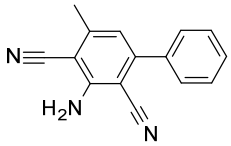
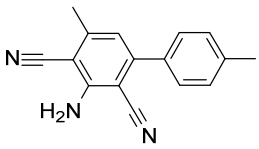
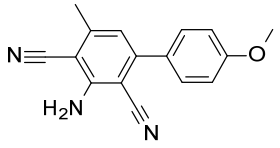
Synthetic route to compounds **B1A-B7A** has been outlined in the scheme below:

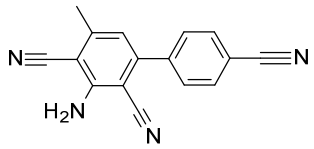
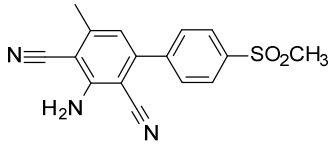
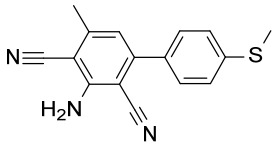


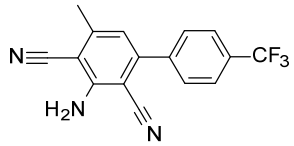
R_1 = H (**B1A**), CH_3 (**B2A**), OCH_3 (**B3A**), CN (**B4A**), SO_2CH_3 (**B5A**), SCH_3 (**B6A**), CF_3 (**B7A**)

Appropriate derivative of benzaldehyde (4.0 mmol), malononitrile (661 mg, 10.0 mmol) and acetone (0.73 cm3, 10.0 mmol) were placed in pressure vial. Powdered sodium hydroxide (240 mg, 6.0 mmol) was added and obtained viscous mixture was stirred overnight in temperature 50 °C. Then cool water was added and resulting precipitate was collected by filtration. Pure product in form of yellow powder was obtained after crystallization from ethanol.

Structure and purity of obtained products 2-amino-4-methyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile derivatives

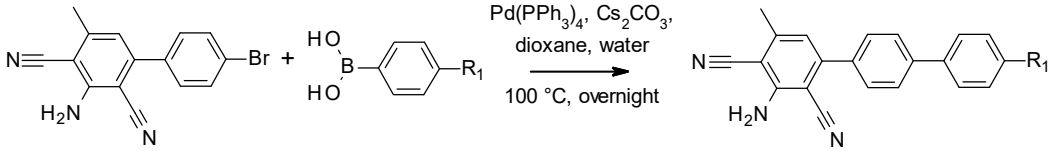
B1A  *2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile*	From benzaldehyde (424 mg, 4.0 mmol). Yield: 300 mg (23%). ^{1}H NMR (400 MHz, DMSO) δ 7.57 – 7.48 (m, 5H), 6.75 (s, 1H), 6.70 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.41, 149.58, 148.19, 137.63, 129.26, 128.63, 128.35, 119.05, 116.11, 115.47, 95.68, 92.70, 20.92. Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.2; H, 4.8; N, 18.0. Found: C, 77.5; H, 5.0; N, 17.6. MS (ESI), m/z (%): 234 (100%, $[M+H]^+$). Purity (LC): 98%.
B2A  *2-amino-4-(4-methylphenyl)-6-methyl-benzene-1,3-dicarbonitrile*	From 4-methylbenzaldehyde (481 mg, 4.0 mmol). Yield: 187 mg (19%). ^{1}H NMR (400 MHz, DMSO) δ 7.45 – 7.40 (m, 2H), 7.35 – 7.29 (m, 2H), 6.71 (s, 1H), 6.66 (s, 2H), 2.43 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.44, 149.58, 148.07, 138.97, 134.74, 129.20, 128.26, 118.93, 116.21, 115.53, 95.41, 92.61, 20.92, 20.82. Anal. Calcd for $C_{16}H_{13}N_3$: C, 77,7; H, 5,3; N, 17.0. Found: C, 77.9; H, 5.4; N, 16.7. MS (ESI), m/z (%): 248 (100%, $[M+H]^+$). Purity (LC): 94%.
B3A  *2-amino-4-(4-methoxyphenyl)-6-methyl-benzene-1,3-dicarbonitrile*	From 4-methoxybenzaldehyde (545 mg, 4.0 mmol). Yield 193 mg (18%). ^{1}H NMR (400 MHz, DMSO) δ 7.53 – 7.47 (m, 2H), 7.09 – 7.04 (m, 2H), 6.72 (s, 1H), 6.63 (s, 2H), 3.82 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 160.12, 153.50, 149.28, 147.94, 129.83, 129.73, 118.88, 116.37, 115.59, 114.07, 95.08, 92.46, 55.31, 20.92. Anal. Calcd for $C_{16}H_{13}N_3O$: C, 73.0; H, 5.0; N, 16.0. Found: C, 73.1; H, 5.2; N, 15.7. MS (ESI), m/z (%): 264 (100%, $[M+H]^+$). Purity (LC): 96%.

B4A  *2-amino-4-(4-cyanophenyl)-6-methyl-benzene-1,3-dicarbonitrile*	From 4-cyanobenzaldehyde (524 mg, 4.0 mmol). Yield: 304 mg (29%). ^{1}H NMR (400 MHz, DMSO) δ 8.03 – 7.97 (m, 2H), 7.78 – 7.71 (m, 2H), 6.82 (s, 2H), 6.78 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.34, 148.59, 147.71, 142.17, 132.55, 129.49, 118.92, 118.40, 115.75, 115.26, 111.94, 96.58, 92.52, 20.95. Anal. Calcd for $C_{16}H_{10}N_4$: C, 74.4; H, 3.9; N, 21.7. Found: C, 74.2; H, 4.2; N, 21.8. MS (ESI), m/z (%): 259 (59%, $[M+H]^+$], 300 (100%, $[M+CH_3CN]^+$). Purity (LC): 96%.
B5A  *2-amino-4-methyl-6-(4-methylsulfonylphenyl)benzene-1,3-dicarbonitrile*	From 4-(methylsulfonyl)benzaldehyde (737 mg, 4.0 mmol). Yield: 370 mg (30%). ^{1}H NMR (400 MHz, DMSO) δ 8.10 – 8.04 (m, 2H), 7.84 – 7.78 (m, 2H), 6.82 (s, 2H), 6.79 (s, 1H), 3.31 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.37, 148.60, 147.77, 142.48, 141.34, 129.51, 127.23, 119.03, 115.81, 115.28, 96.55, 92.58, 43.30, 20.97. Anal. Calcd for $C_{16}H_{13}N_3O_2S$: C, 61.7; H, 4.2; N, 13.5; S, 10.3. Found: C, 61.8; H, 4.5; N, 13.3; S, 10.1. MS (ESI), m/z (%): 312 (100%, $[M+H]^+$). Purity (LC): 96%.
B6A  *2-amino-4-methyl-6-(4-methylsulfanylphenyl)benzene-1,3-dicarbonitrile*	From 4-(methylsulfanyl)benzaldehyde (609 mg, 4.0 mmol). Yield: 395 mg (35%). ^{1}H NMR (400 MHz, DMSO) δ 7.50 – 7.46 (m, 2H), 7.39 – 7.36 (m, 2H), 6.72 (s, 1H), 6.67 (s, 2H), 2.53 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.48, 148.99, 148.14, 140.25, 133.72, 128.84, 125.50, 118.83, 116.21, 115.51, 95.48, 92.43, 20.94, 14.27. Anal. Calcd for : C16H13N3S: C, 68.8; H, 4.7; N, 15.0; S, 11.5. Found: C, 68.8; H, 4.5; N, 15.2; S, 11.5. MS (ESI), m/z (%): 290 (100%, $[M+H]^+$). Purity (LC): 97%.

B7A  *2-amino-4-methyl-6-[4-(trifluoromethyl)phenyl]benzene-1,3-*	From 4-(trifluoromethyl)benzaldehyde (696 mg, 4.0 mmol). Yield: 238 mg (20%). ^{1}H NMR (400 MHz, DMSO) δ 7.93 – 7.86 (m, 2H), 7.80 – 7.73 (m, 2H), 6.81 (s, 2H), 6.79 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.36, 148.55, 147.98, 141.68, 129.64, 129.40, 129.32, 125.54 (q, *J* = 3.6 Hz), 118.99, 115.83, 115.30, 96.44, 92.64, 20.95. Anal. Calcd for : $C_{16}H_{10}F_3N_3$: C, 63.8; H, 3.3; N, 13.9; Found: C, 64.0; H, 3.7; N, 13.5. MS (ESI), m/z (%): 302 (72%, $[M+H]^+$), 343 (100%, $[M+CH_3CN]^+$). Purity (LC): 98%.

Synthesis - General procedure for derivatives of 2-amino-4-methyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile

Synthetic route to compounds **B1-B7** has been outlined in the scheme below:

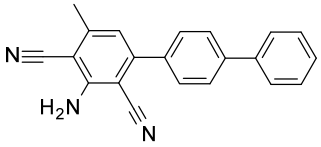


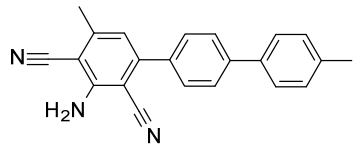
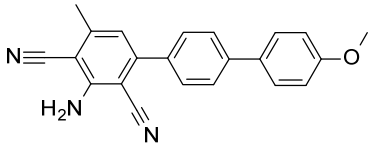
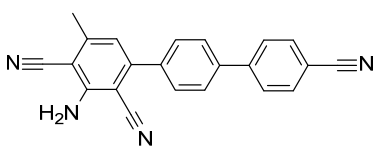
B8A

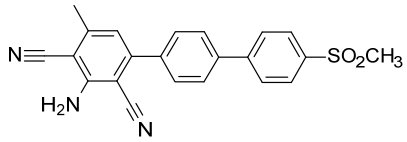
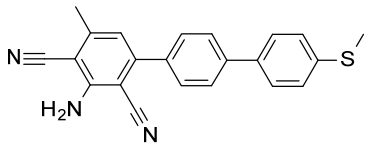
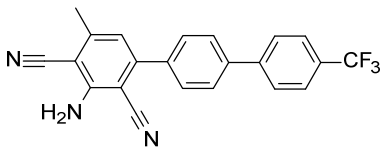
R_1 = H (**B1**), CH_3 (**B2**), OCH_3 (**B3**), CN (**B4**), SO_2CH_3 (**B5**), SCH_3 (**B6**) or CF_3 (**B7**)

Appropriate derivative of phenylboronic acid (0.72 mmol), 2-amino-4-(4-bromophenyl)-6-methyl-benzene-1,3-dicarbonitrile (187 mg, 0.60 mmol), cesium carbonate (375 mg, 1.20 mmol), tetrakis(triphenylphosphine)palladium(0) (15 mg, 0.01 mmol), 1,4-dioxane (4.0 cm3) and water (1.0 cm3) were placed under nitrogen in the pressure vial. Mixture was stirred and heated overnight in temperature 100 °C. After evaporation of solvents the residue was adsorbed on silica gel and purified by column chromatography on silica gel using chloroform as eluent.

Structure and purity of obtained products of of 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives

B1  *2-amino-4-methyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile*	From phenylboronic acid (88 mg, 0.72 mmol). Yield: 150 mg (87%). ^{1}H NMR (400 MHz, DMSO) δ 7.85 – 7.80 (m, 2H), 7.77 – 7.73 (m, 2H), 7.67 – 7.62 (m, 2H), 7.53 – 7.47 (m, 2H), 7.44 – 7.38 (m, 1H), 6.81 (s, 1H), 6.71 (s, 2H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.48, 149.08, 148.21, 140.94, 139.16, 136.59, 129.04, 129.03, 127.92, 126.84, 126.76, 118.99, 116.21, 115.49, 95.71, 92.53, 20.96.

	Anal. Calcd for: $C_{21}H_{15}N_3$: C, 81.5; H, 4.9; N, 13.6; Found: C, 81.6; H, 5.3; N, 13.2. MS (ESI), m/z (%): 310 (100%, $[M+H]^+$). Purity (LC): 96%.
B2  *2-amino-4-[4-(4-methylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*	From 4-methylphenylboronic acid (98 mg, 0.72 mmol). Yield: 140 mg (72%). ^{1}H NMR (400 MHz, DMSO) δ 7.83 – 7.77 (m, 2H), 7.68 – 7.60 (m, 4H), 7.34 – 7.27 (m, 2H), 6.80 (s, 1H), 6.71 (s, 2H), 2.46 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.48, 149.14, 148.20, 140.86, 137.34, 136.26, 136.25, 129.65, 128.99, 126.57, 126.53, 118.97, 116.22, 115.50, 95.65, 92.51, 20.95, 20.70. Anal. Calcd for: $C_{22}H_{17}N_3$: C, 81.7; H, 5.3; N, 13.0; Found: C, 81.8; H, 5.5; N, 12.9. MS (ESI), m/z (%): 324 (100%, $[M+H]^+$). Purity (LC): 97%.
B3  *2-amino-4-[4-(4-methoxyphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*	From 4-methoxyphenylboronic acid (109 mg, 0.72 mmol). Yield: 180 mg (88%). ^{1}H NMR (400 MHz, DMSO) δ 7.80 – 7.75 (m, 2H), 7.73 – 7.67 (m, 2H), 7.64 – 7.58 (m, 2H), 7.09 – 7.03 (m, 2H), 6.79 (s, 1H), 6.70 (s, 2H), 3.81 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 159.28, 153.49, 149.18, 148.17, 140.62, 135.81, 131.42, 128.97, 127.89, 126.23, 118.95, 116.25, 115.51, 114.48, 95.59, 92.49, 55.21, 20.96. Anal. Calcd for: $C_{22}H_{17}N_3O$: C, 77.9; H, 5.0; N, 12.4; Found: C, 78.2; H, 5.2; N, 12.1. MS (ESI), m/z (%): 340 (100%, $[M+H]^+$). Purity (LC): 97%.
B4  *2-amino-4-[4-(4-cyanophenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*	From 4-cyanophenylboronic acid (106 mg, 0.72 mmol). Yield: 158 mg (79%). ^{1}H NMR (400 MHz, DMSO) δ 8.01 – 7.95 (m, 4H), 7.94 – 7.89 (m, 2H), 7.71 – 7.66 (m, 2H), 6.80 (s, 1H), 6.74 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.46, 148.75, 148.29, 143.61, 138.95, 137.85, 132.92, 129.23, 127.67, 127.29, 118.98, 118.79, 116.13, 115.44, 110.47, 95.91, 92.53, 20.96. Anal. Calcd for: $C_{22}H_{14}N_4$: C, 79.0; H, 4.2; N, 16.8; Found: C, 78.8; H, 4.3; N, 16.9. MS (ESI), m/z (%): 335 (100%, $[M+H]^+$). Purity (LC): 99%.

B5  *2-amino-4-[4-(4-methylsulfonylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*	From 4-(methylsulfonyl)phenylboronic acid (144 mg, 0.72 mmol). Yield: 40 mg (17%). ^{1}H NMR (400 MHz, DMSO) δ 8.07 – 8.00 (m, 4H), 7.95 – 7.91 (m, 2H), 7.72 – 7.67 (m, 2H), 6.82 (s, 1H), 6.75 (s, 2H), 3.28 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.47, 148.81, 148.31, 139.99, 139.13, 137.80, 133.58, 129.24, 127.71, 127.69, 127.41, 119.01, 116.15, 115.45, 95.90, 92.55, 43.52, 20.97. Anal. Calcd for: $C_{22}H_{17}N_3O_2S$: C, 68.2; H, 4.4; N, 10.8; S, 8.3; Found: C, 68.3; H, 4.7; N, 10.5; S, 8.1. MS (ESI), m/z (%): 388 (100%, $[M+H]^+$). Purity (LC): 97%.
B6  *2-amino-4-[4-(4-methylsulfanylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*	From 4-(methylsulfanyl)phenylboronic acid (121 mg, 0.72 mmol). Yield: 190 mg (89%). ^{1}H NMR (400 MHz, DMSO) δ 7.84 – 7.78 (m, 2H), 7.74 – 7.68 (m, 2H), 7.65 – 7.60 (m, 2H), 7.40 – 7.35 (m, 2H), 6.79 (s, 1H), 6.71 (s, 2H), 2.53 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.49, 149.08, 148.20, 140.27, 138.25, 136.39, 135.48, 129.05, 127.14, 126.42, 126.32, 118.96, 116.22, 115.49, 95.67, 92.50, 20.96, 14.55. Anal. Calcd for: $C_{22}H_{17}N_3S$: C, 74.3; H, 4.8; N, 11.8; S, 9.0; Found: C, 74.5; H, 5.0; N, 11.6; S, 8.8. MS (ESI), m/z (%): 356 (100%, $[M+H]^+$). Purity (LC): 94%.
B7  *2-amino-4-methyl-6-[4-[4-(trifluoromethyl)phenyl]phenyl]benzene-1,3-dicarbonitrile*	From 4-(trifluoromethyl)phenylboronic acid (187 mg, 0.72 mmol). Yield: 190 mg (89%). ^{1}H NMR (400 MHz, DMSO) δ 8.02 – 7.96 (m, 2H), 7.93 – 7.88 (m, 2H), 7.88 – 7.82 (m, 2H), 7.72 – 7.66 (m, 2H), 6.81 (s, 1H), 6.74 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 153.47, 148.84, 148.28, 143.18, 139.30, 137.59, 131.61, 130.50, 129.20, 127.61, 127.26, 125.86 (q, J = 3.6 Hz), 118.99, 116.15, 115.45, 95.87, 92.55, 20.96. Anal. Calcd for: C22H14F3N3: C, 70.0; H, 3.7; N, 11.1; Found: C, 70.4; H, 4.0; N, 10.8. Composition: C: 70% H: 3,7% F: 15,1% N: 11,1% Molecular Formula: C22H14F3N3 MS (ESI), m/z (%): 378 (100%, $[M+H]^+$). Purity (LC): 97%.

Cyclic voltammetry curves showing oxidation and reduction processes of 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives in acetonitrile.

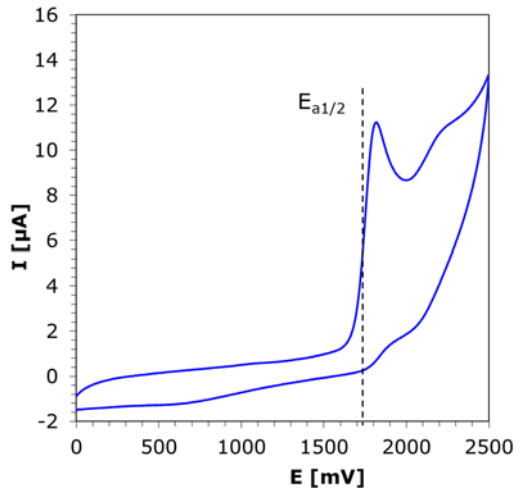


Figure S1: Cyclic voltammogram curves of the B1 oxidation in acetonitrile.

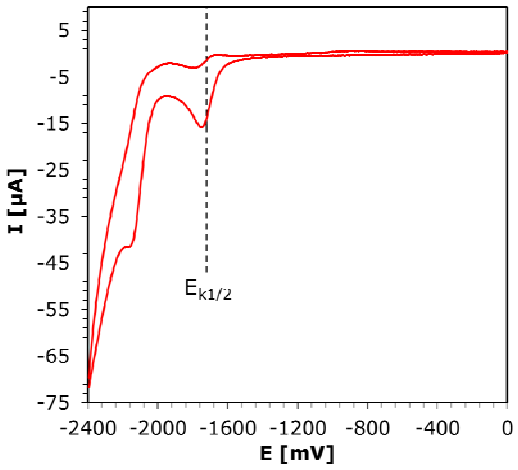


Figure S2: Cyclic voltammogram curves of the B1 reduction in acetonitrile.

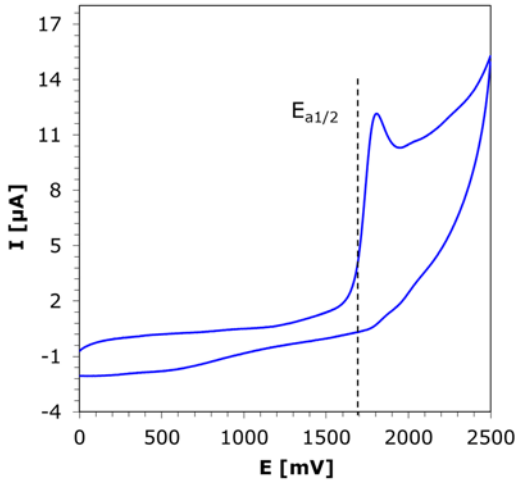


Figure S3: Cyclic voltammogram curves of the B2 oxidation in acetonitrile.

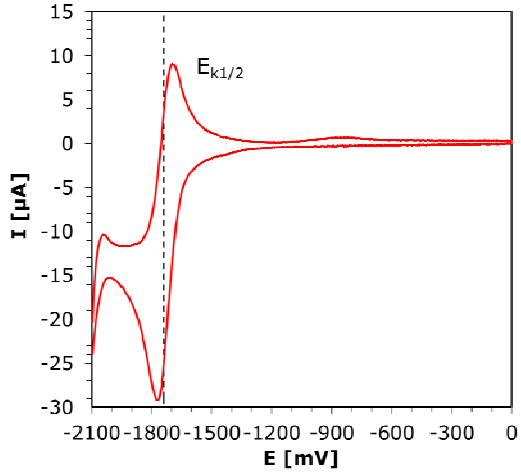


Figure S4: Cyclic voltammogram curves of the B2 reduction in acetonitrile.

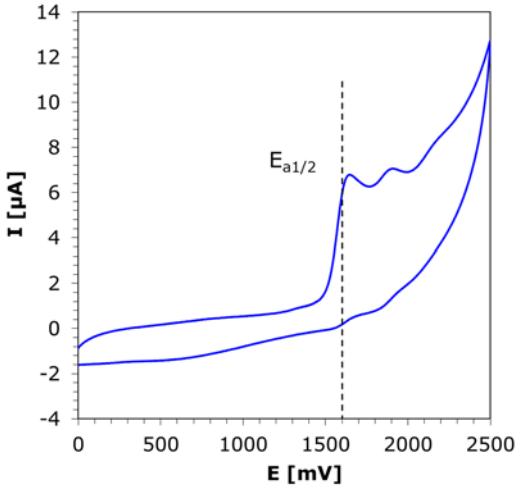


Figure S5: Cyclic voltammogram curves of the B3 oxidation in acetonitrile.

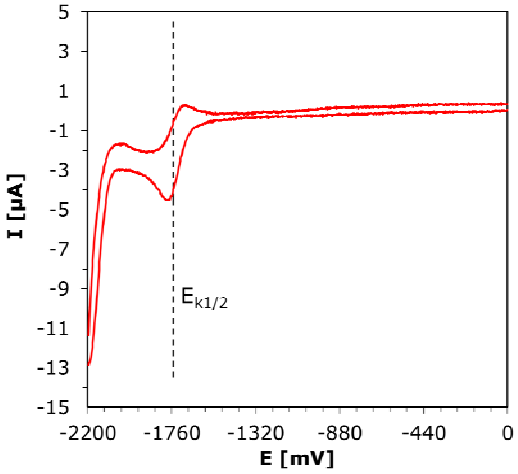


Figure S6: Cyclic voltammogram curves of the B3 reduction in acetonitrile.

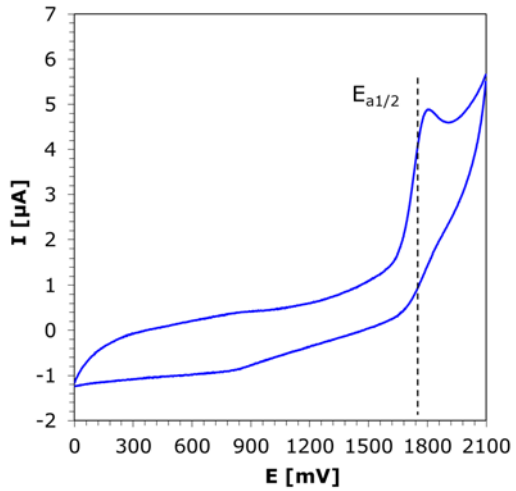


Figure S7: Cyclic voltammogram curves of the B4 oxidation in acetonitrile.

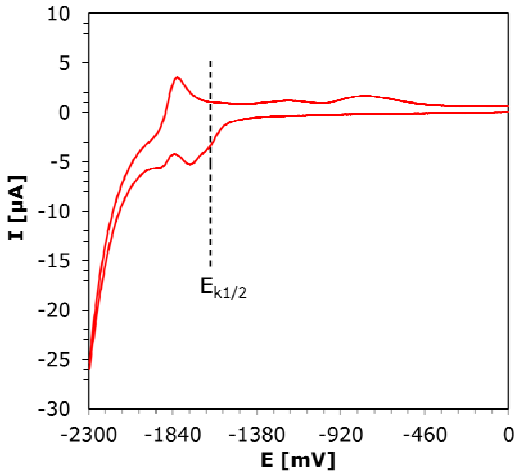


Figure S8: Cyclic voltammogram curves of the B4 reduction in acetonitrile.

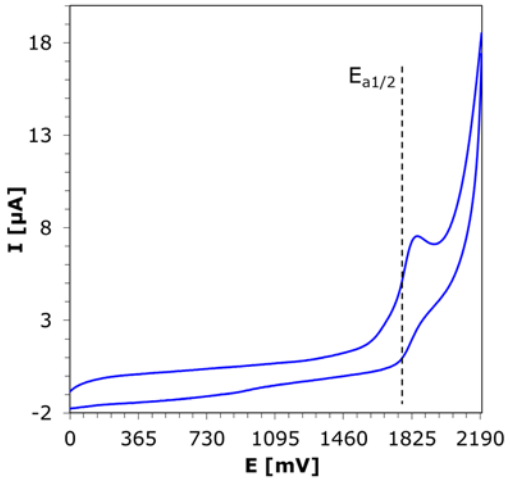


Figure S9: Cyclic voltammogram curves of the B5 oxidation in acetonitrile.

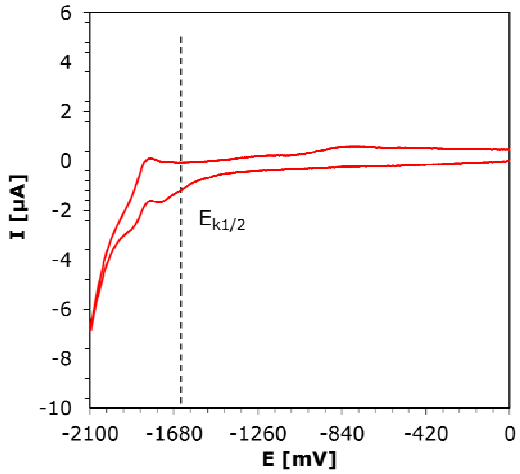


Figure S10: Cyclic voltammogram curves of the B5 reduction in acetonitrile.

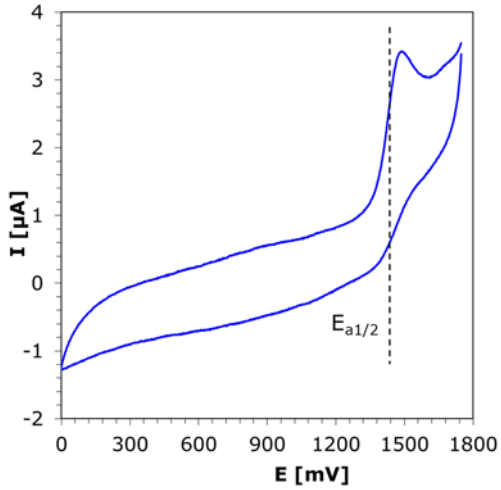


Figure S11: Cyclic voltammogram curves of the B6 oxidation in acetonitrile.

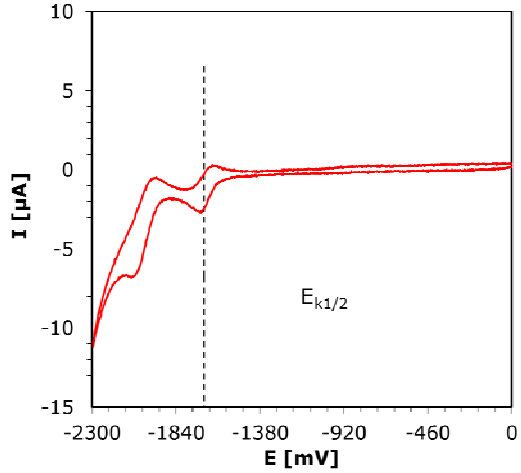


Figure S12: Cyclic voltammogram curves of the B6 reduction in acetonitrile.

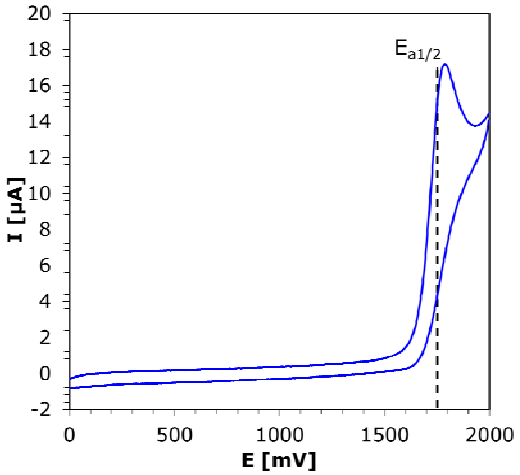


Figure S13: Cyclic voltammogram curves of the B7 oxidation in acetonitrile.

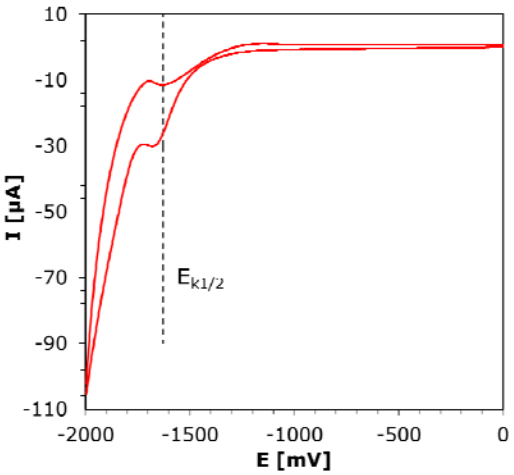


Figure S14: Cyclic voltammogram curves of the B7 reduction in acetonitrile.

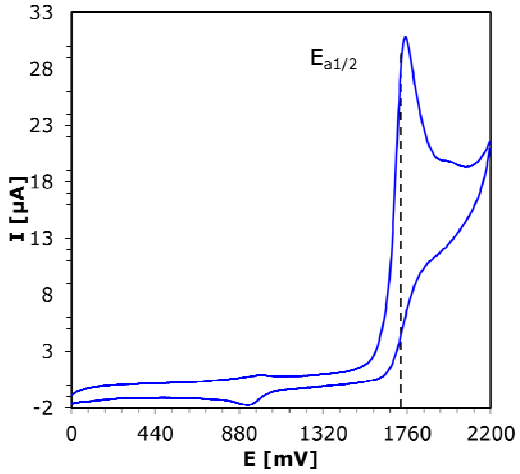


Figure S15: Cyclic voltammogram curves of the B1A oxidation in acetonitrile.

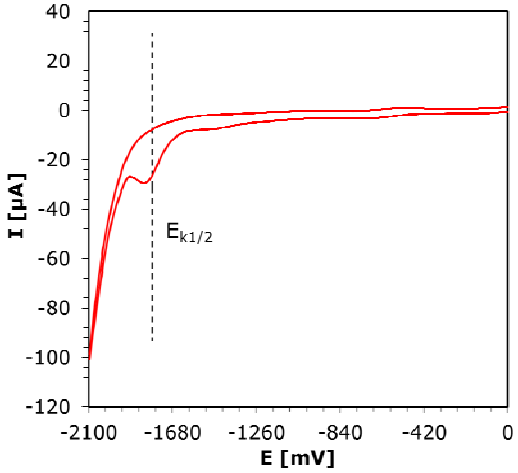


Figure S16: Cyclic voltammogram curves of the B1A reduction in acetonitrile.

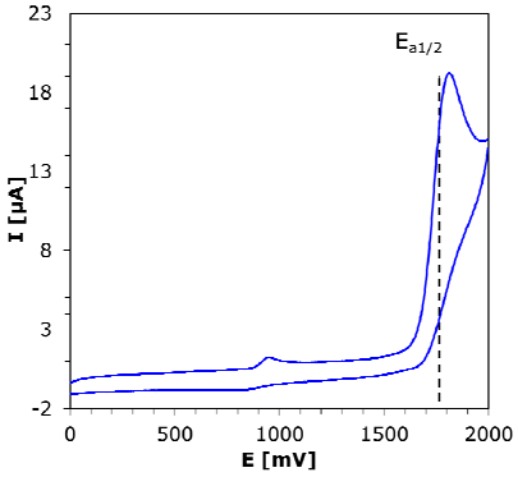


Figure S17: Cyclic voltammogram curves of the B2A oxidation in acetonitrile.

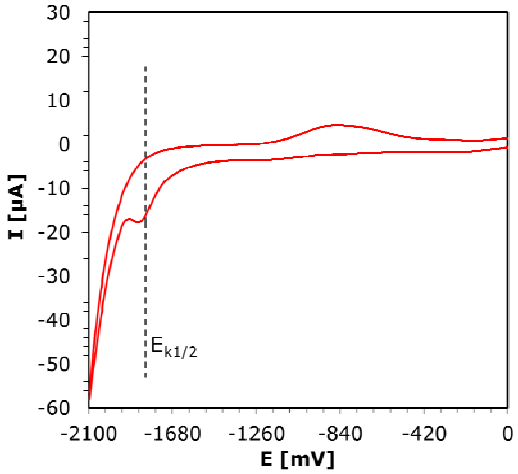


Figure S18: Cyclic voltammogram curves of the B2A reduction in acetonitrile.

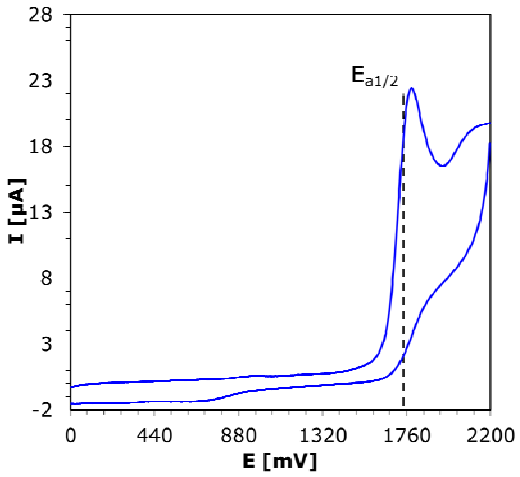


Figure S19: Cyclic voltammogram curves of the B3A oxidation in acetonitrile.

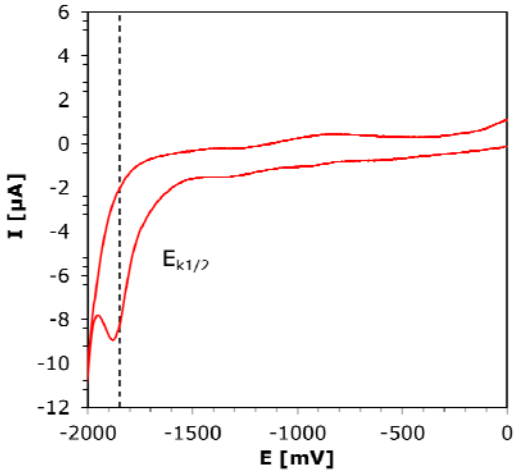


Figure S20: Cyclic voltammogram curves of the B3A reduction in acetonitrile.

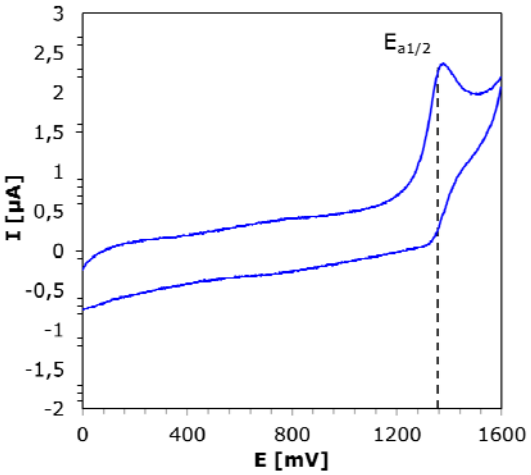


Figure S21: Cyclic voltammogram curves of the B4A oxidation in acetonitrile.

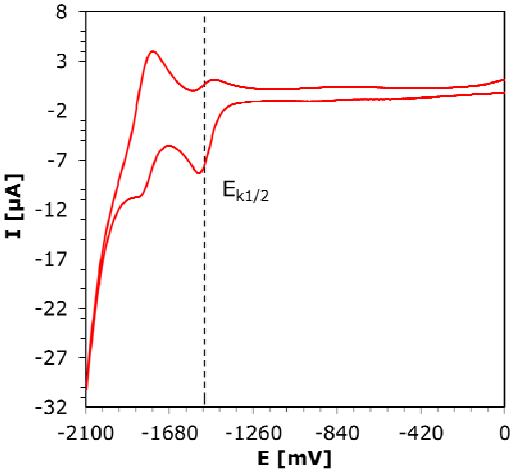


Figure S22: Cyclic voltammogram curves of the B4A reduction in acetonitrile.

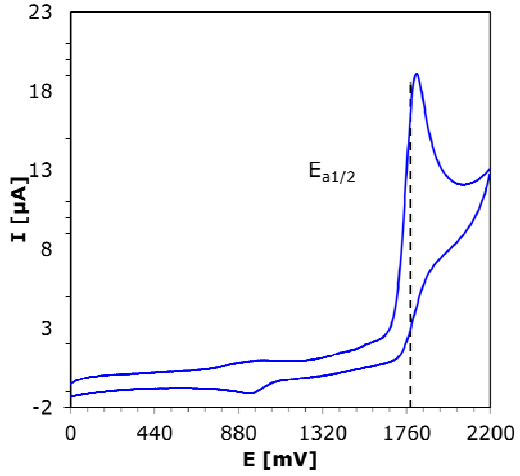


Figure S23: Cyclic voltammogram curves of the B5A oxidation in acetonitrile.

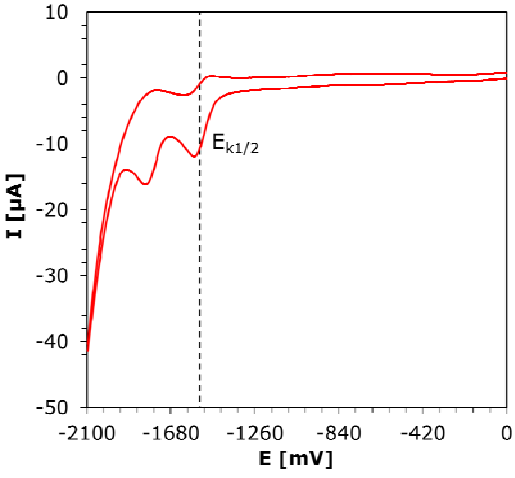


Figure S24: Cyclic voltammogram curves of the B5A reduction in acetonitrile.

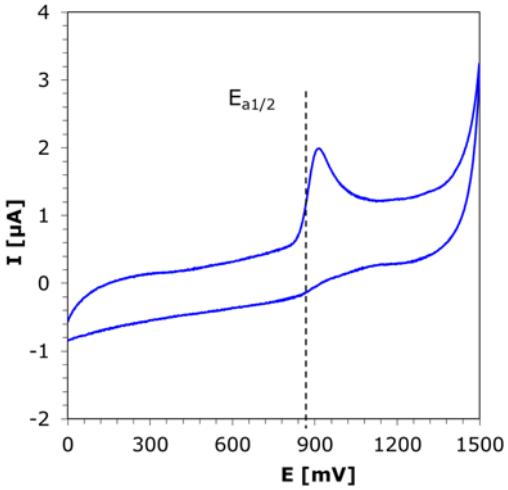


Figure S25: Cyclic voltammogram curves of the B6A oxidation in acetonitrile.

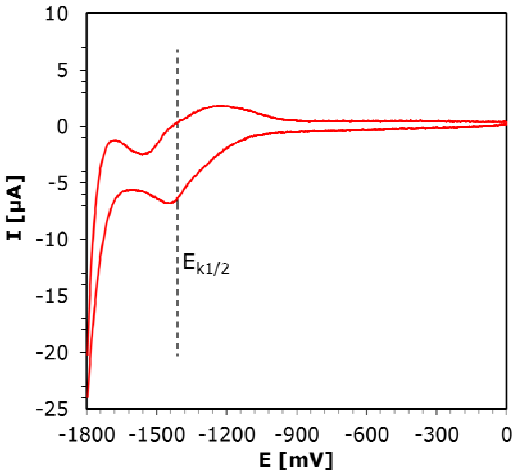


Figure S26: Cyclic voltammogram curves of the B6A reduction in acetonitrile.

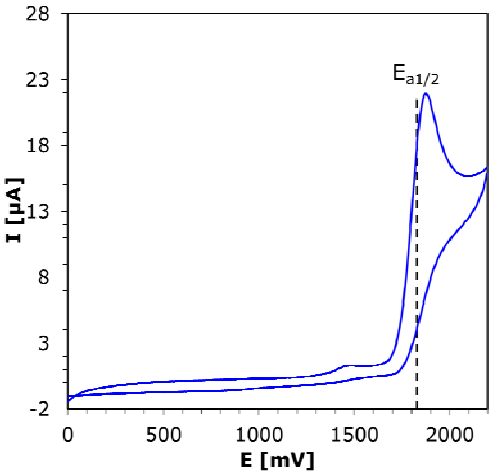


Figure S27: Cyclic voltammogram curves of the B7A oxidation in acetonitrile.

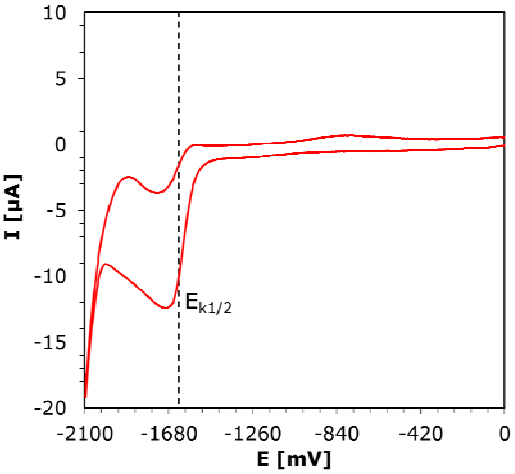


Figure S28: Cyclic voltammogram curves of the B7A reduction in acetonitrile.

Emission and excitation spectra for the determination of the excited singlet state energy for investigated of 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives in acetonitrile.

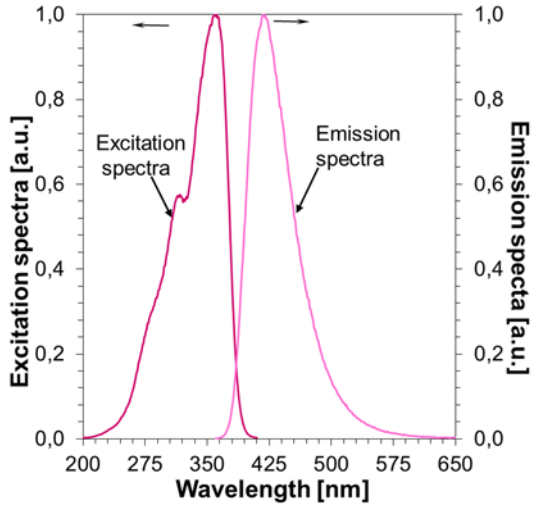


Figure S29: Emission and excitation spectra for the determination of the excited singlet state energy for B1 derivative.

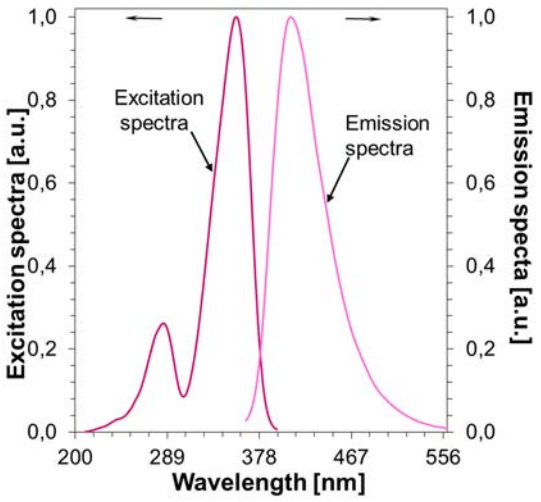


Figure S30: Emission and excitation spectra for the determination of the excited singlet state energy for B1A derivative.

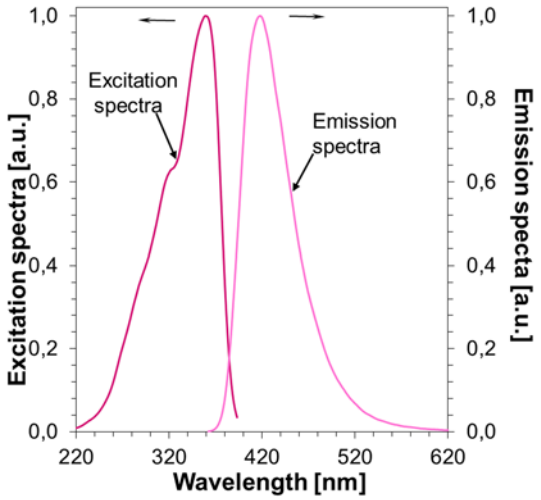


Figure S31: Emission and excitation spectra for the determination of the excited singlet state energy for B2 derivative.

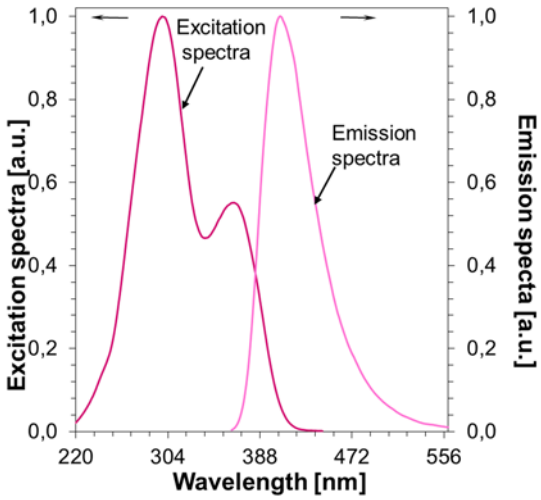


Figure S32: Emission and excitation spectra for the determination of the excited singlet state energy for B2A derivative.

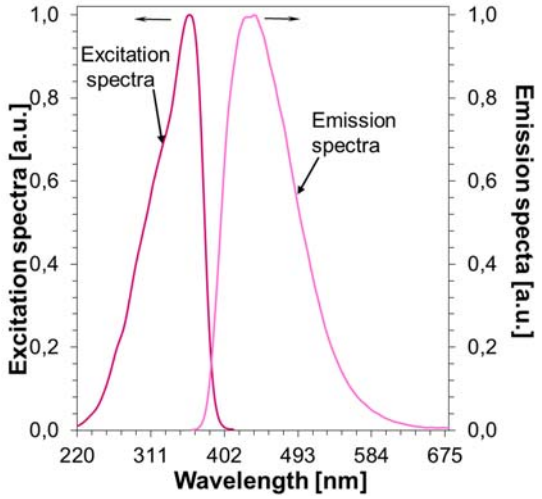


Figure S33: Emission and excitation spectra for the determination of the excited singlet state energy for B3 derivative.

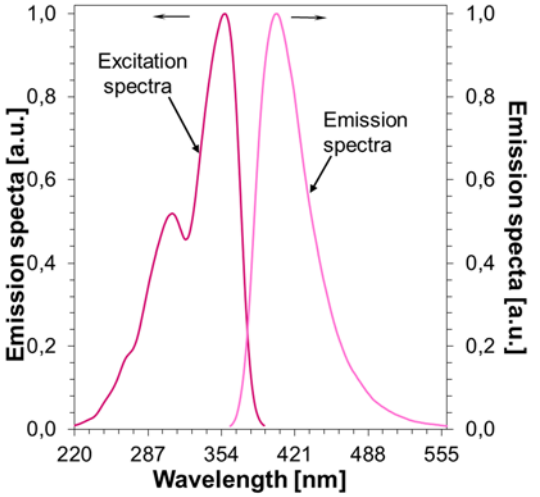


Figure S34: Emission and excitation spectra for the determination of the excited singlet state energy for B3A derivative.

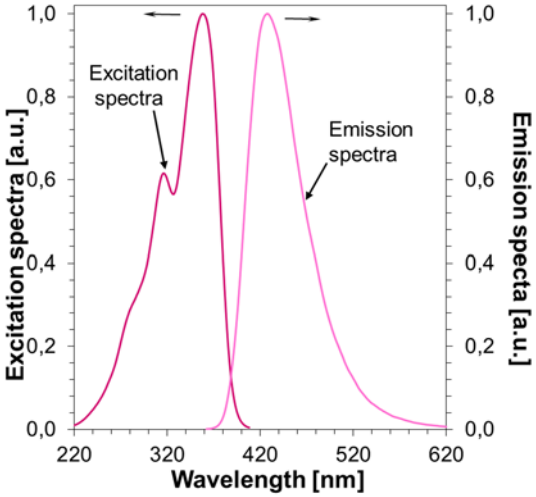


Figure S35: Emission and excitation spectra for the determination of the excited singlet state energy for B4 derivative.

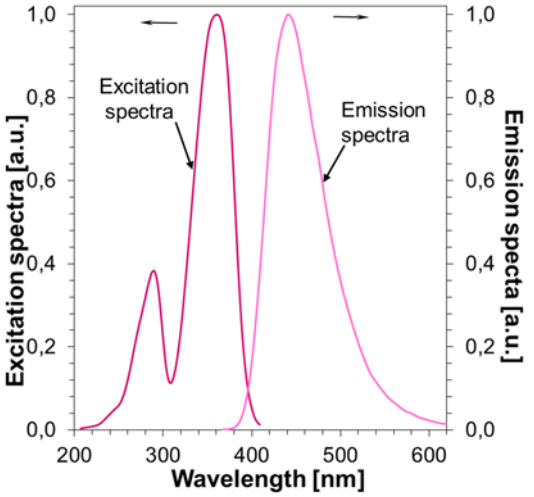


Figure S36: Emission and excitation spectra for the determination of the excited singlet state energy for B4A derivative.

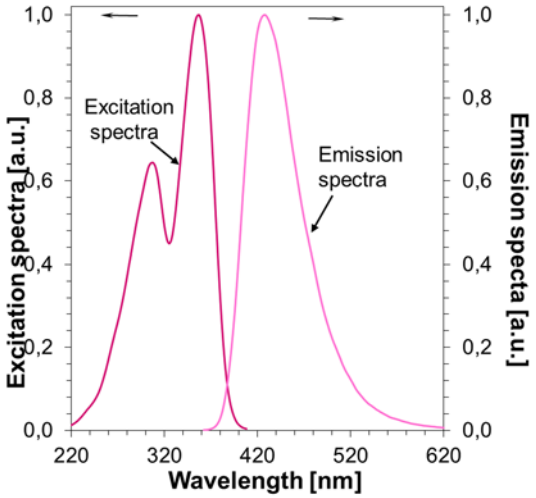


Figure S37: Emission and excitation spectra for the determination of the excited singlet state energy for B5 derivative.

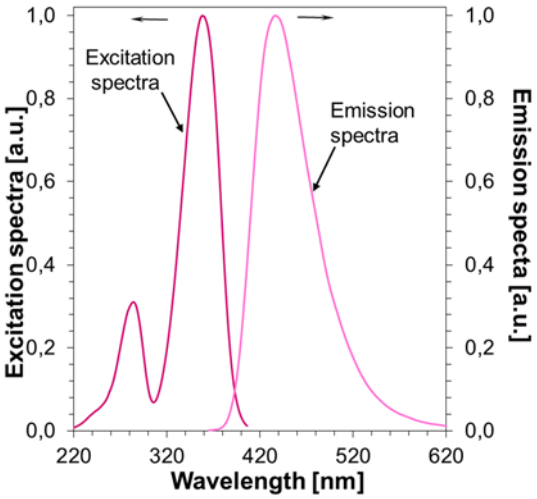


Figure S38: Emission and excitation spectra for the determination of the excited singlet state energy for B5A derivative.

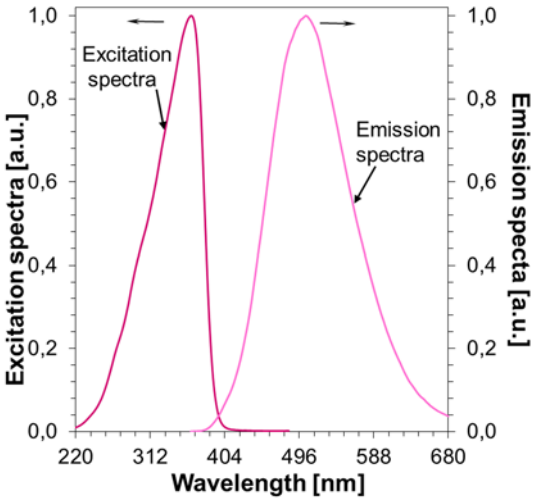


Figure S39: Emission and excitation spectra for the determination of the excited singlet state energy for B6 derivative.

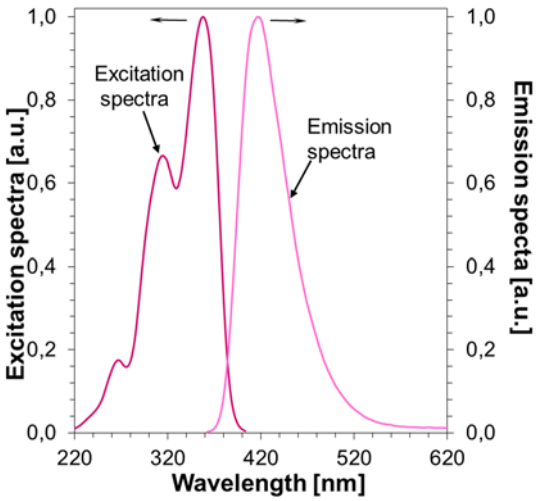


Figure S40: Emission and excitation spectra for the determination of the excited singlet state energy for B6A derivative.

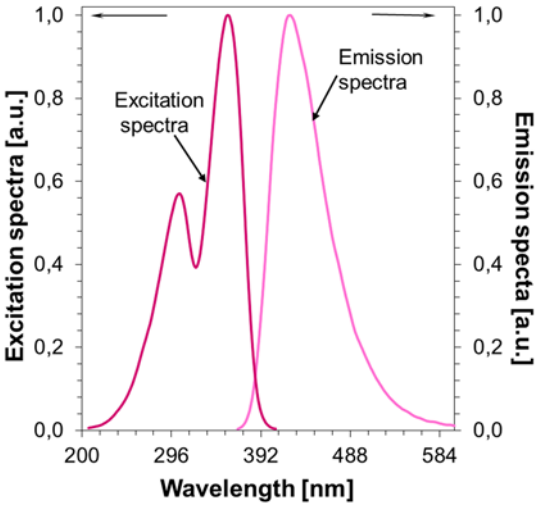


Figure S41: Emission and excitation spectra for the determination of the excited singlet state energy for B7 derivative.

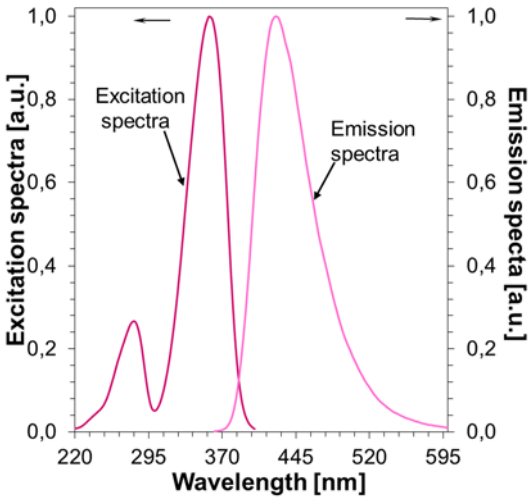
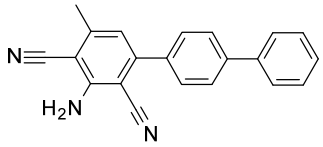
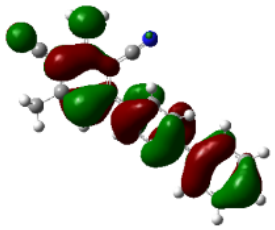
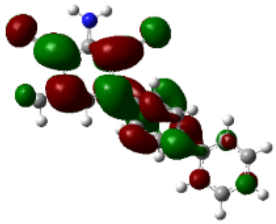
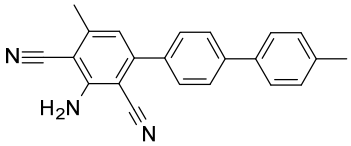
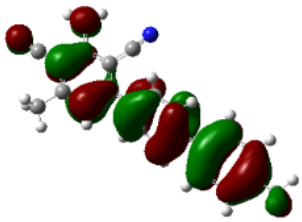
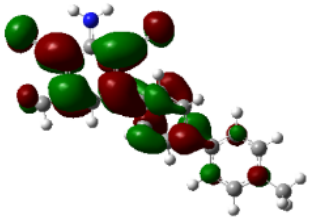
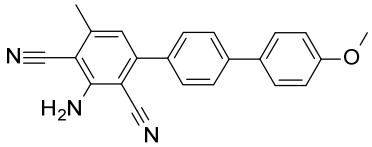
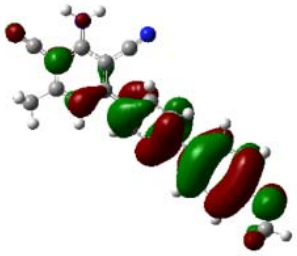
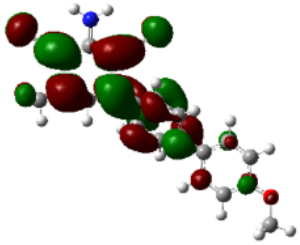
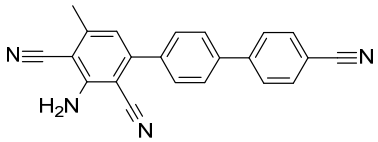
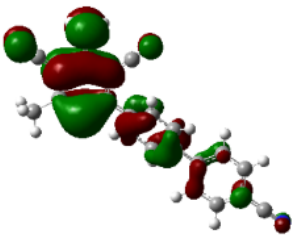
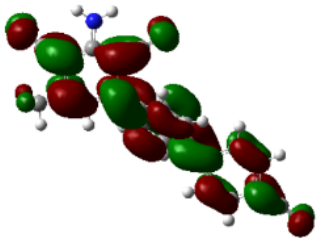
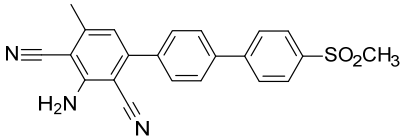
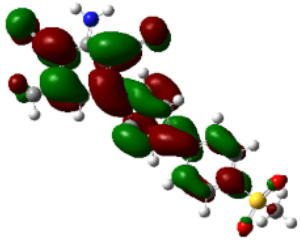


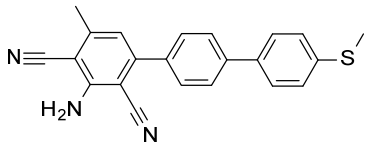
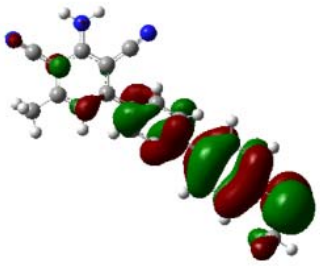
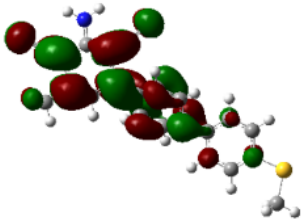
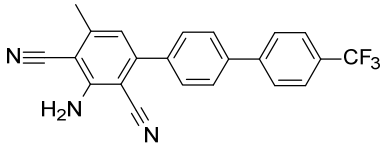
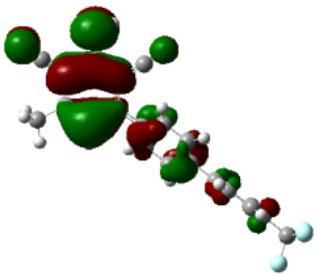
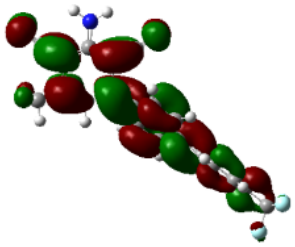
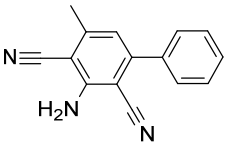
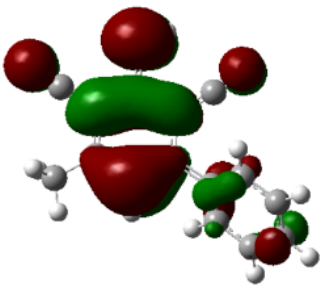
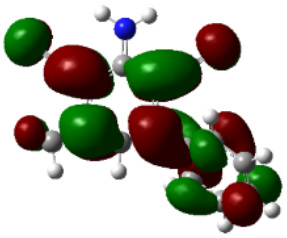
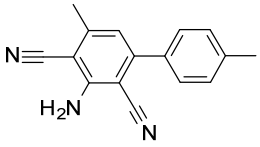
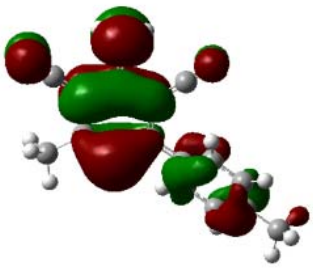
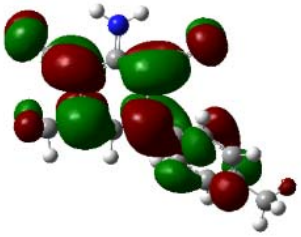
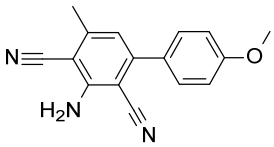
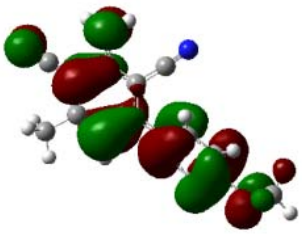
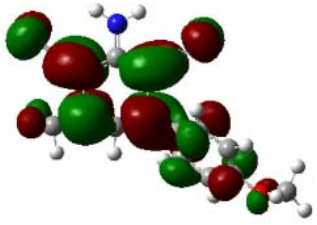
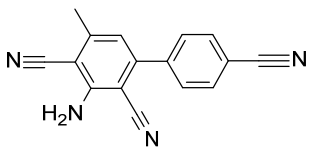
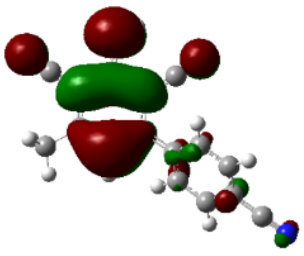
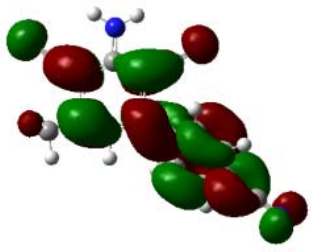
Figure S42: Emission and excitation spectra for the determination of the excited singlet state energy for B7A derivative.

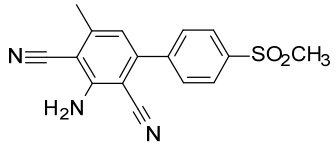
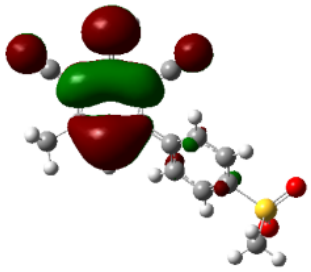
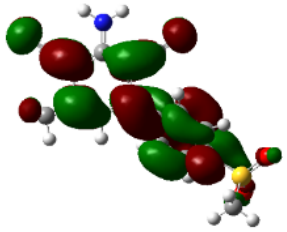
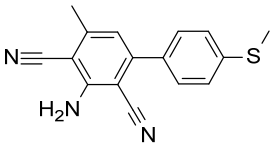
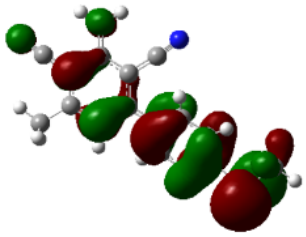
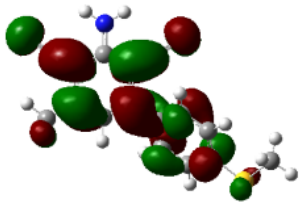
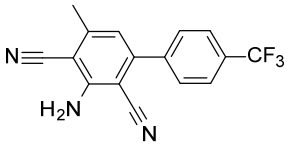
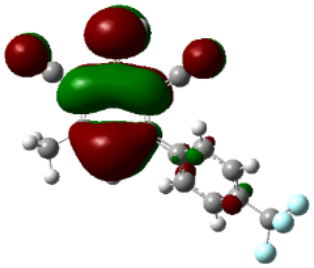
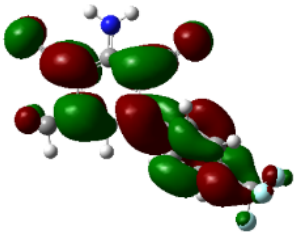
catalysts

MDPI

The optimized structures and HOMO and LUMO orbitals of investigated 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives free molecules determined with the use of uB3LYP/6-31G* level of theory

Compound	HOMO	LUMO
B1  *2-amino-4-methyl-6-(4 phenylphenyl)benzene-1,3-dicarbonitrile*		
B2  *2-amino-4-[4-(4-methylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*		
B3  *2-amino-4-[4-(4-methoxyphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*		
B4  *2-amino-4-[4-(4-cyanophenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*		
B5  *2-amino-4-[4-(4-methylsulfonylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*		

B6  *2-amino-4-[4-(4-methylsulfanylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile*		
B7  *2-amino-4-methyl-6-[4-[4-(trifluoromethyl)phenyl]phenyl]benzene-1,3-dicarbonitrile*		
B1A  *2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile*		
B2A  *2-amino-4-(4-methylphenyl)-6-methyl-benzene-1,3-dicarbonitrile*		
B3A  *2-amino-4-(4-methoxyphenyl)-6-methyl-benzene-1,3-dicarbonitrile*		
B4A  *2-amino-4-(4-cyanophenyl)-6-methyl-benzene-1,3-dicarbonitrile*		

B5A  *2-amino-4-methyl-6-(4-methylsulfonylphenyl)benzene-1,3-dicarbonitrile*		
B6A  *2-amino-4-methyl-6-(4-methylsulfanylphenyl)benzene-1,3-dicarbonitrile*		
B7A  *2-amino-4-methyl-6-[4-(trifluoromethyl)phenyl]benzene-1,3-*		

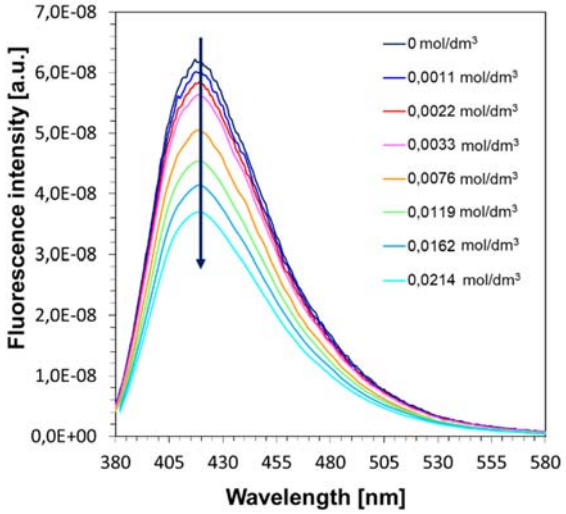


Figure S43: Fluorescence quenching of B1.

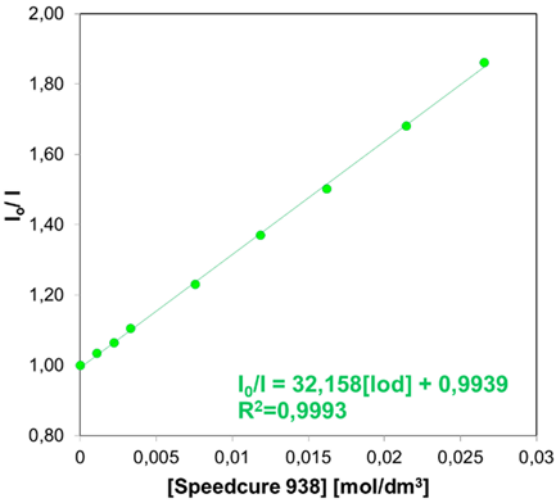


Figure S44: Stern-Volmer treatment for the B1/Iod fluorescence quenching.

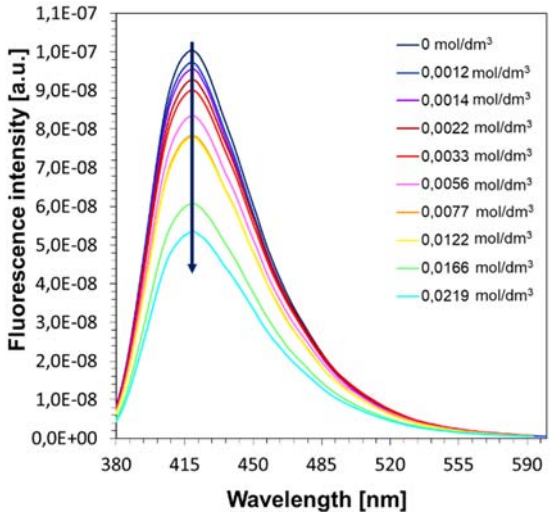


Figure S45: Fluorescence quenching of B2.

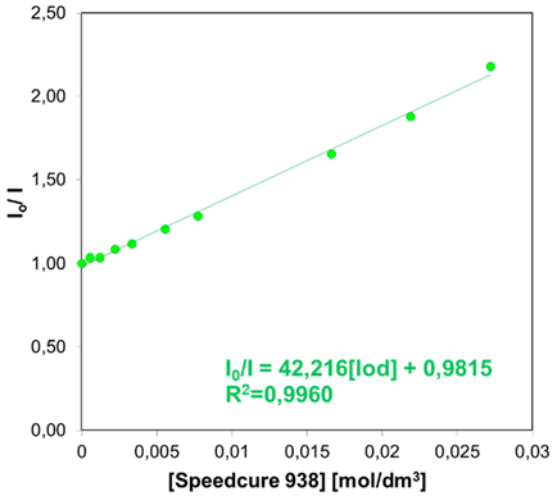


Figure S46: Stern-Volmer treatment for the B2/Iod fluorescence quenching.

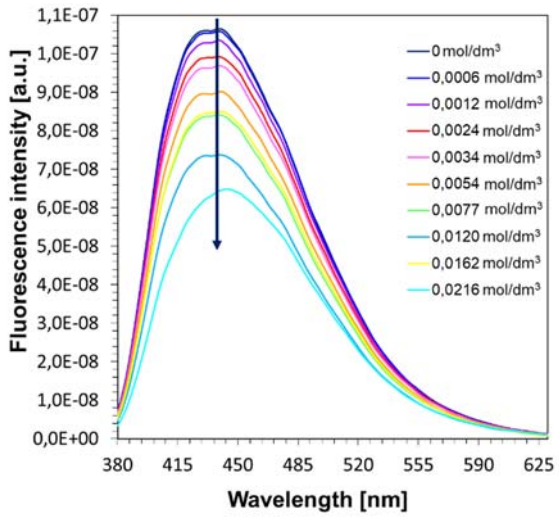


Figure S47: Fluorescence quenching of B3.

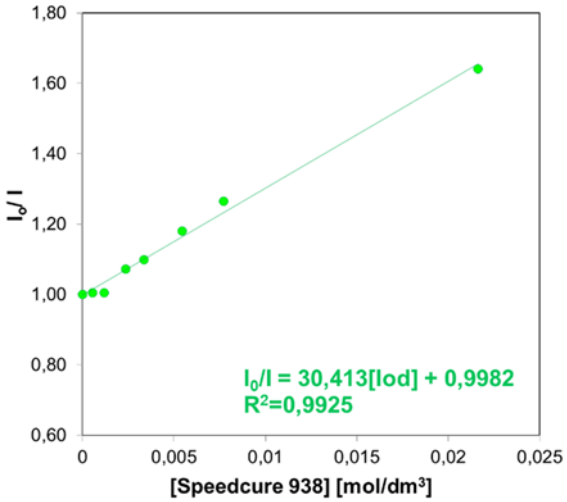


Figure S48: Stern-Volmer treatment for the B3/Iod fluorescence quenching.

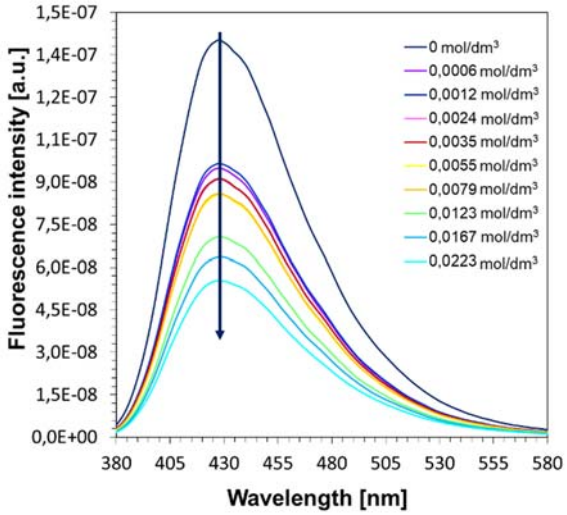


Figure S49: Fluorescence quenching of B4.

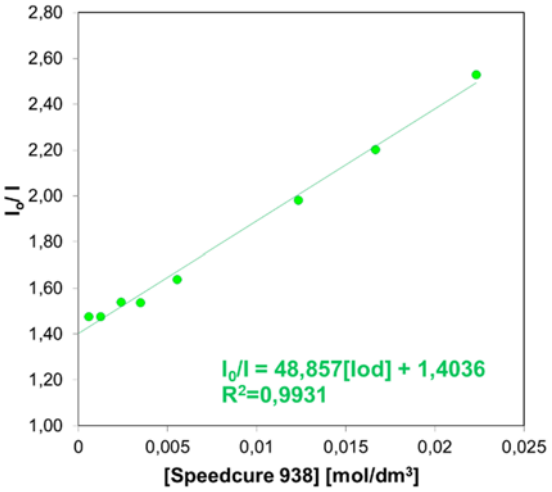


Figure S50: Stern-Volmer treatment for the B4/Iod fluorescence quenching.

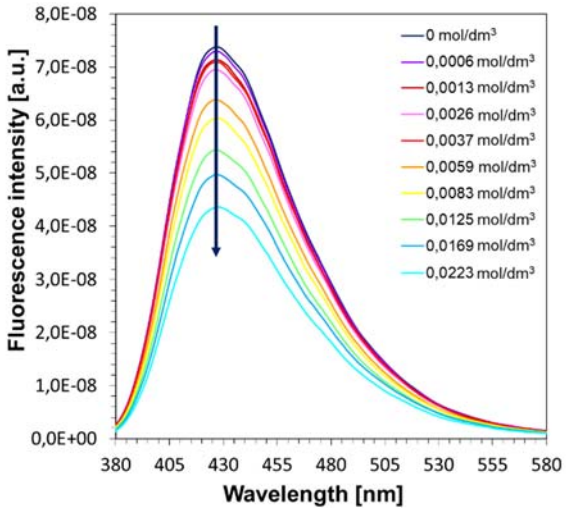


Figure S51: Fluorescence quenching of B5.

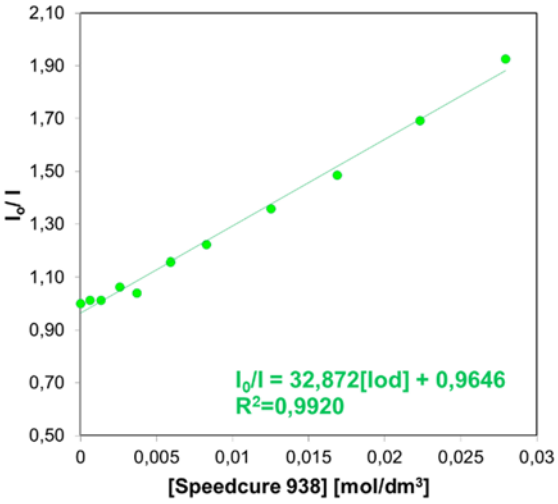


Figure S52: Stern-Volmer treatment for the B5/Iod fluorescence quenching.

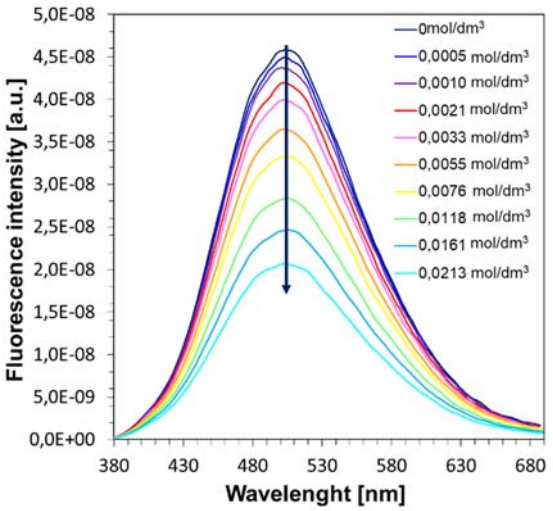


Figure S53: Fluorescence quenching of B6.

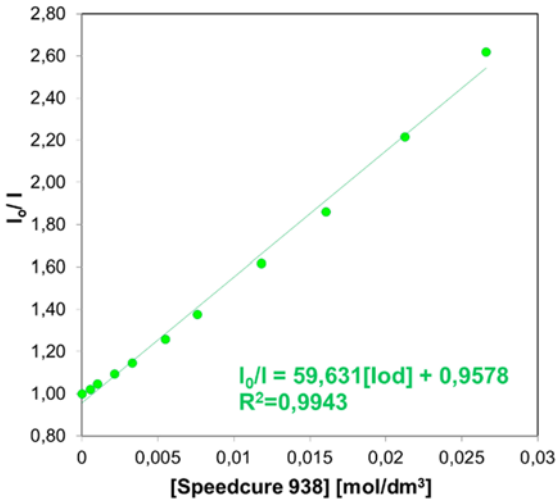


Figure S54: Stern-Volmer treatment for the B6/Iod fluorescence quenching.

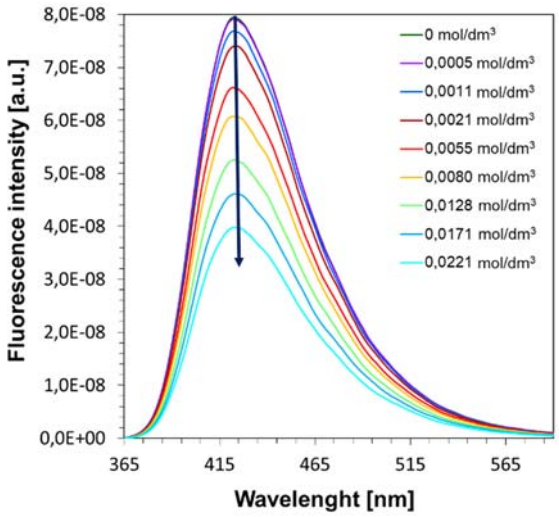


Figure S55: Fluorescence quenching of B7.

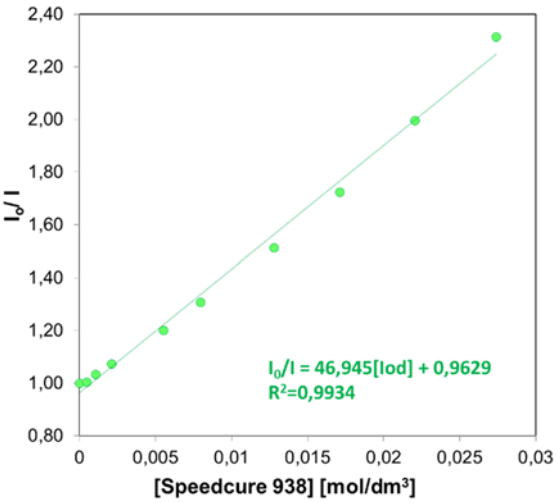


Figure S56: Stern-Volmer treatment for the B7/Iod fluorescence quenching.

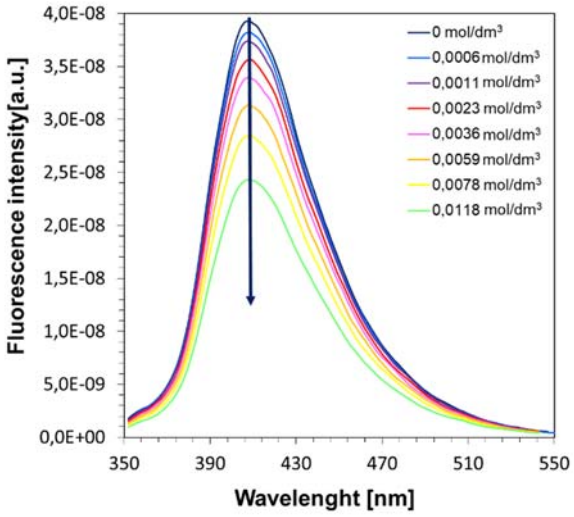


Figure S57: Fluorescence quenching of B1A.

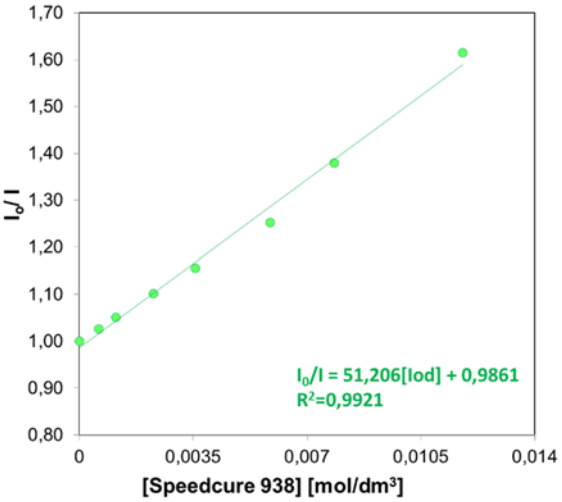


Figure S58: Stern-Volmer treatment for the B1A/Iod fluorescence quenching.

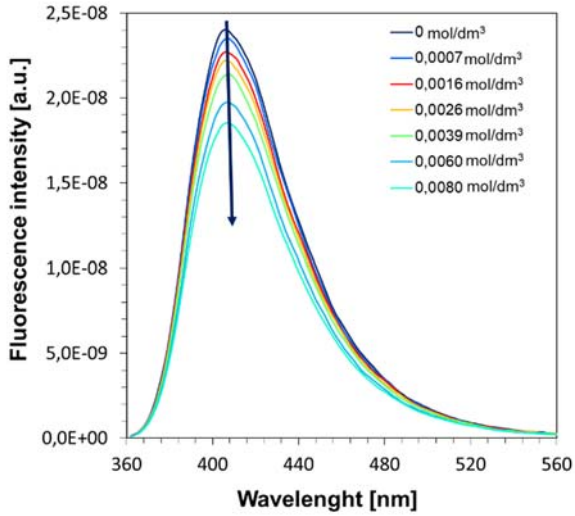


Figure S59: Fluorescence quenching of B2A.

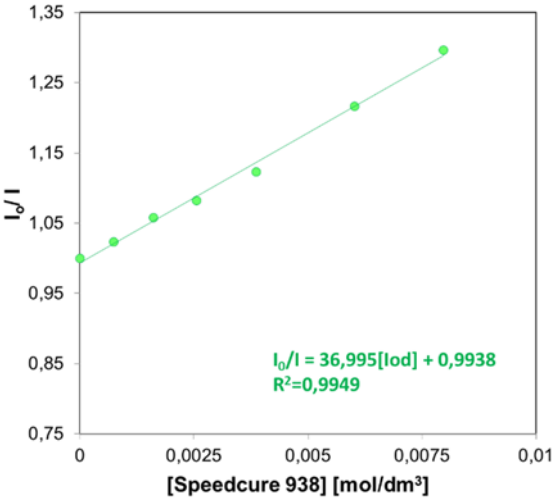


Figure S60: Stern-Volmer treatment for the B2A/Iod fluorescence quenching.

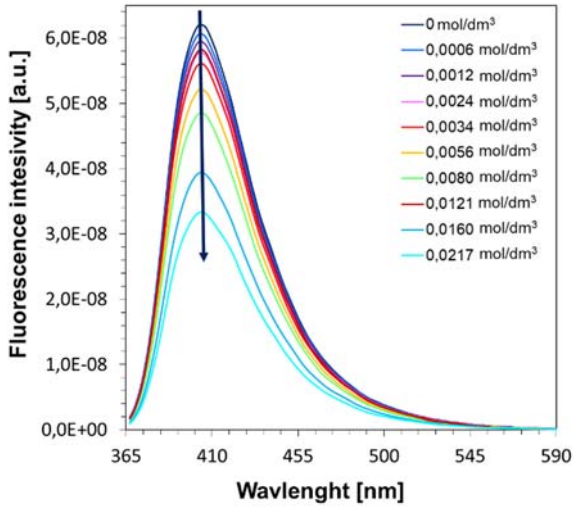


Figure S61: Fluorescence quenching of B3A.

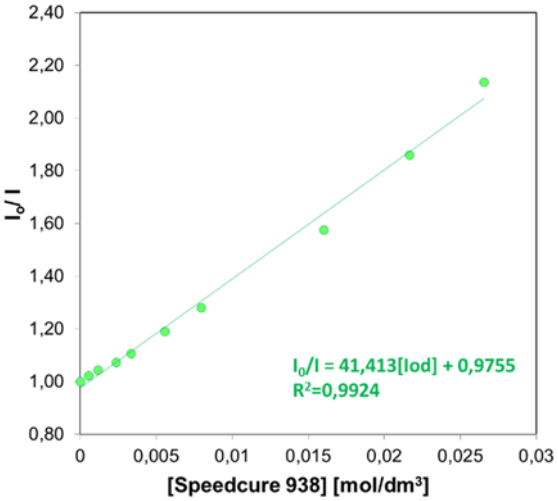


Figure S62: Stern-Volmer treatment for the B3A/Iod fluorescence quenching.

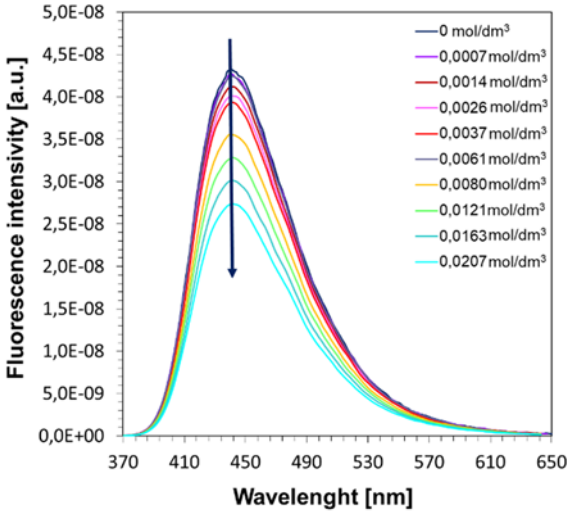


Figure S63: Fluorescence quenching of B4A.

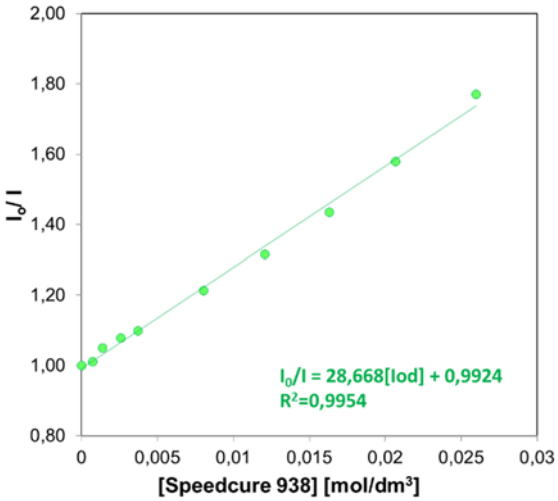


Figure S64: Stern-Volmer treatment for the B4A/Iod fluorescence quenching.

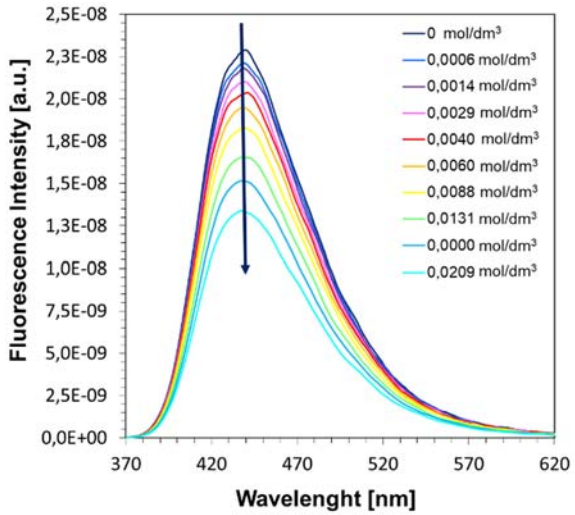


Figure S65: Fluorescence quenching of B5A.

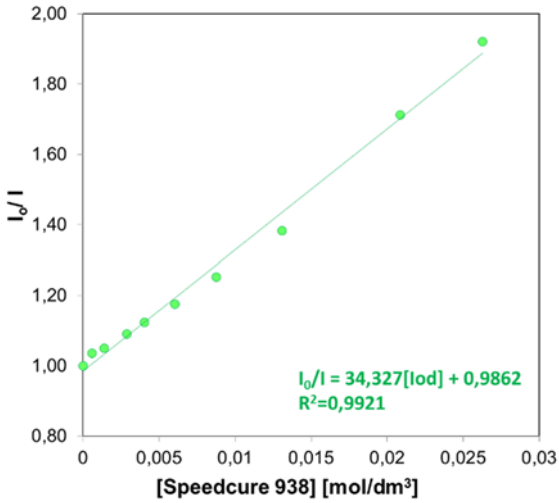


Figure S66: Stern-Volmer treatment for the B5A/Iod fluorescence quenching.

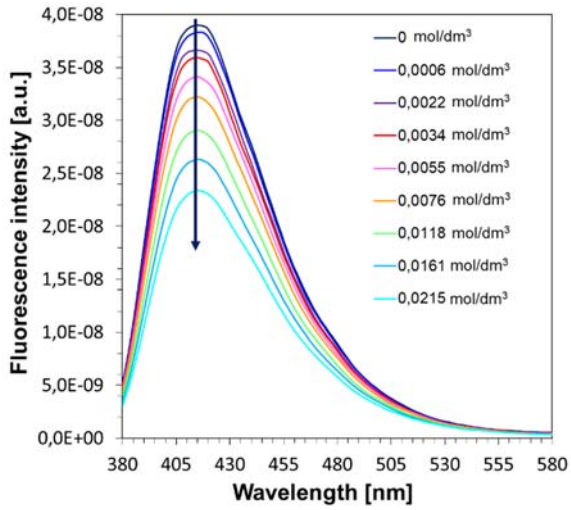


Figure S67: Fluorescence quenching of B6A.

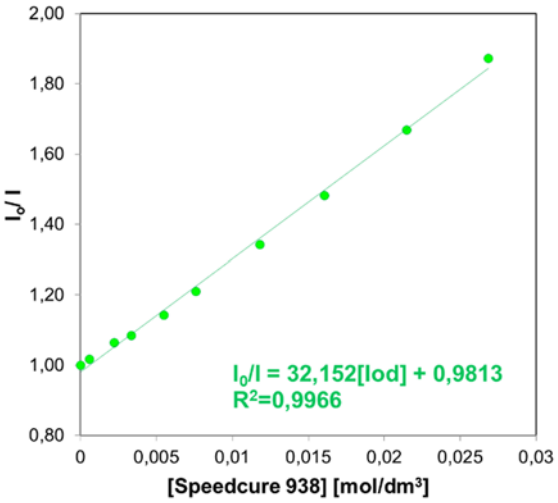


Figure S68: Stern-Volmer treatment for the B6A/Iod fluorescence quenching.

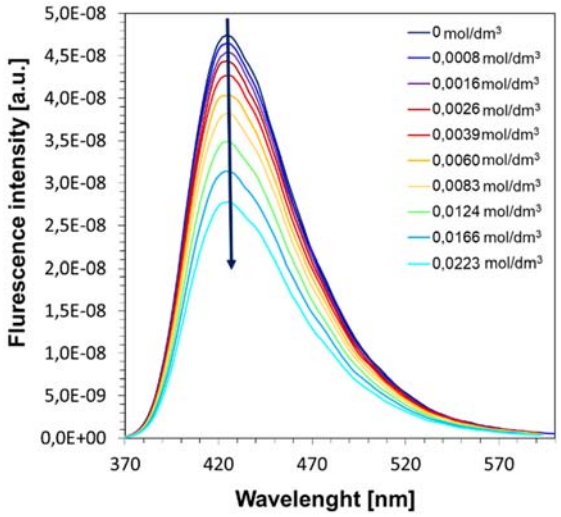


Figure S69: Fluorescence quenching of B7A.

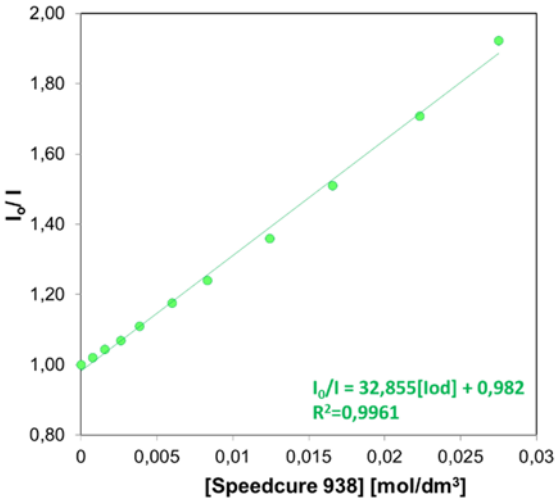


Figure S70: Stern-Volmer treatment for the B7A/Iod fluorescence quenching.

Fluorescence quenching with EDB of investigated 2-amino-4,6-diphenyl-benzene-1,3-dicarbonitrile derivatives together with Stern-Volmer correlation

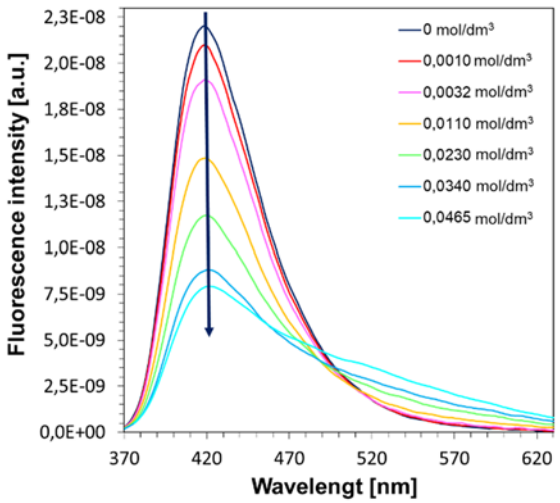


Figure S71: Fluorescence quenching of B1.

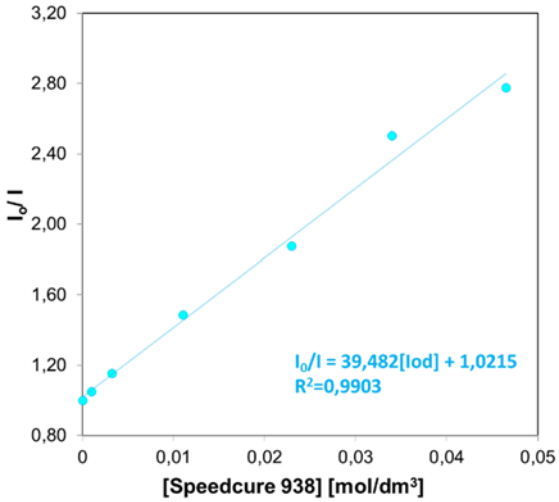


Figure S72: Stern-Volmer treatment for the B1/EDB fluorescence quenching.

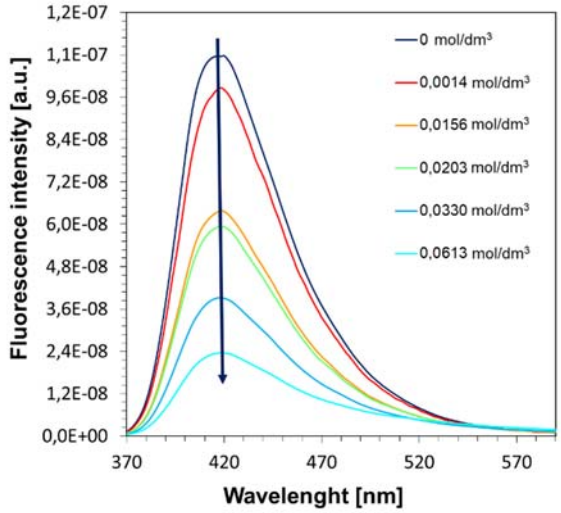


Figure S73: Fluorescence quenching of B2.

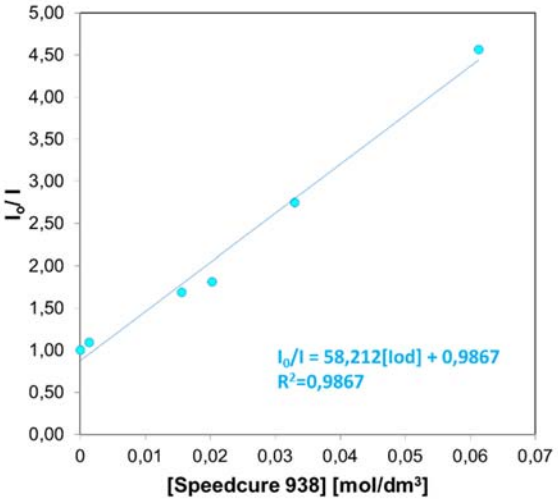


Figure S74: Stern-Volmer treatment for the B2/EDB fluorescence quenching.

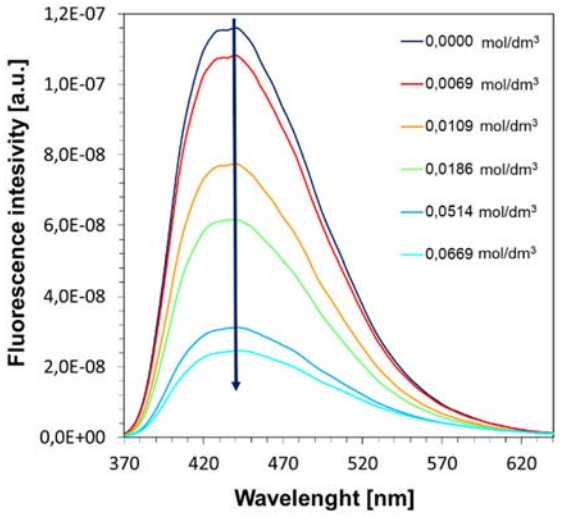


Figure S75: Fluorescence quenching of B3.

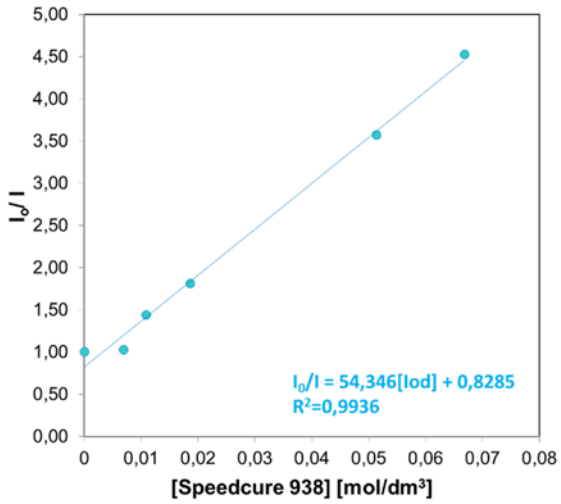


Figure S76: Stern-Volmer treatment for the B3/EDB fluorescence quenching.

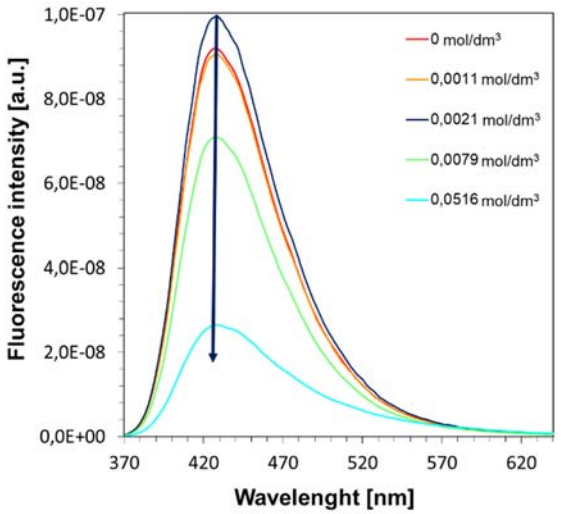


Figure S77: Fluorescence quenching of B4.

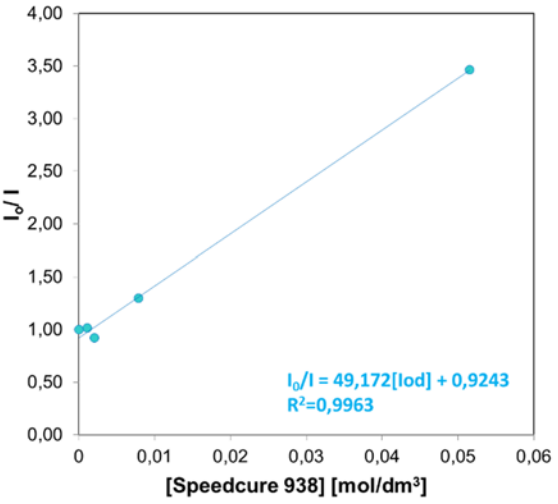


Figure S78: Stern-Volmer treatment for the B4/EDB fluorescence quenching.

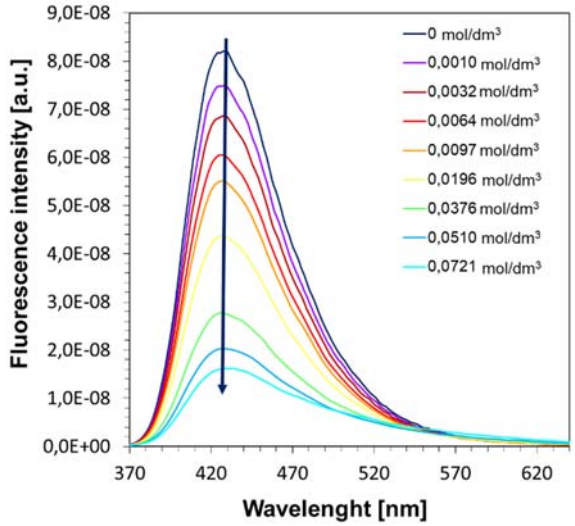


Figure S79: Fluorescence quenching of B5.

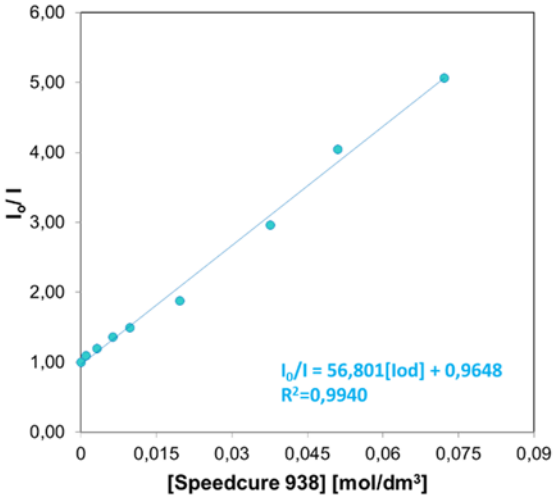


Figure S80: Stern-Volmer treatment for the B5/EDB fluorescence quenching.

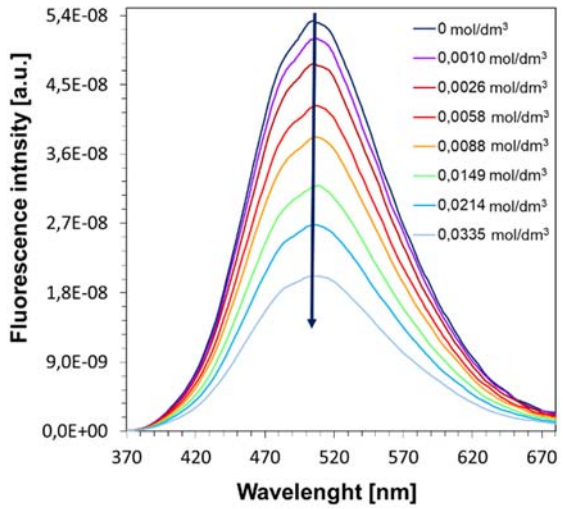


Figure S81: Fluorescence quenching of B6.

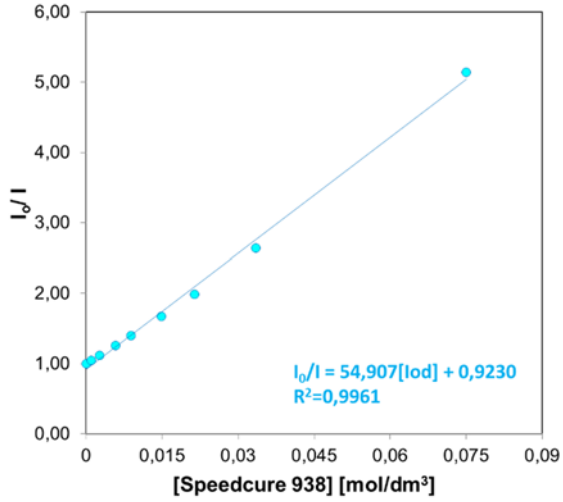


Figure S82: Stern-Volmer treatment for the B6/EDB fluorescence quenching.

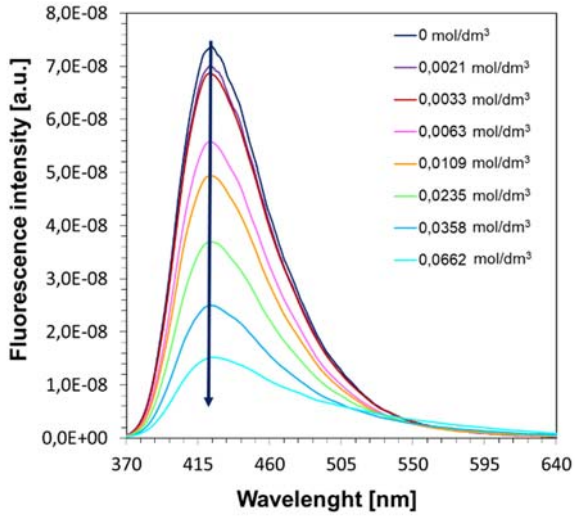


Figure S83: Fluorescence quenching of B7.

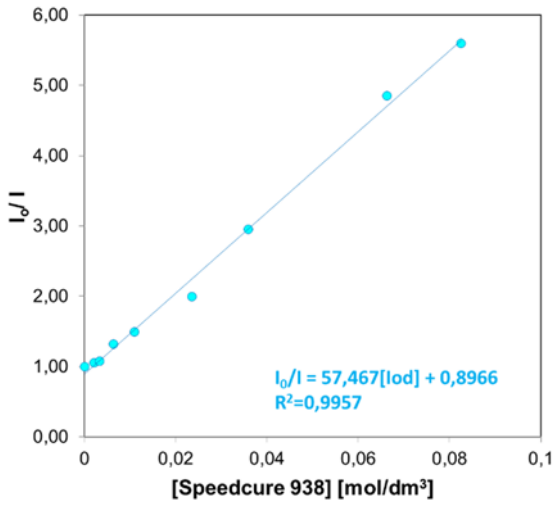


Figure S84: Stern-Volmer treatment for the B7/EDB fluorescence quenching.

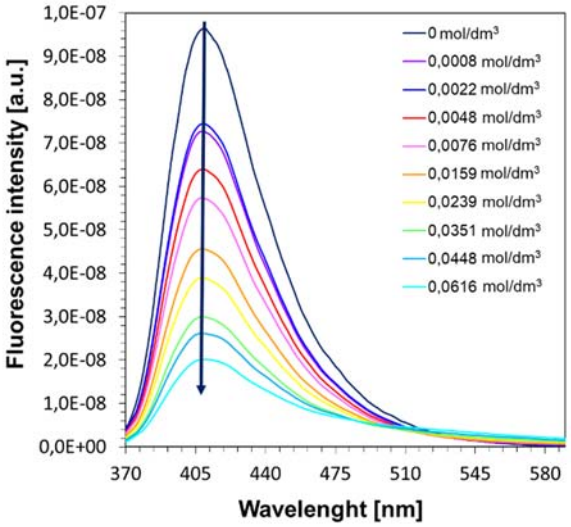


Figure S85: Fluorescence quenching of B1A.

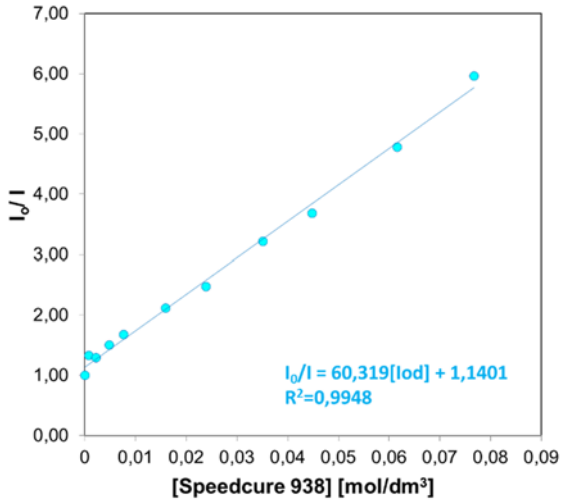


Figure S86: Stern-Volmer treatment for the B1A/EDB fluorescence quenching.

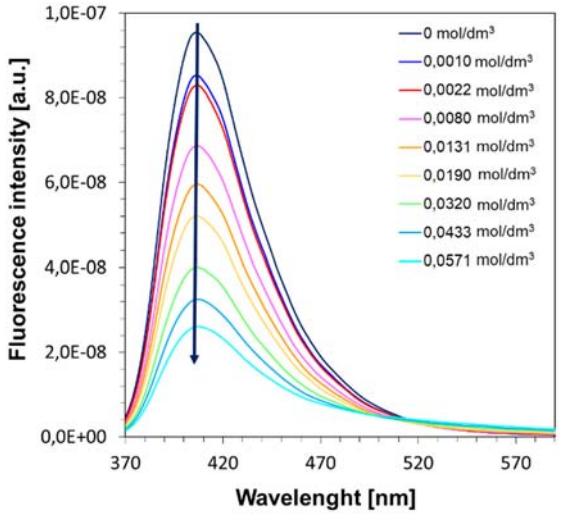


Figure S87: Fluorescence quenching of B2A.

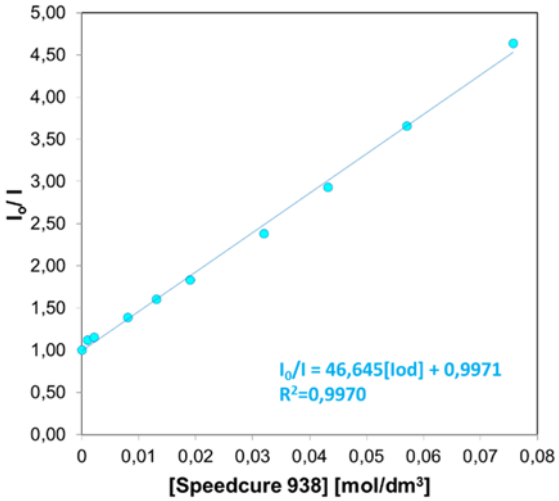


Figure S88: Stern-Volmer treatment for the B2A/EDB fluorescence quenching.

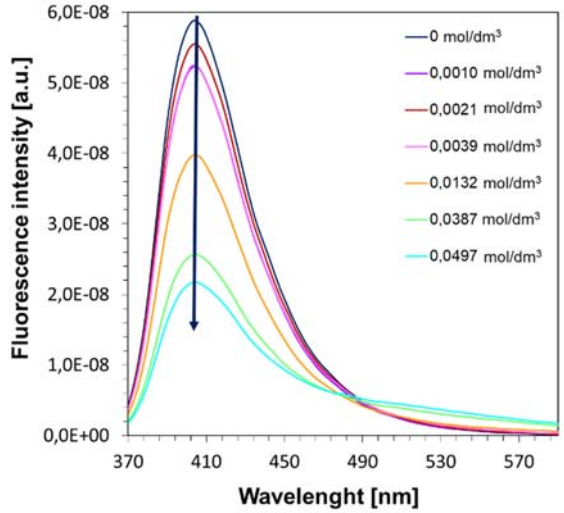


Figure S89: Fluorescence quenching of B3A.

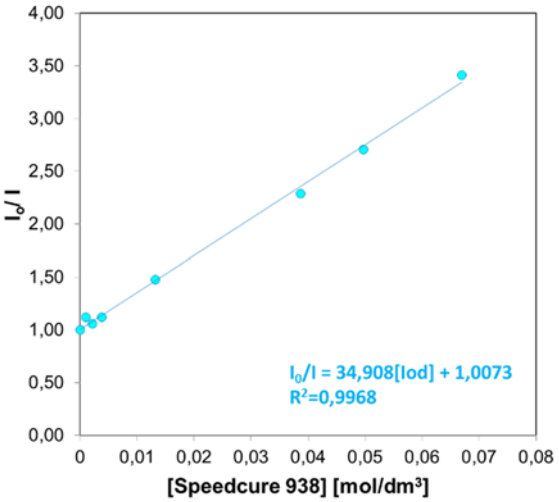


Figure S90: Stern-Volmer treatment for the B3A/EDB fluorescence quenching.

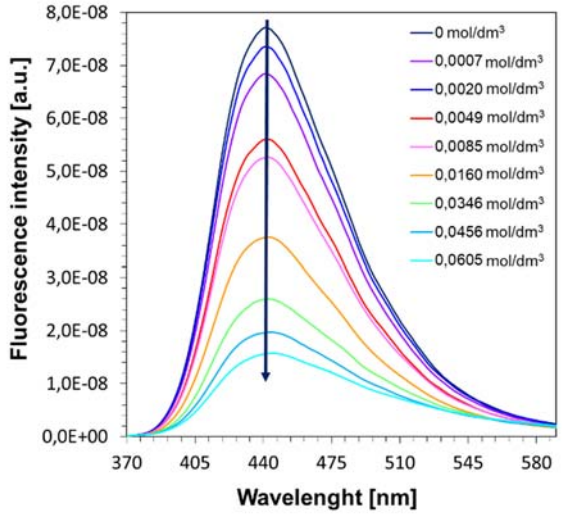


Figure S91: Fluorescence quenching of B4A.

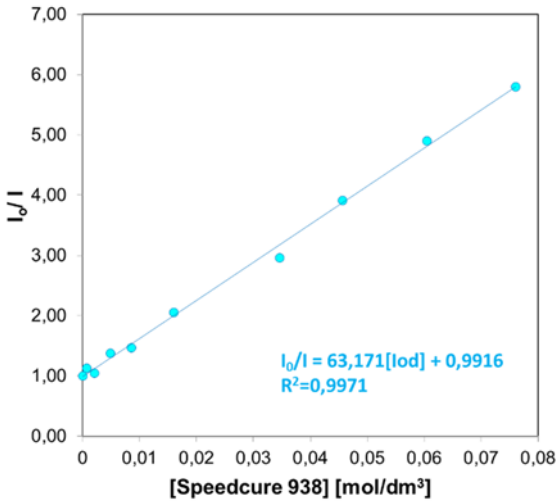


Figure S92: Stern-Volmer treatment for the B4A/EDB fluorescence quenching.

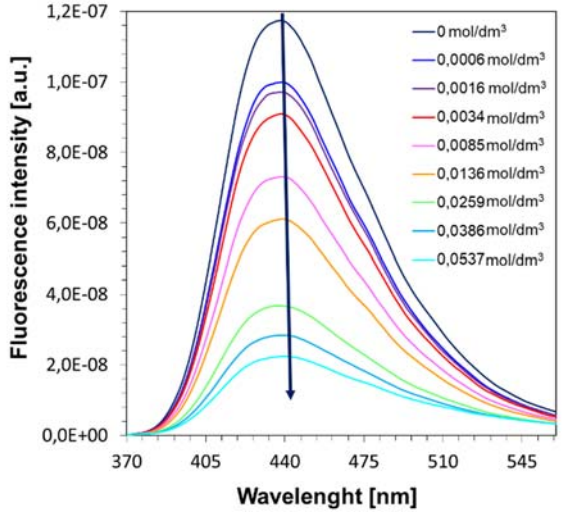


Figure S93: Fluorescence quenching of B5A.

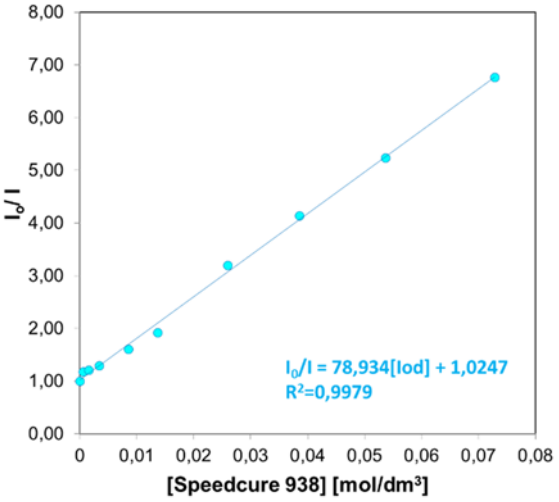


Figure S94: Stern-Volmer treatment for the B5A/EDB fluorescence quenching.

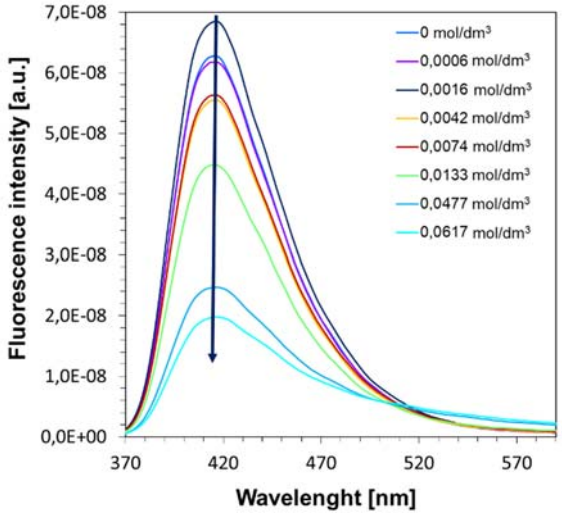


Figure S95: Fluorescence quenching of B6A.

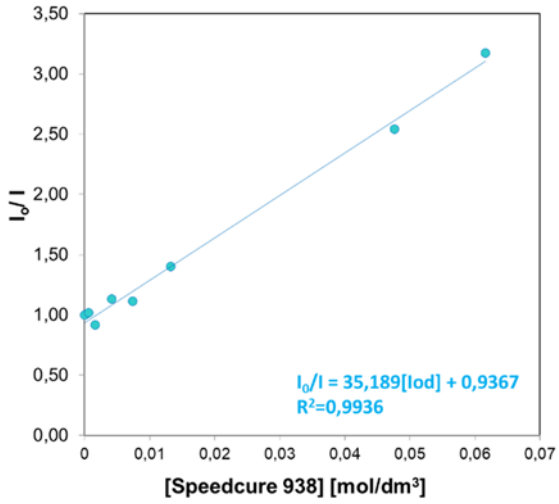


Figure S96: Stern-Volmer treatment for the B6A/EDB fluorescence quenching.

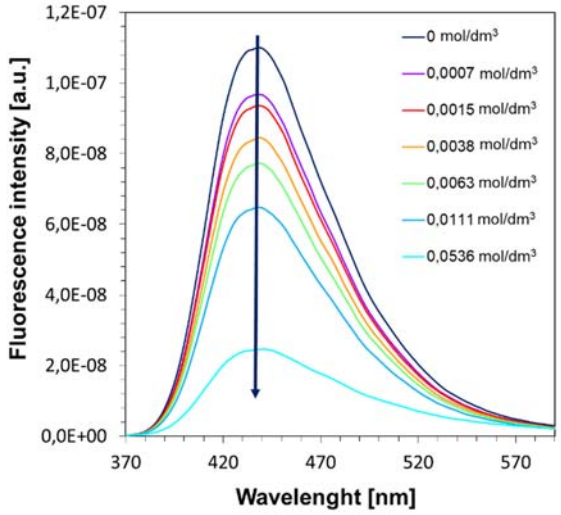


Figure S97: Fluorescence quenching of B7A.

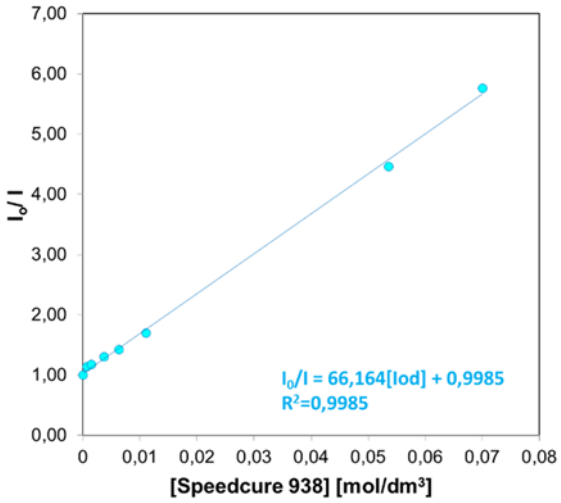


Figure S98: Stern-Volmer treatment for the B7A/EDB fluorescence quenching.

Examples of steady state photolysis upon exposure with LED @365nm for B6 and B6A in acetonitrile

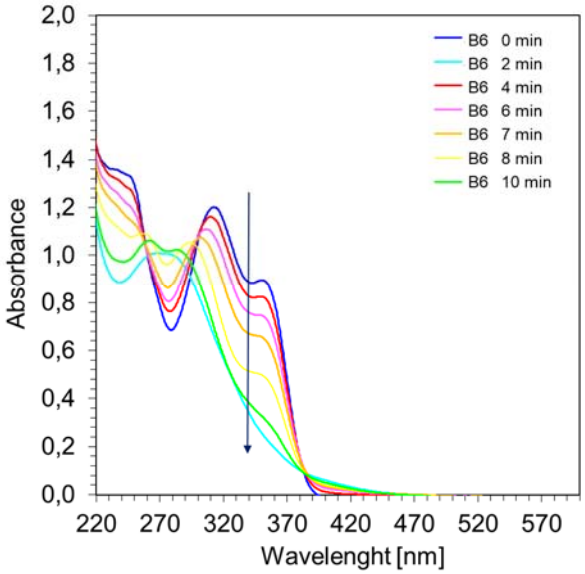


Figure S99: Photolysis of B6 in ACN under 365nm (190mW/cm²).

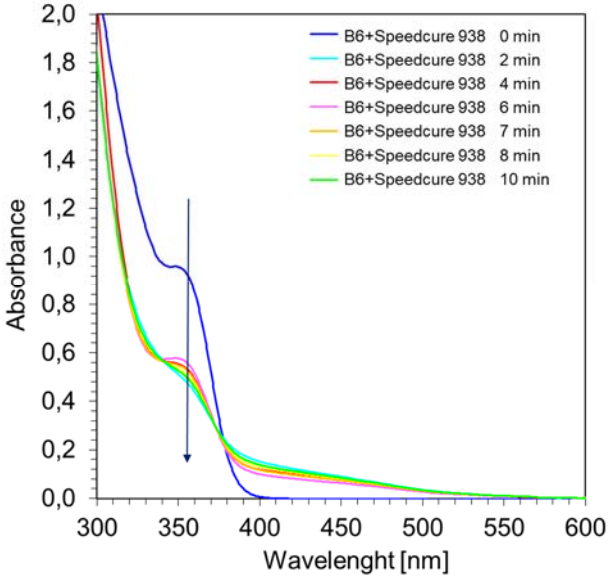


Figure S100: Photolysis of B6 + Speedcure 938 (concentration: $1{,}59 \cdot 10^{-3}$ [mol/dm³]) in ACN under 365nm (190mW/cm²).

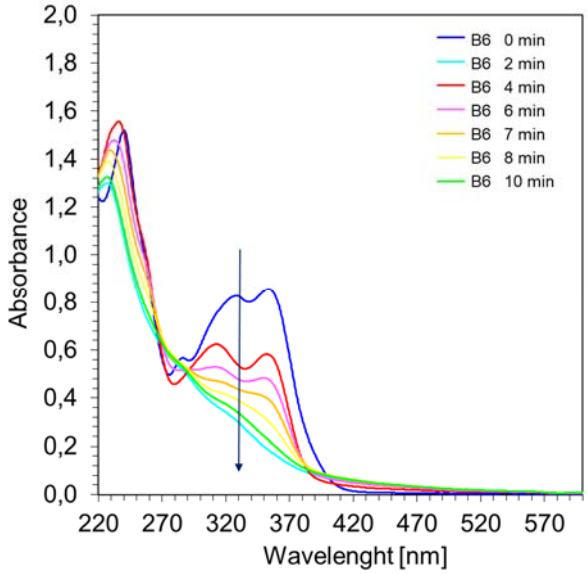


Figure S101: Photolysis of B6A in ACN under 365nm (190mW/cm^2).

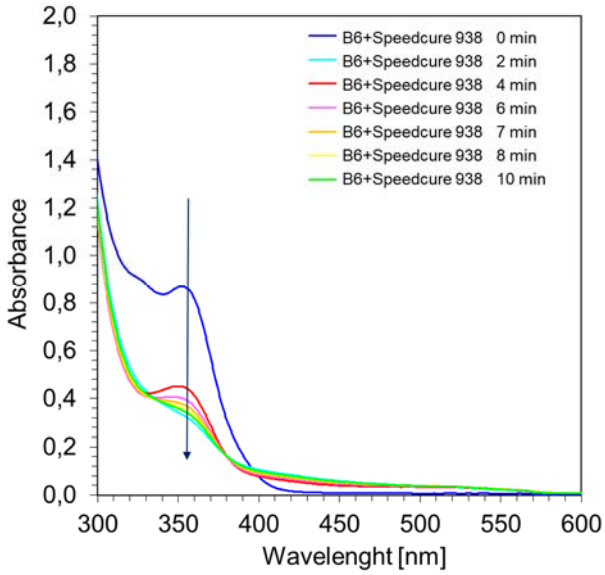


Figure S102: Photolysis of B6A + Speedcure 938 (concentration: 1,59·10^{-3} [mol/dm^3]) in ACN under 365nm (190mW/cm^2).

Photopolymerization profiles of various photopolymerization processes during the formation of interpenetrating polymer networks with the use of photoinitiating system based on Speedcure 938 and 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives in the role of photosensitizers.

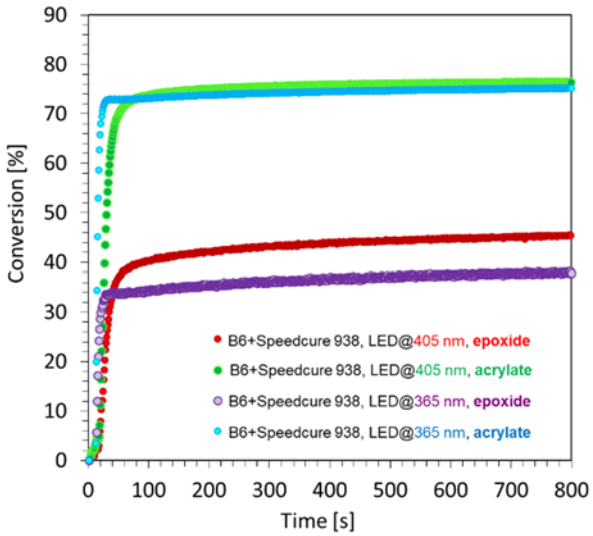


Figure S103: Polymerization profiles carried out in laminate for the system:
CADE/TMPTA (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

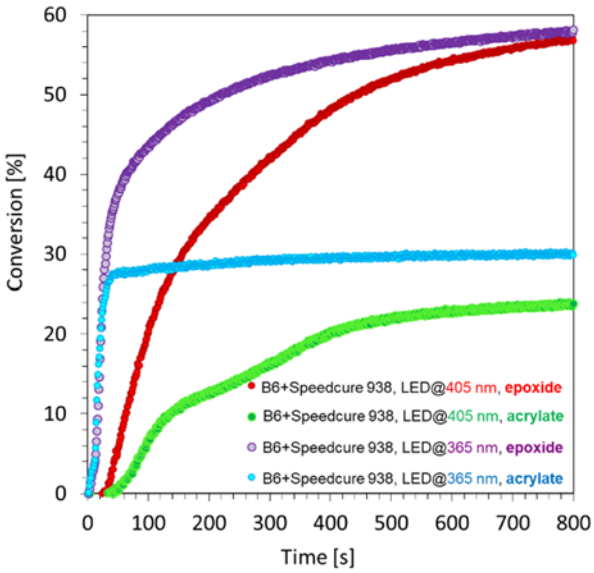


Figure S104: Polymerization profiles carried out in the air for the system:
CADE/TMPTA (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

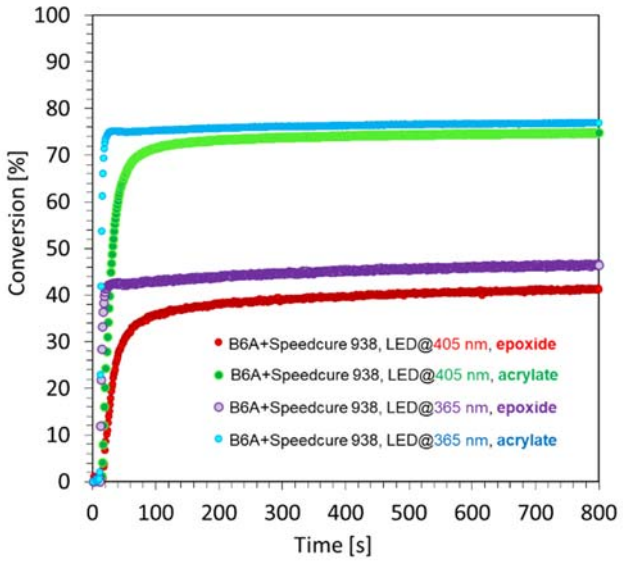


Figure S105: Polymerization profiles carried out in laminate for the system:
CADE/TMPTA (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

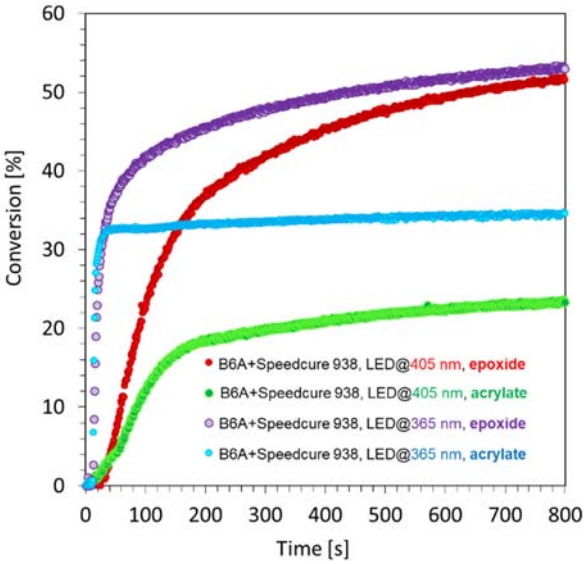


Figure S106: Polymerization profiles carried out in the air:
CADE/TMPTA (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

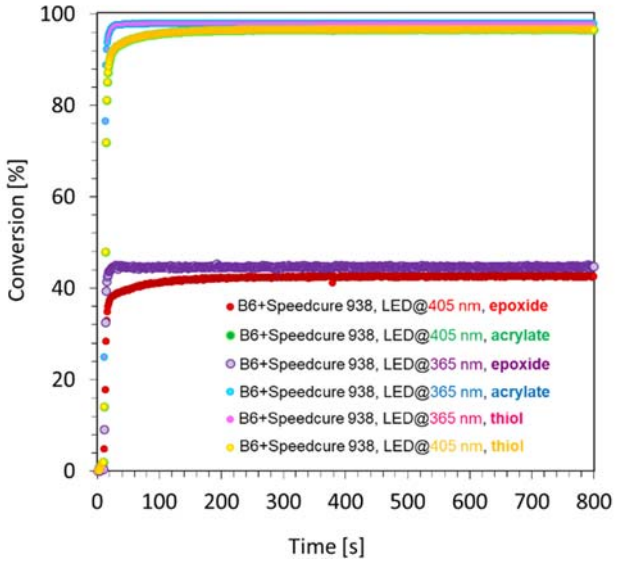


Figure S107: Polymerization profiles carried out in laminate for the system:
CADE/TMPTA/TMPMP (40/40/20 %w/w/w)
+ B6/Iod (0,1/1 %w/w).

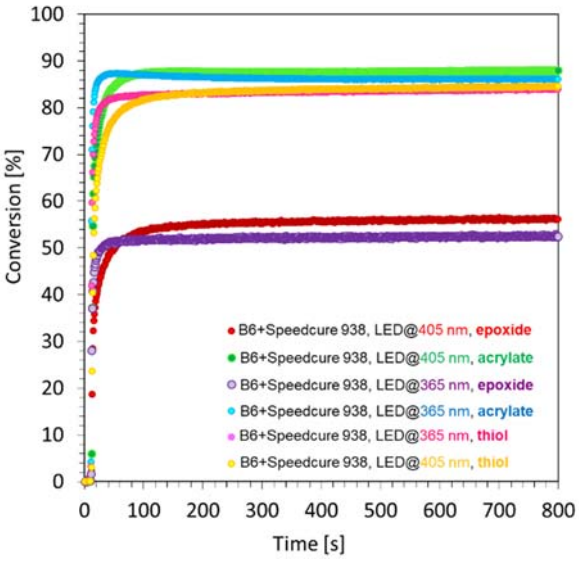


Figure S108: Polymerization profiles carried out in the air:
CADE/TMPTA/ TMPMP (40/40/20 %w/w/w)
+ B6/Iod (0,1/1 %w/w).

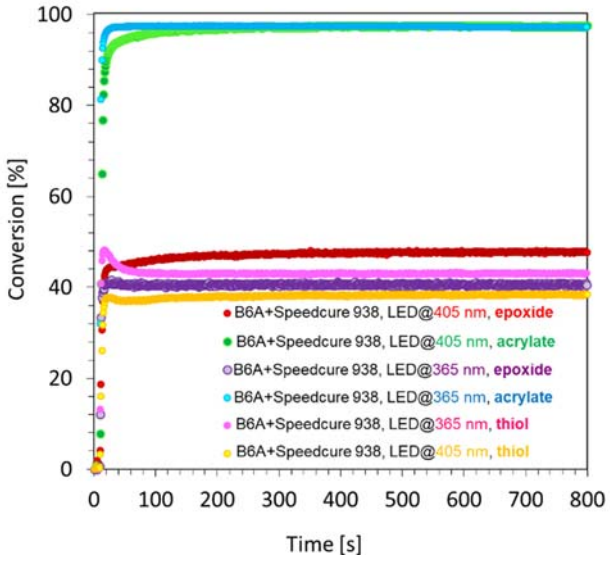


Figure S109: Polymerization profiles carried out in laminate for the system: CADE/TMPTA/TMPMP (40/40/20 %w/w/w) + B6A/Iod (0,1/1 %w/w).

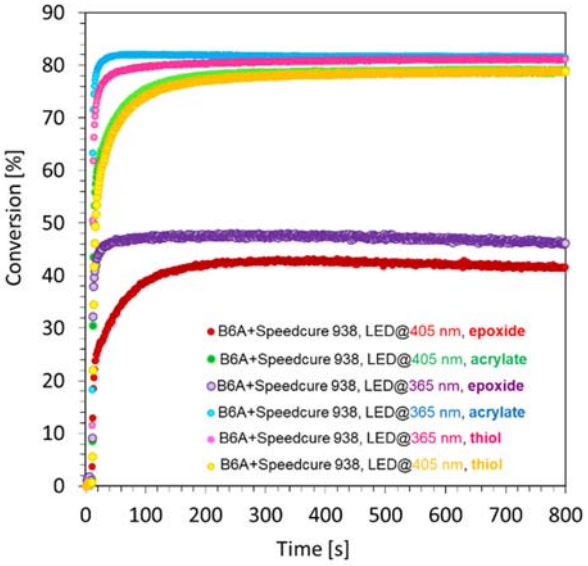


Figure S110: Polymerization profiles carried out in the air: CADE/TMPTA/ TMPMP (40/40/20 %w/w/w) + B6A/Iod (0,1/1 %w/w).

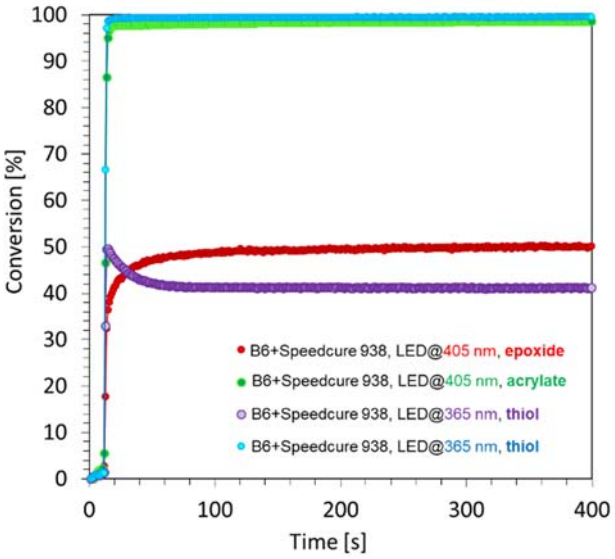


Figure S111: Polymerization profiles carried out in laminate for the system: TMPTA/TMPMP (50/50 %w/w) + B6/Iod (0,1/1 %w/w).

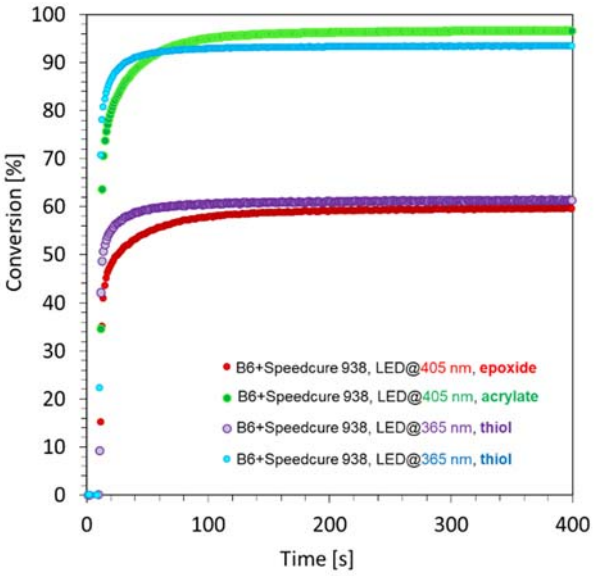


Figure S112: Polymerization profiles carried out in the air: TMPTA/TMPMP (50/50 %w/w) + B6/Iod (0,1/1 %w/w).

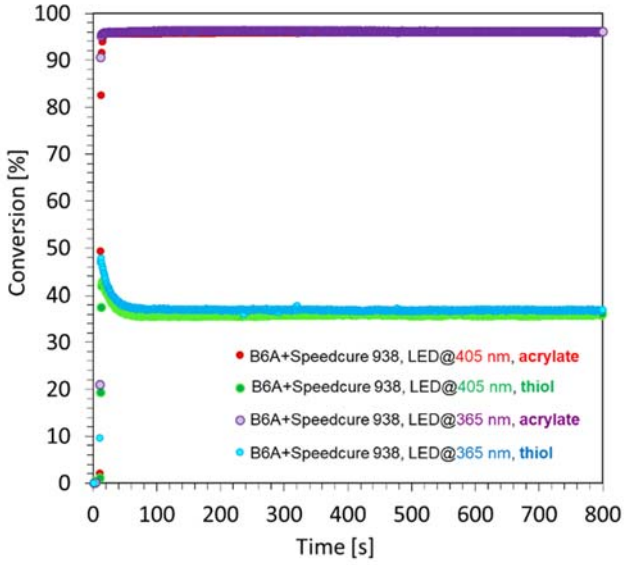


Figure S113: Polymerization profiles carried out in laminate for the system:
TMPTA/TMPMP (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

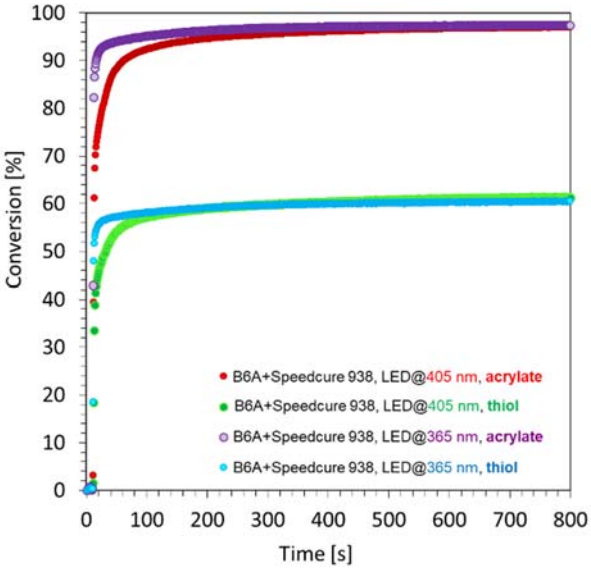


Figure S114: Polymerization profiles carried out in the air:
TMPTA/TMPMP (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

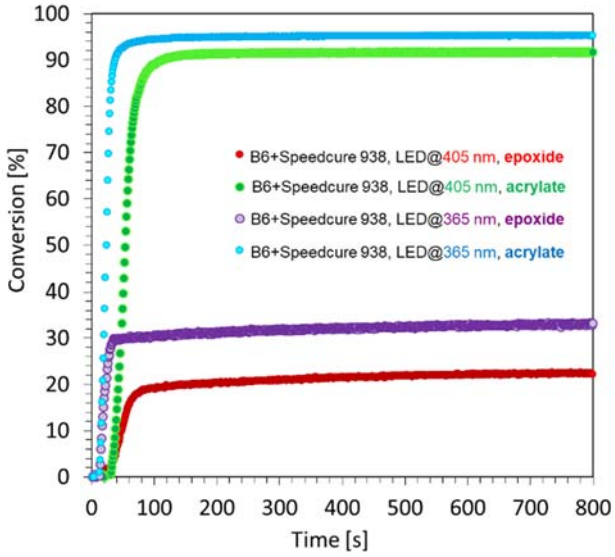


Figure S115: Polymerization profiles carried out in laminate for the system:
CADE/M100 (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

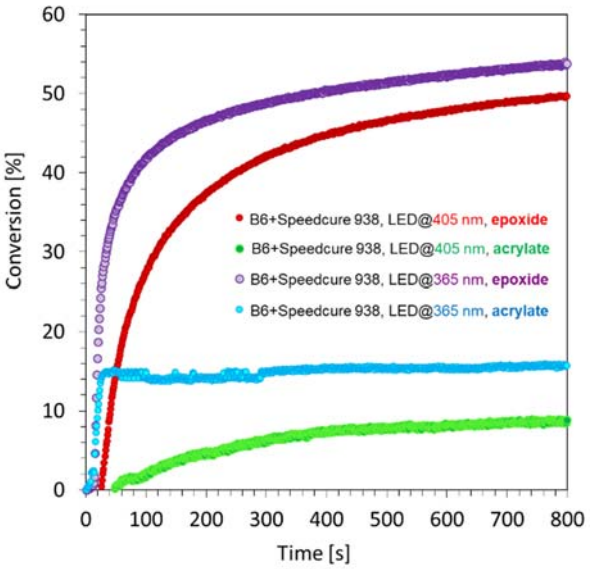


Figure S116: Polymerization profiles carried out in the air:
CADE/M100 (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

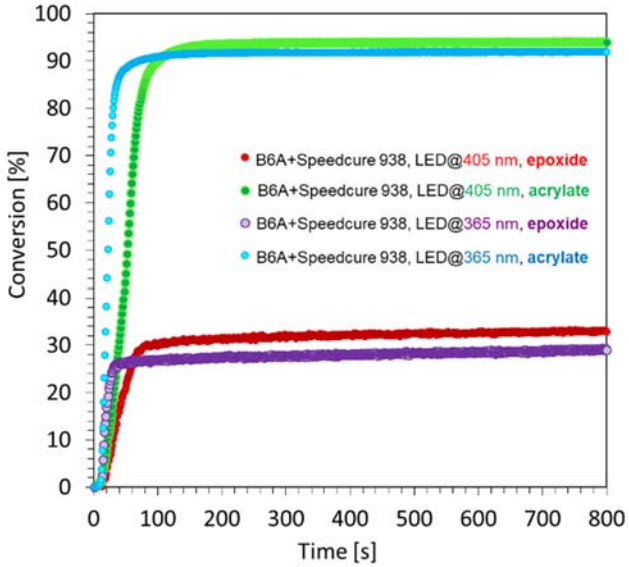


Figure S117: Polymerization profiles carried out in laminate for the system:
CADE/M100 (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

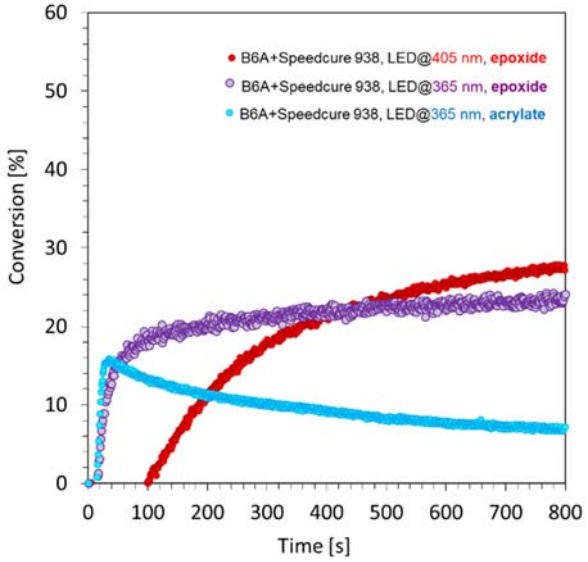


Figure S118: Polymerization profiles carried out in the air:
CADE/M100 (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

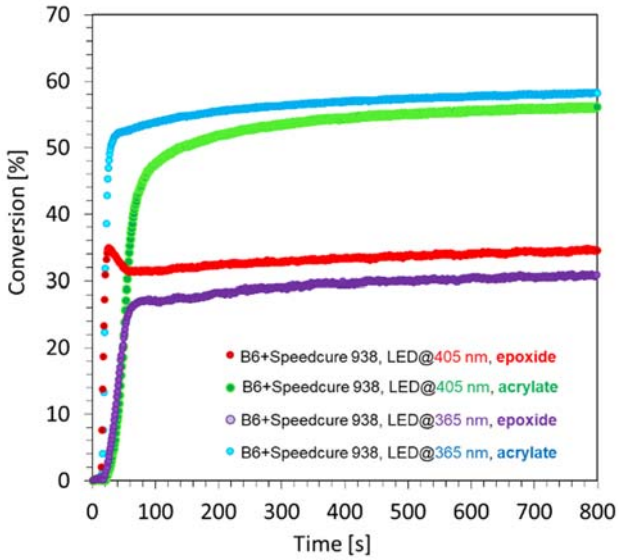


Figure S119: Polymerization profiles carried out in laminate for the system:
TMPTA/M100 (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

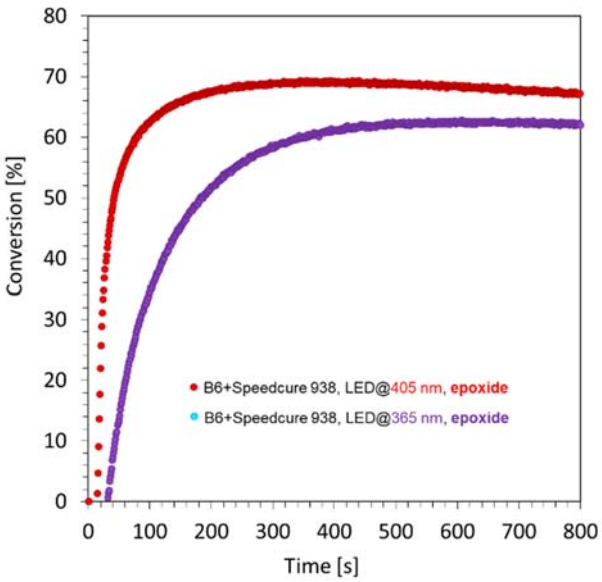


Figure S120: Polymerization profiles carried out in the air:
TMPTA/M100 (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

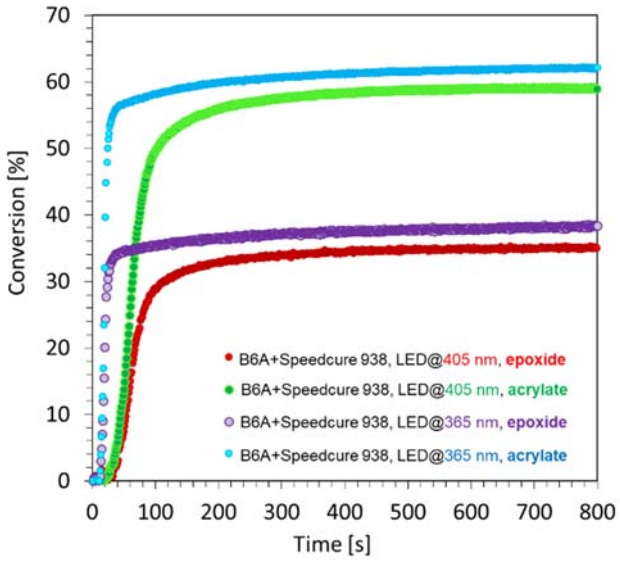


Figure S121: Polymerization profiles carried out in laminate for the system:
TMPTA/M100 (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

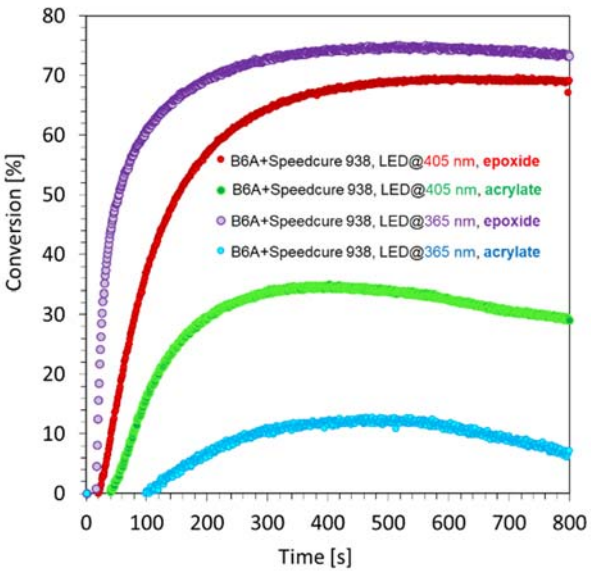


Figure S122: Polymerization profiles carried out in the air:
TMPTA/M100 (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

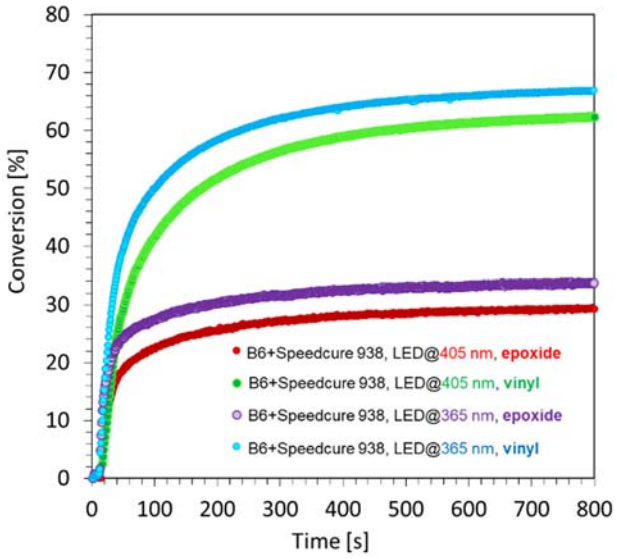


Figure S123: Polymerization profiles carried out in laminate for the system:
CADE/TEGDVE (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

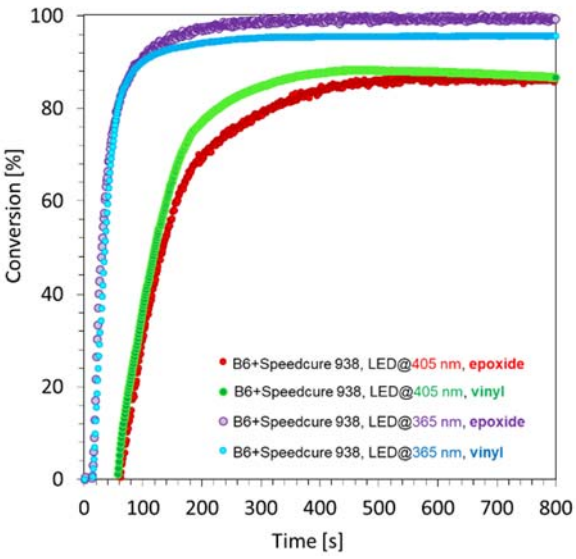


Figure S124: Polymerization profiles carried out in the air:
CADE/TEGDVE (50/50 %w/w)
+ B6/Iod (0,1/1 %w/w).

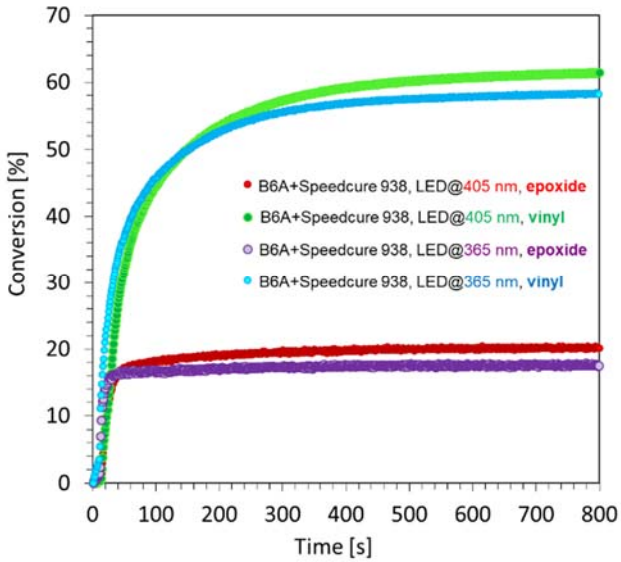


Figure S125: Polymerization profiles carried out in laminate for the system:
CADE/TEGDVE (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

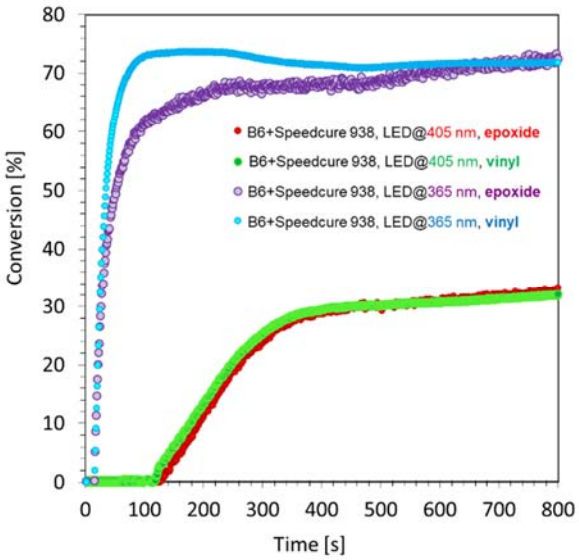


Figure S126: Polymerization profiles carried out in the air:
CADE/TEGDVE (50/50 %w/w)
+ B6A/Iod (0,1/1 %w/w).

[1]HNMR spectra of synthesized compounds

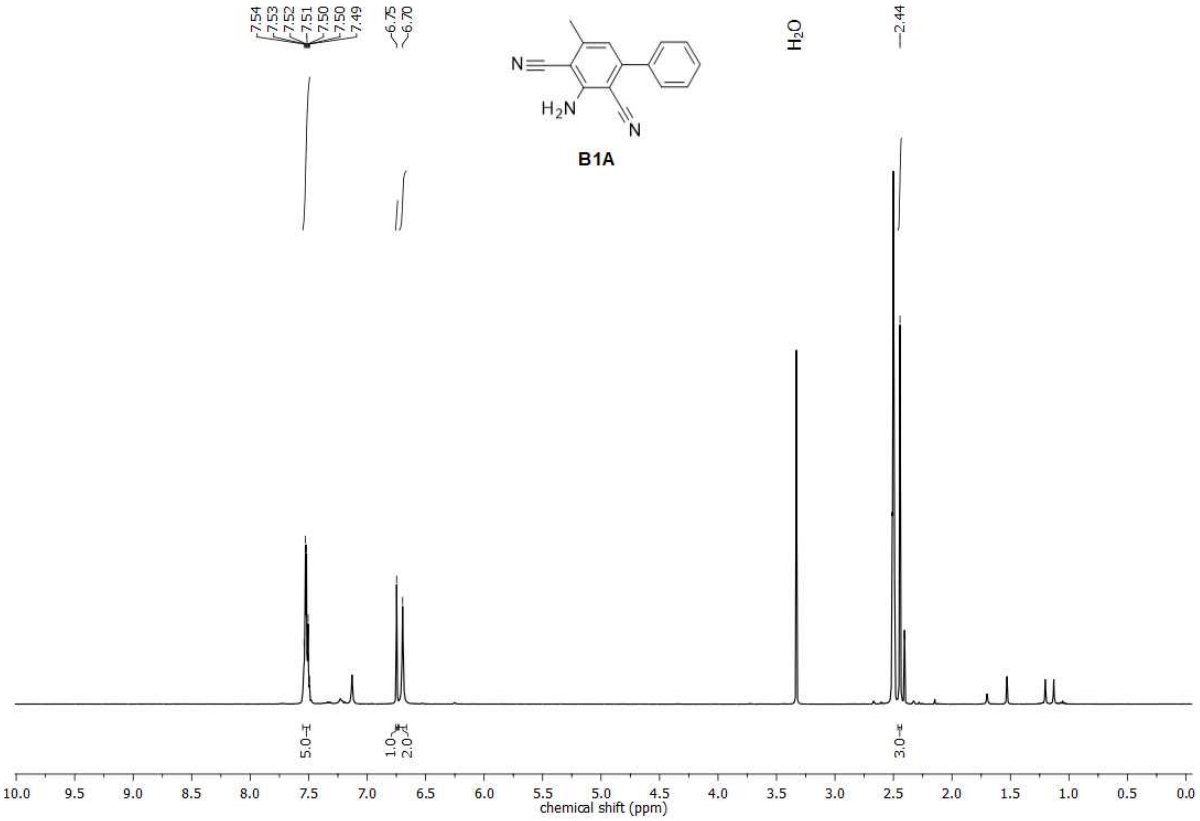


Figure S127: [1]HNMR of 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile (B1A).

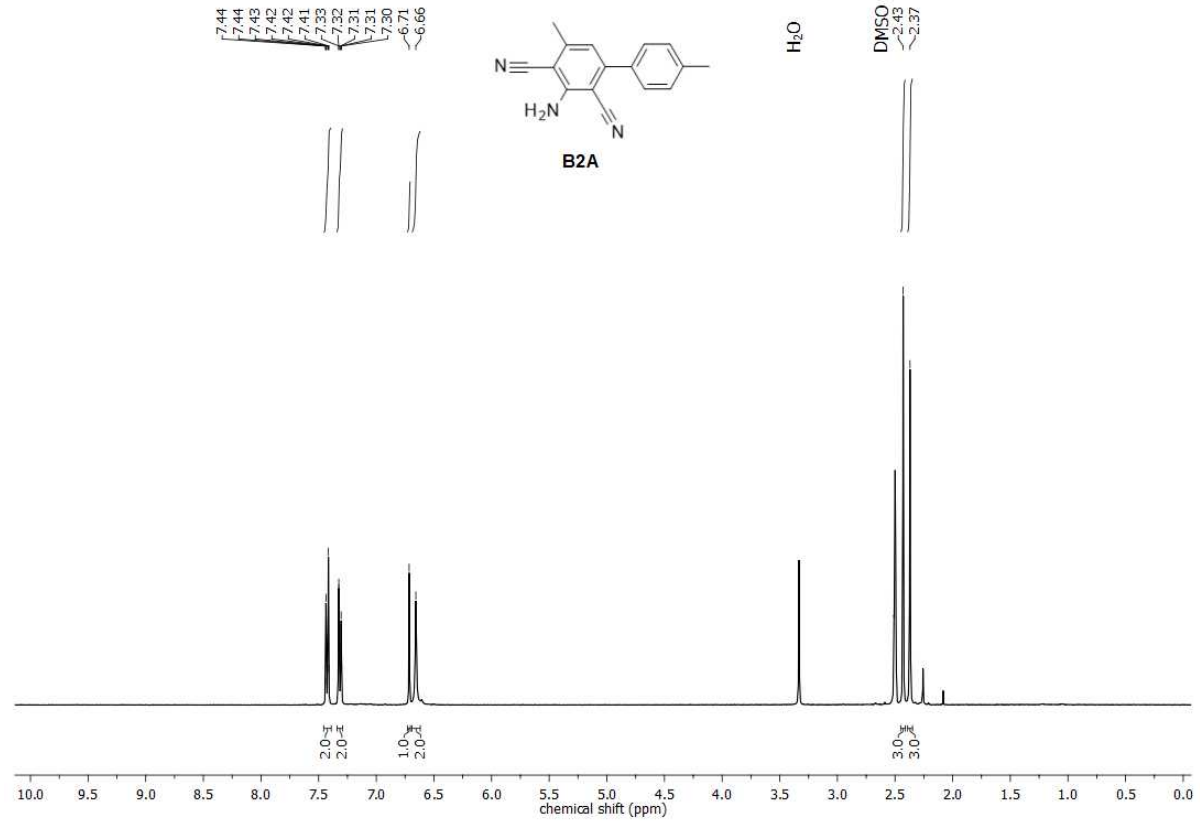


Figure S128: [1]HNMR of 2-amino-4-(4-methylphenyl)-6-methyl-benzene-1,3-dicarbonitrile (B2A).

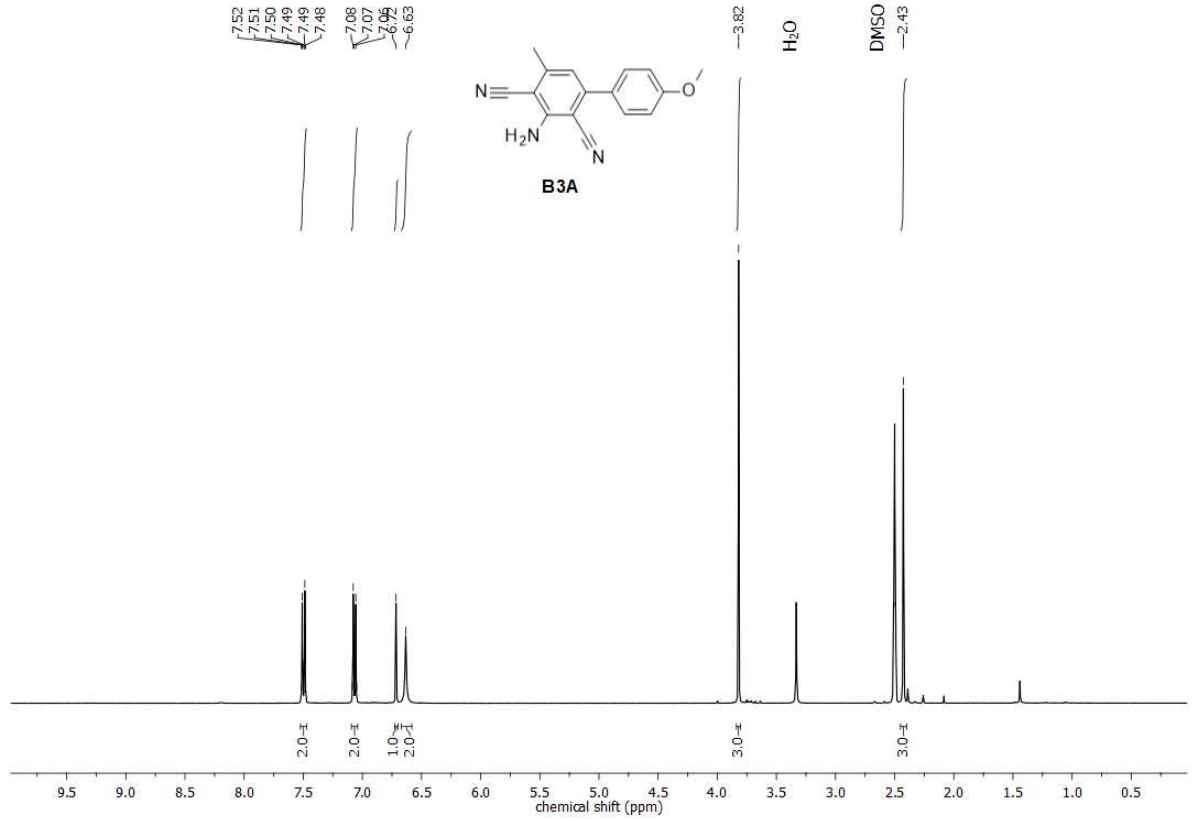


Figure S129: [1]HNMR of 2-amino-4-(4-methoxyphenyl)-6-methyl-benzene-1,3-dicarbonitrile (B3A).

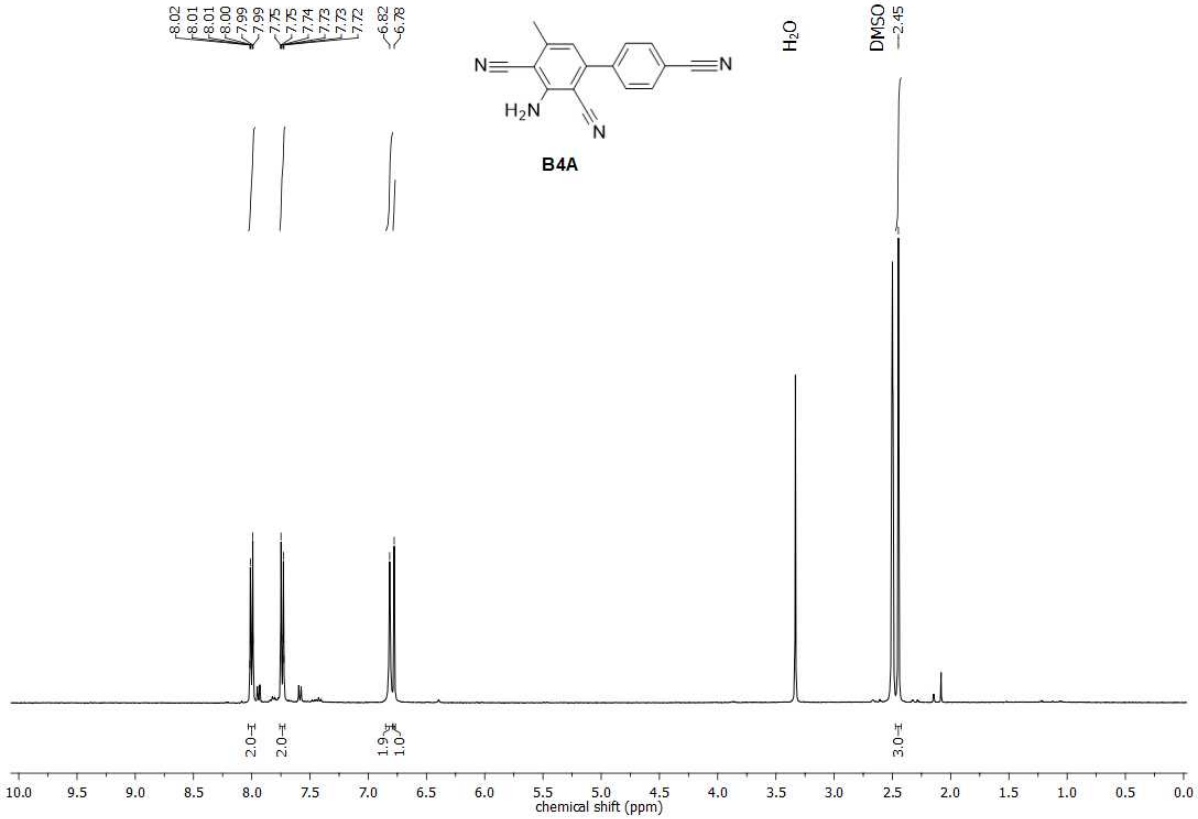


Figure S130: [1]HNMR of 2-amino-4-(4-cyanophenyl)-6-methyl-benzene-1,3-dicarbonitrile (B4A).

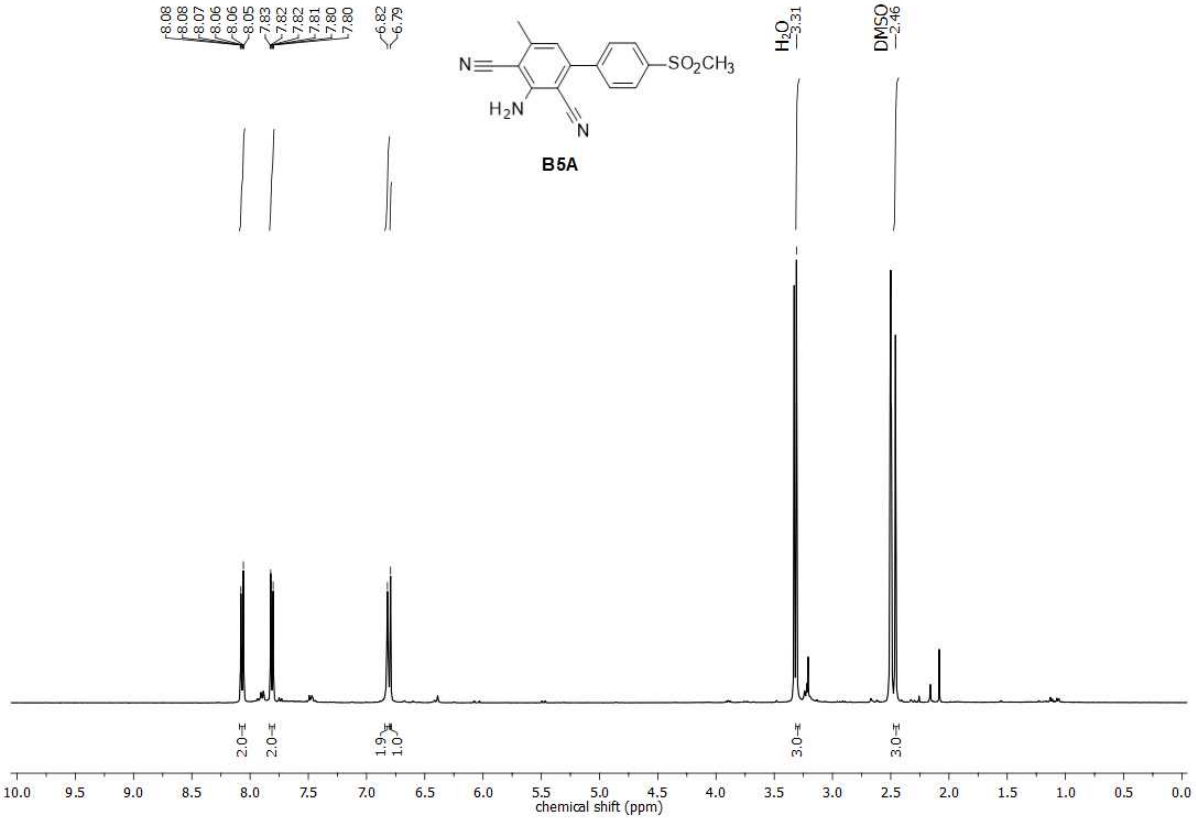


Figure S131: [1]HNMR of 2-amino-4-methyl-6-(4-methylsulfonylphenyl)benzene-1,3-dicarbonitrile (B5A).

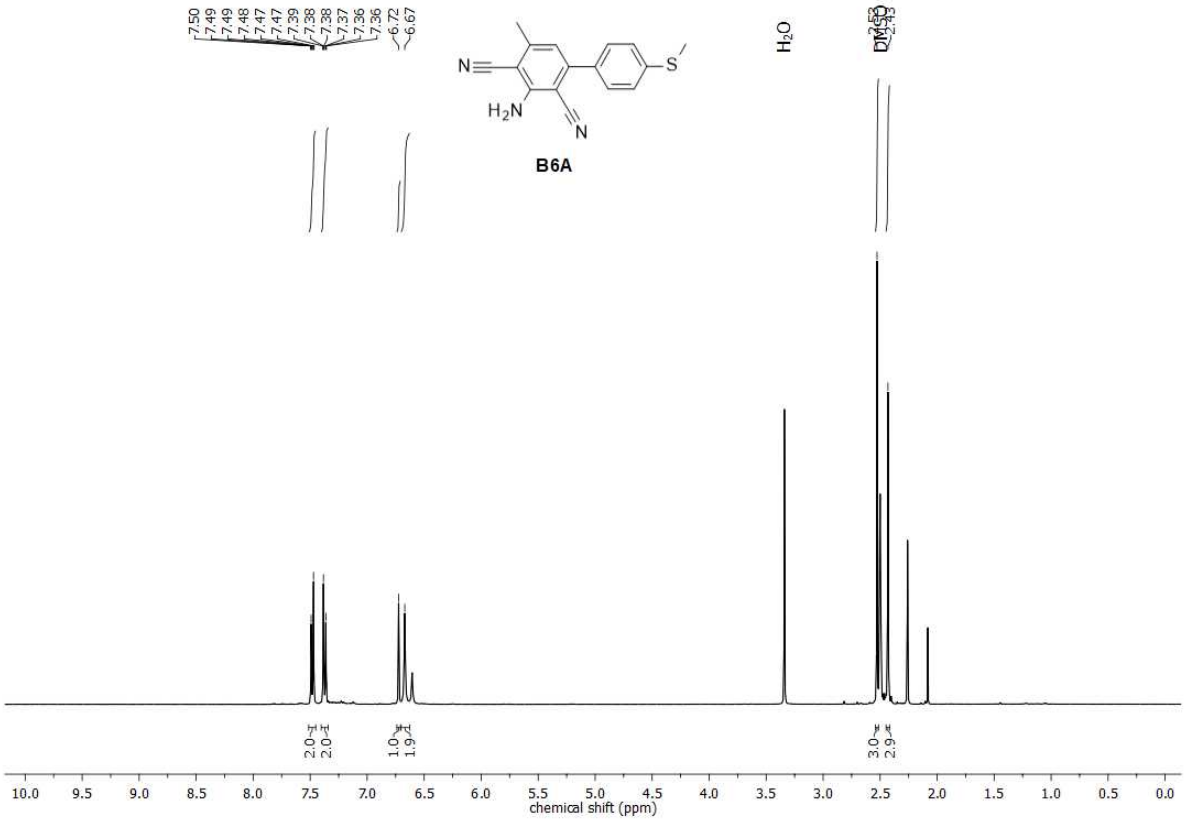


Figure S132: [1]HNMR of 2-amino-4-methyl-6-(4-methylsulfanylphenyl)benzene-1,3-dicarbonitrile (B6A).

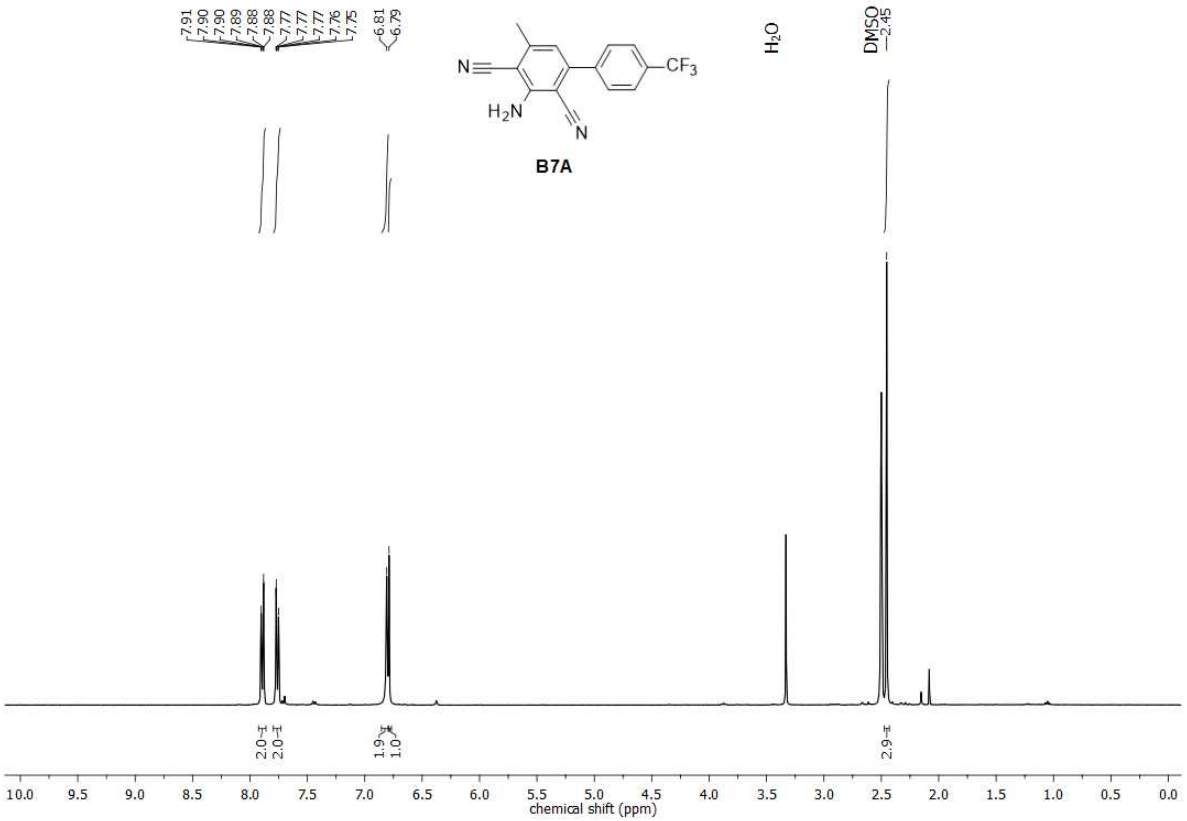


Figure S133: [1]HNMR of 2-amino-4-methyl-6-[4-(trifluoromethyl)phenyl]benzene-1,3-dicarbonitrile (B7A).

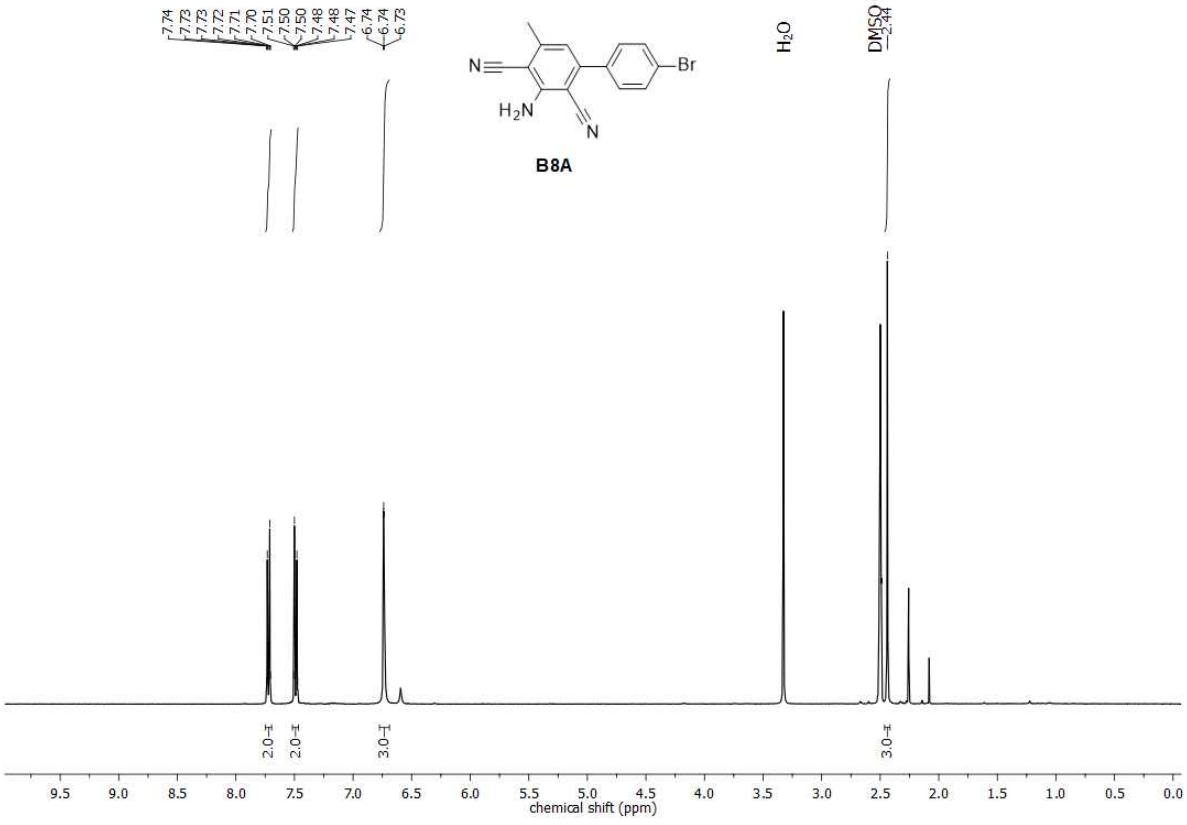


Figure S134: [1]HNMR of 2-amino-4-(4-bromophenyl)-6-methyl-benzene-1,3-dicarbonitrile (B8A).

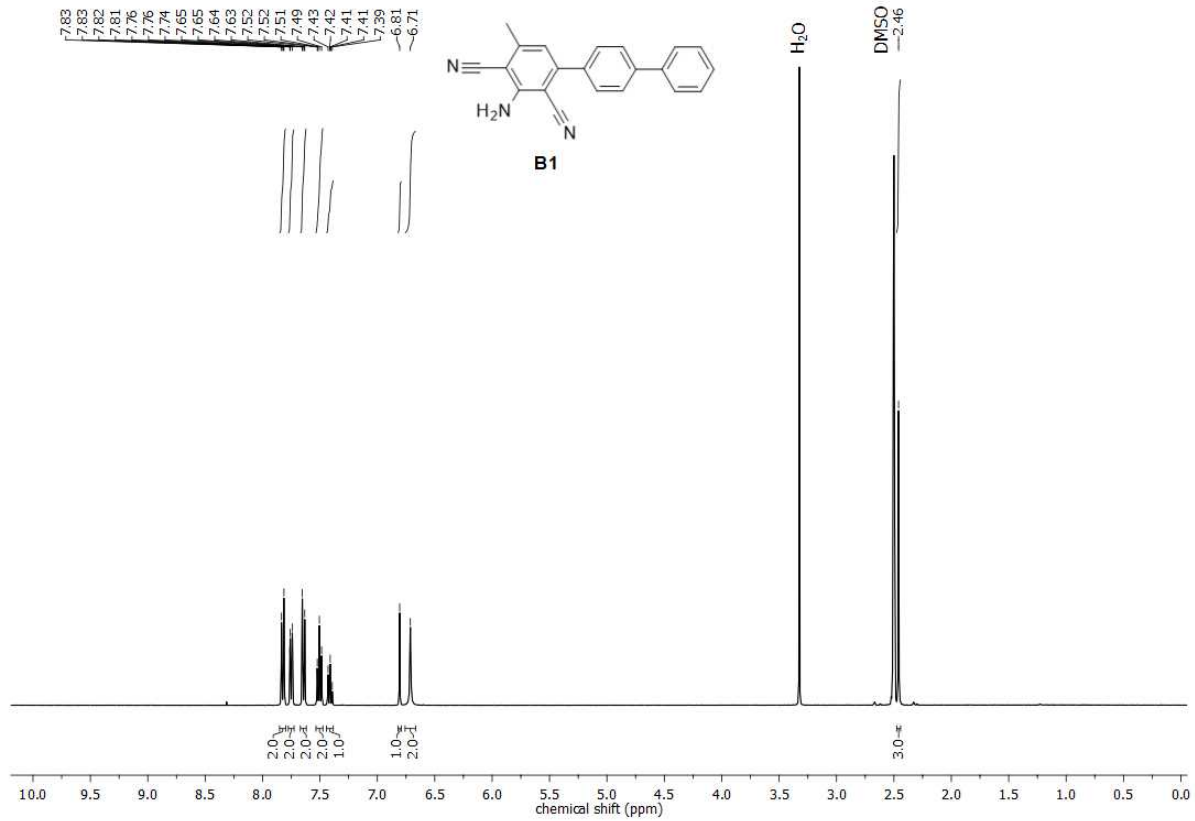


Figure S135: [1]HNMR of 2-amino-4-methyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile (B1).

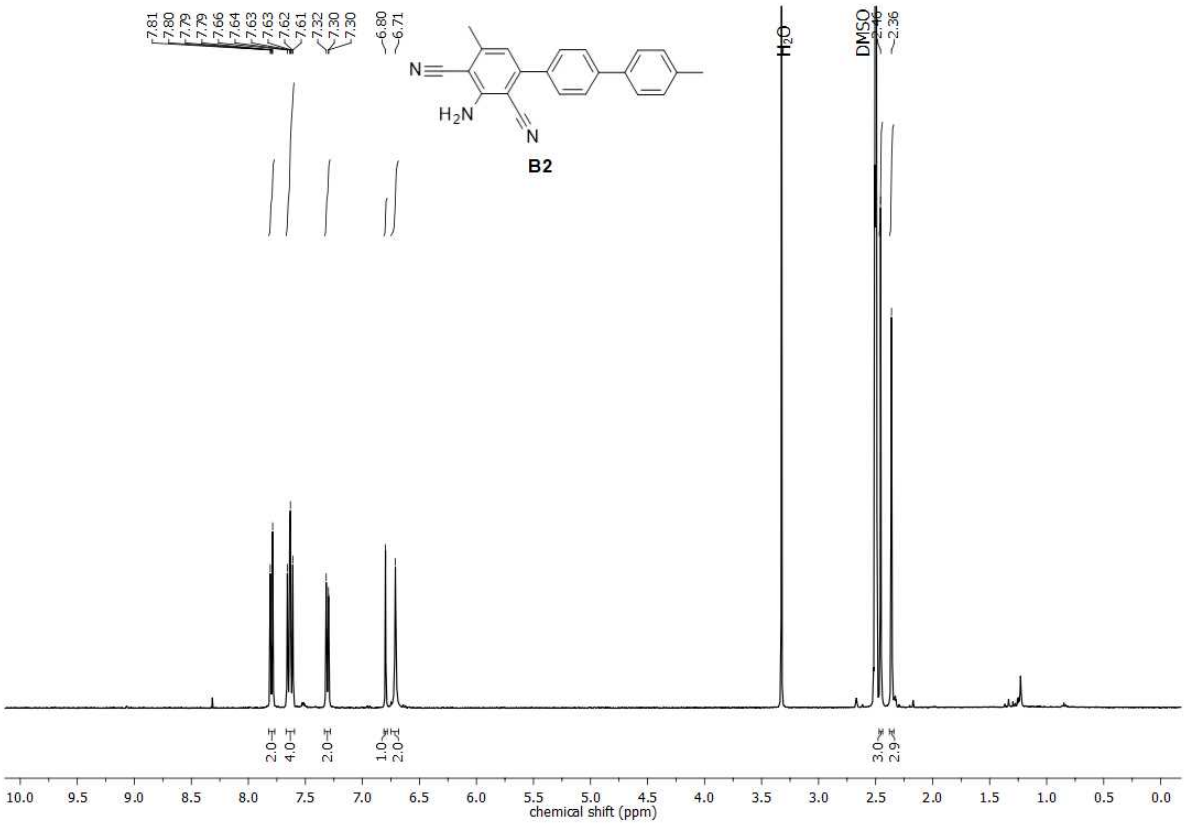


Figure S136: [1]HNMR of 2-amino-4-[4-(4-methylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B2).

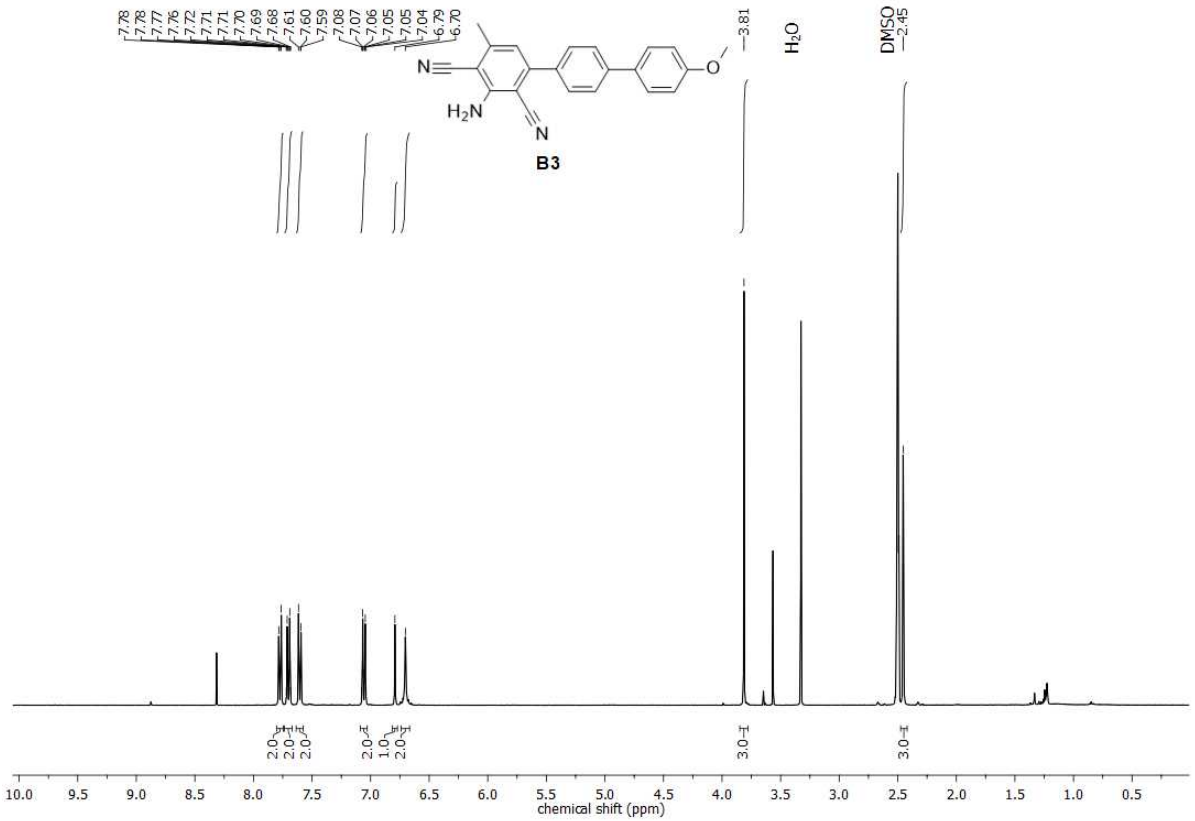


Figure S137: [1]HNMR of 2-amino-4-[4-(4-methoxyphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B3).

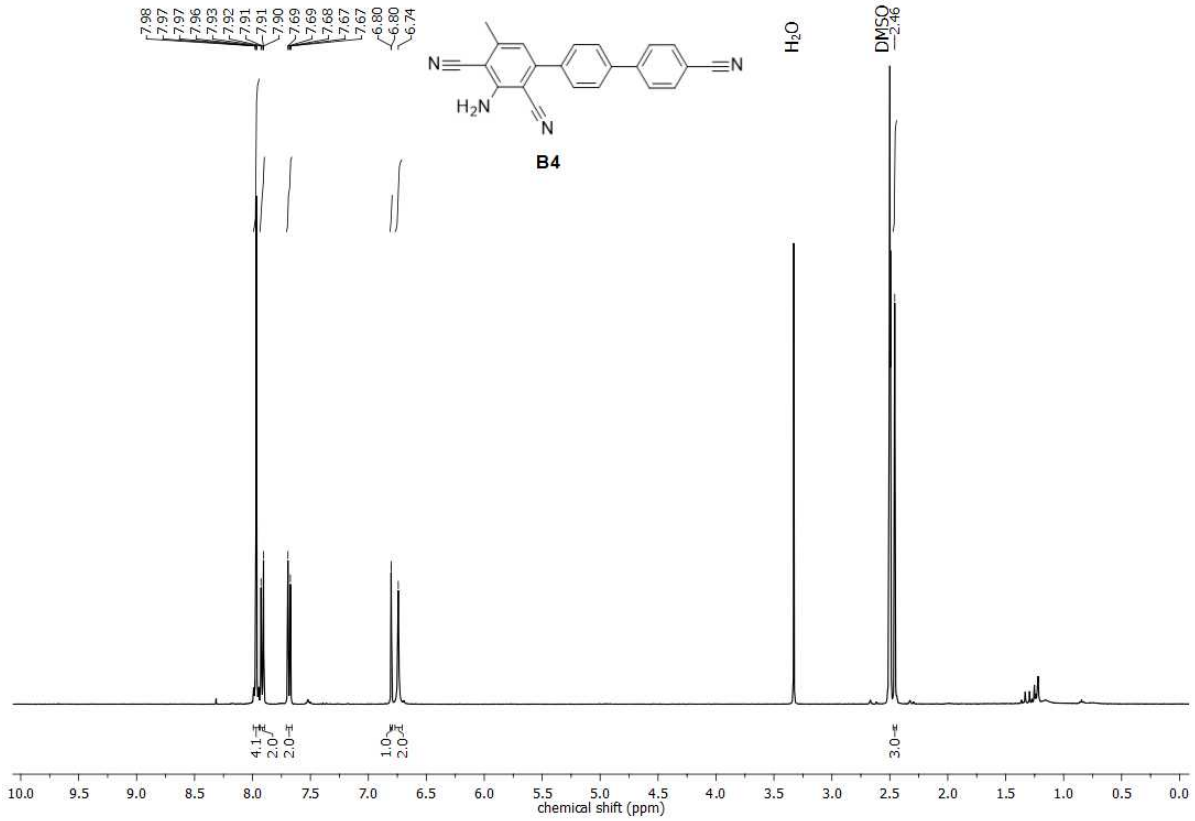


Figure S138: [1]HNMR of 2-amino-4-[4-(4-cyanophenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B4).

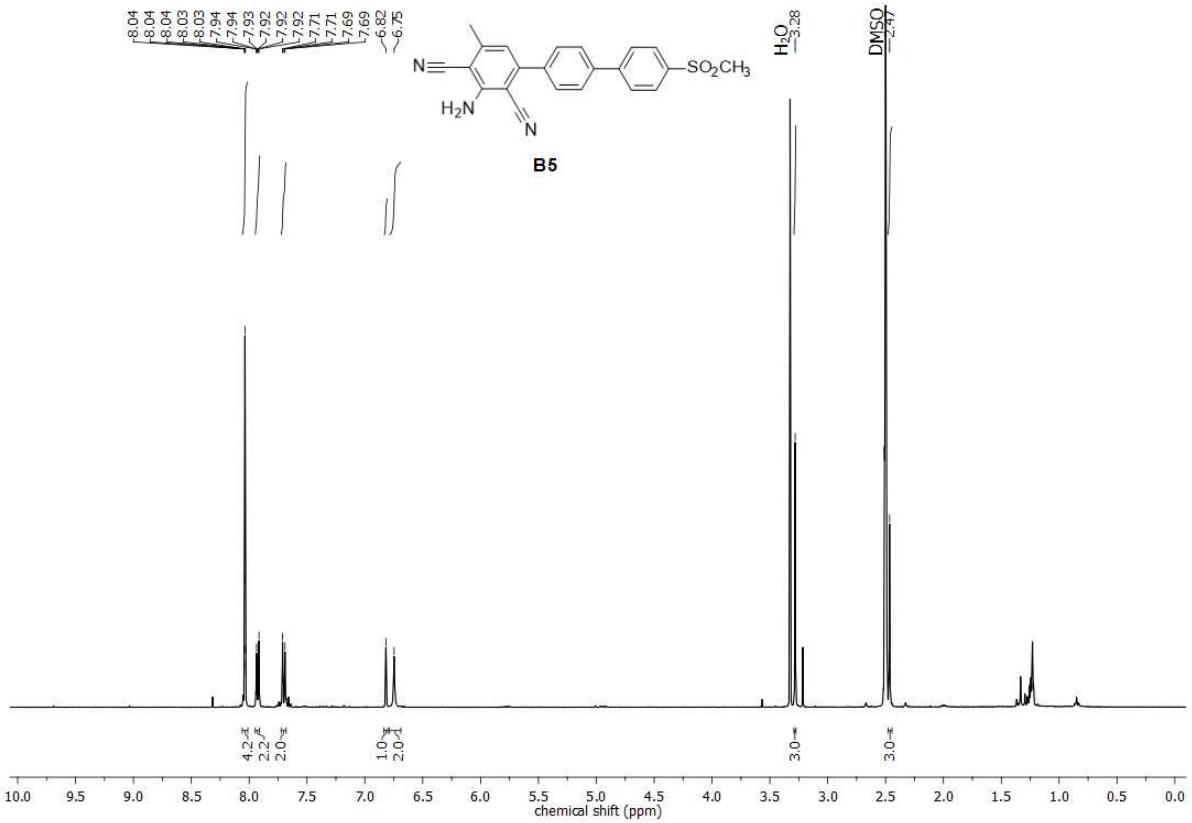


Figure S139: [1]HNMR of 2-amino-4-[4-(4-methylsulfonylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B5).

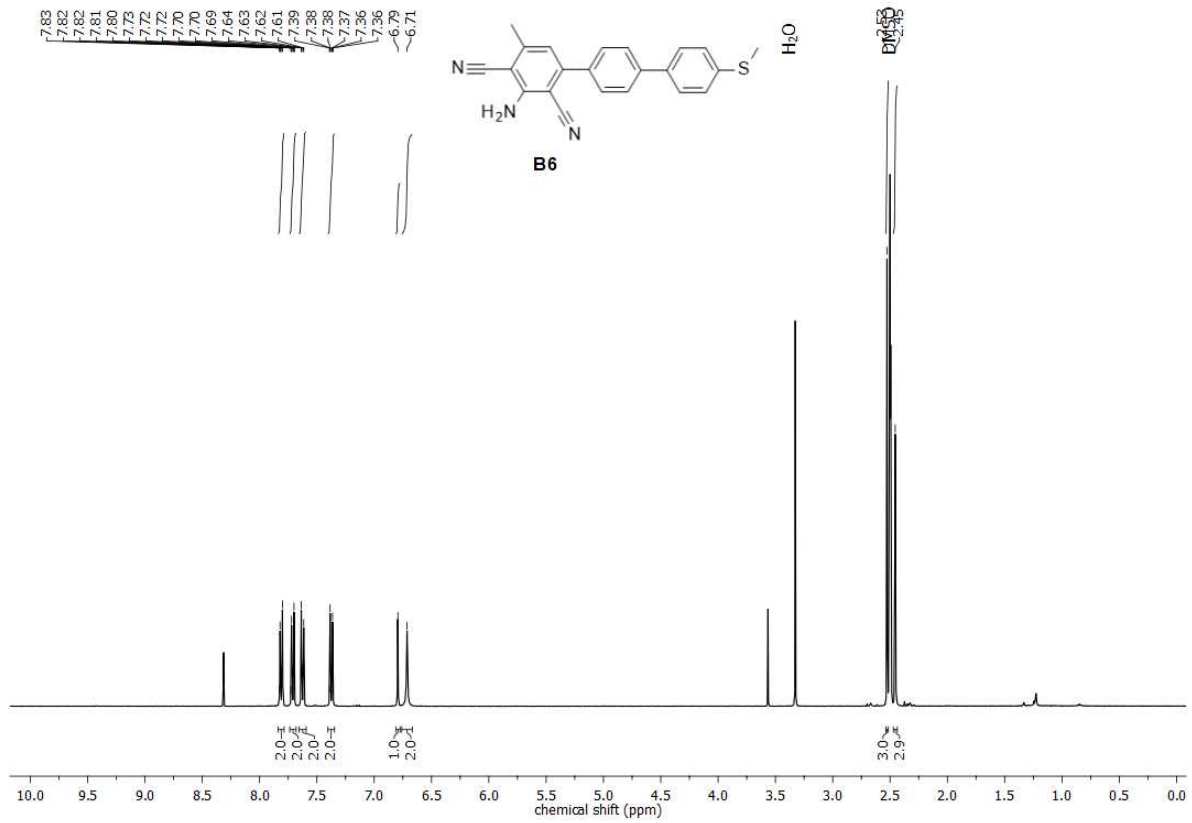


Figure S140: [1]HNMR of 2-amino-4-[4-(4-methylsulfanylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B6).

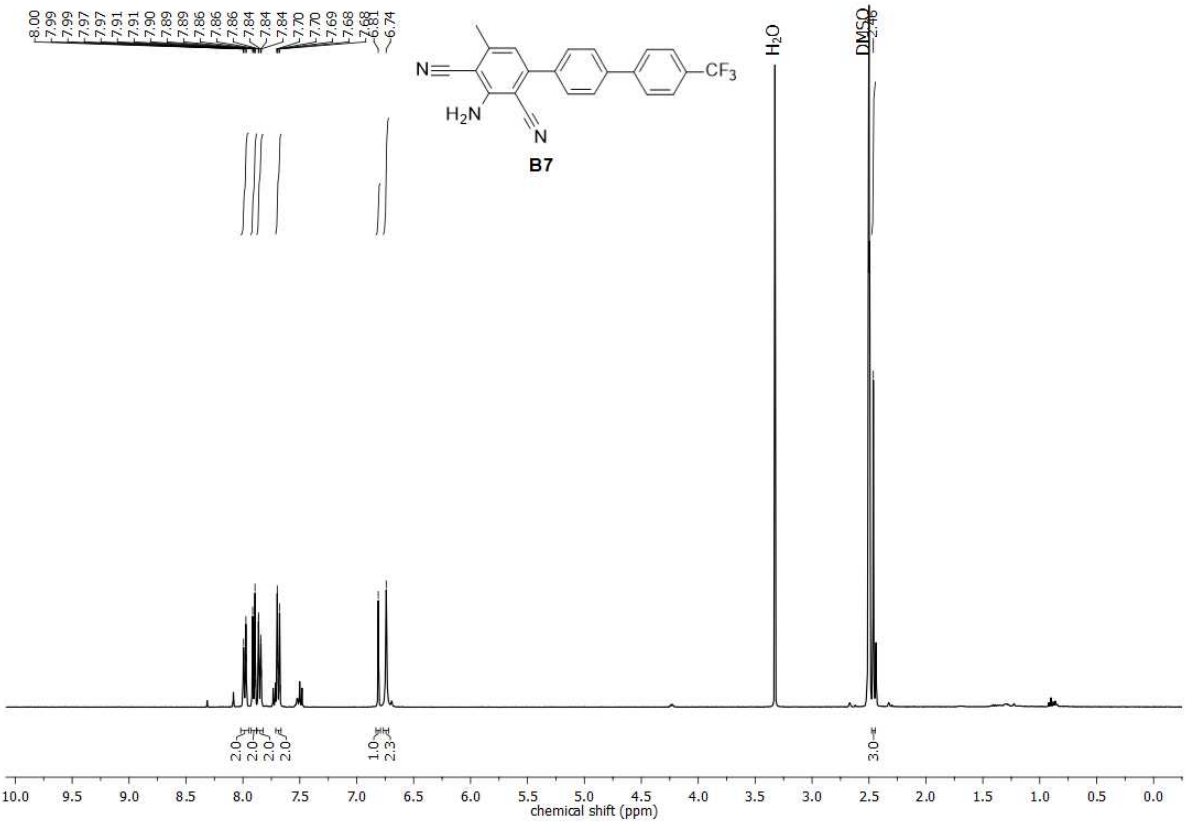


Figure S141: [1]HNMR of 2-amino-4-methyl-6-[4-[4-(trifluoromethyl)phenyl]phenyl]benzene-1,3-dicarbonitrile (B7).

^{13}CNMR spectra of synthesized compounds

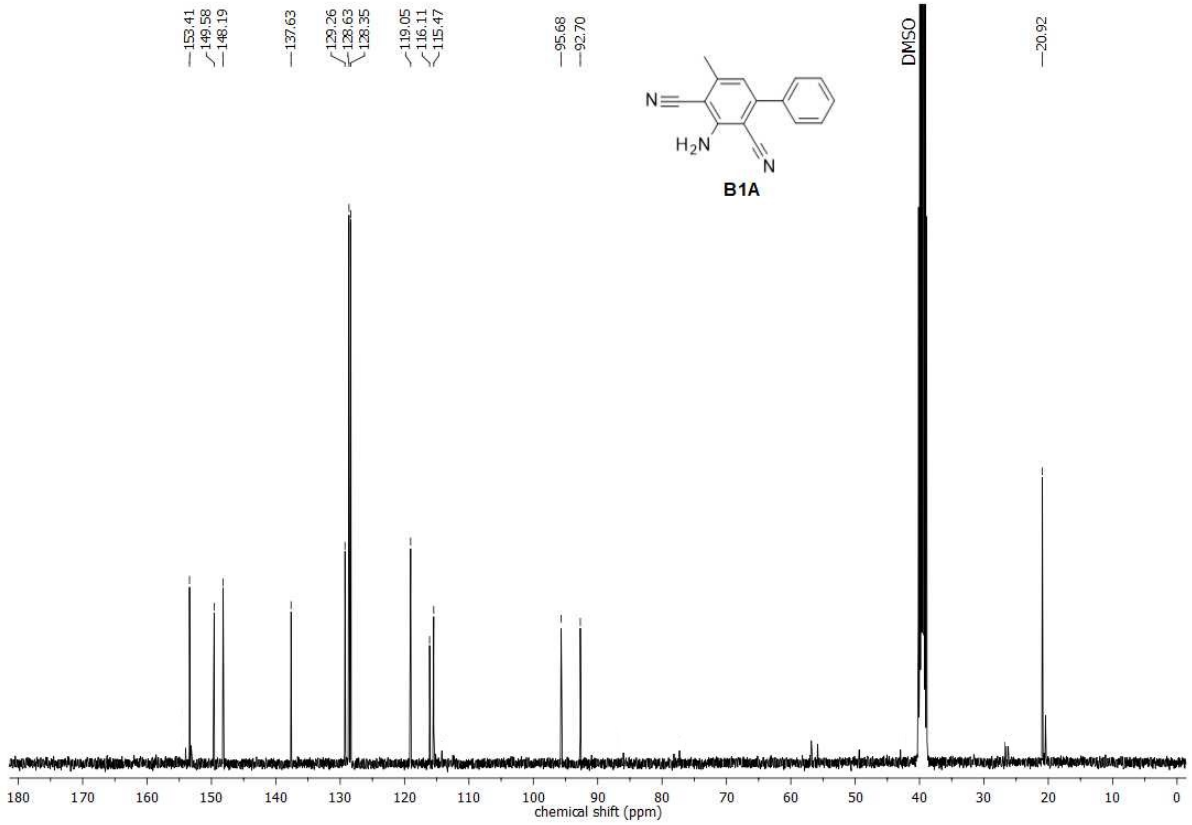


Figure S142: ^{13}CNMR of 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile (B1A).

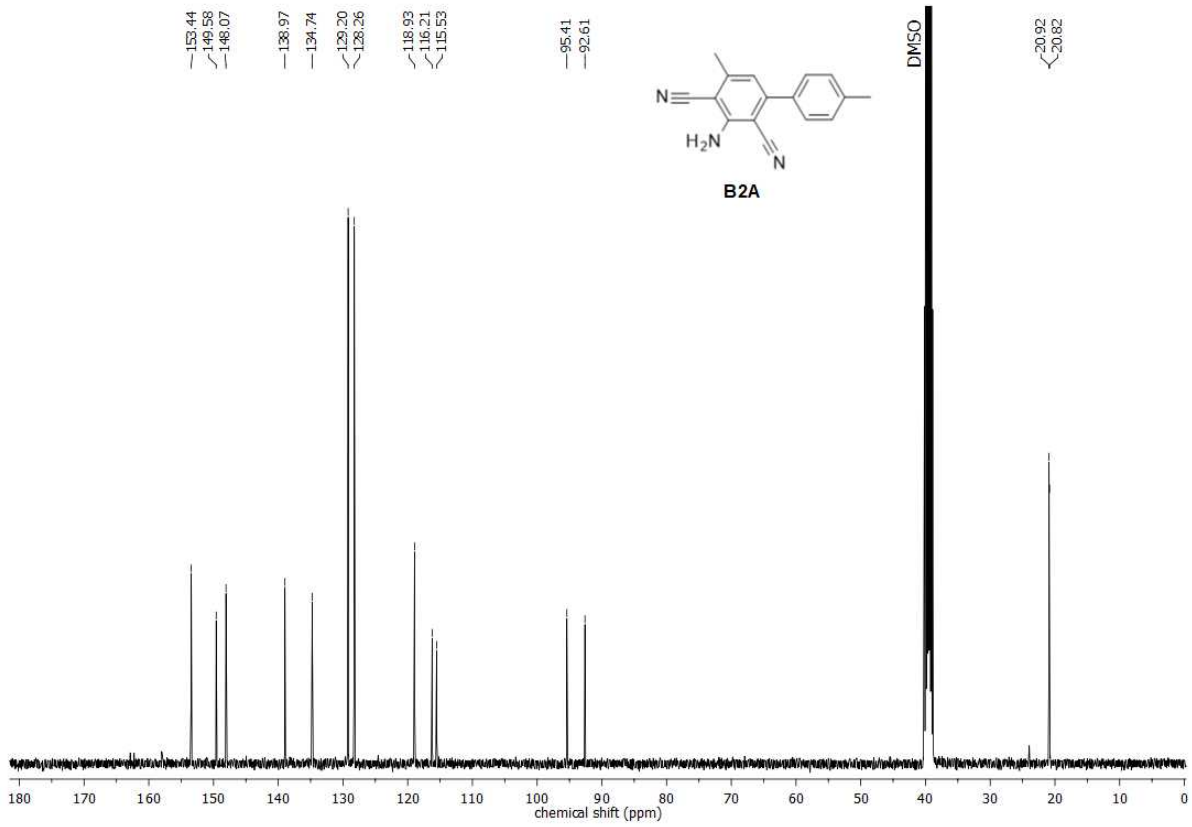


Figure S143: ^{13}CNMR of 2-amino-4-(4-methylphenyl)-6-methyl-benzene-1,3-dicarbonitrile (B2A).

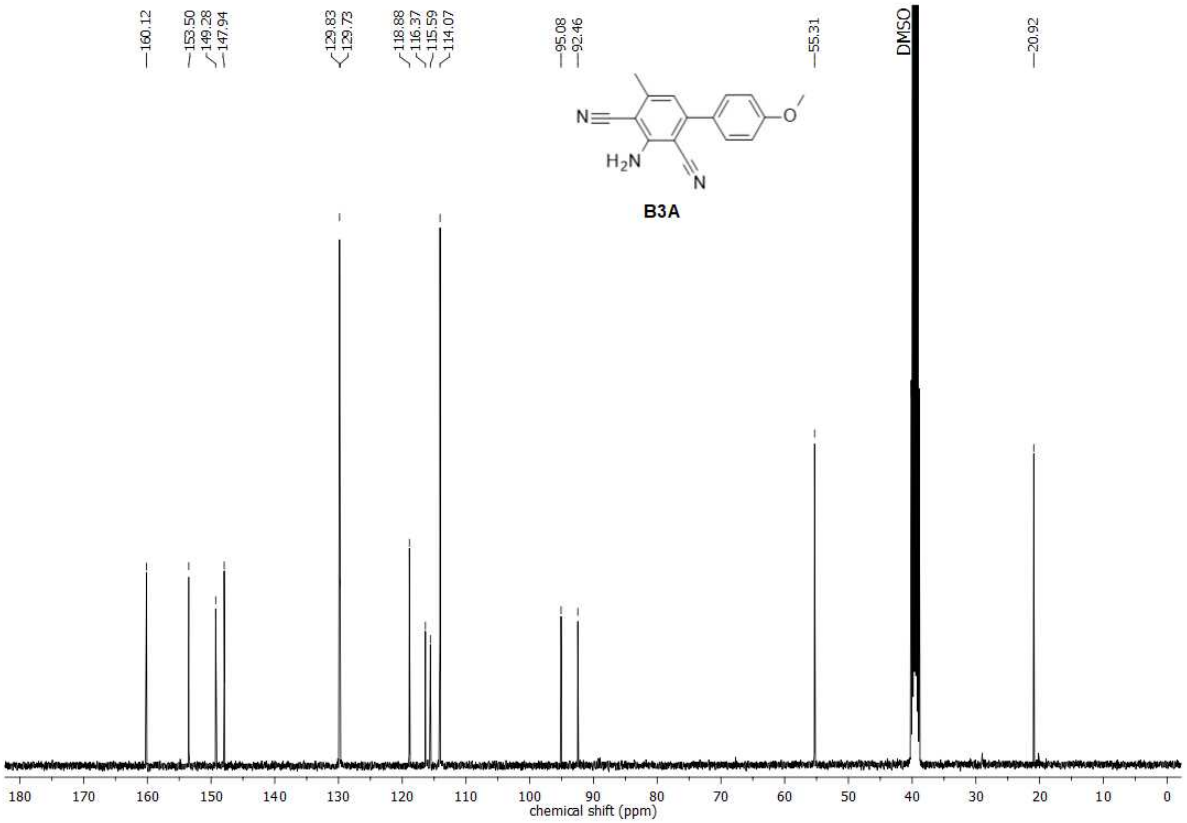


Figure S144: ^{13}CNMR of 2-amino-4-(4-methoxyphenyl)-6-methyl-benzene-1,3-dicarbonitrile (B3A).

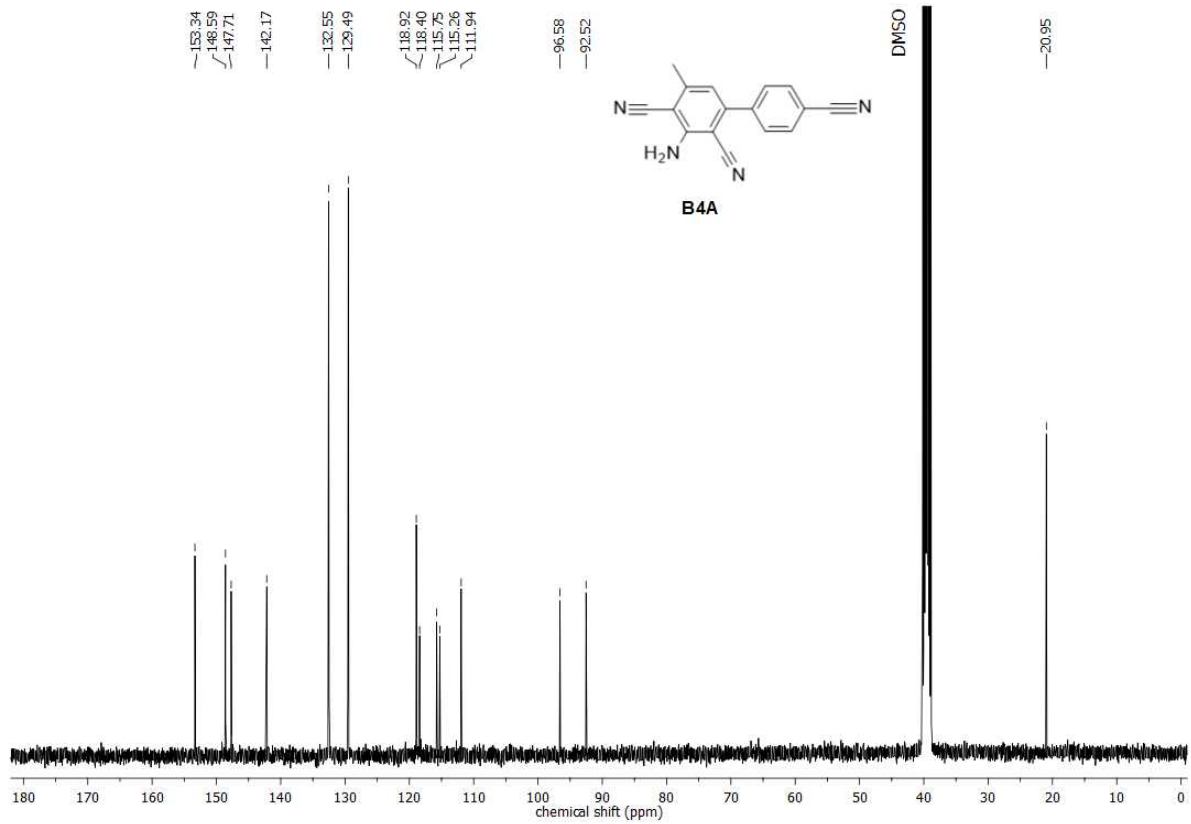


Figure S145: ^{13}CNMR of 2-amino-4-(4-cyanophenyl)-6-methyl-benzene-1,3-dicarbonitrile (B4A).

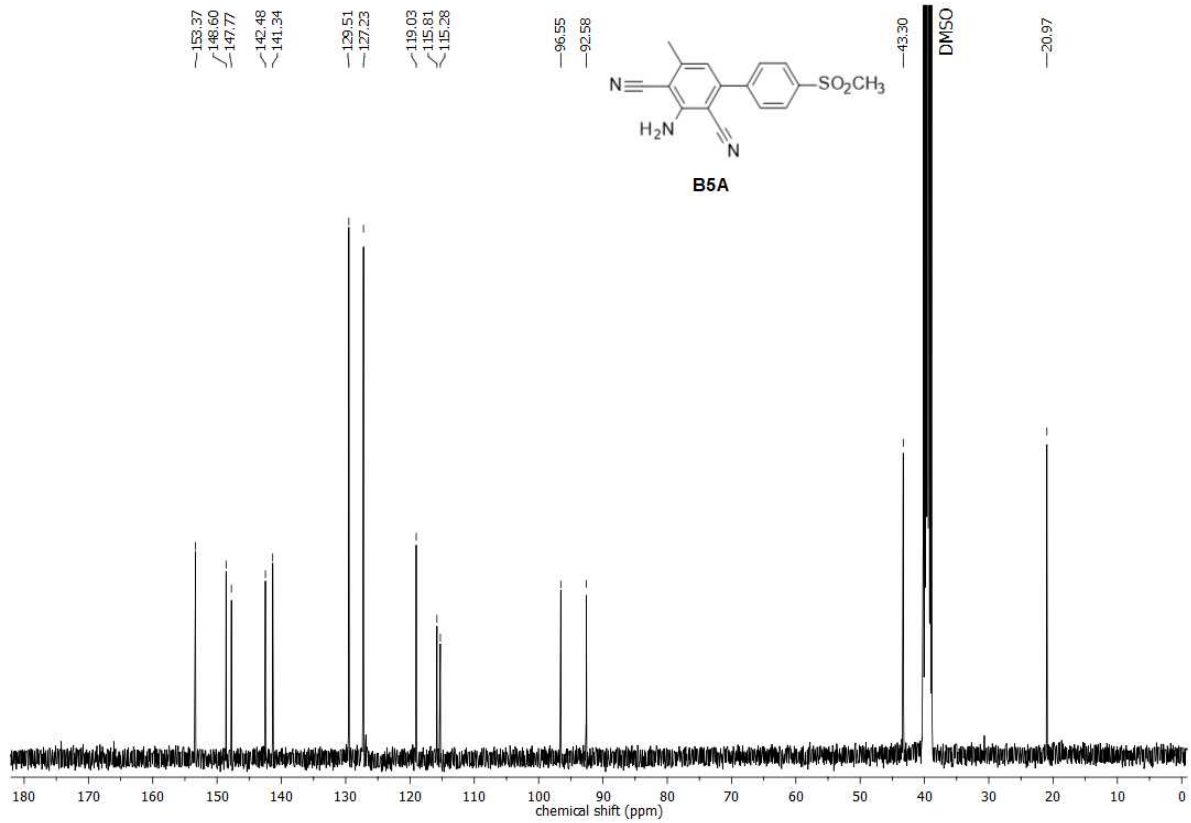


Figure S146: ^{13}CNMR of 2-amino-4-methyl-6-(4-methylsulfonylphenyl)benzene-1,3-dicarbonitrile (B5A).

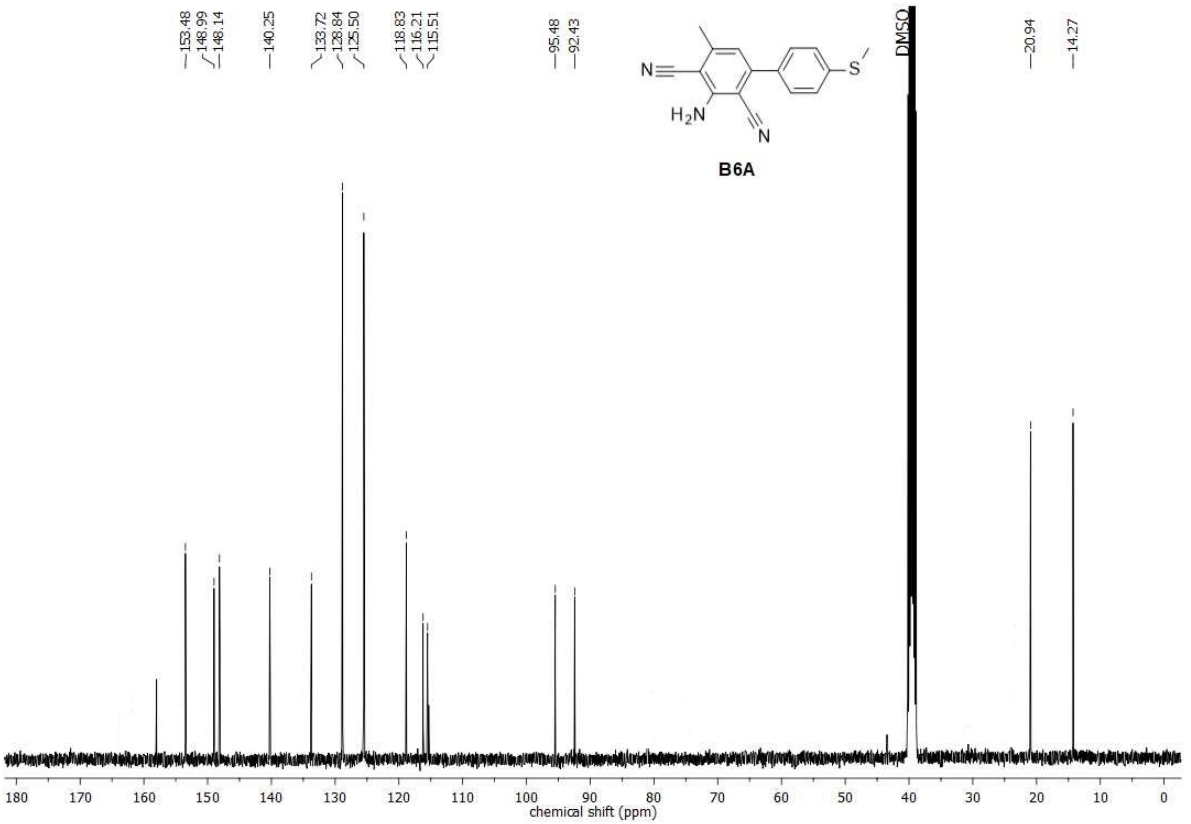


Figure S147: ^{13}CNMR of 2-amino-4-methyl-6-(4-methylsulfanylphenyl)benzene-1,3-dicarbonitrile (B6A).

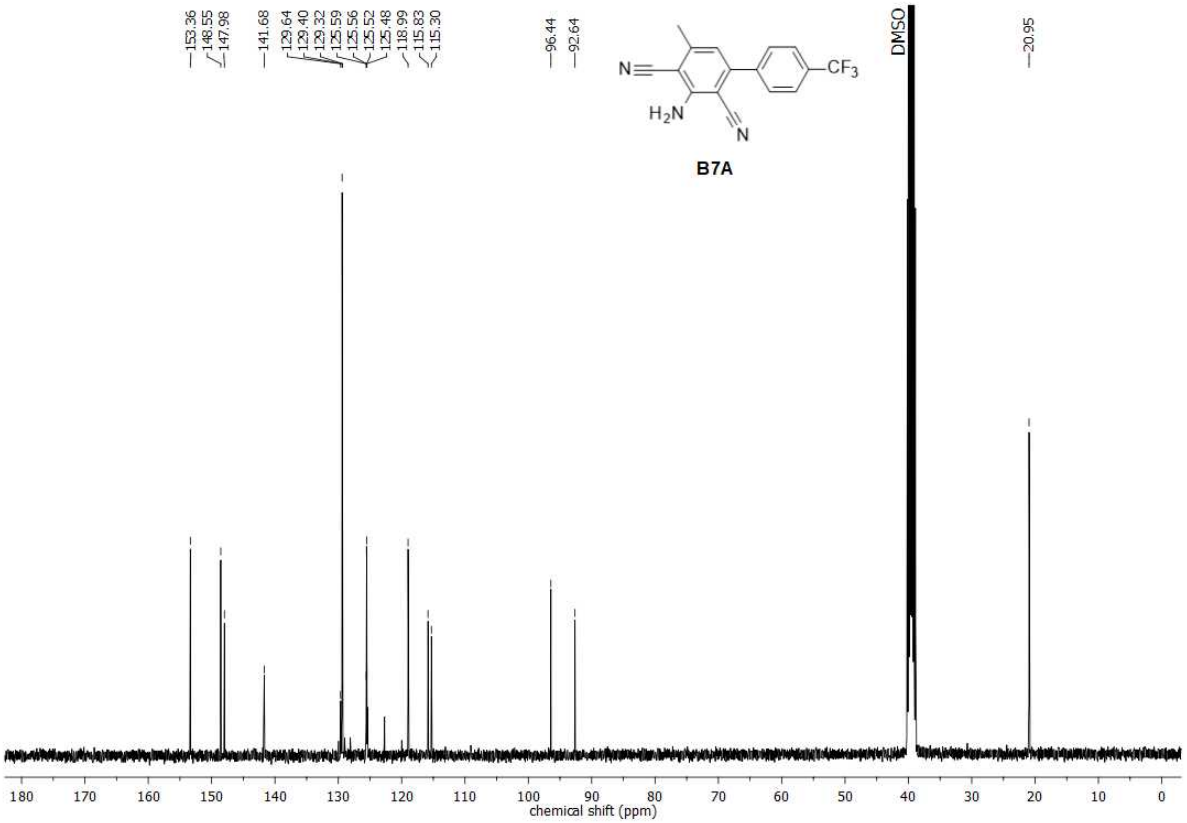


Figure S148: ^{13}CNMR of 2-amino-4-methyl-6-[4-(trifluoromethyl)phenyl]benzene-1,3-dicarbonitrile (B7A).

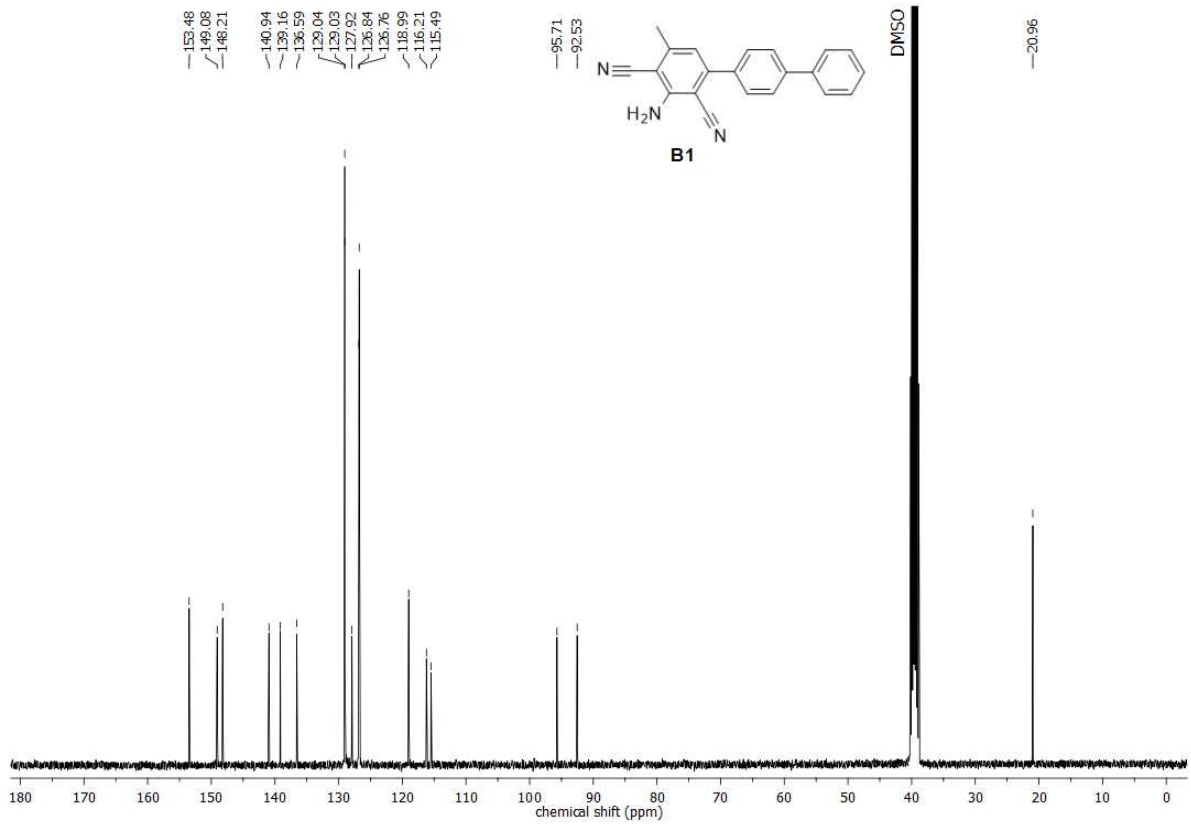


Figure S150: ^{13}CNMR of 2-amino-4-methyl-6-(4-phenylphenyl)benzene-1,3-dicarbonitrile (B1).

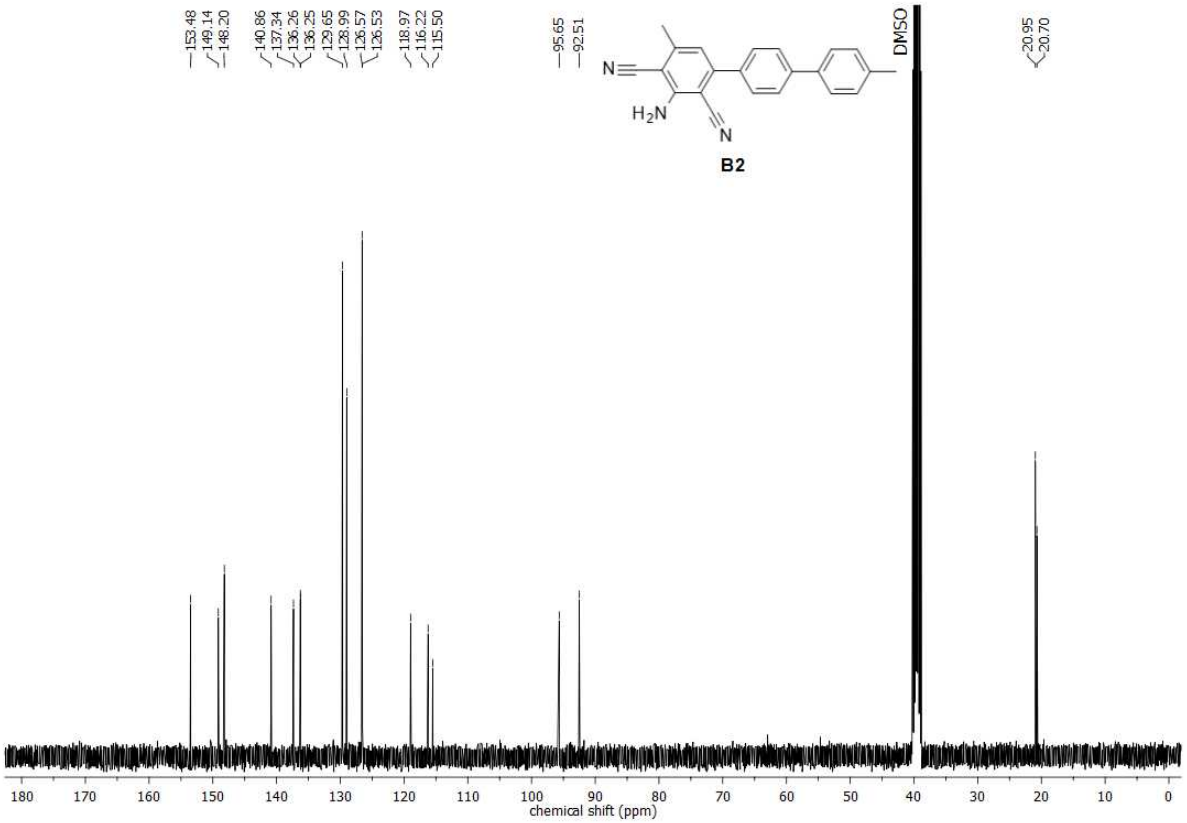


Figure S151: ^{13}CNMR of 2-amino-4-[4-(4-methylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B2).

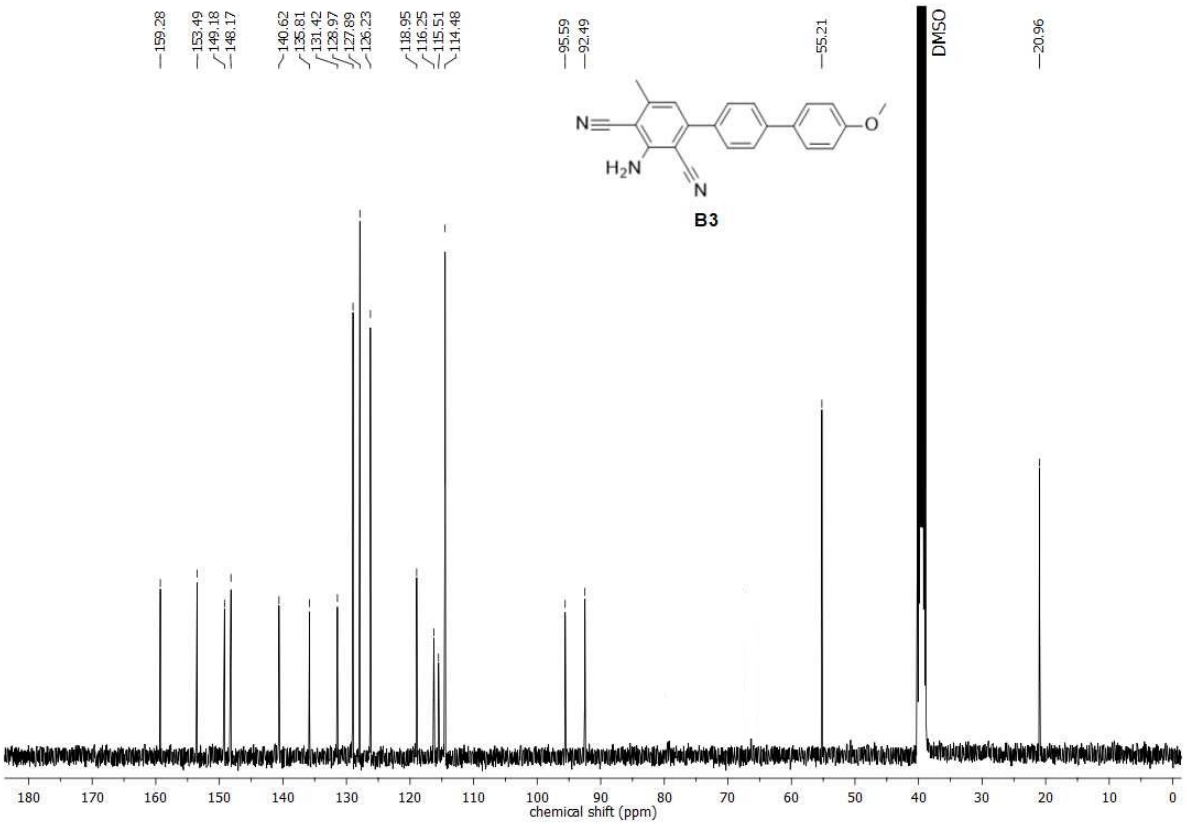


Figure S152: ^{13}CNMR of 2-amino-4-[4-(4-methoxyphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B3).

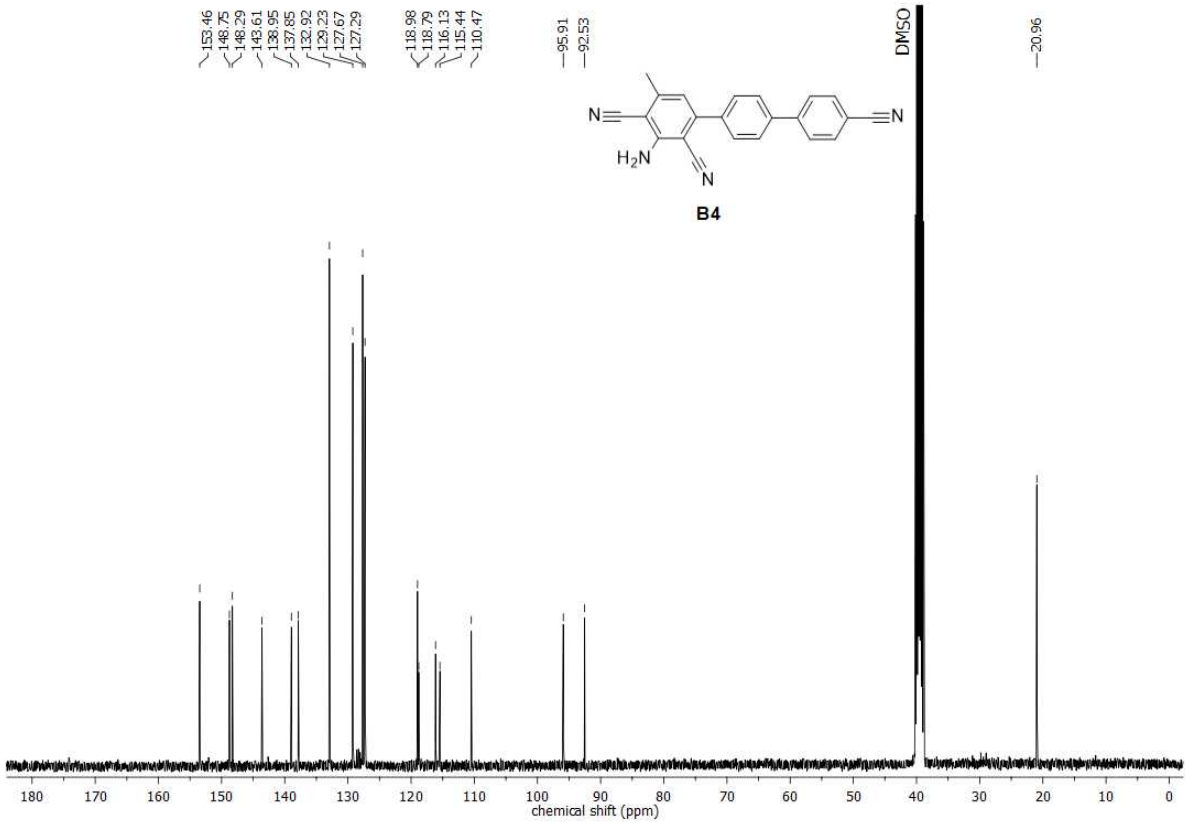


Figure S153: ^{13}CNMR of 2-amino-4-[4-(4-cyanophenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B4).

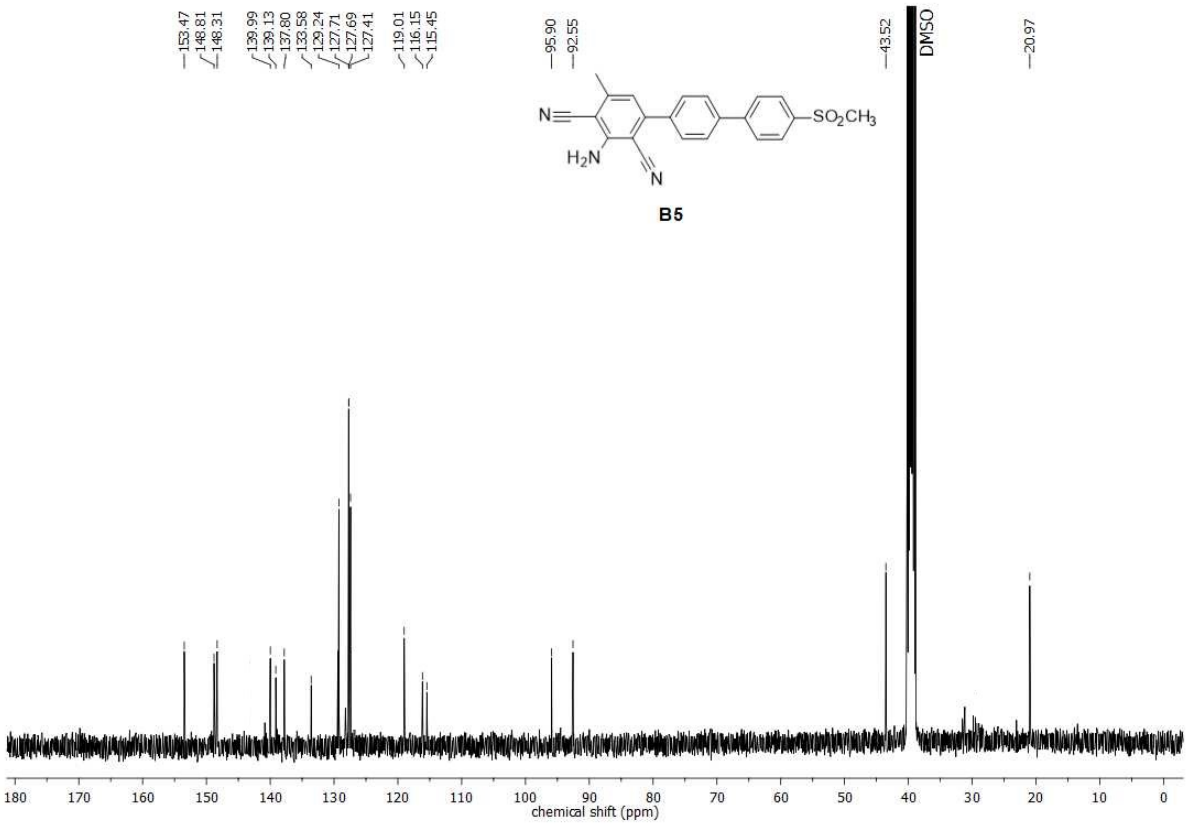


Figure S154: ^{13}CNMR of 2-amino-4-[4-(4-methylsulfonylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B5).

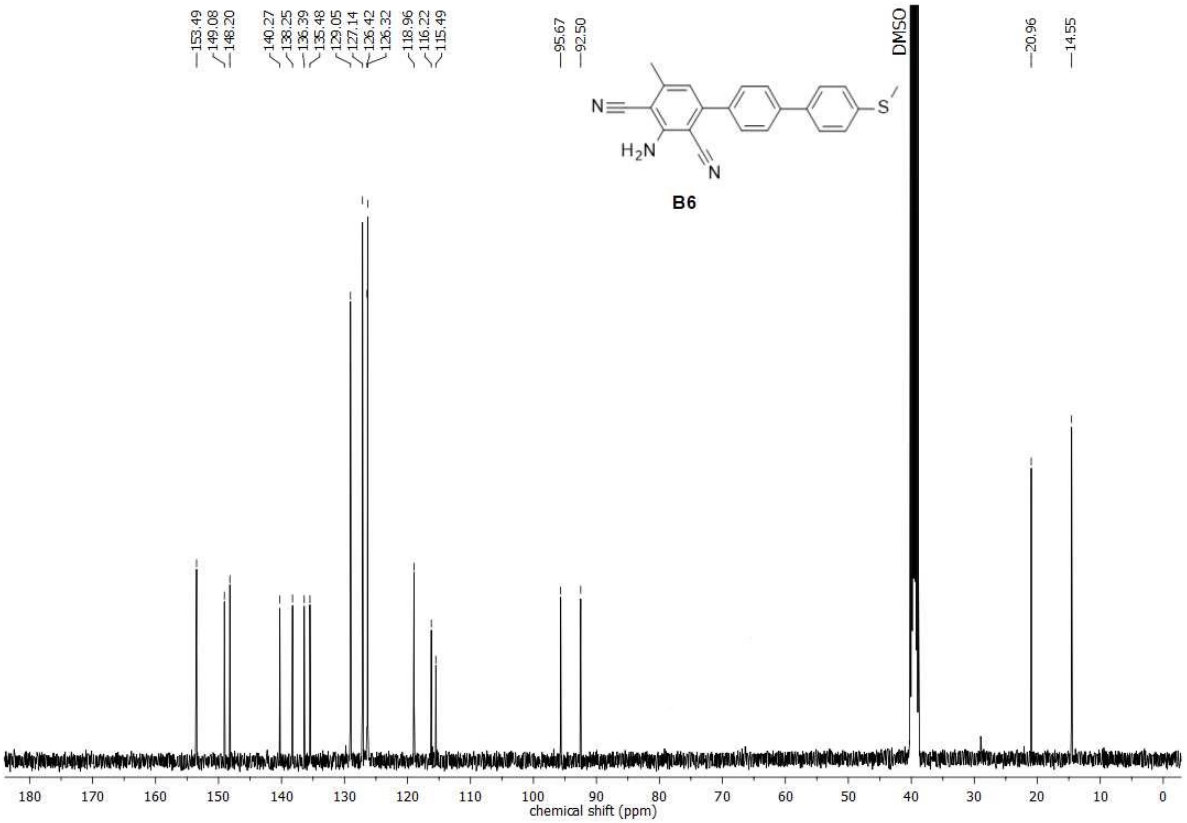


Figure S155: ^{13}CNMR of 2-amino-4-[4-(4-methylsulfanylphenyl)phenyl]-6-methyl-benzene-1,3-dicarbonitrile (B6).

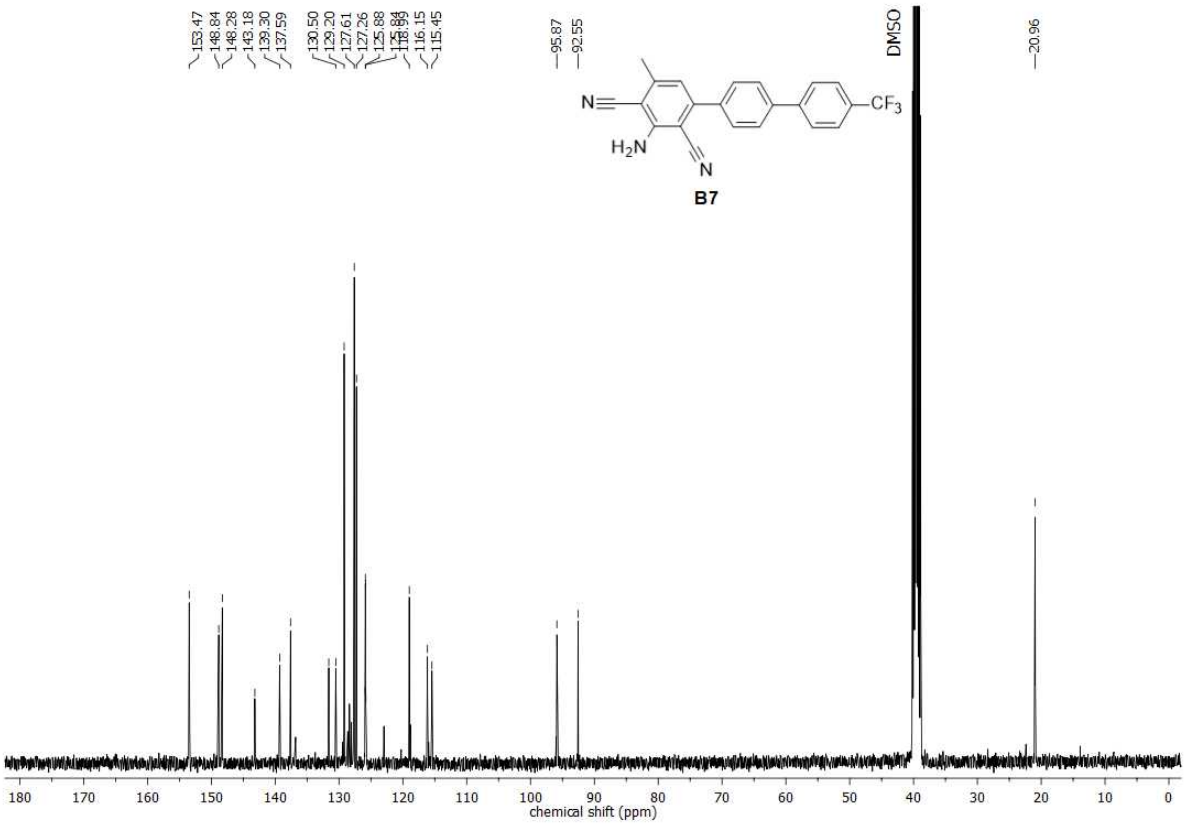


Figure S156: ^{13}CNMR of 2-amino-4-methyl-6-[4-[4-(trifluoromethyl)phenyl]phenyl]benzene-1,3-dicarbonitrile (B7).