**Supporting Information**

# Carbazole Scaffold Based Photoinitiators/Photoredox Catalysts: Toward new High Performance PhotoInitiating Systems and Application in LED Projector 3D Printing Resins.

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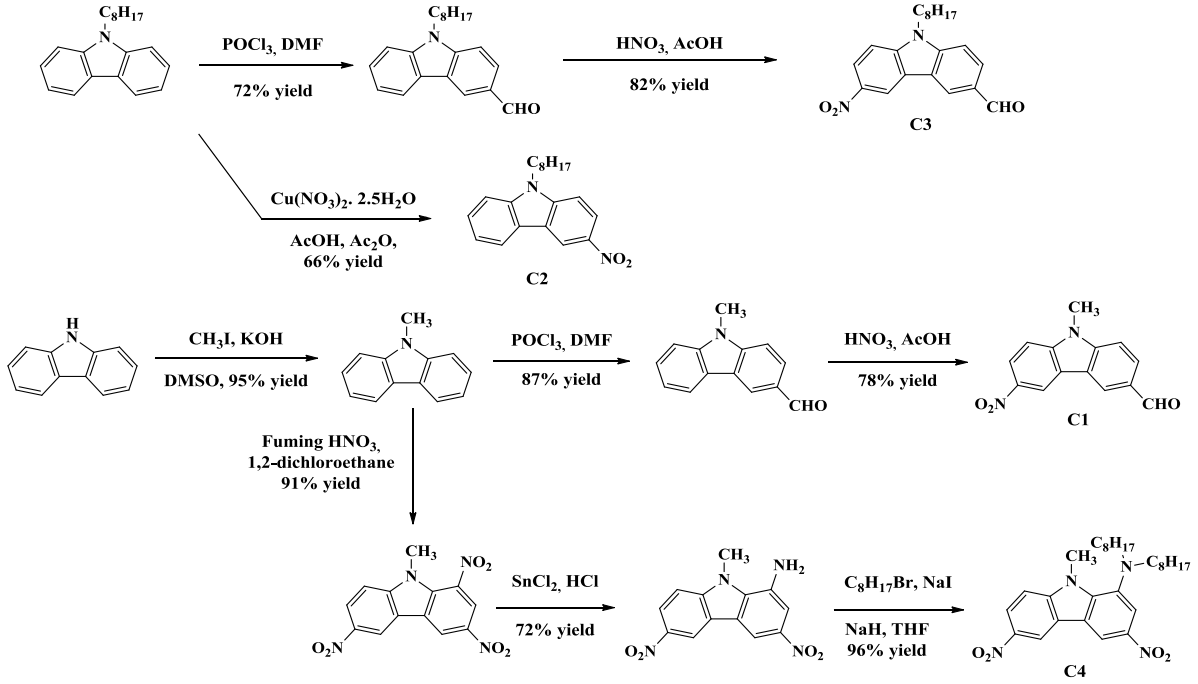
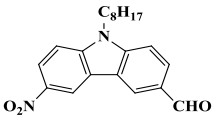
## *Synthesis of the Carbazole Derivatives (C1-C4)*

All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. $^{1}H$ and $^{13}C$ NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: $^{1}H$ (400 MHz) and $^{13}C$ (100 MHz). The $^{1}H$ chemical shifts were referenced to the solvent peak $CDCl_3$ (7.26 ppm), DMSO (2.49 ppm) and the $^{13}C$ chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm), DMSO (49.5 ppm). All these carbazole photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%) which was checked by high field NMR analysis. 3-Formyl-9-octyl-9*H*-carbazole [1] was synthesized as previously reported in the literature, without modifications and obtained in similar yields. The synthetic procedure for the preparation of C1-C4 is given in Scheme 1.



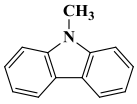

**Scheme 1.** The synthetic procedure for the preparation of C1-C4.

**Synthesis of 9-octyl-6-nitro-9*H*-carbazole-3-carbaldehyde C3**



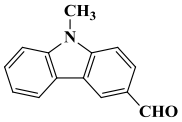
To a solution of 3-formyl-9-octylcarbazole (15 g, 48.79 mmol) in glacial acetic acid (65 mL) was slowly added at room temperature to a solution of fuming $HNO_3$ (2.4 mL) in 22 mL glacial acetic acid. After addition, stirring was maintained for 6 hours. The reaction mixture was diluted with 100 mL water, and the solid material was filtered off, washed several times with water and dried under vacuum (14.10 g, 82% yield). $^1$H NMR ($CDCl_3$) δ (ppm): 0.86 (t, 3H, J = 6.5 Hz), 1.24-1.35 (m, 10H), 1.92 (qt, 2H, J = 7.1 Hz), 4.40 (t, 2H, J = 7.2 Hz), 7.49 (d, 1H, J = 9.1 Hz), 7.57 (d, 1H, J = 8.6 Hz), 8.12 (dd, 1H, J = 8.6 Hz, J = 1.3 Hz), 8.44 (dd, 1H, J = 9.1 Hz, J = 2.2 Hz), 8.66 (d, 1H, J = 0.8 Hz), 9.06 (d, 1H, J = 2.1 Hz), 10.1 (s, 1H); $^{13}$C NMR ($CDCl_3$) δ (ppm): 14.0, 22.6, 27.2, 28.9, 29.1, 29.2, 31.7, 44.0, 109.2, 110.1, 117.5, 122.5, 122.7, 123.0, 124.6, 128.2, 130.0, 141.6, 144.3, 145.2, 191.3; HRMS (ESI MS) m/z: theor: 353.1860 found: 353.1862 ($[M+H]^+$ detected).

**Synthesis of 9-methyl-9*H*-carbazole**



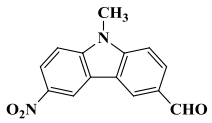

1-Iodomethane (14.2 g, 100 mmol) and potassium hydroxide (33.9 g, 605.4 mmol) were added to a solution of carbazole (18.5 g, 101.1 mmol) in DMSO (200 mL) under stirring. The reaction mixture was stirred for 24 h at 80°C. The reaction was quenched with water. A white precipitate formed. It was filtered off, washed several times with water and pentane, and finally dried under vacuum. It was used without any further purification (19.05 g, 95% yield). $^{1}$H NMR (DMSO-$d_6$) δ (ppm): 3.87 (s, 3H), 7.21 (t, 2H, J = 7.2 Hz), 7.47 (t, 2H, J = 7.2 Hz), 7.58 (d, 2H, J = 8.0 Hz), 8.15 (d, 2H, J = 7.5 Hz); $^{13}$C NMR (DMSO-$d_6$) δ (ppm): 28.9, 129.0, 118.6, 120.1, 121.9, 125.6, 140.6; HRMS (ESI MS) m/z: theor: 181.0891 found: 181.0895 ($[M]^{+\cdot}$ detected).

**Synthesis of 9-methyl-9*H*-carbazole-3-carbaldehyde**



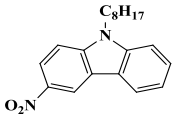

A solution of DMF (25 mL) containing 9-methyl-9*H*-carbazole (4.5 g, 25 mmol) was cooled to 0°C. $POC1_3$ (2.3 mL) was slowly added at 0°C and the solution was allowed to stir to room temperature for one hour. Then, the solution mixture was heated at 130°C for 4 hours. After cooling, the solution was poured into ice water/aq. NaOH solution. Solvents were removed under reduced pressure. Water was added and the solution was extracted with chloroform several times. The organic phases were combined, dried over magnesium sulfate and the solvent removed under vacuum. The residue was purified by column chromatography ($SiO_2$) using chloroform as the eluent (4.55 g, 87% yield). $^{1}$H NMR ($CDCl_3$) δ (ppm): 3.83 (s, 3H), 7.33 (td, 1H, J = 7.9 Hz, J = 0.9 Hz), 7.39-7.42 (m, 2H), 7.54 (td, 1H, J = 7.1 Hz, J = 1.2 Hz), 7.99 (dd, 1H, J = 8.5 Hz, J = 1.6 Hz), 8.12 (d, 1H, J = 7.7 Hz), 8.55 (d, 1H, J = 1.2 Hz); $^{13}$C NMR ($CDCl_3$) δ (ppm): 29.3, 108.7, 109.1, 110.6, 120.4, 120.6, 122.9, 123.8, 126.8, 127.2, 128.5, 140.7, 144.5, 191.8; HRMS (ESI MS) m/z: theor: 209.0841 found: 209.0838 ($[M]^{+\cdot}$ detected).

**Synthesis of 9-methyl-6-nitro-9*H*-carbazole-3-carbaldehyde C1**



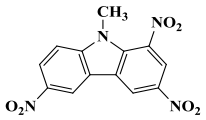

To a solution of 3-formyl-9-methylcarbazole (9 g, 42.86 mmol) in glacial acetic acid (65 mL) was slowly added at room temperature to a solution of fuming $HNO_3$ (2.1 mL) in 22 mL glacial acetic acid. After addition, stirring was maintained for 6 hours. The reaction mixture was diluted with 100 mL water, and the solid material was filtered off, washed several times with water and dried under vacuum (8.50 g, 78% yield). $^1$H NMR (DMSO-$d_6$) δ (ppm): 4.01 (s, 3H), 7.83-7.88 (m, 2H), 8.09 (d, 1H, J = 8.6 Hz), 8.41 (dd, 1H, J = 9.0 Hz, J = 2.2 Hz), 8.99 (s, 1H), 9.28 (d, 1H, J = 1.8 Hz), 10.09 (s, 1H); $^{13}$C NMR (DMSO-$d_6$) δ (ppm): 29.9, 110.3, 110.9, 117.7, 121.98, 122.04, 122.2, 125.0, 127.8, 129.6, 140.9, 144.7, 145.4, 191.9; HRMS (ESI MS) m/z: theor: 255.0764 found: 255.0765 ($[M+H]^+$ detected).

**Synthesis of 3-nitro-9-octyl-9*H*-carbazole C2**



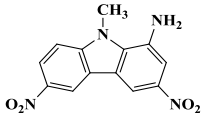

$Cu(NO_3)_2 \times 2.5H_2O$ (4.65 g, 20 mmol) in a mixture of acetic acid (45 mL) and acetic anhydride (90 mL) was slowly added at room temperature to a solution of 9-octyl-9*H*-carbazole (10.06 g, 36 mmol) dissolved in a mixture of acetic acid (45 mL) and acetic anhydride (90 mL). Stirring was maintained overnight. The mixture was then poured into distilled water (500 mL). The precipitate was collected by filtration, washed with water (3×300 mL), and dried under vacuum (7.70 g, 66% yield). Analyses were consistent with those previously reported.[2] $^1$H NMR ($CDCl_3$) δ (ppm): 0.86 (t, 3H, J = 6.5 Hz), 1.24-1.35 (m, 10H), 1.89 (qt, 2H, J = 7.1 Hz), 4.34 (t, 2H, J = 7.2 Hz), 7.35 (t, 1H, J = 7.9 Hz), 7.39 (d, 1H, J = 9.1 Hz), 7.47 (d, 1H, J = 8.2 Hz), 7.56 (t, 1H, J = 8.2 Hz), 8.16 (d, 1H, J = 7.8 Hz), 8.38 (dd, 1H, J = 9.1 Hz, J = 2.2 Hz), 9.02 (d, 1H, J = 2.2 Hz); $^{13}$C NMR ($CDCl_3$) δ (ppm): 14.0, 22.6, 27.2, 28.9, 29.1, 29.3, 31.7, 43.6, 108.2, 109.7, 117.4, 120.7, 121.0, 121.6, 122.5, 122.8, 127.3, 140.6, 141.6, 143.5; HRMS (ESI MS) m/z: theor: 325.1911 found: 325.1914 ($[M+H]^+$ detected).

**Synthesis of 9-methyl-1,3,6-trinitro-9*H*-carbazole**



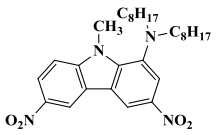
*N*-methylcarbazole (5.2 g, 0.028 mol) was dissolved in 1,2-dichloroethane (50 mL) and the solution was cooled with an ice-water bath. A mixture of fuming nitric acid (95-98%, 23 mL) and 1,2-dichloroethane (23 mL) was added over 1 h with vigorous stirring while maintaining the temperature below 10°C. After completion of the addition, the mixture was heated at 40-50°C for 3.5 h. After cooling to room temperature, the product was filtered, washed several times with water and dried to give 8.3 g of the title compound (91% yield). $^{1}$H NMR (DMSO-$d_6$) δ (ppm): 3.98 (s, 3H), 8.10 (d, 1H, J = 9.6 Hz), 8.56 (dd, 1H, J = 9.6 Hz, J = 2.1 Hz), 8.96 (s, 1H), 9.65 (d, 1H, J = 1.8 Hz), 9.90 (s, 1H); Anal. Calc. for $C_{13}H_8N_4O_6$: C, 49.4; H, 2.5; N, 17.7 Found: C, 49.6, H, 2.6; N, 17.4%; HRMS (ESI MS) m/z: theor: 316.0444 found: 316.0448 ($[M]^{+\cdot}$ detected)

**Synthesis of 9-methyl-3,6-dinitro-9*H*-carbazol-1-amine**



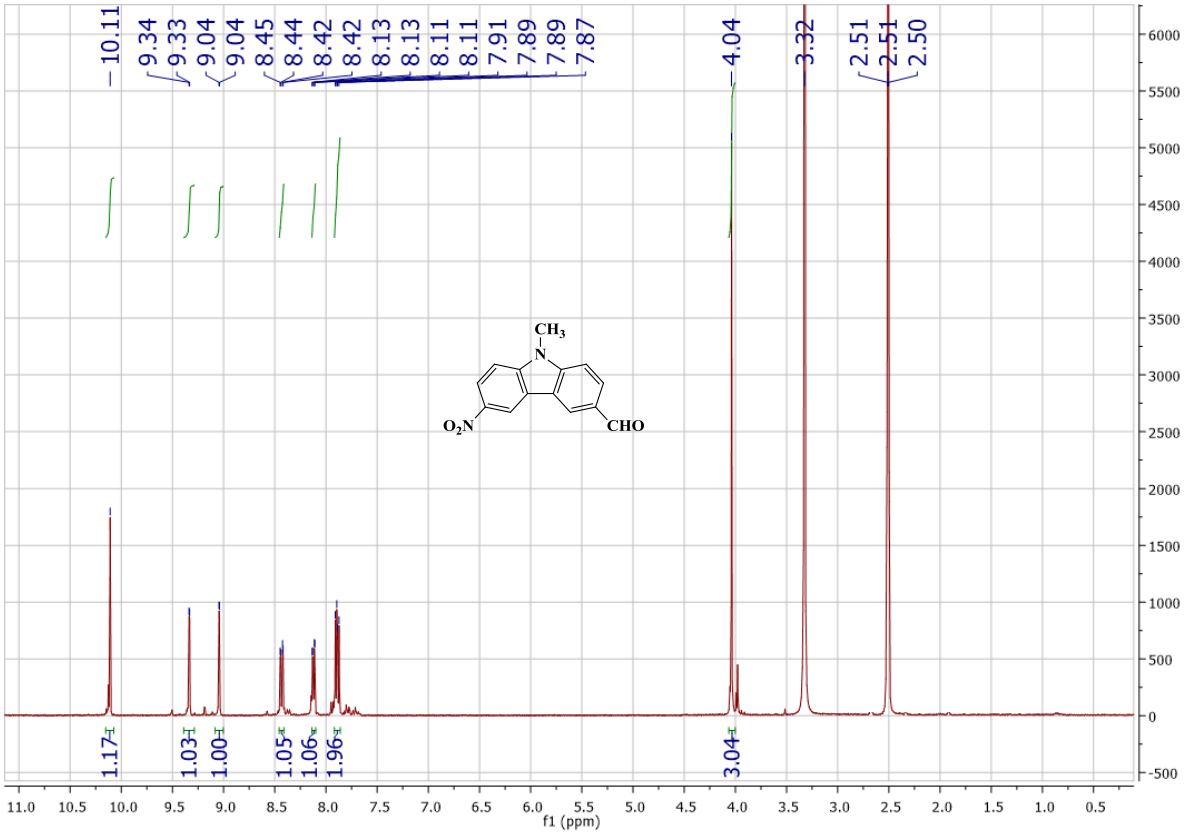
9-Methyl-1,3,6-trinitro-9*H*-carbazole (1.30 g, 4.11 mmol) was mixed with tin(II) chloride (7.0 g, 31 mmol) in conc. hydrochloric acid (7.0 mL) and refluxed for three days. The yellow precipitate was filtered off, washed several times with conc. HCl, and dried under vacuum (0.85 g, 72% yield). $^{1}$H NMR (DMSO-$d_6$) δ (ppm): 4.25 (s, 3H), 5.75 (s, 2H), 7.72 (d, 1H, J = 2.1 Hz), 7.81 (d, 1H, J = 9.2 Hz), 8.35 (dd, 1H, J = 9.2 Hz, J = 2.2 Hz), 8.71 (d, 1H, J = 2.1 Hz), 9.30 (d, 1H, J = 2.1 Hz); $^{13}$C NMR (DMSO-$d_6$) δ (ppm): 32.7, 107.5, 107.9, 110.5, 118.0, 121.9, 122.2, 123.2, 134.6, 136.1, 140.8, 142.1, 145.1

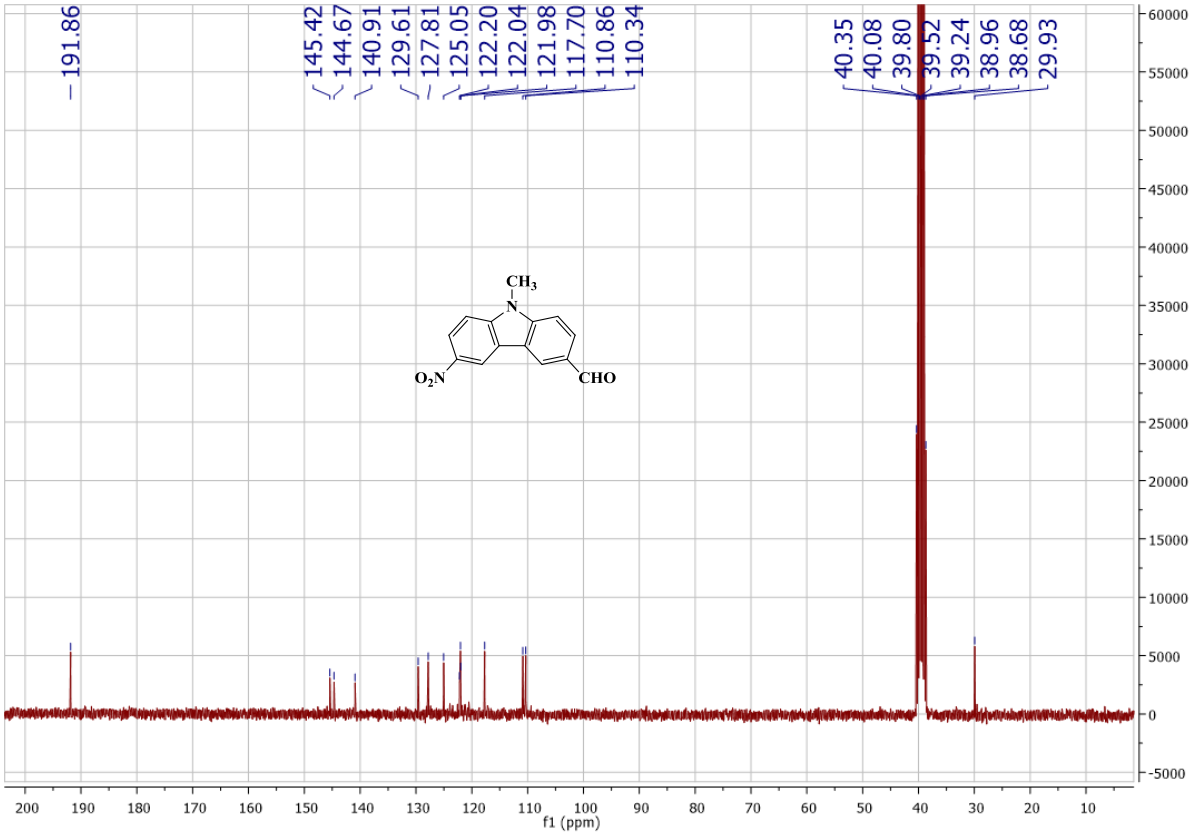
**Synthesis of 9-methyl-3,6-dinitro-*N,N*-dioctyl-9*H*-carbazol-1-amine C4**



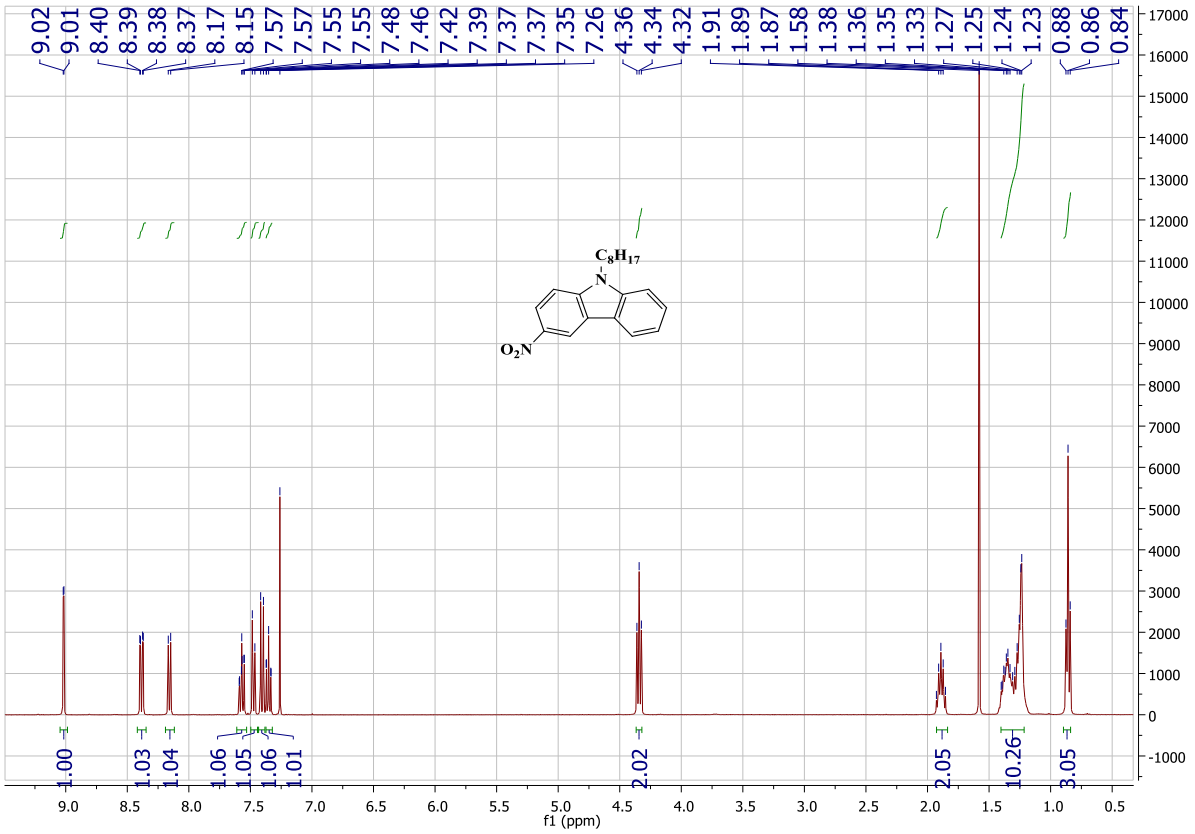
9-Methyl-3,6-dinitro-9*H*-carbazol-1-amine (1 g, 3.49 mmol), NaI (0.5 g, 3.34 mmol) and bromooctane (1.68 g, 8.73 mmol, 2.5 eq.) were suspended in 100 mL dry THF and NaH (1 g, 41.67 mmol) was added by portion at 0°C. The reaction mixture was heated at reflux overnight. After cooling, water was added. The solution was extracted with DCM several times. The organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$) using DCM as the eluent (1.71 g, 96% yield). $^1$H NMR ($CDCl_3$) δ (ppm): 0.84 (t, 6H, J = 6.0 Hz), 1.24-1.35 (m, 20H), 3.08-3.19 (m, 4H), 4.39 (s, 3H), 7.51 (d, 1H, J = 9.0 Hz), 8.19 (d, 1H, J = 1.8 Hz), 8.47 (dd, 1H, J = 2.0 Hz, J = 9.0 Hz), 8.81 (d, 1H, J = 1.9 Hz), 9.05 (d, 1H, J = 1.8 Hz); $^{13}$C NMR ($CDCl_3$) δ (ppm): 14.0, 22.5, 26.2, 27.3, 29.2, 29.3, 31.7, 54.6, 77.2, 109.6, 113.2, 117.2, 117.3, 122.8, 123.0, 124.2, 138.2, 140.9, 142.0, 142.1, 146.1; HRMS (ESI MS) m/z: theor: 511.3279 found: 511.3282 ($[M+H]^+$ detected).

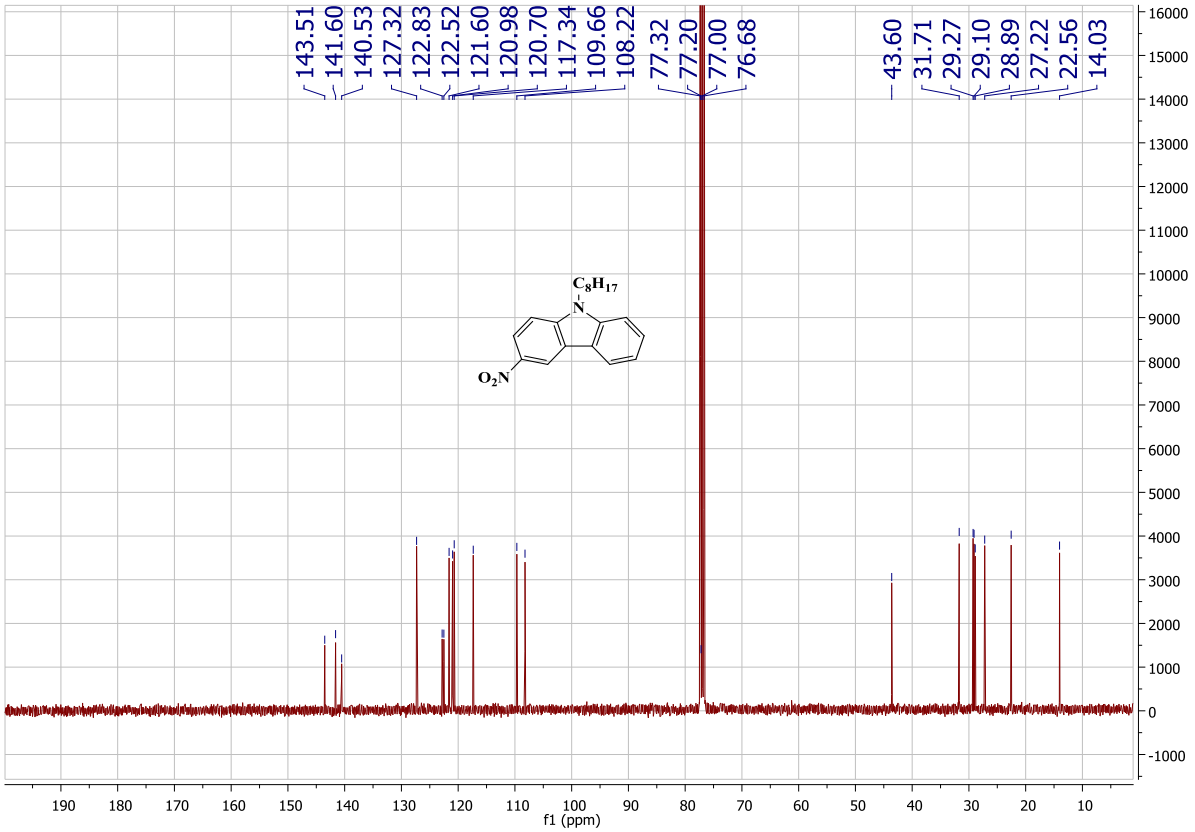
## 9-Methyl-6-nitro-9*H*-carbazole-3-carbaldehyde C1



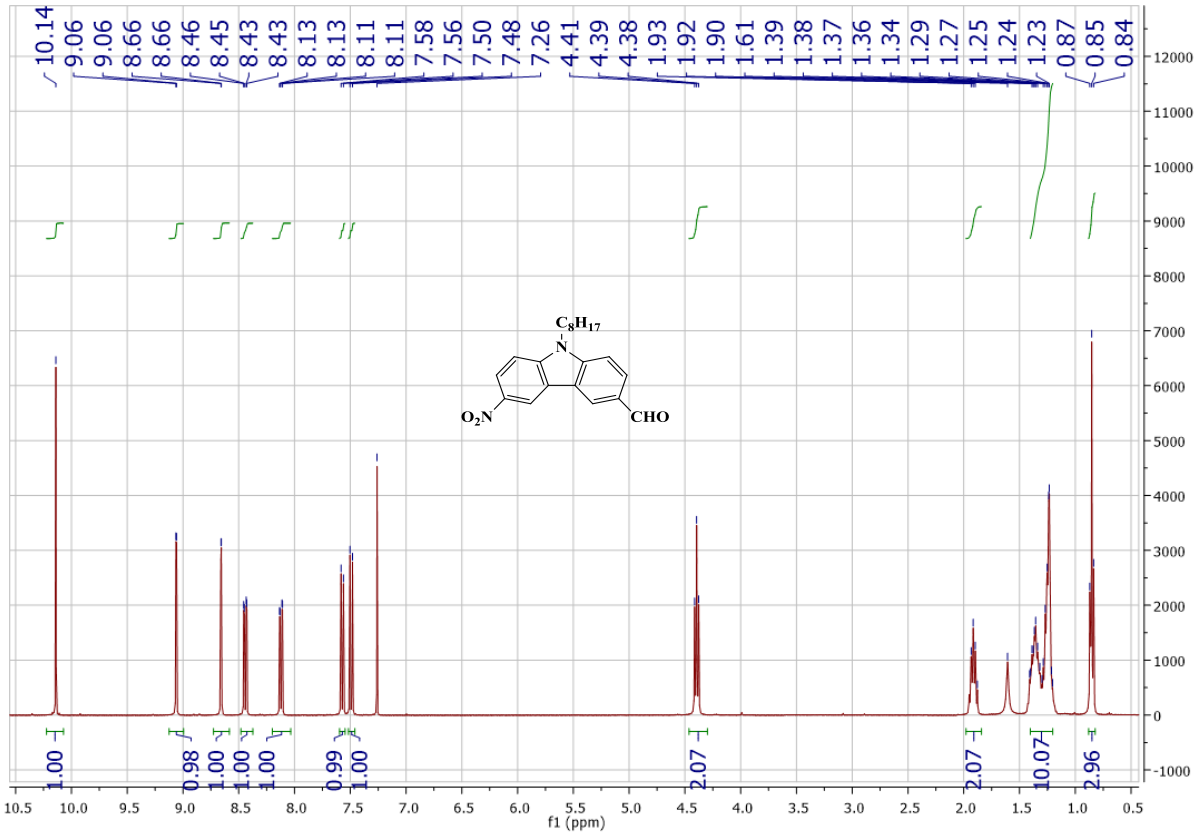



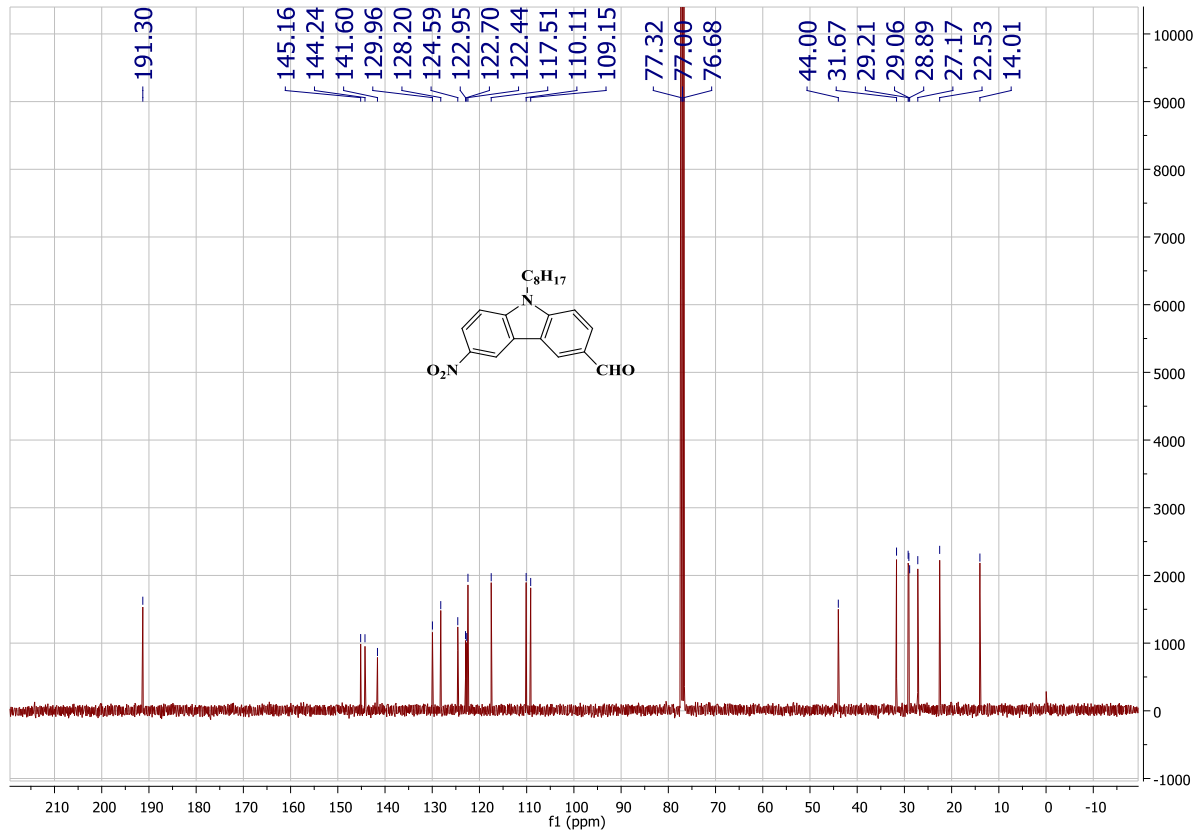
## 3-Nitro-9-octyl-9*H*-carbazole C2



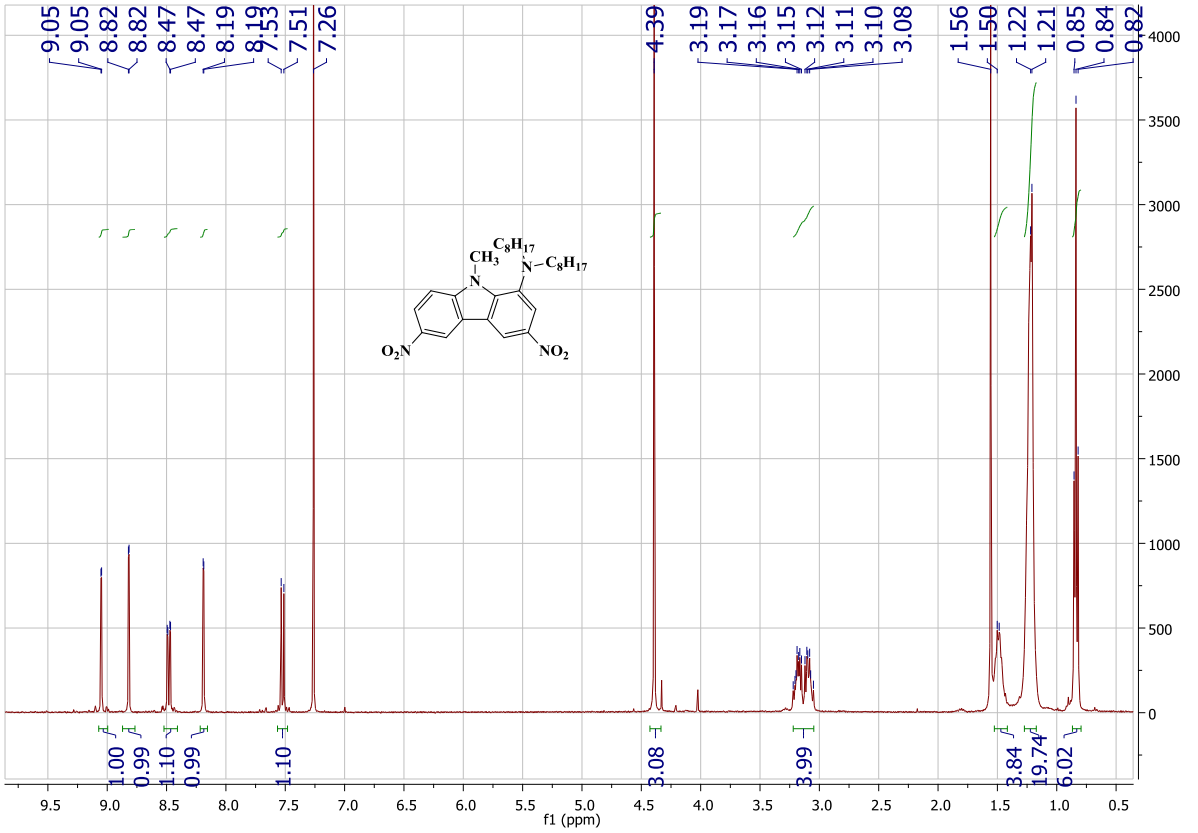



## 9-Octyl-6-nitro-9*H*-carbazole-3-carbaldehyde C3



**9-Methyl-3,6-dinitro-*N*,*N*-dioctyl-9*H*-carbazol-1-amine C4**



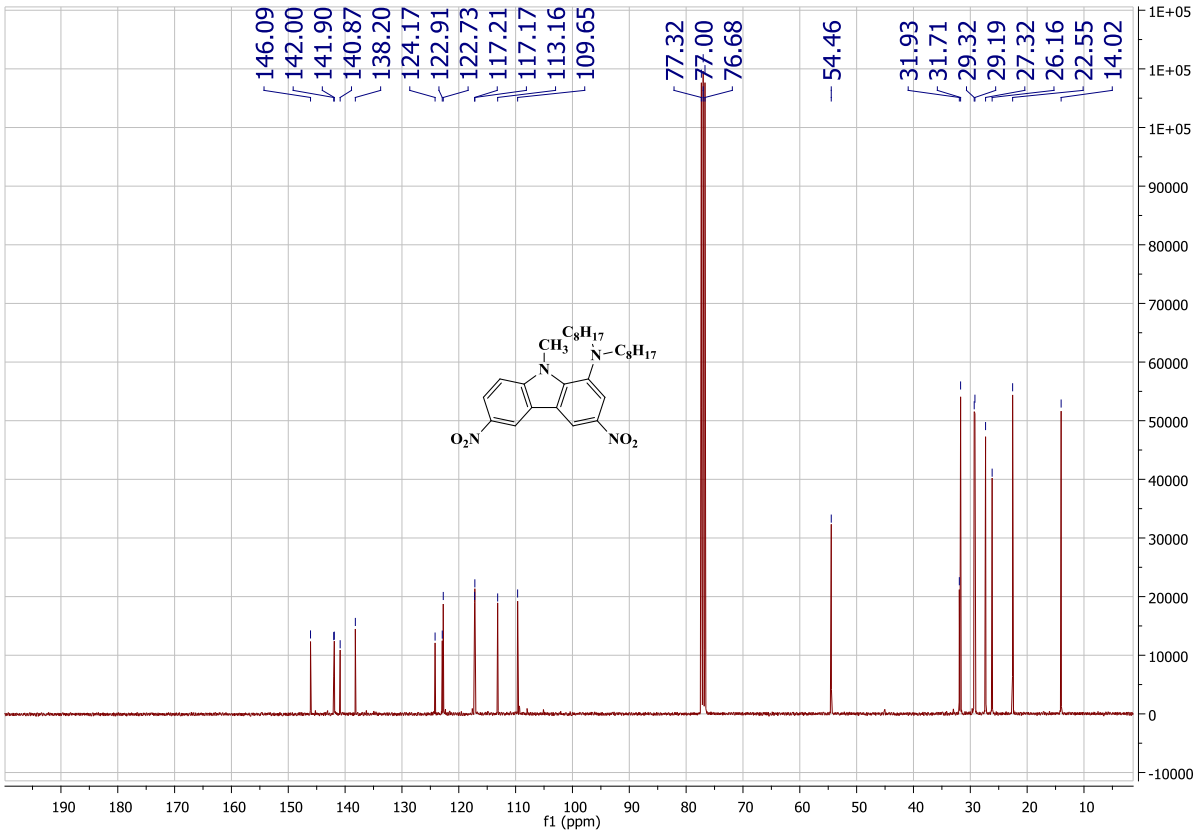



**Figure S1.** Calculated Uv-visible absorption spectra of carbazole derivatives (MPW1PW91/6-31g(d) level of theory).

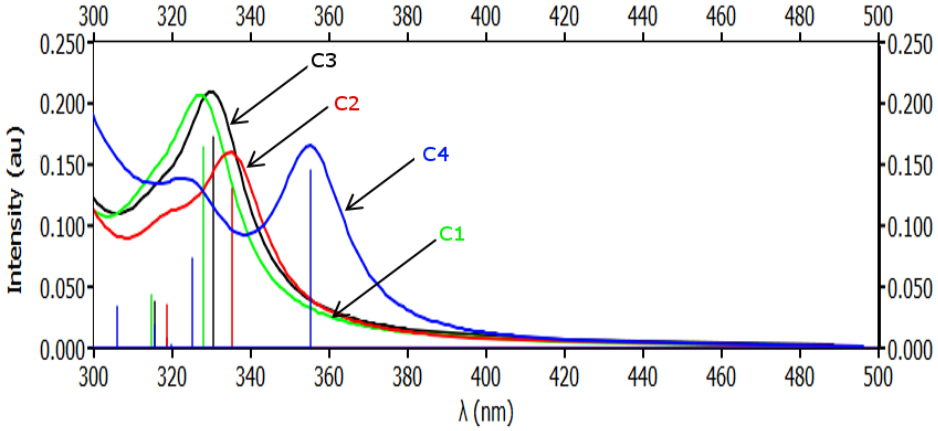



**Figure S2.** Uv-visible maximum absorption wavelengths of the carbazole derivatives in acetonitrile vs. calculated ones (MPW1PW91/6-31g(d) level of theory).

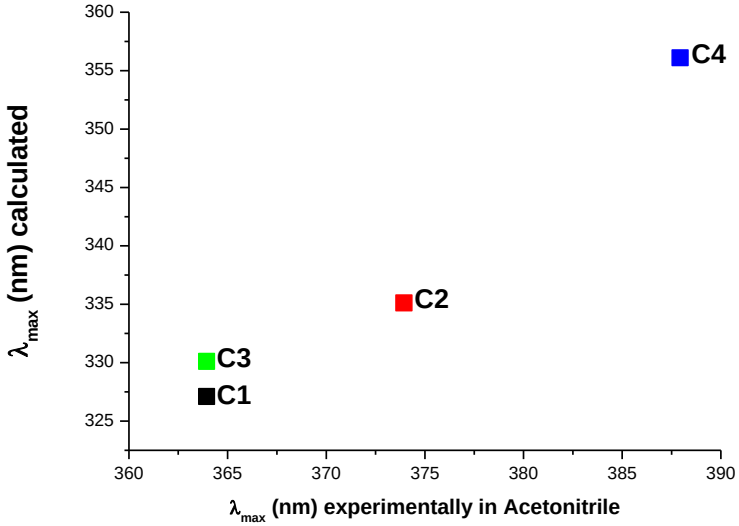
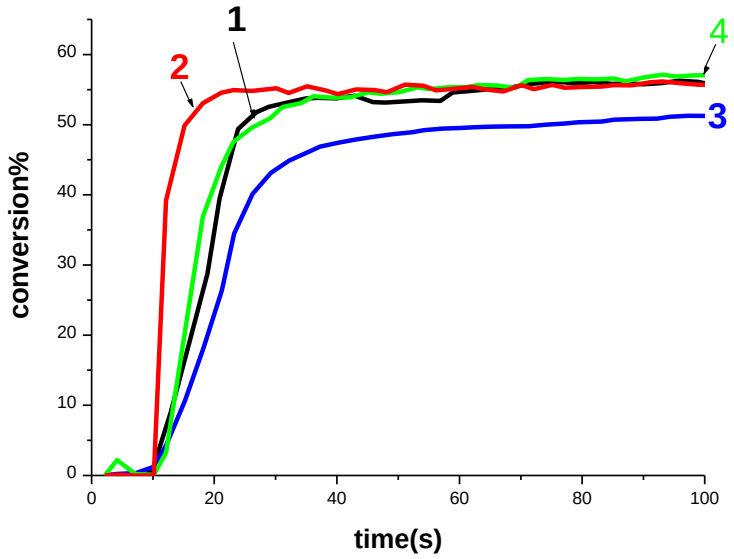



**Figure S3**. Polymerization profiles of TMPTA (acrylate function conversion vs. irradiation time) in laminate upon exposure to LED@405 nm in the presence of: (1) C2/Iod (0.5%/1% w/w); (2) C2/Iod/EDB (0.5%/1%/1.5% w/w); (3) C4/Iod (0.5%/1% w/w) and (4) C4/Iod/EDB (0.5%/1% w/w). (25µm thin sample) irradiation starts at t=10s.




**References:**

[1] Tehfe, M.-A.; Dumur, F.; Graff, B.; Morlet-Savary, F.; Gigmes, D.; Fouassier, J.-P.; Lalevée, J. Push–pull (Thio)barbituric Acid Derivatives in Dye Photosensitized Radical and Cationic Polymerization Reactions under 457/473 Nm Laser Beams or Blue LEDs. *Polym. Chem.* **2013**, *4* (13), 3866–3875 DOI: 10.1039/C3PY00372H.

[2] Dey, G.; Gupta, A.; Mukherjee, T.; Gaur, P.; Chaudhary, A.; Mukhopadhyay, S. K.; Nandi, C. K.; Ghosh, S. Functional Molecular Lumino-Materials to Probe Serum Albumins: Solid Phase Selective Staining Through Noncovalent Fluorescent Labeling. *ACS Appl. Mater. Interfaces* **2014**, *6* (13), 10231–10237 DOI: 10.1021/am501619g.