catalysts

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Supporting information

Novel push-pull dyes derived from 1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)-dione as versatile photoinitiators for photopolymerization and their related applications: 3D-printing and fabrication of photocomposites

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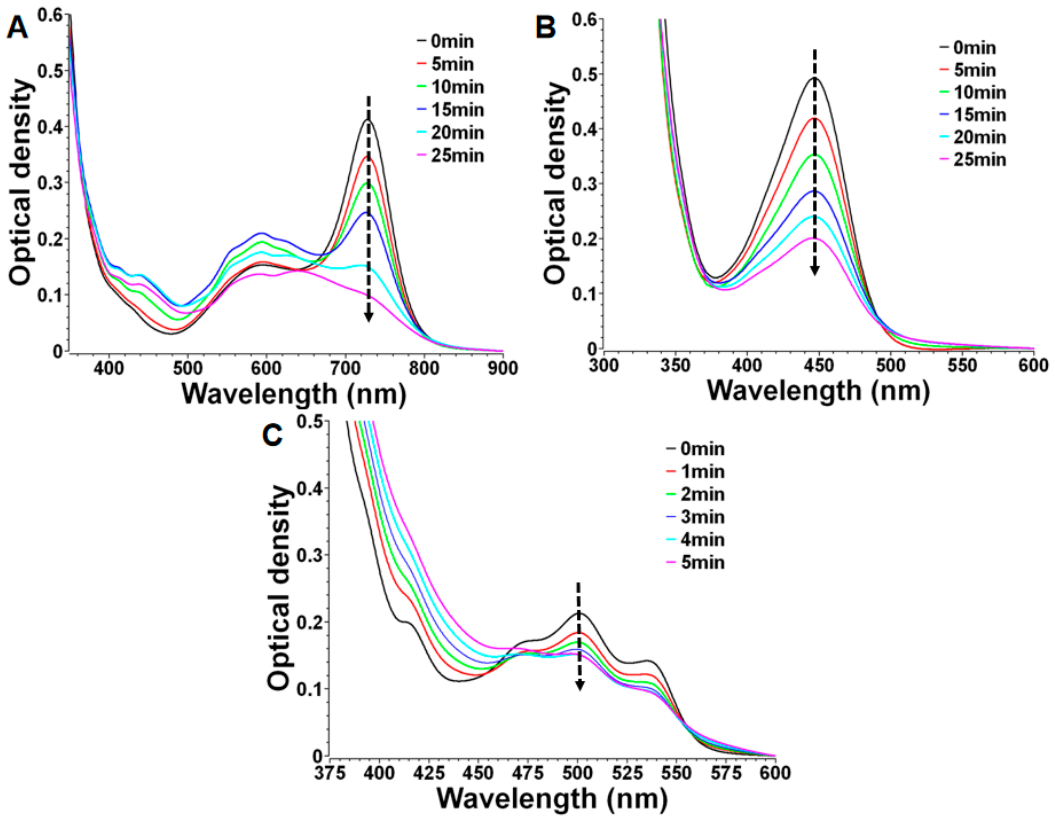


Figure S1. UV-vis absorption spectra of **(A)** dye 5 (6.92×10^{-6} M in acetonitrile), Iodonium (Speedcure 938, 1.46×10^{-4} M in acetonitrile) and amine (Speedcure EDB, 4.07×10^{-4} M in acetonitrile); **(B)** dye 6 (1.02×10^{-5} M in acetonitrile), Iodonium (Speedcure 938, 1.46×10^{-4} M in acetonitrile) and amine (Speedcure EDB, 4.07×10^{-4} M in acetonitrile); **(C)** dye 7 (1.26×10^{-5} M in acetonitrile w/w), Iodonium (Speedcure 938, 2.92×10^{-2} M in acetonitrile) and amine (Speedcure EDB, 8.14×10^{-2} M in acetonitrile) upon exposure to LED@405nm under air in the solvent of acetonitrile.

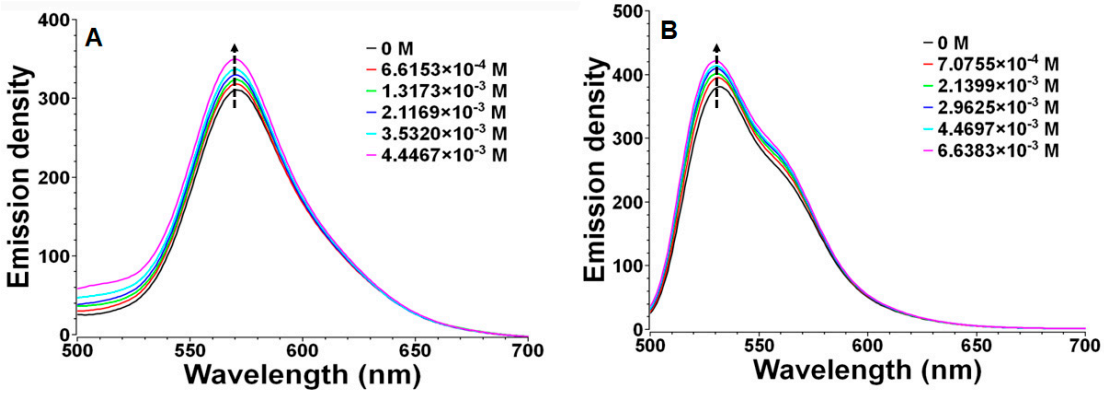


Figure S2. Fluorescence quenching of **(A)** dye 8 (8.51×10^{-6} M in acetonitrile); **(B)** dye 9 (8.54×10^{-6} M in acetonitrile) by Iodonium salts (Speedcure 938).

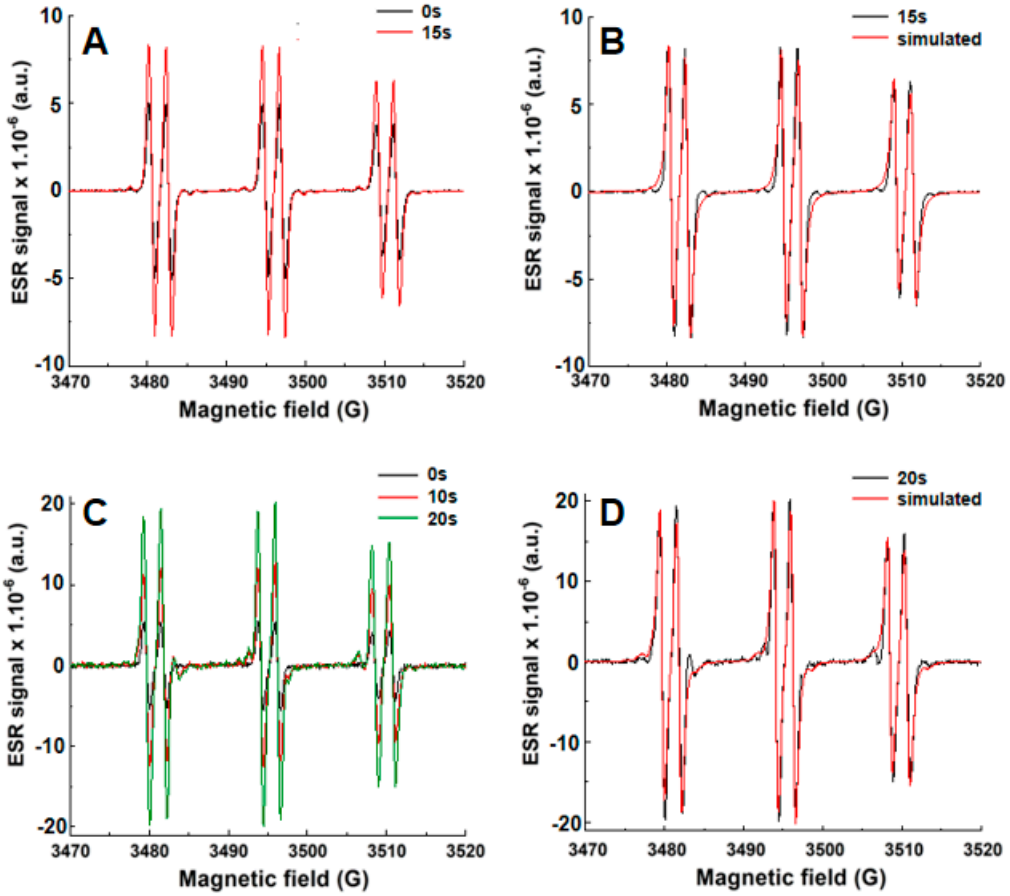
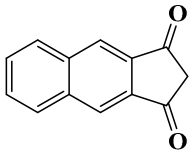


Figure S3. ESR spectra obtained from ESR-spin trapping experiment using PBN = 2 mg/mL (as spin trap agent); Iodonium salt = 12.6 mg/mL and dye **9**= 0.8 mg/mL in *tert*-butylbenzene under N_2. **(a)** dye **9**/Iod PIS, Irradiation time = 15 s (red) and = 0 s (black) spectra; **(b)** dye **9**/Iod PIS, Irradiation time = 15 s (black) and simulated (red) spectra; **(c) dye 9/amine PIS,** Irradiation time = 20 s (green), = 10 s (red) and = 0 s (black) spectra, respectively; **(d) dye 9/amine PIS,** Irradiation time = 20 s (black) and simulated (red) spectra.

Synthetic procedures

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 peaks: DMSO (2.49 ppm), $CDCl_3$ (7.26 ppm) and the ^{13}C chemical shifts were referenced to the solvent peaks: DMSO (49.5 ppm), $CDCl_3$ (77.0 ppm), respectively. All photoinitiators were prepared with analytical purity up to accepted standards for new organic compounds (>98%), which were checked by high field NMR analysis.

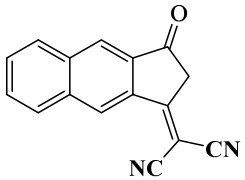
Synthesis of 1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)-dione **EA1**



Chemical Formula: $C_{13}H_8O_2$
Molecular Weight: 196.2050

Following the literature described by : "Pigot, C.; Noirbent, G.; Bui, T.-T.; Péralta, S.; Gigmes, D.; Nechab, M.; Dumur, F. Push-Pull Chromophores Based on the Naphthalene Scaffold: Potential Candidates for Optoelectronic Applications. *Materials* **2019**, *12* (8), 1342. https://doi.org/10.3390/ma12081342."

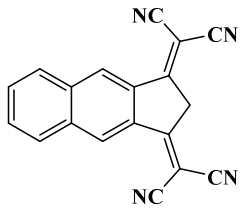
Synthesis of 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene) malononitrile **EA2**



Chemical Formula: $C_{16}H_8N_2O$
Molecular Weight: 244.2530

In a dried two-necked 100 mL flask, 1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)-dione (2) (5 g, 25.5 mmol, M = 196.21 g/mol) and malononitrile (5 g, 75 mmol M = 66.06 g/mol) were dissolved in ethanol (110 mL), and then anhydrous sodium acetate (8.4 g) was slowly added while stirring. After stirring for 2 h, the reaction mixture was poured into ice-water, and acidifed to pH = 1–2 by the addition of hydrochloric acid. The resulting precipitate was collected by filtration and washed with water giving the crude product 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile (4.17 g, 67 % yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ : 9.18 (brs, 1H), 8.48 (brs, 1H), 8.13 (brs, 2H), 7.80 (brs, 2H), 3.84 (brs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ : 195.43, 166.72, 136.60, 136.55, 135.96, 135.72, 131.07, 130.95, 130.88, 130.80, 130.65, 128.25, 126.04, 112.83, 112.53, 78.77, 44.78; HRMS (ESI MS) m/z: theor: 244.0637; found: 244.0640, $M^{+\cdot}$ detected.

Synthesis of 2,2'-(1*H*-cyclopenta[b]naphthalene-1,3(2*H*)-diylidene)dimalononitrile **EA3**

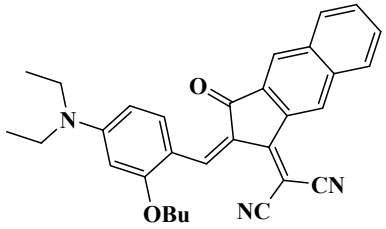


Chemical Formula: $C_{19}H_8N_4$
Molecular Weight: 292.3010

In a dried two-necked 100 mL flask, 1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)-dione (2) (3.5 g, 17.3 mmol, M = 196.21 g/mol) and malononitrile (2.8 g, 42.4 mmol, M = 66.06 g/mol) were dissolved in 2-ethoxyethanol (50 mL), and then anhydrous sodium acetate (3.8 g) was slowly added while

stirring. After refluxed overnight, the reaction mixture was poured into ice-water, and acidified to pH = 1–2 by the addition of concentrated hydrochloric acid. The resulting precipitate was collected by filtration and washed with EtOH. The filtrate was evaporated and a filtration on a plug of silica enabled to get it in pure form (2.1 g, 41% yield). ^{1}H NMR (300 MHz, DMSO-d_6) δ : 8.46 (s, 1H), 8.06 (t, *J* = 6.0 Hz, 2H), 7.93 (s, 1H), 7.72 – 7.58 (m, 2H), 6.19 (s, 1H); Deprotonated form is detected by NMR in this highly polar solvent; Anal. calc. for $C_{19}H_8N_4$: C, 78.1, H, 2.8, N, 19.2; found: C 77.9, H 2.8, O 19.3; HRMS (ESI MS) m/z: theor: 292.0749; found: 292.0753, $M^{+\cdot}$ detected.

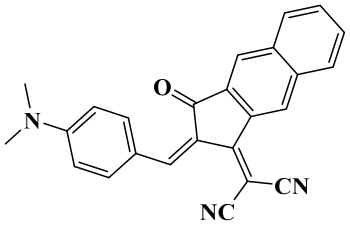
Dye 1: Synthesis of 2-(2-(3-butoxy-4-(diethylamino)benzylidene)-3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*] naphthalen-1-ylidene)malononitrile.



Chemical Formula: $C_{31}H_{29}N_3O_2$
Molecular Weight: 475.5920

In a round bottom flask, 2-butoxy-4-(diethylamino)benzaldehyde (0.456 g, 1.8 mmol, M = 249.35 g/mol) and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene) malononitrile (0.445 g, 1.8 mmol, M = 244.25 g/mol) were mixed in ethanol (40 mL). A few drops of *N,N*-diisopropylethylamine (DIPEA) were added. Then, the mixture was placed in a pre-heated bath at 90 °C. Progress of the reaction was monitored by TLC. After cooling, the resulting precipitate was filtered off, washed several times with EtOH and pentane. 0.744 g (87% yield) of a dark solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 9.10-9.08 (m, 2H), 8.84 (s, 1H), 8.24 (brs, 1H), 8.10 – 7.93 (m, 2H), 7.68 – 7.57 (m, 2H), 6.44 (dd, *J* = 9.5, 2.2 Hz, 1H), 6.00 (d, *J* = 2.2 Hz, 1H), 4.07 (t, *J* = 6.4 Hz, 2H), 3.54 (q, *J* = 7.1 Hz, 4H), 1.99 – 1.86 (m, 2H), 1.56 (d, *J* = 13.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ : 164.57, 164.15, 156.25, 142.62, 139.01, 135.97, 135.19, 134.11, 130.40, 129.84, 128.90, 128.67, 125.40, 123.35, 122.53, 116.85, 114.08, 105.74, 92.62, 77.32, 77.00, 76.69, 68.63, 45.46, 30.89, 19.35, 13.83, 12.88; HRMS (ESI MS) m/z: theor: 476.2333; found: 476.2336 $[M+H]^+$ detected.

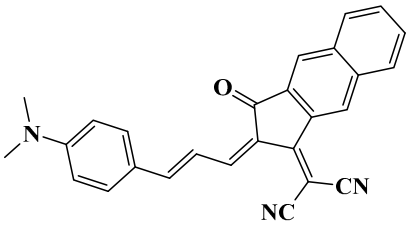
Dye 2 Synthesis of 2-(2-(4-(dimethylamino)benzylidene)-3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile.



Chemical Formula: $C_{25}H_{17}N_3O$
Molecular Weight: 375.4310

In a round bottom flask, 4-(dimethylamino)benzaldehyde (0. 272 g, 1.8 mmol, M = 149.19 g/mol) and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene) malononitrile (0.445 g, 1.8 mmol, M = 244.25 g/mol) were mixed in ethanol (40 mL). A few drops of DIPEA were added. Then, the mixture was placed in a pre-heated bath at 90 °C. Progress of the reaction was monitored by TLC. After cooling, the resulting precipitate was filtered off, washed several times with EtOH and pentane. 0.459 g (68% yield) of a dark solid was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 9.14 (s, 1H), 8.65 – 8.28 (m, 4H), 8.06 (s, 2H), 7.66 (s, 2H), 6.79 (s, 2H), 3.23 (s, 6H); Anal. calc. for $C_{25}H_{17}N_3O$: C 80.0, H11.2, O 4.3; found: C 79.8, H 11.3, O 4.5; HRMS (ESI MS) m/z: theor: 376.1444 found: 375.1372 ($[M+H]^+$ detected).

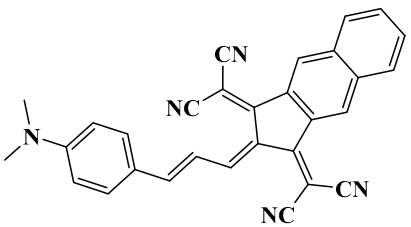
Dye 3: Synthesis of 2-{(2*E*)-3-[4-(dimethylamino)phenyl]prop-2-en-1-ylidene}-3- oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene]propanedinitrile.



Chemical Formula: $C_{27}H_{19}N_3O$
Molecular Weight: 401.4690

In a round bottom flask, (*E*)-3-(4-(dimethylamino)phenyl)acrylaldehyde (0. 315 g, 1.8 mmol, M = 175.23 g/mol) and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1- ylidene)malononitrile (0.445 g, 1.8 mmol, M = 244.25 g/mol) were mixed in ethanol (40 mL). A few drops of DIPEA were added. Then the mixture was placed in a pre-heated bath at 90 °C. Progress of the reaction was monitored by TLC. After cooling, the resulting precipitate was filtered off, washed several times with EtOH and pentane. 0.318 g (44% yield) of a dark solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) : 9.15 (brs, 1 H), 8.78 (brs, 1 H), 8.61 (brs, 1 H), 8.32 (brs, 1 H), 8.02–8.08 (brs, 2 H), 7.66–7.68 (m, 4 H), 7.46 (*d*, *J* = 14.8 Hz, 1 H), 6.72 (brs, 2 H), 3.15 (*s*, 6 H); Anal. calc. for $C_{27}H_{19}N_3O$: C 80.8, H 4.8, O 4.0; found: C 80.6, H 4.6, O 4.1; HRMS (ESI MS) m/z: theor: 402.1601 found: 402.1600 ($[M+H]^+$ detected).

Dye 4: Synthesis of (*E*)-2,2'-(2-(3-(4-(dimethylamino)phenyl)allylidene)-1*H*- cyclopenta[*b*] naphthalene-1,3(2*H*)-diylidene)dimalononitrile.

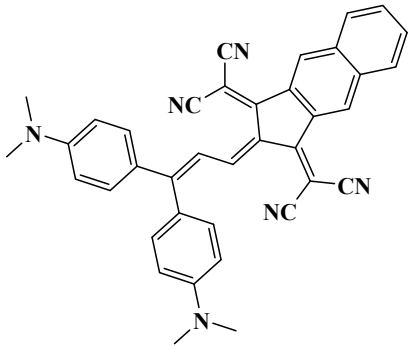


Chemical Formula: $C_{30}H_{19}N_5$
Molecular Weight: 449.5170

In a round bottom flask, (*E*)-3-(4-(dimethylamino)phenyl)acrylaldehyde (0. 275 g, 1.56 mmol, M = 175.23 g/mol) and 2,2'-(1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)- diylidene)dimalononitrile (0.458 g, 1.56 mmol, M = 292.30 g/mol) were mixed in Ac_2O (20 mL). Then the mixture was placed in a

pre-heated bath at 90 °C and then heated to reflux overnight. After cooling and evaporation of the solvent, addition of pentane/diethyl ether to the residue allowed the formation of a dark solid, which was separated by filtration, washed several times with EtOH and pentane. 0.260g (37% yield) of solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.91 (d, *J* = 62.4 Hz, 2H), 8.65 (d, *J* = 8.1 Hz, 1H), 7.94 (s, 2H), 7.60 (m, 5H), 7.46 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 2H), 3.07 (s, 6H); Anal. calc. for $C_{30}H_{19}N_5$: C, 80.2; H, 4.3; N, 15.6; found : C, 80.1; H, 4.2; N, 15.6; HRMS (ESI MS) m/z: theor: 450.1713 found: 450.1715 ($[M+H]^+$ detected).

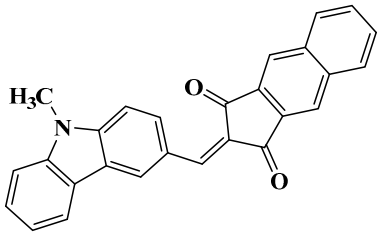
Dye 5: Synthesis of 2,2'-(2-(3,3-*bis*(4-(dimethylamino)phenyl)allylidene)-1*H*-cyclopenta[*b*] naphthalene-1,3(2*H*)-diylidene)dimalononitrile



Chemical Formula: $C_{38}H_{28}N_6$
Molecular Weight: 568.6840

In a round bottom flask, 3,3-bis(4-(dimethylamino)phenyl)acrylaldehyde (0. 459 g, 1.56 mmol, M = 294.40 g/mol) and 2,2'-(1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)-diylidene)dimalononitrile (0.458 g, 1.56 mmol, M = 292.30 g/mol) were mixed in Ac_2O (30 mL). Then the mixture was placed in a pre-heated bath at 90 °C and then heated to reflux overnight. After cooling and evaporation of the solvent, addition of pentane/diethyl ether to the residue allowed the formation of a purple solid, which was separated by filtration, washed several times with EtOH and pentane. 0.372g (42% yield) of solid was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 8.96 (s, 2H), 8.21 (d, *J* = 12.5 Hz, 1H), 7.99 (m, 2H), 7.64 (m, 2H), 7.43-7.41 (m, 4H), 6.79 (m, 5H), 3.14 (s, 12H); Anal. calc. for $C_{38}H_{28}N_6$: C, 80.3; H, 5.0; N, 14.8 found : C, 80.2; H, 4.9; N, 14.6; HRMS (ESI MS) m/z: theor: 569.2448 found: 569.2452 ($[M+H]^+$ detected).

Dye 6: Synthesis of 2-((9-methyl-9*H*-carbazol-3-yl)methylene)-1*H*-cyclopenta[*b*] naphthalene -1,3(2*H*)-dione

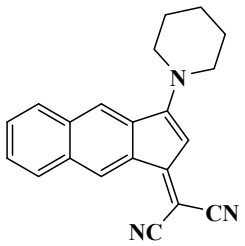


Chemical Formula: $C_{27}H_{17}NO_2$
Molecular Weight: 387.4380

1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)-dione (0.5 g, 2.55 mmol, M = 196.20 g/mol) and 9-methyl-9H-carbazole-3-carbaldehyde (0.53 g, 2.55 mmol, M = 209.25 g/mol) were dissolved in

absolute ethanol (50 mL) and a few drops of piperidine were added. The reaction mixture was refluxed and progress of the reaction was followed by TLC. After cooling, a precipitate formed. It was filtered off, washed several times with ethanol and dried under vacuum. 0.840 g (85% yield) of solid was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 3.91 (s, 3H), 7.37 (t, 1H, *J* = 6.7 Hz), 7.43 (d, 1H, *J* = 7.8 Hz), 7.48 (d,1H, *J* = 8.7 Hz), 7.53 (t, 1H, *J* = 7.3 Hz), 7.66-7.69 (m, 2H), 8.05-8.12 (m, 3H), 8.20 (s, 1H), 8.28 (d, 1H, *J* = 7.3 Hz), 8.48 (d, 2H, *J* = 7.6 Hz), 8.76 (d, 1H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 29.4, 108.8, 109.2, 120.8, 121.0, 123.2, 123.66, 123.68, 123.7, 125.3, 126.8, 127.5, 128.8, 128.9, 129.0, 130.38, 130.40, 133.9, 135.7, 136.3, 136.5, 137.8, 141.7, 144.5, 149.9, 189.5, 190.9; HRMS (ESI MS) m/z: theor: 388.1332 found: 388.1330 ($[M+H]^+$ detected).

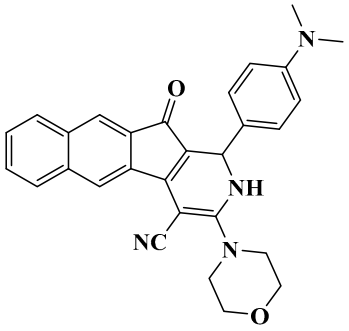
Dye 7: Synthesis of 2-(3-(piperidin-1-yl)-1*H*-cyclopenta[*b*]naphthalen-1-ylidene) malononitrile.



Chemical Formula: $C_{21}H_{17}N_3$
Molecular Weight: 311.3880

In a round bottom flask, (*E*)-3-(4-(dimethylamino)phenyl)acrylaldehyde (0.902, g, 5.15 mmol, M = 175.23 g/mol) and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*] naphthalen-1-ylidene)malononitrile (1.25 g, 5.15 mmol, M = 244.25 g/mol) were mixed in ethanol (40 mL). A few drops of piperidine were added. Then, the mixture was placed in a pre-heated bath at 90 °C and the mixture turned to a deep red color. Progress of the reaction was monitored by TLC and after 15min. of heating, no progress was detected. The solution was cooled to room temperature during which time, a precipitate formed. The insoluble red solid was filtered off, washed several times with EtOH and Et_2O, and dried under vacuum. 1.41 g (88% yield) of a red solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.57 (s, 1H), 7.77–7.89 (m, 3H), 7.52–7.57 (m, 2H), 5.87 (s, 1H), 3.86 (br. s, 4H), 1.85 (br. s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 23.8, 26.1, 51.5, 56.9, 103.1, 116.9, 117.0, 123.7, 124.3, 128.40, 128.41, 129.5, 129.8, 133.1, 133.3, 133.5, 134.3, 161.8, 162.6; HRMS (ESI MS) m/z: theor: 312.1495 found: 312.1492 ($[M]^{+\cdot}$ detected).

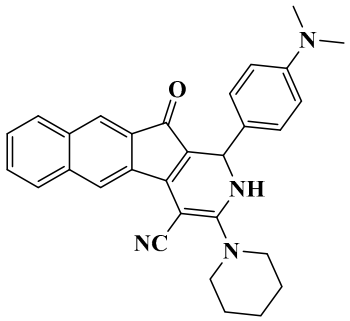
Dye 8: Synthesis of 1-(4-(dimethylamino)phenyl)-3-morpholino-11-oxo-2,11 -dihydro-1*H*-benzo [5,6]indeno [2,1-*c*]pyridine-4-carbonitrile



Chemical Formula: $C_{29}H_{26}N_4O_2$
Molecular Weight: 462.5530

In a round bottom flask, 4-(dimethylamino)benzaldehyde (0. 272 g, 1.8 mmol, M = 149.19 g/mol) and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene)malononitrile (0.445 g, 1.8 mmol, M = 244.25 g/mol) were mixed in ethanol (40 mL). A few drops of morpholine were added. Then, the mixture was placed in a pre-heated bath at 90°C and the mixture immediately turned to a deep red color. After 15 min. of heating (progress of the reaction was monitored by TLC), the reaction was stopped. After cooling, the insoluble red solid was filtered off, washed with EtOH and Et_2O. 0.658 g (79% yield) of a red solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.92 (s, 6H), 3.47–3.52 (m, 4H), 3.72–3.77 (m, 4H), 5.42 (brs, 1H), 5.63 (d, 1H, *J* = 3.9 Hz), 6.68 (d, 2H, *J* = 8.5 Hz), 7.25 (d, 2H, *J* = 8.5 Hz), 7.44–7.52 (m, 2H), 7.74 (s, 1H), 7.79 (d, 1H, *J* = 7.8 Hz), 7.84 (d, 1H, *J* = 7.8 Hz), 8.16 (s, 1H); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.85 (s, 6H), 3.44–3.54 (m, 2H), 3.69–3.78 (m, 6H), 5.49 (s, 1H), 6.68 (d, 2H, *J* = 8.9 Hz), 7.12 (d, 2H, *J* = 8.9 Hz), 7.50–7.58 (m, 2H), 7.78 (s, 1H), 7.89 (d, 1H, *J* = 8.6 Hz), 7.98 (d, 1H, *J* = 8.6 Hz), 8.04 (s, 1H), 8.97 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 48.0, 49.1, 51.5, 59.3, 65.9, 112.4, 117.5, 119.0, 119.8, 120.2, 127.2, 128.0, 129.0, 129.8, 129.9, 131.9, 133.3, 133.6, 134.4, 135.3, 149.9, 153.3, 160.2, 185.9; HRMS (ESI MS) *m*/*z*: theor: 463.2129 found: 463.2126 ([M+H$^+$] detected).

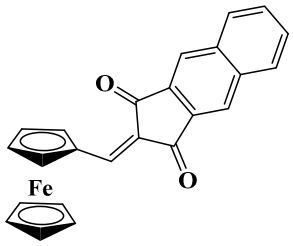
Dye 9: Synthesis of 1-(4-(dimethylamino)phenyl)-11-oxo-3-(piperidin-1-yl)-2,11-dihydro-1*H*-benzo[5,6]indeno[2,1-*c*]pyridine-4-carbonitrile.



Chemical Formula: $C_{30}H_{28}N_4O$
Molecular Weight: 460.5810

In a round bottom flask, 4-(dimethylamino)benzaldehyde (0. 77 g, 5.15 mmol, M = 149.19 g/mol) and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1- ylidene)malononitrile (1.25 g, 5.15 mmol, M = 244.25 g/mol) were mixed in ethanol (40 mL). A few drops of piperidine were added. Then, the mixture was placed in a pre-heated bath at 90°C and the mixture turned immediately to a deep red color. After 15min. of heating (progress of the reaction was monitored by TLC), the reaction was finished. After cooling, the red precipitate was filtered off, washed with EtOH and Et_2O. 0.452 g (14% yield) of a red solid was obtained. ^{1}H NMR (400 MHz, Acetone-d_6) δ : 1.68–1.80 (m, 6H), 2.90 (s, 6H), 3.58–3.87 (m, 4H), 5.59 (d, 2H, *J* = 4.8 Hz), 6.71 (d, 2H, *J* = 8.8 Hz), 7.23 (d, 2H, *J* = 8.8 Hz), 7.48–7.61 (m, 2H), 7.74 (s, 1H), 7.93 (dd, 2H, *J* = 13.7 Hz, J = 7.5 Hz), 8.20 (s, 1H); ^{1}H NMR (400 MHz, $CDCl_3$) δ : 1.72–1.75 (m, 6H), 2.90 (s, 6H), 3.50–3.57 (m, 2H), 3.62–3.68 (m, 2H), 5.57–5.60 (m, 2H), 6.67 (d, 2H, *J* = 8.5 Hz), 7.25 (d, 2H, *J* = 8.5 Hz), 7.40–7.48 (m, 2H), 7.71 (s, 1H), 7.77 (d, 1H, *J* = 7.6 Hz), 7.82 (d, 1H, *J* = 7.6 Hz), 8.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 25.4, 40.2, 40.4, 49.8, 54.2, 80.2, 110.9, 112.4, 120.5, 120.9, 123.5, 124.1, 127.2, 127.9, 128.4, 129.5, 130.1, 131.9, 133.3, 133.7, 134.8, 136.2, 153.6, 157.3, 160.1, 160.2, 187.2; HRMS (ESI MS) *m*/*z*: theor: 461.2336 found: 461.2333 ([M+H$^+$] detected).

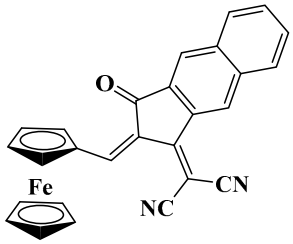
Dye 10: Synthesis of ((1,3-dioxo-1,3-dihydro-2*H*-cyclopenta[*b*]naphthalen-2-ylidene) methyl)ferrocene.



Chemical Formula: $C_{24}H_{16}FeO_2$
Molecular Weight: 392.2350

In a round bottom flask, ferrocenecarboxaldehyde (0.5 g, 2.34 mmol, M = 214.05 g/mol) and 1*H*-cyclopenta[*b*]naphthalene-1,3(2*H*)-dione (0.458 g, 2.34 mmol, M = 196.21 g/mol) were mixed in ethanol (20 mL). A few drops of piperidine were added. Then, the mixture was placed in a pre-heated bath at 90°C. Progress of the reaction was monitored by TLC. After cooling and evaporation of the volatiles, addition of pentane/diethyl ether to the residue allowed the formation of a solid, which was separated by filtration, washed several times with water and pentane. 0.810 g (88% yield) of blue solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.45 (m, 2H), 8.07 (s, 2H), 7.99 (s, 1H), 7.77 – 7.58 (m, 2H), 5.51 (s, 2H), 4.92 (s, 2H), 4.26 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ : 190.45, 150.74, 136.58, 136.46, 130.53, 129.05, 128.94, 123.74, 123.43, 77.88, 75.99, 75.82, 71.15; HRMS (ESI MS) m/z: theor: 393.0573 found: 393.0564 ($[M+H]^+$ detected).

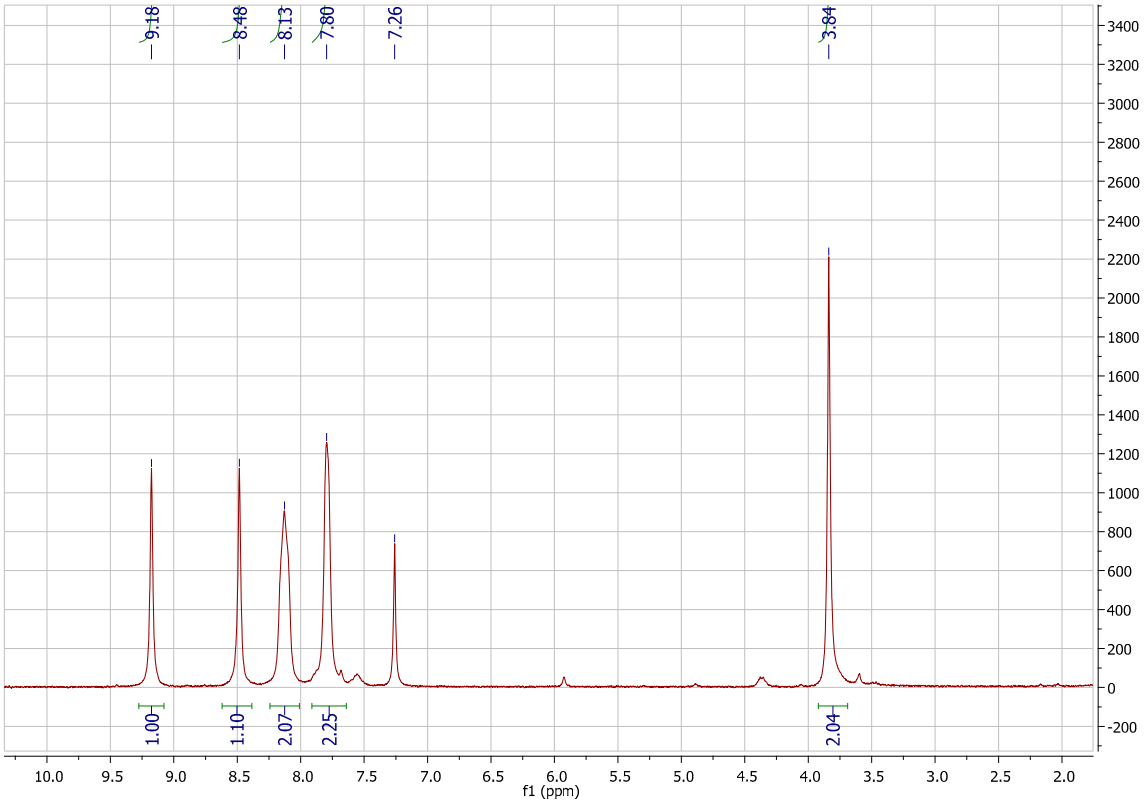
Dye 11: Synthesis of ((1-(dicyanomethylene)-3-oxo-1,3-dihydro-2*H*-cyclopenta[*b*] naphthalen-2-ylidene)methyl)ferrocene.



Chemical Formula: $C_{27}H_{16}FeN_2O$
Molecular Weight: 440.2830

In a round bottom flask, ferrocenecarboxaldehyde (0.415 g, 1.94 mmol, M = 214 g/mol) and 2-(3-oxo-2,3-dihydro-1*H*-cyclopenta[*b*]naphthalen-1-ylidene) malononitrile (0.473 g, 1.94 mmol, M = 244 g/mol) were mixed in ethanol (20 mL). 0.1 mL of DIPEA was added as the catalyst. Then, the mixture was placed in a pre-heated bath at 90 °C. Progress of the reaction was monitored by TLC. After cooling, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2, DCM), allowing the obtention of the product as a green solid (0.2 g, 23% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.51 (s, 1H), 8.33 (s, 1H), 8.05 (ddd, *J* = 18.6, 5.8, 3.3 Hz, 2H), 7.69 (dd, *J* = 6.2, 3.2 Hz, 2H), 5.47 – 5.37 (m, 2H), 5.19 – 5.08 (m, 2H), 4.39 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.22, 161.83, 150.10, 136.36, 135.58, 134.58, 133.70, 130.70, 130.25, 129.79, 129.50, 126.69, 125.32, 124.39, 116.04, 115.93, 78.74, 77.80, 76.37, 72.61; HRMS (ESI MS) m/z: theor: 441.0685 found: 441.0683 ($[M+H]^+$ detected).

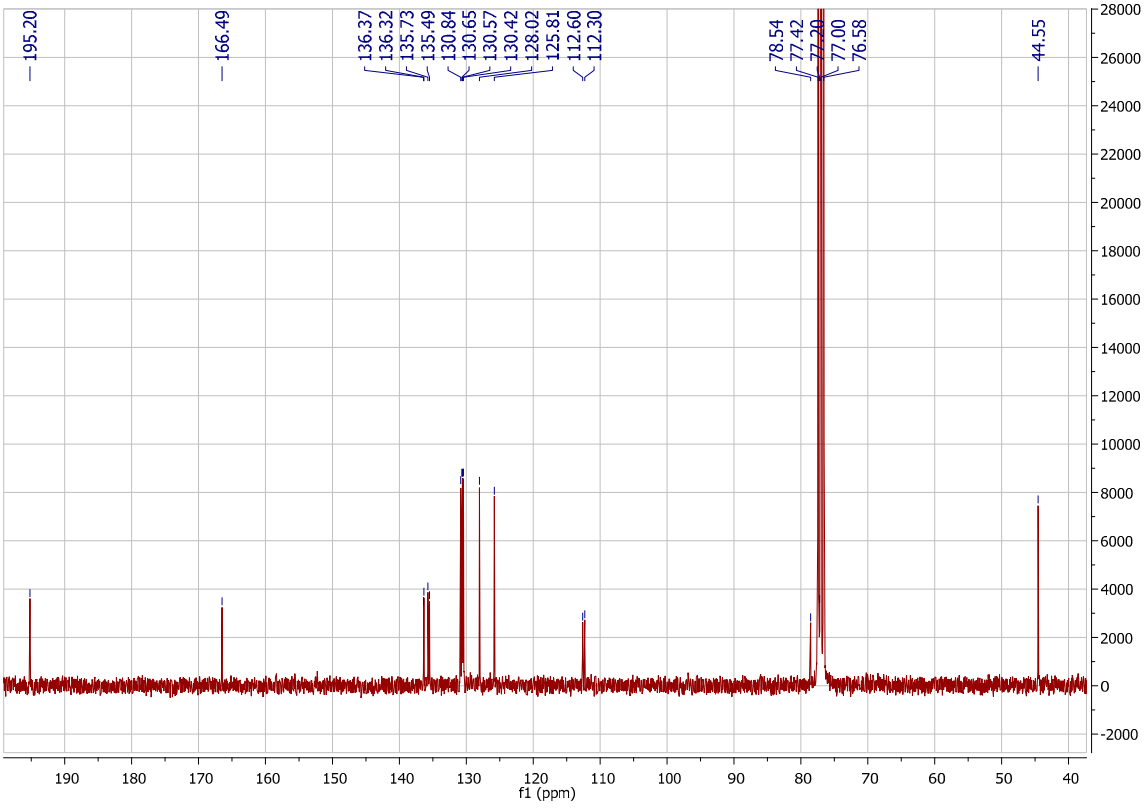
252 ^{1}H NMR spectrum of **EA2**



253

254

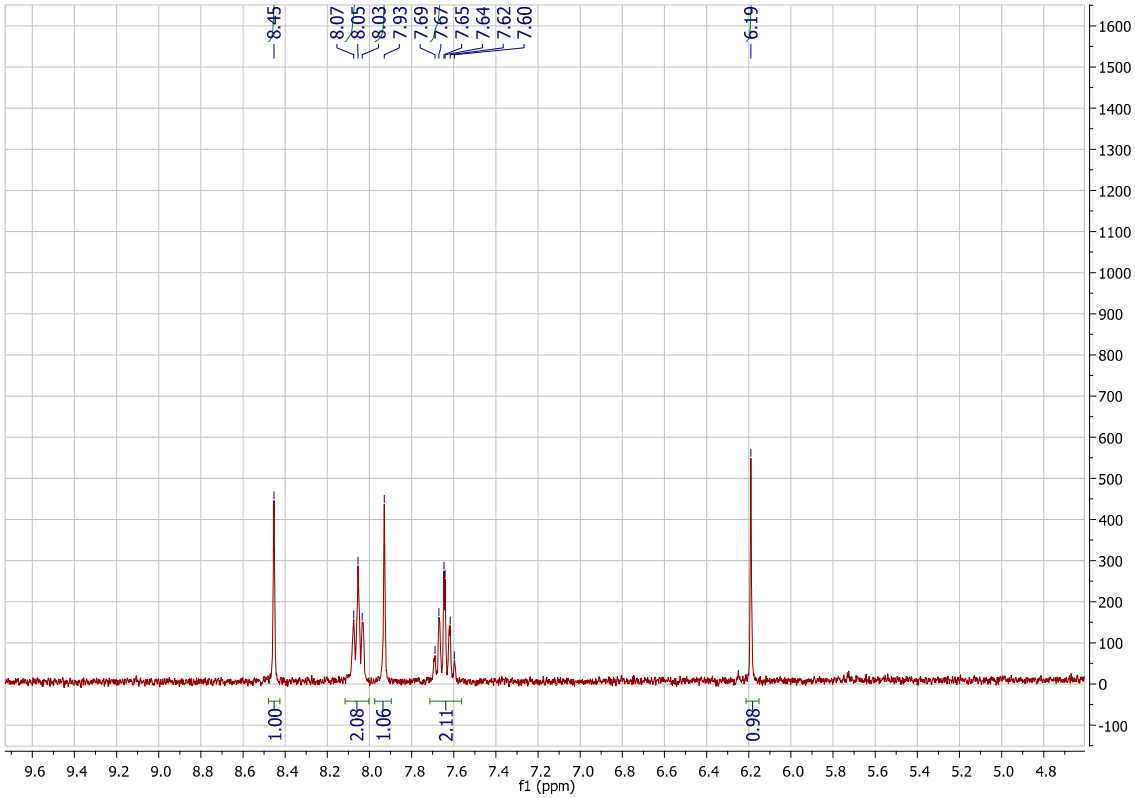
255 ^{13}C NMR spectrum of **EA2**



256

257

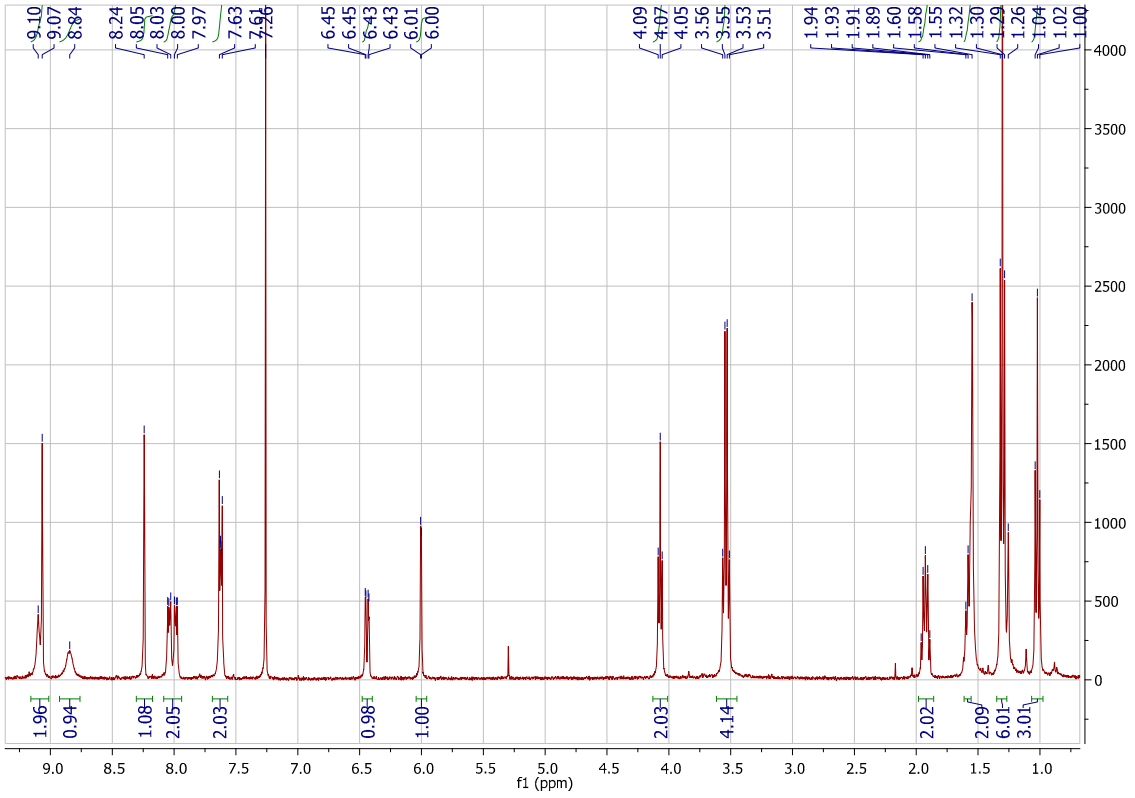
258 ^{1}H NMR spectrum of **EA3**



259

260

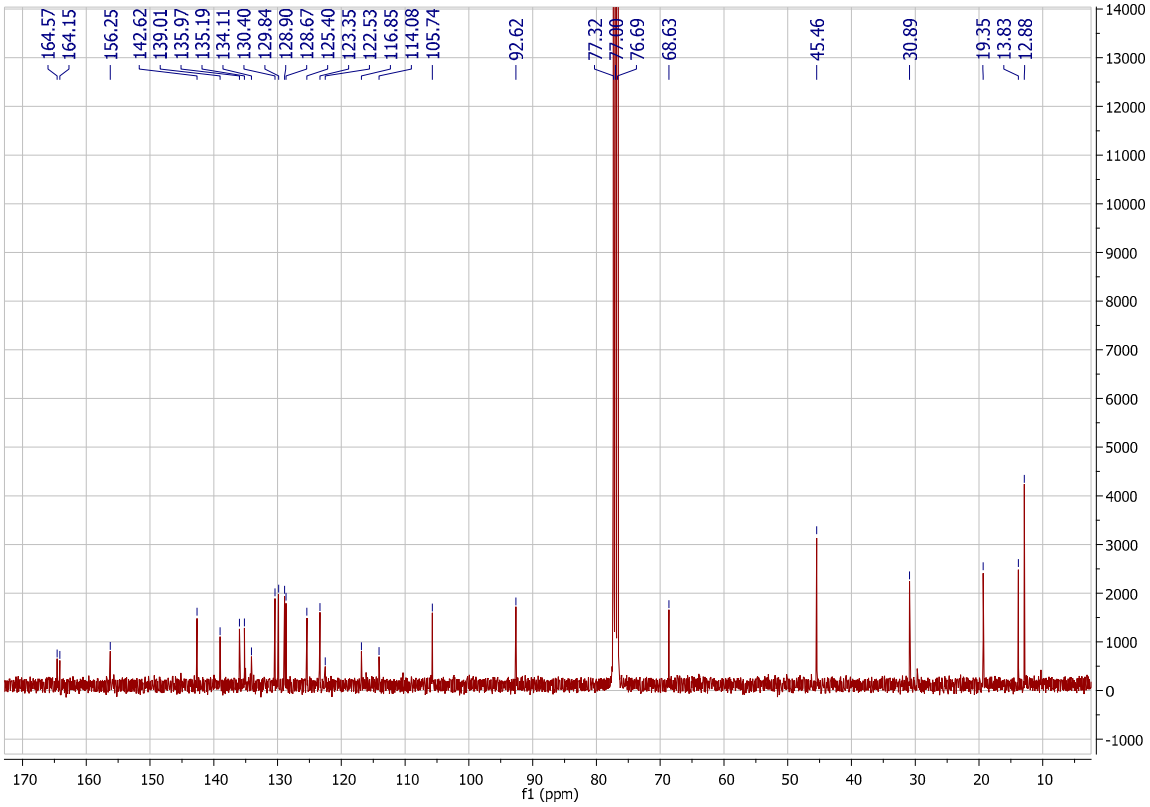
261 ^{1}H NMR spectrum of **dye 1**



262

263

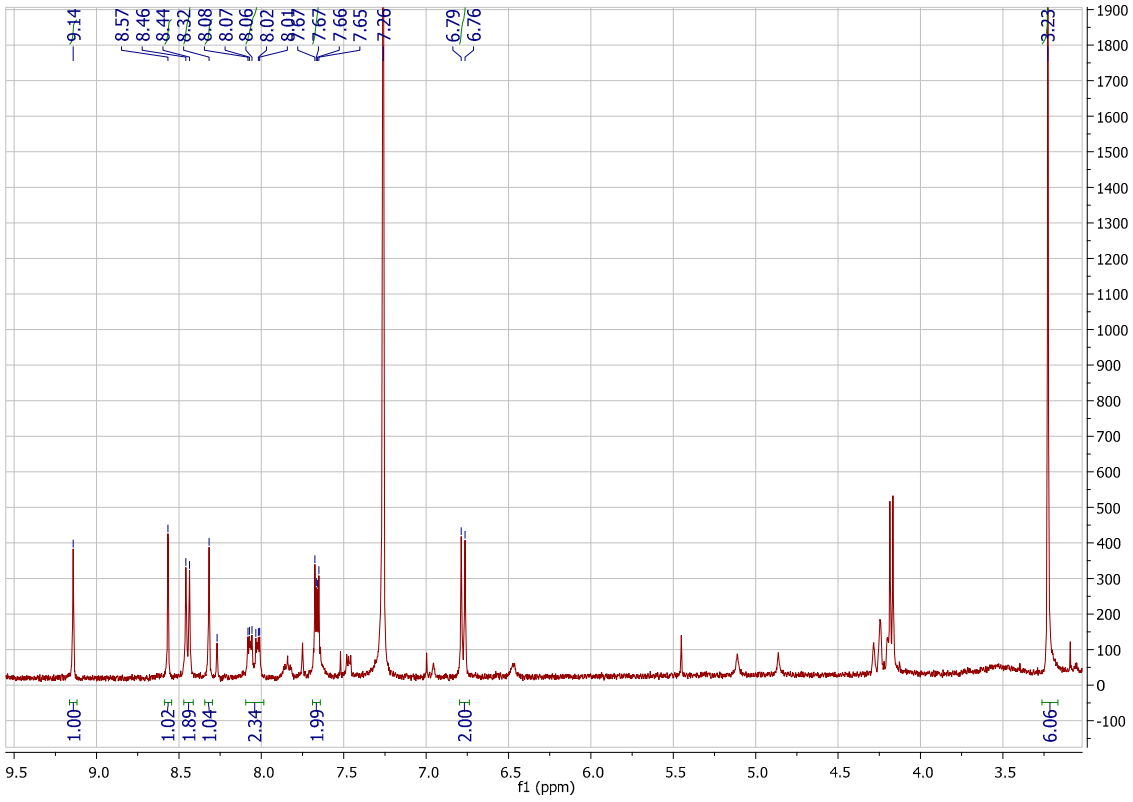
264 ^{13}C NMR spectrum of **dye 1**



265

266

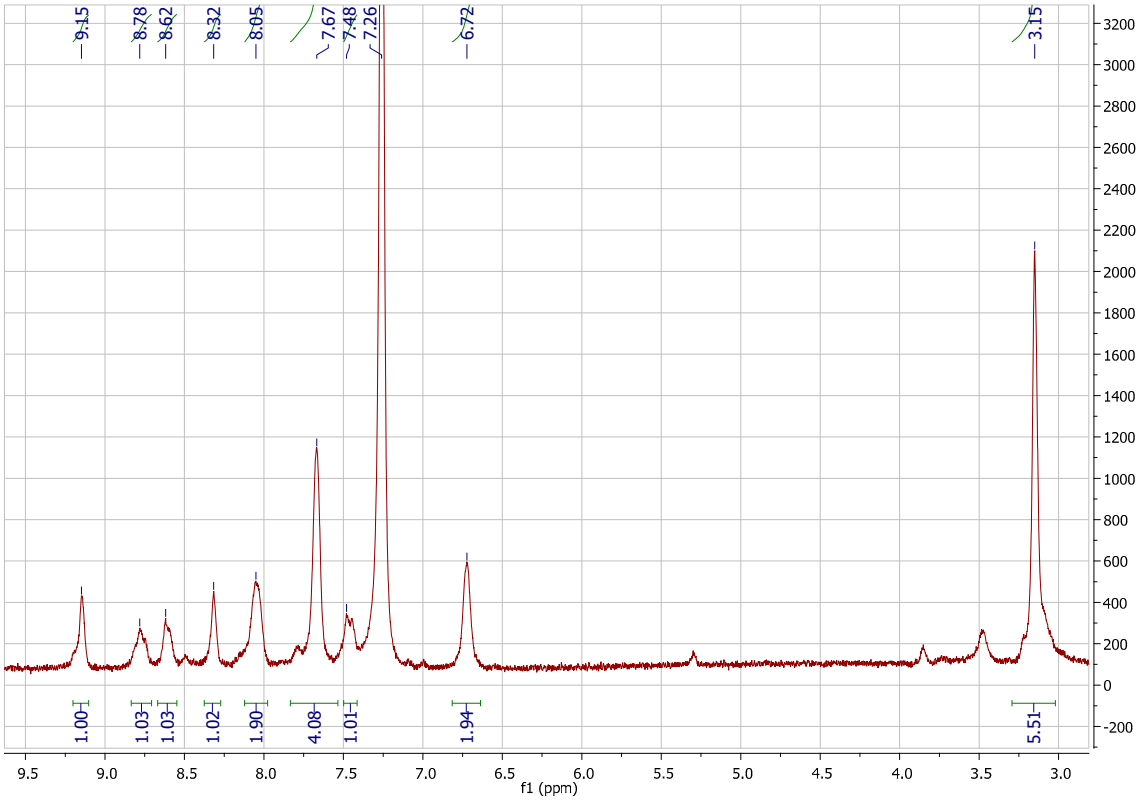
267 ^{1}H NMR spectrum of **dye 2**



268

269

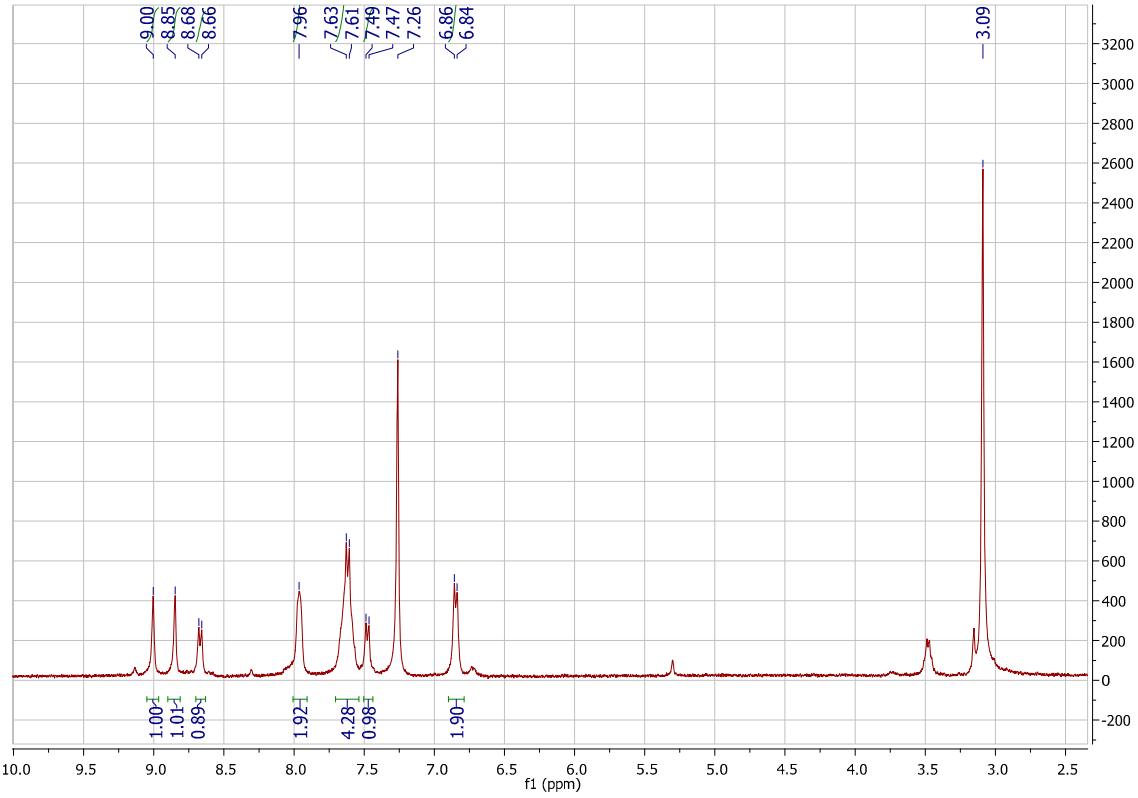
270 ^{1}H NMR spectrum of **dye 3**



271

272

273 ^{1}H NMR spectrum of **dye 4**

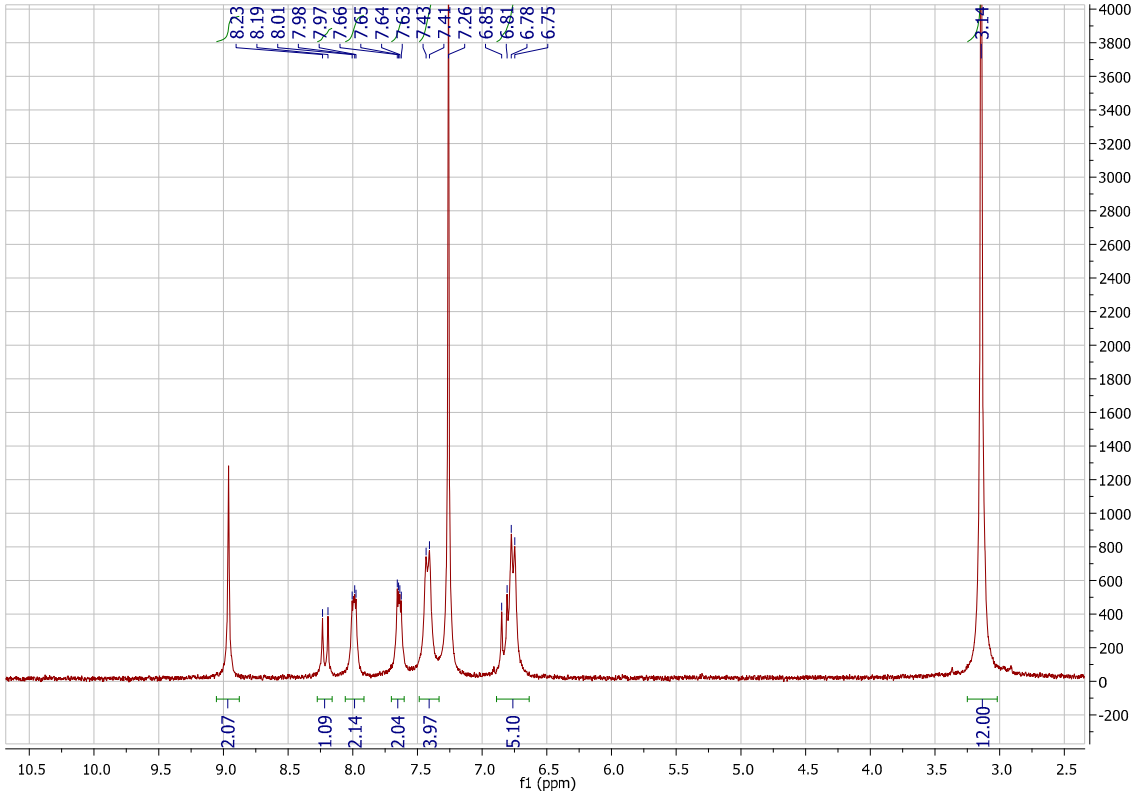


274

275

276

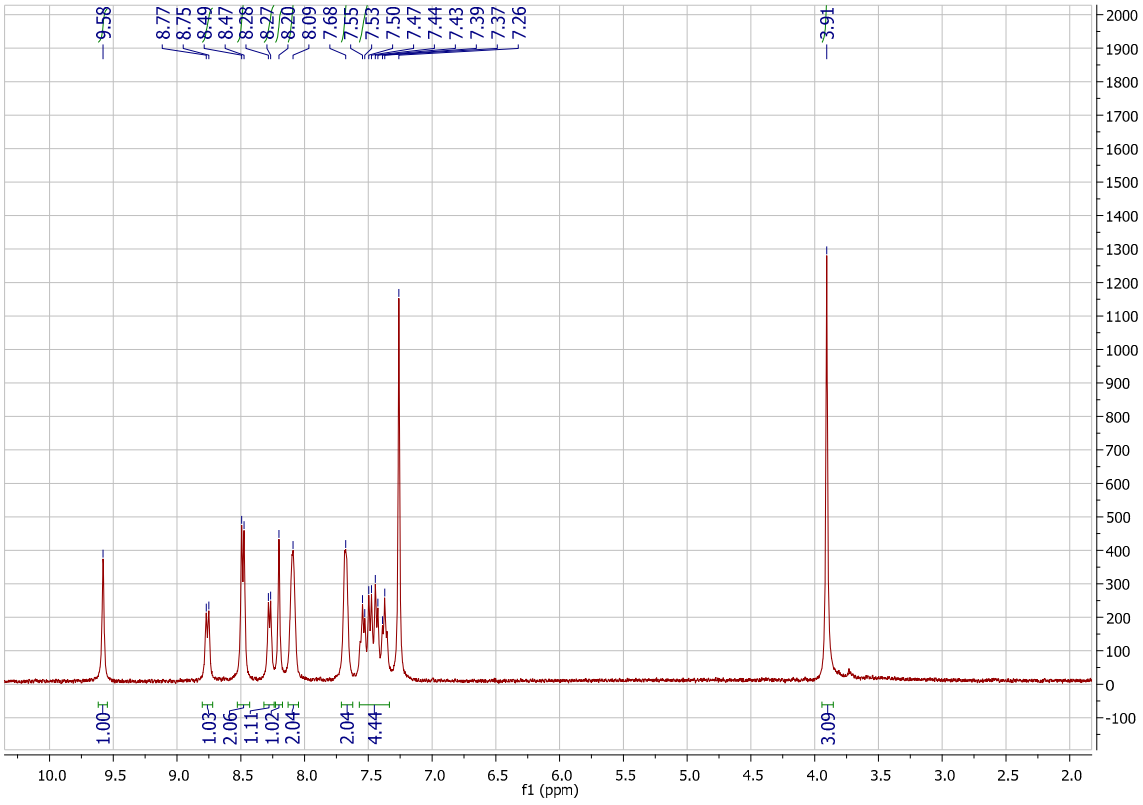
277 ^{1}H NMR spectrum of **dye 5**



278

279

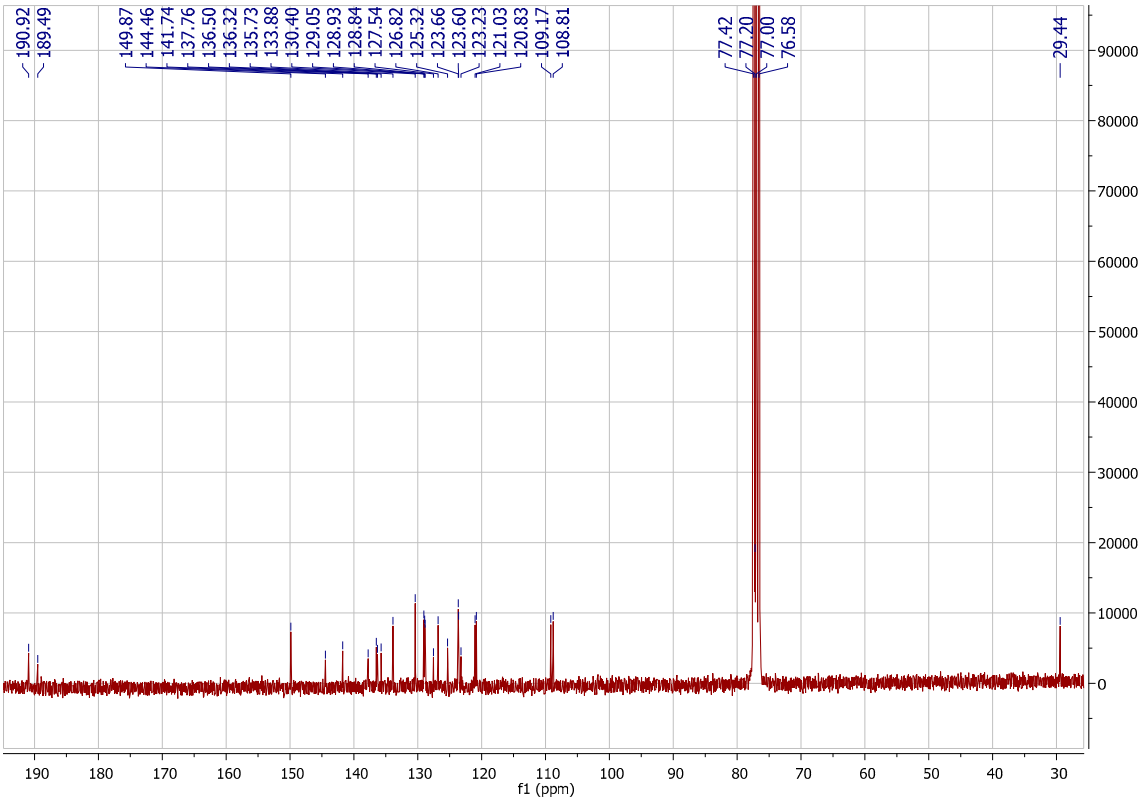
280 ^{1}H NMR spectrum of **dye 6**



281

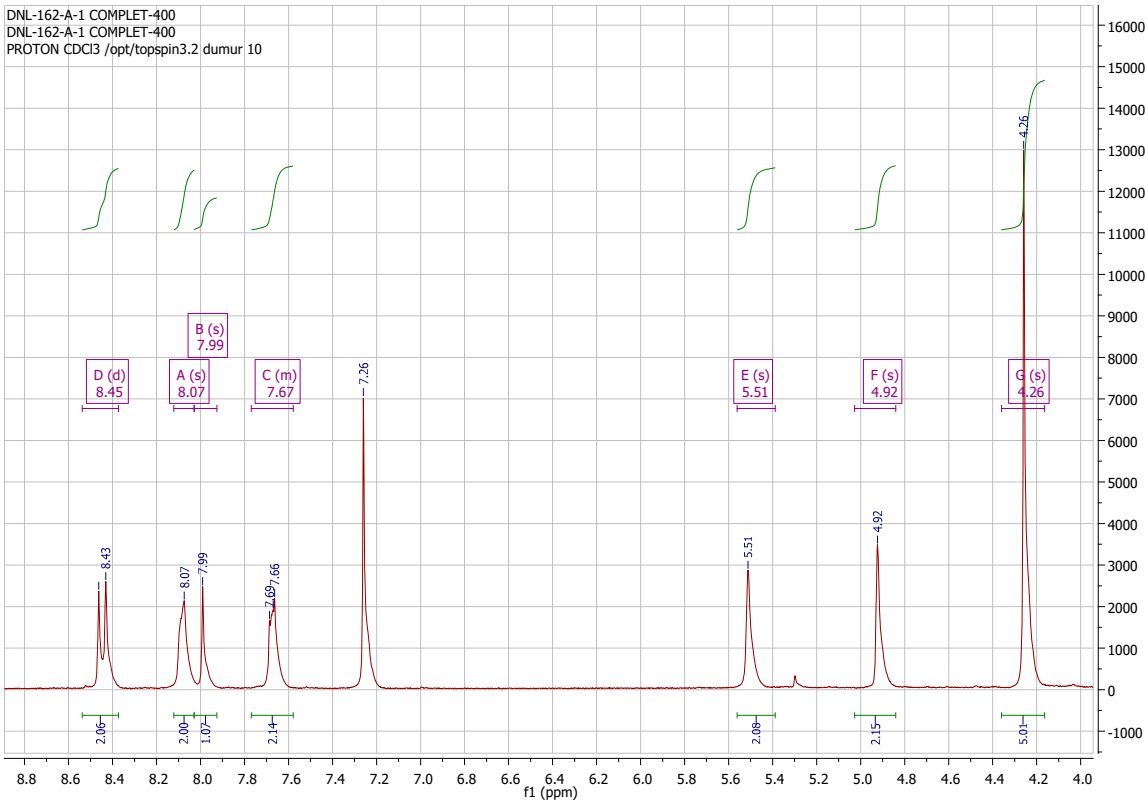
282

283 ^{13}C NMR spectrum of **dye 6**



284
285

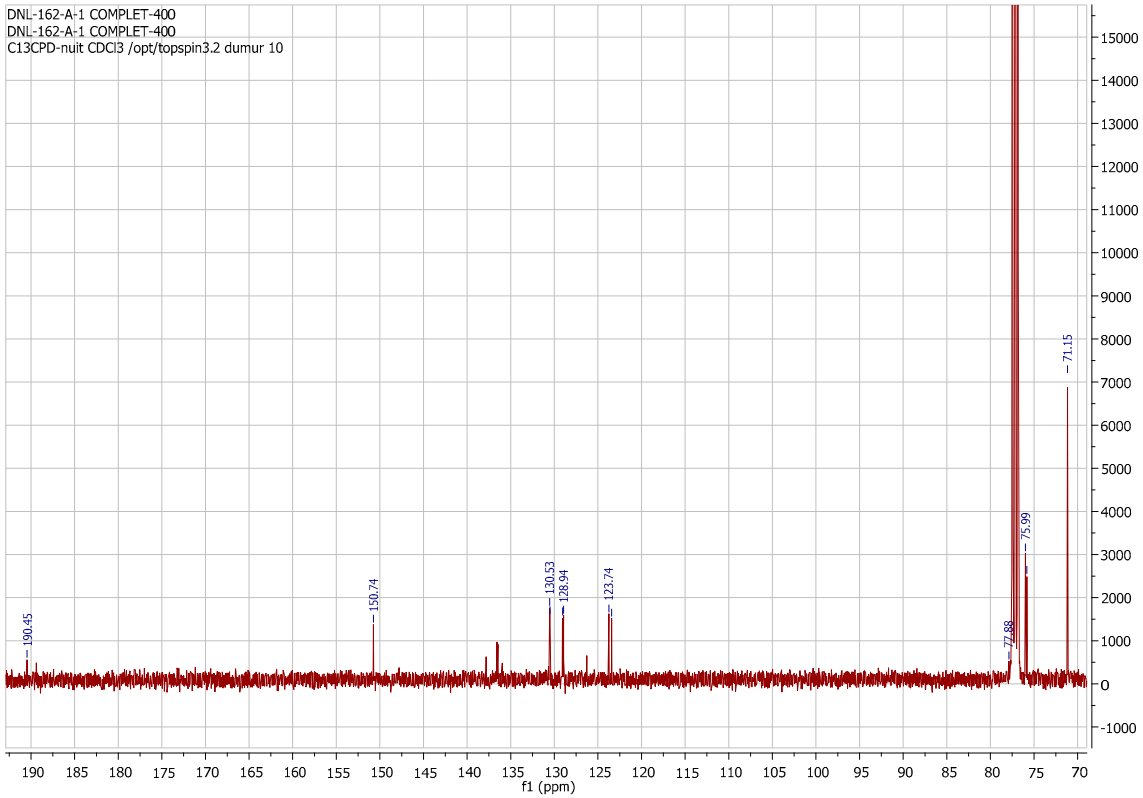
286 ^{1}H NMR spectrum of **dye 10**



287

288

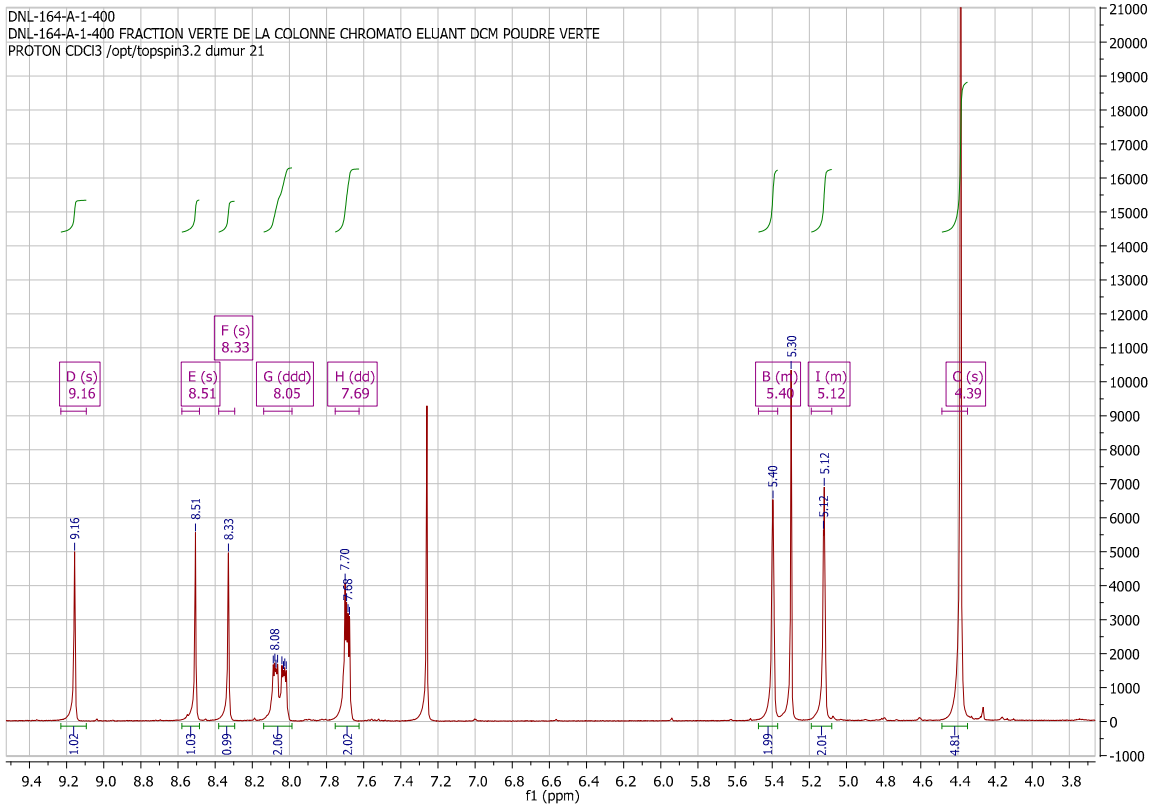
289 ^{13}C NMR spectrum of **dye 10**



290

291

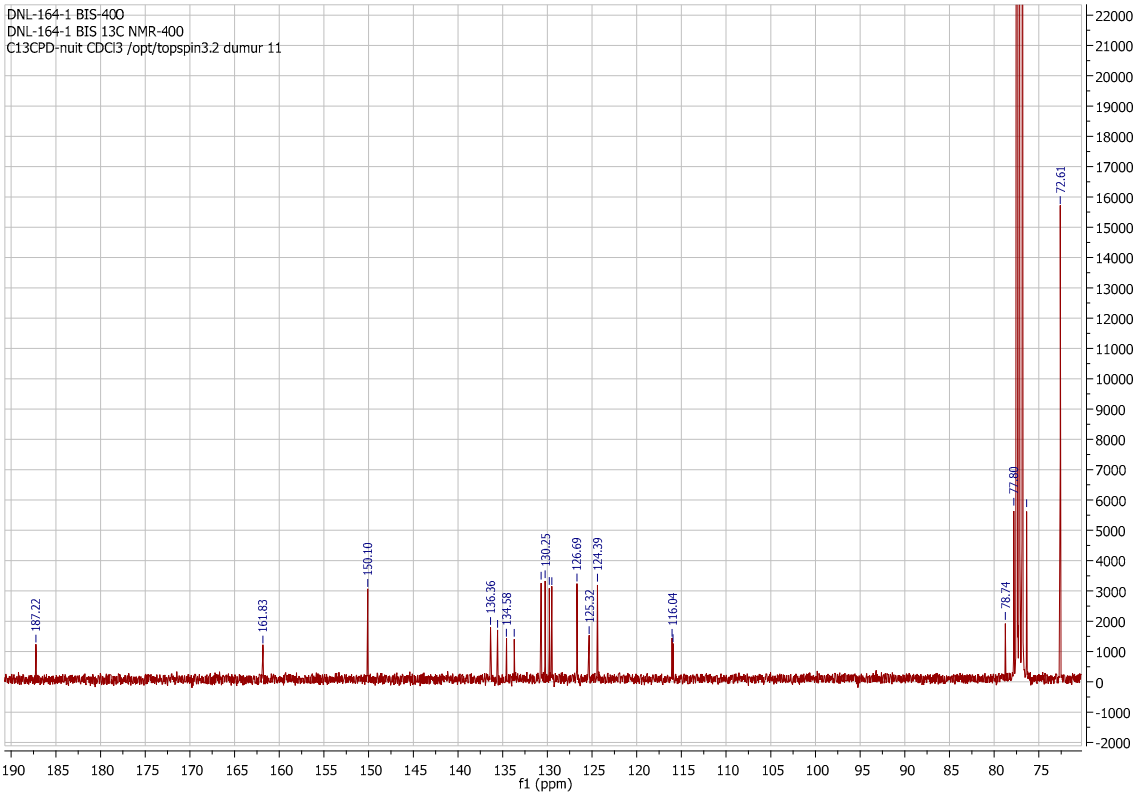
292 ^{1}H NMR spectrum of **dye 11**



293

294

295 ^{13}C NMR spectrum of **dye 11**



296