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Supporting Information

N,N'-Dibutylbarbituric acid as an acceptor moiety in push-pull chromophores

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1. General

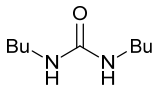
Column chromatography was carried out with silica gel 60 (particle size 0.040-0.063 mm, 230-400 mesh) and commercially available solvents. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with silica gel 60 F254 with visualization by a UV lamp (254 or 360 nm). Melting points (m.p.) were measured in open capillaries and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz at 25 °C with a Bruker AVANCE 400 instrument. Chemical shifts are reported in ppm relative to the signal of Me_4Si. The residual solvent signal in the ^{1}H and ^{13}C NMR spectra was used as an internal reference ($CDCl_3$ 7.25 and 77.23 ppm). Apparent resonance multiplicities are described as s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet), and m (multiplet). One or two set(s) of the signals corresponding to two butyl substituents were observed in ^{13}C spectra of target compounds **1**-**3**. ^{1}H signals of 1,4-phenylene moieties were denoted as CH_{ar}. IR spectra were recorded as neat using HATR adapter on a Perkin-Elmer FTIR Spectrum BX spectrometer. EI-MS spectra were measured on a GC/MS configuration comprised of an Agilent Technologies 6890N gas chromatograph equipped with a 5973 Network MS detector (EI 70 eV, mass range 33–550Da). High resolution MALDI MS spectra were measured on a MALDI mass spectrometer LTQ Orbitrap XL (Thermo Fisher Scientific, Bremen, Germany) equipped with nitrogen UV laser (337 nm, 60 Hz). The LTQ Orbitrap instrument was operated in positive-ion mode over a normal mass range (*m/z* 50 - 1500) with the following setting of tuning parameters: resolution 100,000 at *m/z* = 400, laser energy 17 mJ, number of laser shots 5, respectively. The survey crystal positioning system (survey CPS) was set for the random choice of shot position by automatic crystal recognition. The isolation width $\Delta m/z$ 4, normalised collision energy 25%, activation Q value 0.250, activation time 30 ms and helium as the collision gas were used for

CID experiments in LTQ linear ion trap. The used matrix was 2,5-dihydroxybenzoic acid (DHB). Mass spectra were averaged over the whole MS record (30 s) for all measured samples. UV/Vis spectra were recorded on a HP 8453 spectrophotometer in acetonitrile (c = 2×10^{-5} M). The NLO activities of chromophores **1**-**3** were measured by a conventional Electric Field Induced Second Harmonic (EFISH) generation technique,[1] which provides access to the $\mu\beta$ product, where μ is the ground state permanent dipole moment and β is the vector part of the first hyperpolarizability.[2] Chromophores were dissolved in chloroform at a concentration ~ 10^{-3} M and illuminated with a laser beam emitted by a pulsed Nd:YAG laser, operating with Raman-shifted wavelength at 1907 nm. This wavelength has the advantage of being far from the absorption CT-bands of the measured molecules. In order to orient the chromophore molecules and break the initial centrosymmetry, a high-voltage signal was applied to the solution synchronously with the laser pulses. The generated second harmonic intensity was measured as a function of the length of the optical path. The resulting curves (Maker fringes) were analysed and compared with a reference (quartz crystal) to determine the $\mu\beta$ values. The measurements were repeated at various concentrations to detect any aggregation problems, which can easily be recognized by an abnormal drop in the SHG amplitude.

Compounds **12**-**14** were synthesized according to literature procedures.[3]

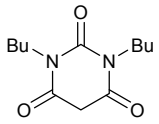
2. Synthesis of intermediates

N,*N*'-Dibutylurea



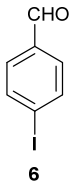
Butyl isocyanate (8.0 ml, 68.5 mmol) was added dropwise to a solution of butylamine (7.0 ml, 68.5 mmol) in CH_2Cl_2 (150 ml) at 0 °C. The reaction mixture was stirred 1 h at 25 °C, the solvent was evaporated *in vacuo* to give the title compound as an off-white solid (11.7 g, 99 %). Mp 68–70 °C (from ether) (lit.,[4] mp 65–70 °C). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 1.02 (6H, t, J = 7.2, 2×CH_3), 1.31–1.35 (4H, m, 2×CH_2), 1.42–1.49 (4H, m, 2×CH_2), 3.11–3.16 (4H, m, 2×CH_2) and 4.50 (2H, s, 2×NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.01, 20.25, 32.56, 40.47 and 158.71. EI-MS (70 eV): *m/z* 172 (M^+, 72%), 130 (27), 106 (27), 101 (35), 74 (44), 57 (46), 44 (100), 41 (75).

N,*N*'-Dibutylbarbituric acid



A reaction mixture of *N*,*N*'-Dibutylurea (0.58 g, 3.37 mmol), malonic acid (0.36 g, 3.37 mmol), acetic acid (4 ml) and acetanhydride (1.2 ml) was stirred at 90 °C for 5 h and subsequently cooled to 25 °C and stirred for additional 12 h. The volatiles were removed *in vacuo* and the residue was purified by column chromatography (SiO_2; EtOAc/Hex 1:3) to afford pure title compound as an off-white amorphous solid (0.74 g, 91 %). Mp 40–45 °C (lit.,[5] 49–50 °C). R_f = 0.30 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.92 (6H, t, J = 7.6, 2×CH_3), 1.28–1.37 (4H, m, 2×CH_2), 1.51–1.58 (4H, m, 2×CH_2), 3.62 (2H, s, CH_2) and 3.83–3.87 (4H, m, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.75, 20.12, 30.07, 39.72, 41.88, 151.48 and 164.75. EI-MS (70 eV): *m/z* 240 (M^+, 5), 185 (100), 98 (20), 86 (20), 70 (22), 56 (25).

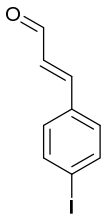
4-Iodobenzenecarbaldehyde (6)



6

*n*Buli (28.4 ml, 45.5 mmol) was slowly added to a solution of **4** (15.0 g, 45.5 mmol) in dry THF (150 ml) at -78 °C under argon and the reaction mixture was stirred for 1,5 h. DMF (3.85 ml, 50.0 mmol) was added and the reaction was allowed to reach 25 °C and was stirred additional 1 h. The reaction mixture was poured into the stirred mixture of KH_2PO_4 (100 ml, sat. aq.) and ether (100 ml). The organic phase was separated and the water layer was extracted with ether (2×50 ml). Combined organic extracts were dried (Na_2SO_4), the solvents were evaporated *in vacuo* and the residue was recrystallized from hexane to afford **6** as an yellow powder (4.6 g, 44 %). The measured analytical data were in accordance with those published in literature.[6]

(*E*)-3-(4-Iodophenyl)propenal (7)

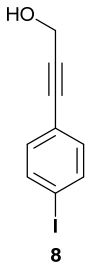


7

4-Iodobenzaldehyde **6** (1.8 g, 7.76 mmol) and (triphenylphosphoranylidene)acetaldehyde (2.36 g, 7.76 mmol) were dissolved in benzene (25 ml) and the reaction mixture was stirred for 5 h. The solvent was evaporated *in vacuo* and the residue was filtered through a plug (SiO_2; CH_2Cl_2). ^{1}H NMR analysis showed presence of both (*E*) and (*Z*) isomers in the ratio of 3:2. Hence, the crude product was dissolved in toluene, small amount of I_2 was added and the reaction mixture was refluxed for 12 h. The solvent was evaporated and the residue was portioned between CH_2Cl_2 (100 ml) and $Na_2S_2O_3$ (100, aq.). The organic layer was seprated, dried (Na_2SO_4), the solvent was evaporated *in vacuo* and the residue was purified by column chromatography (SiO_2; CH_2Cl_2) to provide **7** as an yellow solid (1.17 g, 59 %). Mp 81–83 °C. R_f = 0.77 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 6.70 (1H, dd, J_1 = 7.6, J_2 = 16.0, CH), 7.26–7.29 (2H, m, CH_{ar}), 7.38 (1H, d, J = 16.0, CH); 7.75–7.78 (2H, m, CH_{ar}) and 9.69 (1H, d, J = 7.6, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 98.04, 129.26, 130.00, 133.63,

138.58, 151.47 and 193.58. EI-MS (70 eV): *m/z* 258 (M^+, 46), 131 (100), 103 (48), 77 (30).

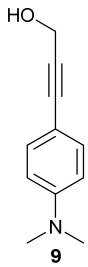
3-(4-Iodophenyl)prop-2-yn-1-ol (8)



8

The title compound was prepared from **4** (3.83 g, 11.61 mmol) and propargyl alcohol (0.65 g, 11.61 mmol) following the general method C and using the mixture of THF/Et_3N (40 ml, 1:1) as a reactiom medium. The crude alcohol was purified by filtration through a plug (SiO_2; CH_2Cl_2) to afford **8** as a slightly orange solid (1.51 g, 51 %). R_f = 0.38 (SiO_2; CH_2Cl_2). The measured analytical data were in accordance with those published in literature.[7]

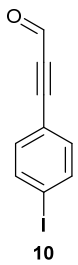
3-[4-(*N*,*N*-Dimethylamino)phenyl]prop-2-yn-1-ol (9)



9

The title compound was prepared from **5** (494 g, 2.0 mmol) and propargyl alcohol (124 mg, 2.20 mmol) following the general Method C and using Et_3N (20 ml) as a reactiom medium. The crude alcohol was purified by column chromatography (SiO_2; CH_2Cl_2) to afford **8** as an yellow solid (235 g, 67 %). R_f = 0.29 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 1.65 (1H, t, *J* = 5.6, OH), 2.96 (6H, s, $N(CH_3)_2$), 4.48 (2H, d, *J* = 5.6, CH_2), 6.61 (2H, d, *J* = 8.8, CH_{ar}) and 7.31 (2H, d, *J* = 8.8, CH_{ar}).^{13}C NMR (100 MHz, $CDCl_3$): δ_C 40.38, 52.11, 85.17, 86.97, 109.37, 111.93, 133.04 and 150.43. EI-MS (70 eV): *m/z* 175 (M^+, 100), 158 (45), 148 (28), 144 (42), 120 (16).

3-(4-Iodophenyl)propynal (10)

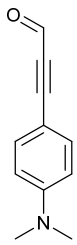


10

Into a solution of alcohol **8** (1.51g, 5.85 mmol) in CH_2Cl_2 (40 ml) Dess-Martin periodinane (2.48 g, 5.85 mmol) was added and the reaction was

stirred at 25 °C for 2 h. The reaction progress was monitored by TLC (SiO_2; CH_2Cl_2). The solvent was evaporated and the crude product was purified by filtration through a plug (SiO_2; CH_2Cl_2) to afford **10** as an orange solid (1.40 g, 94 %). R_f = 0.90 (SiO_2; CH_2Cl_2). Mp 106–109 °C (lit.,[8] 113–114 °C). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 7.15 (2H, d, *J* = 8.8, CH_{ar}), 7.61 (2H, d, *J* = 8.8, CH_{ar}) and 9.25 (1H, s, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 89.42, 93.96, 98.65, 119.01, 134.57, 138.27 and 176,77. EI-MS (70 eV): *m/z* 256 (M^+, 100), 228 (35), 128 (21), 101 (32), 74 (22).

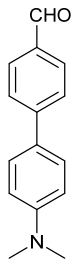
3-[4-(*N*,*N*-Dimethylamino)phenyl]propynal (11)



11

Into a solution of alcohol **9** (235 mg, 1.35 mmol) in CH_2Cl_2 (40 ml) Dess-Martin periodinane (565 mg, 1.35 mmol) was added and the reaction was stirred at 25 °C for 30 min. The reaction progress was monitored by TLC (SiO_2; CH_2Cl_2). The solvent was evaporated and the crude product was purified by column chromatography (SiO_2; CH_2Cl_2) to afford **11** as an yellow-orange solid (175 mg, 76 %). R_f = 0.83 (SiO_2; CH_2Cl_2). The measured analytical data were in accordance with those published in literature.[9]

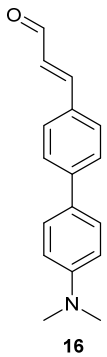
4'-(*N*,*N*-Dimethylamino)biphenyl-4-carbaldehyde (15)



15

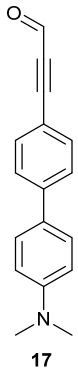
The title compound was prepared from **6** (232 mg, 1.0 mmol) and **12** (259 mg, 1.05 mmol) following the general Method A. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **15** as an yellow solid (202 mg, 90 %). The measured analytical data were in accordance with those published in literature.[10]

(2*E*)-3-[4'-(*N*,*N*-Dimethylamino)biphenyl-4-yl]propenal (16)


16

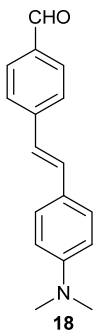
The title compound was prepared from **7** (129 mg, 0.5 mmol) and **12** (131 mg, 0.53 mmol) following the general Method A. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **16** as an yellow-orange solid (118 mg, 94 %). Mp 228–232 °C. R_f = 0.45 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 3.01 (6H, s, $N(CH_3)_2$), 6.72 (1H, dd, J_1 = 16.0, J_2 = 8.0, CH), 6.79 (2H, d, J = 8.8, CH_{ar}), 7.49 (1H, d, J = 16.0, CH), 7.55 (2H, d, J = 8.8, CH_{ar}), 7.60 (4H, m, CH_{ar}) and 9.70 (1H, d, J = 8.0, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 40.63, 112.80, 126.66, 127.50, 127.80, 127.92, 129.32, 131.72, 144.37, 150.68, 153.05 and 194.02. EI-MS (70 eV): *m/z* 251 (M^+, 100), 222 (15), 207 (35), 178 (20), 152 (13), 111 (13).

3-[4'-(*N*,*N*-Dimethylamino)biphenyl-4-yl]propynal (17)


17

The title compound was prepared from **10** (200 mg, 0.78 mmol) and **12** (203 mg, 0.82 mmol) following the general Method A. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **17** as an yellow solid (140 mg, 72 %). Mp > 300 °C. R_f = 0.77 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 3.01 (6H, s, $N(CH_3)_2$), 6.78 (2H, d, J = 9.2, CH_{ar}), 7.53 (2H, d, J = 9.2, CH_{ar}), 7.61 (4H, m, CH_{ar}) and 9.43 (1H, s, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 40.58, 89.47, 96.63, 112.74, 116.42, 126.28, 127.10, 128.00, 134.14, 144.38, 150.75 and 177.04. HR-FT-MALDI-MS (DHB) *m/z*: 250.1226 ($[M+H]^+$), $C_{17}H_{16}NO^+$ requires 250.1226.

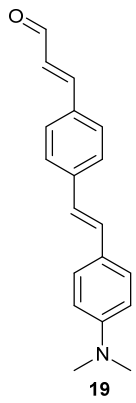
4-{(*E*)-2-[4-(*N*,*N*-Dimethylamino)phenyl]ethenyl}benzenecarbaldehyde (18)


18

The title compound was prepared from **6** (233 mg, 1.0 mmol) and **13** (155 mg, 1.05 mmol) following the general Method B. The crude product was

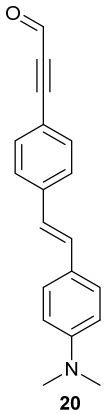
purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **18** as an yellow solid (230 mg, 92 %). The measured analytical data were in accordance with those published in literature.[11]

(2*E*)-3-(4-{(*E*)-2-[4-(*N*,*N*-Dimethylamino)phenyl]ethenyl}phenyl)propenal (19)



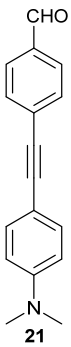
The title compound was prepared from **7** (258 mg, 1.0 mmol) and **13** (155 mg, 1.05 mmol) following the general Method B. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **19** as an yellow-orange solid (255 mg, 92 %) with a cinnamonic smell. Mp > 300 °C. R_f = 0.60 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 3.00 (6H, s, $N(CH_3)_2$), 6.67–6.73 (3H, m, CH + CH_{ar}), 6.90 (1H, d, *J* = 16.0, CH), 7.14 (1H, d, *J* = 16.0, CH), 7.42–7.47 (3H, m, CH + CH_{ar}), 7.49–7.54 (4H, m, CH_{ar}) and 9.69 (1H, d, *J* = 8.0, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 40.58, 112.49, 123.16, 125.17, 126.67, 127.72, 128.20, 129.23, 131.30, 132.31, 141.74, 150.67, 152.88 and 194.00. EI-MS (70 eV): *m/z* 277 (M^+, 64), 253 (11), 207 (100), 191 (11), 96 (10).

3-(4-{(*E*)-2-[4-(*N*,*N*-Dimethylamino)phenyl]ethenyl}phenyl)propynal (20)



The title compound was prepared from **10** (110 mg, 1.0 mmol) and **13** (155 mg, 1.05 mmol) following the general Method B. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **20** as an orange solid (75 mg, 64 %). Mp > 300 °C. R_f = 0.83 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 3.01 (6H, s, $N(CH_3)_2$), 6.78 (2H, d, *J* = 9.2, CH_{ar}), 7.53 (2H, d, *J* = 9.2, CH_{ar}), 7.61 (4H, m, CH_{ar}) and 9.43 (1H, s, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 40.58, 89.47, 96.63, 112.74, 116.42, 122.89, 124.97, 126.28, 127.10, 128.00, 134.14, 144.38, 150.75 and 177.04. HR-FT-MALDI-MS (DHB) *m/z*: 276.1383 ($[M+H]^+$), $C_{19}H_{18}NO^+$ requires 276.1383.

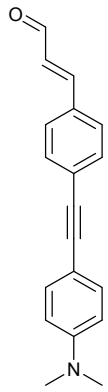
4-{2-[4-(*N*,*N*-Dimethylamino)phenyl]ethynyl}benzenecarbaldehyde (21)



21

The title compound was prepared from **6** (232 mg, 1.0 mmol) and **14** (152 mg, 1.05 mmol) following the general Method C. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **21** as an yellow solid (203 mg, 82 %). The measured analytical data were in accordance with those published in literature.[12]

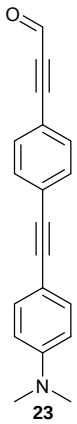
(2*E*)-3-(4-{2-[4-(*N*,*N*-Dimethylamino)phenyl]ethynyl}phenyl)propenal (22)



22

The title compound was prepared from **7** (258 mg, 1.0 mmol) and **14** (152 mg, 1.05 mmol) following the general Method C. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **22** as a yellow-orange solid (258 mg, 94 %) with a cinnamonic smell. Mp 216–220 °C. R_f = 0.55 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 3.00 (6H, s, $N(CH_3)_2$), 6.65 (2H, d, J = 9.2, CH_{ar}), 6.70 (1H, dd, J_1 = 16.0, J_2 = 7.6 Hz, CH), 7.40–7.46 (3H, m, CH + CH_{ar}), 7.50–7.54 (4H, m, CH_{ar}) and 9.69 (1H, d, J = 7.6, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 40.37, 87.49, 94.37, 109.45, 111.96, 127.59, 128.62, 128.65, 131.93, 132.93, 133.15, 150.60, 152.23 and 193.80. HR-FT-MALDI-MS (DHB) *m/z*: 276.1378 ($[M+H]^+$), $C_{19}H_{18}NO^+$ requires 276.1383.

3-(4-{2-[4-(*N*,*N*-Dimethylamino)phenyl]ethynyl}phenyl)propynal (23)

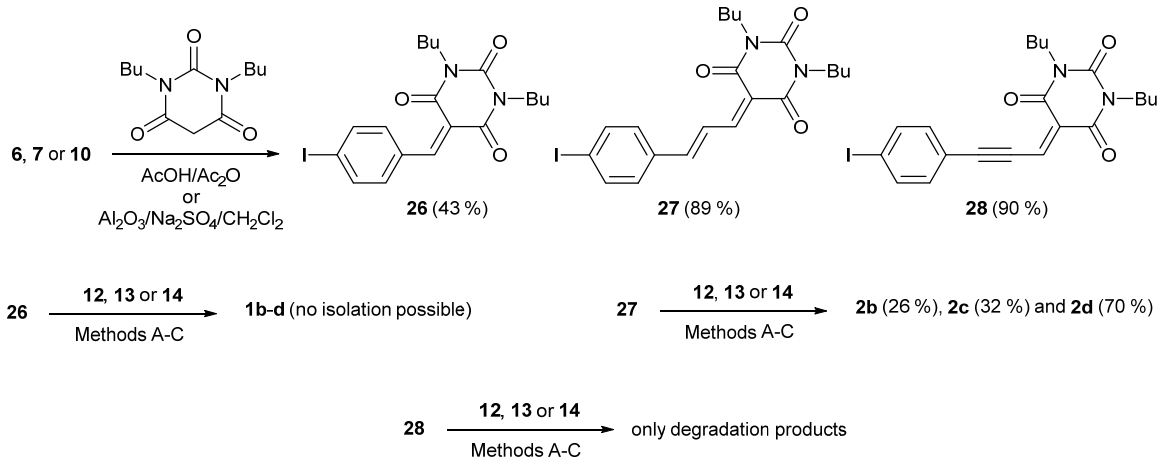


23

The title compound was prepared from **10** (256 mg, 1.0 mmol) and **14** (152 mg, 1.05 mmol) following the general Method C. The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **23** as an yellow-orange solid (169 mg, 62 %). Mp 175–179 °C. R_f = 0.88 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 3.00 (6H, s, $N(CH_3)_2$), 6.65 (2H, d, J = 8.8, CH_{ar}), 7.40 (2H, d, J = 8.8, CH_{ar}), 7.49 (2H, d, J = 8.8, CH_{ar}), 7.54 (2H, d, J = 8.8, CH_{ar}) and 9.42 (1H, s, CH=O). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 40.36, 87.23, 89.91,

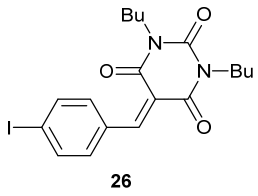
95.33, 95.36, 109.23, 111.95, 117.94, 127.83, 131.53, 133.20, 133.40, 150.67 and 176.84. HR-FT-MALDI-MS (DHB) *m/z*: 274.1221 ($[M+H]^+$), $C_{19}H_{16}NO^+$ requires 274.1226.

3. Alternative synthetic route to 1-3



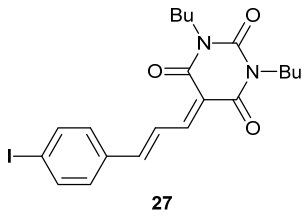
Scheme S1. Attempted alternative synthetic route to **1**-**3**.

Intermediate 26


26

Aldehyde **6** (930 mg, 3.88 mmol) and *N*,*N*'-dibutylbarbituric acid (900 mg, 3.88 mmol) were refluxed in acetic acid (100 ml) and acetanhydride (5 ml) for 2 h. The crude product, obtained by evaporation of the solvents *in vacuo*, was purified by crystallization from ethanol. Compound **26** was obtained as an yellow solid (758 mg, 43 %). Mp 73–76 °C. R_f = 0.4 (SiO_2; CH_2Cl_2/Hex 1:1). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.91–0.97 (6H, m, 2×CH_3), 1.32–1.40 (4H, m, 2×CH_2), 1.55–1.66 (4H, m, 2×CH_2), 3.89–3.98 (4H, m, 2×NCH_2), 7.72 (2H, d, *J* = 8.4, CH_{ar}), 7.80 (2H, d, *J* = 8.4, CH_{ar}) and 8.42 (s, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.96, 20.35, 20.38, 30.28, 42.06, 42.65, 100.76, 118.65, 132.34, 134.55, 137.77, 150.84, 157.71, 160.26 and 162.20. EI-MS (70 eV): *m/z* 454 (M^+, 10), 281 (11), 253 (12), 207 (100), 191 (12), 133 (10), 96 (12).

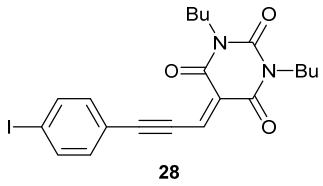
Intermediate 27



27

Aldehyde **7** (1.07 g, 4.17 mmol) and *N*,*N*'-dibutylbarbituric acid (1.0 g, 4.17 mmol) were reacted for 3 h according to the general method for the Knoevenagel condensation (see the main text). The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **27** as an orange solid (1.77 g, 89 %). Mp 137–143 °C. R_f = 0.83 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.91–0.97 (6H, m, 2×CH_3), 1.34–1.41 (4H, m, 2×CH_2), 1.58–1.64 (4H, m, 2×CH_2), 3.91–3.96 (4H, m, 2×NCH_2), 7.30 (1H, d, *J* = 15.6, CH), 7.37 (2H, d, *J* = 8.4, CH_{ar}), 7.75 (2H, d, *J* = 8.4, CH_{ar}), 8.15 (1H, d, *J* = 12.0, CH) and 8.58 (1H, dd, J_1 = 15.6, J_2 = 12.0, CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.97, 13.99, 20.35, 20.44, 30.32, 30.38, 41.72, 42.22, 98.38, 115.53, 125.91, 130.45, 134.94, 138.52, 151.05, 152.36, 156.68, 161.6 and 162.11. EI-MS (70 eV): *m/z* 480 (M^+, 78), 241 (44), 207 (100), 127 (56).

Intermediate 28



28

Aldehyde **10** (128 mg; 0.5 mmol) and *N*,*N*'-dibutylbarbituric acid (120 mg, 0.5 mmol) were reacted for 1 h according to the general method for the Knoevenagel condensation (see the main text). The crude product was purified by column chromatrography (SiO_2; CH_2Cl_2) to afford **28** as an yellow solid (215 mg, 90 %). Mp 98–104 °C. R_f = 0.83 (SiO_2; CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$): δ_H 0.90–0.95 (6H, m, 2×CH_3), 1.33–1.40 (4H, m, 2×CH_2), 1.56–1.64 (4H, m, 2×CH_2), 3.91–3.94 (4H, m, 2×NCH_2), 7.37 (2H, d, *J* = 8.4, CH_{ar}), 7.72 (1H, s, CH) and 7.75 (2H, d, *J* = 8.4, CH_{ar}). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 13.94, 13.96, 20.32, 20.37, 29.90, 30.26, 41.89, 42.28, 90.76, 98.50, 115.73, 121.39, 126.13, 134.67, 135.90, 138.18, 150.72, 159.23 and 161.06. HR-FT-MALDI-MS (DHB) *m/z*: 479.0831 ($[M+H]^+$), $C_{21}H_{24}N_2O_3^+$ requires 479.0826.

4. Crystallography

The X-ray data for coloured crystals of chromophores **1a** and **2a** were obtained at 150K using Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK_α radiation (λ = 0.71073 Å), a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.[13] The absorption was corrected by integration methods.[14] Structures were solved by direct methods (Sir92)[15] and refined by full matrix least-square based on F^2 (SHELXL97).[16] Hydrogen atoms were mostly localized on a difference Fourier map, however to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $H_{iso}(H) = 1.2\ U_{eq}$(pivot atom) or of $1.5U_{eq}$ for the methyl moiety with C-H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms on sp^2 carbon atoms, respectively.

$R_{int} = \sum |F_o^2 - F_{o,mean}^2| / \sum F_o^2$, GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$ for all data, $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$ for observed data, $wR(F^2) = [\sum(w(F_o^2 - F_c^2)^2)/(\sum w(F_o^2)^2)]^{½}$ for all data.

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 932395 and 932394 for **1a** and **2a**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

Crystallographic data for **1a**: $C_{21}H_{29}N_3O_3$, M = 371.47, triclinic, *P -1*, *a* = 7.8780(4), *b* = 8.8850(8), *c* = 14.7671(16)Å, α = 82.567(7), β = 84.778(7), γ = 76.935(6)°, Z = 2, V = 996.38(15)Å^3, D_c = 1.238 g.cm^{-3}, μ = 0.083 mm^{-1}, T_{min}/T_{max} = 0.697/0.837; -10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19; 18454 reflections measured (θ_{max} = 27.49°), 18398 independent (R_{int} = 0.0513), 2710 with $I > 2\sigma(I)$, 244 parameters, *S* = 1.127, *R1*(obs.

data) = 0.0720, *wR2*(all data) = 0.1436; max., min. residual electron density = 0.302, -0.222 eÅ^{-3}.

Crystallographic data for **2a**: $C_{23}H_{31}N_3O_3$, M = 397.51, triclinic, *P -1*, *a* = 7.6351(12), *b* = 8.8110(8), *c* = 16.5849(19) Å, α = 77.500(9), β = 86.211(10), γ = 76.035(10)°, Z = 2, V = 1057.0(2)Å^3, D_c = 1.249 g.cm^{-3}, μ = 0.083 mm^{-1}, T_{min}/T_{max} = 0.965/ 0.994; -9 ≤ h ≤ 9, -11 ≤ k ≤ 10, -21 ≤ l ≤ 21; 22704 reflections measured (θ_{max} = 27.50°), 22654 independent (R_{int} = 0.0325), 3926 with $I > 2\sigma(I)$, 262 parameters, *S* = 1.091, *R1*(obs. data) = 0.0484, *wR2*(all data) = 0.1149; max., min. residual electron density = 0.300, -0.225 eÅ^{-3}.

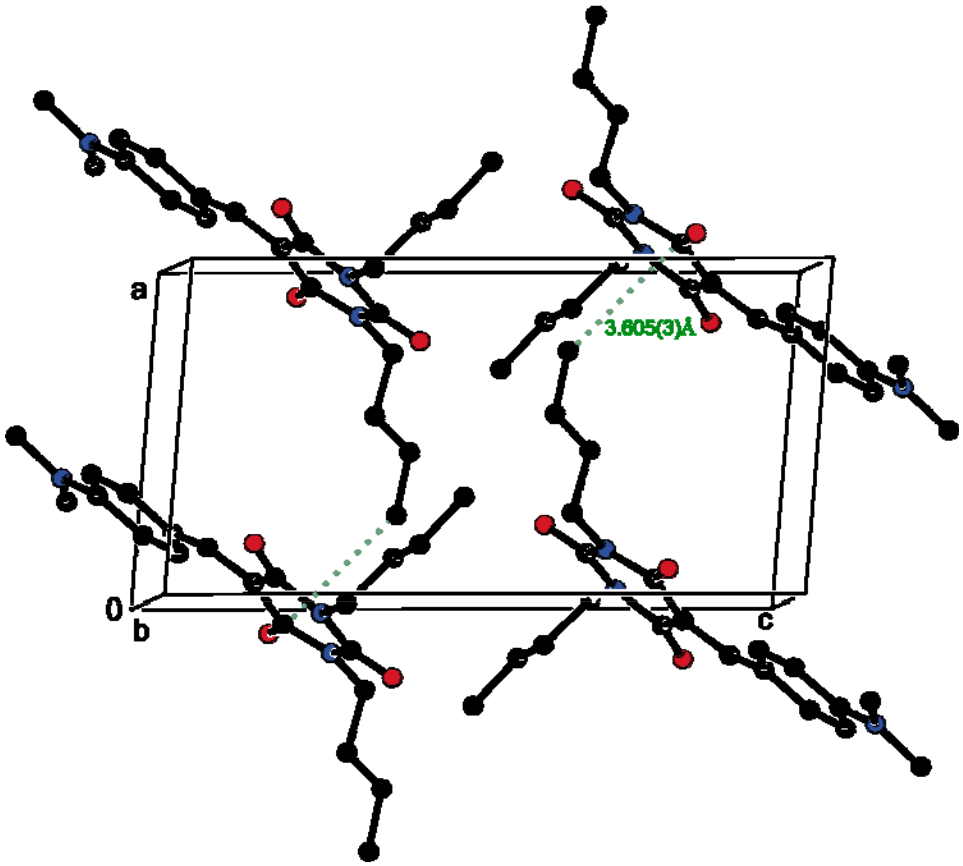


Fig. S1 Crystal packing of chromophore **1a**.

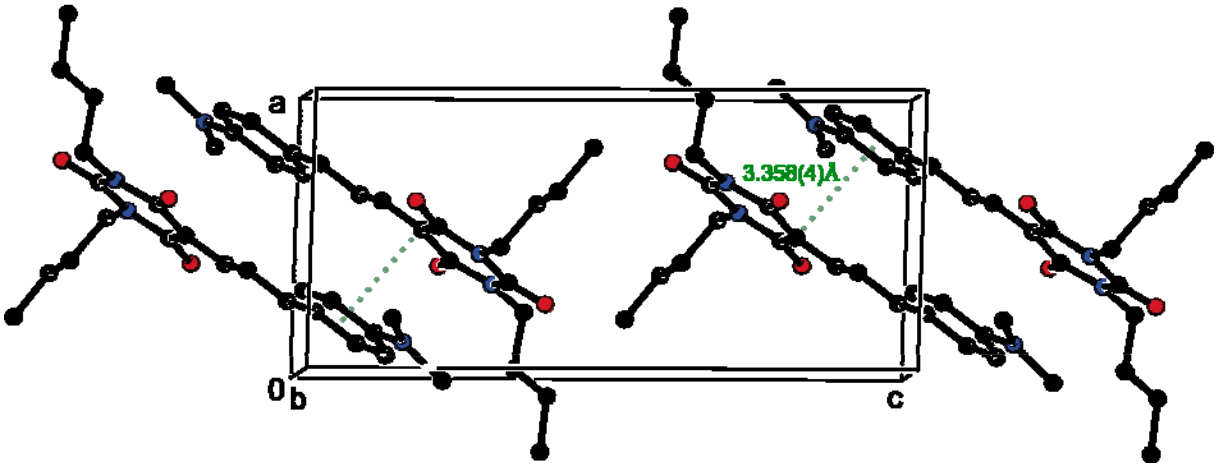


Fig. S2 Crystal packing of chromophore **2a**.

5. Electrochemistry

Electrochemical measurements were carried out in acetonitrile containing 0.1 M Bu_4NPF_6 in a three electrode cell by cyclic voltammetry (CV) and rotating disc voltammetry (RDV). The working electrode was platinum disc (2 mm in diameter) for CV and RDV experiments. As the reference and auxiliary electrodes were used saturated calomel electrode (SCE) separated by a bridge filled with supporting electrolyte and Pt wire, respectively. All potentials are given *vs.* SCE. Voltammetric measurements were performed using a potentiostat PGSTAT 128N (AUTOLAB, Metrohm Autolab B.V., Utrecht, The Netherlands) operated via NOVA 1.9 software.

Table S1. Full electrochemical data for chromophores **1a**-**d**, **2a**-**d** and **3a**-**d** measured by CV and RDV.

Comp.	E^o [V][a]	ΔE_p [mV][b]	E_p [V][c]	$E_{1/2}$(RDV) [V][d]
1a	+0.99	70		+0.99
			-1.27	-1.26
1b	+0.77	68		+0.77
			-1.07	-1.02
1c			+1.81	+0.58
			+1.43	-1.01
	+0.58	76		
			-1.01	
			-1.73	
1d			+0.82	+0.79
			-0.97	-0.95
			-1.72	
2a			+1.75	+0.81
	+0.80	59		-1.04
			-1.05	
2b			+1.53	+0.76
	+0.75	71		-0.92
			-0.93	
2c			+1.33	+0.59
	+0.59	68		-0.93 (inhib.)
			-0.92	
2d	+1.03	68		+0.78
			+0.81	-0.83
			-0.91	
	-1.22	100		
	-1.59	75		
3a			+1.27	+1.24
	+0.94	66		+0.94
			-0.99	-0.97
3b			+1.61	+0.77
	+0.77	66		-0.87
			-0.88	
3c	+0.56	102		+0.58
			-0.91	-0.87
3d			+0.81	+0.80
			-0.86	-0.79
			-1.61	

[a] $E^o = (E_{p,c} + E_{p,a})/2$ where $E_{p,c}$ and $E_{p,a}$ correspond to the cathodic and anodic peak potentials, respectively. [b] $\Delta E_p = E_{ox} - E_{red}$ (reversible redox process). [c] E_p = irreversible peak potential. [d] $E_{1/2}$ = half-wave potential measured by RDV. All potentials are given vs. SCE.

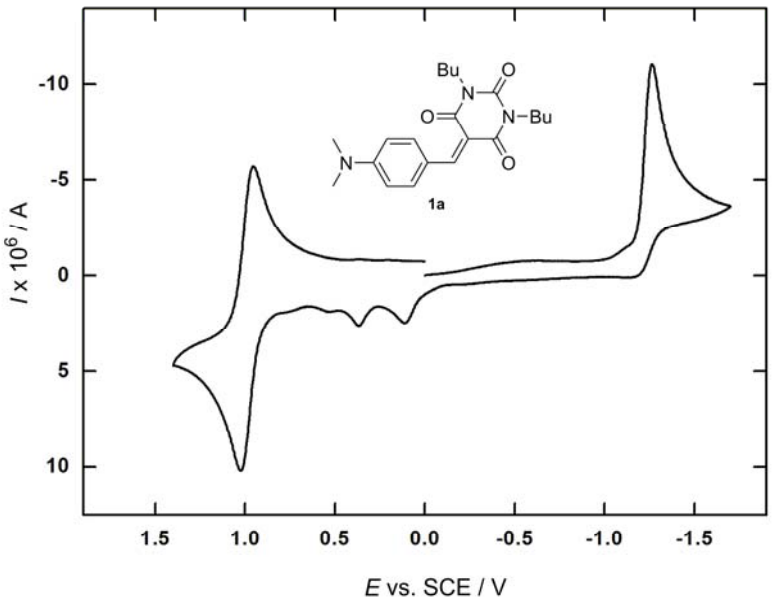


Fig. S3 Representative CV curve of the oxidation and reduction of compound **1a** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

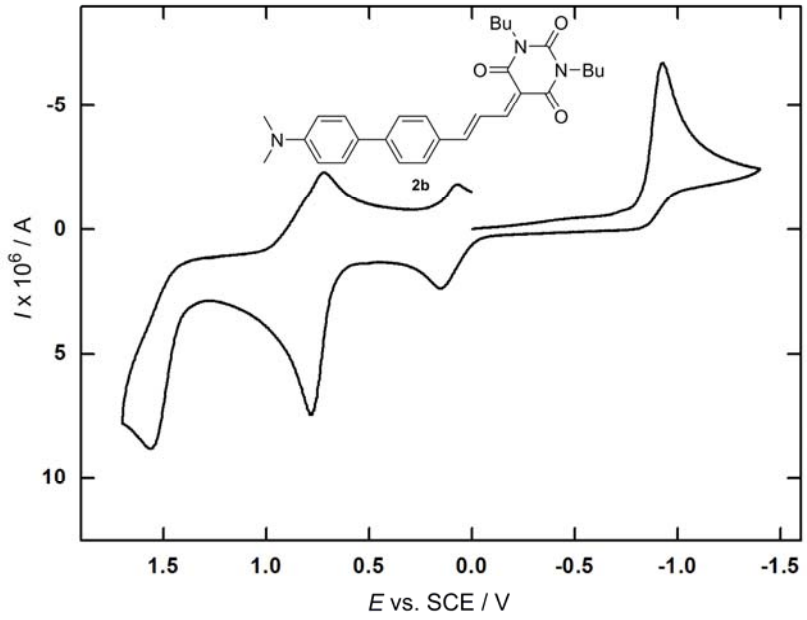


Fig. S4 Representative CV curve of the oxidation and reduction of compound **2b** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

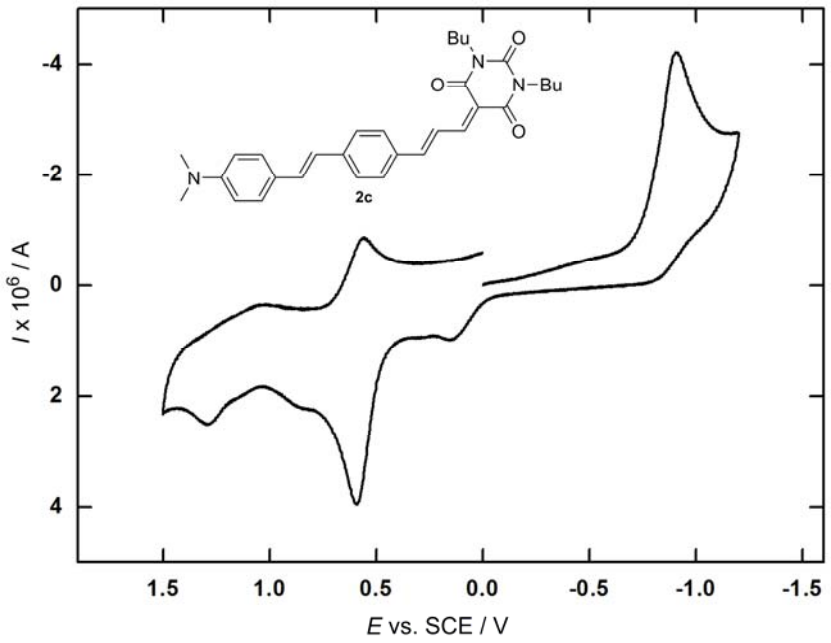


Fig. S5 Representative CV curve of the oxidation and reduction of compound **2c** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

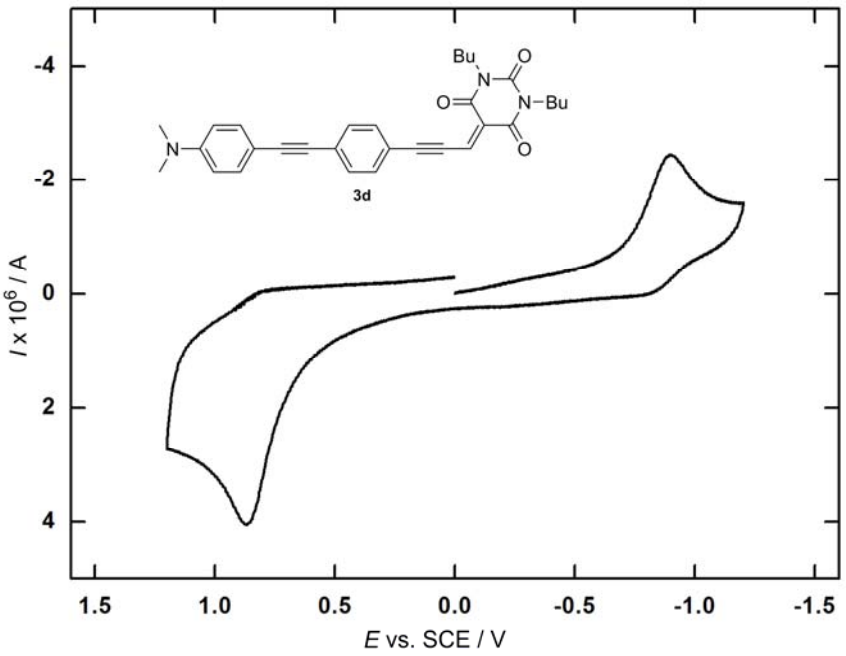


Fig. S6 Representative CV curve of the oxidation and reduction of compound **3d** at Pt electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

6. UV/Vis spectra

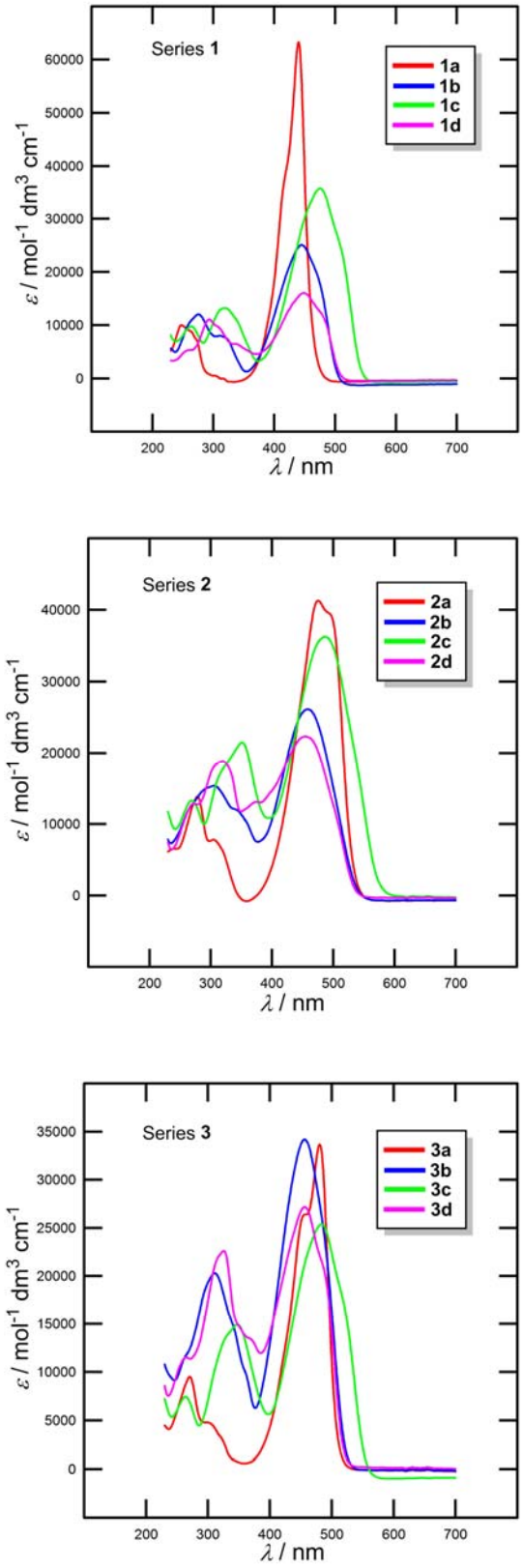


Fig. S7 UV/Vis absorption spectra of chromophores in series **1**-**3** measured in cyclohexane (c = 2 × 10^{-5} M).

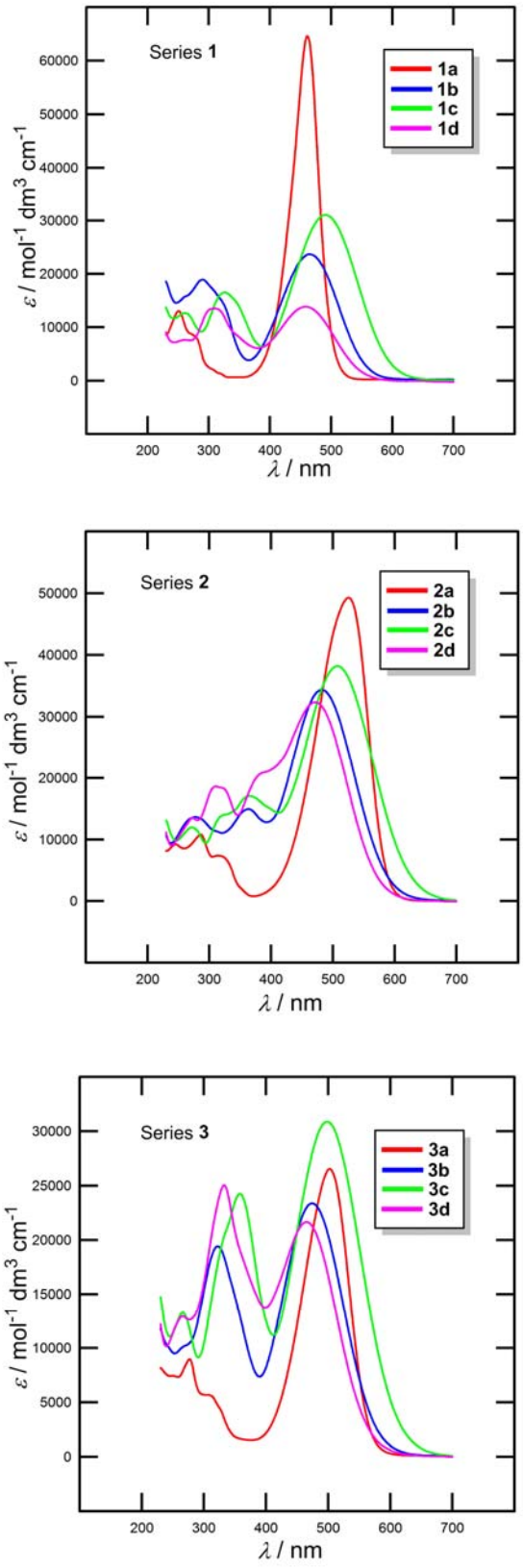


Fig. S8 UV/Vis absorption spectra of chromophores in series **1**-**3** measured in dichloromethane (c = 2 × 10^{-5} M).

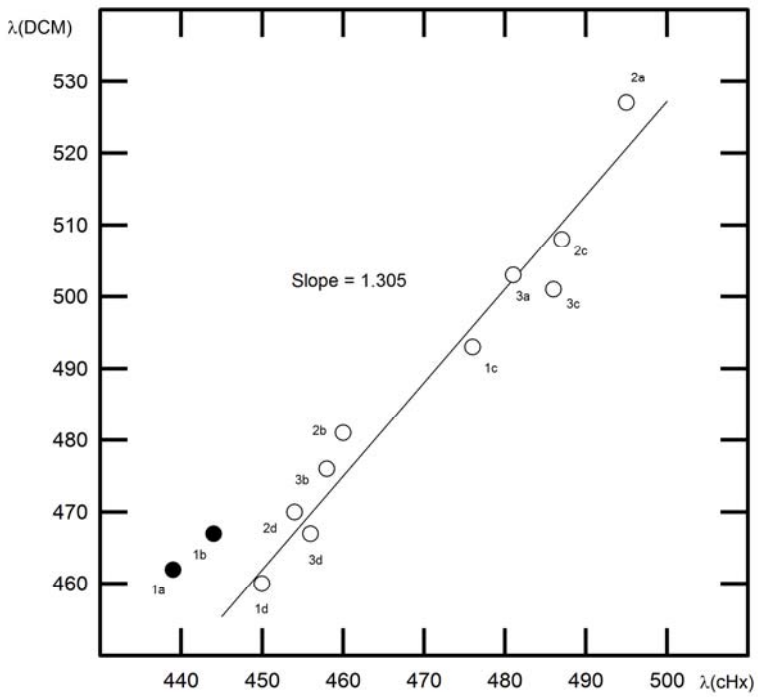


Fig. S9 Dependence of the λ_{max} values measured in dichloromethane (DCM) and cyclohexane (cHx) with orthogonal linear fit.

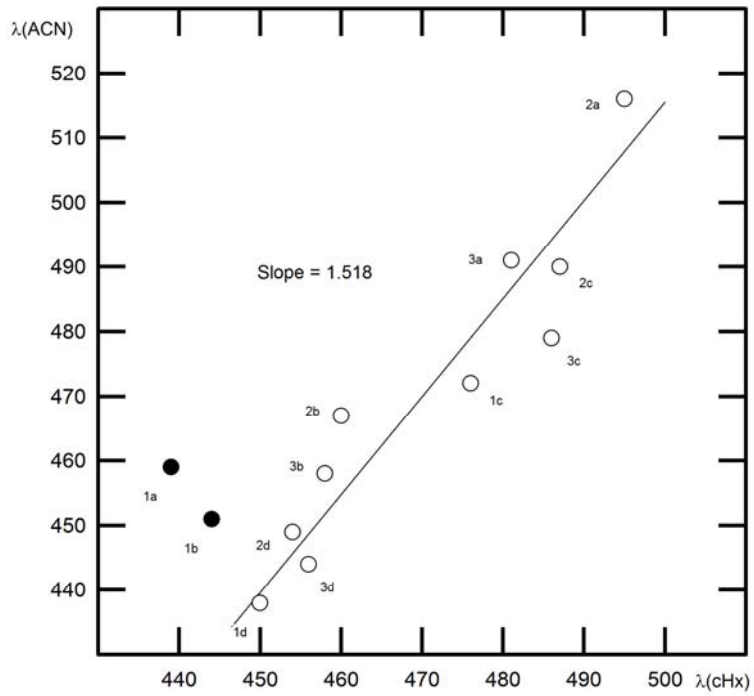


Fig. S10 Dependence of the λ_{max} values measured in acetonitrile (ACN) and cyclohexane (cHx) with orthogonal linear fit.

7. HOMO and LUMO localizations

The following figures have been derived from calculations using PM7 method implemented MOPAC2012.[17] The visualizations have been performed in OPchem.[18]

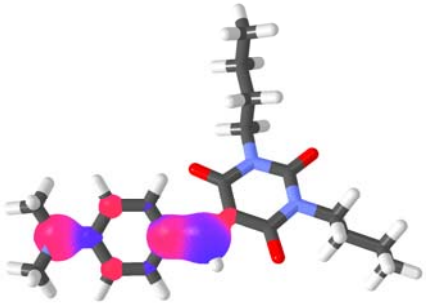


Fig. S11 HOMO (red) and LUMO (blue) localizations in chromophore **1a**

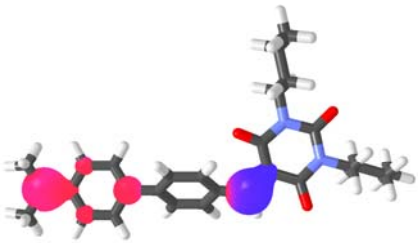


Fig. S12 HOMO (red) and LUMO (blue) localizations in chromophore **1b**

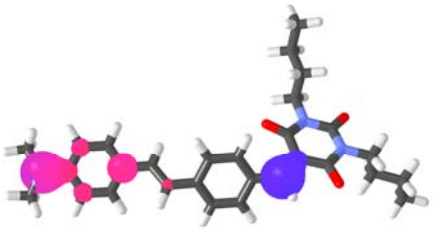


Fig. S13 HOMO (red) and LUMO (blue) localizations in chromophore **1c**

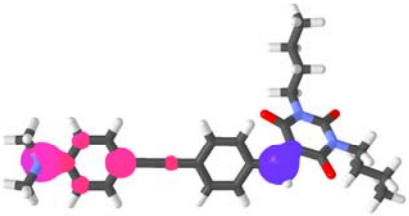


Fig. S14 HOMO (red) and LUMO (blue) localizations in chromophore **1d**

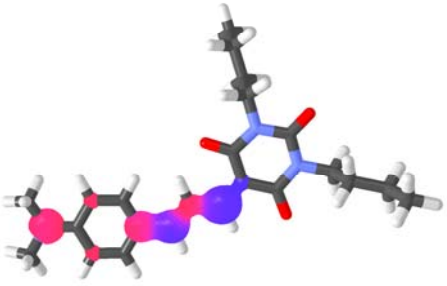


Fig. S15 HOMO (red) and LUMO (blue) localizations in chromophore **2a**

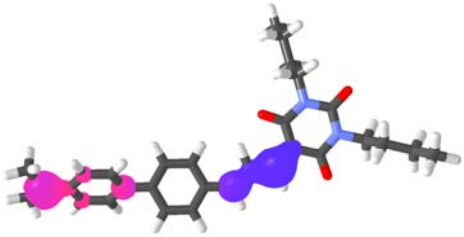


Fig. S16 HOMO (red) and LUMO (blue) localizations in chromophore **2b**

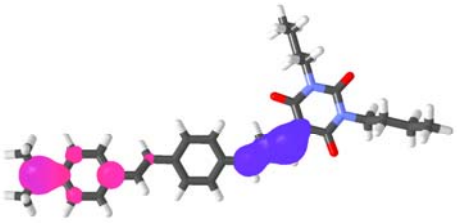


Fig. S17 HOMO (red) and LUMO (blue) localizations in chromophore **2c**

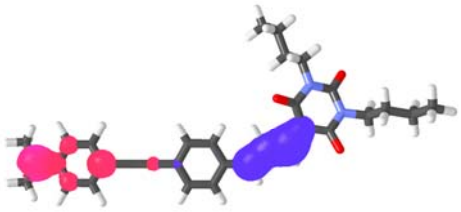


Fig. S18 HOMO (red) and LUMO (blue) localizations in chromophore **2d**

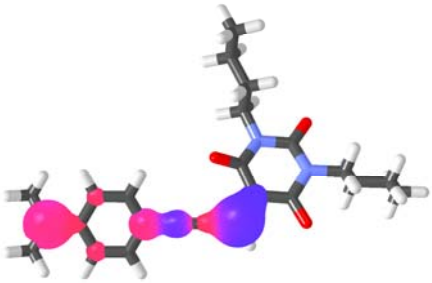


Fig. S19 HOMO (red) and LUMO (blue) localizations in chromophore **3a**

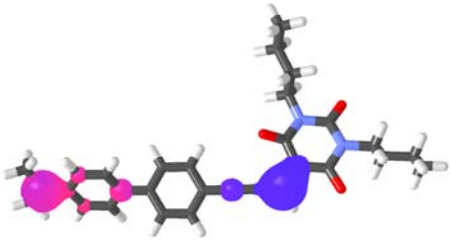


Fig. S20 HOMO (red) and LUMO (blue) localizations in chromophore **3b**

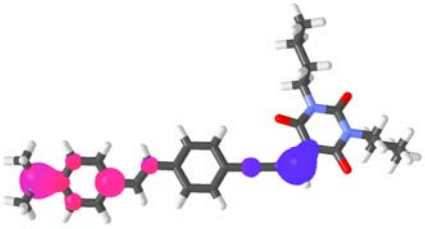


Fig. S21 HOMO (red) and LUMO (blue) localizations in chromophore **3c**

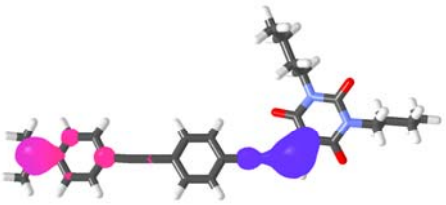


Fig. S22 HOMO (red) and LUMO (blue) localizations in chromophore **3d**

8. ^{1}H and ^{13}C NMR Spectra of Target Compounds 1-3

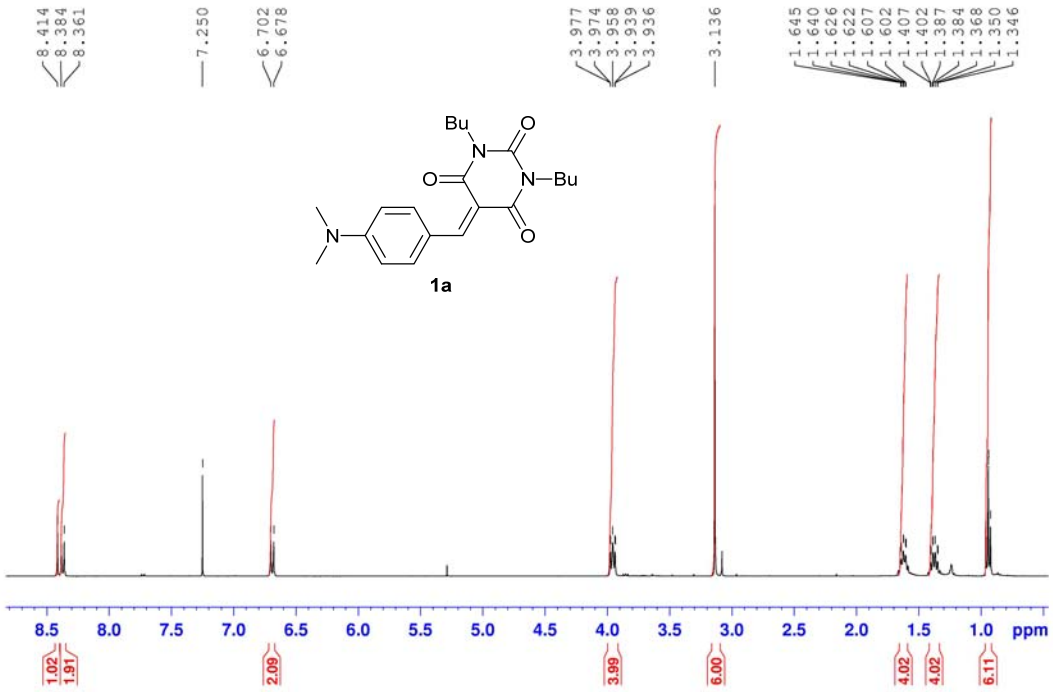


Fig. S23 ^{1}H NMR spectrum of chromophore **1a** ($CDCl_3$, 400 MHz, 25 °C)

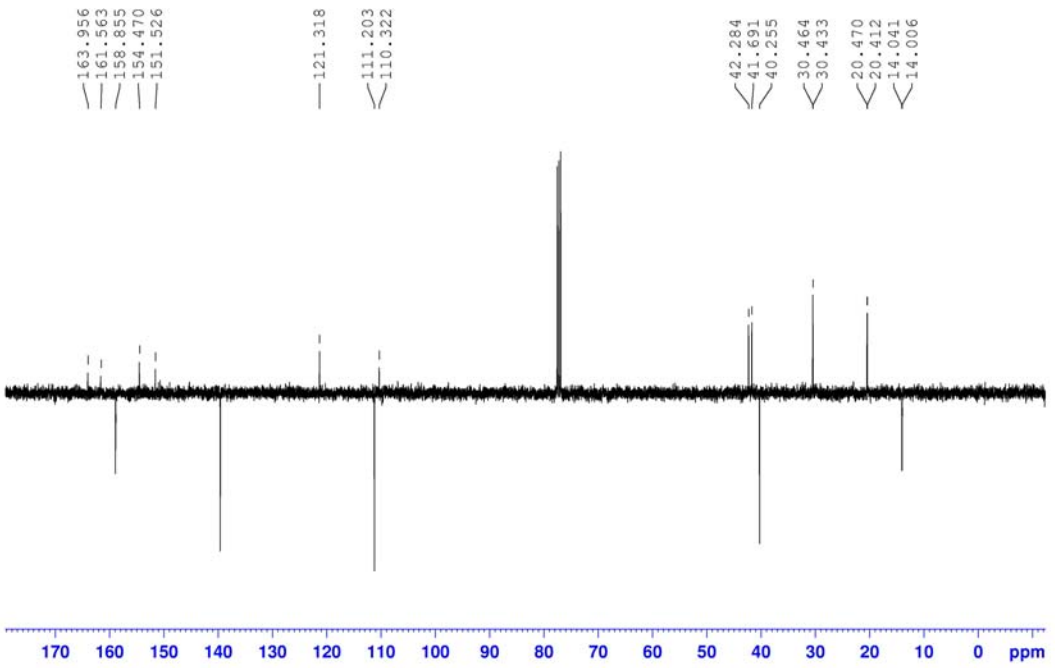


Fig. S24 ^{13}C NMR APT spectrum of chromophore **1a** ($CDCl_3$, 100 MHz, 25 °C)

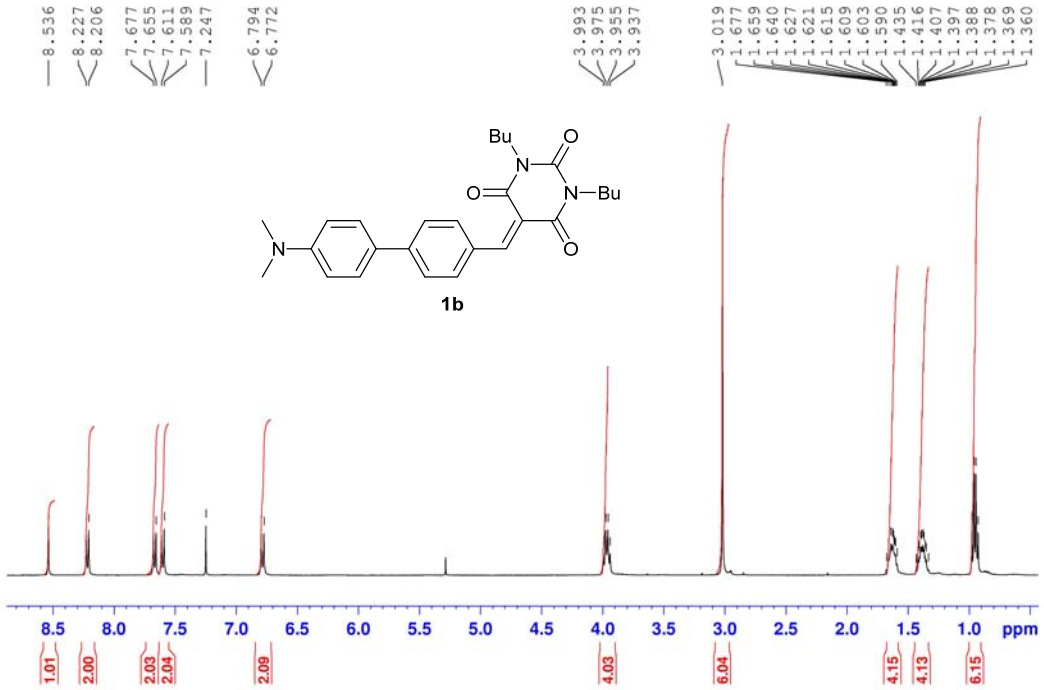


Fig. S25 ^{1}H NMR spectrum of chromophore **1b** ($CDCl_3$, 400 MHz, 25 °C)

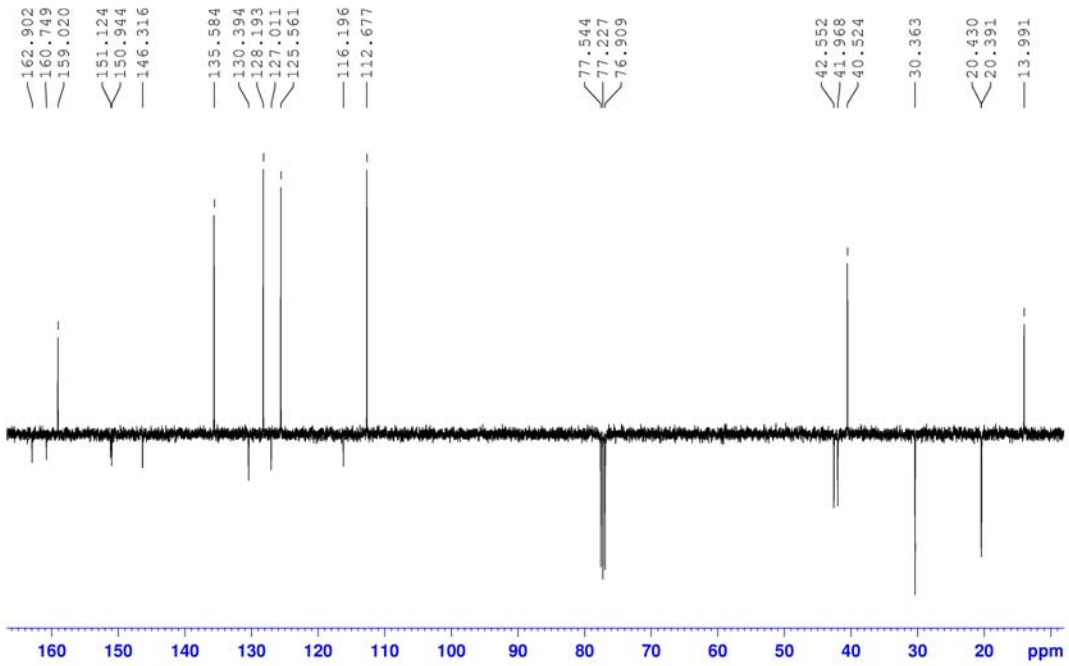


Fig. S26 ^{13}C NMR APT spectrum of chromophore **1b** ($CDCl_3$, 100 MHz, 25 °C)

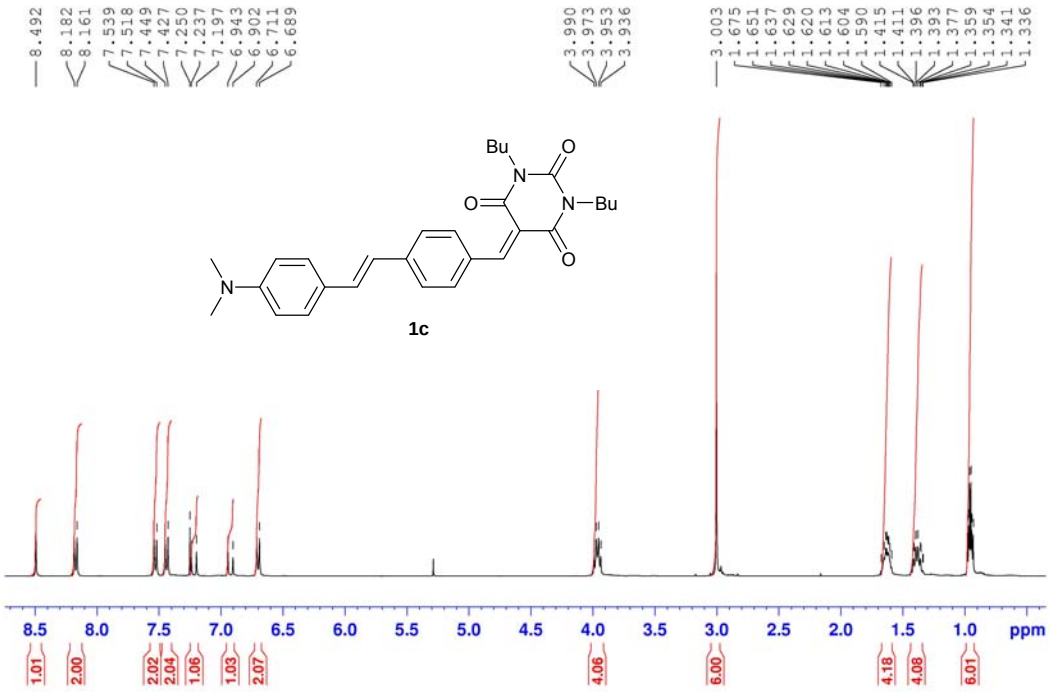


Fig. S27 ^{1}H NMR spectrum of chromophore **1c** ($CDCl_3$, 400 MHz, 25 °C)

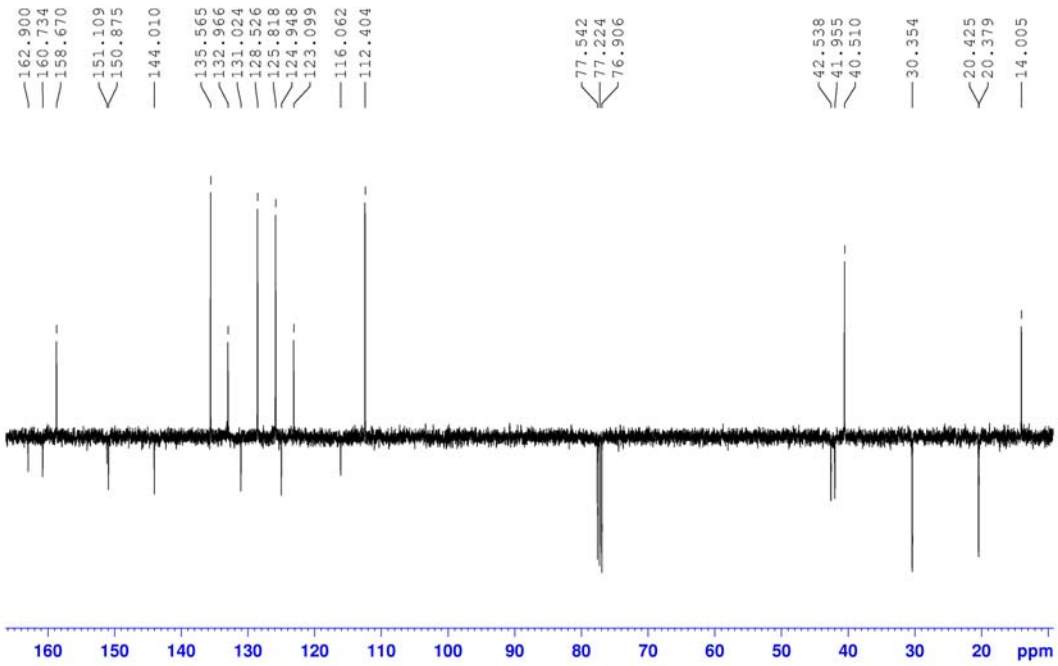


Fig. S28 ^{13}C NMR APT spectrum of chromophore **1c** ($CDCl_3$, 100 MHz, 25 °C)

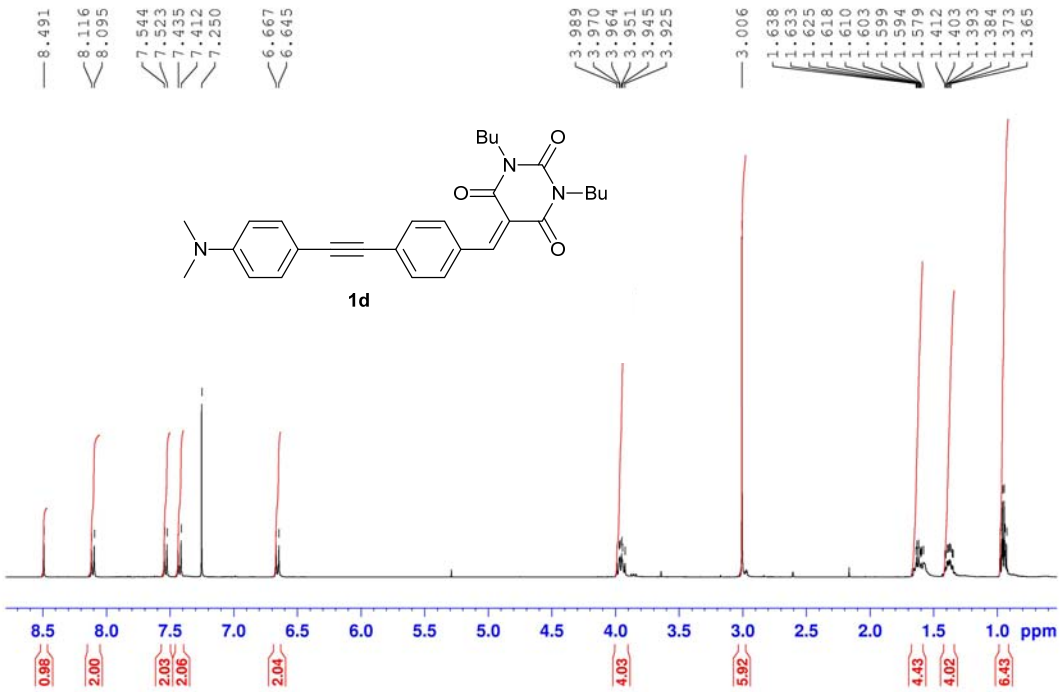


Fig. S29 ^{1}H NMR spectrum of chromophore **1d** ($CDCl_3$, 400 MHz, 25 °C)

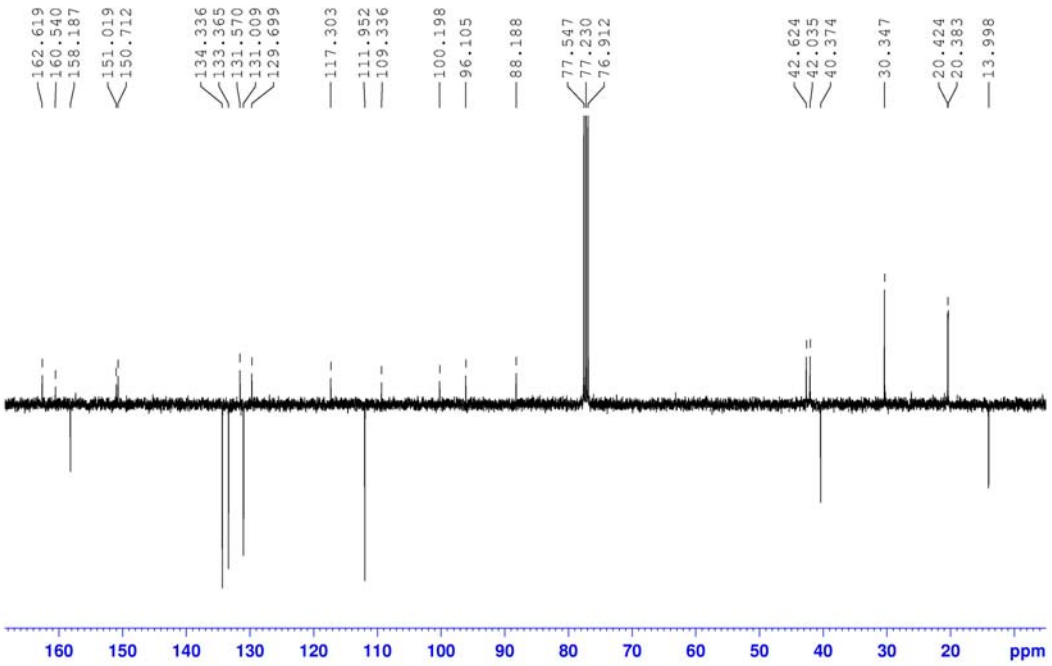


Fig. S30 ^{13}C NMR APT spectrum of chromophore **1d** ($CDCl_3$, 100 MHz, 25 °C)

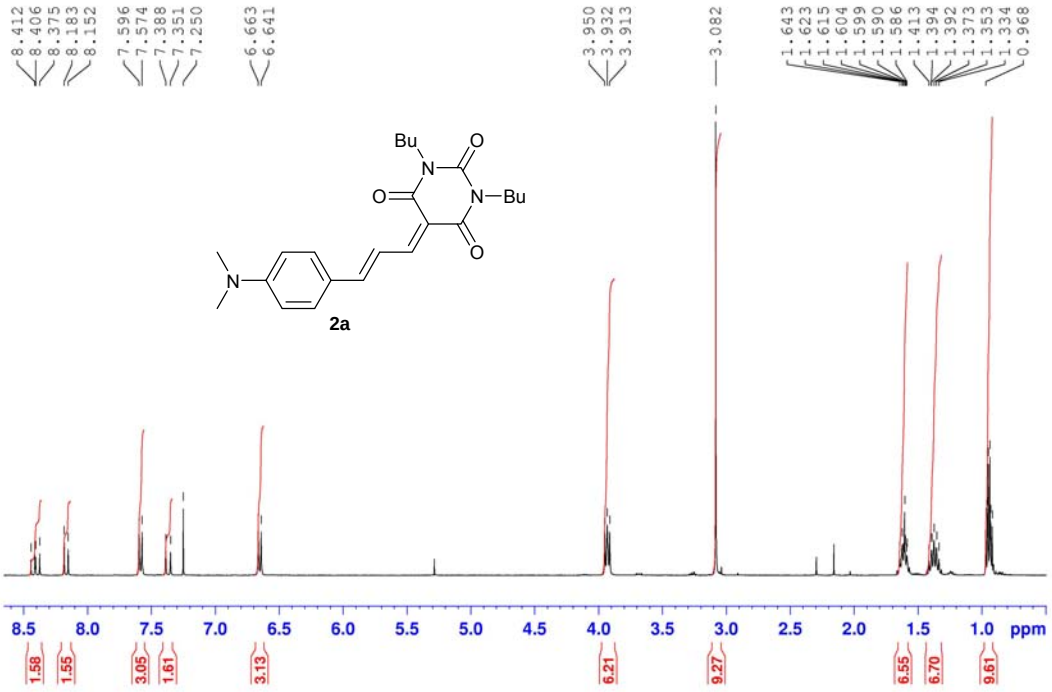


Fig. S31 ^{1}H NMR spectrum of chromophore **2a** ($CDCl_3$, 400 MHz, 25 °C)

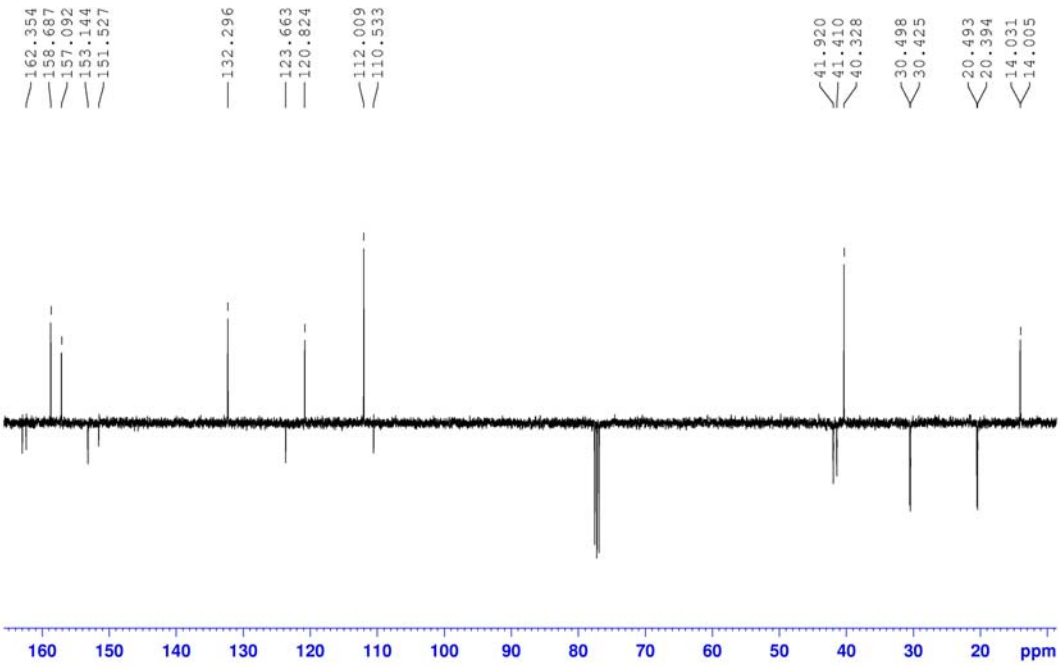


Fig. S32 ^{13}C NMR APT spectrum of chromophore **2a** ($CDCl_3$, 100 MHz, 25 °C)

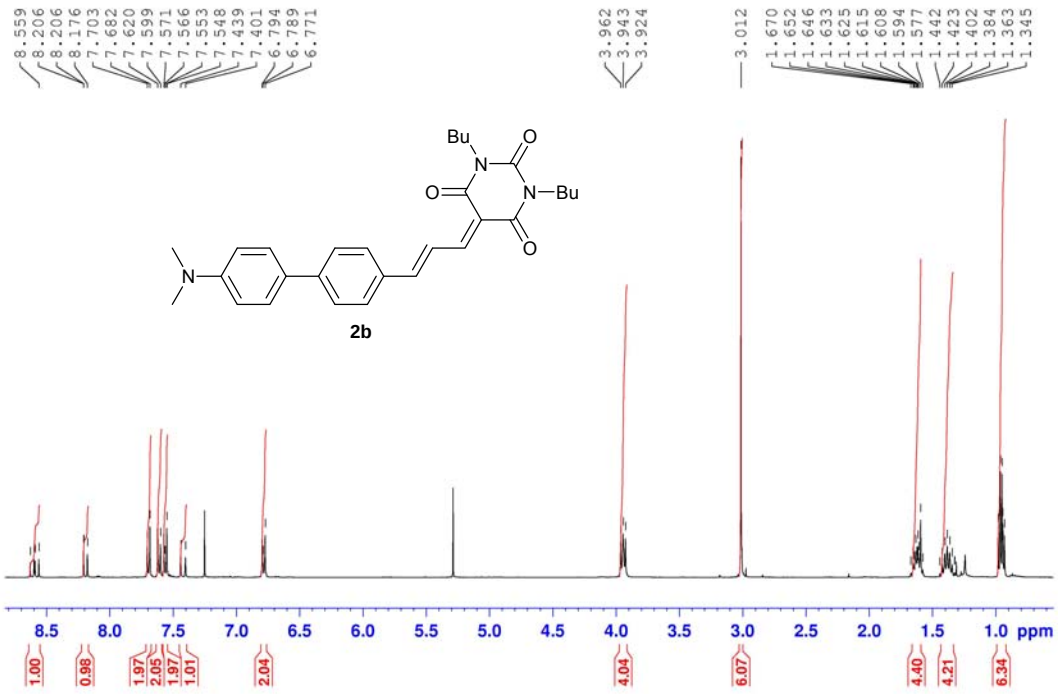


Fig. S33 ^{1}H NMR spectrum of chromophore **2b** ($CDCl_3$, 400 MHz, 25 °C)

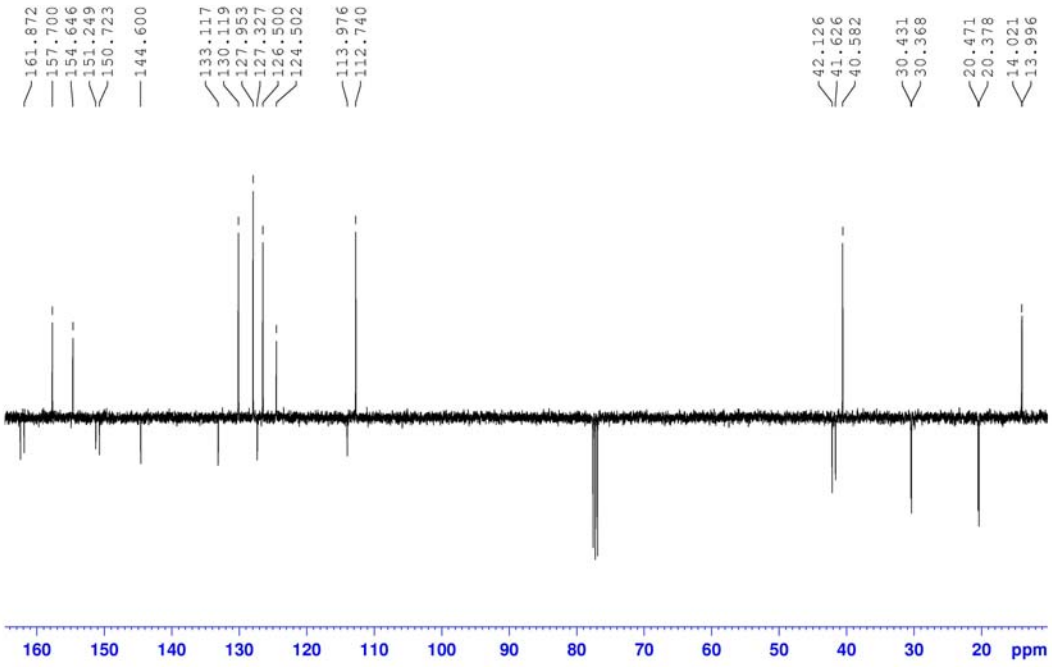


Fig. S34 ^{13}C NMR APT spectrum of chromophore **2b** ($CDCl_3$, 100 MHz, 25 °C)

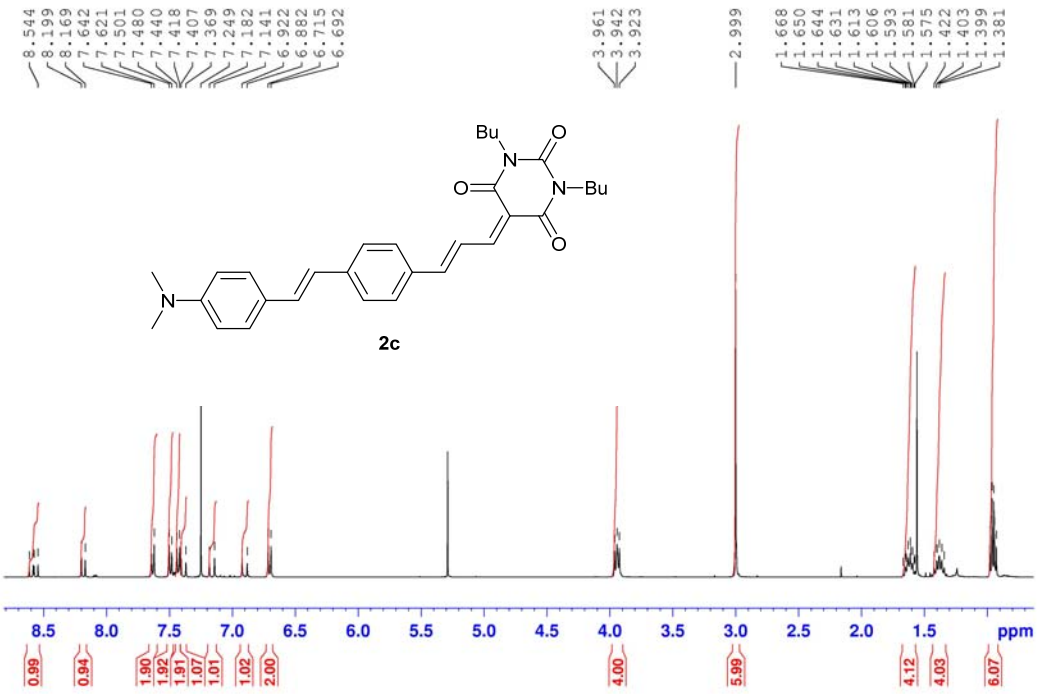


Fig. S35 ^{1}H NMR spectrum of chromophore **2c** ($CDCl_3$, 400 MHz, 25 °C)

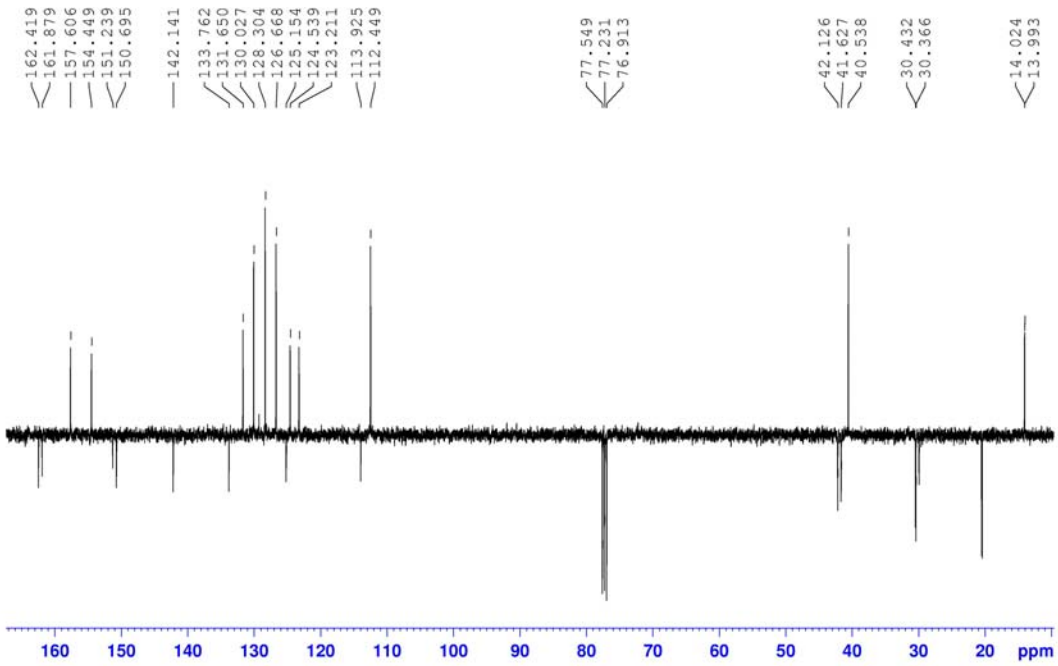


Fig. S36 ^{13}C NMR APT spectrum of chromophore **2c** ($CDCl_3$, 100 MHz, 25 °C)

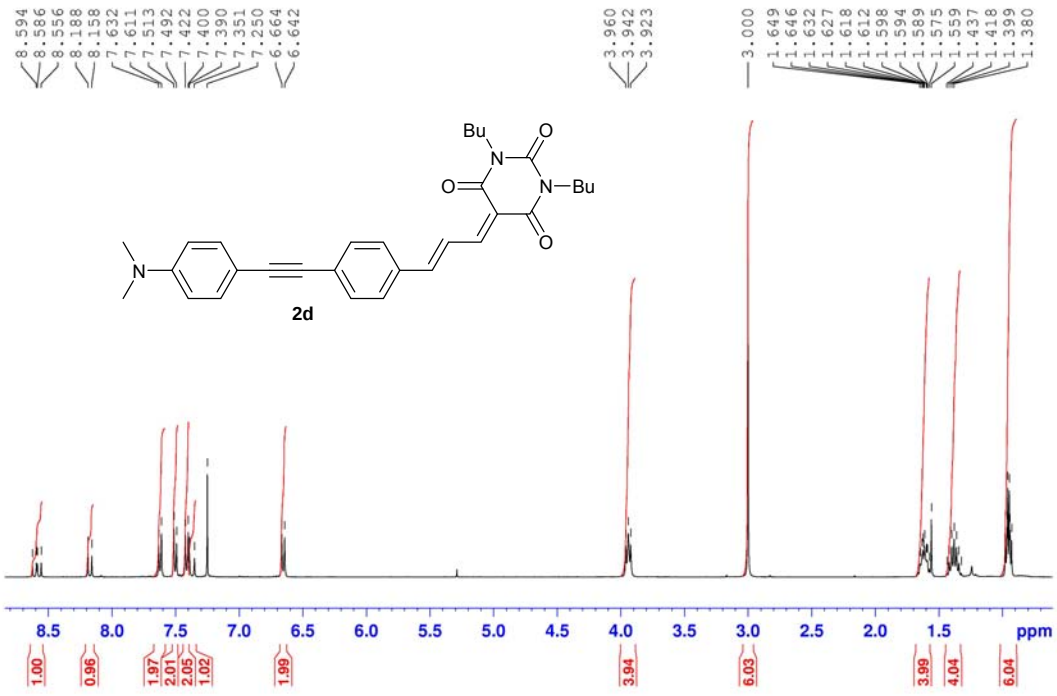


Fig. S37 ^{1}H NMR spectrum of chromophore **2d** ($CDCl_3$, 400 MHz, 25 °C)

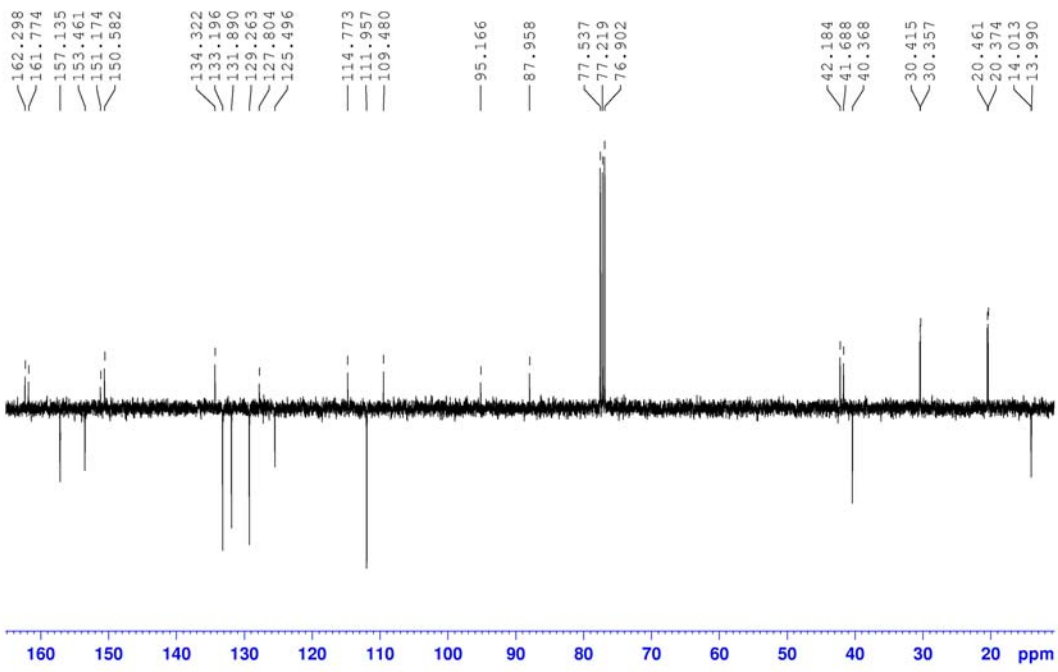


Fig. S38 ^{13}C NMR APT spectrum of chromophore **2d** ($CDCl_3$, 100 MHz, 25 °C)

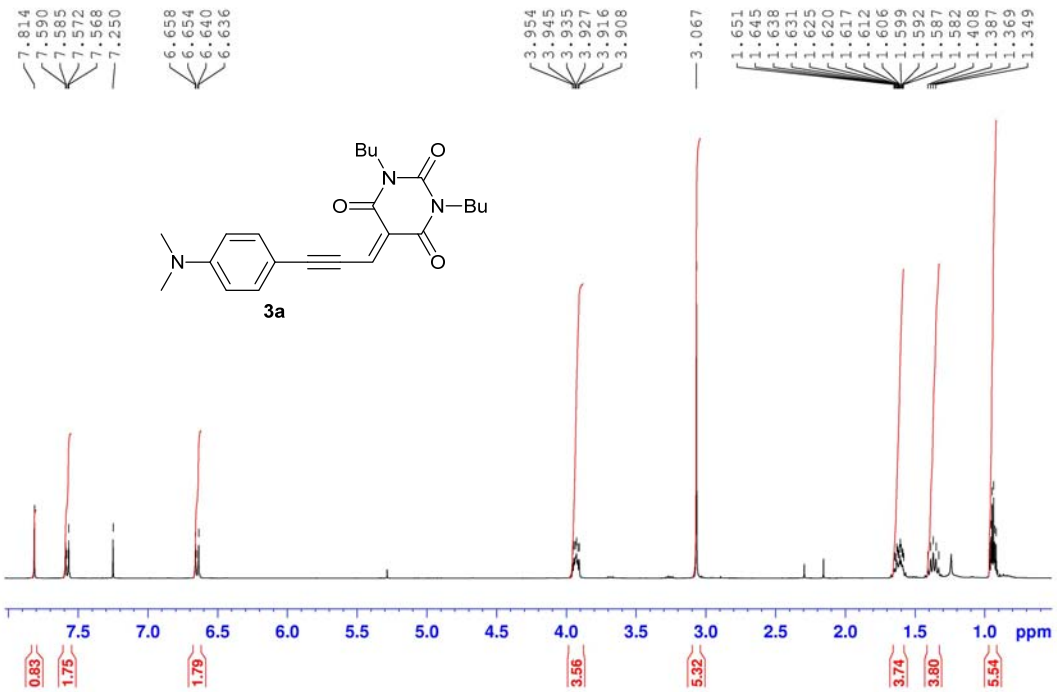


Fig. S39 ^{1}H NMR spectrum of chromophore **3a** ($CDCl_3$, 400 MHz, 25 °C)

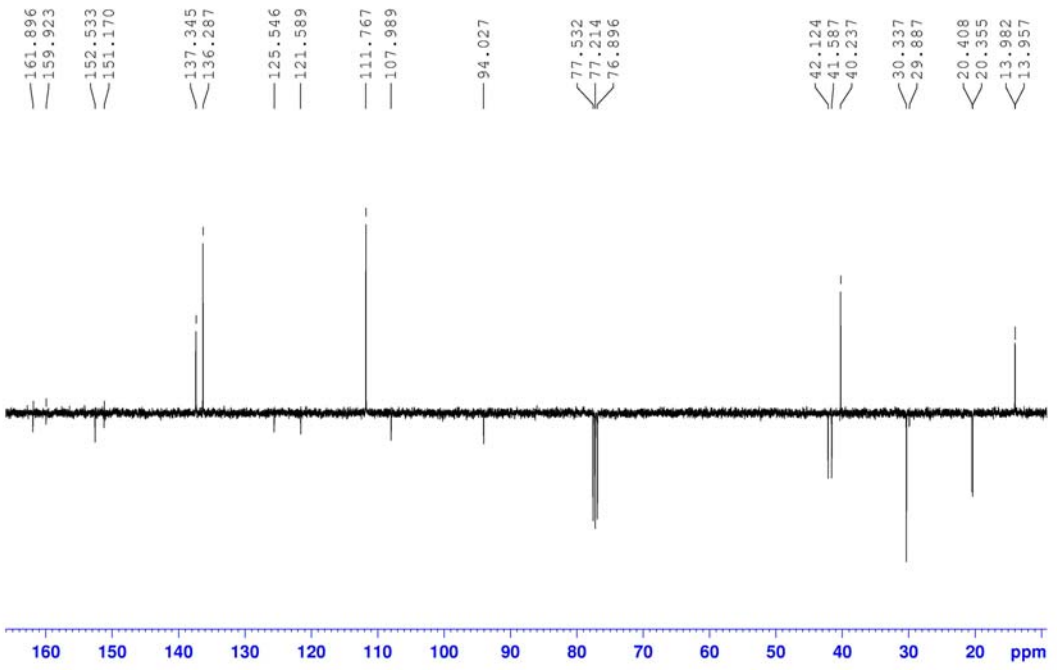


Fig. S40 ^{13}C NMR APT spectrum of chromophore **3a** ($CDCl_3$, 100 MHz, 25 °C)

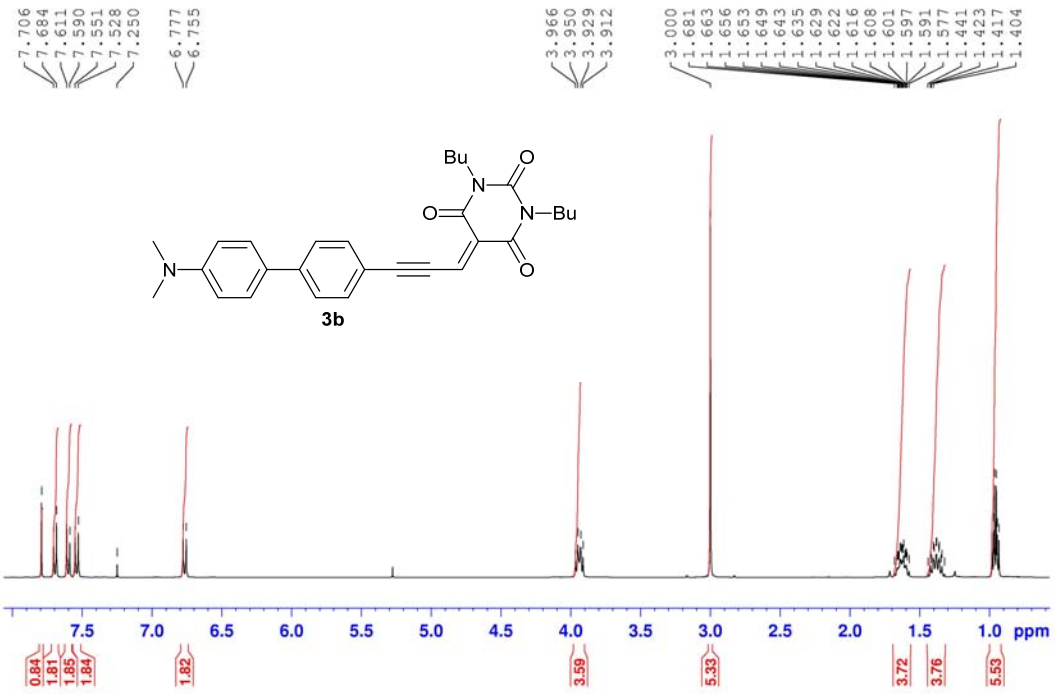


Fig. S41 ^{1}H NMR spectrum of chromophore **3b** ($CDCl_3$, 400 MHz, 25 °C)

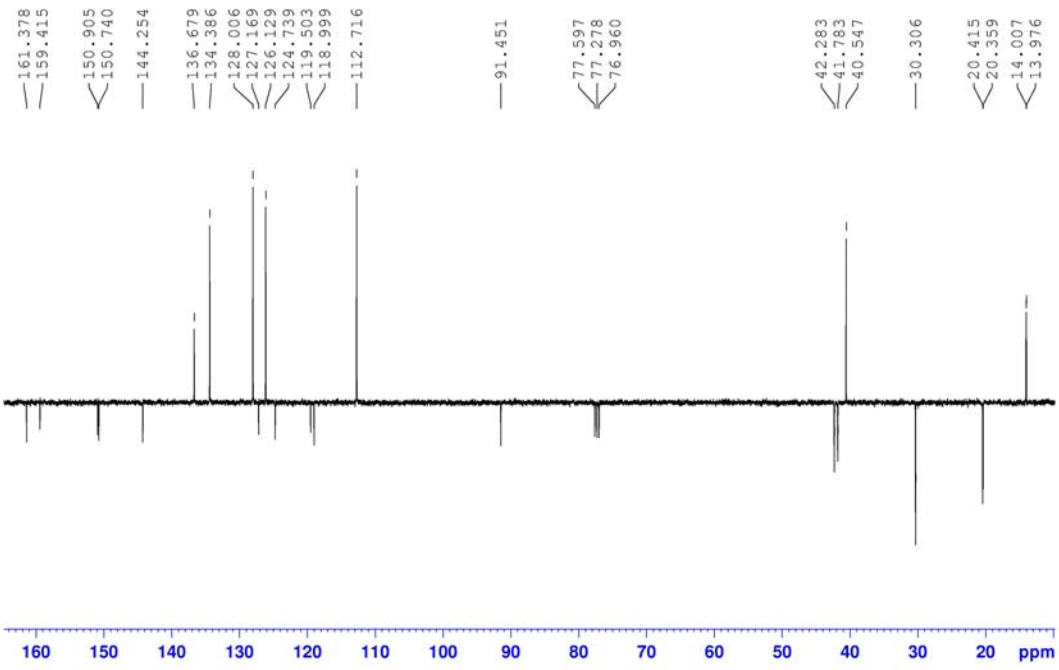


Fig. S42 ^{13}C NMR APT spectrum of chromophore **3b** ($CDCl_3$, 100 MHz, 25 °C)

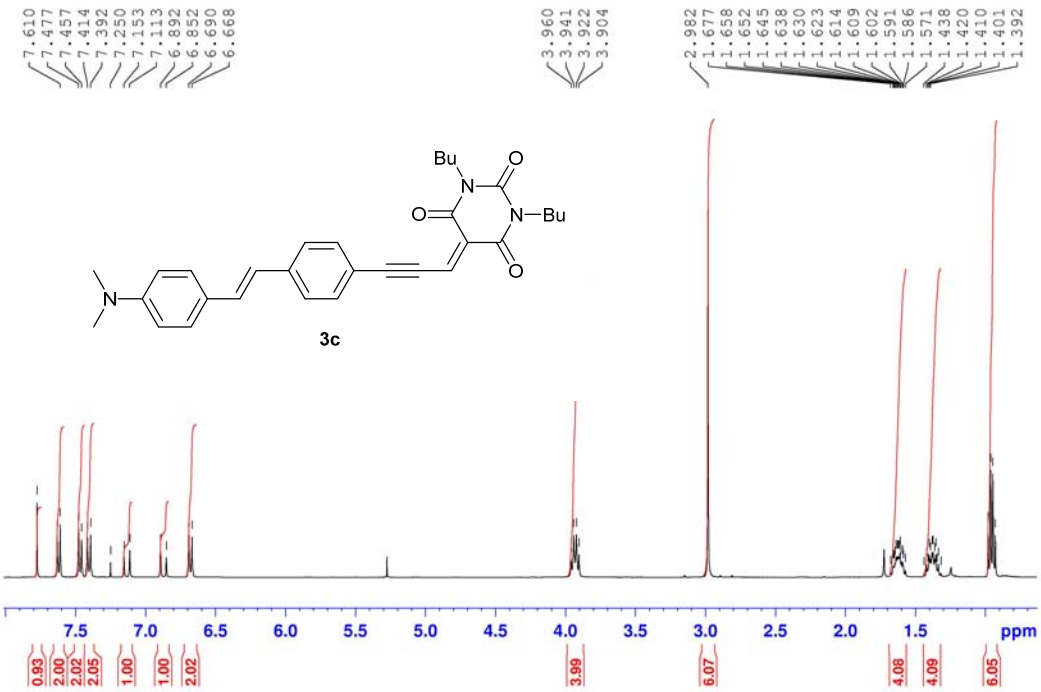


Fig. S43 ^{1}H NMR spectrum of chromophore **3c** ($CDCl_3$, 400 MHz, 25 °C)

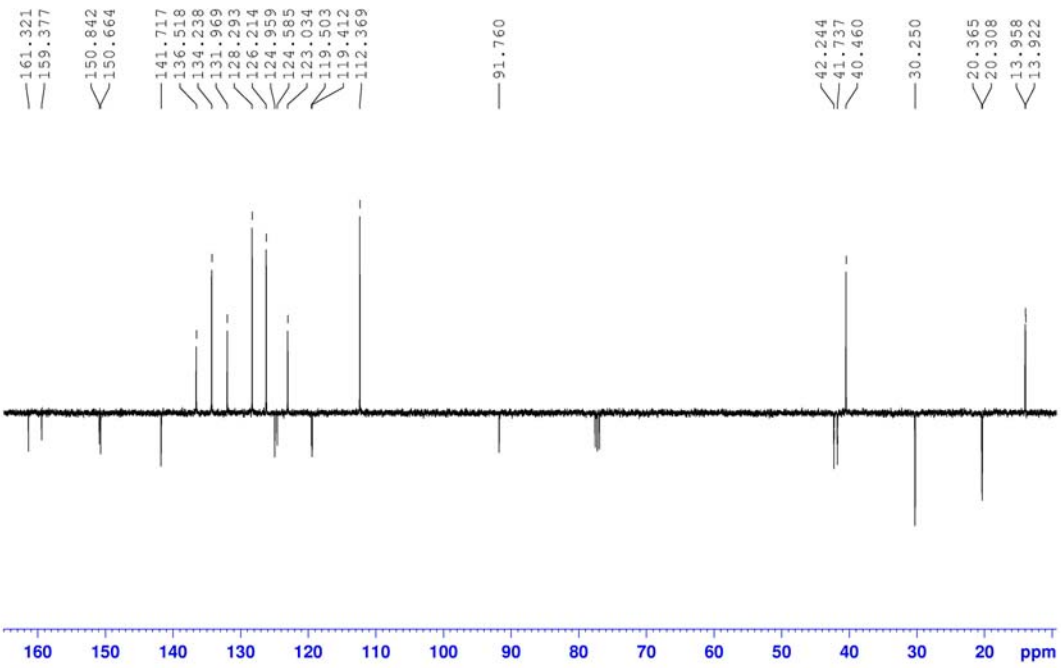


Fig. S44 ^{13}C NMR APT spectrum of chromophore **3c** ($CDCl_3$, 100 MHz, 25 °C)

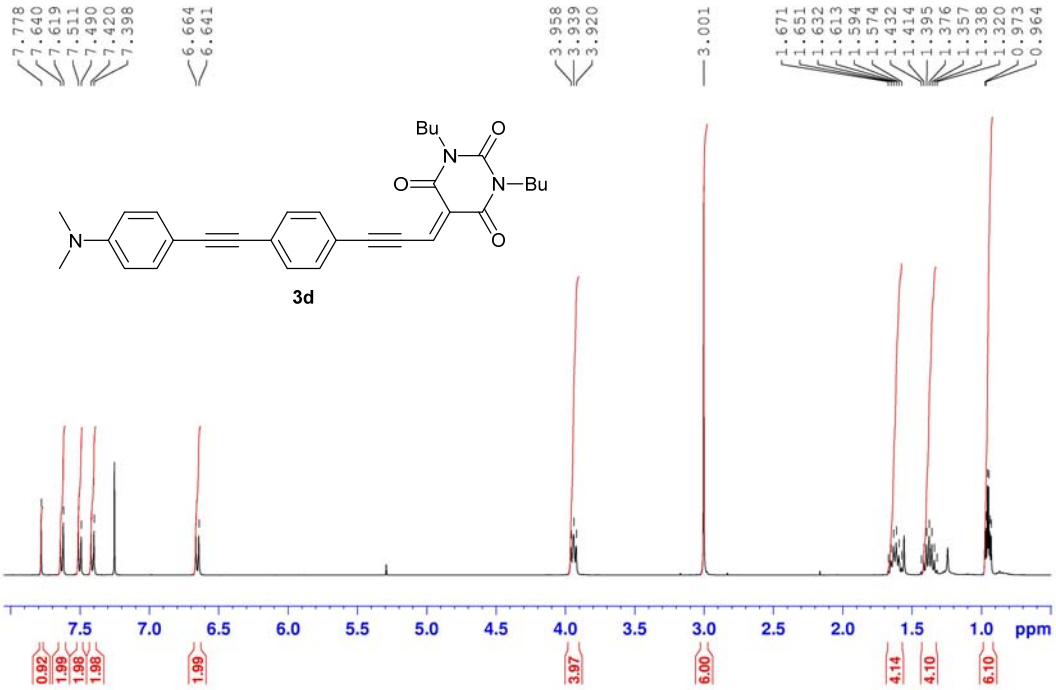


Fig. S45 ^{1}H NMR spectrum of chromophore **3d** ($CDCl_3$, 400 MHz, 25 °C)

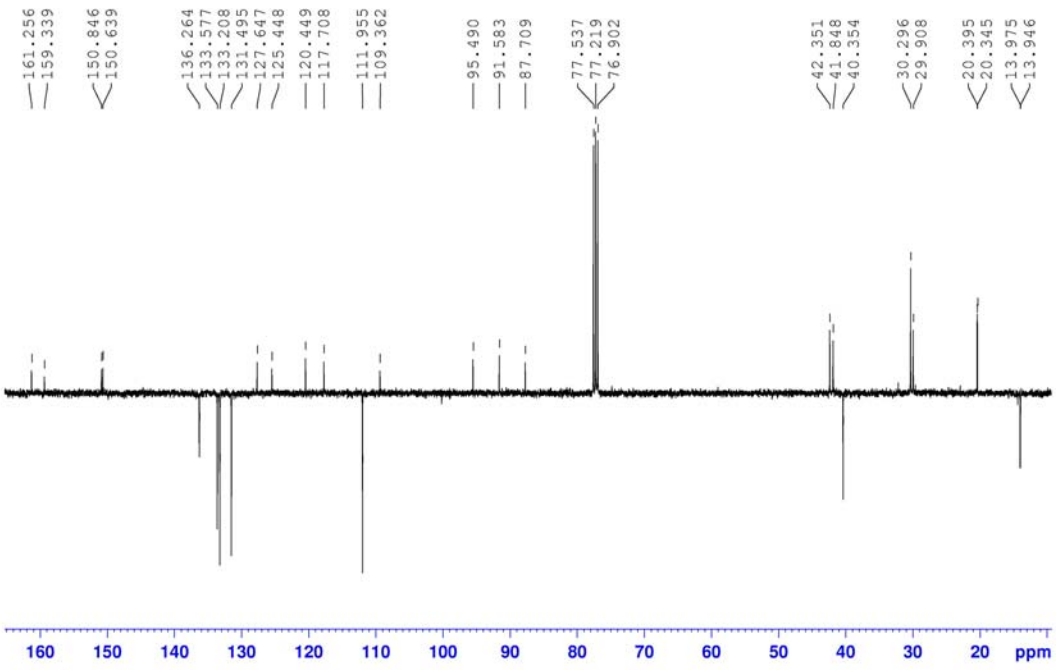


Fig. S46 ^{13}C NMR APT spectrum of chromophore **3d** ($CDCl_3$, 100 MHz, 25 °C)

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