ORGANIC & BIOMOLECULAR CHEMISTRY

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Cycloaddition reactions of polyenic Donor-π-Acceptor systems with an electron-rich alkyne: access to new chromophores with second-order optical nonlinearities

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2.3. NMR spectra for new compounds

1. General Experimental Methods

Infrared measurements were carried out in nujol mulls using a Perkin-Elmer Fourier Transform Infrared 1600 spectrometer. Melting points were obtained on a Gallenkamp apparatus in open capillaries and are uncorrected. Elemental analysis was performed with a Perkin-Elmer 240C microanalyzer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker ARX300 or a Bruker AV400 at 300 or 400 MHz and 75 or 100 MHz respectively; δ values are given in ppm (relative to TMS) and J values in Hz. The apparent resonance multiplicity is described as a s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). ^{1}H-^{1}H COSY experiments were recorded at 400 MHz in order to establish peaks assignment and spatial relationships. Selective ge-1D NOESY experiments (mixing time: 0.6-1.2 s; selective 180 pulse: 20-40 ms) were recorded at 300 MHz for compound **5b**, in order to determine the regio- and torquoselectivity of the reaction and the conformation of TCF moiety. Electrospray mass spectra were recorded on a Bruker Q-ToF spectrometer; accurate mass measurements were achieved using sodium formate as external reference. Electronic spectra were recorded with an UV-Vis UNICAM UV4 spectrophotometer. The spectra were measured in CH_2Cl_2 and in dioxane. The absorption wavelengths are reported in nm with log ε in parenthesis; shoulders are indicated as sh. Cyclic voltammetry measurements were performed with a μ-Autolab ECO-Chemie potentiostat, using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon, in CH_2Cl_2, with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 100 mV s^{-1}.

X-Ray data collection were carried out on a diffractometer equipped with a graphite monochromator utilizing Mo Kα radiation (λ = 0.71073 Å). The diffraction frames (compounds **7c** and **10**) were integrated and corrected for absorption using the CrysAlis RED package.[1] For compound **5a** the CrysAlis RED package[2] was used. The structures were solved by direct methods.[3] All refinements were carried out using SHELXL-97[4] against the F^2 data

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(1) CrysAlisPro, Oxford Diffraction Ltd.,Version 1.171.34.44 (release 25-10-2010 CrysAlis171. NET) (compiled Oct 25 2010,18:11:34).

(2) CrysAlisPro, Oxford Diffraction Ltd., Version 1.171.32.19 (release 28-02-2008 CrysAlis171. NET) (compiled Feb 28 2008,12:10:31).

(3) (a) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343–350. (b) Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786–790.

(4) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

using full-matrix least squares methods. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at idealized positions and assigned isotropic displacement parameters 1.2 times the U_{iso} value of the corresponding bonding partner (1.5 times for methyl hydrogen atoms, except C22 and C23 (1.2 times) in **5a**).

All theoretical calculations were performed by using the Gaussian 09[5] program. The molecular geometries were optimized using the B3P86[6] functional and the 6-31G*[7] basis set. Solvent effect was studied by placing the solute in a cavity within the solvent reaction field and using the Polarizable Continuum Model (PCM).[8]

For NLO measurements, see Section 7, page S53.

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(5) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

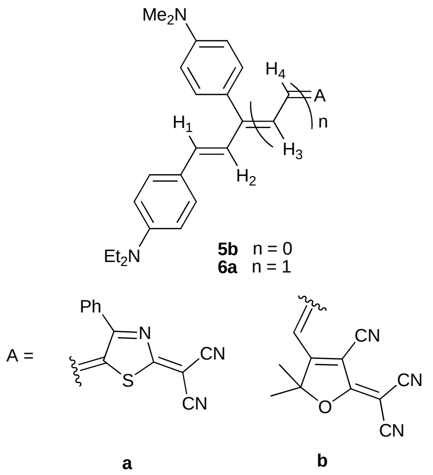
(6) The B3P86 Functional consists of Becke's three parameter hybrid functional (Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648–5652) with the nonlocal correlation provided by the Perdew 86 expression: Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822–8824.

(7) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(8) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999-3093.

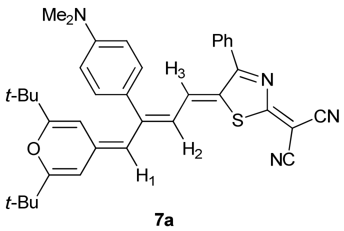
2. NMR studies

2.1. Analysis of the $^3J_{HH}$ in the study of the structure of compounds 5b, 6a, 7a



	δ ($^3J_{HH}$)			
Compd	**H_1**	**H_2**	**H_3**	**H_4**
5b	7.01 (15.3 Hz)	7.14 (15.3 Hz)	-	-
6a	7.13 (15.3 Hz)	6.99 (15.3 Hz)	6.62 (12.8 Hz)	7.63 (12.8 Hz)

Figure S1: Chemical shift (δ, ppm) and $^3J_{HH}$ (Hz) for compounds **5b** and **6a** (Spectra recorded in CD_2Cl_2 at 400 MHz).



7a

	δ ($^3J_{HH}$)		
Compd	**H_1**	**H_2**	**H_3**
7a	6.10	6.58 (13.3 Hz)	7.46 (13.3 Hz)

Figure S2: Chemical shift (δ, ppm) and $^3J_{HH}$ (Hz) for compound **7a** (Spectrum recorded in CD_2Cl_2 at 300 MHz).

2.2. Study of the torquoselectivity in the formation of compound 5b

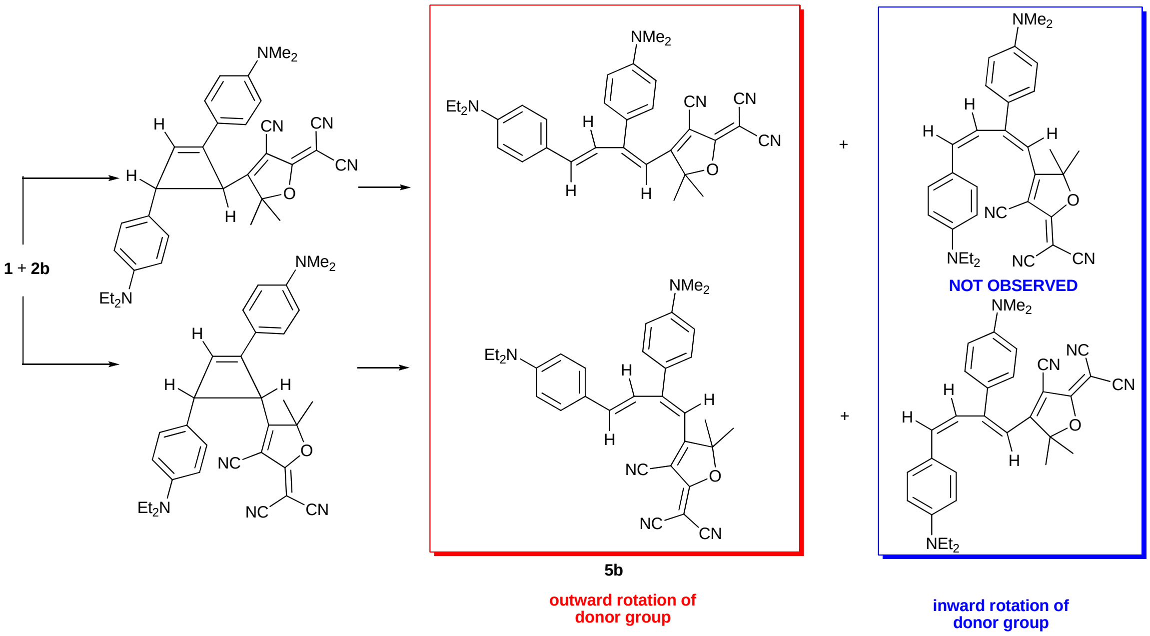


Figure S3: Torquoselective formation of **5b**.

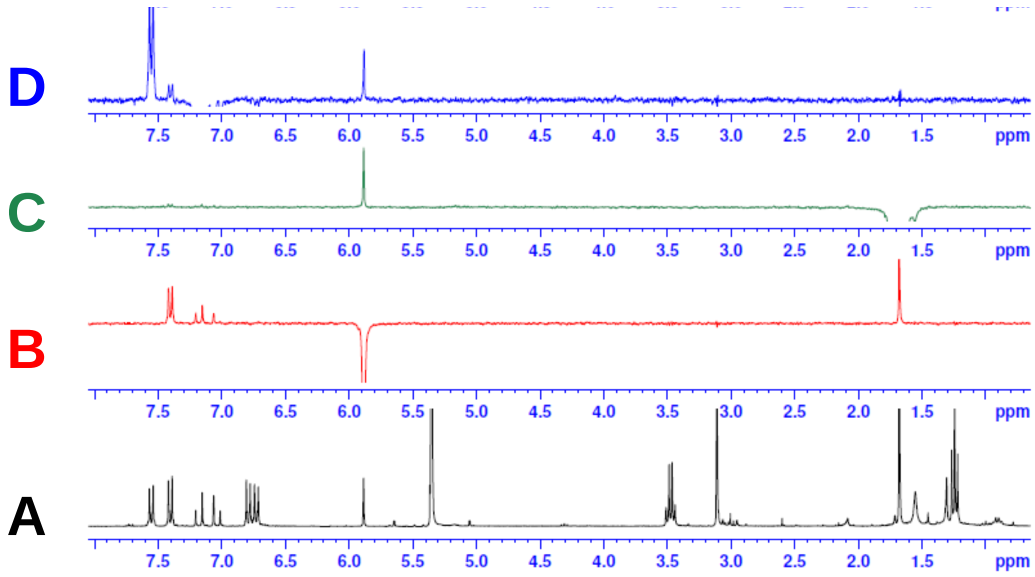
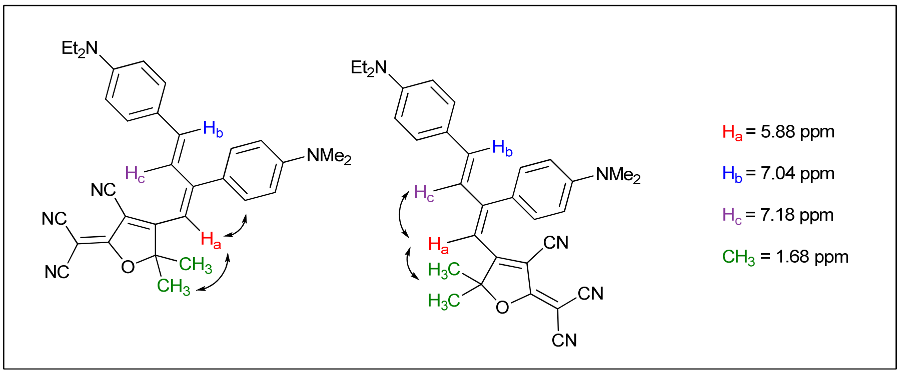


Figure S4: Selective NOE experiments for compound **5b** (300 MHz, 298 K, CD_2Cl_2).



A) ^{1}H spectrum.

B) Spectrum after saturation of H_a ($\delta = 5.88$ ppm) (mixing time: 1.1 s).

C) Spectrum after saturation of CH_3 ($\delta = 1.68$ ppm) (mixing time: 0.6 s).

D) Spectrum after saturation of H_c ($\delta = 7.18$ ppm) (mixing time: 1.2 s)

2.3. NMR spectra for new compounds

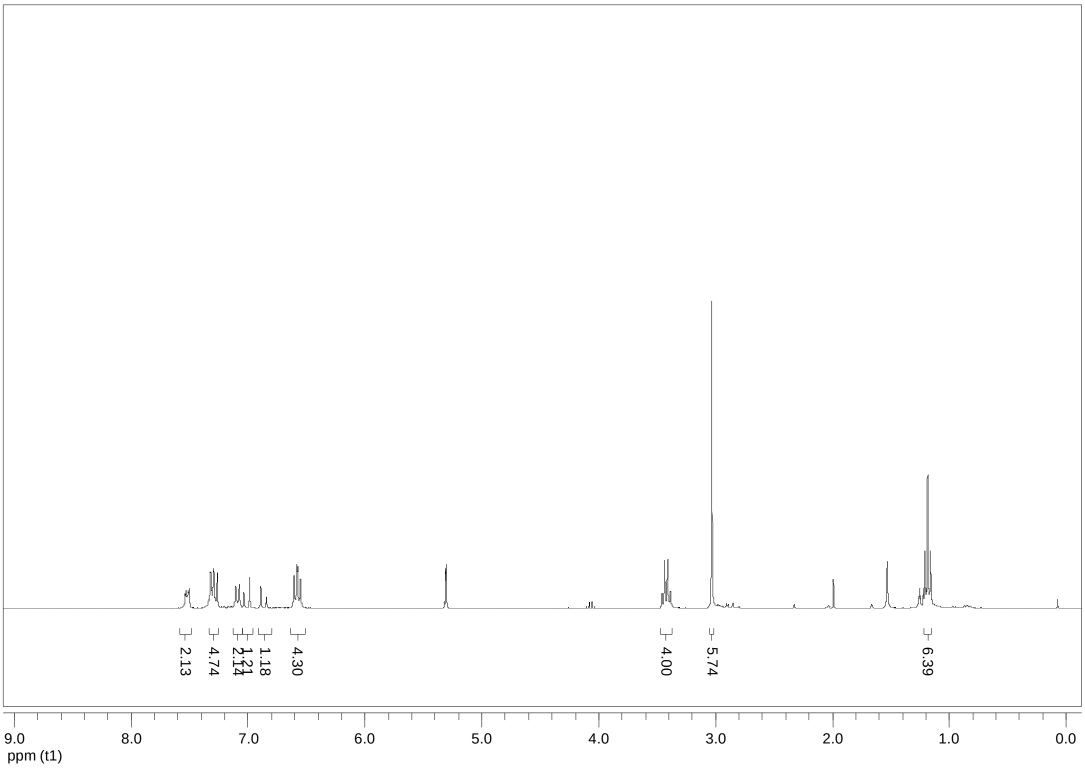
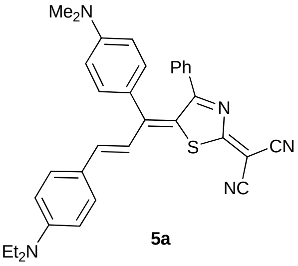


Figure S5: ^{1}H-NMR spectrum of compound **5a** (300 MHz, CD_2Cl_2).



5a

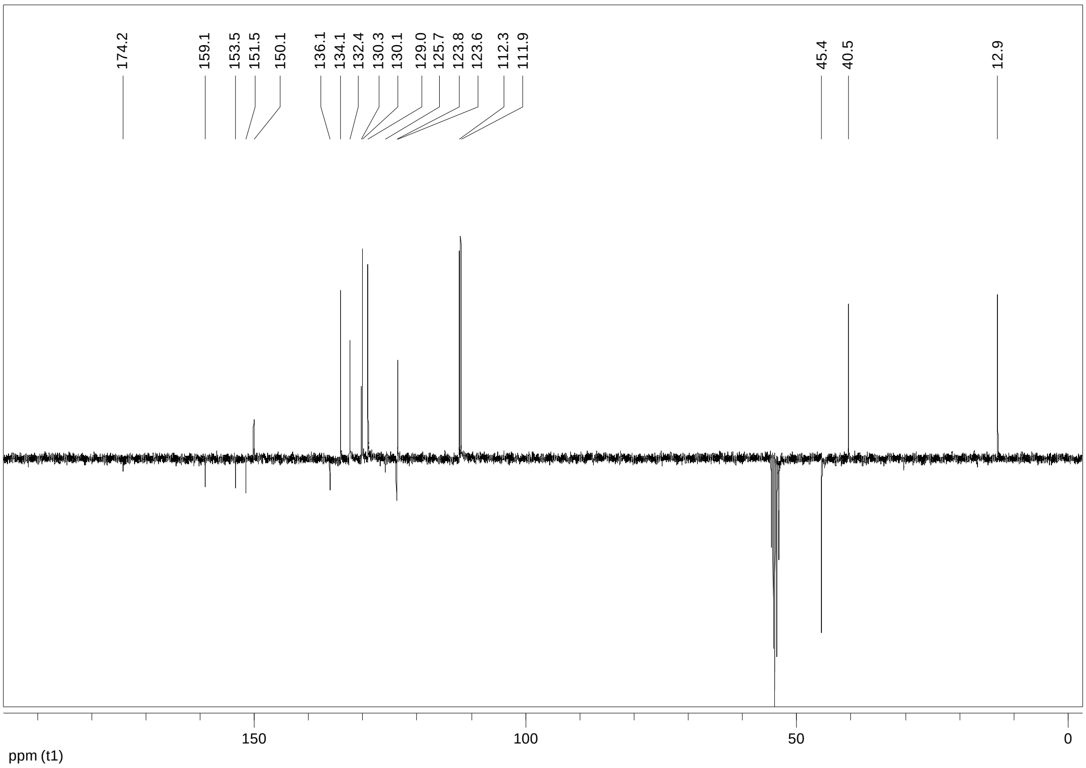
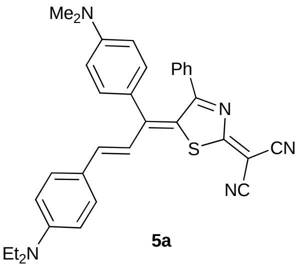


Figure S6: ^{13}C-NMR (APT) spectrum of compound **5a** (75 MHz, CD_2Cl_2).



5a

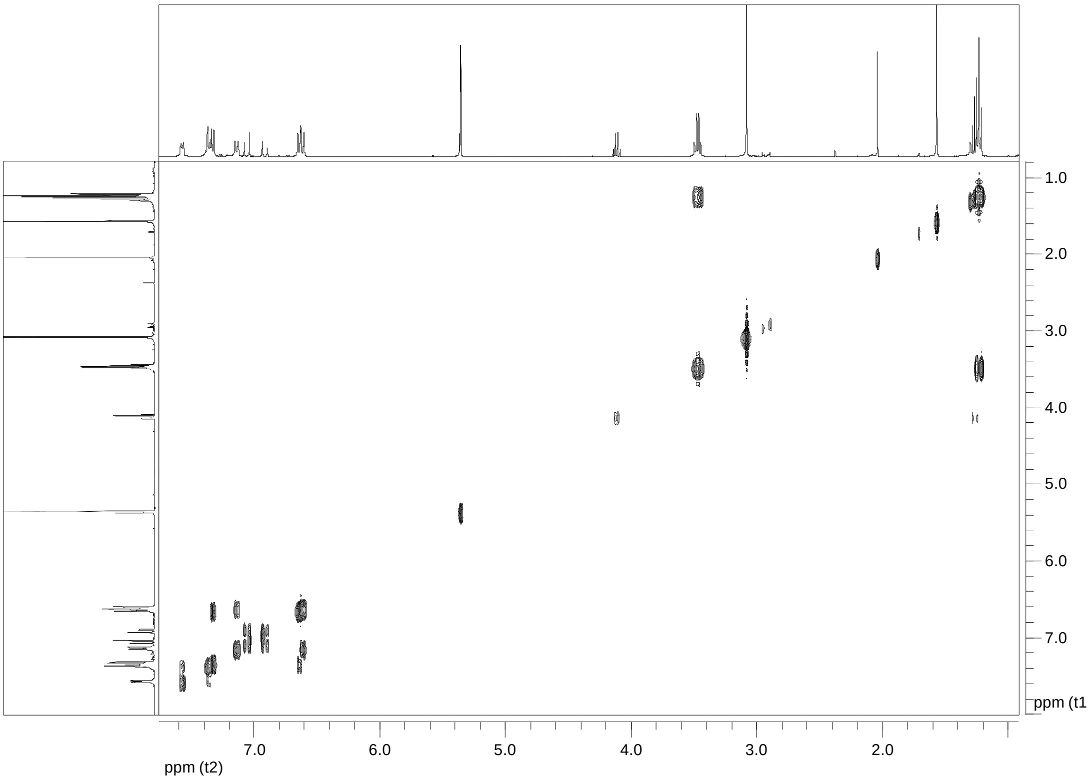
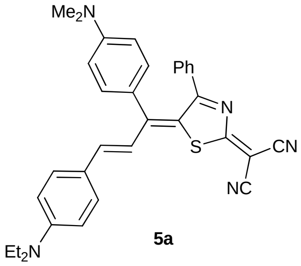


Figure S7: ^{1}H-^{1}H COSY spectrum of compound **5a** (400 MHz, CD_2Cl_2).



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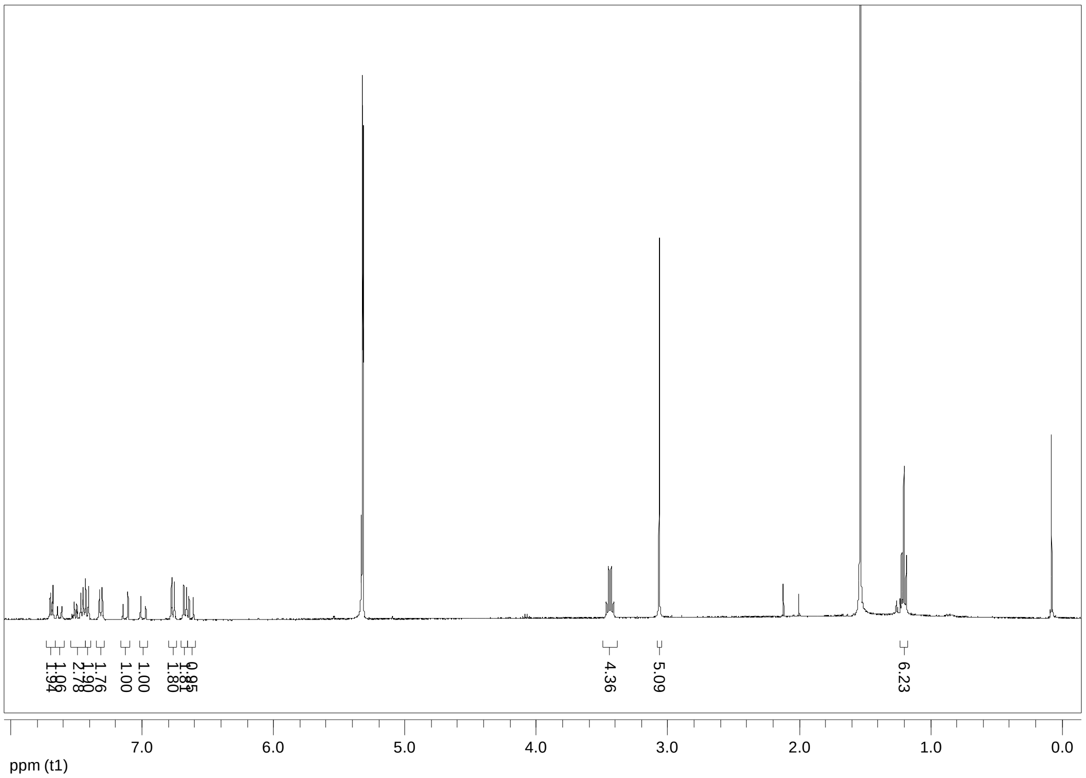
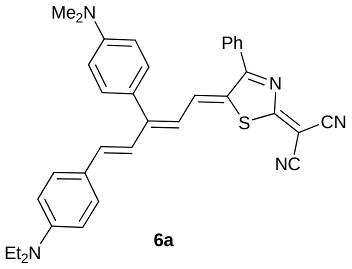


Figure S8: ^{1}H-NMR spectrum of compound **6a** (400 MHz, CD_2Cl_2).



6a

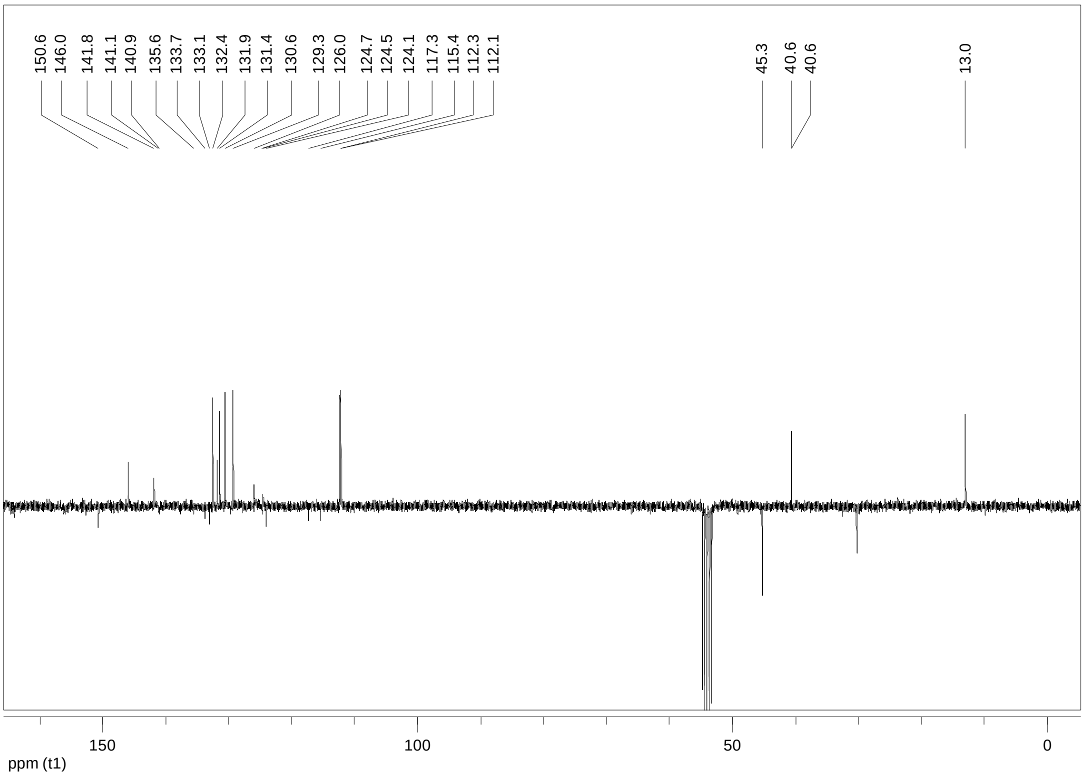
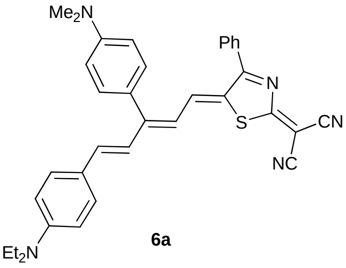


Figure S9: ^{13}C-NMR (APT) spectrum of compound **6a** (75 MHz, CD_2Cl_2).



6a

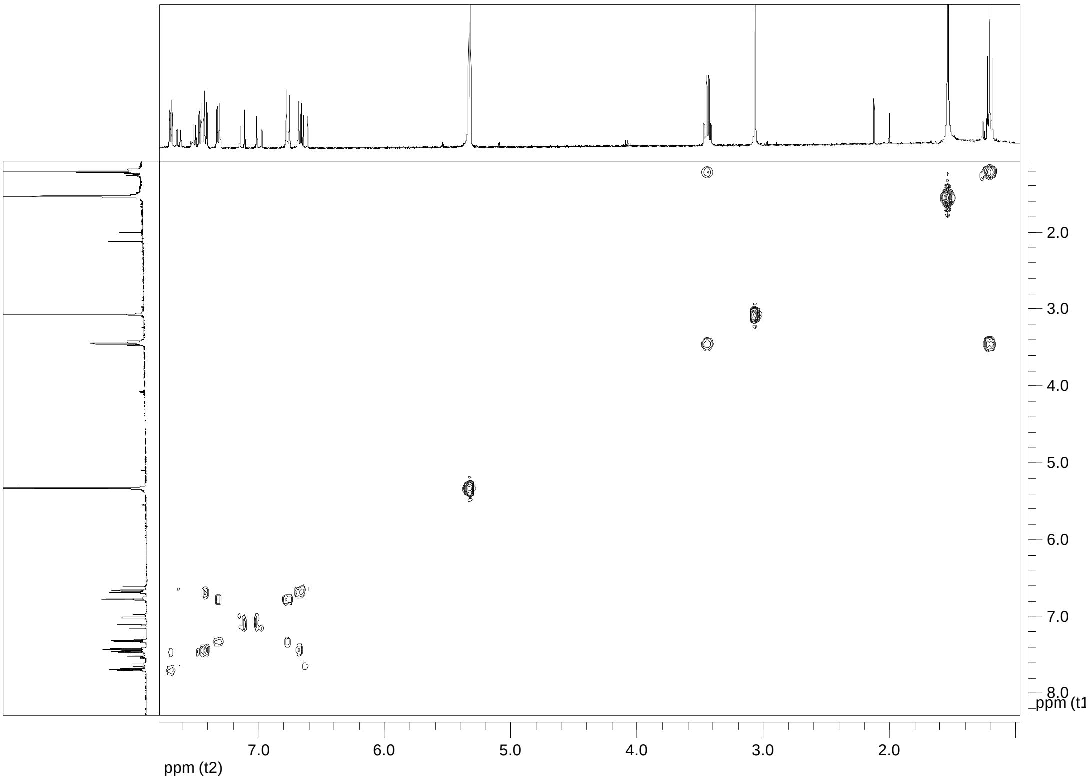
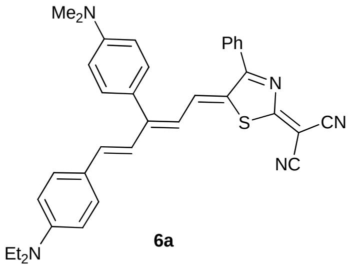


Figure S10: ^{1}H-^{1}H COSY spectrum of compound **6a** (400 MHz, CD_2Cl_2).



6a

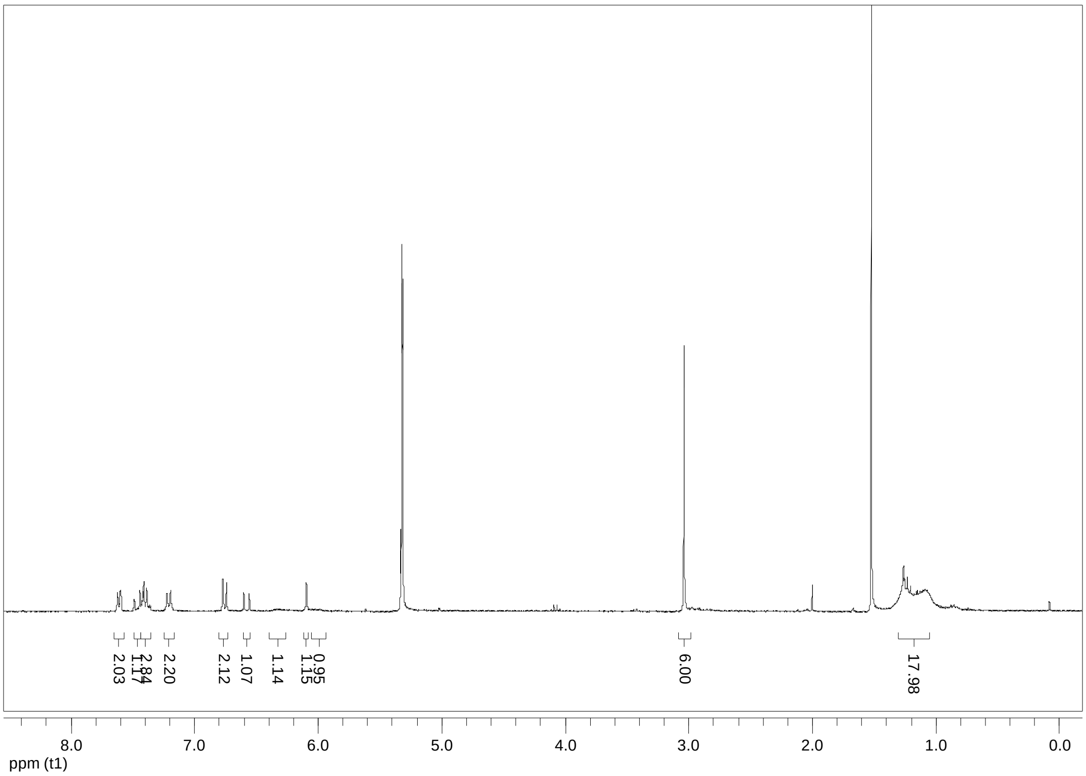
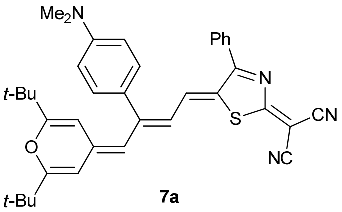


Figure S11: ^{1}H-NMR spectrum of compound **7a** (300 MHz, CD_2Cl_2).



7a

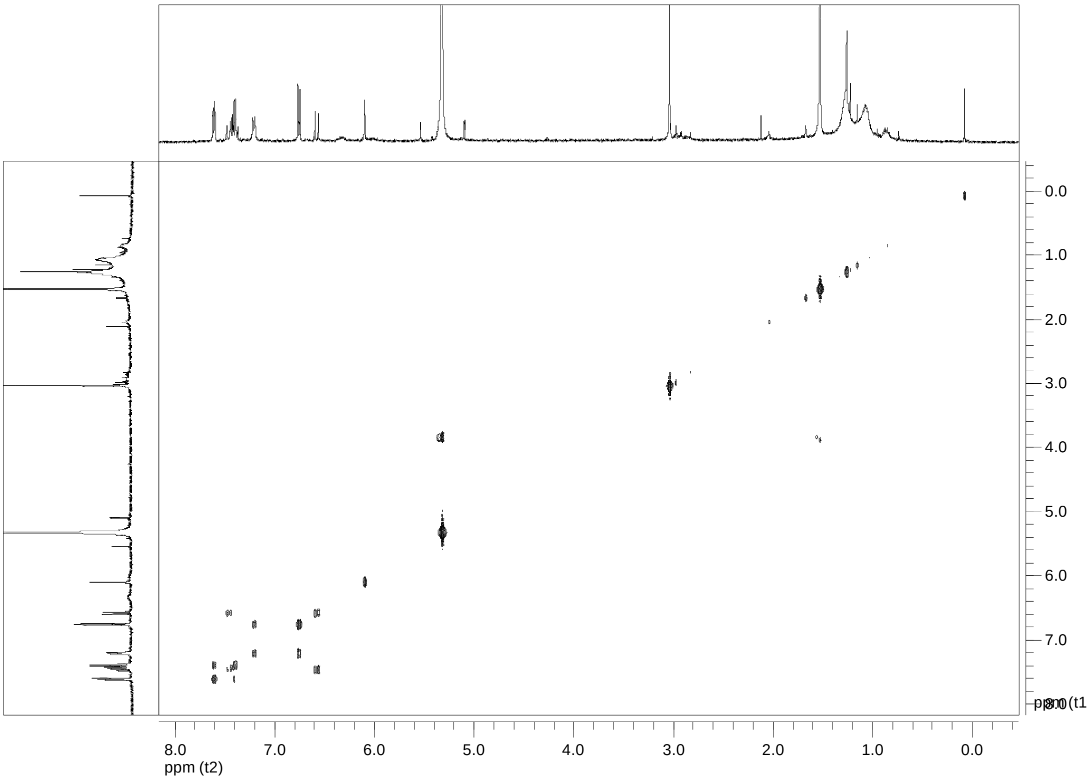
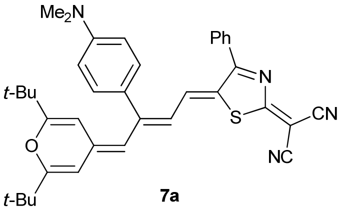


Figure S12: ^{1}H-^{1}H COSY spectrum of compound **7a** (400 MHz, CD_2Cl_2).



7a

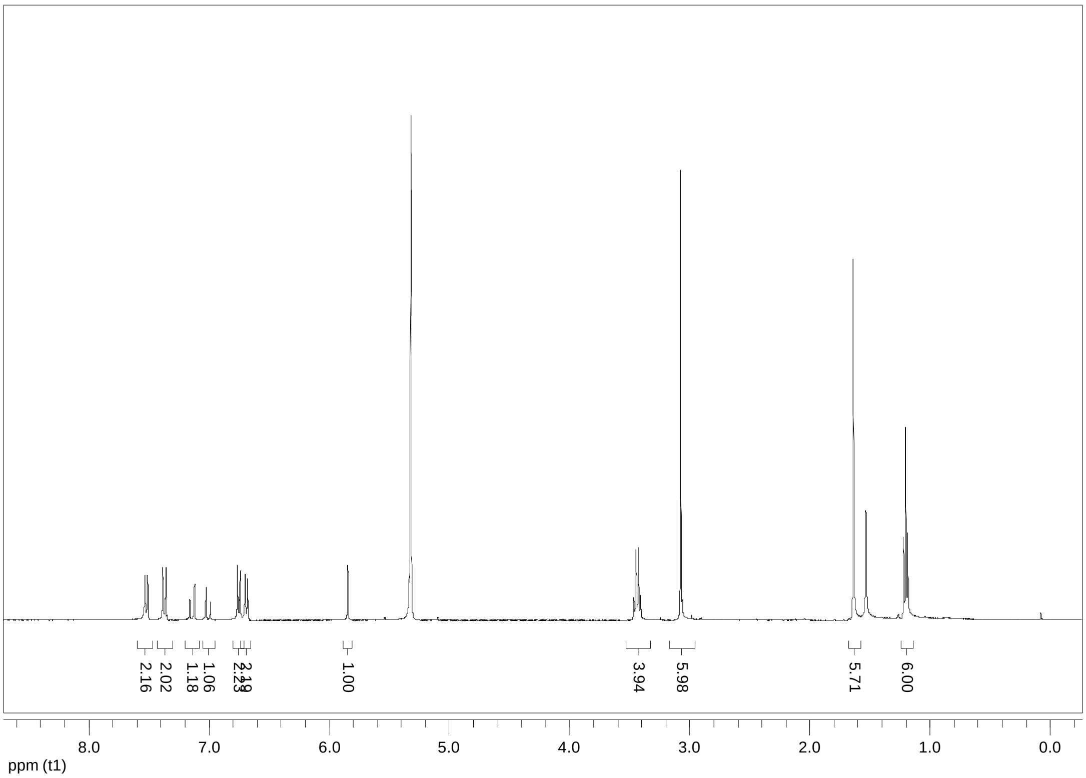
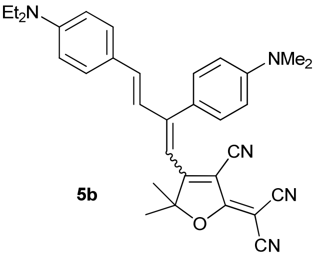


Figure S13: ^{1}H-NMR spectrum of compound **5b** (400 MHz, CD_2Cl_2).



5b

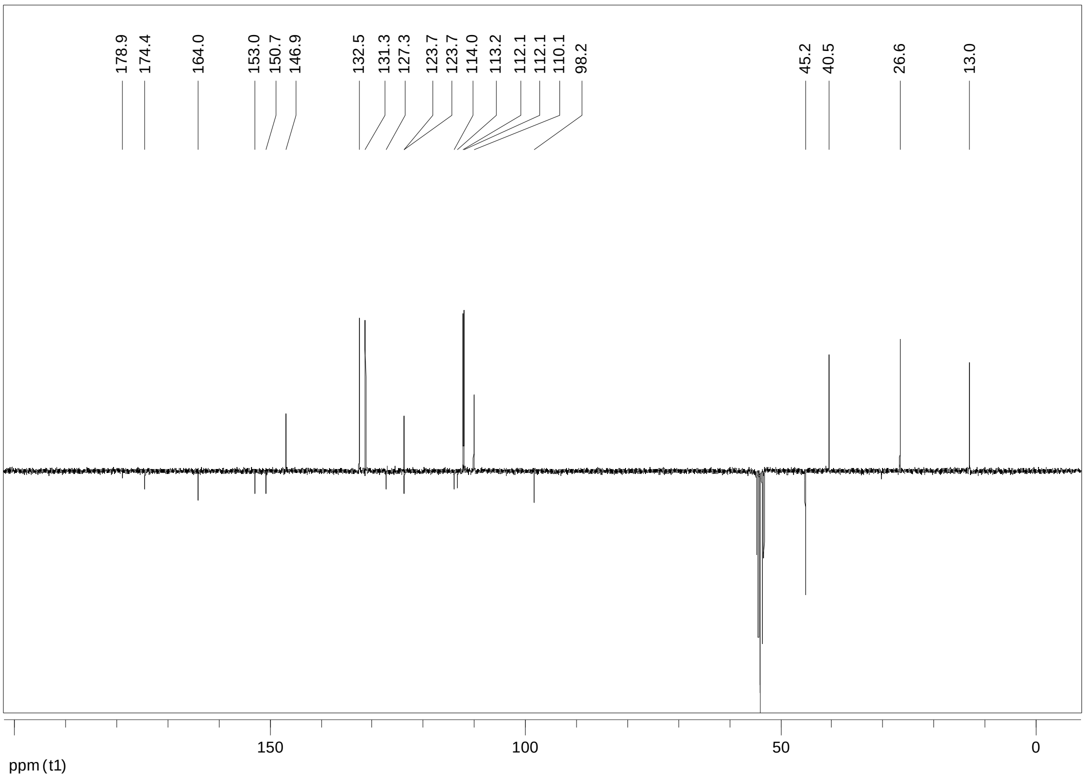
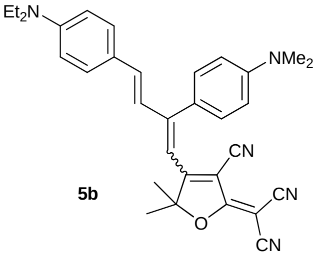


Figure S14: ^{13}C-NMR (APT) spectrum of compound **5b** (75 MHz, CD_2Cl_2).



5b

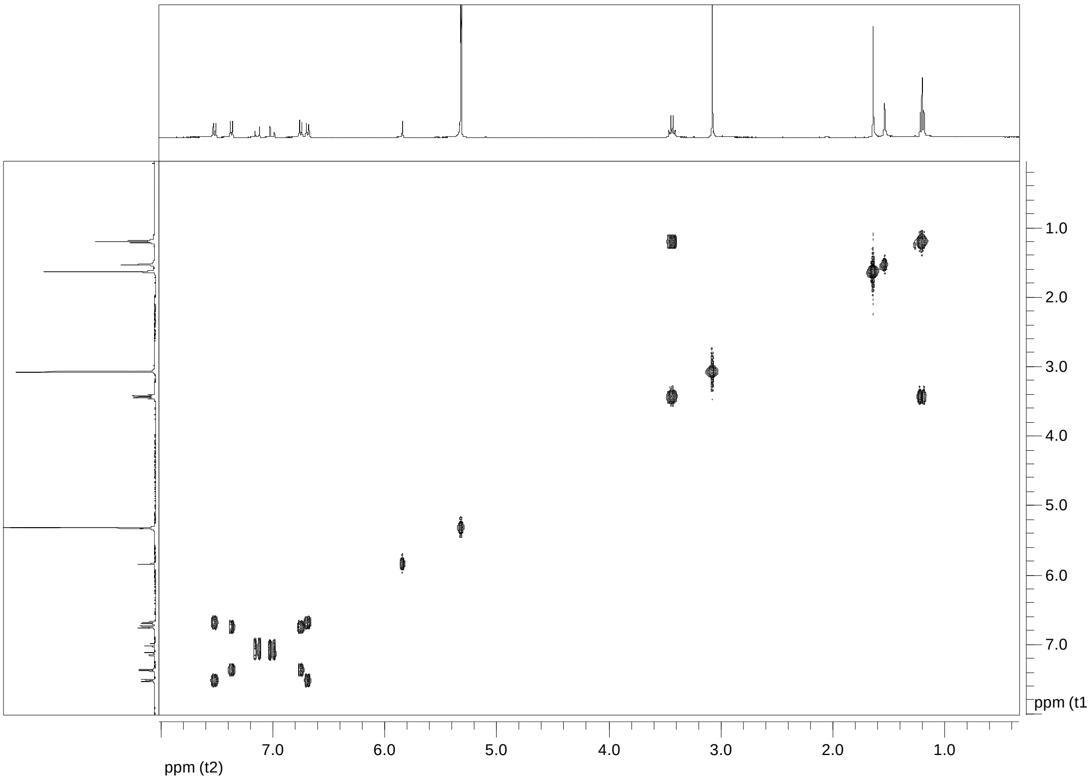
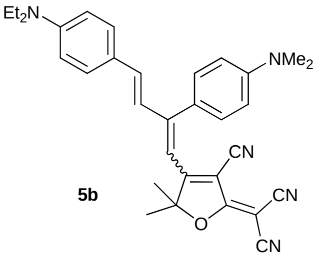


Figure S15: ^{1}H-^{1}H COSY spectrum of compound **5b** (400 MHz, CD_2Cl_2).



5b

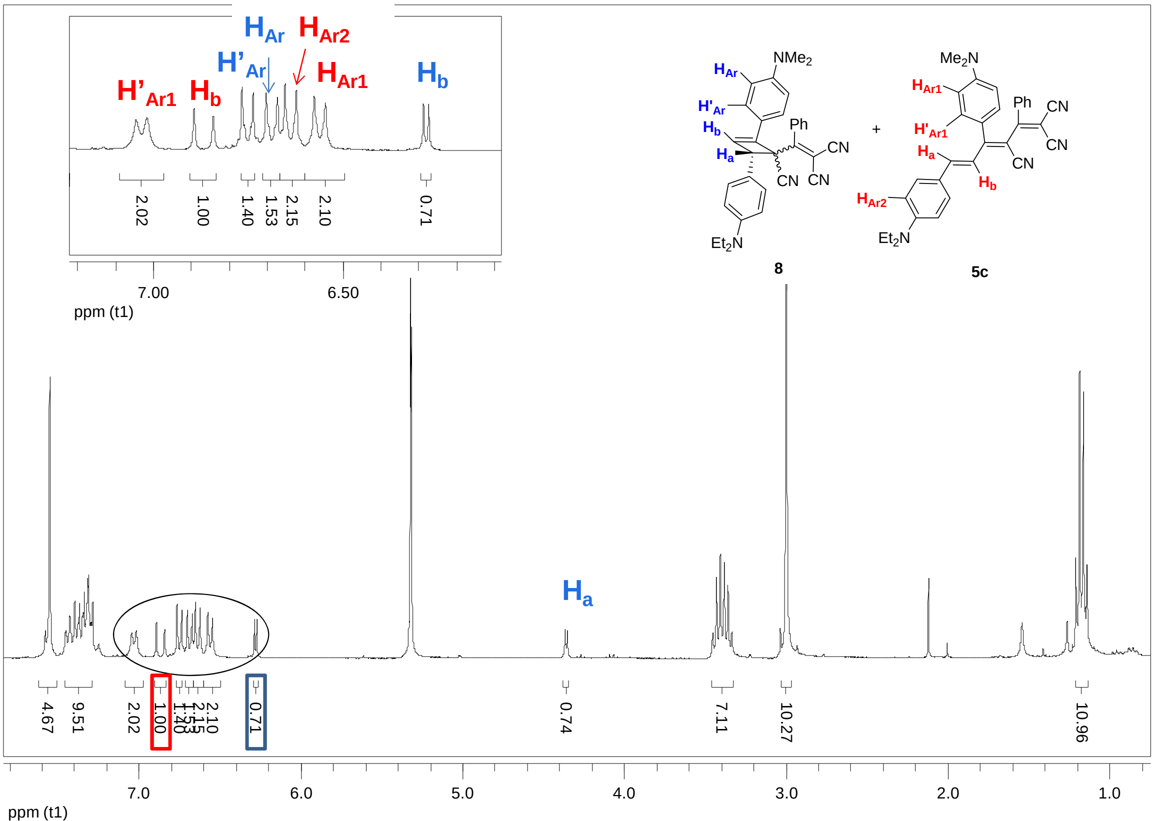
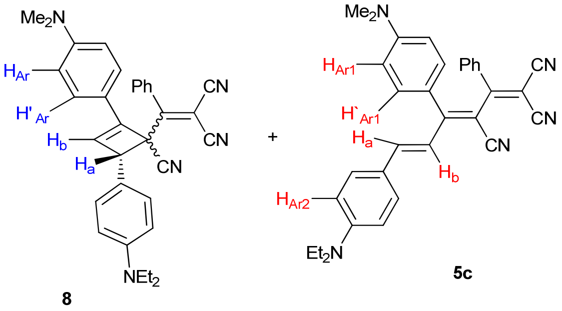


Figure S16: ^{1}H-NMR spectrum of mixture **5c**+**8** (ratio 10/7) (300 MHz, CD_2Cl_2).



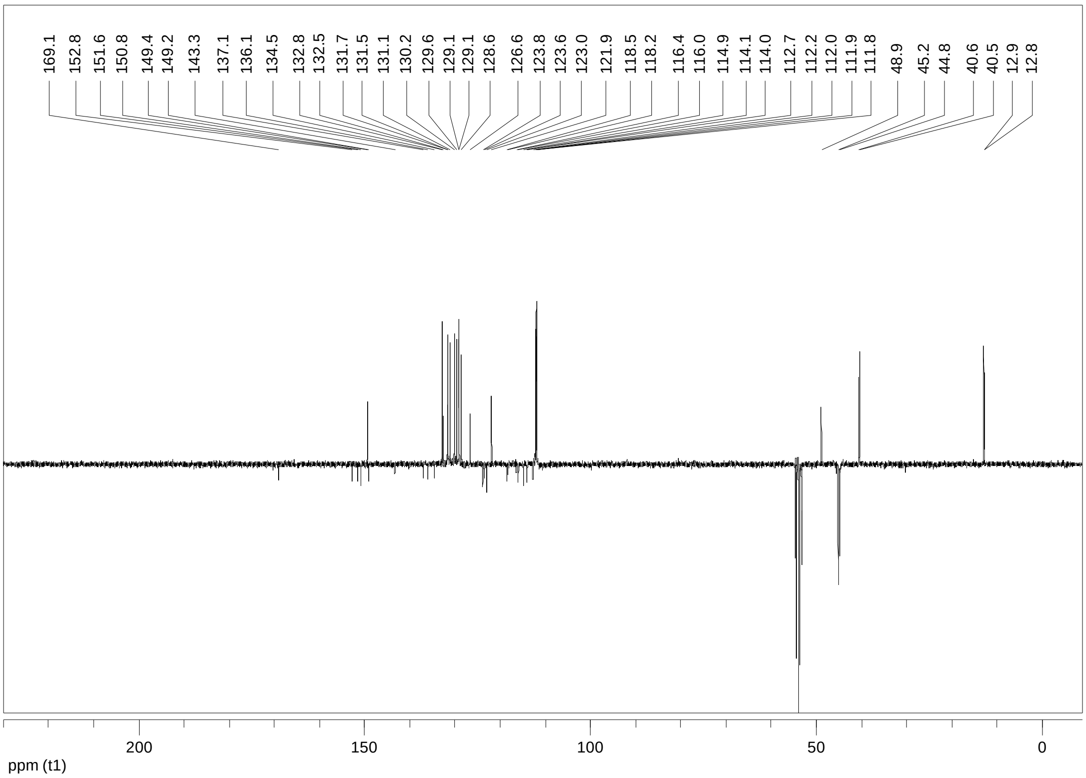
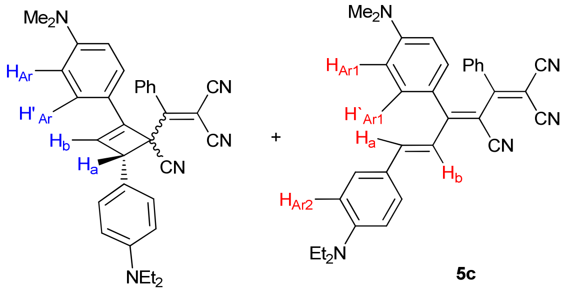


Figure S17: ^{13}C-NMR (APT) spectrum of mixture **5c**+**8** (ratio 10/7) (75 MHz, CD_2Cl_2).



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5c

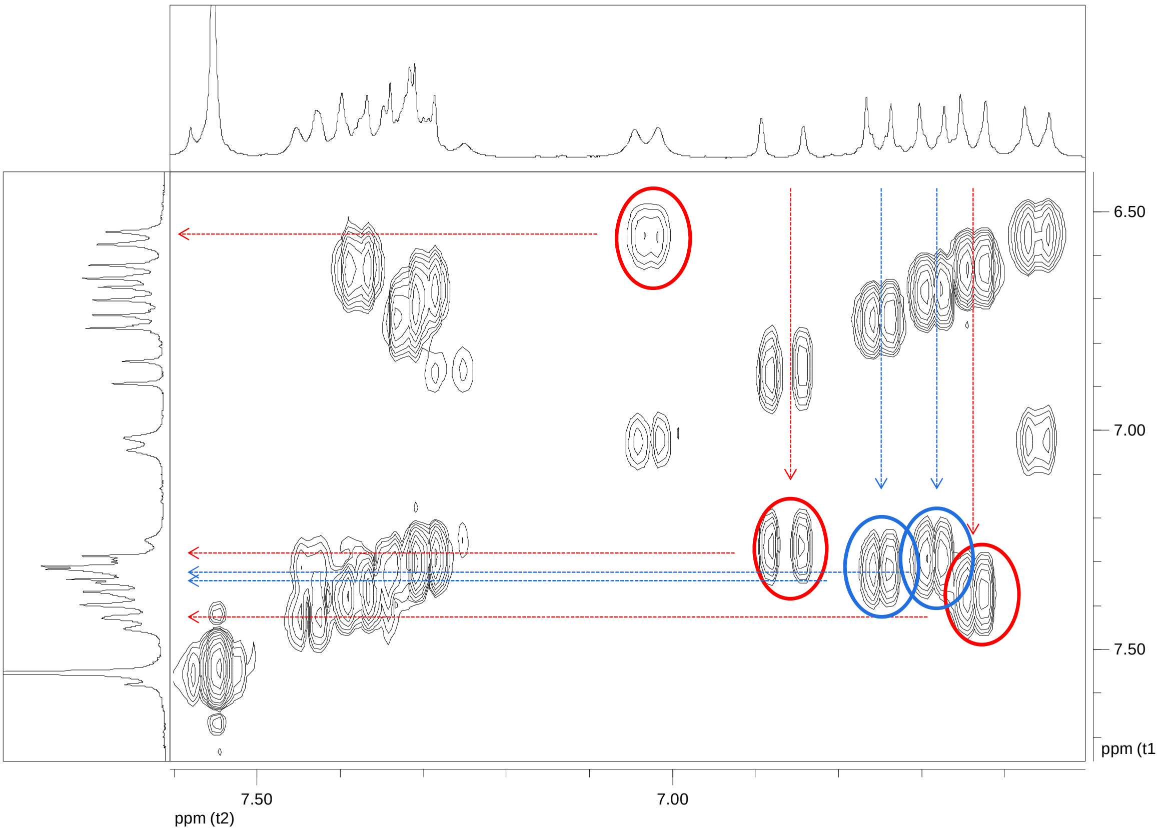
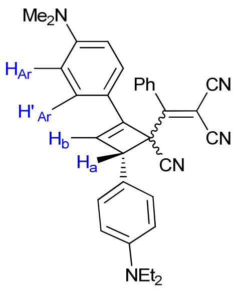


Figure S18: ^{1}H-^{1}H COSY spectrum of mixture **5c**+**8** (ratio 10/7) (400 MHz, CD_2Cl_2).



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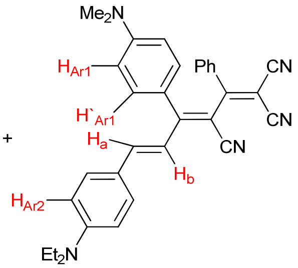
+



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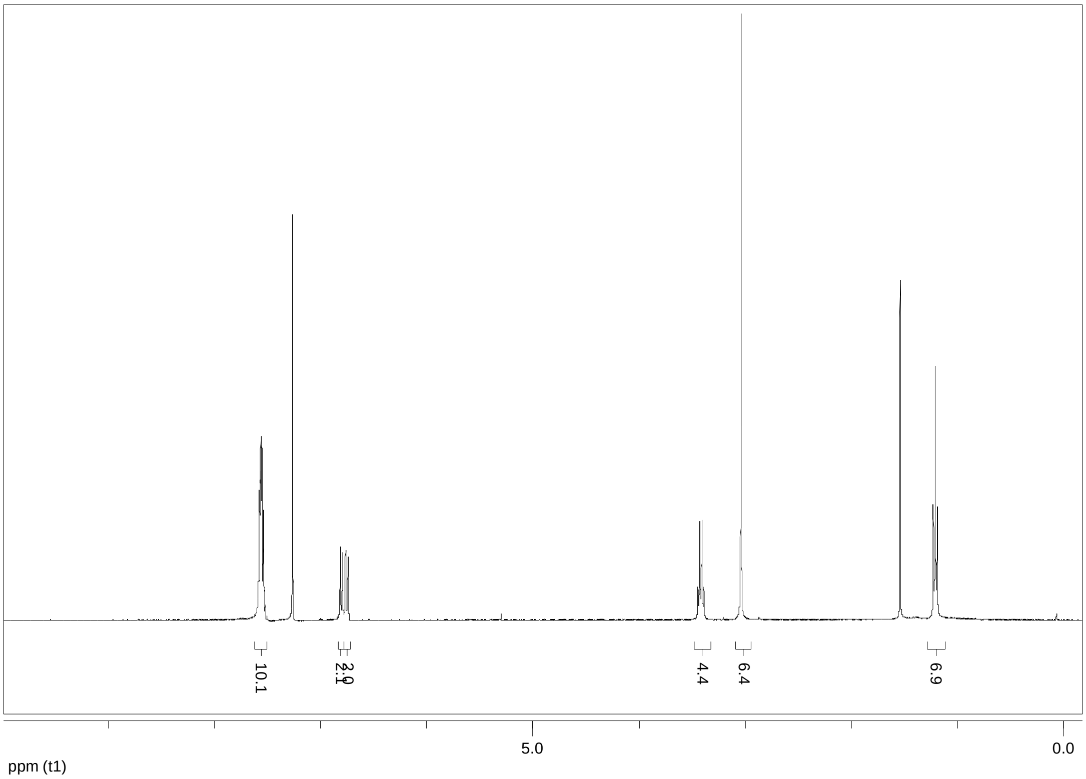
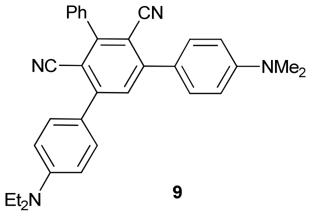


Figure S19: ^{1}H-NMR spectrum of compound **9** (400 MHz, CDCl$_3$).



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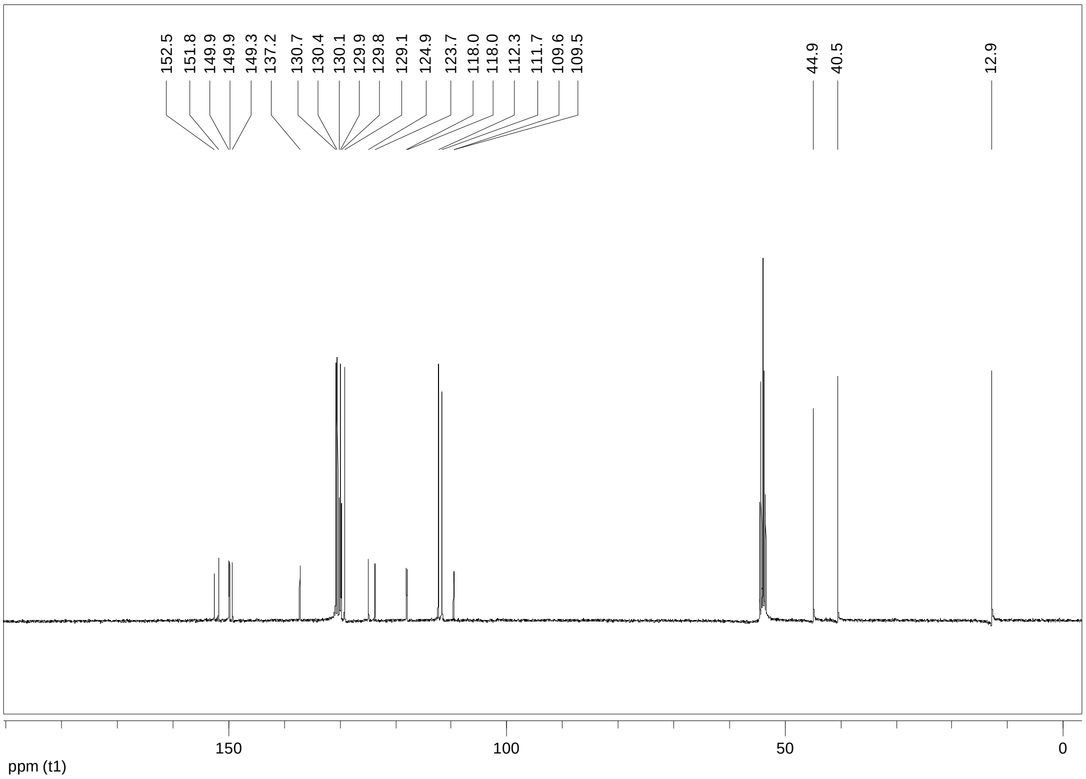
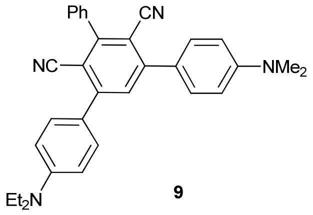


Figure S20: ^{13}C-NMR spectrum of compound **9** (100 MHz, CD_2Cl_2).



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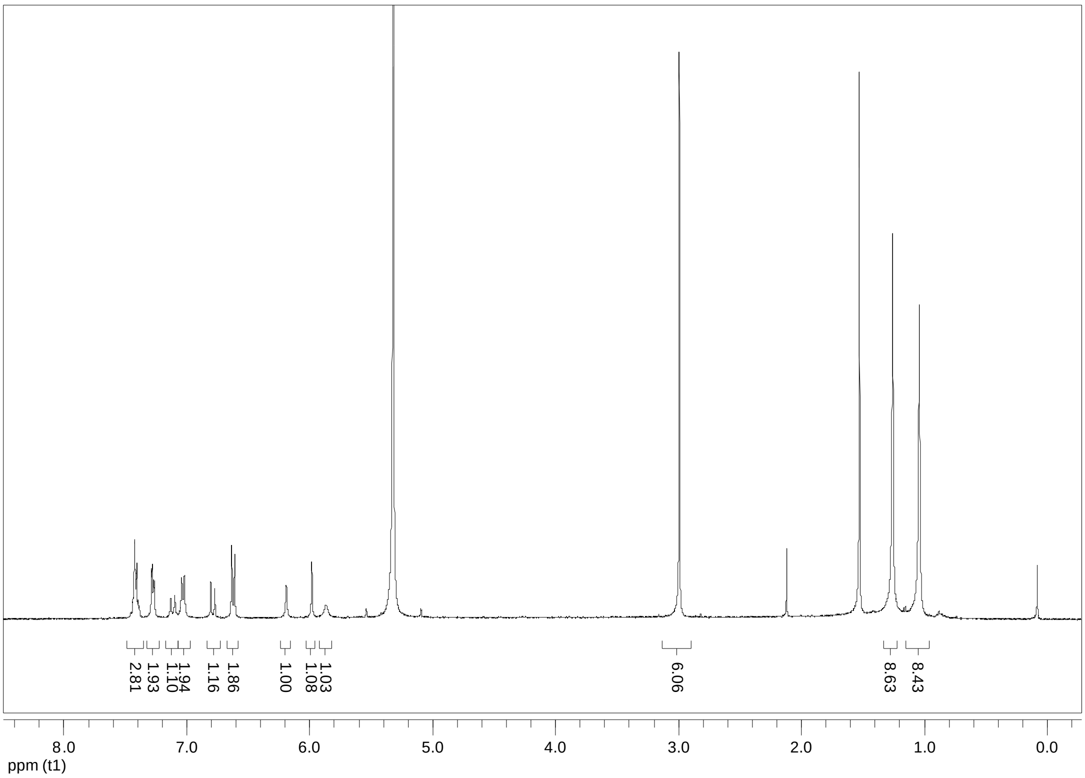
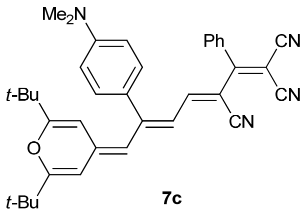


Figure S21: ^{1}H-NMR spectrum of compound **7c** (400 MHz, CD_2Cl_2).



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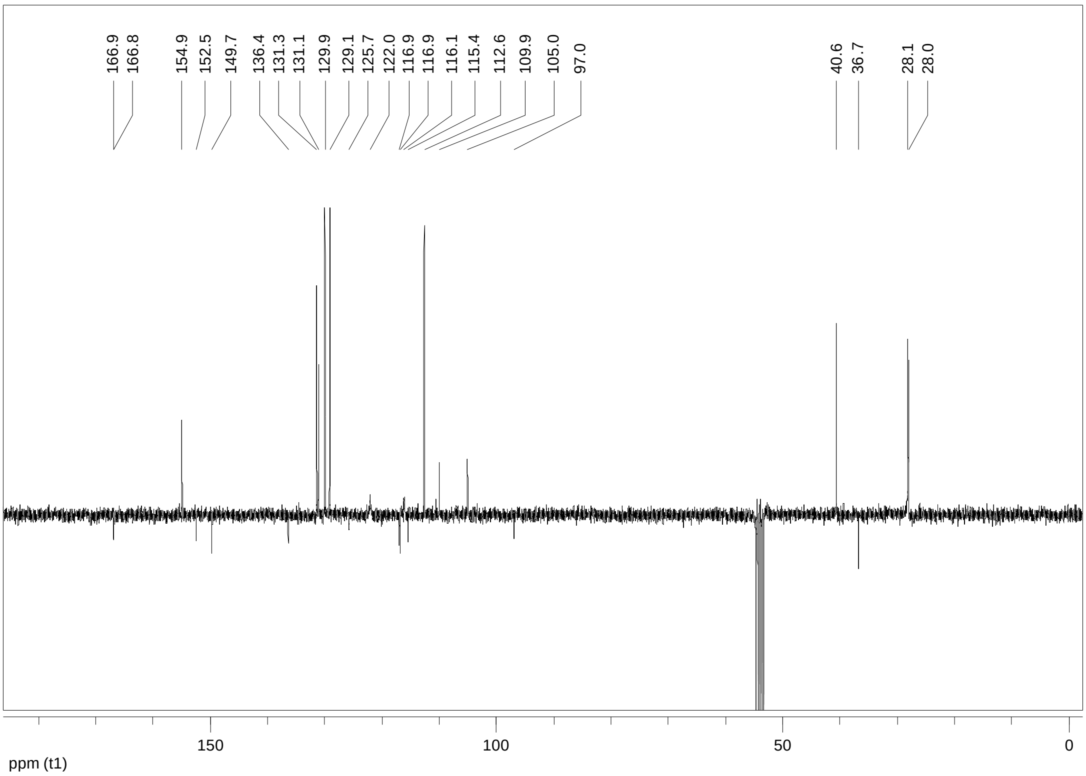
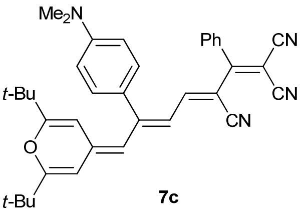


Figure S22: ^{13}C-NMR (APT) spectrum of compound **7c** (75 MHz, CD_2Cl_2).



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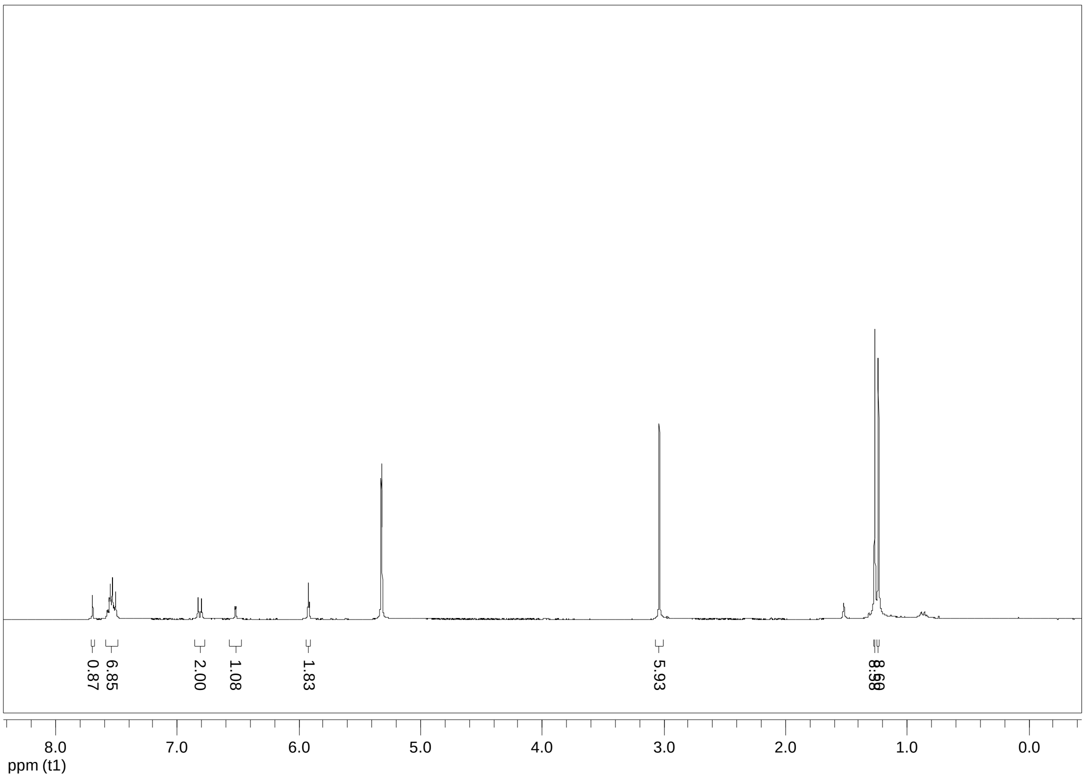
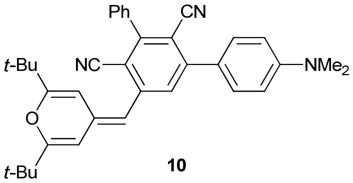


Figure S23: ^{1}H-NMR spectrum of compound **10** (300 MHz, CD_2Cl_2).



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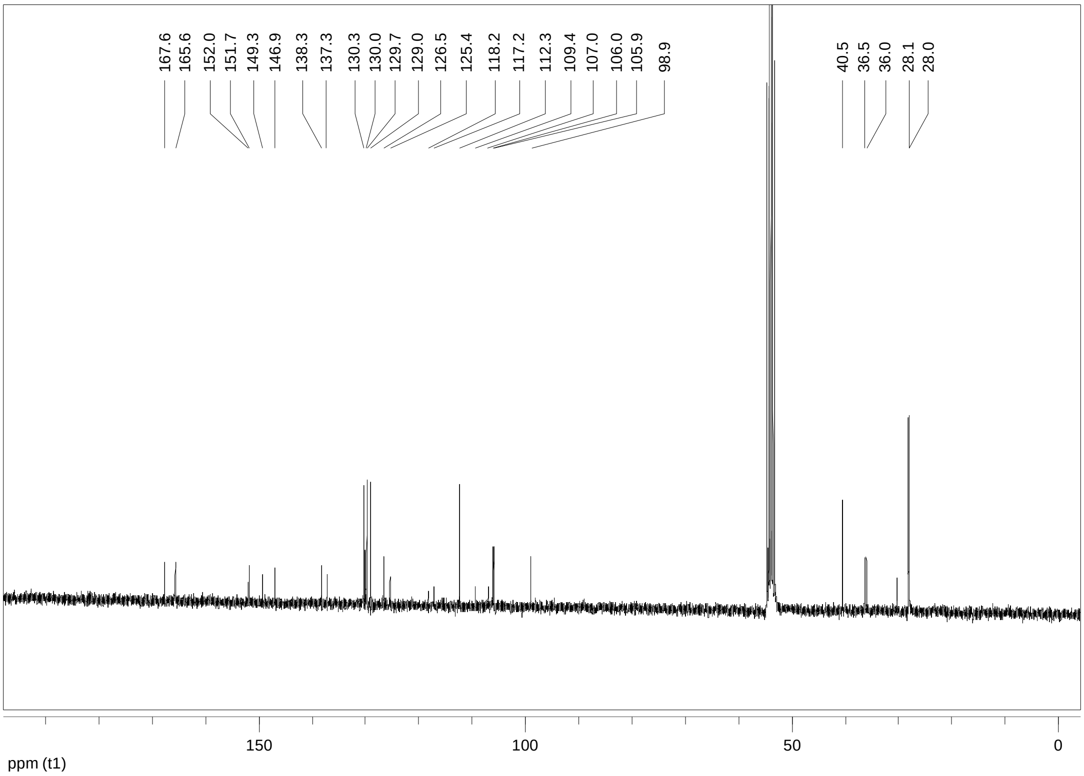
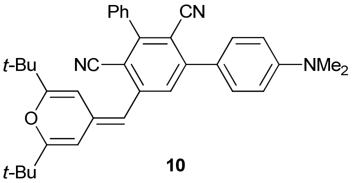


Figure S24: ^{13}C-NMR spectrum of compound **10** (75 MHz, CD_2Cl_2).



10

3. Non-concerted dipolar mechanisms

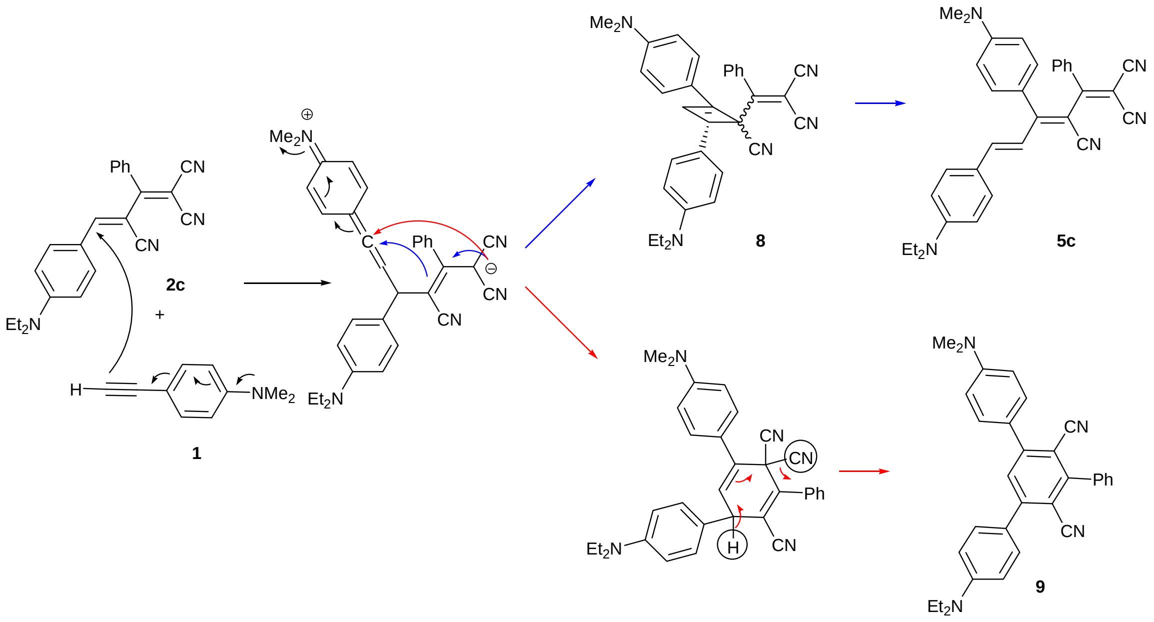


Figure S25: Non-concerted dipolar mechanism for the [2+2] (blue line) and [4+2] (red line) cycloaddition of **1** with **2c** in formation of a mixture of **5c** and **8** and **9** respectively.

4.- X-ray Diffraction

Crystal data for **5a**:

Single crystals were obtained by slow diffusion of hexane into a solution of the chromophore in AcOEt at room temperature: $C_{33}H_{31}N_5S$, M_r = 529.69, crystal dimensions 0.37 x 0.12 x 0.06 mm, triclinic space group P-1 (no. 2), ρ_{calcd} = 1.248 g cm^{-3}, Z = 2, a = 8.5856(3), b = 13.3808(10), c = 13.8389(9) Å, α = 66.612(7), β = 77.281(4), γ = 77.711(5), V = 1409.37(15) Å^3 at 298(1) K. Number of measured and unique reflections 23380 and 4939, respectively (R_{int}=0.0973). Final R(*F*)=0.0419, wR(F^2)=0.0365 for 354 parameters and 1804 reflections with I› 4σ(I) (corresponding R-values based on all 4939 reflections 0.1598 and 0.0424).

Crystal data and structure refinement for 5a.

Identification code	5a
Empirical formula	C33 H31 N5 S
Formula weight	529.69
Temperature	298(1) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 8.5856(3) A alpha = 66.612(7) deg. b = 13.3808(10) A beta =77.281(4)deg. c = 13.8389(9) A gamma = 77.711(5)deg.
Volume	1409.37(15) A^3
Z, Calculated density	2, 1.248 Mg/m^3
Absorption coefficient	0.146 mm^-1

F(000)	560
Crystal size	0.37 x 0.12 x 0.06 mm
Theta range for data collection	2.67 to 25.00 deg.
Limiting indices	-6<=h<=10, -15<=k<=15, -16<=l<=16
Reflections collected / unique	23380 / 4939 [R(int) = 0.0973]
Completeness to theta = 25.00	99.3 %
Max. and min. transmission	0.9913 and 0.9480
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4939 / 0 / 354
Goodness-of-fit on F^2	0.805
Final R indices [I>2sigma(I)]	R1 = 0.0419, wR2 = 0.0365
R indices (all data)	R1 = 0.1598, wR2 = 0.0424
Largest diff. peak and hole	0.130 and -0.146 e.A^-3

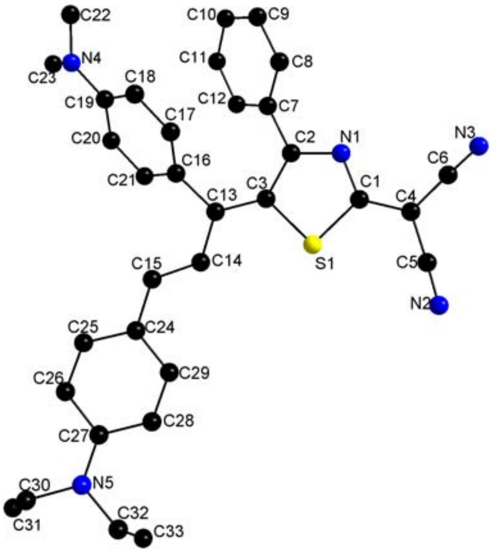


Figure S26: Molecular structure of compound **5a**.

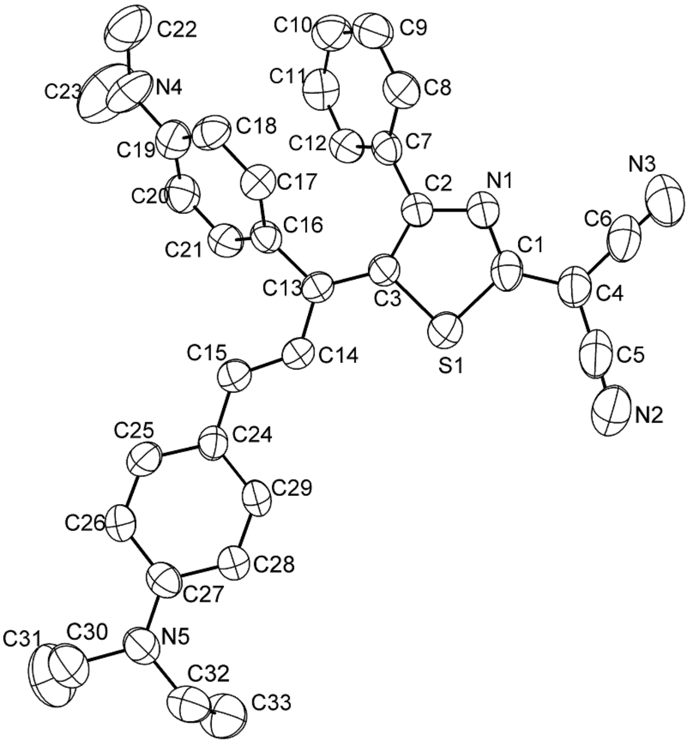


Figure S27: ORTEP view of **5a**

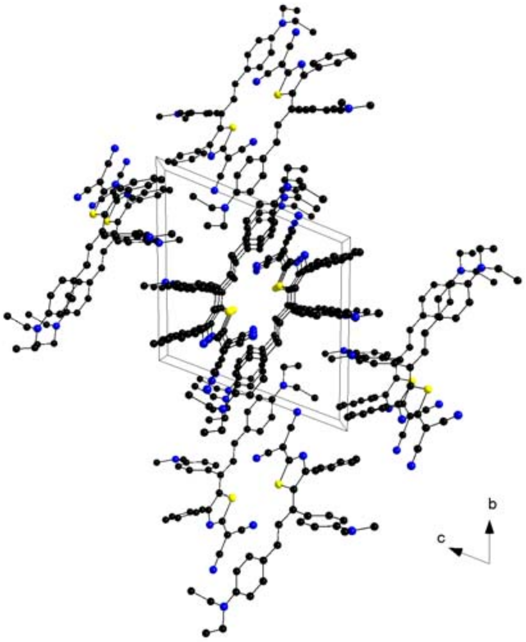


Figure S28: Crystal packing of **5a** viewed along the [100] direction.

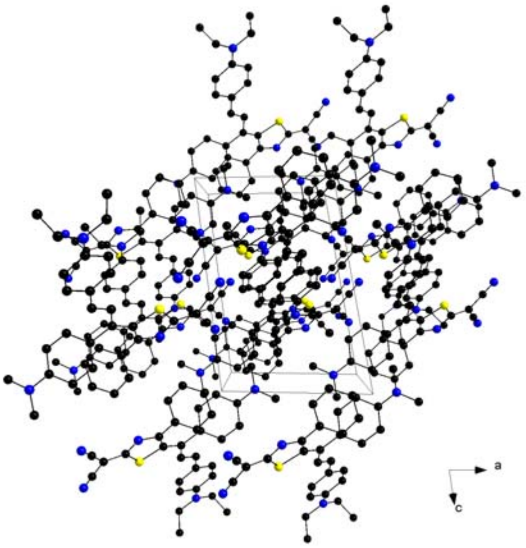


Figure S29: Crystal packing of **5a** viewed along the [010] direction.

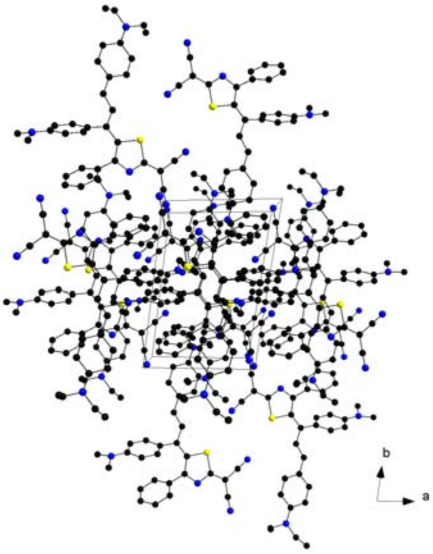


Figure S30: Crystal packing of **5a** viewed along the [001] direction.

Crystal data for **7c**:

Single crystals were obtained by slow diffusion of hexane into a concentrated solution of the chomophore in $CHCl_3$ at room temperature: $C_{37}H_{38}N_4O$, M_r = 554.71, crystal dimensions 0.29 x 0.24 x 0.04 mm, monoclinic space group $P2_1/c$ (no. 14), ρ_{calcd} = 1.170 g cm^{-3}, Z = 4, a = 9.8471(5), b = 28.4321(15), c = 11.7509(8) Å, β = 106.763(6), V = 3150.1(3) Å^3 at 150(1) K. Number of measured and unique reflections 24720 and 7462, respectively (R_{int}=0.0914). Final R(*F*)=0.0685, wR(F^2)=0.0916 for 387 parameters and 3573 reflections with I› 4σ(I) (corresponding R-values based on all 7462 reflections 0.1690 and 0.1209).

Crystal data and structure refinement for 7c.

Identification code	7c	
Empirical formula	C37 H38 N4 O	
Formula weight	554.71	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P21/c	
Unit cell dimensions	a = 9.8471(5) A	alpha = 90 deg.
	b = 28.4321(15) A	beta = 106.763(6)
	c = 11.7509(8) A	gamma = 90 deg.
Volume	3150.1(3) A^3	
Z, Calculated density	4, 1.170 Mg/m^3	
Absorption coefficient	0.071 mm^-1	
F(000)	1184	

Crystal size	0.29 x 0.24 x 0.04 mm
Theta range for data collection	3.05 to 28.87 deg.
Limiting indices	-12<=h<=12, -38<=k<=36, -15<=l<=15
Reflections collected / unique	24720 / 7462 [R(int) = 0.0914]
Completeness to theta = 27.50	98.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9972 and 0.9797
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7462 / 0 / 387
Goodness-of-fit on F^2	0.984
Final R indices [I>2sigma(I)]	R1 = 0.0685, wR2 = 0.0916
R indices (all data)	R1 = 0.1690, wR2 = 0.1209
Largest diff. peak and hole	0.218 and -0.221 e.A^-3

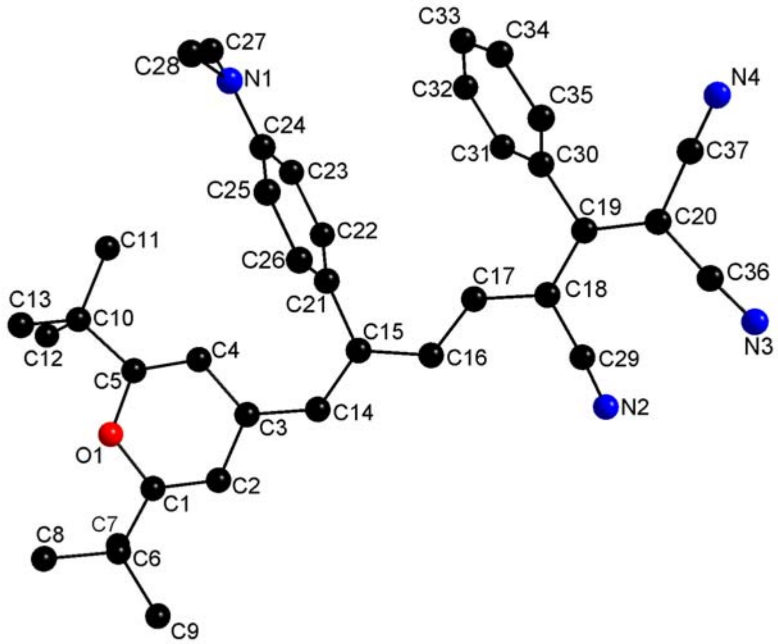


Figure S31: Molecular structure of compound **7c**.

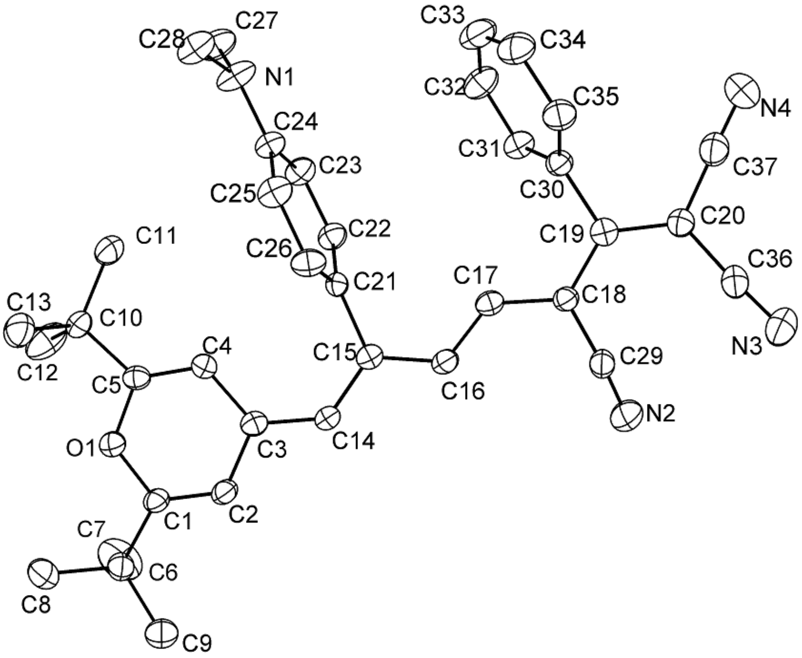


Figure S32: ORTEP view of **7c**.

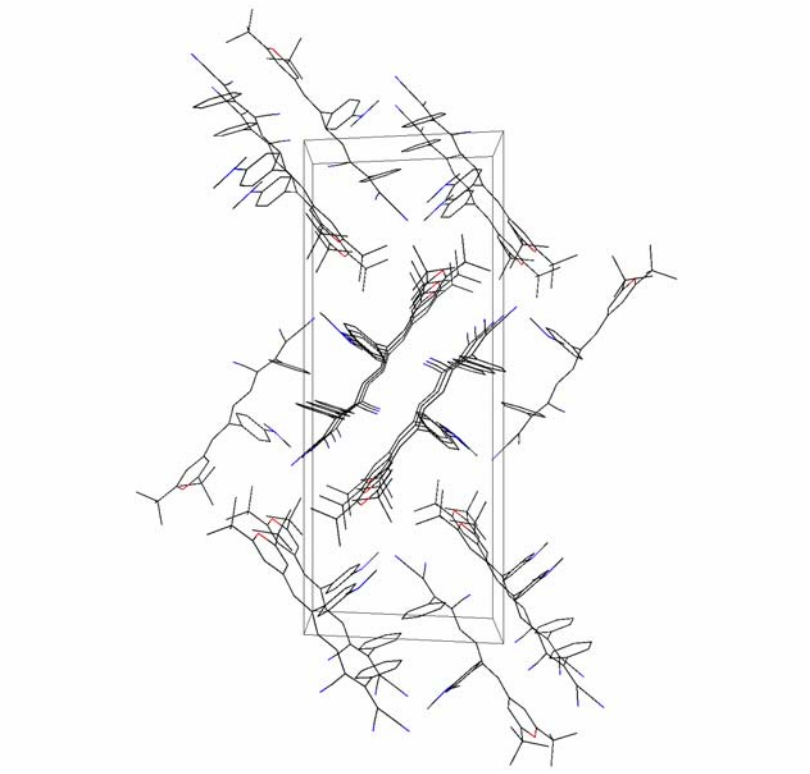


Figure S33: Crystal packing of **7c** viewed along the [100] direction.

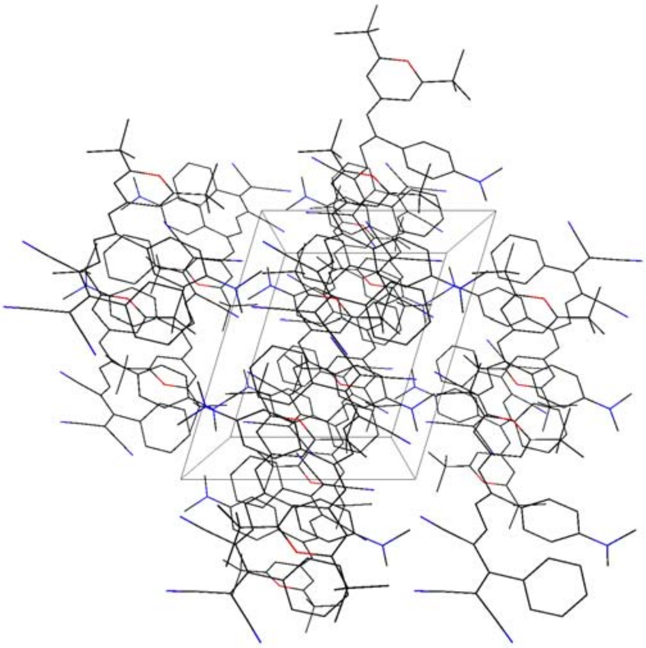


Figure S34: Crystal packing of **7c** viewed along the [010] direction.

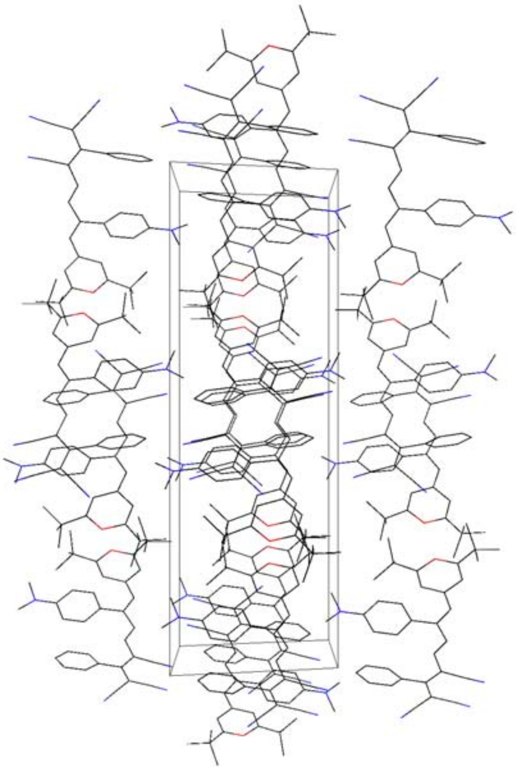


Figure S35: Crystal packing of **7c** viewed along the [001] direction.

Crystal data for **10**:

Single crystals were obtained by slow diffusion of hexane into a concentrated solution of the chromophore in CH_2Cl_2 at room temperature: $C_{36}H_{37}N_3O$, M_r = 527.69, crystal dimensions 0.34 x 0.05 x 0.04 mm, triclinic space group P-1 (no. 2), ρ_{calcd} = 1.152 g cm^{-3}, Z = 2, a = 5.9702(5), b = 12.9502(14), c = 20.426(2) Å, α = 104.108(9), β = 92.797(8), γ = 95.045(8), V = 1521.6(3) Å^3 at 150(1) K. Number of measured and unique reflections 9971 and 5343, respectively (R_{int}=0.0851). Final R(*F*)=0.0804, wR(F^2)=0.0971 for 361 parameters and 2142 reflections with I› 4σ(I) (corresponding R-values based on all 5343 reflections 0.0804 and 0.1405).

Crystal data and structure refinement for 10.

Identification code	10
Empirical formula	C36 H37 N3 O
Formula weight	527.69
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.9702(5) A alpha = 104.108(9) deg. b = 12.9502(14) A beta = 92.797(8) deg. c = 20.426(2) A gamma = 95.045(8) deg.
Volume	1521.6(3) A^3
Z, Calculated density	2, 1.152 Mg/m^3
Absorption coefficient	0.069 mm^-1
F(000)	564

Crystal size	0.34 x 0.05 x 0.04 mm
Theta range for data collection	2.93 to 25.00 deg.
Limiting indices	-7<=h<=7, -15<=k<=11, -23<=l<=24
Reflections collected / unique	9971 / 5343 [R(int) = 0.0851]
Completeness to theta = 25.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9972 and 0.9768
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5343 / 0 / 361
Goodness-of-fit on F^2	0.968
Final R indices [I>2sigma(I)]	R1 = 0.0804, wR2 = 0.0971
R indices (all data)	R1 = 0.2233, wR2 = 0.1405
Largest diff. peak and hole	0.194 and -0.207 e.A^-3

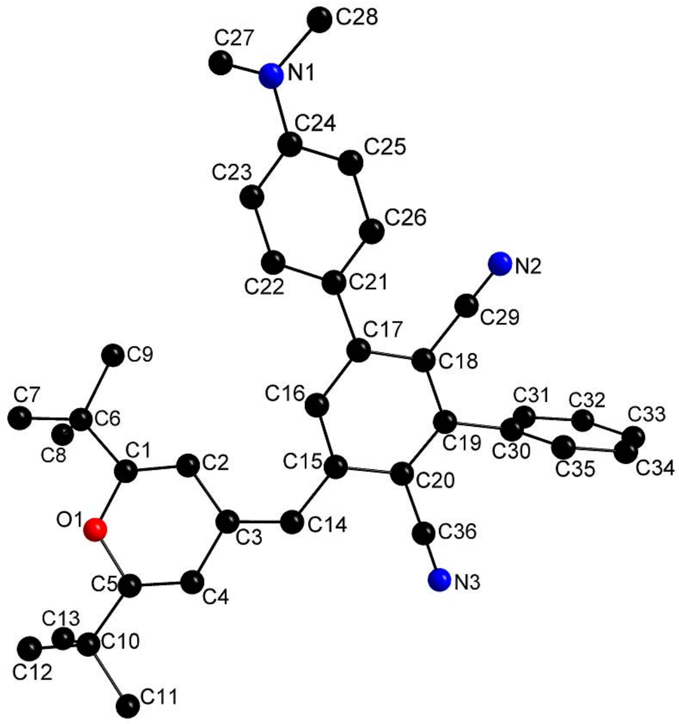


Figure S36: Molecular structure of compound **10**.

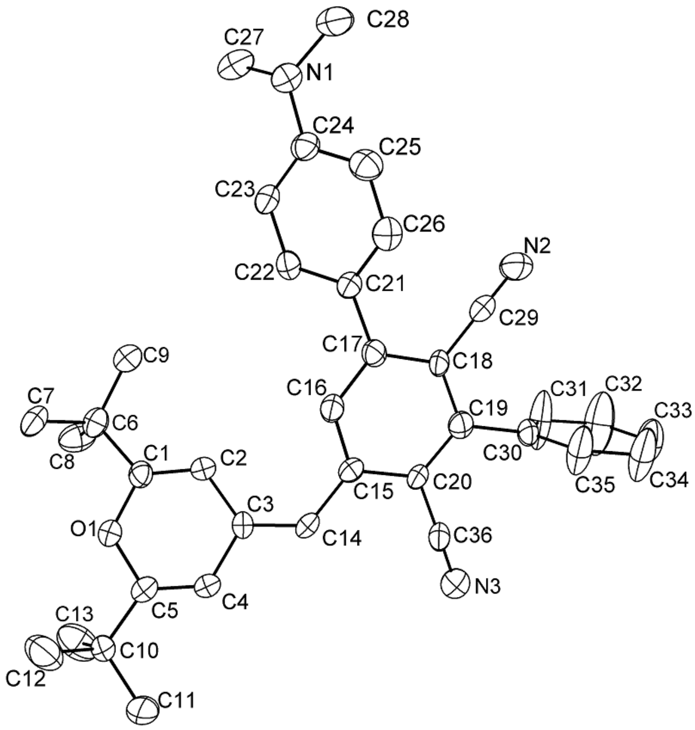


Figure S37: ORTEP view of **10**.

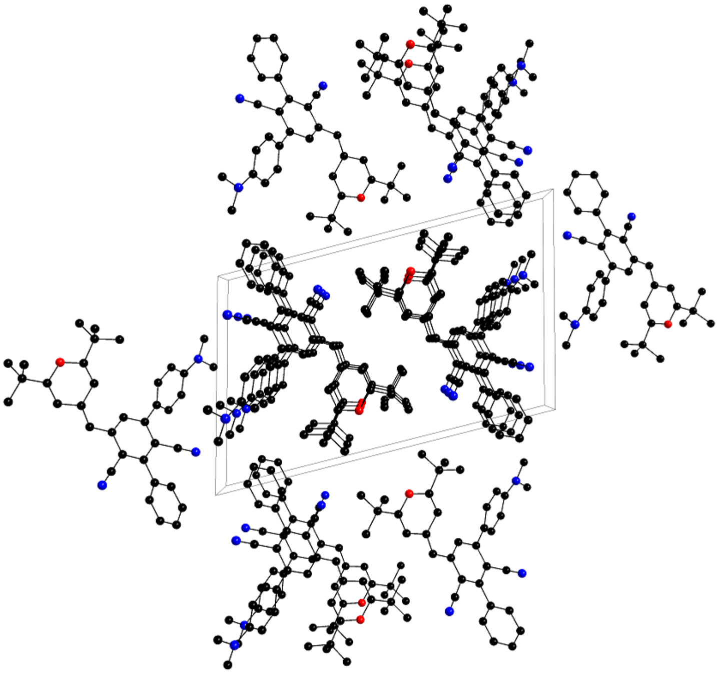


Figure S38: Crystal packing of **10** viewed along the [100] direction.

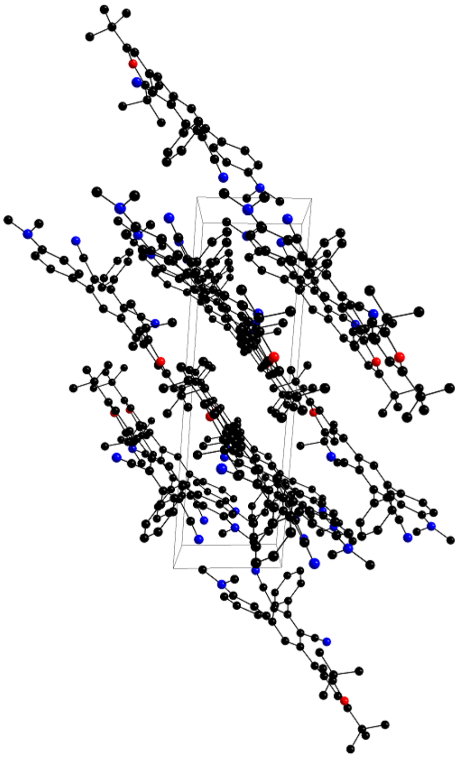


Figure S39: Crystal packing of **10** viewed along the [010] direction.

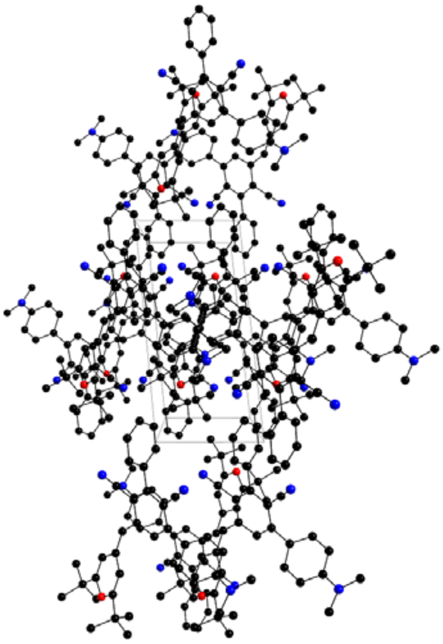


Figure S40: Crystal packing of **10** viewed along the [001] direction.

5. UV-vis spectra

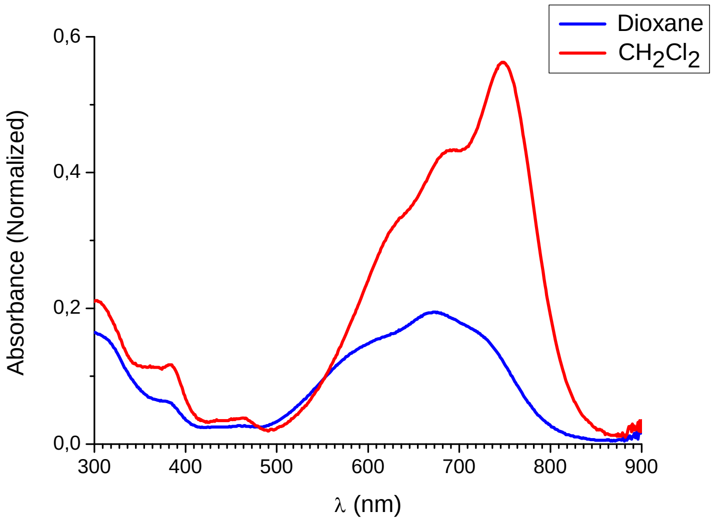


Figure S41: Normalized UV-vis absorption of compound **5a** (10^{-5} M) in dioxane and in CH_2Cl_2.

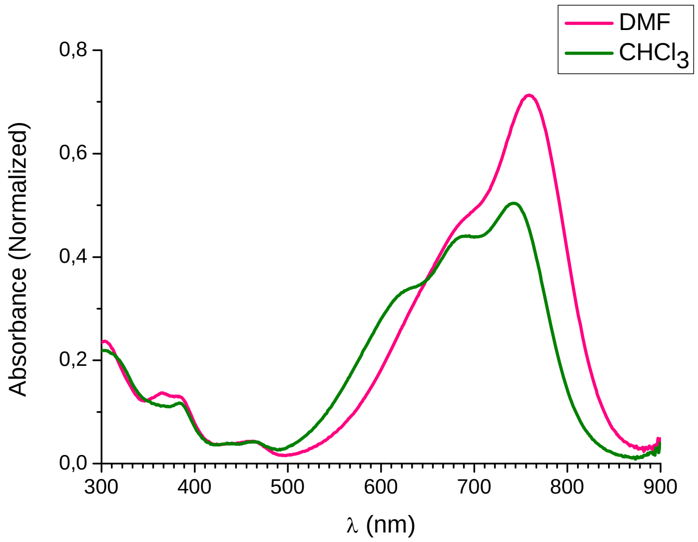


Figure S42: Normalized UV-vis absorption of compound **5a** (10^{-5} M) in DMF and in $CHCl_3$.

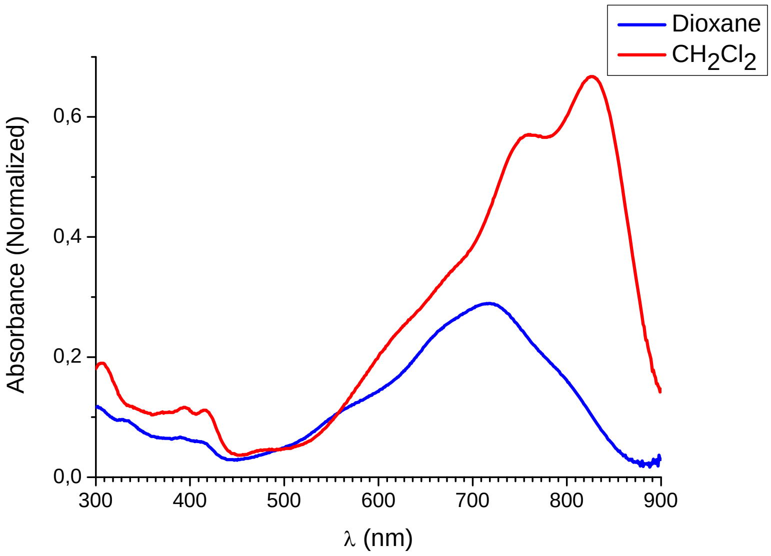


Figure S43: Normalized UV-vis absorption of compound **6a** (10^{-5} M) in dioxane and in CH_2Cl_2.

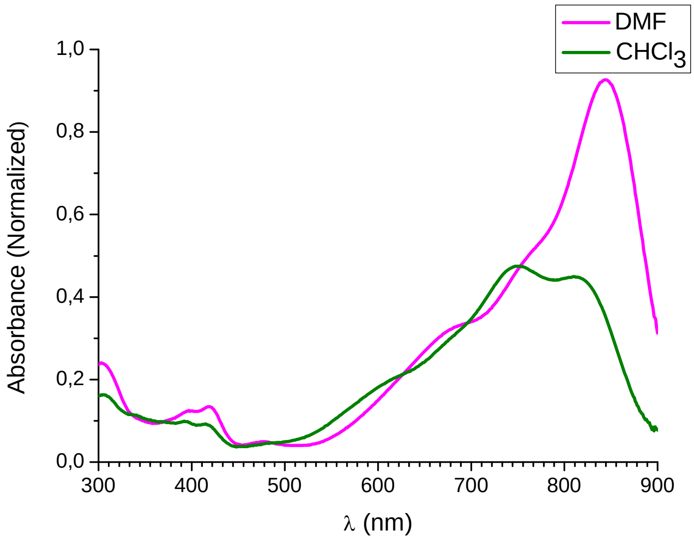


Figure S44: Normalized UV-vis absorption of compound **6a** (10^{-5} M) in DMF and in $CHCl_3$.

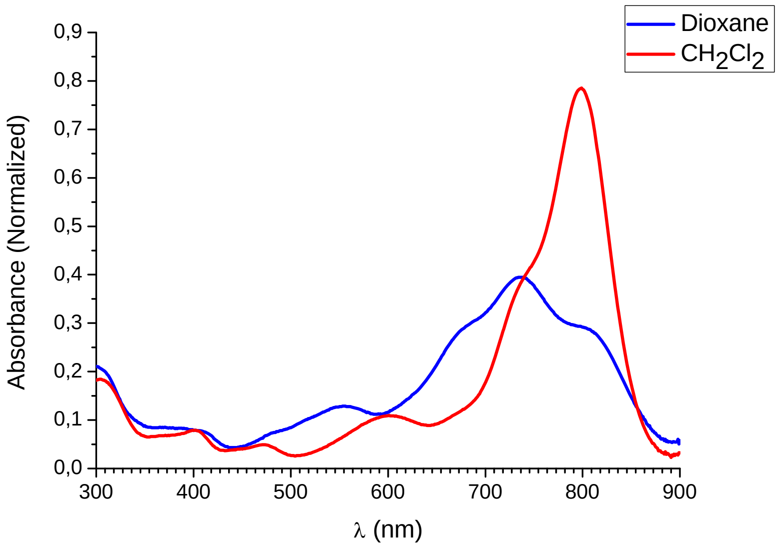


Figure S45: Normalized UV-vis absorption of compound **7a** (10^{-5} M) in dioxane and in CH_2Cl_2.

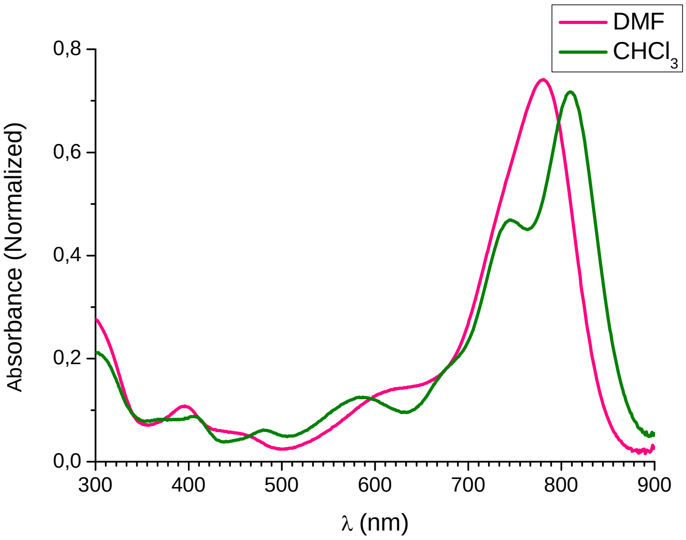


Figure S46: Normalized UV-vis absorption of compound **7a** (10^{-5} M) in DMF and in $CHCl_3$.

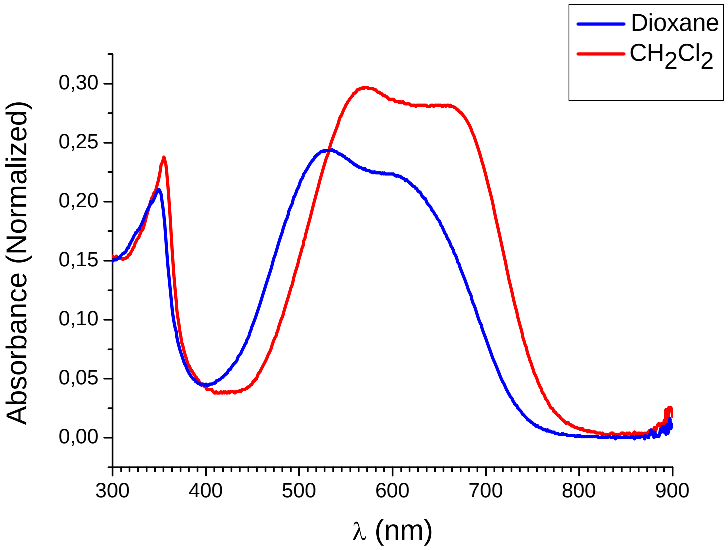


Figure S47: Normalized UV-vis absorption of compound **5b** (10^{-5} M) in dioxane and in CH_2Cl_2.

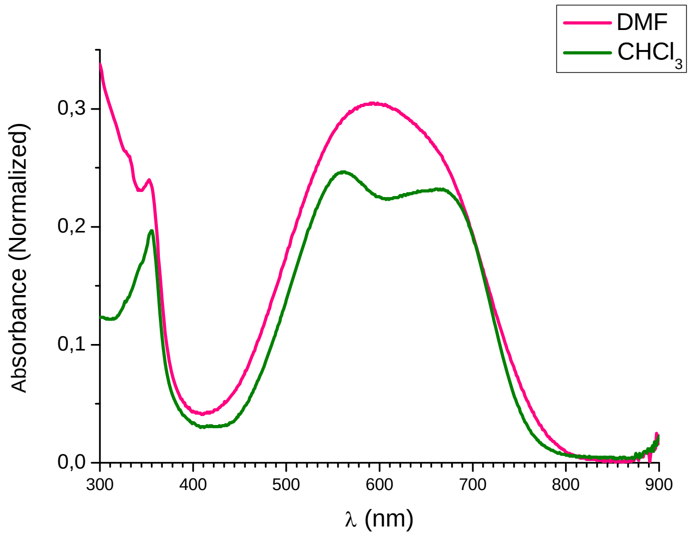


Figure S48: Normalized UV-vis absorption of compound **5b** (10^{-5} M) in DMF and in $CHCl_3$.

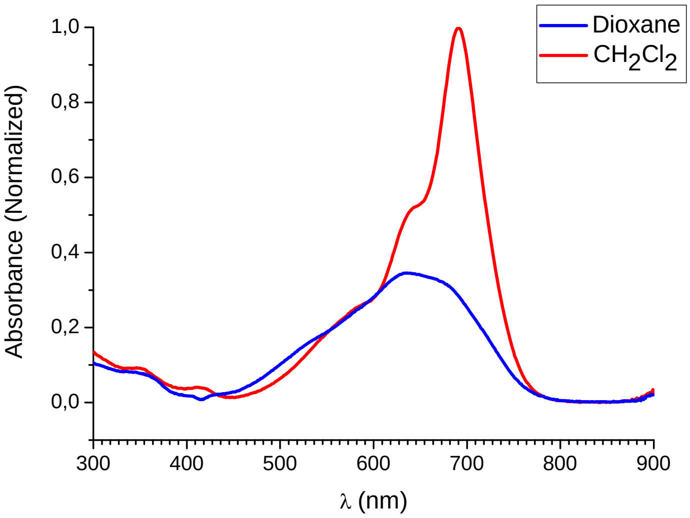


Figure S49: Normalized UV-vis absorption of compound **7c** (10^{-5} M) in dioxane and in CH_2Cl_2.

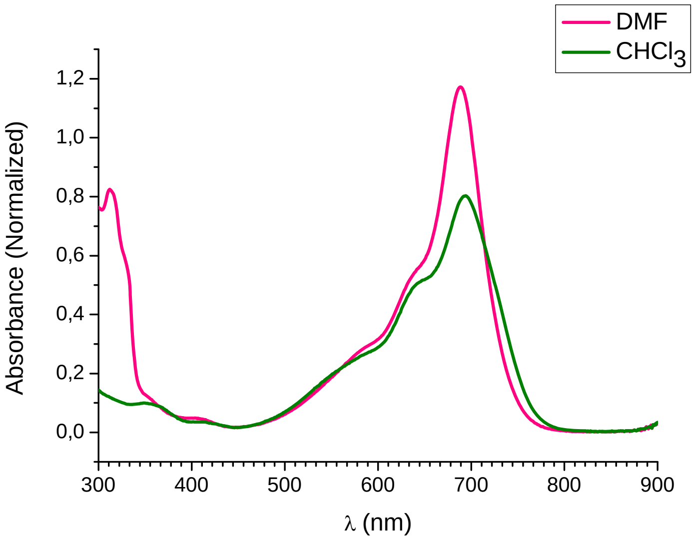


Figure S50: Normalized UV-vis absorption of compound **7c** (10^{-5} M) in DMF and in $CHCl_3$.

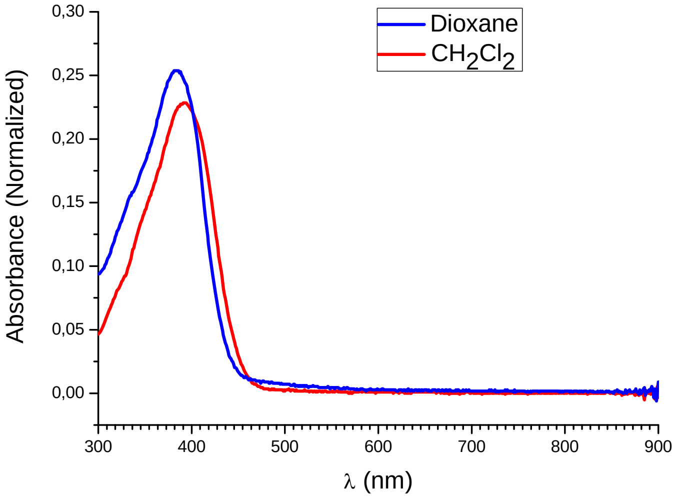


Figure S51: Normalized UV-vis absorption of compound **9** (10^{-5} M) in dioxane and in CH_2Cl_2.

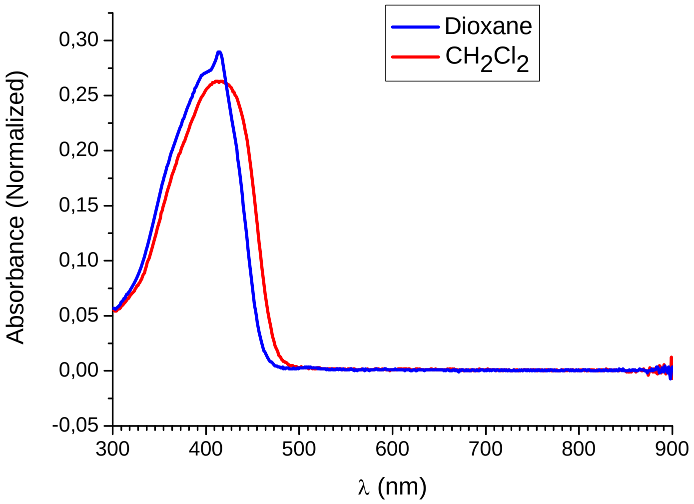


Figure S52: Normalized UV-vis absorption of compound **10** (10^{-5} M) in dioxane and in CH_2Cl_2.

6. Theoretical calculations

Cartesian coordinates and energies of optimized geometries used in theoretical calculations (PCM (CH_2Cl_2)-B3P86/6-31G*)

5a

```
                         Standard orientation:
---------------------------------------------------------------------
Center     Atomic      Atomic             Coordinates (Angstroms)
Number     Number       Type             X           Y           Z
---------------------------------------------------------------------
    1          6           0        1.625079    1.174890    0.029025
    2          6           0        3.010345    1.260550    0.327005
    3         16           0        1.070279    2.784891   -0.442226
    4          6           0        2.711832    3.379263   -0.285735
    5          6           0        3.061411    4.710617   -0.571368
    6          7           0        3.584427    2.456012    0.131027
    7          6           0        4.403100    5.135703   -0.456208
    8          7           0        5.506529    5.506810   -0.367747
    9          6           0        2.087583    5.643722   -0.981422
   10          7           0        1.263661    6.400718   -1.318742
   11          6           0        3.855883    0.215604    0.936461
   12          6           0        5.198488    0.117218    0.549267
   13          6           0        3.377808   -0.618084    1.954814
   14          6           0        6.036012   -0.820251    1.143423
   15          1           0        5.574312    0.782485   -0.221395
   16          6           0        4.220083   -1.547806    2.554069
   17          1           0        2.350090   -0.522744    2.289453
   18          6           0        5.549031   -1.656958    2.146298
   19          1           0        7.072516   -0.893290    0.826969
   20          1           0        3.839818   -2.182383    3.349286
   21          1           0        6.204703   -2.385043    2.615301
   22          6           0        0.722394    0.084733    0.005954
   23          6           0       -3.082892   -0.288862   -0.102059
   24          6           0       -3.661919    0.789180    0.608017
   25          6           0       -3.977956   -1.210307   -0.691266
   26          6           0       -5.023397    0.940349    0.715001
   27          1           0       -3.024940    1.527272    1.086245
   28          6           0       -5.343756   -1.075196   -0.594959
   29          1           0       -3.572505   -2.058925   -1.237031
   30          6           0       -5.921938    0.012889    0.113606
   31          1           0       -5.406633    1.796780    1.255895
   32          1           0       -5.973854   -1.826915   -1.054054
   33          7           0       -7.268766    0.162333    0.215702
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     34          6           0       -7.874792    1.209146    1.031896
     35          1           0       -8.841552    0.826916    1.374711
     36          1           0       -7.274678    1.358914    1.933759
     37          6           0       -8.198655   -0.710979   -0.492546
     38          1           0       -7.781308   -0.965528   -1.470975
     39          1           0       -9.099713   -0.122862   -0.693435
     40          6           0       -1.677583   -0.488610   -0.250783
     41          6           0       -0.670194    0.350652    0.158788
     42          1           0       -1.389644   -1.396752   -0.777660
     43          1           0       -0.935237    1.312891    0.591881
     44          6           0       -8.562255   -1.967870    0.290550
     45          1           0       -9.281758   -2.569069   -0.274578
     46          1           0       -7.679507   -2.583837    0.487001
     47          1           0       -9.016600   -1.710233    1.252792
     48          6           0       -8.070255    2.521906    0.281251
     49          1           0       -8.554065    3.258877    0.930269
     50          1           0       -7.114090    2.934958   -0.054282
     51          1           0       -8.704113    2.376935   -0.599560
     52          6           0        1.202962   -1.267358   -0.235792
     53          6           0        2.238658   -1.518288   -1.158299
     54          6           0        0.655049   -2.382154    0.431057
     55          6           0        2.694563   -2.793576   -1.411439
     56          1           0        2.664264   -0.687528   -1.712913
     57          6           0        1.116368   -3.662940    0.208733
     58          1           0       -0.116478   -2.225446    1.179063
     59          6           0        2.151242   -3.912180   -0.728490
     60          1           0        3.470690   -2.932702   -2.154117
     61          1           0        0.685672   -4.479364    0.775763
     62          7           0        2.604055   -5.173672   -0.964624
     63          6           0        3.699121   -5.395224   -1.889311
     64          1           0        4.601224   -4.852268   -1.582082
     65          1           0        3.437635   -5.082078   -2.907918
     66          6           0        2.014048   -6.302061   -0.271178
     67          1           0        0.936319   -6.370095   -0.462424
     68          1           0        2.168623   -6.238812    0.813682
     69          1           0        2.478395   -7.221572   -0.626341
     70          1           0        3.935813   -6.458547   -1.913164
 ---------------------------------------------------------------------
E(RB3P86) =  -1953.15647132     A.U.
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6a

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                        Standard orientation:
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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
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      2          6           0       -4.546351   -0.875213    0.333743
      3         16           0       -3.051602   -2.910670   -0.230184
      4          6           0       -4.807117   -3.020711   -0.170023
      5          6           0       -5.488886   -4.223225   -0.410888
      6          7           0       -5.418366   -1.869350    0.134488
      7          6           0       -6.899839   -4.267651   -0.351289
      8          7           0       -8.064759   -4.325937   -0.307842
      9          6           0       -4.787034   -5.407281   -0.718386
     10          7           0       -4.186723   -6.377268   -0.970623
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     12          6           0       -6.266072    0.893459    0.130181
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     19          1           0       -7.712499    2.473151    0.003506
     20          1           0       -4.439800    3.128001    2.711486
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     23          6           0        4.144892   -0.187780   -0.079903
     24          6           0        4.472109   -1.466299    0.427757
     25          6           0        5.226448    0.621475   -0.492854
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     32          1           0        7.317903    0.879754   -0.729661
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     36          1           0        7.843432   -2.960919    1.661239
     37          6           0        9.259234   -0.732307   -0.347687
     38          1           0        8.947564   -0.235589   -1.271054
     39          1           0       10.042954   -1.439622   -0.637203
     40          6           0        2.811684    0.317086   -0.191042
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7a

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13	7	0	5.795115	-0.867082	0.044867
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15	7	0	9.001419	-2.477956	0.665295
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22	1	0	6.409778	1.519097	0.916391
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24	1	0	3.342579	1.336208	-2.082619
25	6	0	5.174895	4.001998	-1.052033
26	1	0	6.710578	3.938003	0.459316
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29	8	0	-5.522410	-1.250247	0.133108
30	6	0	-1.375366	-1.468514	-0.447853
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32	1	0	-1.073359	-2.463221	-0.771673
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35	6	0	0.992612	-1.093826	-0.210623
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37	6	0	-5.592434	0.854064	1.233622
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45	1	0	-7.211450	2.176363	0.668609
46	1	0	-6.062013	1.867104	-0.646901
47	1	0	-6.984094	1.003447	2.885648
48	1	0	-7.025340	-0.572389	2.077112
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50	6	0	-5.994704	-3.368690	-0.838734

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     67          1           0        0.627872    1.158774    1.667370
     68          6           0       -1.489305    2.944504   -1.026664
     69          1           0       -1.750032    1.017759   -1.903252
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     79          1           0       -1.459747    5.623880   -1.925986
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7c

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9	6	0	1.100246	-1.730417	0.000325
10	6	0	2.390761	-1.230393	-0.008981
11	6	0	3.569359	-1.992693	-0.170508
12	6	0	4.870305	-1.410410	-0.106078
13	6	0	6.022565	-2.012229	-0.625785
14	6	0	7.325065	-1.536446	-0.313646
15	7	0	8.416833	-1.199713	-0.077709
16	6	0	6.013303	-3.112425	-1.523530
17	7	0	6.068361	-3.982212	-2.298802
18	6	0	5.021094	-0.093337	0.557844
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20	6	0	4.704290	1.329333	2.493692
21	6	0	5.334694	2.380266	1.829508
22	6	0	5.806650	2.198249	0.530909
23	6	0	5.658174	0.967436	-0.099538
24	6	0	3.411286	-3.391873	-0.379627
25	7	0	3.206334	-4.534518	-0.490084
26	1	0	-2.364428	0.730069	-0.746430
27	1	0	-3.387327	-3.097318	1.000600
28	1	0	-1.167349	-2.685985	0.625793
29	1	0	0.968502	-2.809866	-0.045765
30	1	0	2.526363	-0.159865	0.112163
31	1	0	4.053969	-0.718805	2.378938
32	1	0	4.340394	1.464301	3.507903
33	1	0	5.457466	3.339827	2.323314
34	1	0	6.291362	3.016144	0.006228
35	1	0	6.019007	0.828771	-1.114257
36	6	0	-5.033089	1.495819	-1.111733
37	6	0	-5.914530	2.159972	-0.038160
38	6	0	-3.968165	2.490790	-1.577400
39	6	0	-5.903617	1.081350	-2.311628
40	1	0	-6.699049	1.483423	0.312471
41	1	0	-5.316739	2.472894	0.824567
42	1	0	-6.395066	3.048804	-0.460073
43	1	0	-3.338316	2.070801	-2.368577
44	1	0	-4.461597	3.380178	-1.981564
45	1	0	-3.322598	2.810394	-0.752573
46	1	0	-6.379560	1.969228	-2.740653
47	1	0	-5.298581	0.607754	-3.091973
48	1	0	-6.690723	0.383078	-2.013512
49	6	0	-0.004125	0.515890	0.031350
50	6	0	0.656263	1.174973	-1.019241
51	6	0	-0.578600	1.318624	1.031268
52	6	0	0.729484	2.555719	-1.083397
53	1	0	1.092518	0.588840	-1.823304

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     54          6           0       -0.493724    2.698116    0.997316
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     59          7           0        0.247793    4.725374   -0.111282
     60          6           0       -0.364085    5.524935    0.929387
     61          1           0        0.077208    5.320069    1.913698
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     72          1           0       -6.446808   -1.667989    2.742972
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     74          1           0       -7.890596   -2.477938    2.107472
     75          1           0       -6.410196   -3.502634   -1.188170
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     77          1           0       -7.335611   -2.012007   -0.917127
     78          1           0       -6.613452   -4.571888    1.700043
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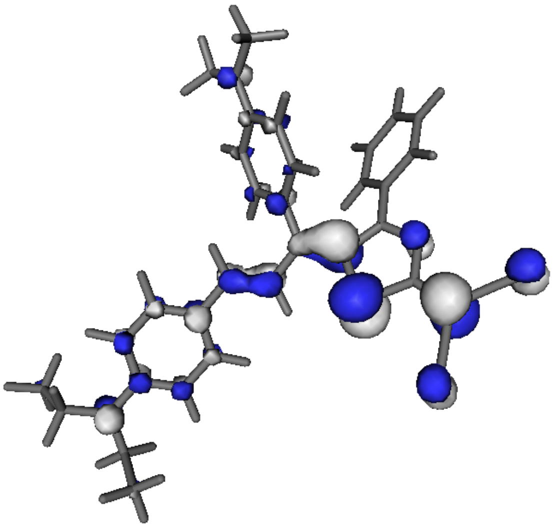	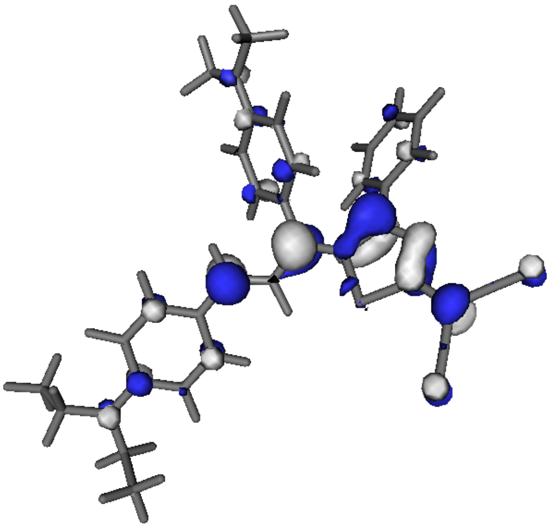
HOMO: –5.79 eV	**LUMO**: –3.67 eV

Figure S53: HOMO and LUMO contour plots (PCM-B3P86/6-31G*//B3P86-31G* in CH_2Cl_2) for compound **5a.**

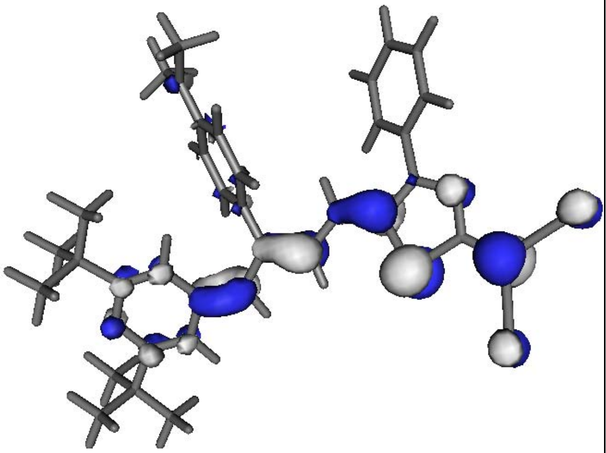	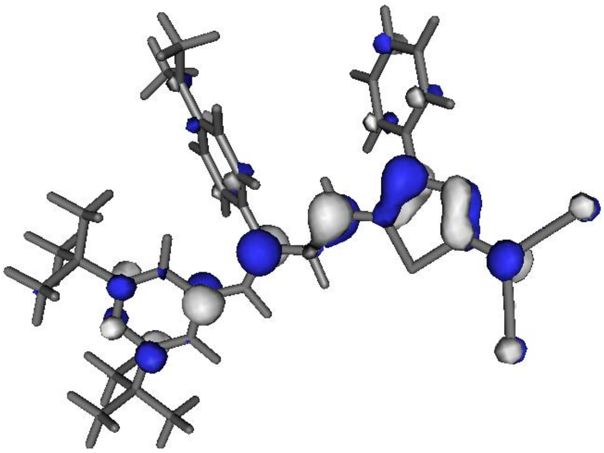
HOMO: –5.68 eV	**LUMO**: –3.64 eV

Figure S54: HOMO and LUMO contour plots (PCM-B3P86/6-31G*//B3P86-31G* in CH_2Cl_2) for compound **7a.**

7. NLO measurements

Electric field induced second harmonic generation (EFISH) measurements have been performed using as the fundamental radiation the 1.9 μm output of a H_2 Raman shifter pumped by a Q-switched Nd:YAG laser. This laser operates at 1064 nm, with a repetition rate of 10 Hz and pulse width of 8 ns. A computer controlled NLO spectrometer completes the SHG experimental set-up. The 1.9 μm incident light is split in two beams. The less intense one is directed to a *N*-(4-nitrophenyl)-(L)-prolinol (NPP) powder sample whose SH signal is used as a reference in order to reduce the effects of laser fluctuations. The other beam is passed through a linear polarizer and focused into the EFISH wedge shaped liquid cell. Voltage pulses of 5 kV and 3 μs are applied across the cell (2 mm gap between the electrodes) synchronously with the laser pulses. The harmonic signals from both the EFISH cell and the NPP reference are measured with two photomultipliers. Interference filters are used to remove the residual excitation light beyond the sample and the reference.

The molecular $\mu\beta$ values have been determined in dichloromethane for all compounds. As a rule, three solutions of concentration in the range (1×10^{-4}M–8×10^{-4}M) were measured. The effect of absorption at harmonic wavelength (953 nm) of compound **6a** has been corrected following ref.[9]. $\mu\beta_0$ values were extrapolated using a two-level dispersion model.[10] Under the same experimental conditions $\mu\beta_0$ deduced for DR1 was 480×10^{-48} esu, quite close to the value reported in the same solvent by Dirk et al.[11]

---

(9) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446–457.
(10) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664–2668.
(11) Dirk, C. W.; Katz, H. E.; Schilling, M. L.; King, L. A. *Chem. Mater.* **1990**, *2*, 700–705.