SUPPORTING INFORMATION FOR

4*H*-Pyran-4-ylidenes: Strong Proaromatic Donors for Organic Nonlinear Optical Chromophores

Raquel Andreu,[†] Laura Carrasquer,[†] Santiago Franco,[†] Javier Garín[*,†], Jesús Orduna,[†] Natalia Martínez de Baroja,[†] Belén Villacampa, [‡] Raquel Alicante,[‡] and Magali Allain. [§]*

[†]Departamento de Química Orgánica, ICMA, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain. [‡]Departamento de Física de la Materia Condensada, ICMA, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain. [§]Laboratoire de Chimie, Ingénierie Moleculaire et Matériaux d'Angers (UMR CNRS 6200), Université d'Angers, 2, Boulevard Lavoisier, 49045-Angers CEDEX, France.

TABLE OF CONTENTS

General Experimental Methods:

Infrared measurements were carried out in nujol mulls using a Fourier Transform Infrared spectrometer. — Melting points are uncorrected. — ^{1}H- and ^{13}C-NMR spectra were recorded 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. — ^{1}H-^{1}H COSY experiments were recorded at 300 MHz or 400 MHz in order to establish peaks assignment and spatial relationships. — Selective ge-1D NOESY experiments (mixing time: 1-2 s; selective 180 pulse: 20-40 ms) were recorded at 300 MHz for compound **4b**, in order to determine the stereochemistry of the HC=C(CN) and the (NH_2)C-C(CN) bonds. 2D-EXSY experiments (mixing time: 20 ms) were recorded at 300 MHz for compound **4b,** in order to show the exchange between H3 and H5 protons of the pyranylidene unit. — EI Mass spectra were recorded at 70 eV. — MALDI-ToF Mass Spectra were recorded using dithranol as matrix. — Electrospray mass spectra were recorded on a Q-ToF spectrometer; accurate mass measurements were achieved using sodium formate as external reference. — Cyclic voltammetry measurements were performed 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}. — Thermogravimetric analysis (TGA) were carried out at 10ºC/min in nitrogen atmosphere from 40ºC to 600ºC; from 600ºC to 750 ºC heating was continued in synthetic air atmosphere. — Differential scanning calorimetry (DSC) measurements were carried out at 10ºC/min; the apparatus was calibrated with indium (156ºC; 28.4 J/g).

Analytical data for *N*-((1*E*, 3*E*)-5-(1,3-diethyl-4,6-dioxo-2-thioxo-tetrahydropyrimidin-5*H*-ylidene)penta-1,3-dienyl)-*N*-phenylacetamide (8').

Mp 206–208ºC. IR (Nujol, cm^{-1}) 1691 (C=O), 1655 (C=C), 1184 (C=S). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 13.7 Hz, 1H), 8.06 (d, *J* = 12.6 Hz, 1H), 7.74 (dd, *J* = 13.8 Hz, *J'* = 13.1 Hz, 1H), 7.60–7.54 (m, 3H), 7.28–7.19 (m, 3H), 5.38 (dd, *J* = 13.3 Hz, *J'* = 11.8 Hz, 1H), 4.54–4.45 (m, 4H), 1.98 (s, 3H), 1.27 (t, *J* = 6.8 Hz, 3H), 1.24 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 184.4, 177.2, 169.0, 167.7, 159.0, 148.6, 144.3, 138.7, 137.0, 130.4, 129.4, 129.0, 128.5, 121.8, 113.4, 43.3, 43.0, 23.2, 12.3, 12.0. MS (EI^+): *m/z* 397 ($M^{+\cdot}$, 20), 354 (25), 143 (100), 77(30). Anal. Calcd. for $C_{21}H_{23}N_3O_3S$: C 63.45, H 5.83, N 10.57. Found: C 63.26, H 5.60, N 10.29.

Analytical data for *N*-((1*E*, 3*E*, 5*Z*)-5-(5-oxo-3-phenylisoxazol-4 (5*H*)-ylidene)penta-1,3-dienyl)-*N*-phenylacetamide (9').

Mp 197–199ºC (lit[1] mp: 198–200ºC). IR (Nujol, cm^{-1}) 1725 (C=O), 1688 (C=C), 1542 (C=N). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.12 (d, *J* = 13.8 Hz, 1H), 7.59-7.49 (m, 9H), 7.30 (d, *J* = 12.2 Hz, 1H), 7.20–7.17 (m, 2H), 7.05 (dd, *J* = 14.4 Hz, *J'* = 11.5 Hz, 1H), 5.37 (dd, *J* = 13.8 Hz, *J'* = 11.5 Hz, 1H), 1. 95 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.9, 169.3, 162.3, 152.6, 149.8, 140.6, 138.1, 130.7, 130.6, 129.8, 129.1, 128.2, 128.1, 124.5, 113.4, 113.2, 23.3. MS (EI^+): *m/z* 358 ($M^{+\cdot}$, 45), 316 (95), 271 (100), 224 (35), 156 (55), 77 (60). Anal. Calcd. for $C_{22}H_{18}N_2O_3$: C 73.73, H 5.06, N 7.82. Found: C 73.49, H 4.80, N 7.61.

[1] Brooker, L. G. S.; Keyes, G. H.; Sprague, R. H.; VanDyke, R. H.; VanLare, E.; VanZandt, G.; White, F. L.; Cressman, H. W. J.; Dent, S. G. Jr. *J. Am. Chem. Soc.* **1951**, *73*, 5332-5350.

Compounds 2d–4d: General Procedure. Equimolar quantities of 2,6-di-*tert*-butyl-4-methylpyrylium triflate (**6**) and the corresponding acceptor (**9'-11'**) were treated with triethylamine (2 eq.) and catalytic pyridine under argon atmosphere. The mixture was stirred at room temperature (for **9'-10'**) or at reflux (for **11'**) for 10-30 minutes (TLC monitoring). After cooling, ether (70 mL) was added, and the organic layer was washed with HCl 10% (2×50 mL) and water (2×50 mL), dried ($MgSO_4$) and the solvent evaporated. The crude product was purified by column chromatography on silica gel and/or recrystallization.

(*Z*)-4-[(2*E*,4*E*)-6-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)hexa-2,4-dienylidene]-3-phenyl-5-isoxazolone (2d).

Chromatography eluent: hexane/AcOEt (8:2). Yield: dark blue solid (36%).

Mp 166–168ºC. IR (Nujol, cm^{-1}) 1709 (C=O), 1654 (C=C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (t, J = 13.2 Hz, 1H), 7.60–7.49 (m, 5H), 7.30 (d, J = 12.6 Hz, 1H), 7.18–7.07 (m, 2H), 6.42 (t, J = 12.8 Hz, 1H), 6.23 (d, J = 1.6 Hz, 1H), 5.88 (d, J = 1.6 Hz, 1H), 5.70 (d, J = 12.5 Hz, 1H), 1.25 (s, 9H), 1.22 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 178.0, 170.1, 164.6, 155.4, 149.3, 142.7, 141.3, 130.2, 129.0, 128.3, 126.5, 123.5, 122.2, 113.6, 106.4, 100.0, 42.6, 40.4, 27.9, 27.8. MS (EI^+): *m/z* 429 ($M^{+\cdot}$, 35), 269 (60), 254 (45), 57 (100). Anal. Calcd. for $C_{28}H_{31}NO_3$: C 78.29, H 7.27, N 3.26. Found: C 78.44, H 7.16, N 3.43.

(3*Z*,5*E*,7*E*)-9-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)-2-phenylnona-1,3,5,7-tetraene-1,1,3-tricarbonitrile (3d).

Chromatography eluent: hexane/AcOEt (8:2). Yield after recrystallization from AcOEt/hexane: emerald green solid (28%).

Mp 193–195ºC (dec.). IR (Nujol, cm^{-1}) 2205 (C≡N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56–7.47 (m, 3H), 7.39–7.37 (m, 2H), 7.27–7.19 (m, 2H), 7.06 (t, J = 12.7 Hz, 1H), 6.72 (t, J = 12.9 Hz, 1H), 6.35 (t, J = 12.8 Hz, 1H), 6.34 (d, J = 1.8 Hz, 1H), 5.99 (d, J = 1.8 Hz, 1H), 5.78 (d, J = 12.8 Hz, 1H), 1.26 (s, 9H), 1.25 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.3, 169.1, 166.3, 156.0, 155.2, 145.3, 144.5, 135.0, 131.6, 129.6, 129.1, 126.2, 123.5, 115.6, 115.3, 114.6, 114.1, 107.3, 100.8, 100.3, 60.5, 36.4, 36.1, 27.9, 27.8. MS (EI^+): *m/z* 461 ($M^{+\cdot}$, 50), 269 (60), 254 (40), 193 (50), 153 (40), 57 (73). Anal. Calcd. for $C_{31}H_{31}N_3O$: C 80.66, H 6.77, N 9.10. Found: C 80.92, H 6.52, N 9.28.

(3*Z*,5*E*,7*E*)-2-amino-9-(2,6-di-*tert*-butyl-4*H*-pyran-4-ylidene)nona-1,3,5,7-tetraene-1,1,3-tricarbonitrile (4d).

Chromatography eluent: hexane/AcOEt (65:35). Yield: dark blue solid (49%).

Mp 111–115ºC. IR (Nujol, cm^{-1}) 2209 (C≡N). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.98 (d, J = 12.0 Hz, 1H), 7.26–7.16 (m, 2H), 6.56 (dd, J = 13.3 Hz, J' = 12.3 Hz, 1H), 6.31 (d, J = 1.8 Hz, 1H), 6.30 (dd, J = 13.5 Hz, J' = 12.0 Hz, 1H), 5.91 (d, J = 1.8 Hz, 1H), 5.81 (br s, 2H), 5.70 (d, J = 12.7 Hz, 1H), 1.27 (s, 9H), 1.23 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.5, 155.1, 154.7, 154.2, 144.4, 142.7, 125.0, 122.0, 115.9, 115.6, 115.4, 113.4, 106.6, 100.2, 36.2, 29.7, 27.9, 27.8. MS (EI^+): *m/z* 400 ($M^{+\cdot}$, 60), 57 (100). Anal. Calcd. for $C_{25}H_{28}N_4O$: C 74.97, H 7.05, N 13.99. Found: C 75.18, H 6.89, N 14.26.

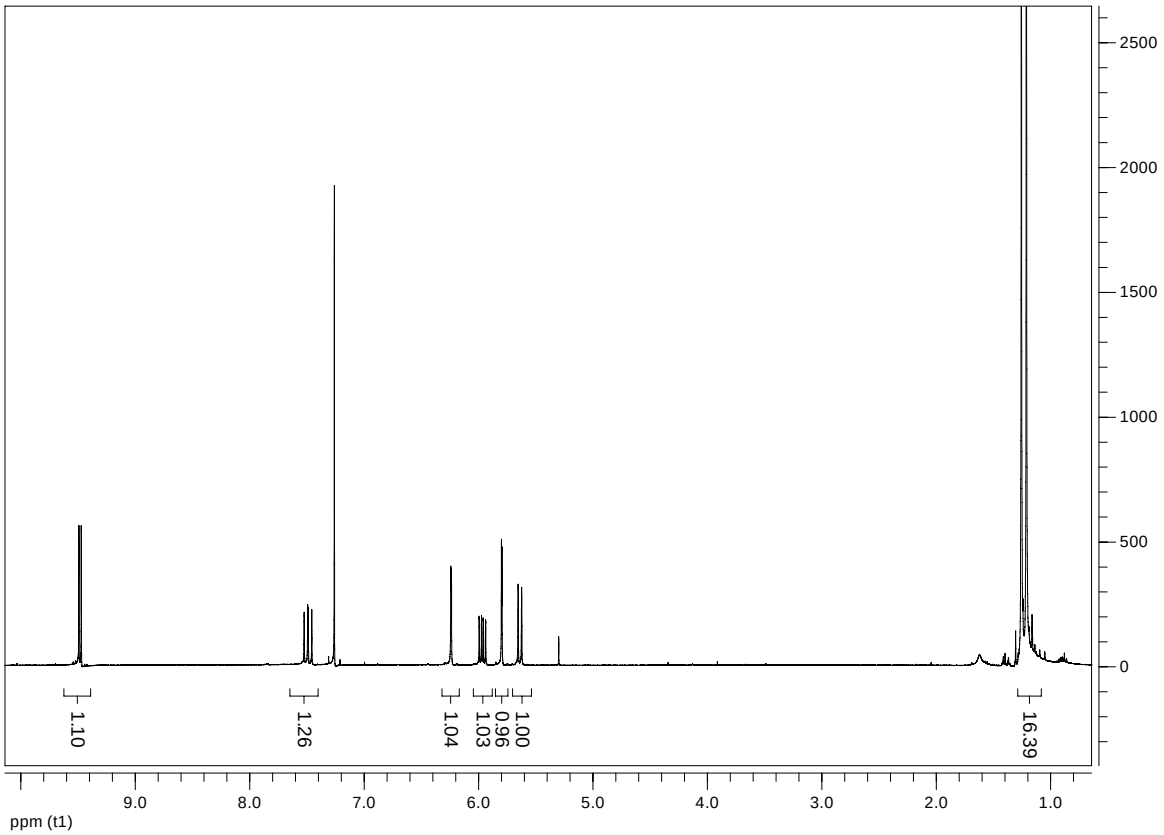
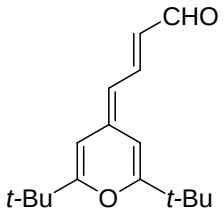


Figure S-1: ^{1}H-NMR spectrum of compound **7c** (100 MHz, $CDCl_3$).



7c

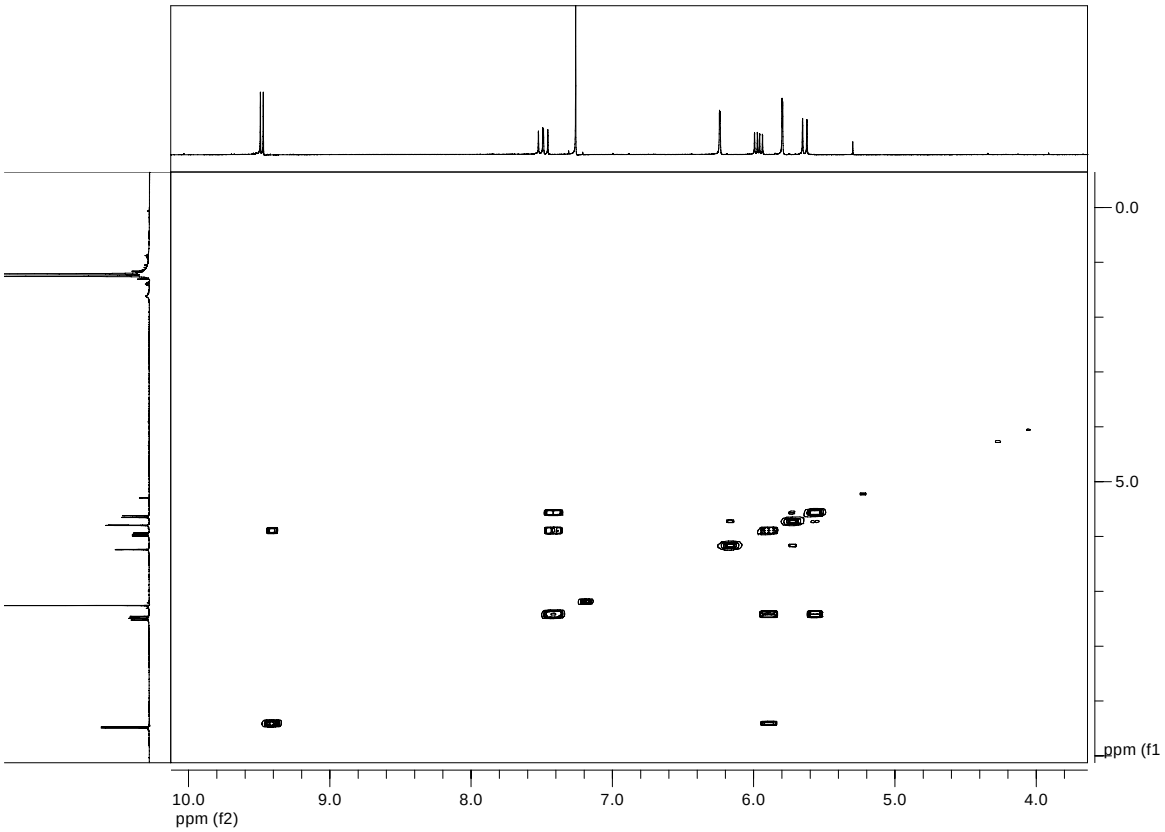
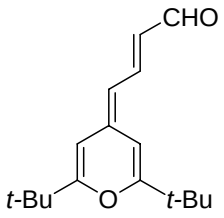


Figure S-2: ^{1}H-^{1}H COSY spectrum of compound **7c** (400 MHz, $CDCl_3$).



7c

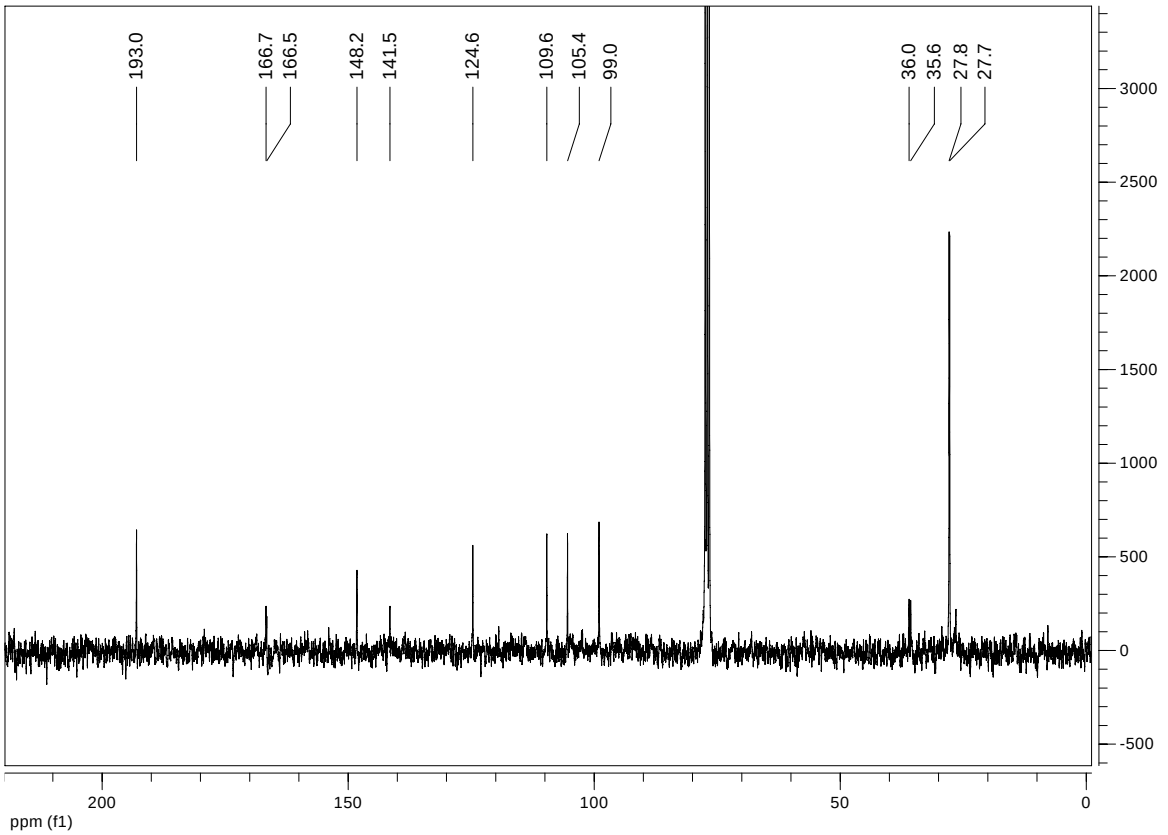
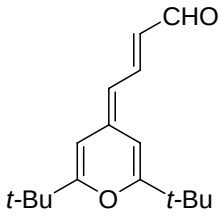


Figure S-3: ^{13}C-NMR spectrum of compound **7c** (75 MHz, $CDCl_3$).



7c

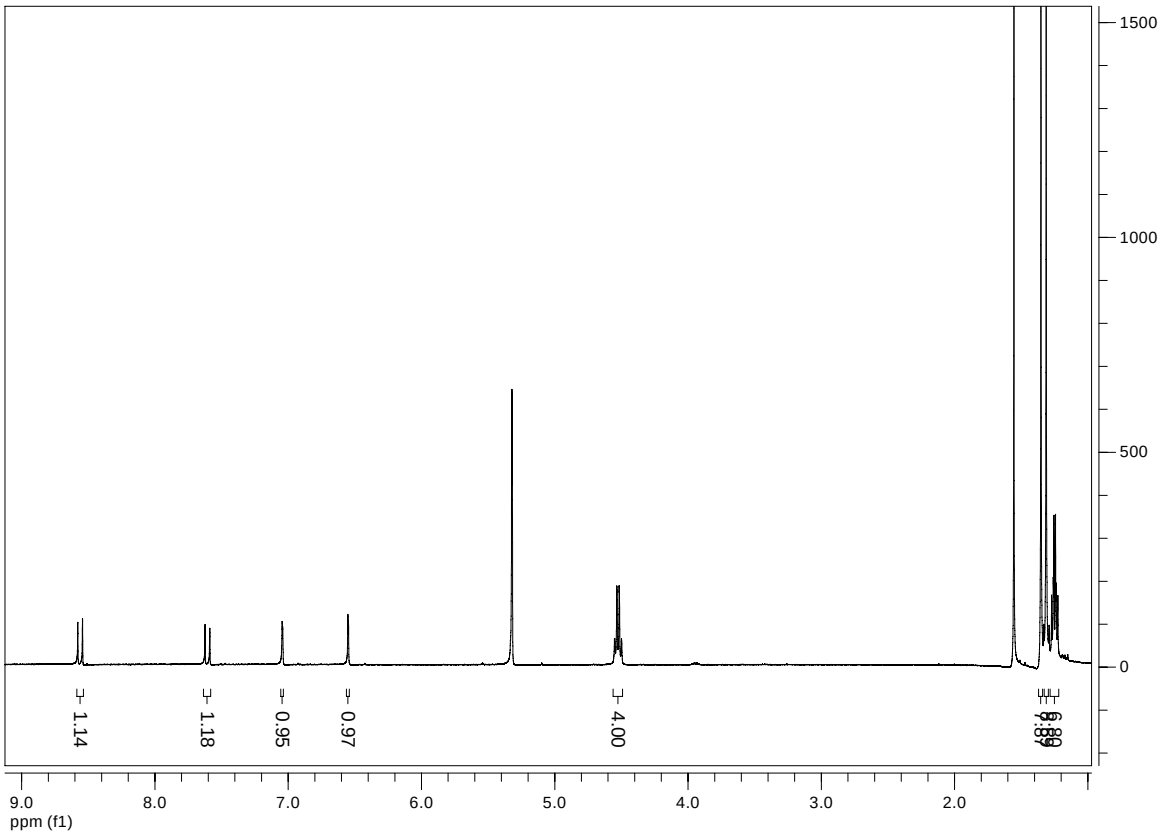
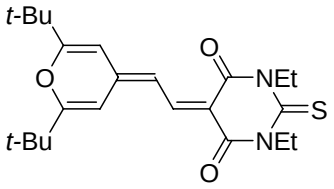


Figure S-4: ^{1}H-NMR spectrum of compound **1b** (400 MHz, CD_2Cl_2).



1b

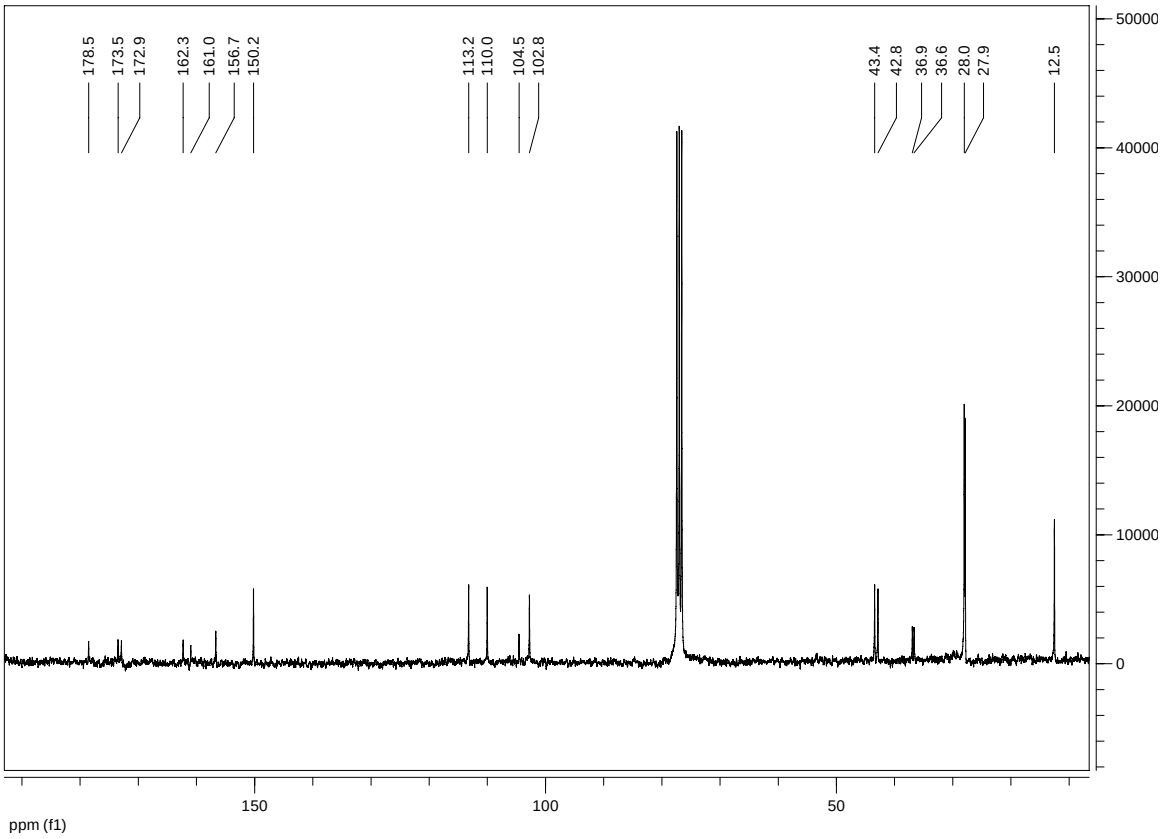
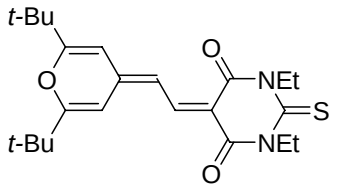


Figure S-5: ^{13}C-NMR spectrum of compound **1b** (75 MHz, $CDCl_3$).



1b

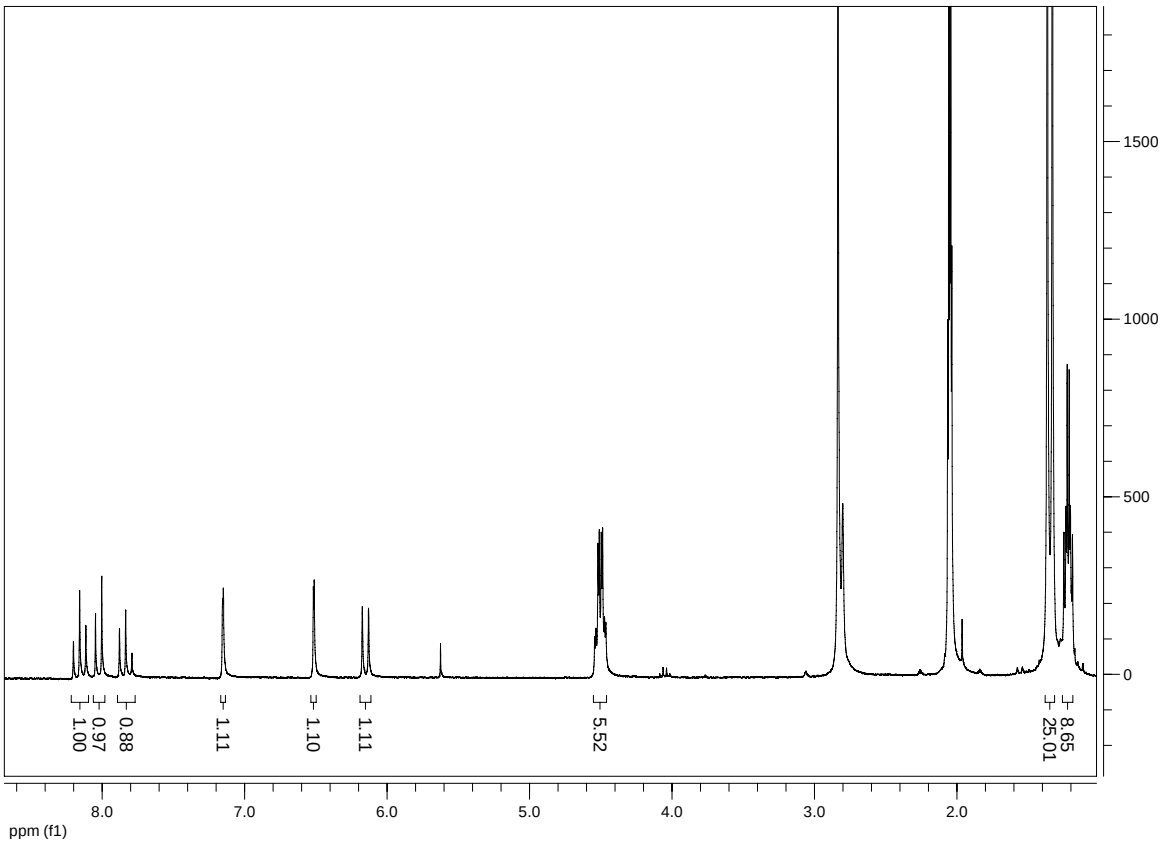
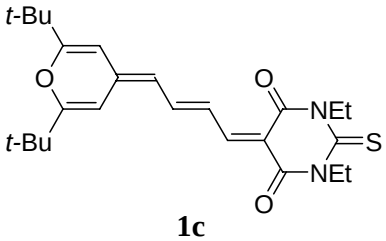


Figure S-6: ^{1}H-NMR spectrum of compound **1c** (300 MHz, C_2D_6CO).



1c

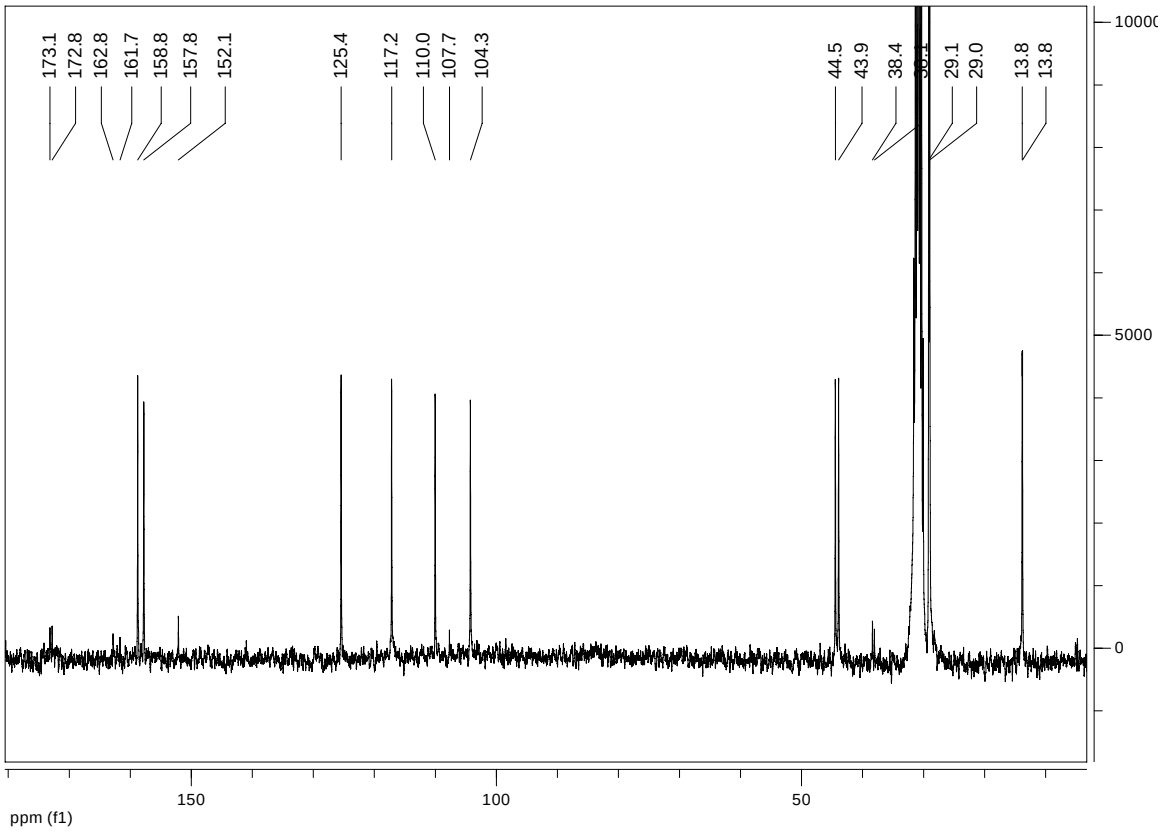
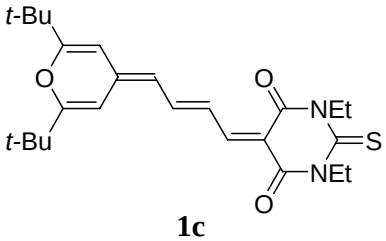


Figure S-7: ^{13}C-NMR spectrum of compound **1c** (75 MHz, C_2D_6CO).



1c

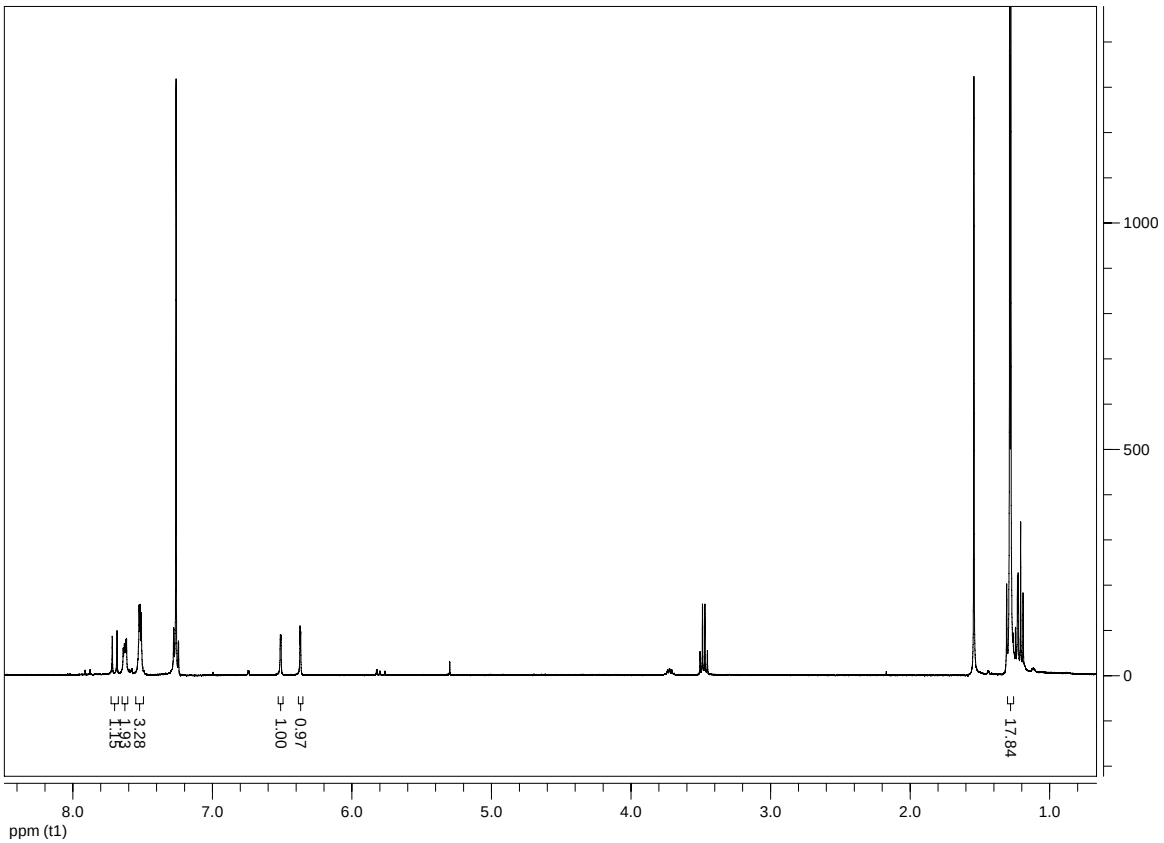
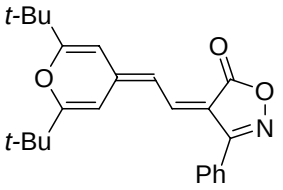


Figure S-8: ^{1}H-NMR spectrum of compound **2b** (400 MHz, $CDCl_3$).



2b

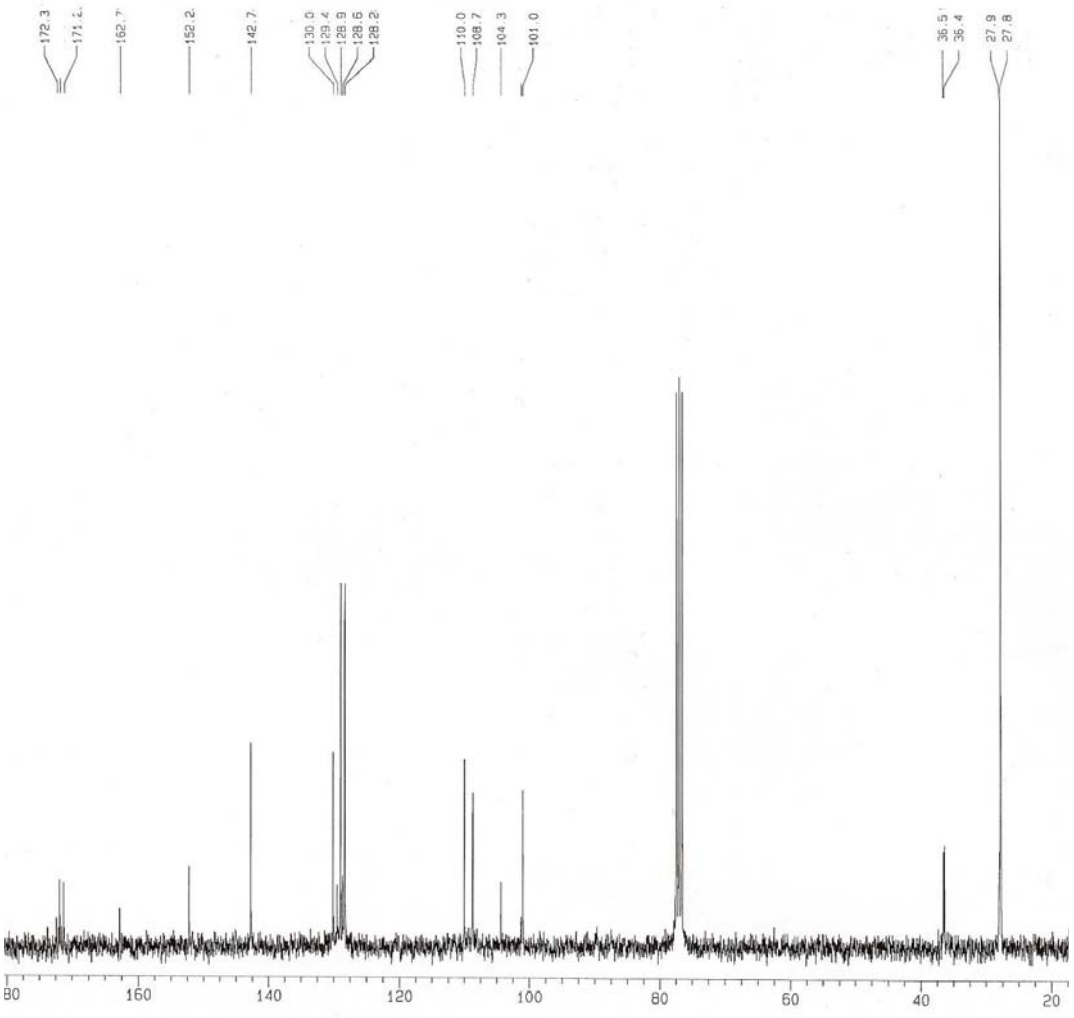
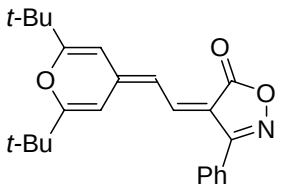


Figure S-9: ^{13}C-NMR spectrum of compound **2b** (75 MHz, $CDCl_3$).



2b

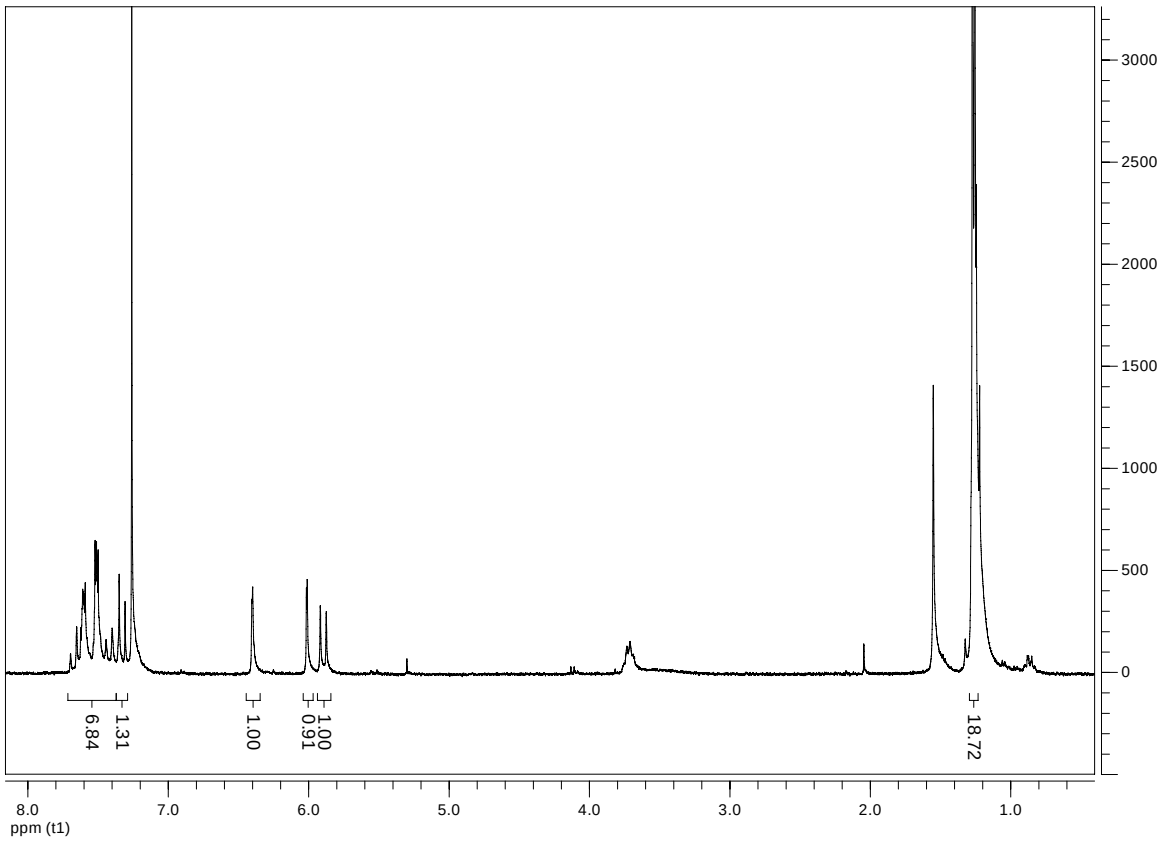
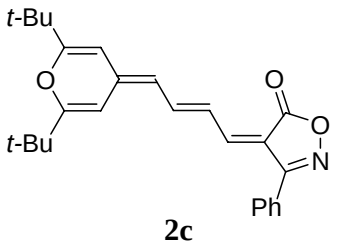


Figure S-10: ^{1}H-NMR spectrum of compound **2c** (300 MHz, $CDCl_3$).



2c

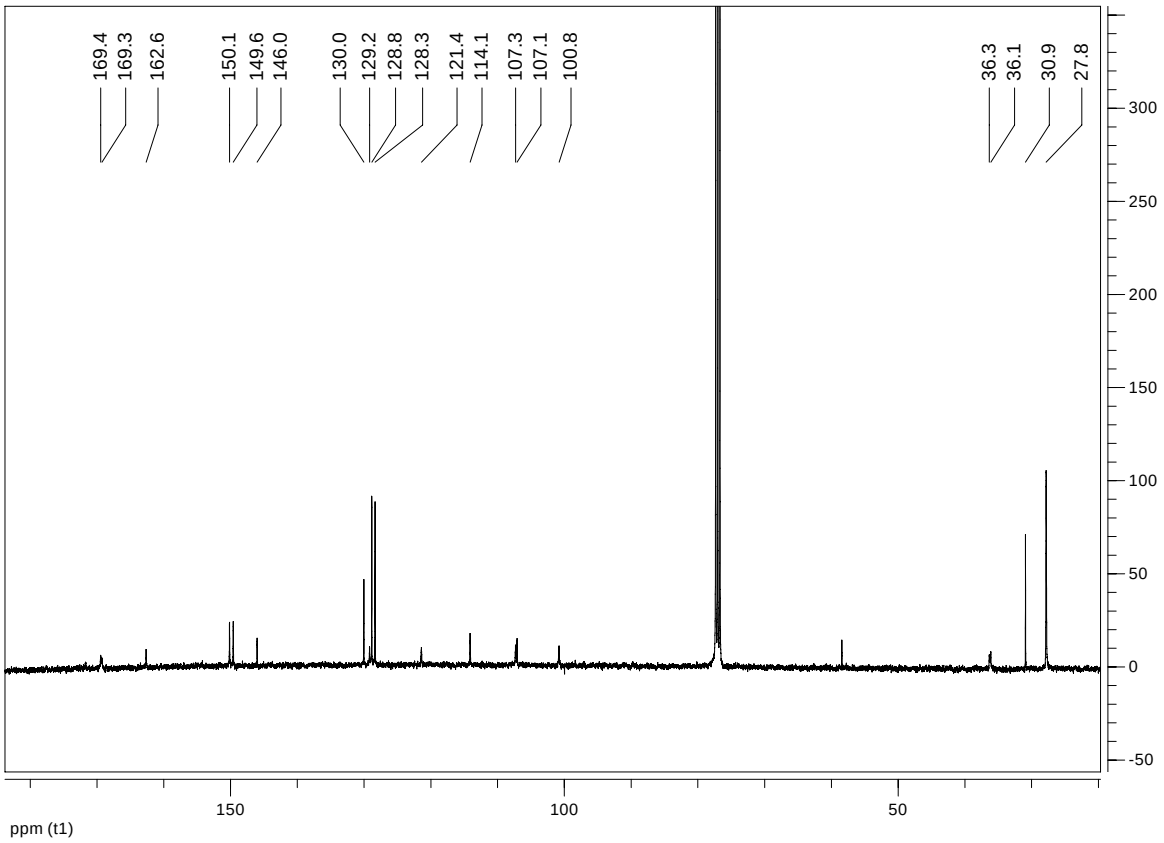
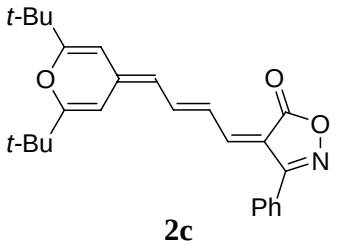


Figure S-11: ^{13}C-NMR spectrum of compound **2c** (100 MHz, $CDCl_3$).



2c

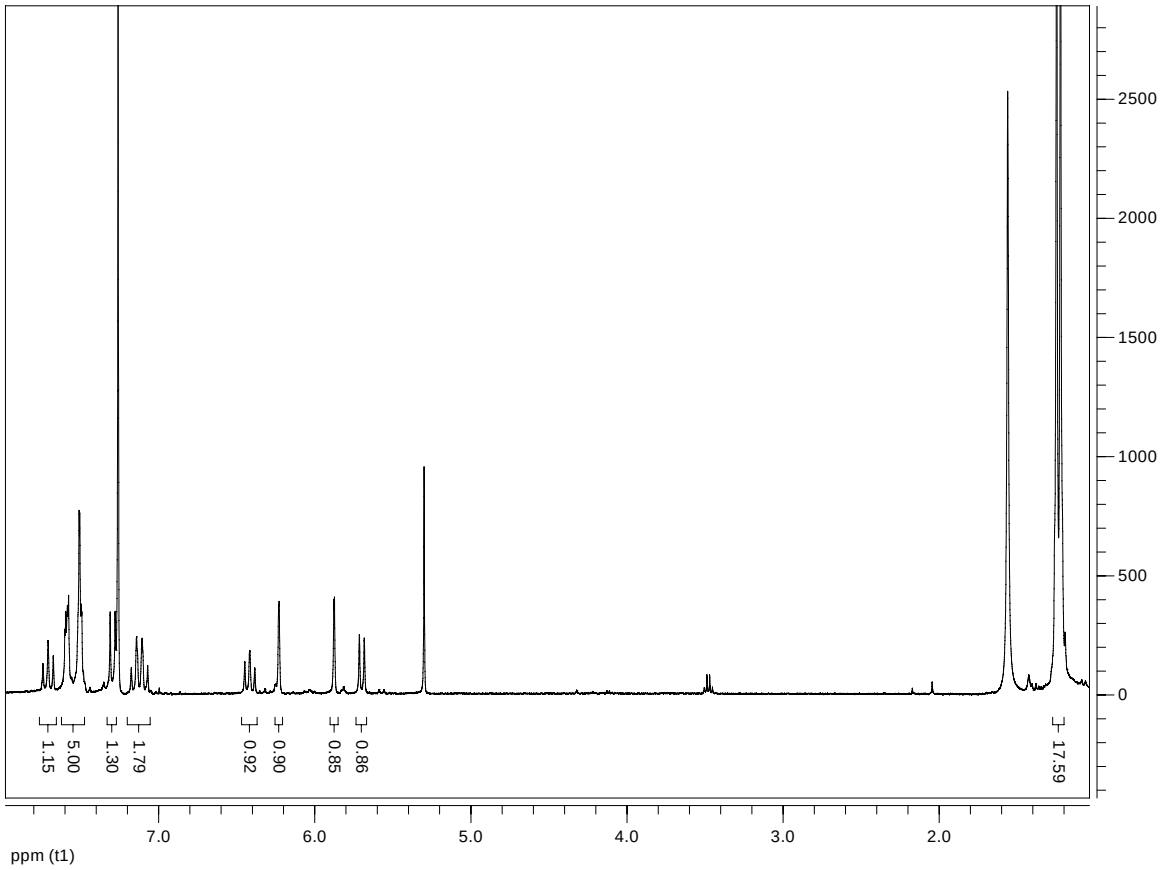
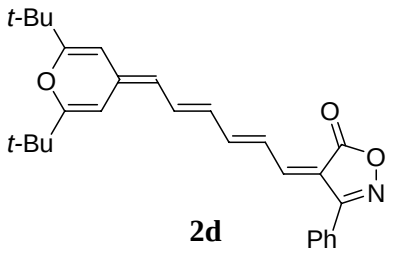


Figure S-12: ^{1}H-NMR spectrum of compound **2d** (400 MHz, $CDCl_3$).



2d

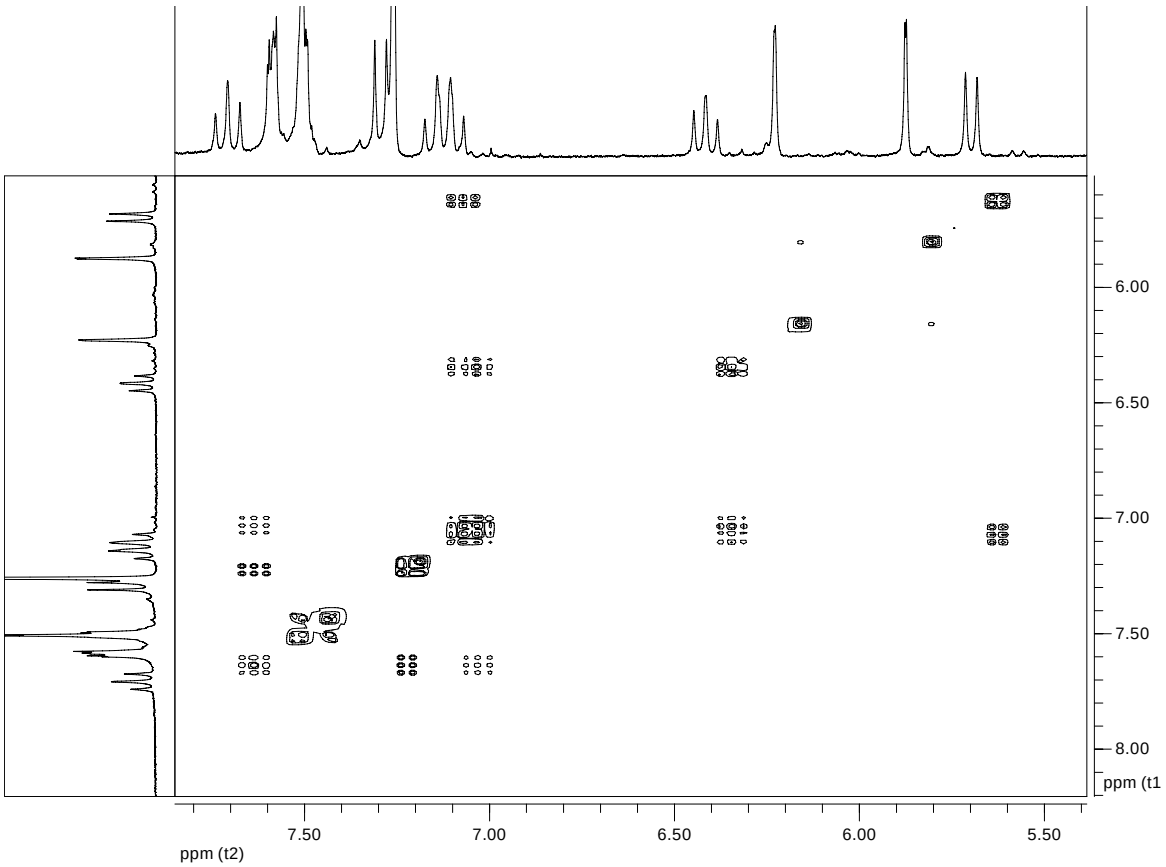
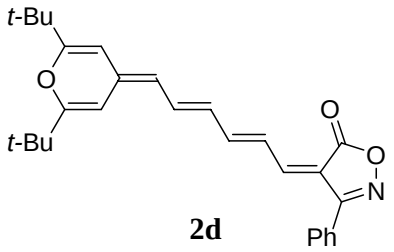


Figure S-13: ^{1}H-^{1}H COSY spectrum of compound **2d** (400 MHz, $CDCl_3$).



2d

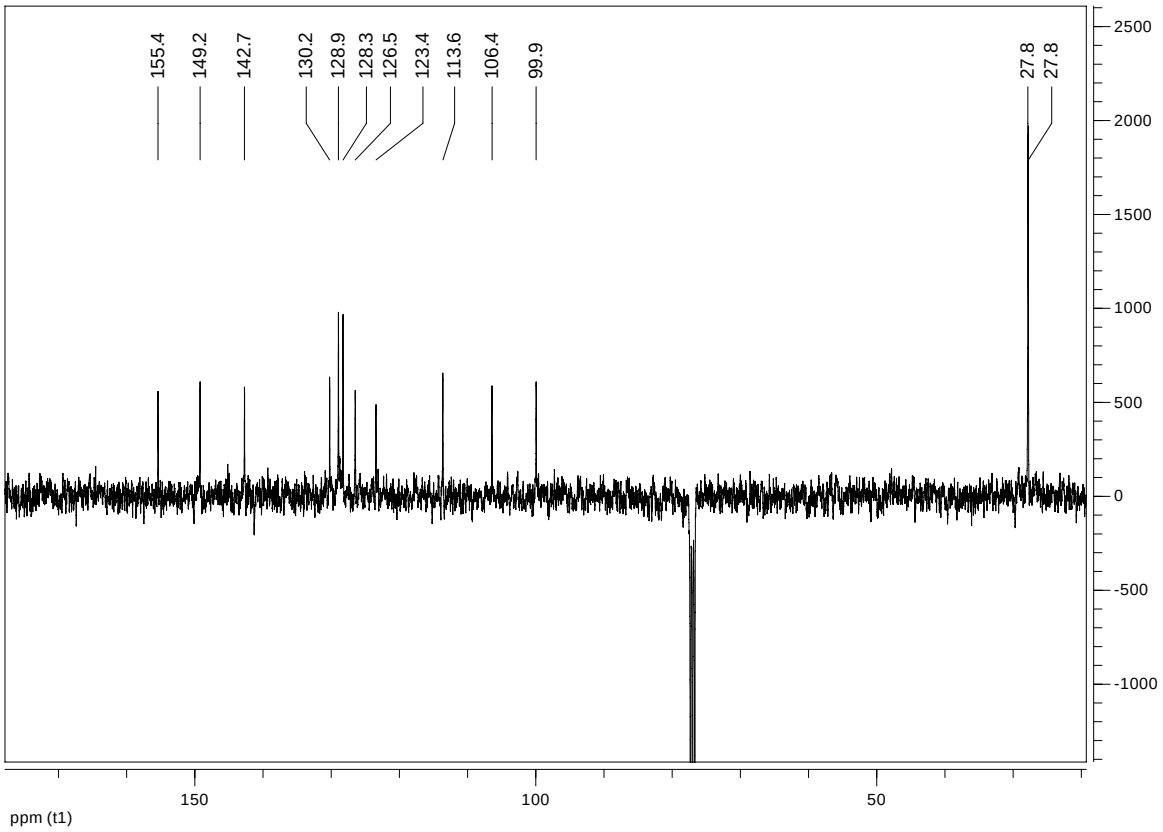
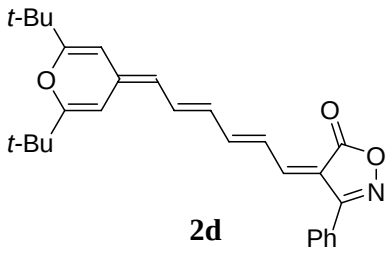


Figure S-14: ^{13}C-NMR (APT) spectrum of compound **2d** (100 MHz, $CDCl_3$).



2d

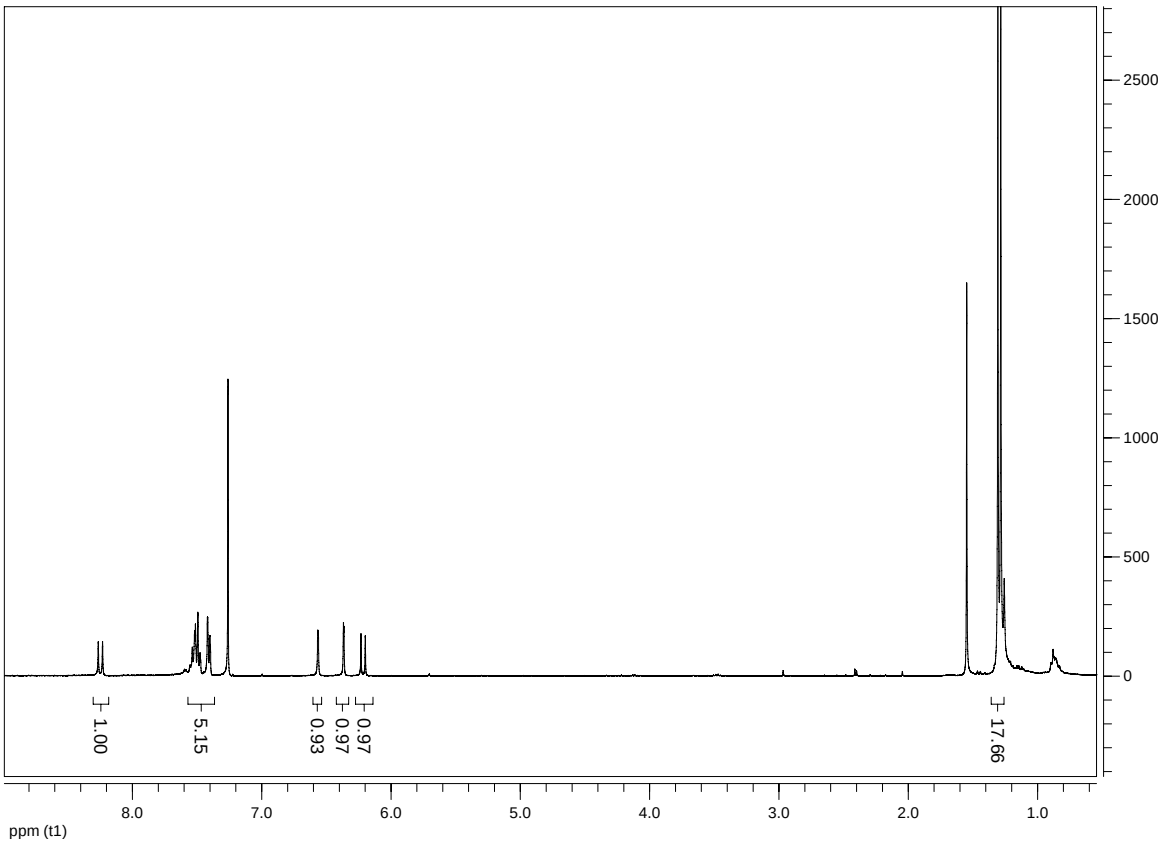
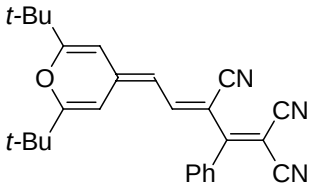


Figure S-15: ^{1}H-NMR spectrum of compound **3b** (400 MHz, $CDCl_3$).



3b

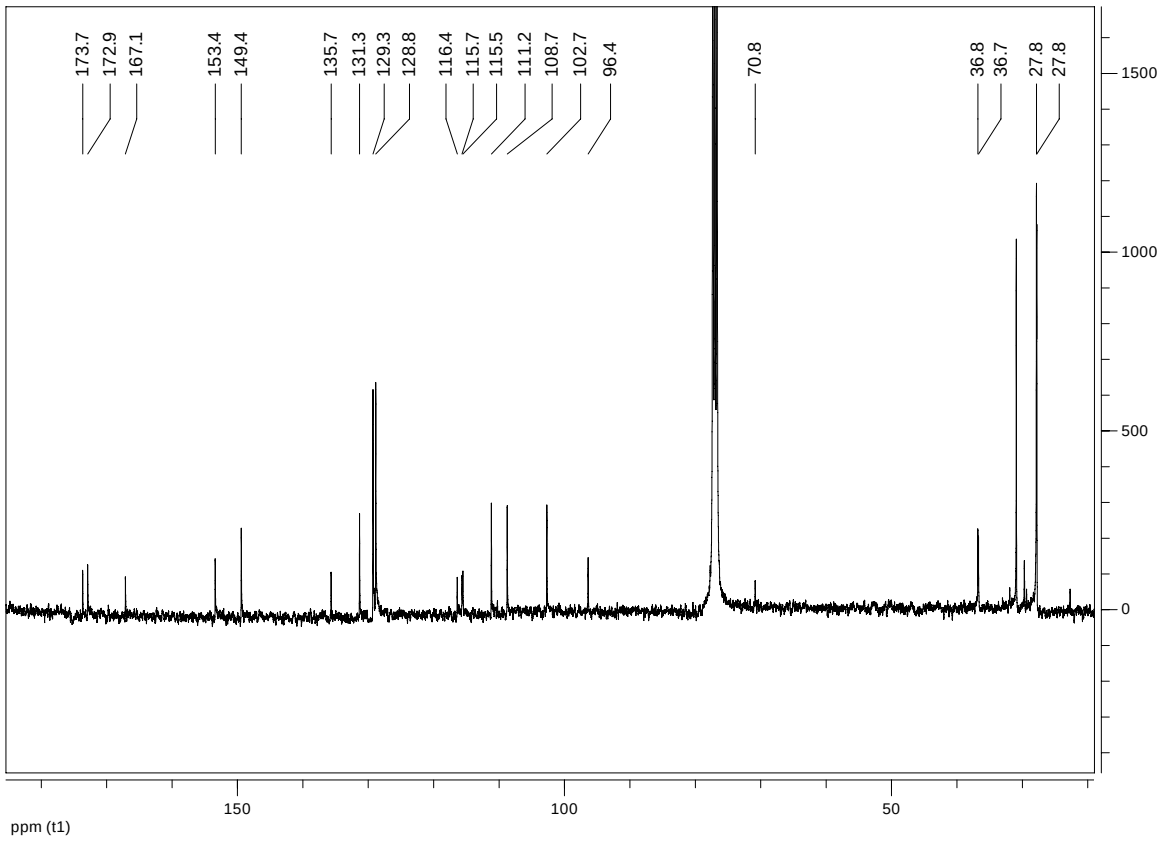
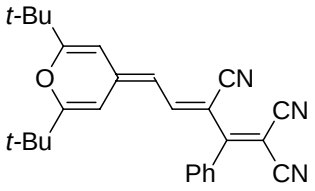


Figure S-16: ^{13}C-NMR spectrum of compound **3b** (100 MHz, $CDCl_3$).



3b

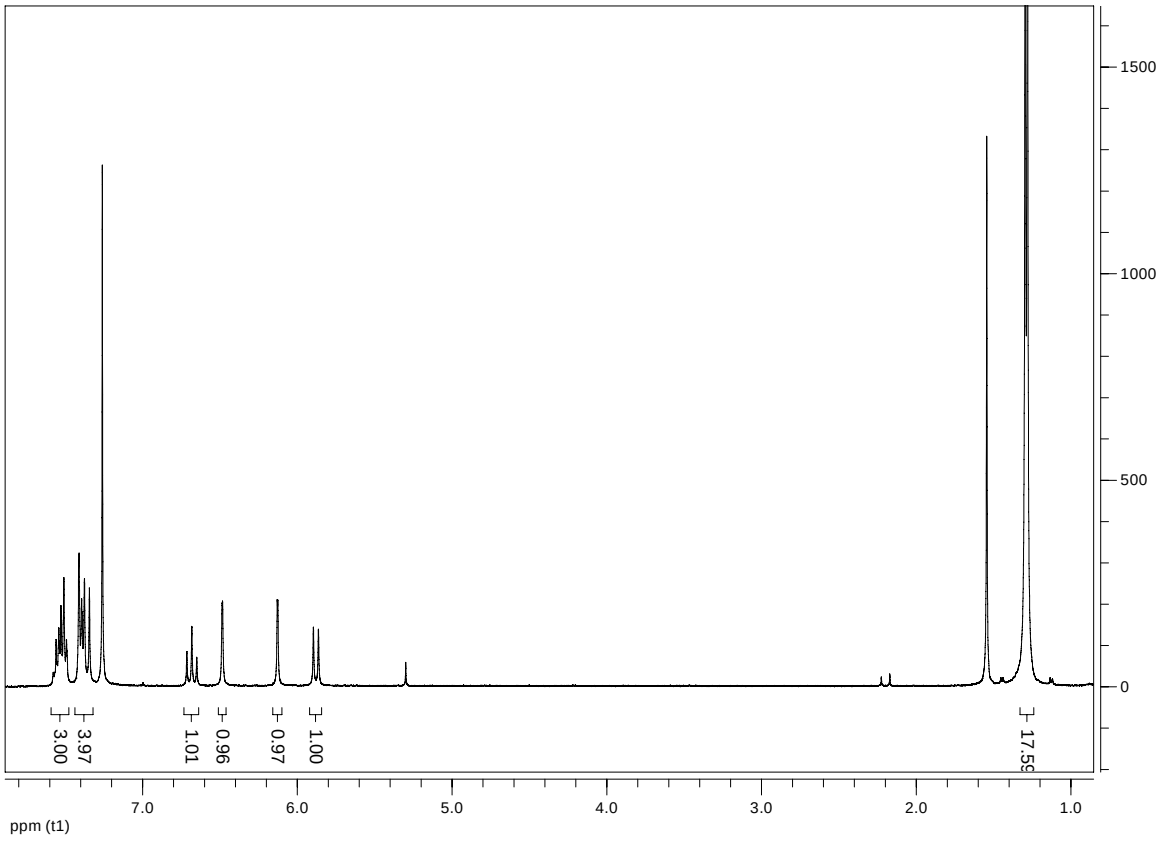
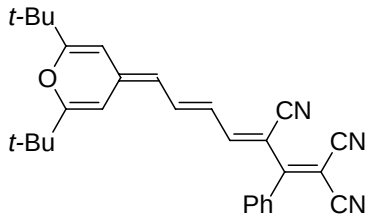


Figure S-17: ^{1}H-NMR spectrum of compound **3c** (400 MHz, $CDCl_3$).



3c

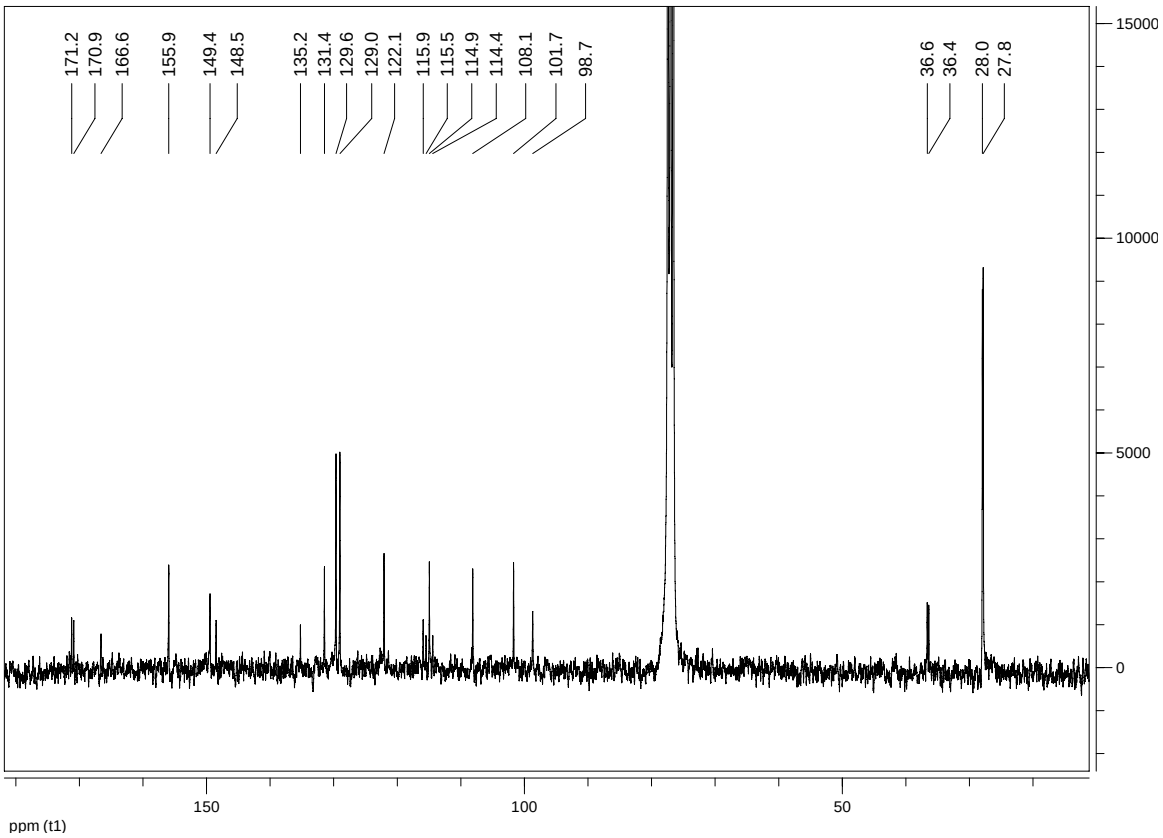
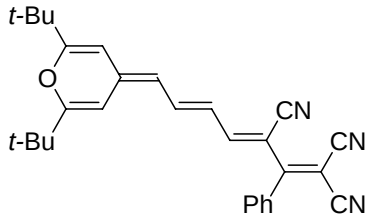


Figure S-18: ^{13}C-NMR spectrum of compound **3c** (75 MHz, $CDCl_3$).



3c

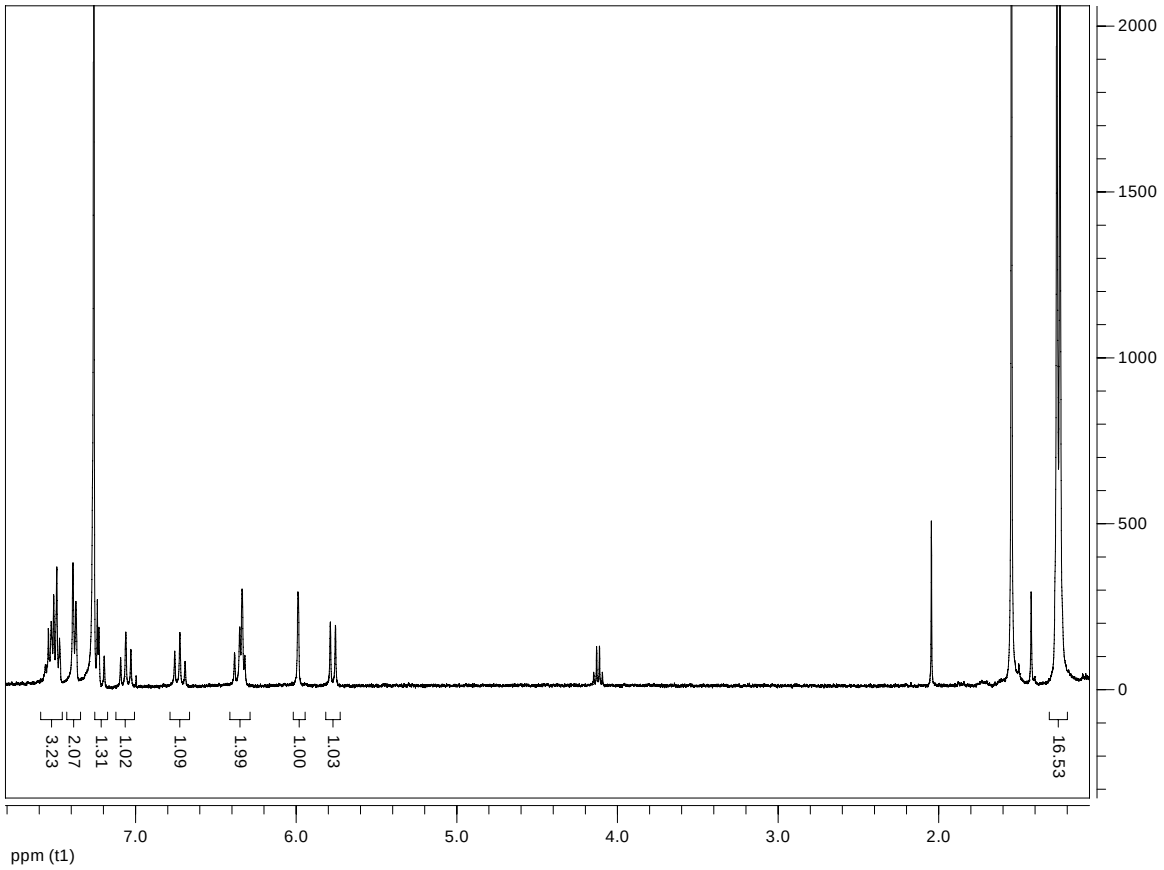
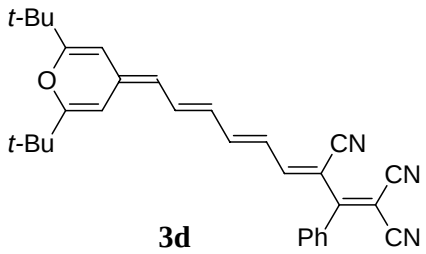


Figure S-19: ^{1}H-NMR spectrum of compound **3d** (400 MHz, $CDCl_3$).



3d

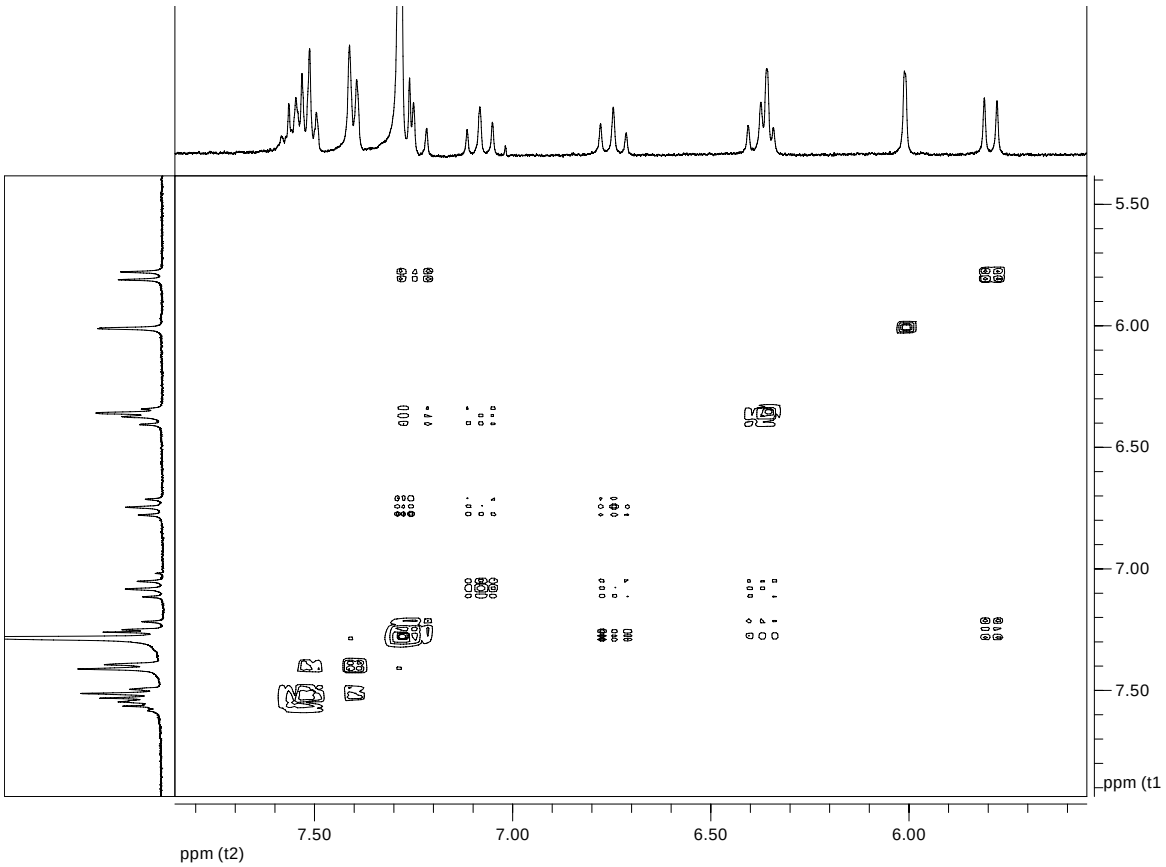
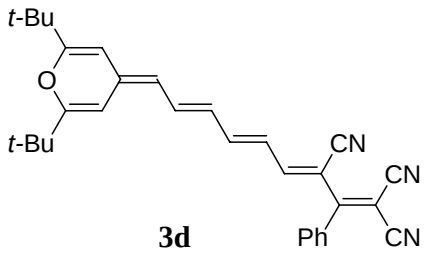


Figure S-20: ^{1}H-^{1}H COSY spectrum of compound **3d** (400 MHz, $CDCl_3$).



3d

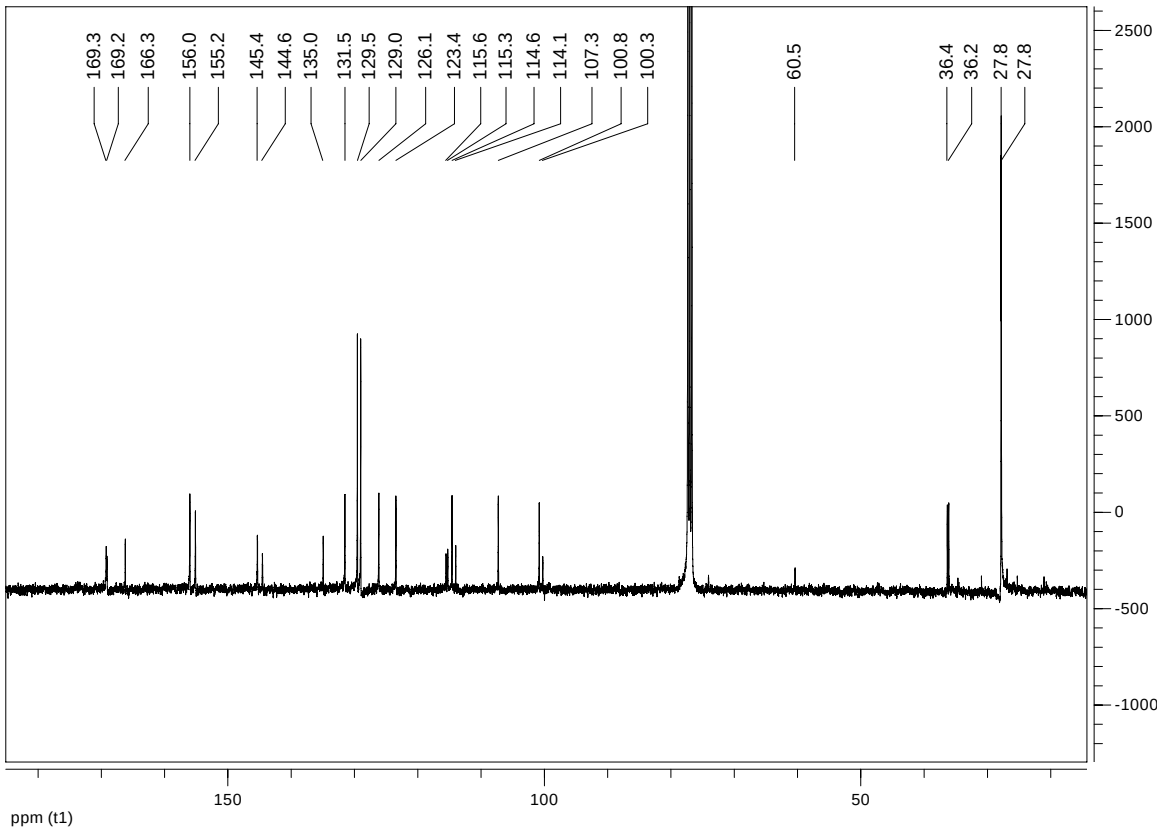
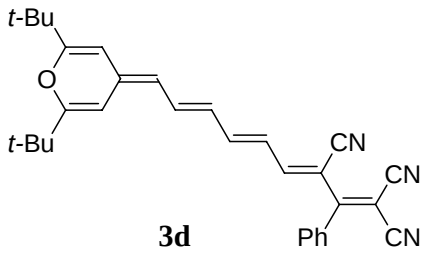


Figure S-21: ^{13}C-NMR spectrum of compound **3d** (100 MHz, $CDCl_3$).



3d

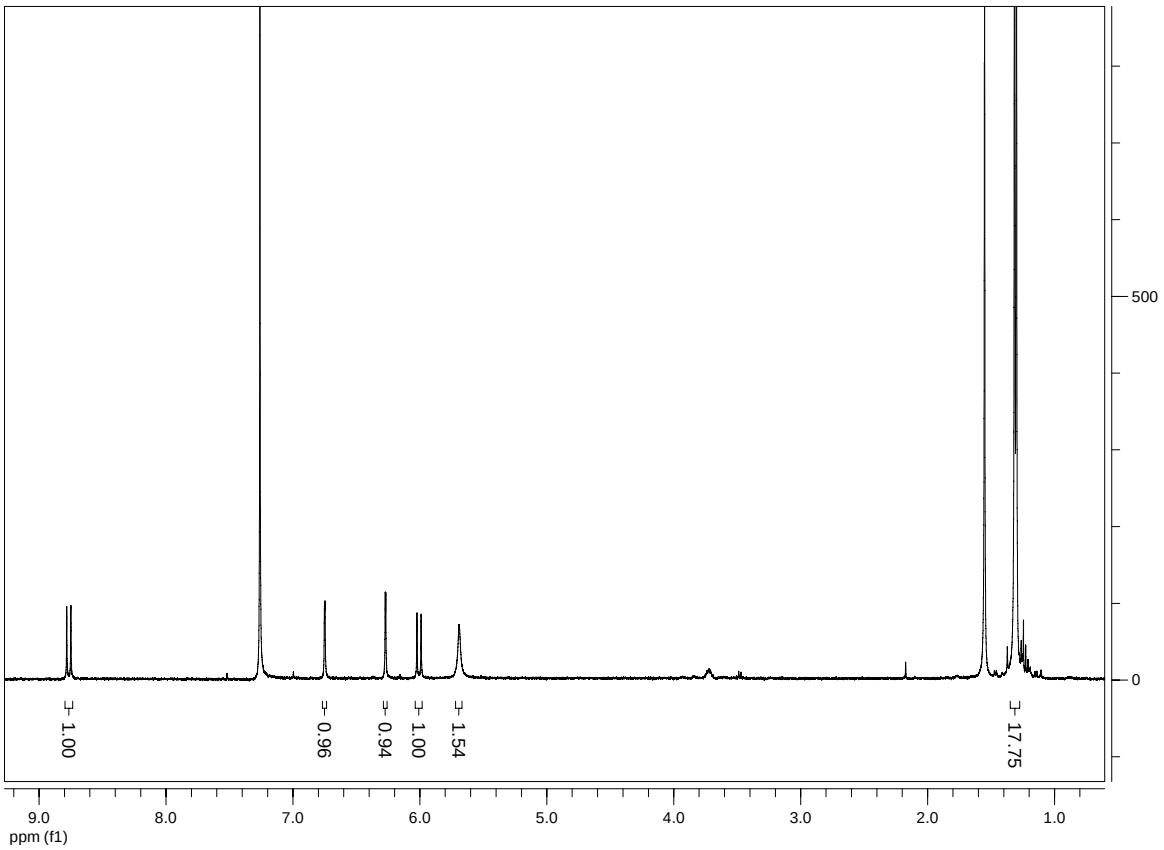
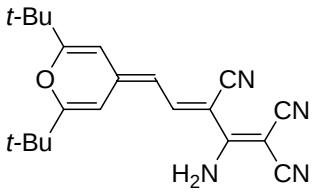


Figure S-22: ^{1}H-NMR spectrum of compound **4b** (400 MHz, $CDCl_3$).



4b

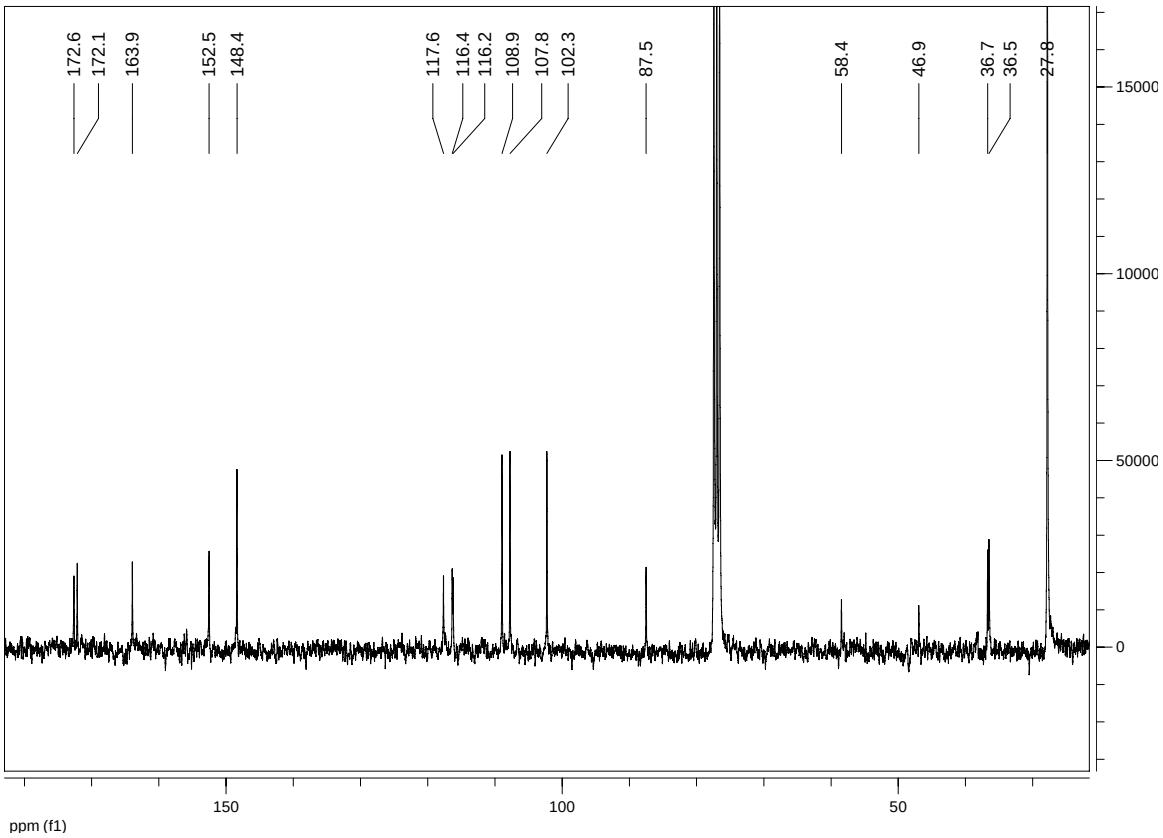
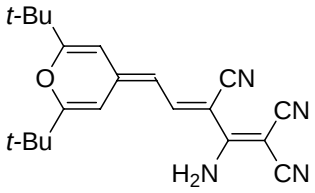


Figure S-23: ^{13}C spectrum of compound **4b** (75 MHz, $CDCl_3$).



4b

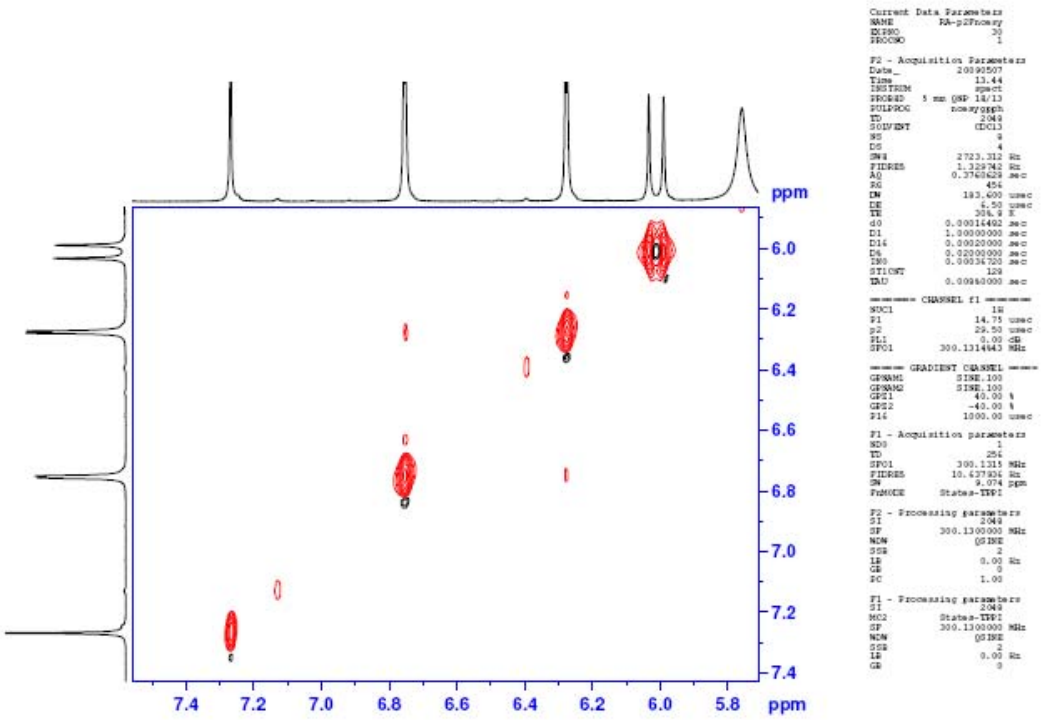
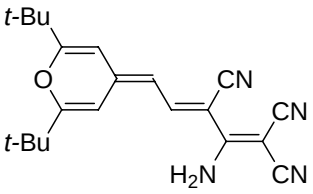


Figure S-24: 2D ^{1}H-EXSY experiment for compound **4b** (300 MHz, 30ºC, $CDCl_3$). (mixing time: 20 ms).



4b

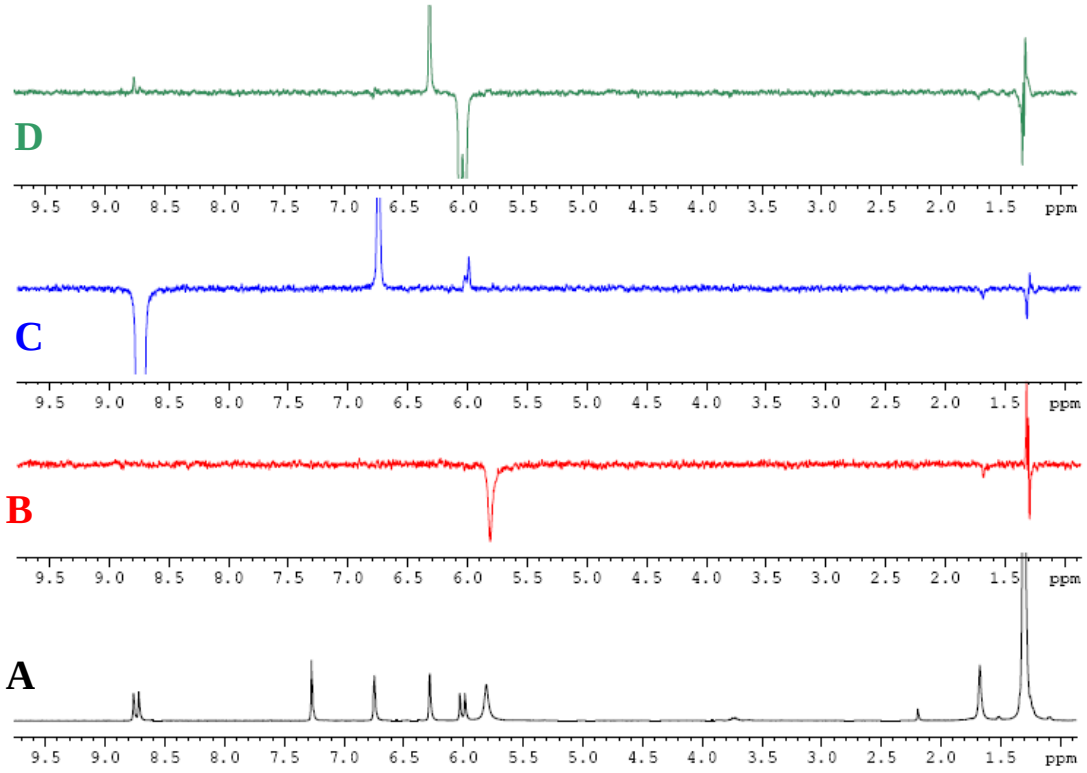


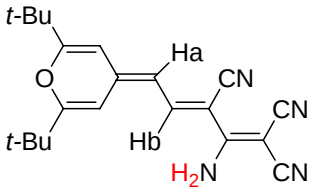
Figure S-25: Selective NOE experiments for compound **4b** (300 MHz, 0ºC, $CDCl_3$).

A) ^1H spectrum.

B) Spectrum after saturation of NH_2 (δ = 5.82 ppm) (mixing time: 1 s).

C) Spectrum after saturation of Hb (δ = 8. 74 ppm) (mixing time: 1 s).

D) Spectrum after saturation of Ha (δ = 6. 01 ppm) (mixing time: 1.87 s).



4b

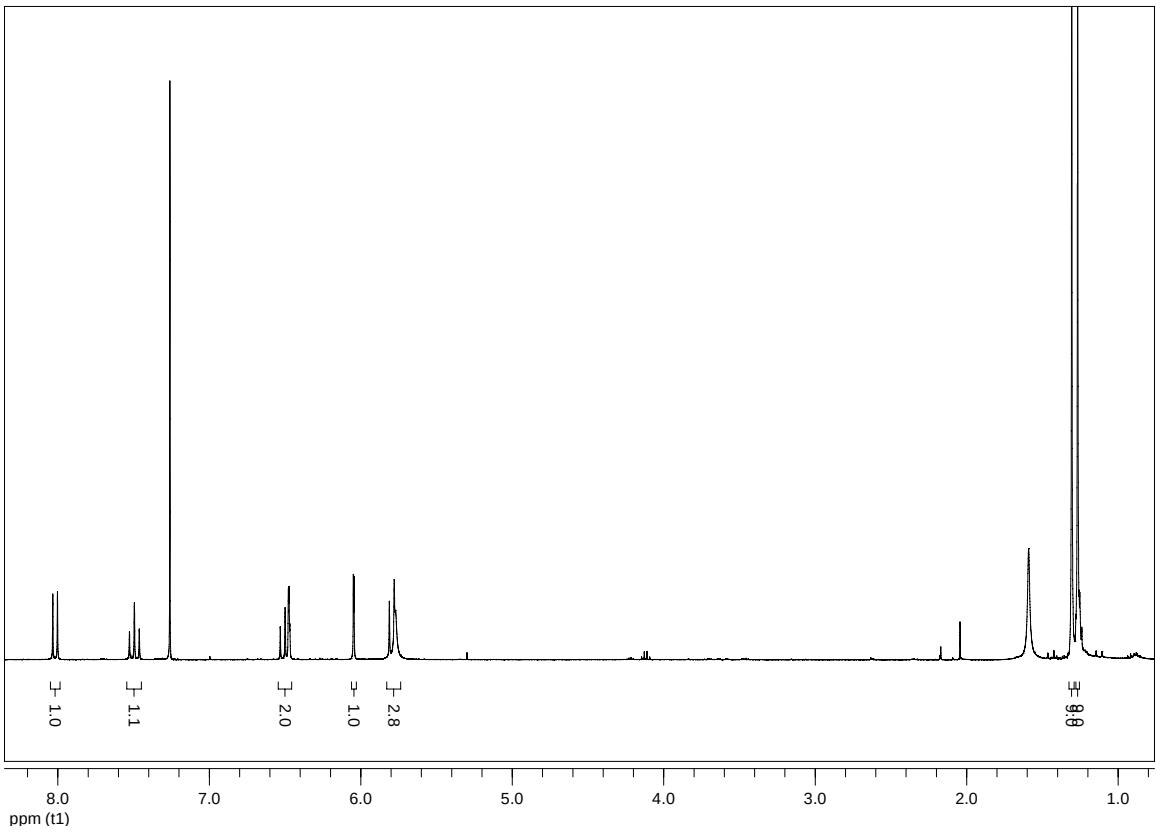
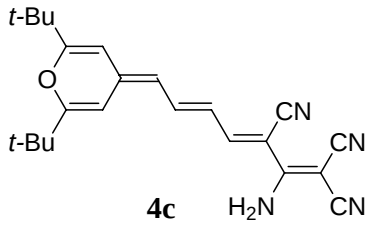


Figure S-26: ^{1}H-NMR spectrum of compound **4c** (400 MHz, $CDCl_3$).



4c

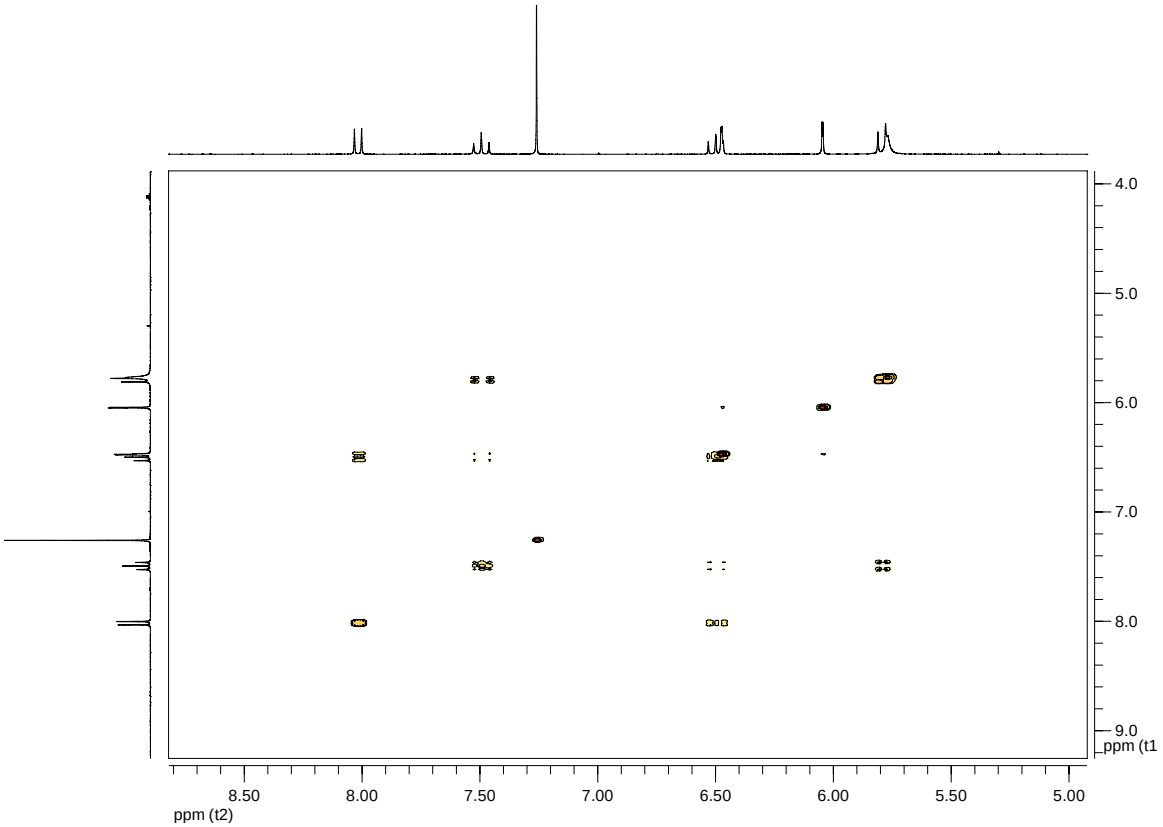
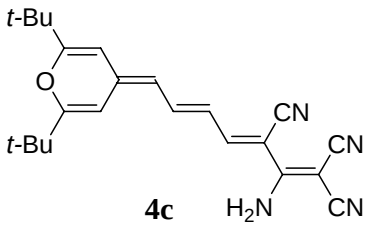


Figure S-27: ^{1}H-^{1}H COSY spectrum of compound **4c** (400 MHz, $CDCl_3$).



4c

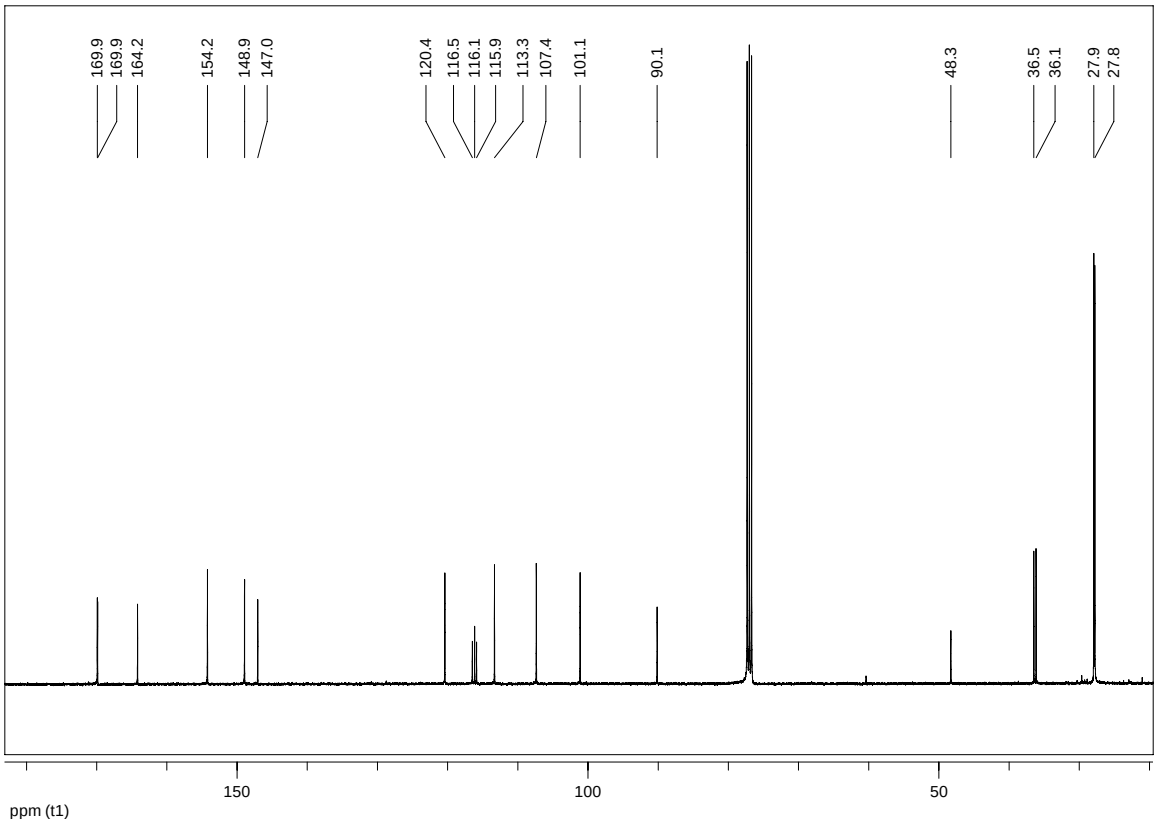
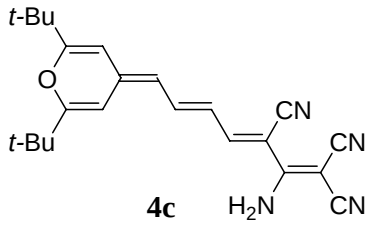


Figure S-28: ^{13}C spectrum of compound **4c** (100 MHz, $CDCl_3$).



4c

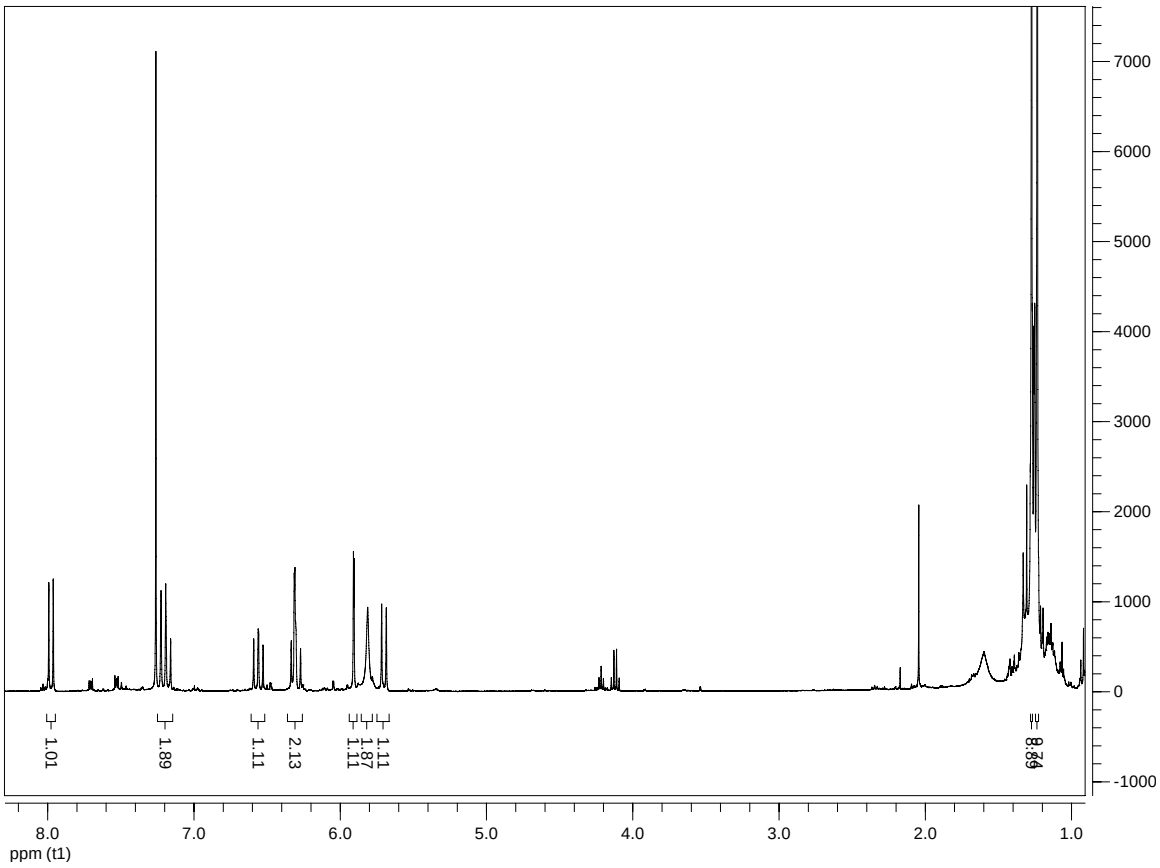
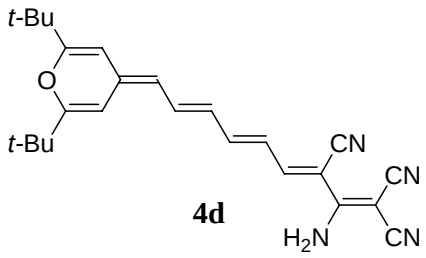


Figure S-29: ^{1}H-NMR spectrum of compound **4d** (400 MHz, $CDCl_3$).



4d

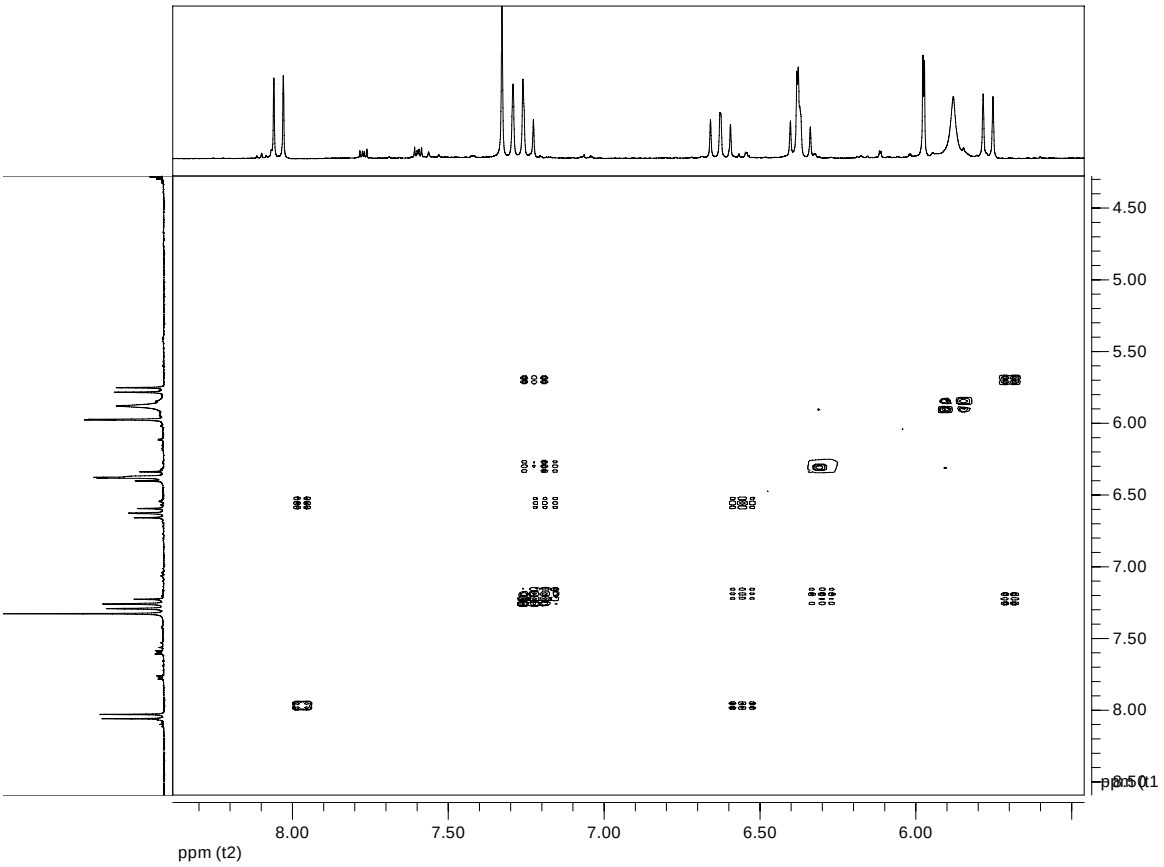
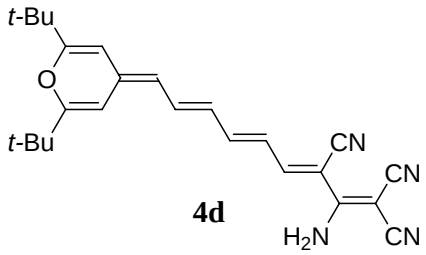


Figure S-30: ^{1}H-^{1}H COSY spectrum of compound **4d** (400 MHz, $CDCl_3$).



4d

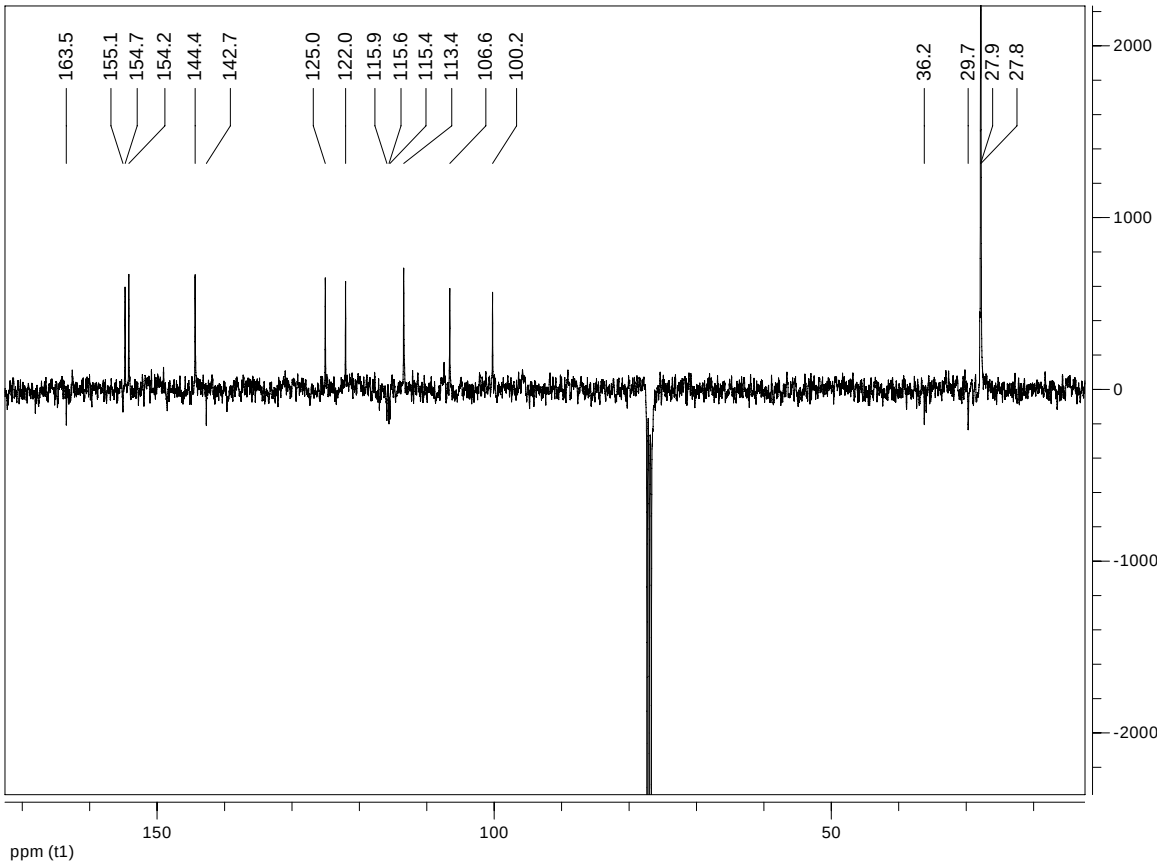
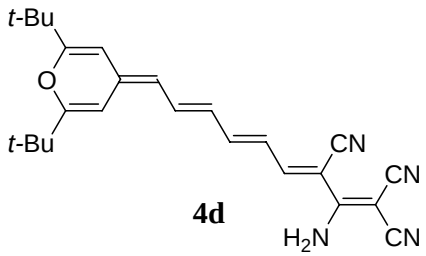


Figure S-31: ^{13}C spectrum (APT) of compound **4d** (100 MHz, $CDCl_3$).



4d

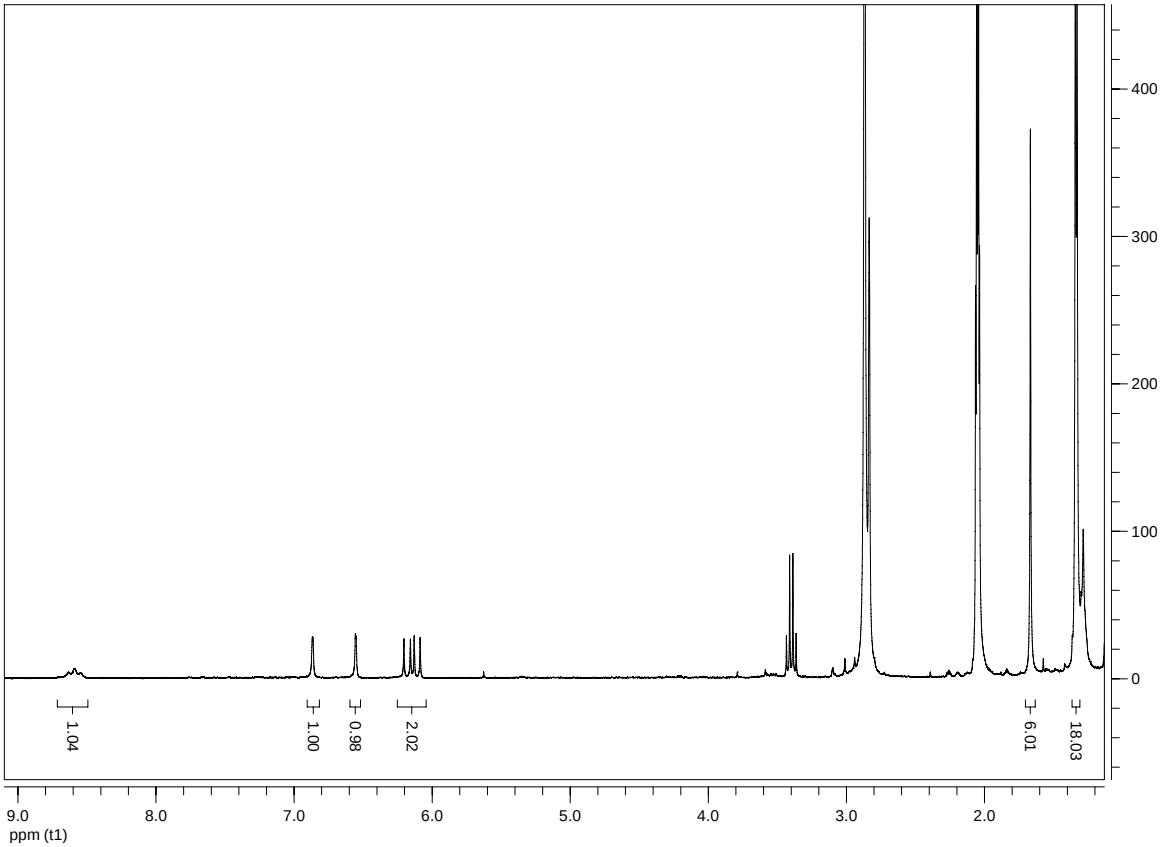
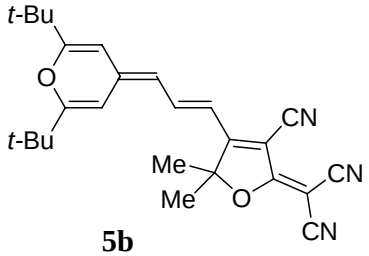


Figure S-32: ^{1}H spectrum of compound **5b** (300 MHz, C_2D_6CO).



5b

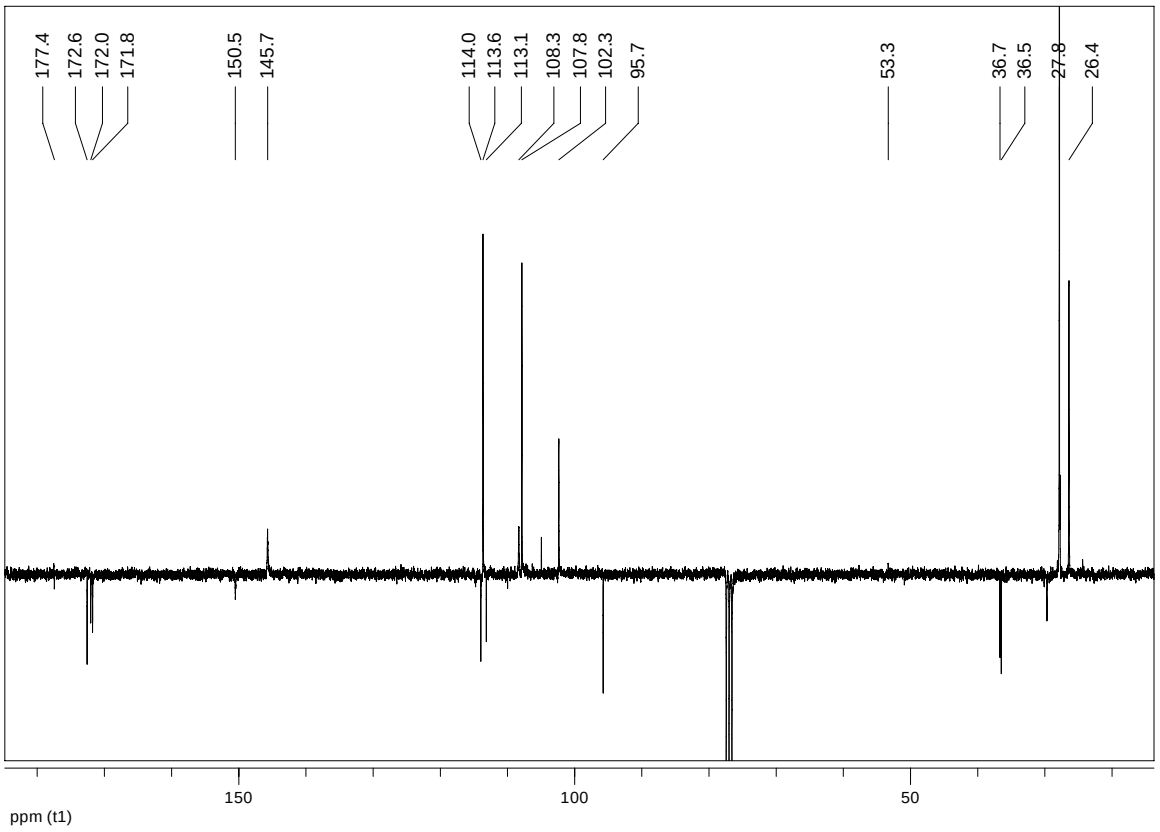
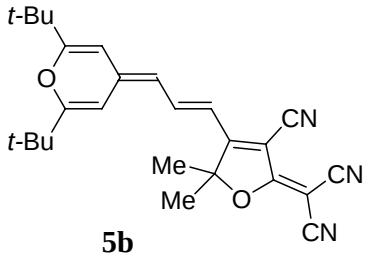


Figure S-33: ^{13}C spectrum of compound **5b** (75 MHz, $CDCl_3$).



5b

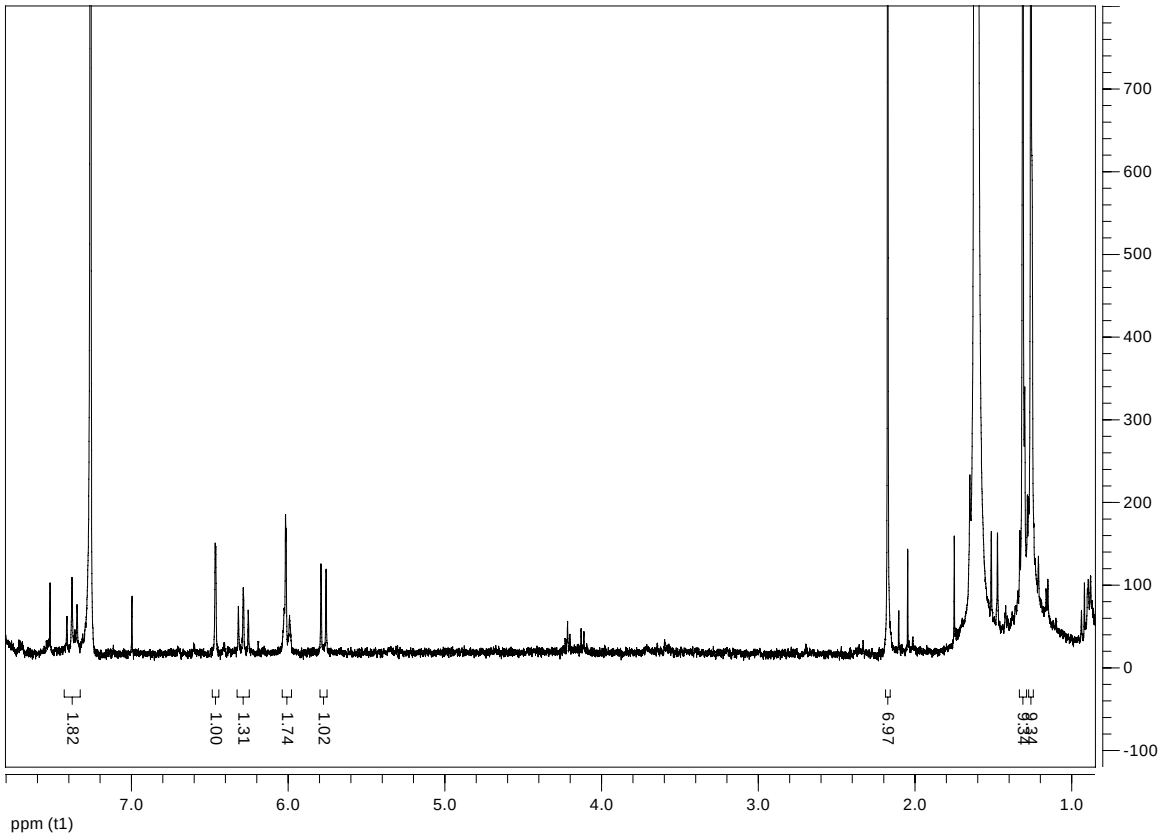
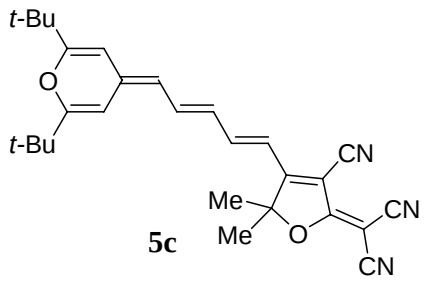


Figure S-34: ^{1}H spectrum of compound **5c** (400 MHz, $CDCl_3$).



5c

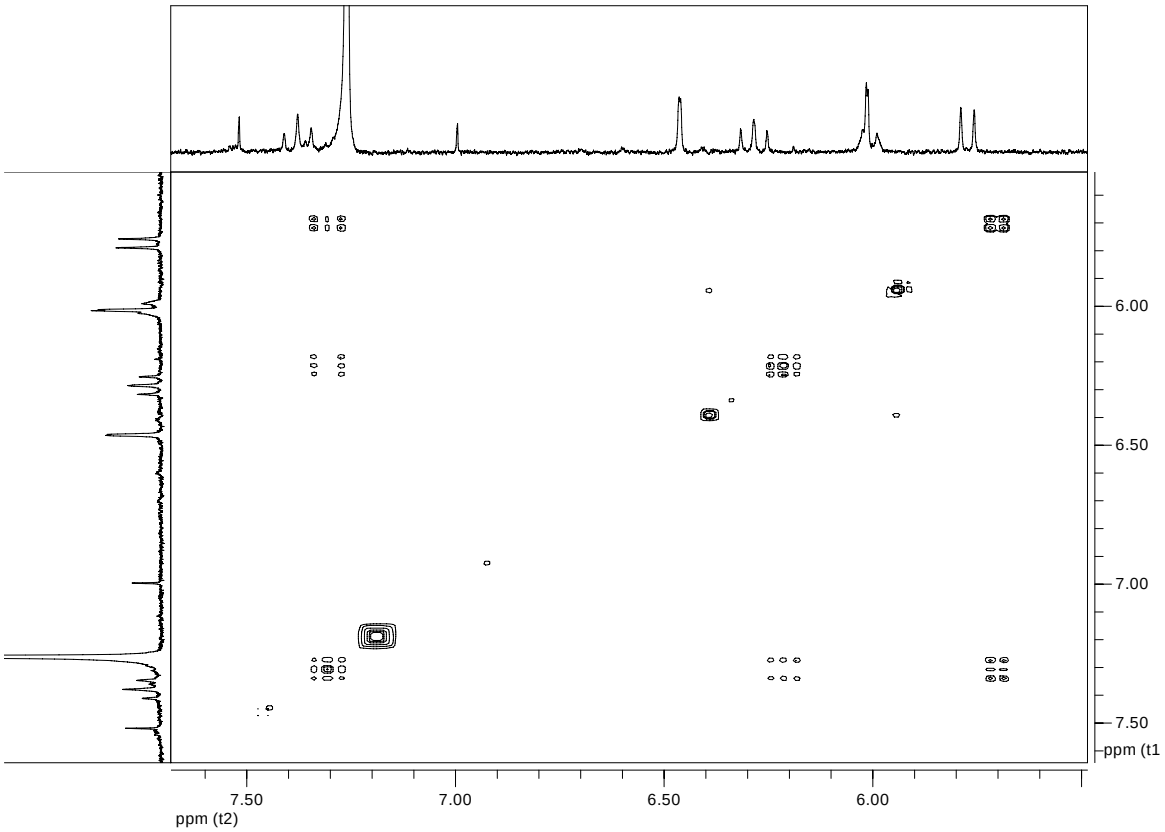
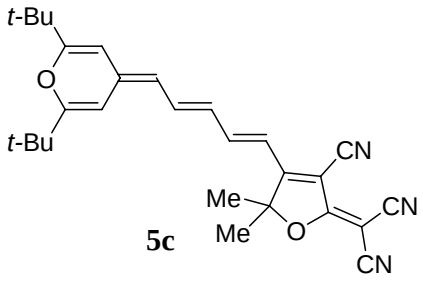


Figure S-35: ^{1}H-^{1}H COSY spectrum of compound **5c** (400 MHz, $CDCl_3$).



5c

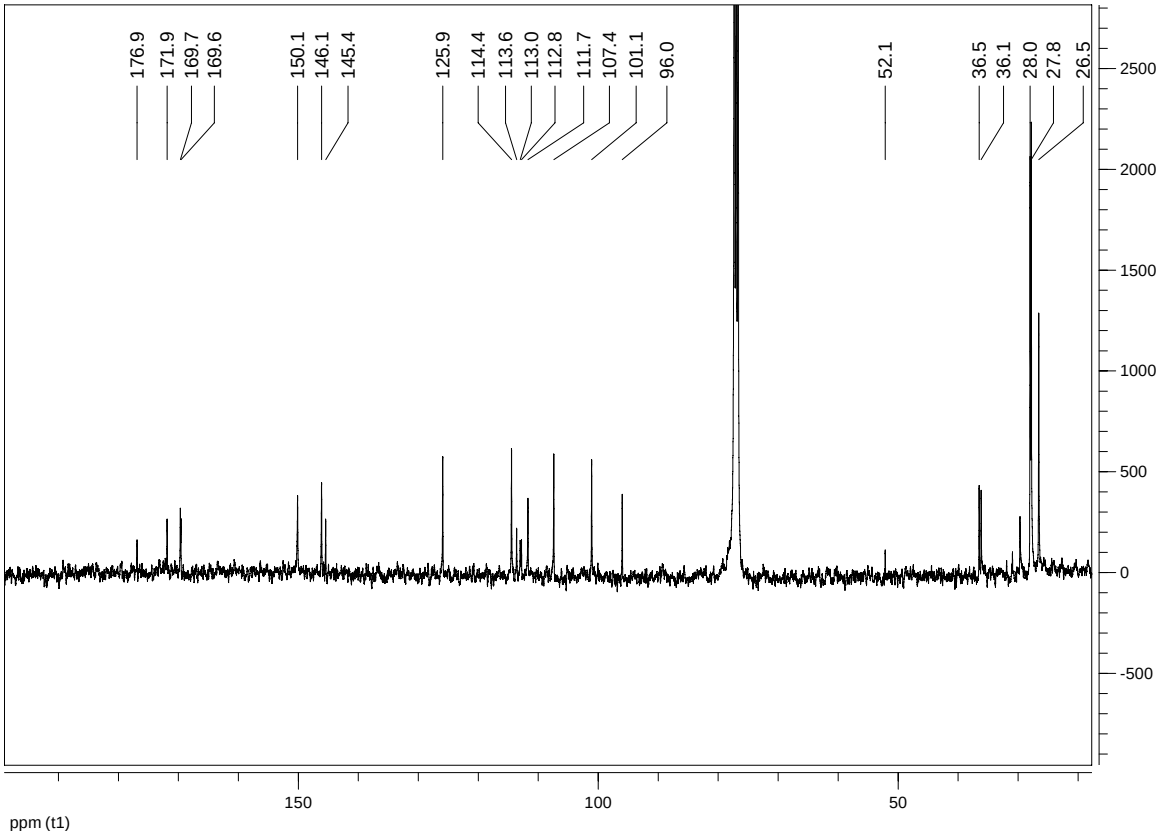
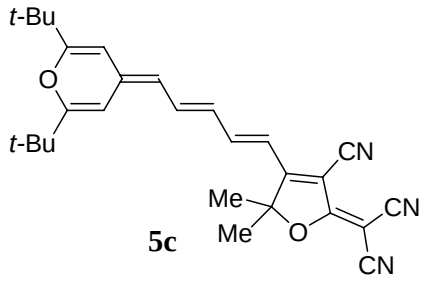


Figure S-36: ^{13}C spectrum of compound **5c** (100 MHz, $CDCl_3$).



5c

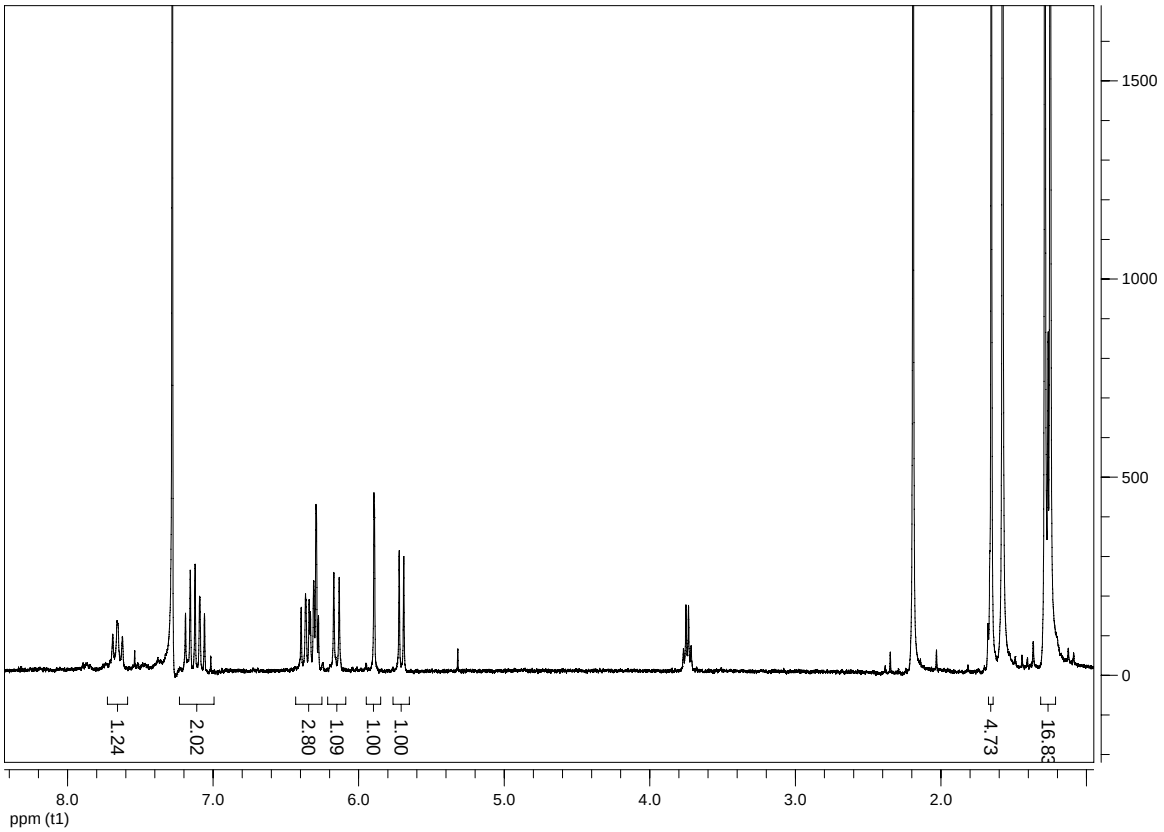
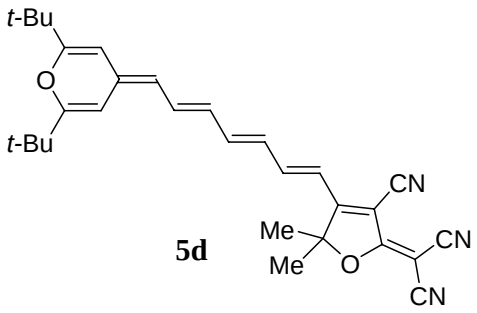


Figure S-37: ^{1}H spectrum of compound **5d** (400 MHz, $CDCl_3$).



5d

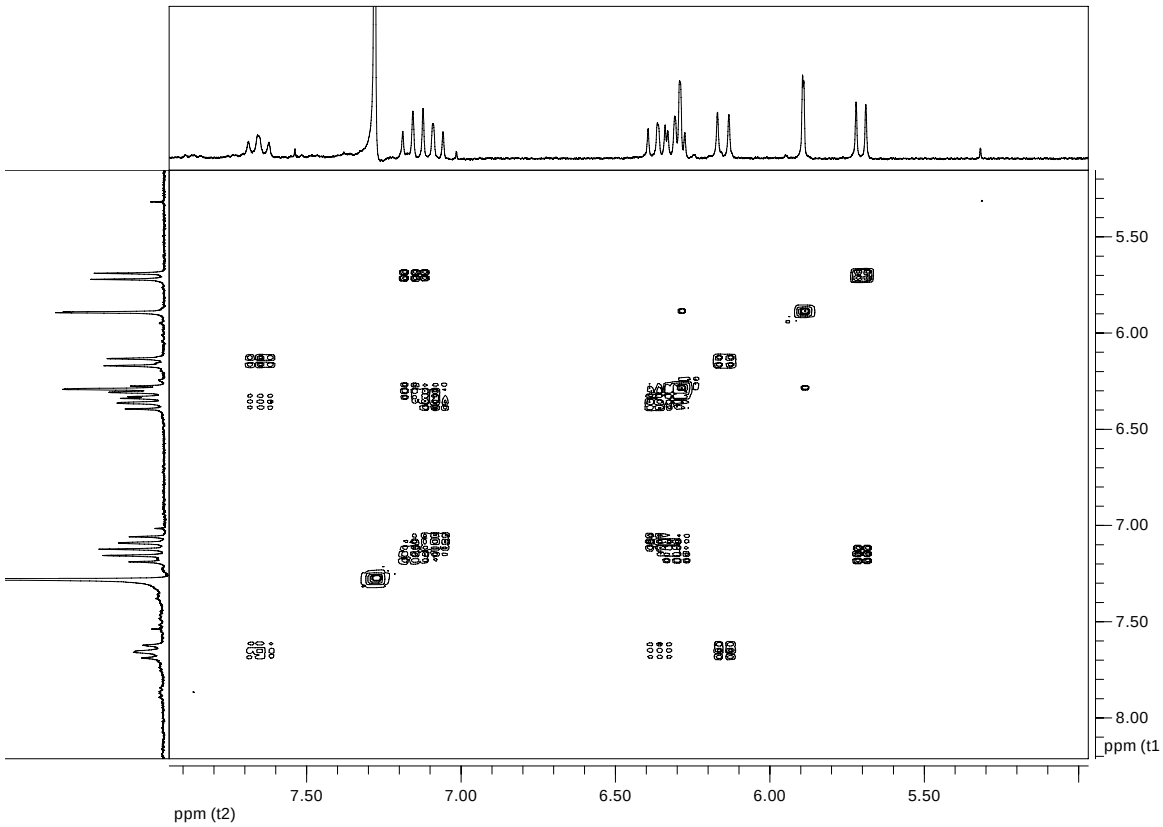
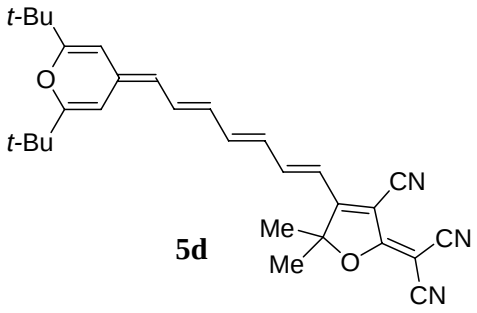


Figure S-38: ^{1}H-^{1}H COSY spectrum of compound **5d** (400 MHz, $CDCl_3$).



5d

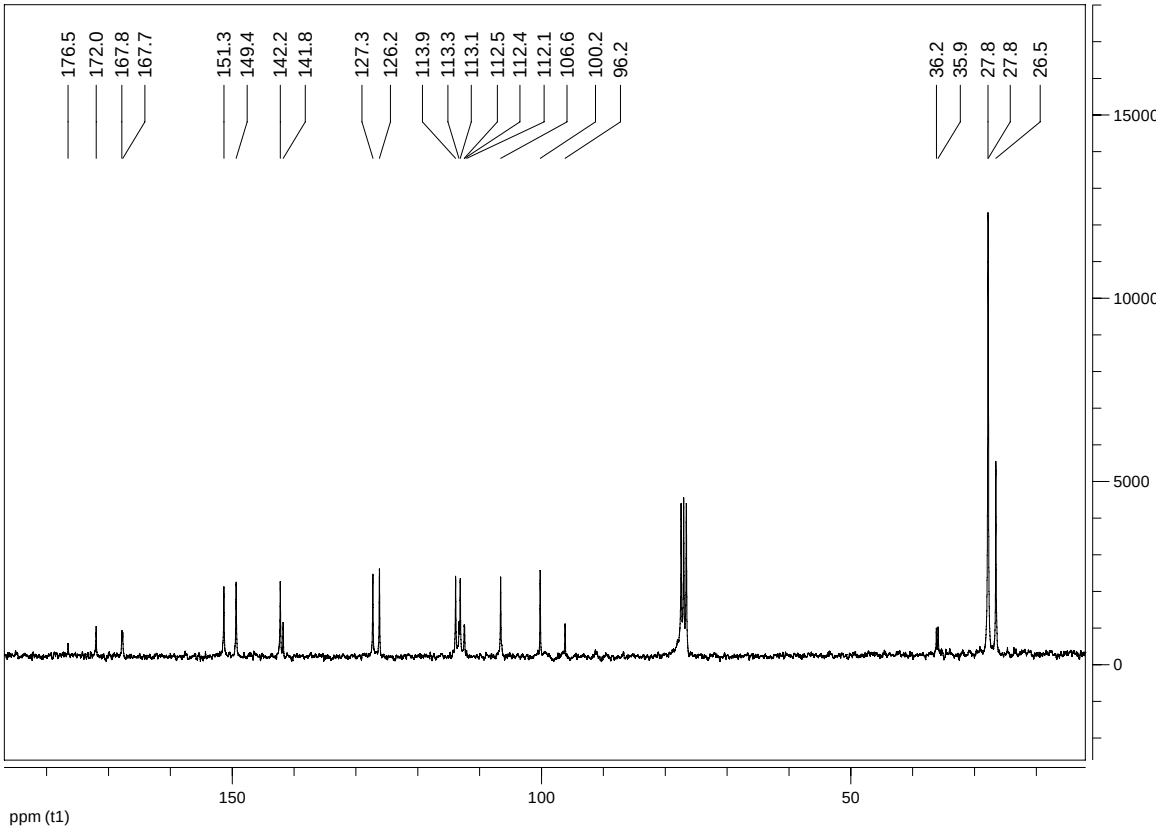
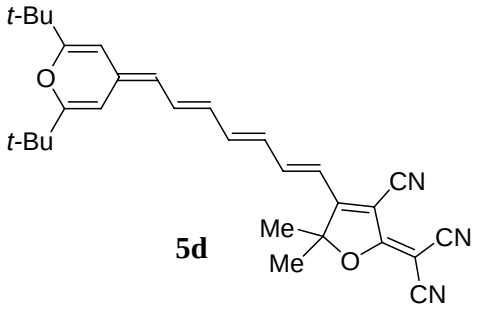


Figure S-39: ^{13}C spectrum of compound **5d** (75 MHz, $CDCl_3$).



5d

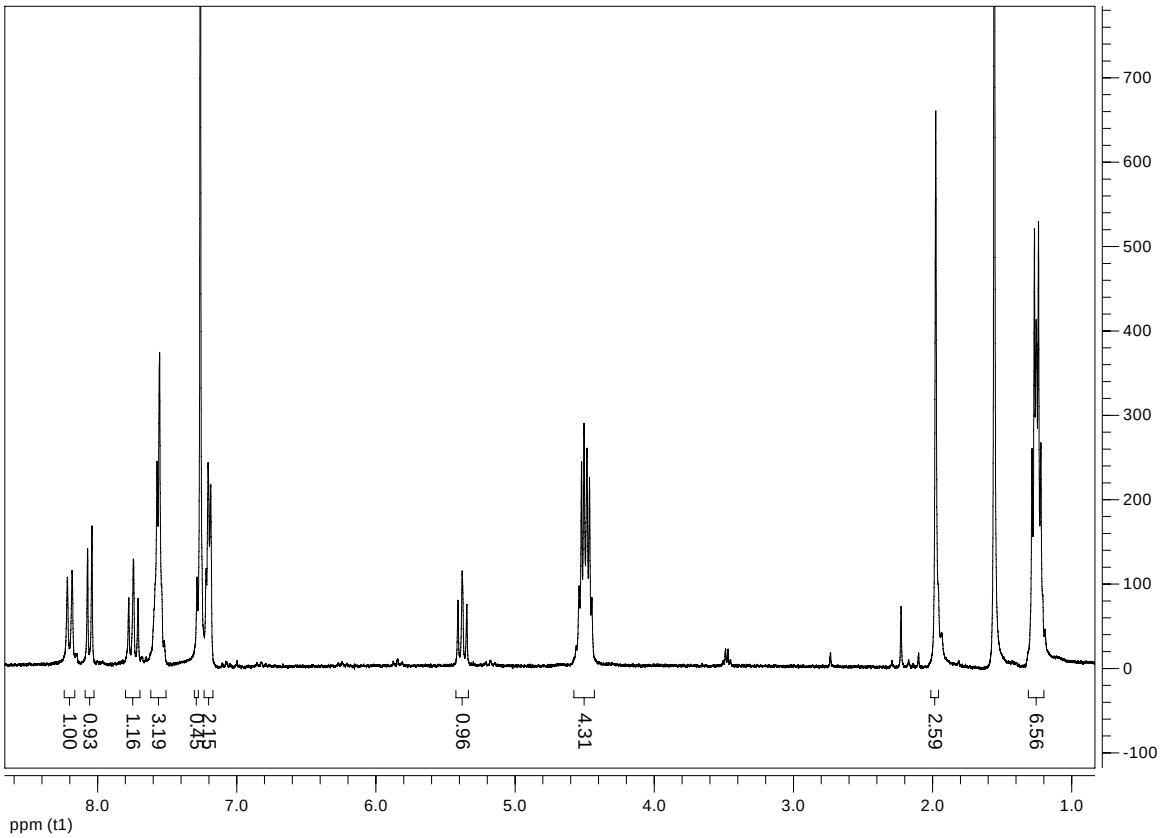
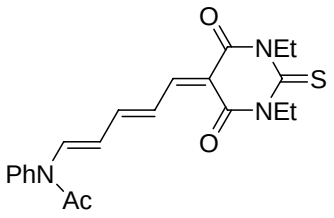


Figure S-40: ^{1}H spectrum of compound **8'** (400 MHz, $CDCl_3$).



8'

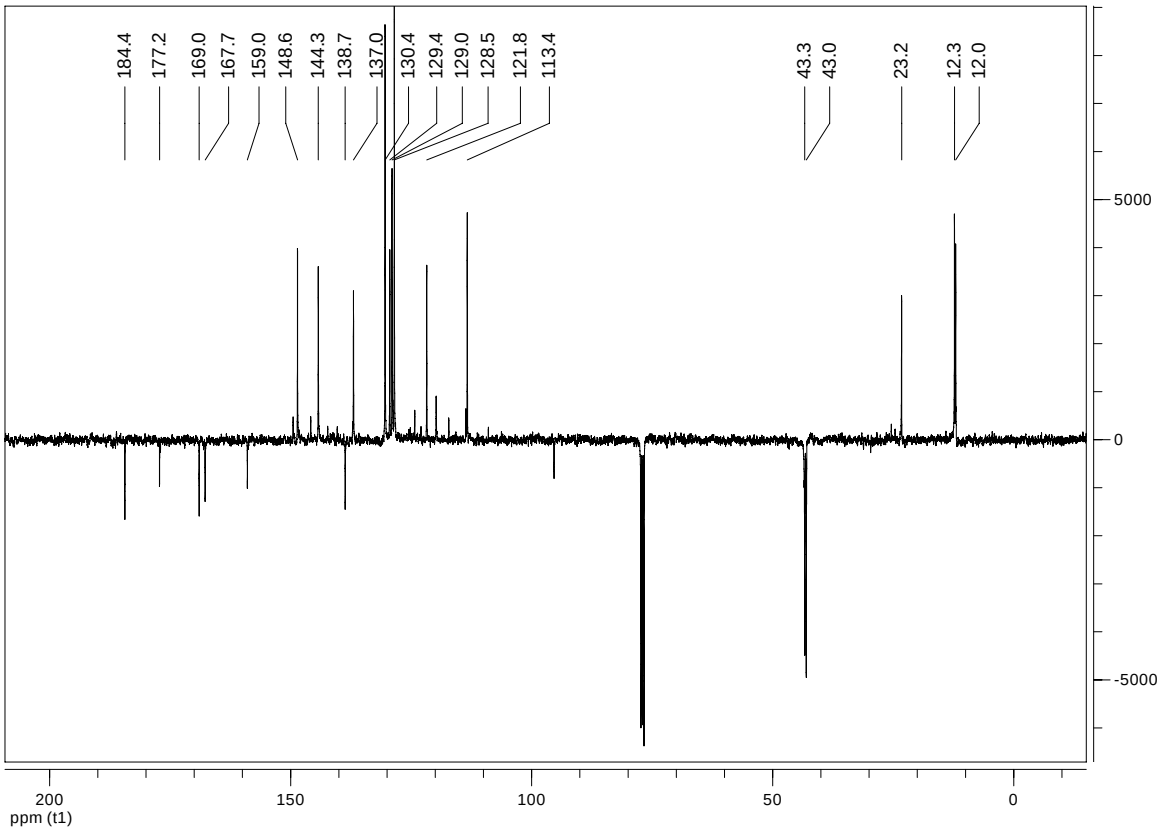
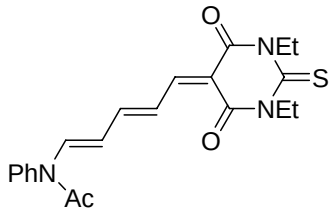


Figure S-41: ^{13}C spectrum (APT) of compound **8'** (100 MHz, $CDCl_3$).



8'

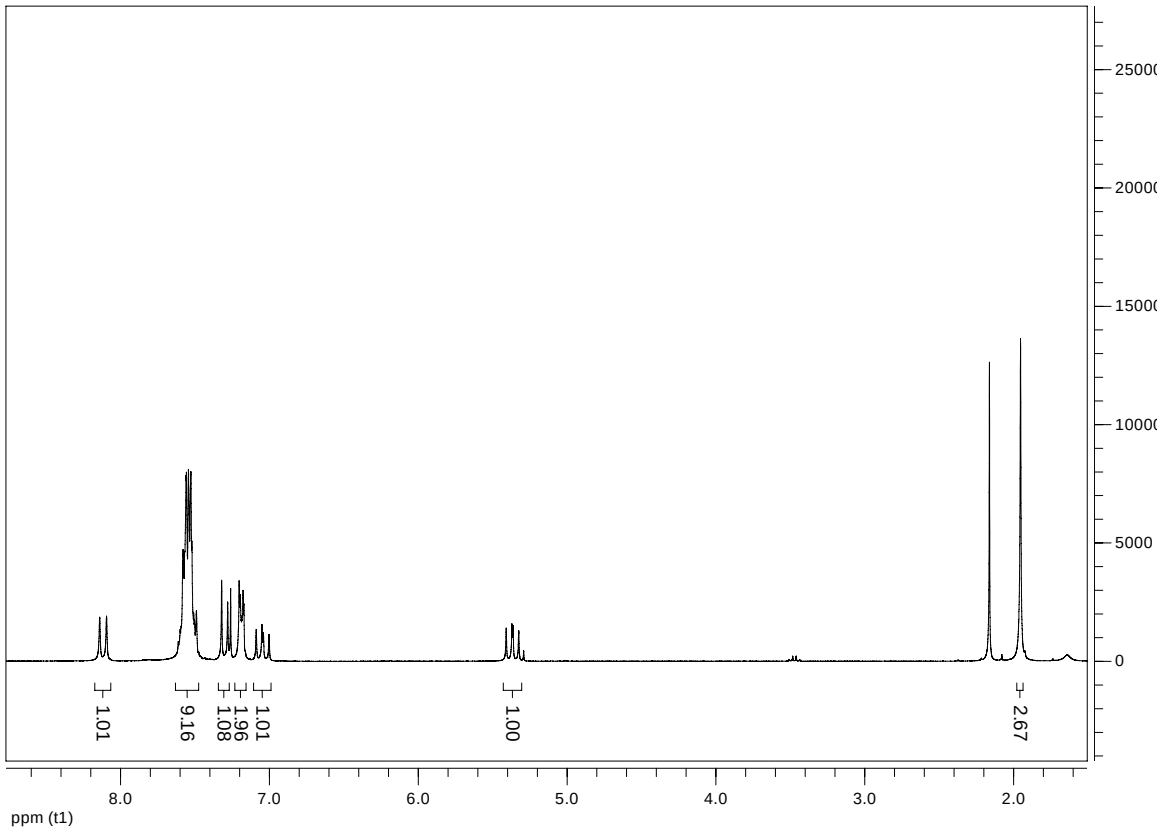
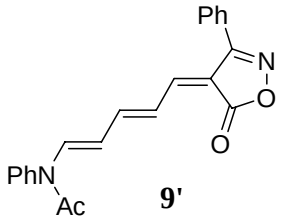


Figure S-42: ^{1}H spectrum of compound **9'** (300 MHz, $CDCl_3$).



9'

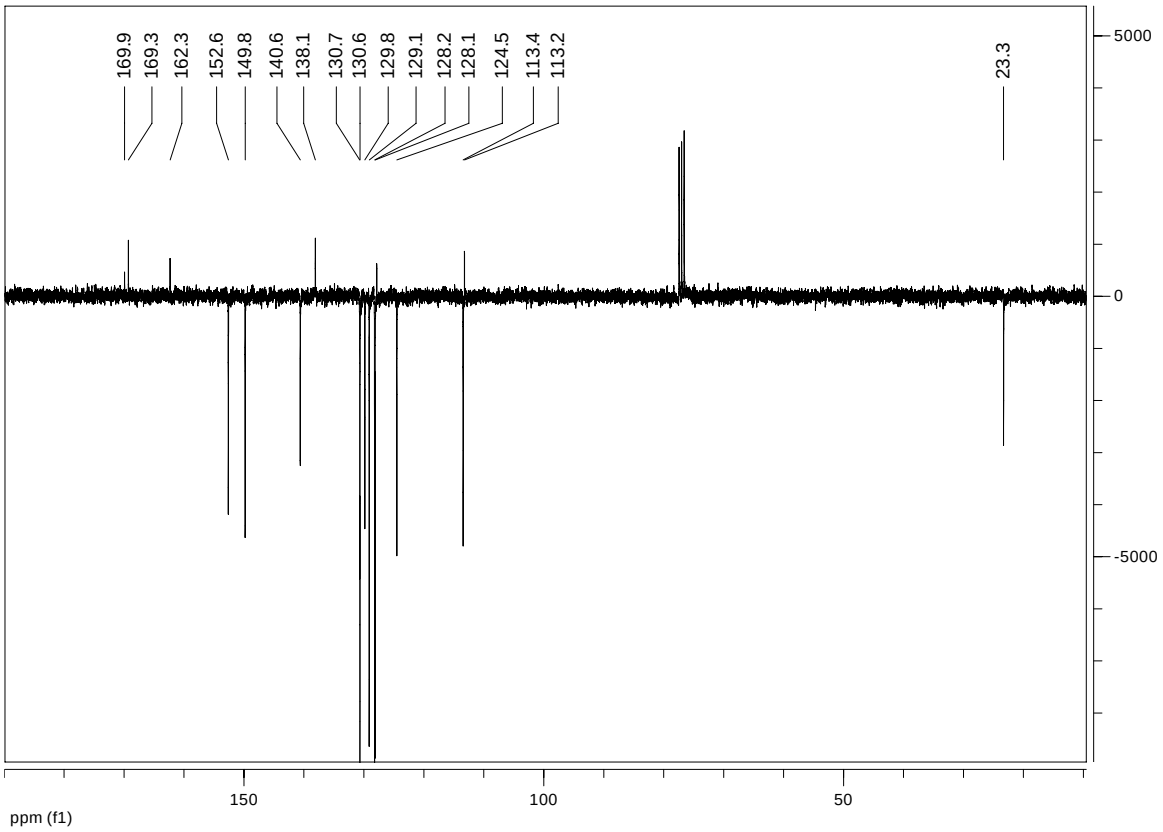
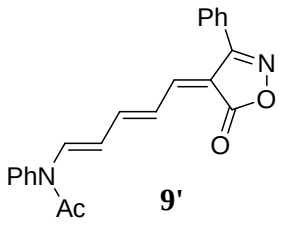


Figure S-43: ^{13}C spectrum (APT) of compound **9'** (75 MHz, $CDCl_3$).



9'

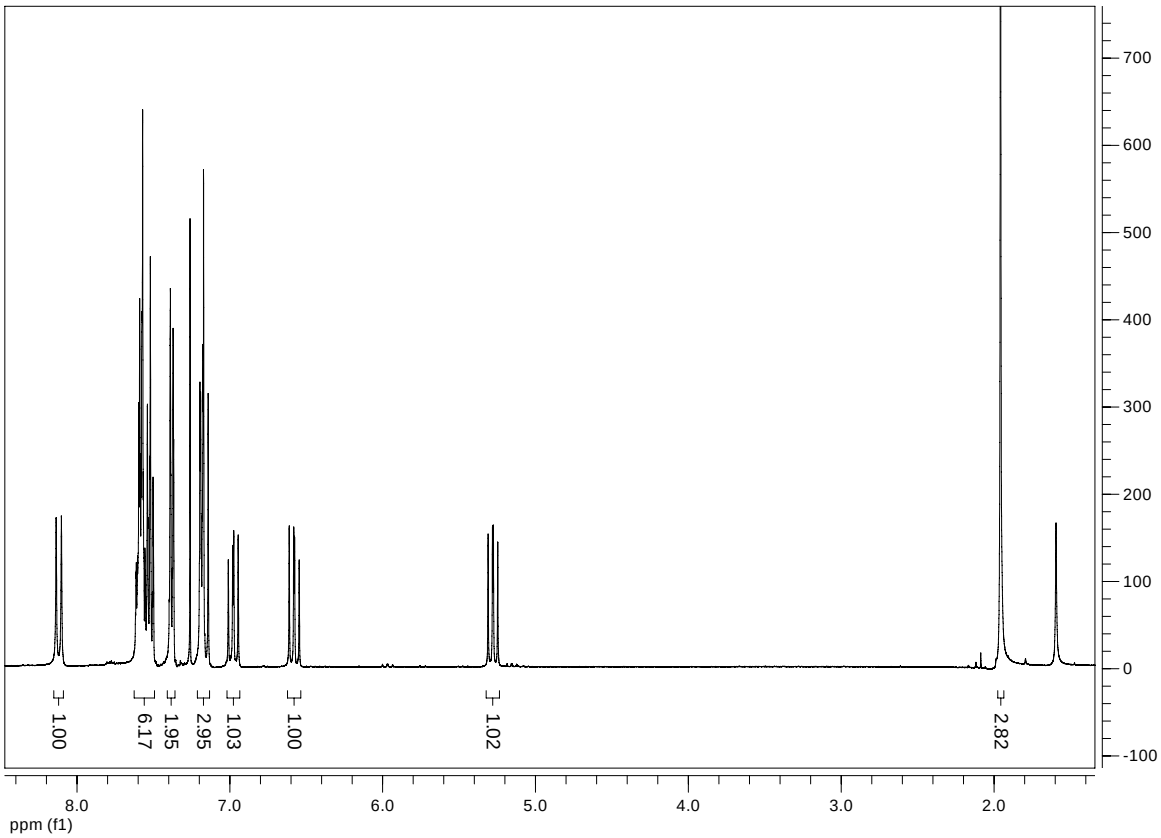
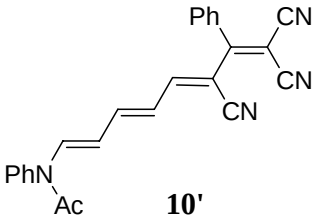


Figure S-44: ^{1}H spectrum of compound **10'** (400 MHz, $CDCl_3$).



10'

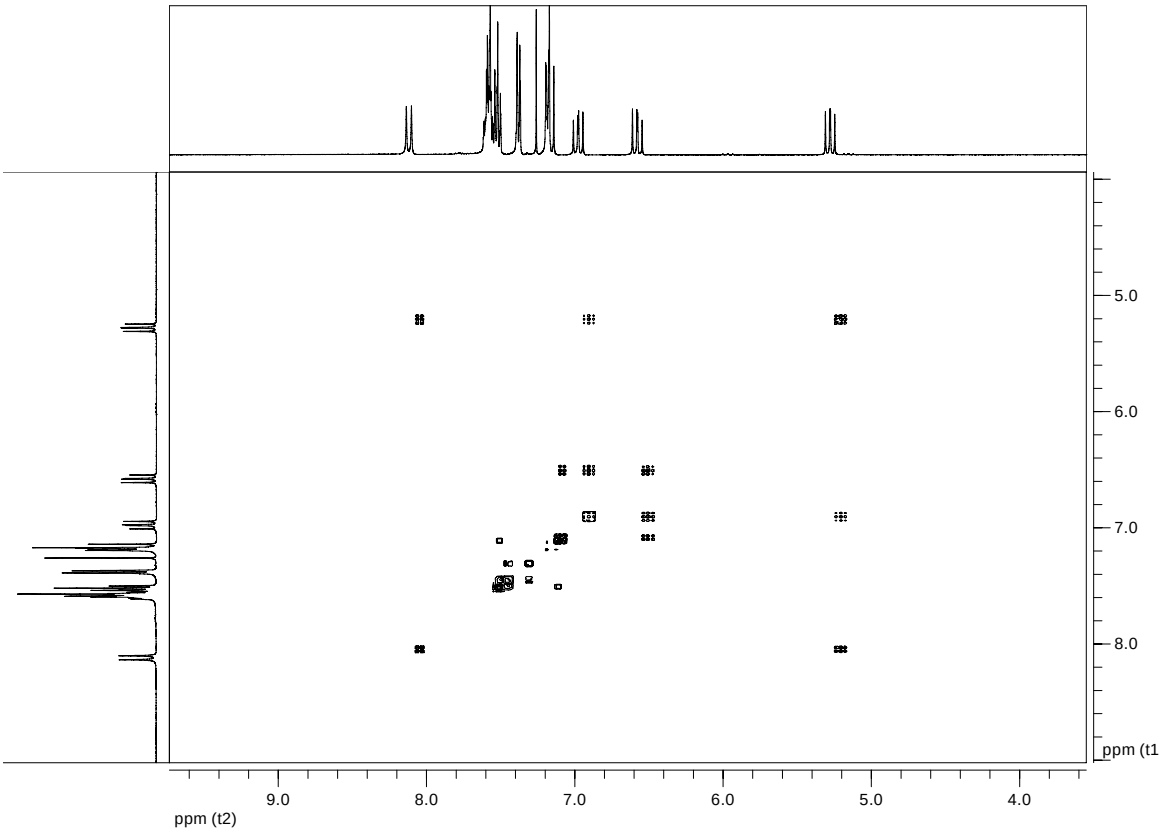
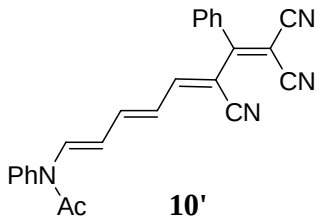


Figure S-45: ^{1}H-^{1}H COSY spectrum of compound **10'** (400 MHz, $CDCl_3$).



10'

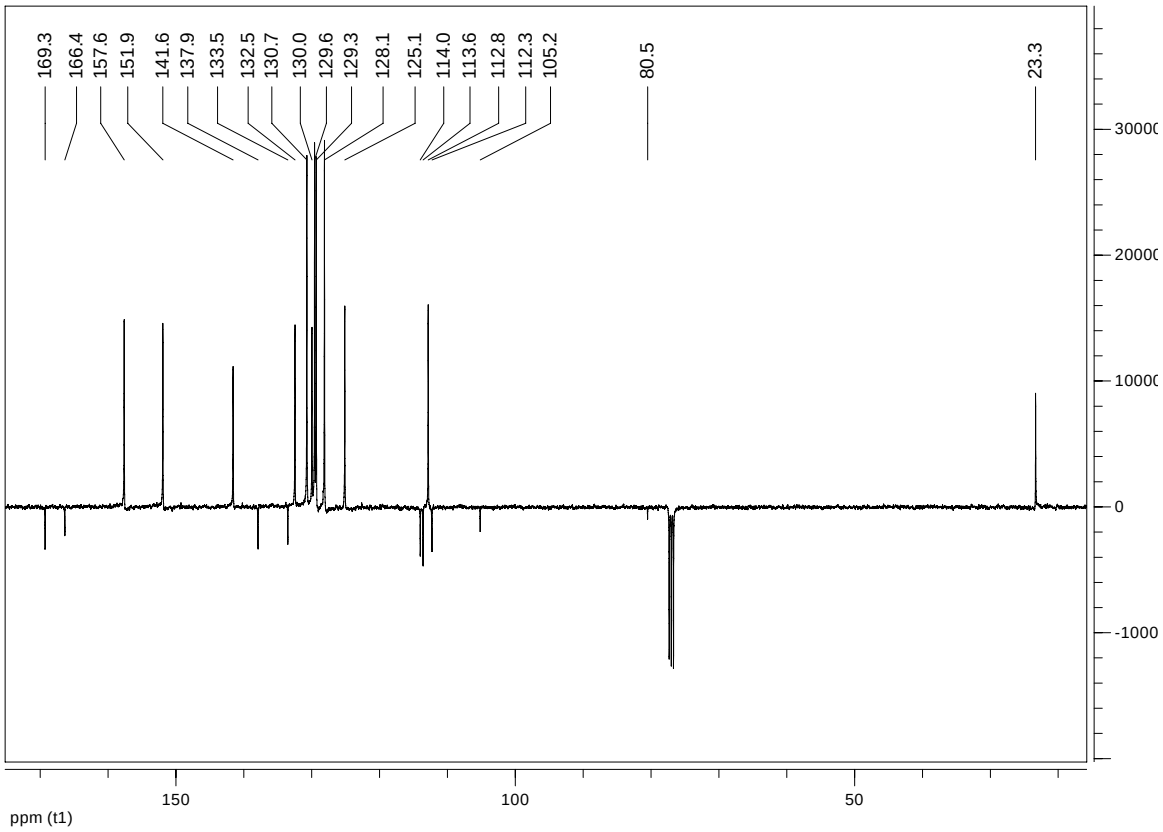
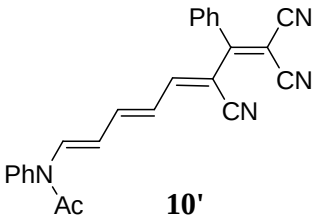


Figure S-46: ^{13}C spectrum (APT) of compound **10'** (100 MHz, $CDCl_3$).



10'

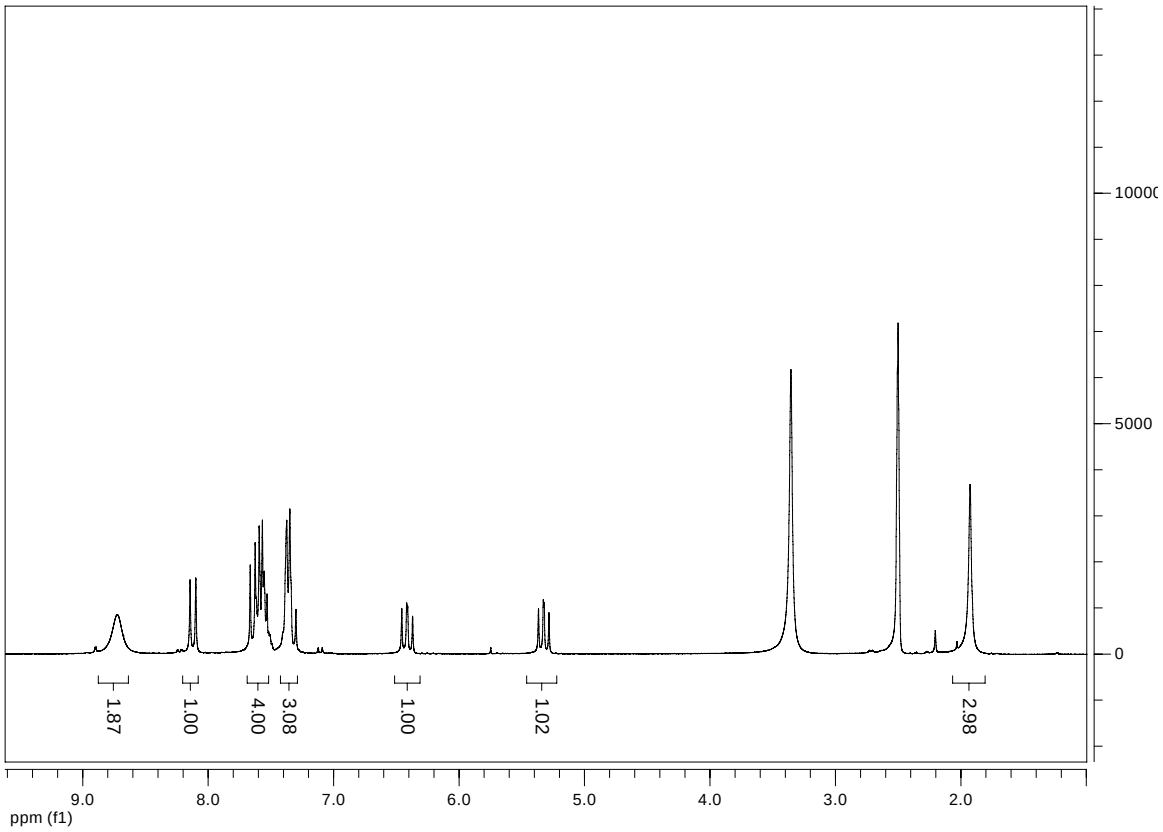
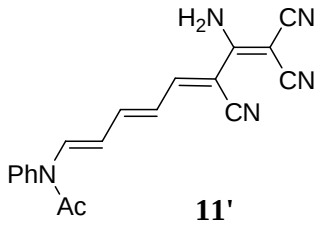


Figure S-47: ^{1}H spectrum of compound **11'** (300 MHz, DMSO-d_6).



11'

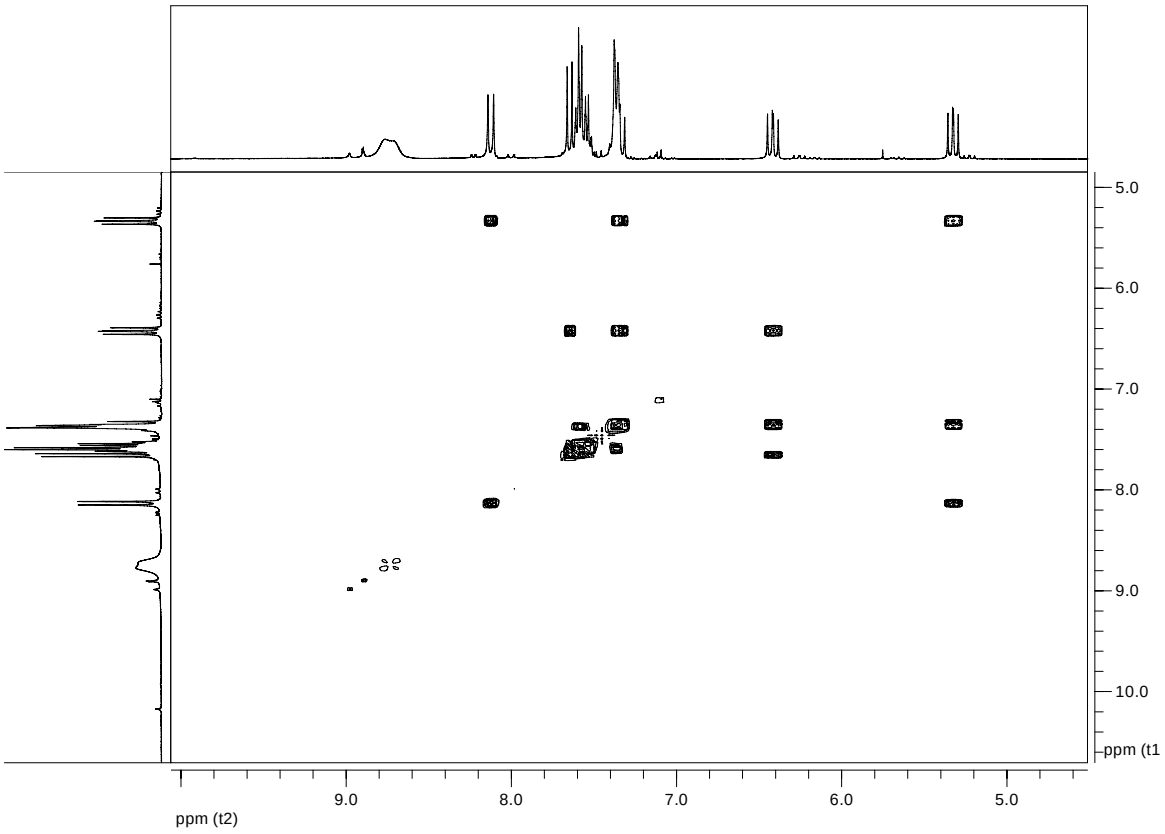
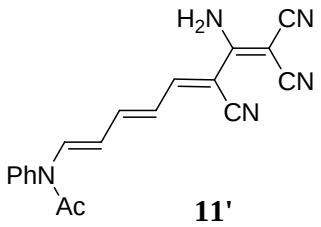


Figure S-48: ^{1}H-^{1}H COSY spectrum of compound **11'** (400 MHz, DMSO-d_6).



11'

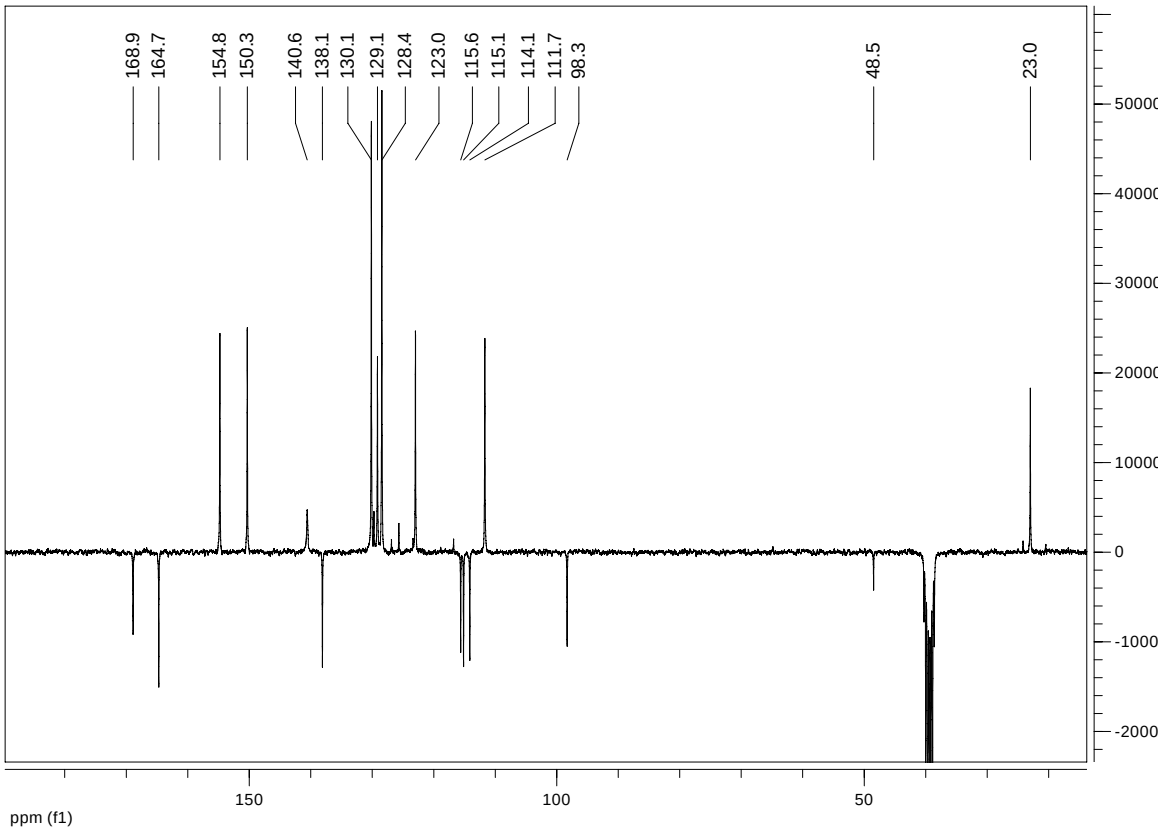
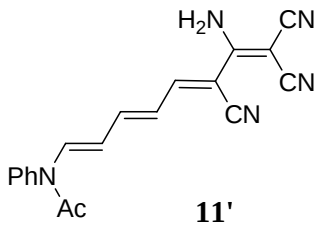


Figure S-49: ^{13}C spectrum (APT) of compound **11'** (75 MHz, DMSO-d_6).



11'

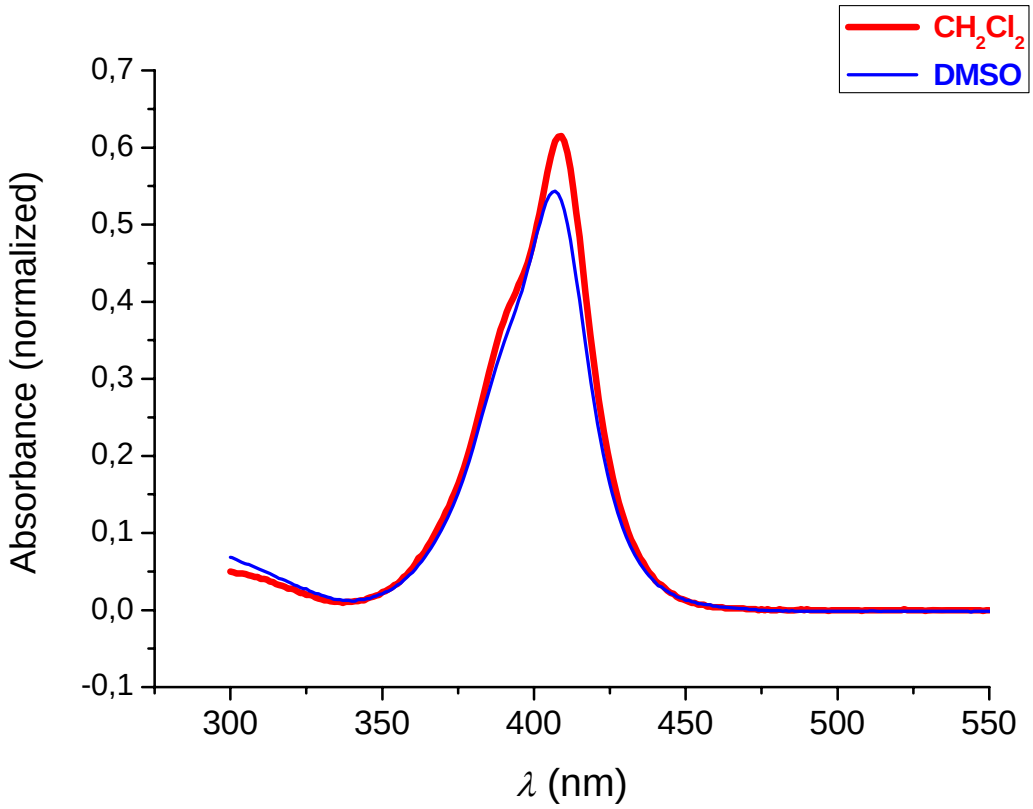
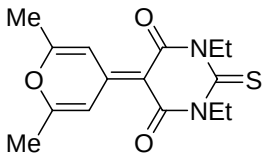


Figure S-50: Normalized UV-vis absorption of compound **1a**. (10^{-5} M)



1a

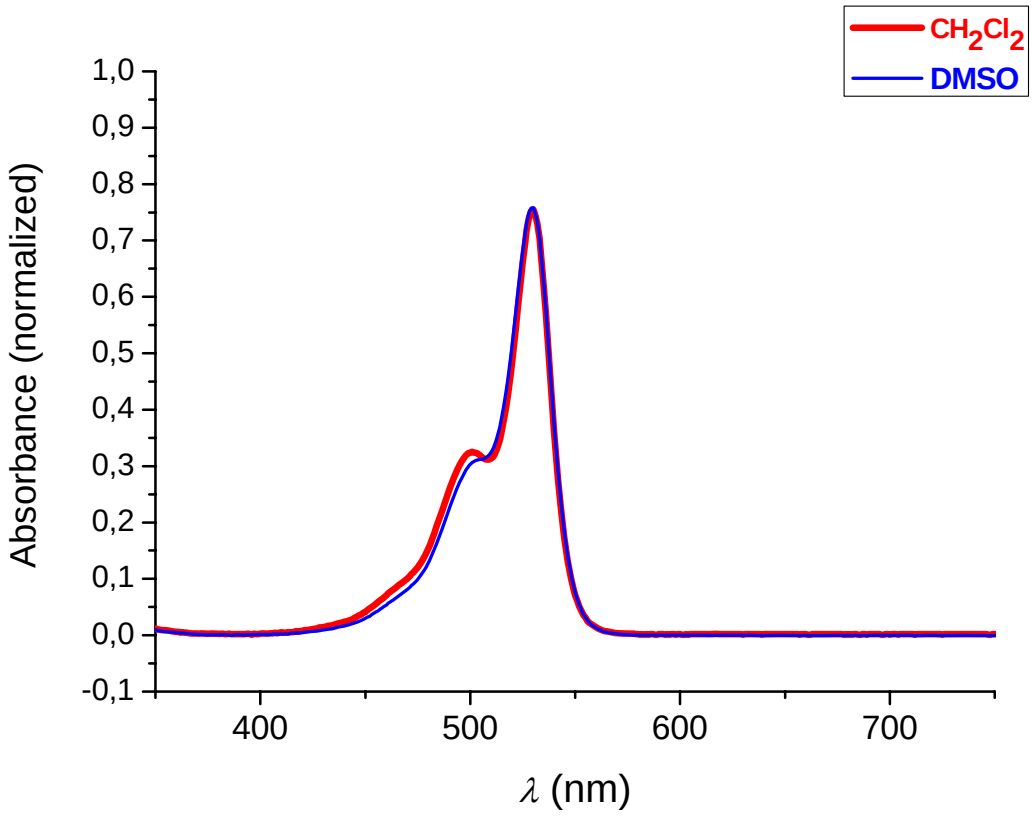
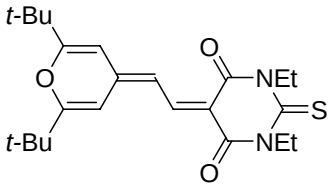


Figure S-51: Normalized UV-vis absorption of compound **1b**. (5×10^{-6} M)



1b

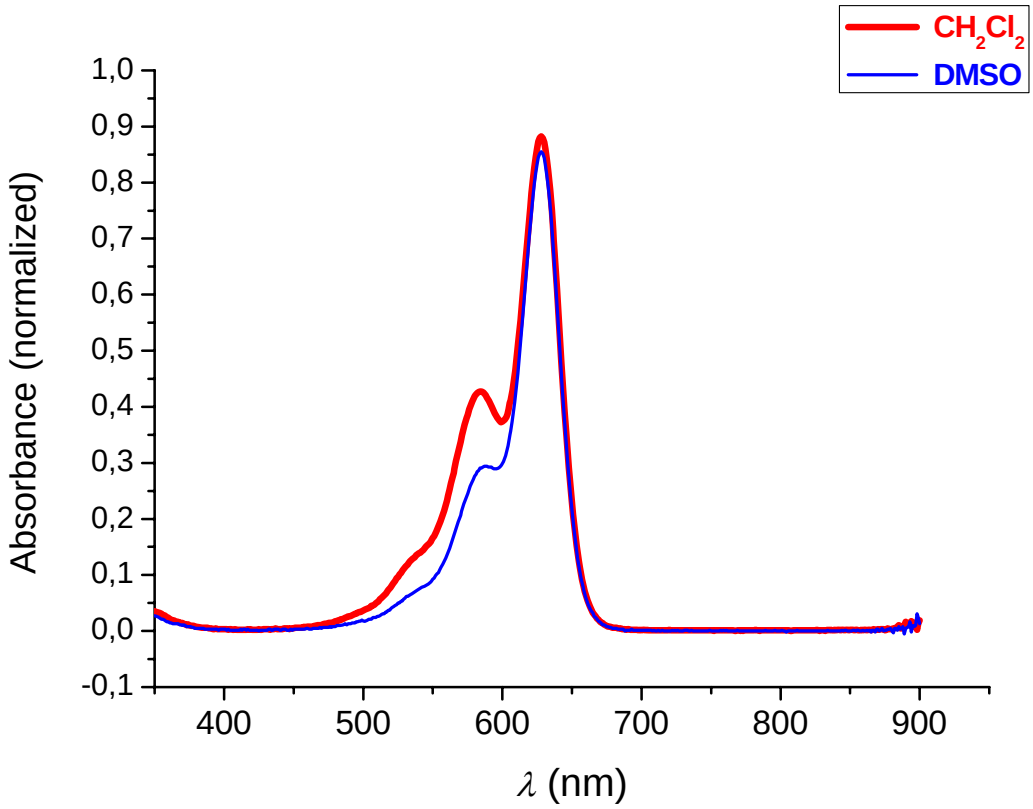
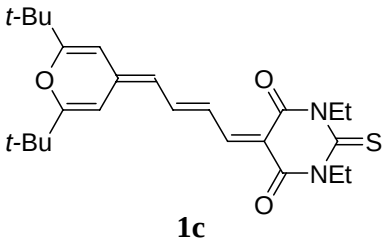


Figure S-52: Normalized UV-vis absorption of compound **1c**. (5×10^{-6} M)



1c

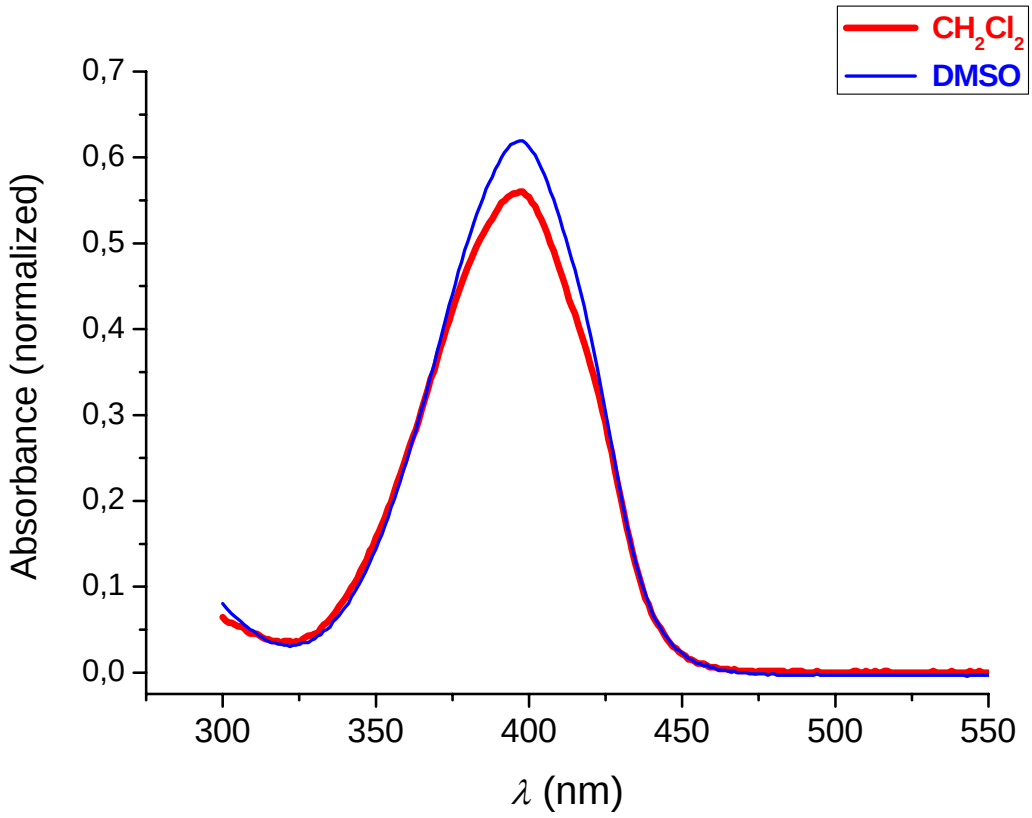
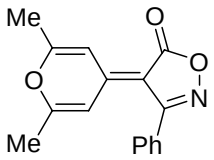


Figure S-53: Normalized UV-vis absorption of compound **2a**. (2.5×10^{-5} M)



2a

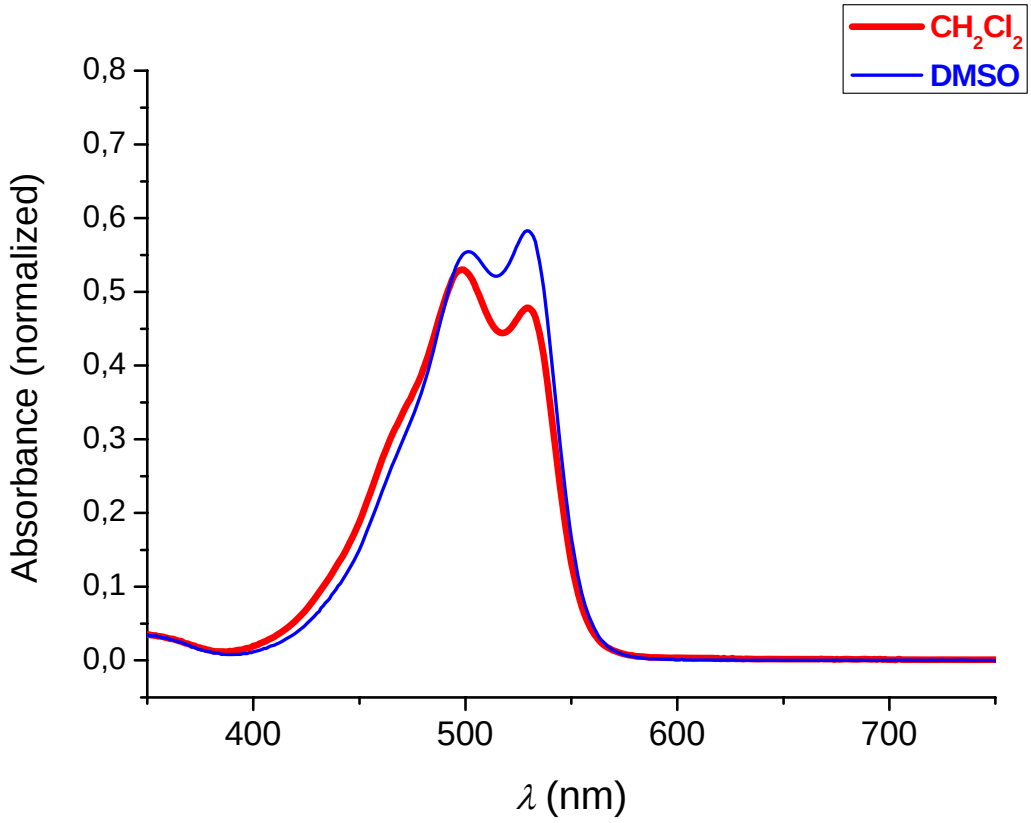
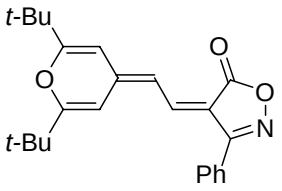


Figure S-54: Normalized UV-vis absorption of compound **2b**. (10^{-5} M)



2b

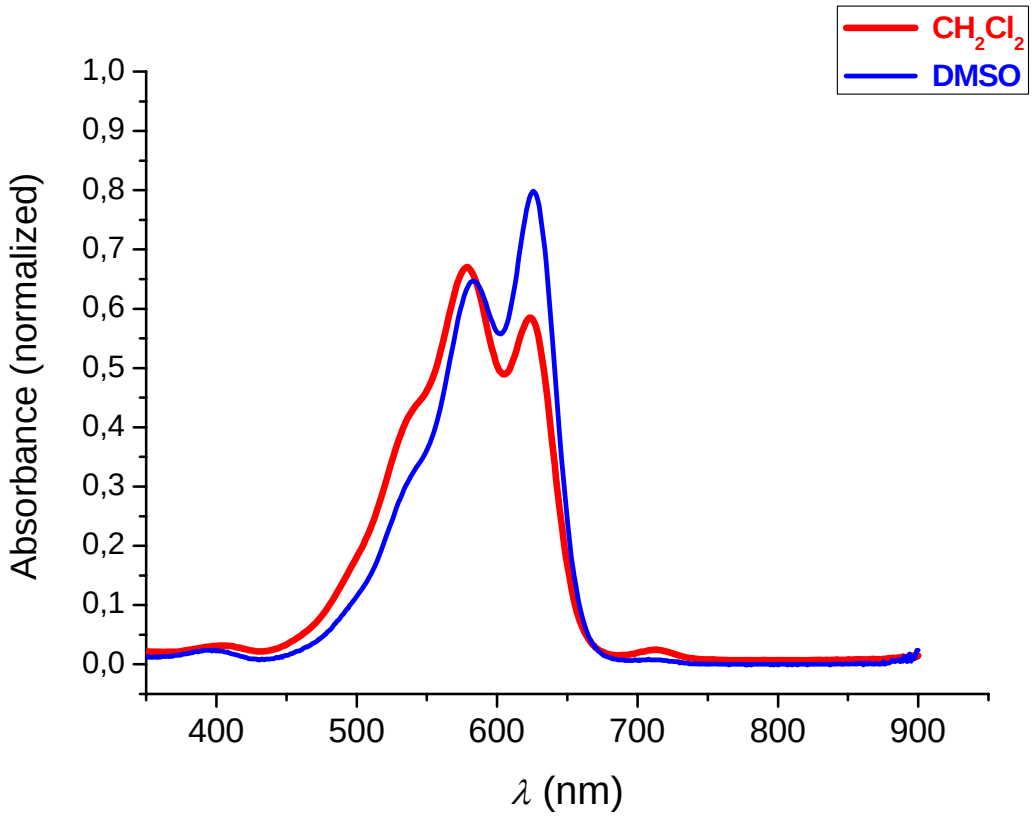
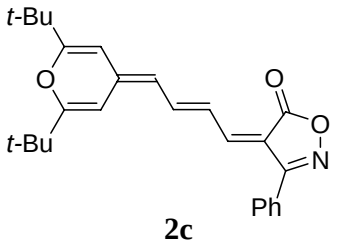


Figure S-55: Normalized UV-vis absorption of compound **2c**. (10^{-5} M)



2c

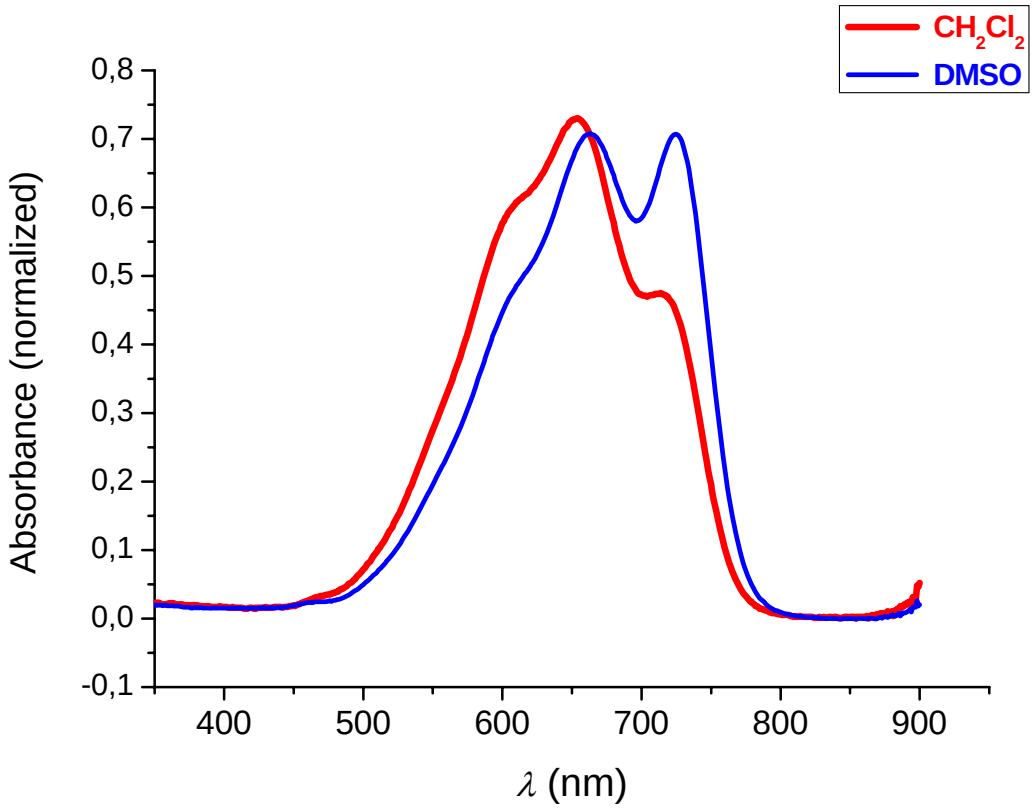
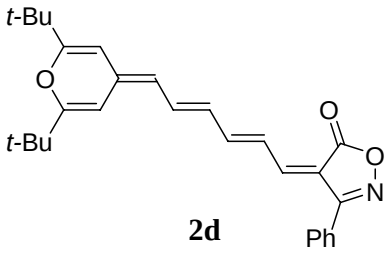


Figure S-56: Normalized UV-vis absorption of compound **2d**. (10^{-5} M)



2d

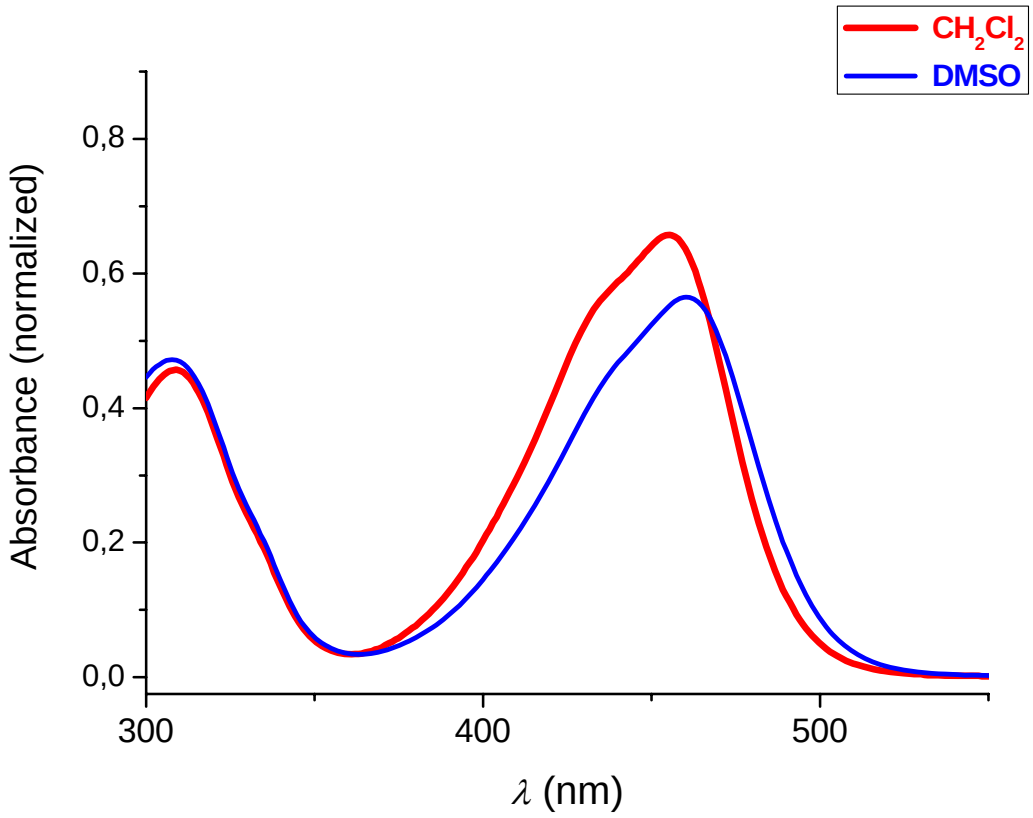
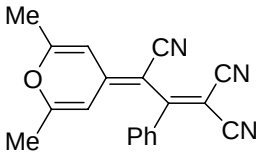


Figure S-57: Normalized UV-vis absorption of compound **3a**. (2.5×10^{-5} M)



3a

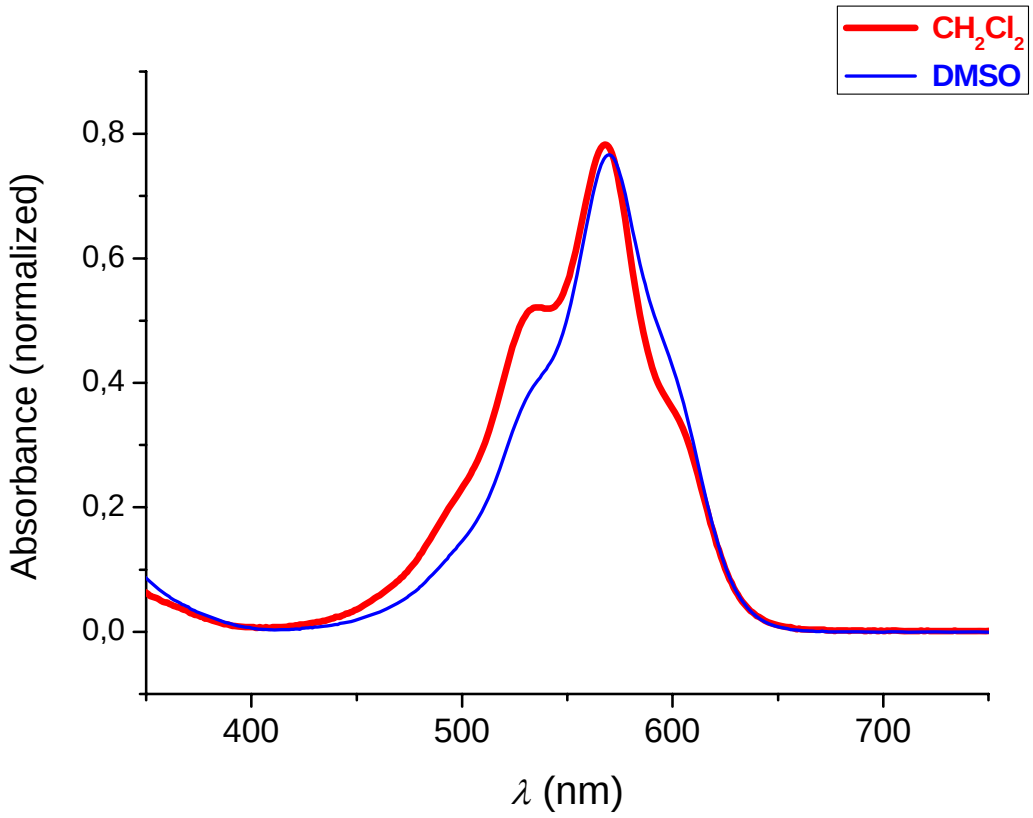
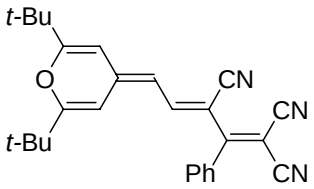


Figure S-58: Normalized UV-vis absorption of compound **3b**. (10^{-5} M)



3b

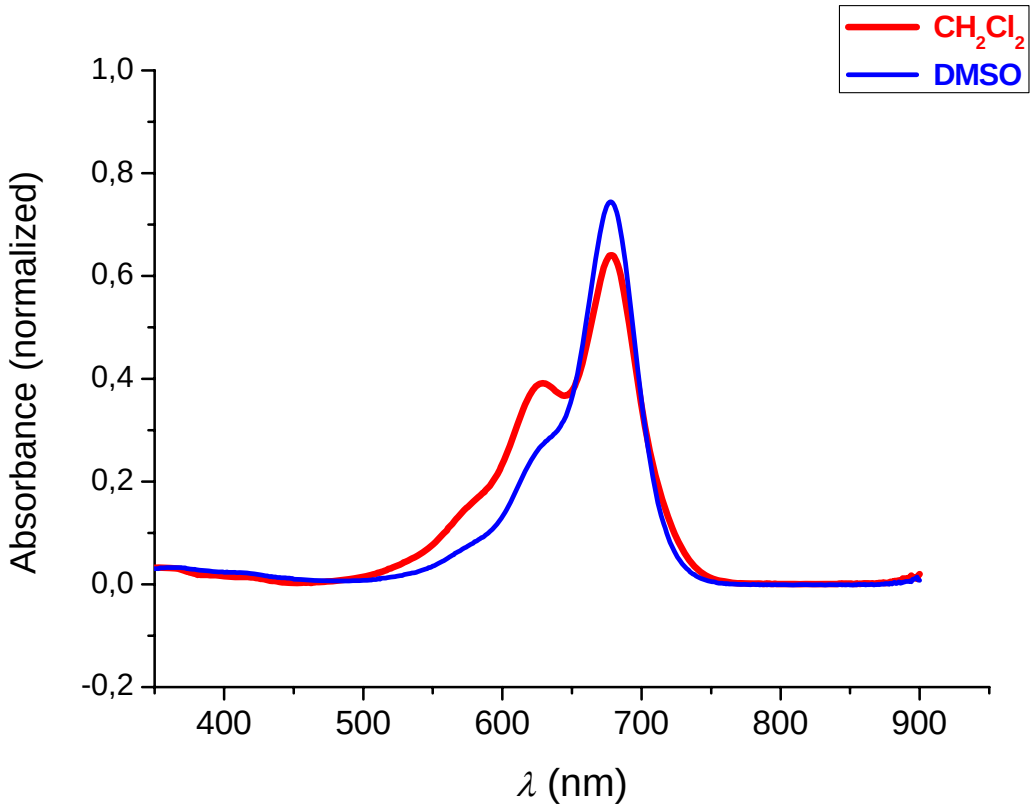
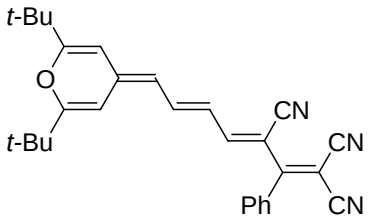


Figure S-59: Normalized UV-vis absorption of compound **3c**. (5×10^{-6} M)



3c

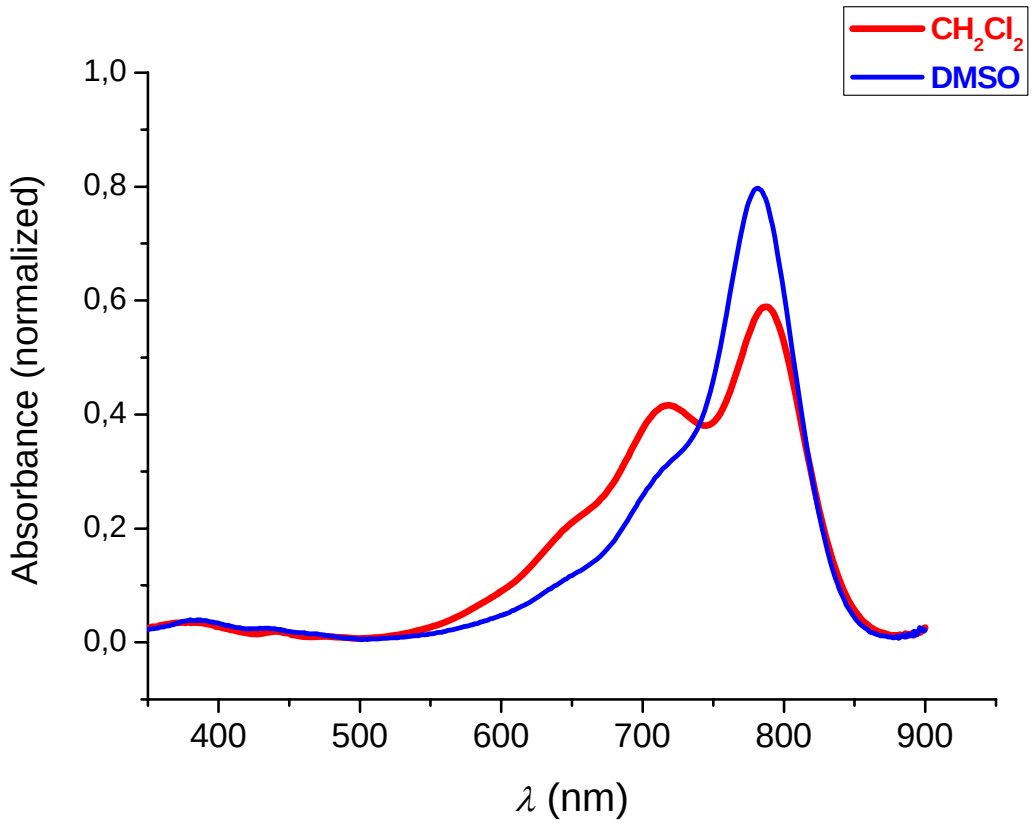
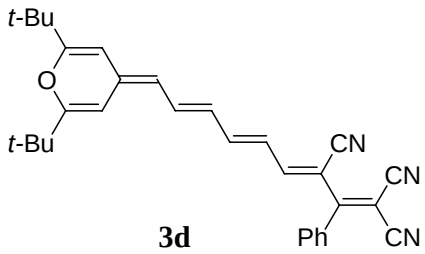


Figure S-60: Normalized UV-vis absorption of compound **3d**. (5×10^{-6} M)



3d

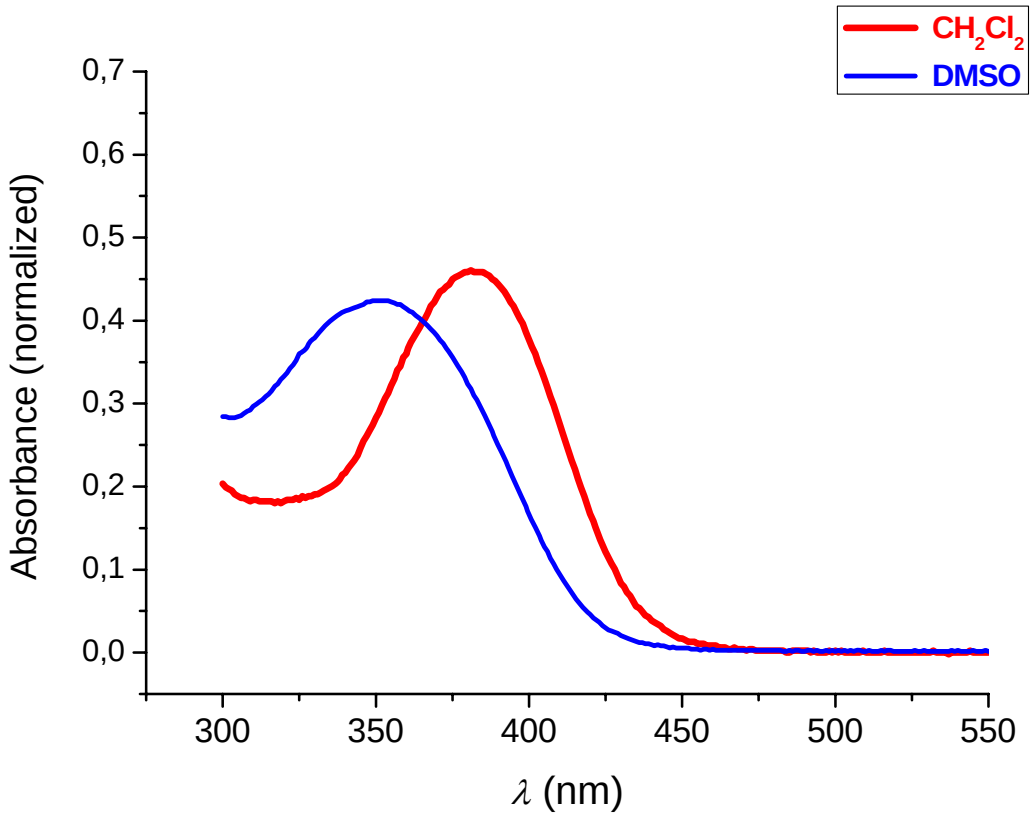
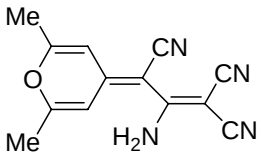


Figure S-61: Normalized UV-vis absorption of compound **4a**. (2.5×10^{-5} M)



4a

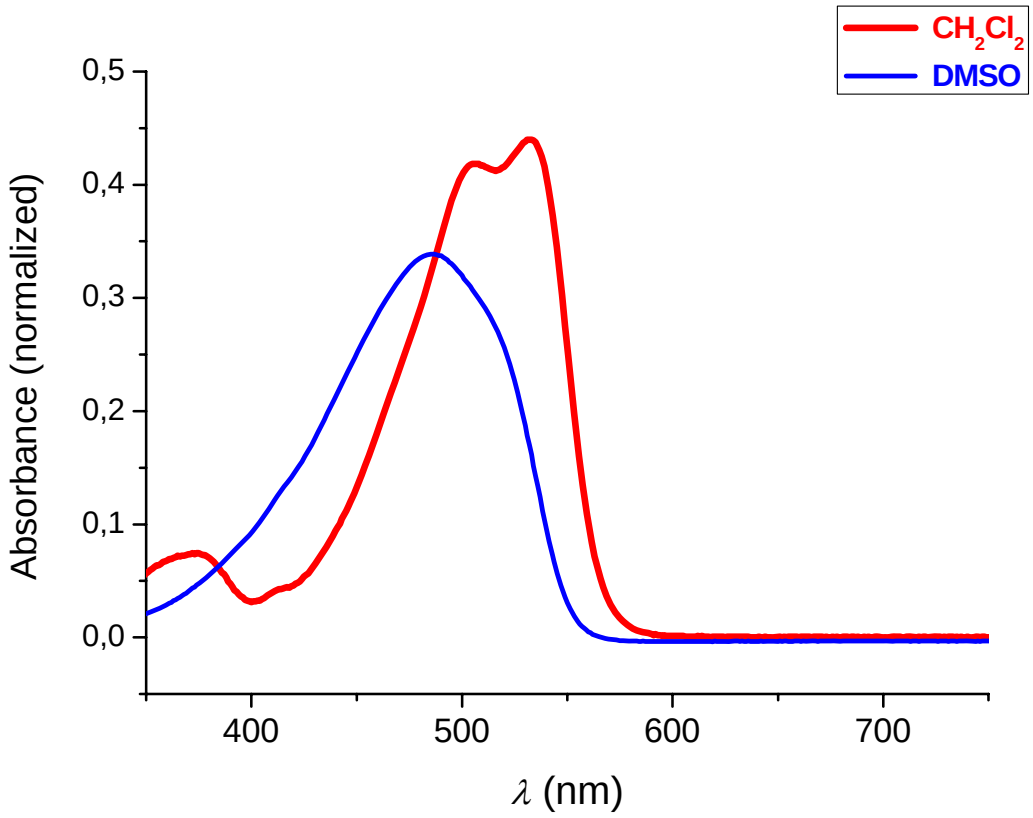
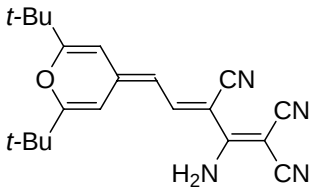


Figure S-62: Normalized UV-vis absorption of compound **4b**. (10^{-5} M)



4b

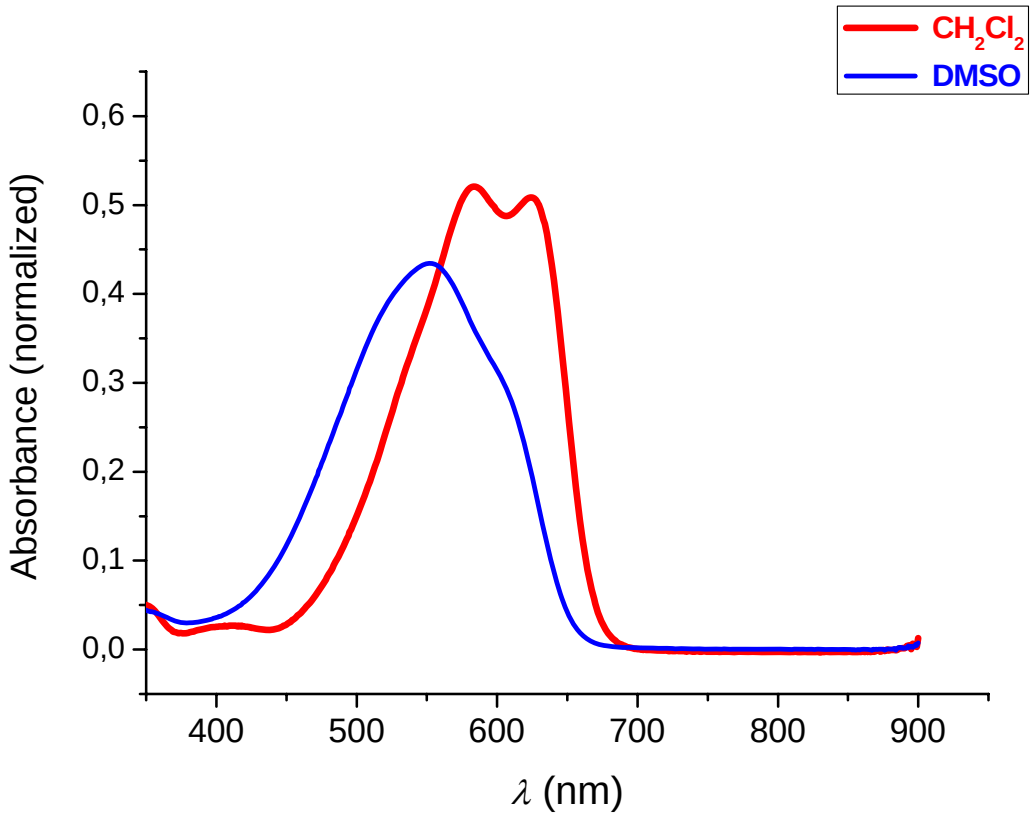
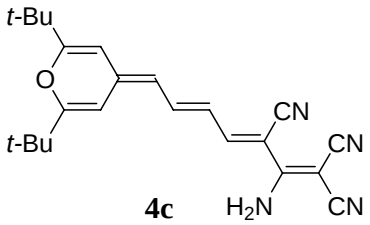


Figure S-63: Normalized UV-vis absorption of compound **4c**. (10^{-5} M)



4c

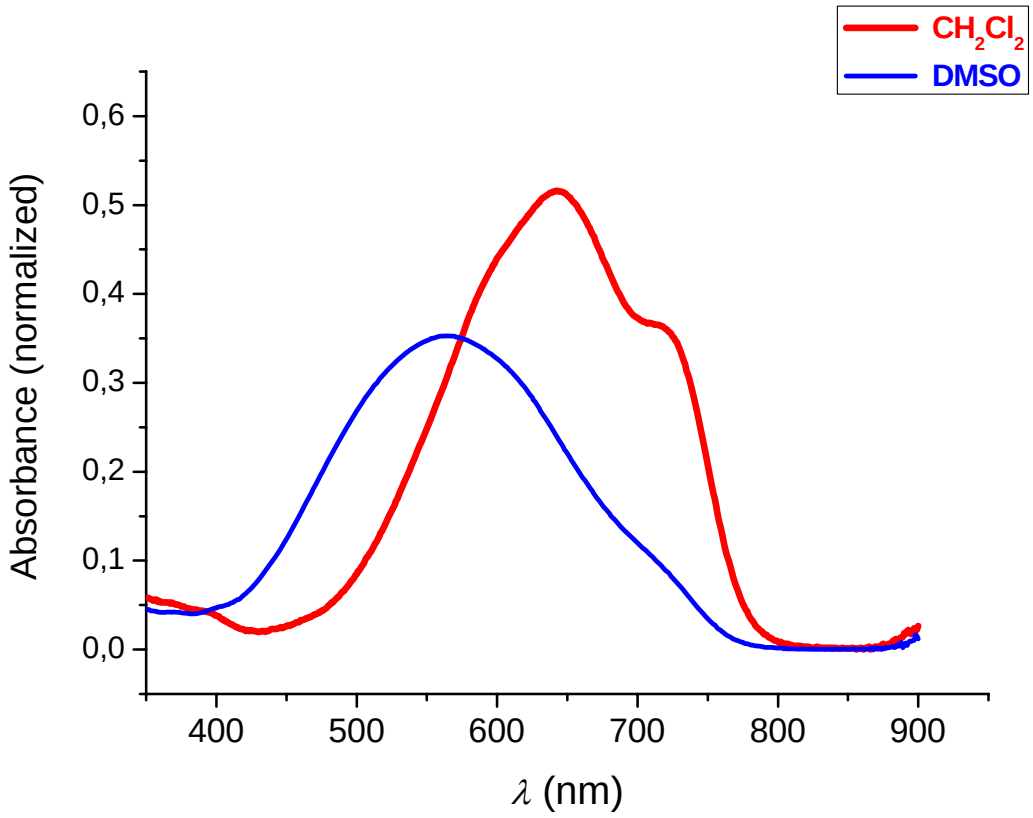
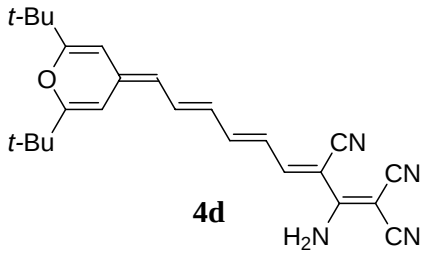


Figure S-64: Normalized UV-vis absorption of compound **4d**. (10^{-5} M)



4d

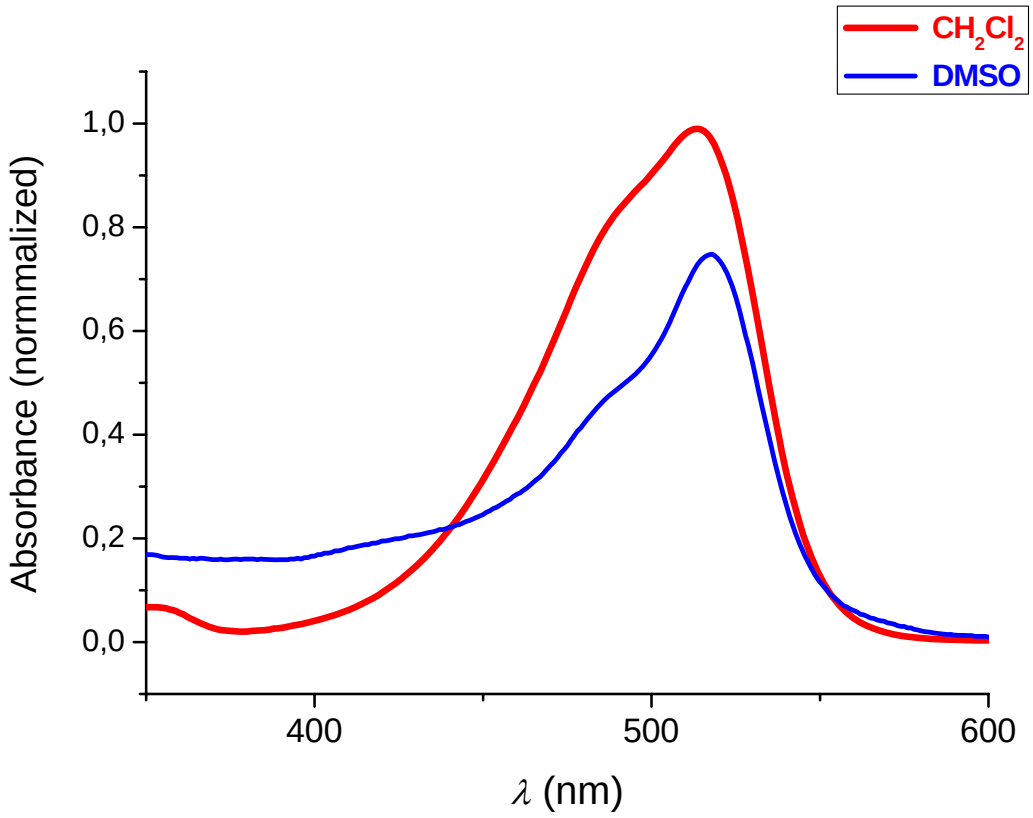
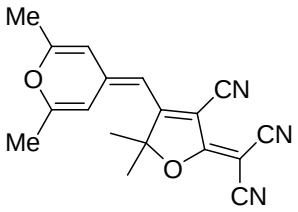


Figure S-65: Normalized UV-vis absorption of compound **5a**. (2.5×10^{-5} M)



5a

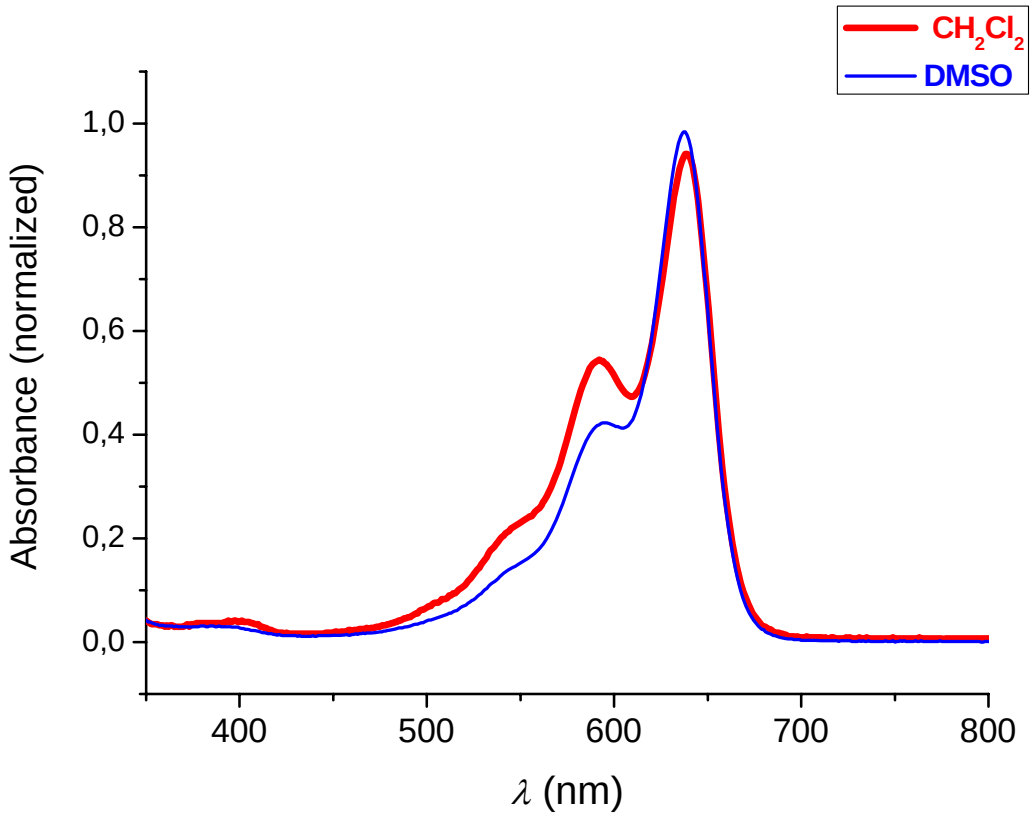
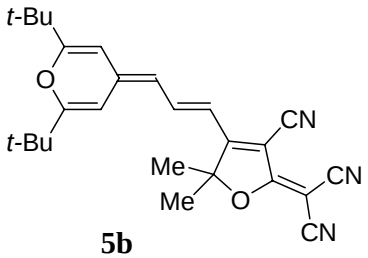


Figure S-66: Normalized UV-vis absorption of compound **5b**. (10^{-5} M)



5b

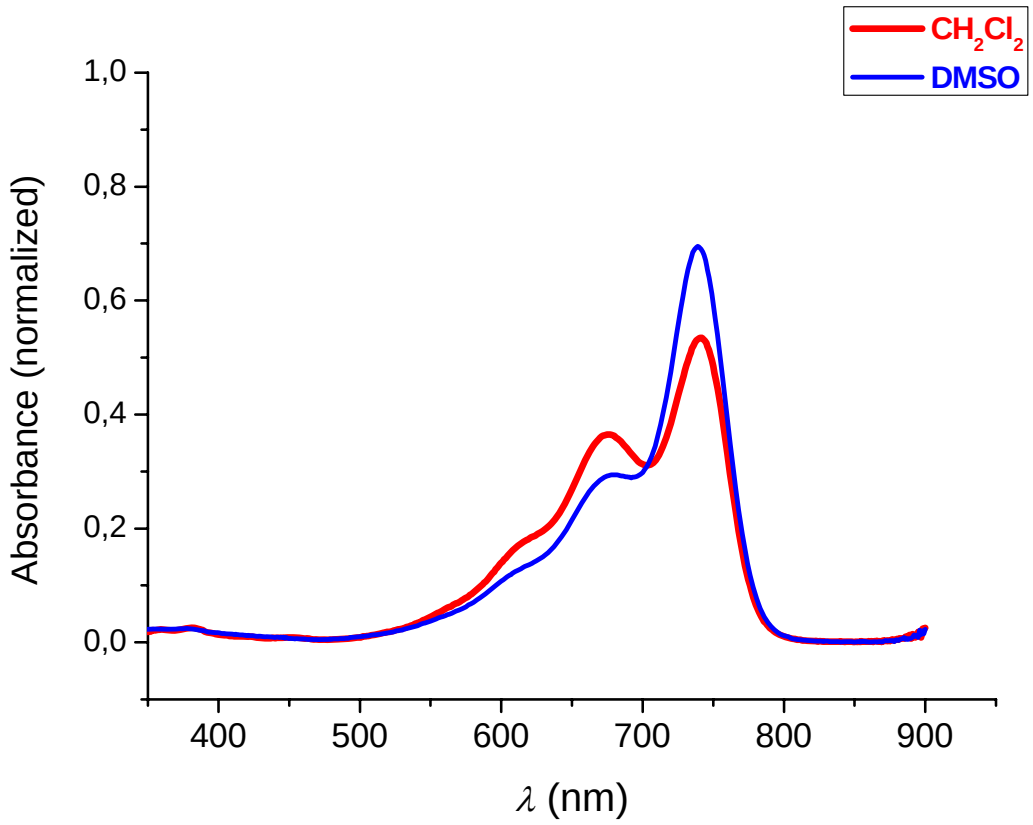
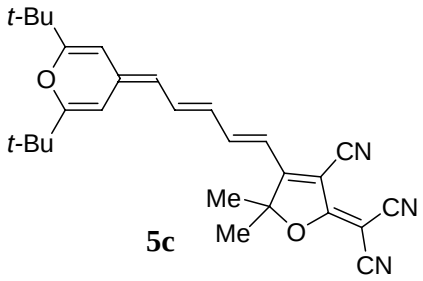


Figure S-67: Normalized UV-vis absorption of compound **5c**. (5×10^{-6} M)



5c

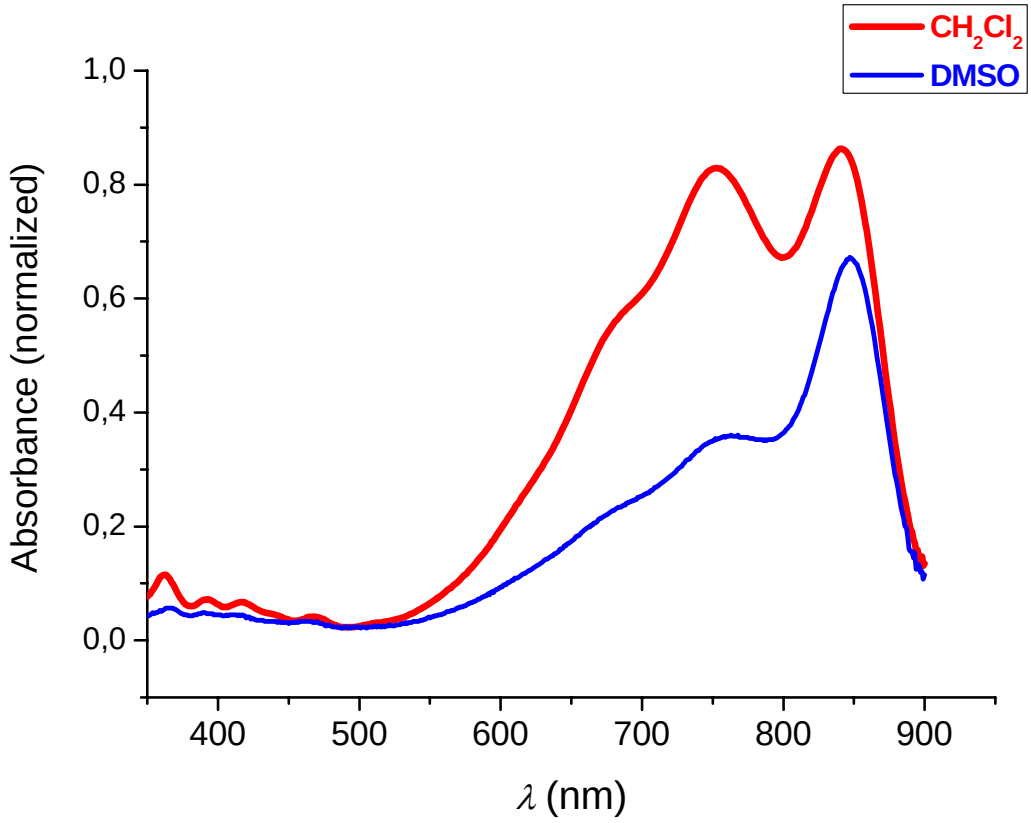
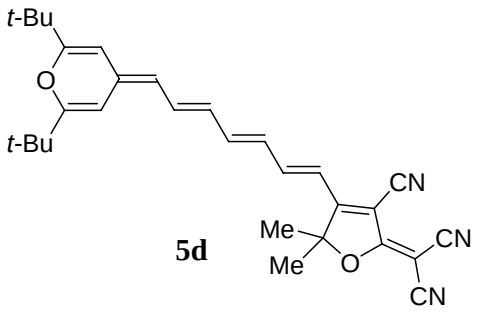


Figure S-68: Normalized UV-vis absorption of compound **5d**. (10^{-5} M)



5d

NLO measurements

Electric field induced second harmonic (EFISH) generation measurements have been performed using as the fundamental excitation the 1.9 μm output of a H_2 Raman shifter pumped by a Q-switched Nd:YAG laser. This laser operates at 1.06 μm, 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 fundamental 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 (electrode gap = 2 mm) 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 $\mu\beta_{1907}$ values have been determined in dichloromethane for all compounds, apart from **4a**, in DMSO. As a rule, at least three solutions of concentration in the range (4×10^{-3} M- 4×10^{-4} M) were measured. $\mu\beta_0$ values have been extrapolated using a two-level dispersion model.[2] Under the same experimental conditions $\mu\beta_0$ deduced for azo dye DR1 was 480 x 10^{-48} esu, quite close to the value reported in the same solvent by Dirk et al.[3]

[2] Oudar, J.L.; Chemla, D.S. *J. Chem. Phys*. **1977**, *66*, 2664-2668.
[3] Dirk, C. W.; Katz, H. E.; Schilling, M. L.; King, L. A. *Chem. Mater*. **1990**, *2*, 700-705.

X-ray Single-Crystal Diffraction

X-ray single-crystal diffraction data were collected at 293K on a diffractometer equipped with a graphite monochromator utilizing MoKα radiation (λ = 0.71073Å). The structures were solved by direct methods using SIR92[4] and refined on F^2 by full matrix least-squares techniques using SHELX-97[5] package with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogens atoms were treated with a riding model.

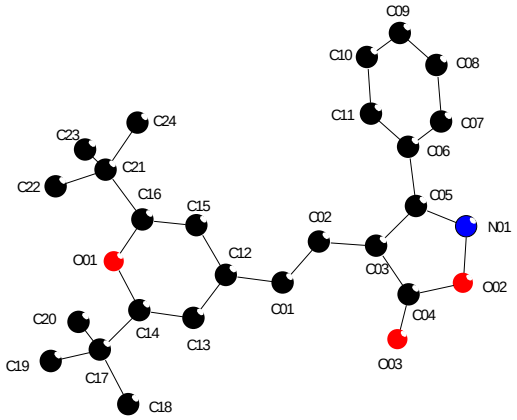
Crystal data for **2b**:

Black prism (0.65 x 0.46 x 0.29 mm^3), $C_{24}H_{27}N_1O_3$, Mr = 377.47, monoclinic, space group $P2_1/n$, a = 10.340(1) Å, b = 12.560(1) Å, c = 16.843(2) Å, β = 91.12(1)°, V = 2187.0(4) $Å^3$, Z = 4, ρcalc = 1.146 gcm^{-3}, μ (MoKα) = 0.075 mm^{-1}, F(000) = 808, 16867 reflections collected in the 2.02 - 25.86° θ range, 4188 unique (R_{int} = 0.095), restraints / parameters = 0 / 253, R1 = 0.0440 and wR2 = 0.0973 using 2208 reflections with I>2σ(I), R1 = 0.0994 and wR2 = 0.1139 using all data, GOF = 0.881, -0.110 < Δρ < 0.115 $e.Å^{-3}$.

[4] Altomare, A.; Cascarano, G.; Giacovazzo. C.; Guagliardi, A. *J. Appl. Cryst.* **1993**, *26*, 343-350.
[5] SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB (and SHELXA)] - Programs for Crystal Structure Analysis (Release 97-2). Sheldrick, G.M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

Crystal data and structure refinement for 2b.

Identification code	**2b**
Empirical formula	C24 H27 N O3
Formula weight	377.47
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 10.3400(10) A alpha = 90 deg. b = 12.5600(10) A beta = 91.120(10) deg. c = 16.843(2) A gamma = 90 deg.
Volume	2187.0(4) A^3
Z, Calculated density	4, 1.146 Mg/m^3
Absorption coefficient	0.075 mm^-1
F(000)	808
Crystal size	0.65 x 0.46 x 0.29 mm
Theta range for data collection	2.02 to 25.86 deg.
Limiting indices	-12<=h<=12, -15<=k<=15, -20<=l<=20
Reflections collected / unique	16867 / 4188 [R(int) = 0.0952]
Completeness to theta = 25.86	99.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4188 / 0 / 253
Goodness-of-fit on F^2	0.881
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.0973 [2208 Fo]
R indices (all data)	R1 = 0.0994, wR2 = 0.1139
Largest diff. peak and hole	0.115 and -0.110 e.A^-3



Atomic coordinates and equivalent isotropic displacement parameters for 2b.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(01)	1.05025(17)	0.06960(14)	0.88273(9)	0.0537(4)
C(02)	0.97061(18)	0.11741(13)	0.93796(9)	0.0524(4)
C(03)	1.00968(17)	0.16100(14)	1.00976(9)	0.0530(4)
C(04)	1.1412(2)	0.16718(16)	1.03956(11)	0.0653(5)
C(05)	0.9343(2)	0.21119(13)	1.06937(9)	0.0567(5)
C(06)	0.7926(2)	0.21926(14)	1.07571(9)	0.0592(5)
C(07)	0.7365(2)	0.30670(17)	1.11172(11)	0.0781(6)
C(08)	0.6047(3)	0.3101(2)	1.12300(13)	0.0898(7)
C(09)	0.5268(2)	0.2285(2)	1.09897(12)	0.0852(7)
C(10)	0.5807(2)	0.14184(19)	1.06293(11)	0.0783(6)
C(11)	0.7125(2)	0.13683(16)	1.05132(10)	0.0653(5)
C(12)	1.00599(16)	0.01812(13)	0.81415(9)	0.0485(4)
C(13)	1.09400(16)	-0.03788(13)	0.76528(9)	0.0507(4)
C(14)	1.05348(16)	-0.09550(14)	0.70281(9)	0.0507(4)
C(15)	0.87375(16)	0.01236(13)	0.78875(9)	0.0509(4)
C(16)	0.83676(16)	-0.04530(14)	0.72529(9)	0.0510(4)
C(17)	1.13186(17)	-0.16320(15)	0.64756(10)	0.0595(5)
C(18)	1.27457(19)	-0.1587(2)	0.66978(13)	0.0913(7)
C(19)	1.1122(2)	-0.12094(19)	0.56267(10)	0.0863(7)
C(20)	1.0842(2)	-0.27827(17)	0.65228(14)	0.0865(7)
C(21)	0.70243(18)	-0.06325(17)	0.69213(11)	0.0673(5)
C(22)	0.6953(2)	-0.0253(2)	0.60541(13)	0.1129(10)
C(23)	0.6734(2)	-0.1830(2)	0.69664(16)	0.0988(8)
C(24)	0.60321(19)	-0.0017(2)	0.74000(15)	0.0973(8)
N(01)	1.00641(18)	0.24945(14)	1.12714(9)	0.0744(5)
O(01)	0.92563(11)	-0.09927(10)	0.68244(6)	0.0575(3)
O(02)	1.13841(14)	0.22508(11)	1.10913(7)	0.0790(4)
O(03)	1.24348(15)	0.13257(13)	1.01648(8)	0.0842(5)
H(01)	1.1391	0.0722	0.8922	0.064
H(02)	0.8827	0.1203	0.9253	0.063
H(07)	0.7880	0.3634	1.1284	0.094
H(08)	0.5686	0.3691	1.1474	0.108
H(09)	0.4381	0.2315	1.1069	0.102

H(10)	0.5281	0.0858	1.0461	0.094
H(11)	0.7478	0.0774	1.0269	0.078
H(13)	1.1821	-0.0343	0.7772	0.061
H(15)	0.8117	0.0495	0.8169	0.061
H(18A)	1.3223	-0.2023	0.6339	0.137
H(18B)	1.2873	-0.1844	0.7230	0.137
H(18C)	1.3044	-0.0865	0.6665	0.137
H(19A)	1.1610	-0.1636	0.5267	0.130
H(19B)	1.1412	-0.0484	0.5602	0.130
H(19C)	1.0221	-0.1243	0.5481	0.130
H(20A)	1.1331	-0.3219	0.6170	0.130
H(20B)	0.9943	-0.2812	0.6371	0.130
H(20C)	1.0952	-0.3039	0.7057	0.130
H(22A)	0.6096	-0.0368	0.5842	0.169
H(22B)	0.7563	-0.0645	0.5747	0.169
H(22C)	0.7155	0.0493	0.6032	0.169
H(23A)	0.5878	-0.1964	0.6759	0.148
H(23B)	0.6792	-0.2060	0.7509	0.148
H(23C)	0.7351	-0.2215	0.6659	0.148
H(24A)	0.5182	-0.0145	0.7182	0.146
H(24B)	0.6221	0.0730	0.7376	0.146
H(24C)	0.6070	-0.0251	0.7943	0.146

Bond lengths [A] for 2b.

C(01)-C(02)	1.391(2)
C(01)-C(12)	1.393(2)
C(02)-C(03)	1.381(2)
C(03)-C(05)	1.430(2)
C(03)-C(04)	1.442(3)
C(04)-O(03)	1.215(2)
C(04)-O(02)	1.380(2)
C(05)-N(01)	1.306(2)
C(05)-C(06)	1.474(3)
C(06)-C(11)	1.383(3)
C(06)-C(07)	1.387(3)
C(07)-C(08)	1.380(3)
C(08)-C(09)	1.360(3)
C(09)-C(10)	1.370(3)
C(10)-C(11)	1.382(3)
C(12)-C(13)	1.425(2)
C(12)-C(15)	1.427(2)
C(13)-C(14)	1.338(2)
C(14)-O(01)	1.3601(19)
C(14)-C(17)	1.508(2)
C(15)-C(16)	1.341(2)
C(16)-O(01)	1.3605(19)
C(16)-C(21)	1.504(2)
C(17)-C(18)	1.516(3)
C(17)-C(20)	1.530(3)
C(17)-C(19)	1.535(2)
C(21)-C(24)	1.527(3)
C(21)-C(23)	1.536(3)
C(21)-C(22)	1.537(3)
N(01)-O(02)	1.437(2)

Bond angles [deg] for 2b.

C(02)-C(01)-C(12)	124.45(17)
C(03)-C(02)-C(01)	126.17(17)
C(02)-C(03)-C(05)	129.47(17)
C(02)-C(03)-C(04)	125.73(17)
C(05)-C(03)-C(04)	104.78(15)
O(03)-C(04)-O(02)	119.53(19)
O(03)-C(04)-C(03)	133.65(18)
O(02)-C(04)-C(03)	106.81(18)
N(01)-C(05)-C(03)	111.96(18)
N(01)-C(05)-C(06)	118.34(16)
C(03)-C(05)-C(06)	129.60(15)
C(11)-C(06)-C(07)	118.0(2)
C(11)-C(06)-C(05)	121.12(17)
C(07)-C(06)-C(05)	120.71(18)
C(08)-C(07)-C(06)	120.5(2)
C(09)-C(08)-C(07)	121.1(2)

C(08)-C(09)-C(10)	119.1(2)
C(09)-C(10)-C(11)	120.7(2)
C(10)-C(11)-C(06)	120.67(19)
C(01)-C(12)-C(13)	120.32(16)
C(01)-C(12)-C(15)	124.72(16)
C(13)-C(12)-C(15)	114.90(14)
C(14)-C(13)-C(12)	121.86(16)
C(13)-C(14)-O(01)	120.35(15)
C(13)-C(14)-C(17)	128.79(16)
O(01)-C(14)-C(17)	110.86(14)
C(16)-C(15)-C(12)	121.56(15)
C(15)-C(16)-O(01)	120.47(15)
C(15)-C(16)-C(21)	128.62(16)
O(01)-C(16)-C(21)	110.90(14)
C(14)-C(17)-C(18)	111.02(15)
C(14)-C(17)-C(20)	108.84(14)
C(18)-C(17)-C(20)	109.61(18)
C(14)-C(17)-C(19)	108.47(15)
C(18)-C(17)-C(19)	109.12(16)
C(20)-C(17)-C(19)	109.77(17)
C(16)-C(21)-C(24)	110.68(16)
C(16)-C(21)-C(23)	107.97(16)
C(24)-C(21)-C(23)	109.59(18)
C(16)-C(21)-C(22)	109.46(17)
C(24)-C(21)-C(22)	108.94(19)
C(23)-C(21)-C(22)	110.19(18)
C(05)-N(01)-O(02)	107.19(15)
C(14)-O(01)-C(16)	120.80(12)
C(04)-O(02)-N(01)	109.08(14)

Anisotropic displacement parameters for 2b.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(01)	0.0649(11)	0.0516(11)	0.0448(9)	0.0000(8)	0.0039(8)	-0.0044(9)
C(02)	0.0715(12)	0.0420(10)	0.0437(9)	0.0038(8)	0.0014(8)	-0.0046(8)
C(03)	0.0733(12)	0.0453(11)	0.0405(9)	0.0008(8)	0.0008(8)	-0.0107(9)
C(04)	0.0878(16)	0.0596(13)	0.0485(11)	0.0023(9)	0.0043(10)	-0.0220(11)
C(05)	0.0904(14)	0.0406(11)	0.0392(9)	-0.0014(8)	0.0017(9)	-0.0101(9)
C(06)	0.0902(15)	0.0498(12)	0.0378(9)	-0.0028(8)	0.0029(9)	0.0004(10)
C(07)	0.1118(19)	0.0594(14)	0.0633(12)	-0.0121(10)	0.0048(12)	0.0009(12)

```
  C(08)       0.114(2)   0.0809(18) 0.0748(15)-0.0166(13) 0.0119(13)
0.0244(15)
  C(09)       0.0904(16) 0.097(2)   0.0680(13)-0.0056(13) 0.0038(12)
0.0178(15)
  C(10)       0.0877(17) 0.0802(16) 0.0668(13)-0.0102(12)-0.0010(11)-
0.0003(12)
  C(11)       0.0823(15) 0.0590(13) 0.0548(11)-0.0107(9)  0.0051(9)
0.0010(11)
  C(12)       0.0625(11) 0.0432(10) 0.0401(9)  0.0058(8)  0.0055(8) -
0.0046(8)
  C(13)       0.0538(10) 0.0543(11) 0.0442(9)  0.0022(8)  0.0068(8)
0.0004(8)
  C(14)       0.0553(11) 0.0515(11) 0.0455(9)  0.0021(8)  0.0061(8) -
0.0013(8)
  C(15)       0.0599(11) 0.0462(11) 0.0469(9) -0.0035(8)  0.0107(8)
0.0023(8)
  C(16)       0.0554(11) 0.0491(11) 0.0488(9) -0.0046(8)  0.0086(8)
0.0004(8)
  C(17)       0.0624(12) 0.0615(13) 0.0549(10)-0.0069(9)  0.0151(8)
0.0049(9)
  C(18)       0.0704(15) 0.110(2)   0.0937(15)-0.0237(14) 0.0146(12)
0.0182(13)
  C(19)       0.1115(18) 0.0958(18) 0.0525(11)-0.0079(11) 0.0232(11)
0.0144(13)
  C(20)       0.1041(17) 0.0634(15) 0.0932(15)-0.0143(12) 0.0326(13)
0.0053(12)
  C(21)       0.0585(12) 0.0734(15) 0.0700(12)-0.0166(11) 0.0007(9)
0.0026(10)
  C(22)       0.1007(18) 0.162(3)   0.0749(15)-0.0038(16)-0.0221(13)
0.0189(17)
  C(23)       0.0740(15) 0.0871(18) 0.135(2)  -0.0376(16)-0.0005(13)-
0.0176(13)
  C(24)       0.0576(13) 0.118(2)   0.1167(18)-0.0383(16) 0.0034(12)
0.0087(12)
  N(01)       0.0982(13) 0.0722(12) 0.0528(9) -0.0123(8)  0.0035(9) -
0.0174(10)
  O(01)       0.0574(8)  0.0632(8)  0.0521(6) -0.0154(6)  0.0067(5)
0.0001(6)
  O(02)       0.0930(11) 0.0865(11) 0.0572(8) -0.0102(7) -0.0049(7) -
0.0267(8)
  O(03)       0.0766(10) 0.1027(12) 0.0735(9) -0.0071(8)  0.0033(8) -
0.0195(9)
```

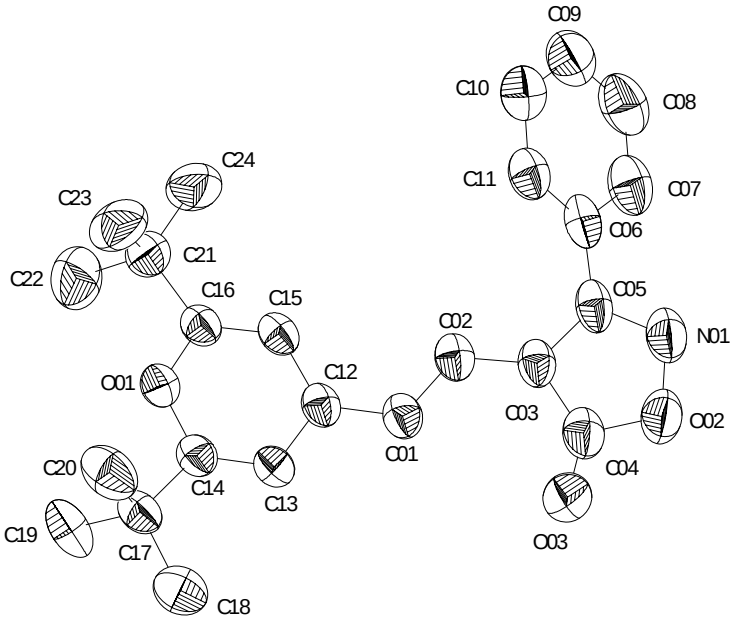


Figure S-69: ORTEP view of **2b**.

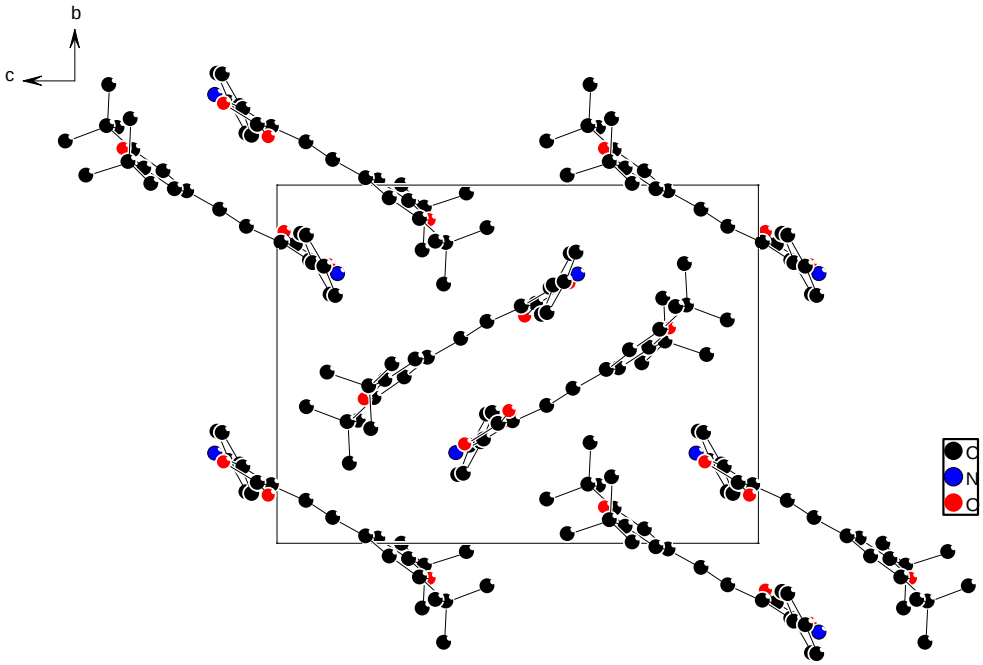


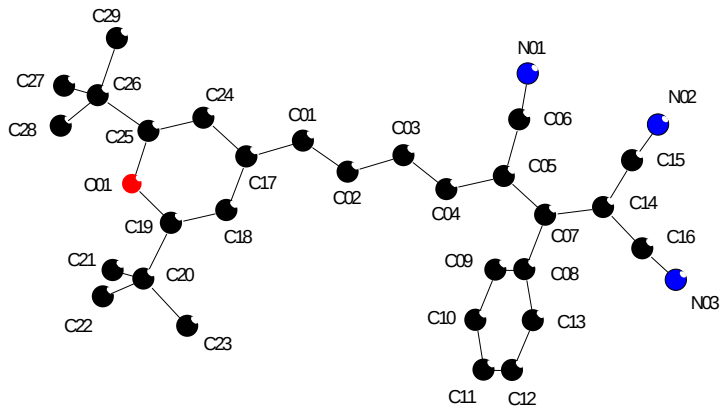
Figure S-70: Molecular packing of **2b** viewed along the [100] direction.

Crystal data for **3c**:

Blue needle (0.80 x 0.13 x 0.10 mm^3), $C_{29}H_{29}N_3O_1$, Mr = 435.55, triclinic, space group P-1, a = 20.485(3) Å, b = 9.563(1) Å, c = 7.049(1) Å, α = 78.92(1)°, β = 81.79(1)°, γ = 76.67(2)°, V = 1311.6(3) $Å^3$, Z = 2, ρcalc = 1.103 gcm^{-3}, μ (MoKα) = 0.068 mm^{-1}, F(000) = 464, 13030 reflections collected in the 2.05 - 25.96° θ range, 4772 unique (R_{int} = 0.063), restraints / parameters = 0 / 298, R1 = 0.0542 and wR2 = 0.01293 using 2305 reflections with I>2σ(I), R1 = 0.1138 and wR2 = 0.1521 using all data, GOF = 0.854, -0.158 < Δρ < 0.325 e.$Å^{-3}$.

Crystal data and structure refinement for 3c.

Identification code	**3c**
Empirical formula	C29 H29 N3 O
Formula weight	435.55
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 20.485(3) A alpha = 78.92(1) deg. b = 9.563(1) A beta = 81.79(1) deg. c = 7.049(1) A gamma = 76.67(2) deg.
Volume	1311.6(3) A^3
Z, Calculated density	2, 1.103 Mg/m^3
Absorption coefficient	0.068 mm^-1
F(000)	464
Crystal size	0.80 x 0.13 x 0.1 mm
Theta range for data collection	2.05 to 25.96 deg.
Limiting indices	-25<=h<=25, -11<=k<=11, -8<=l<=8
Reflections collected / unique	13030 / 4772 [R(int) = 0.0628]
Completeness to theta = 25.96	92.8 %
Absorption correction	none
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4772 / 0 / 298
Goodness-of-fit on F^2	0.854
Final R indices [I>2sigma(I)]	R1 = 0.0542, wR2 = 0.1293 [2305 Fo]
R indices (all data)	R1 = 0.1138, wR2 = 0.1521
Largest diff. peak and hole	0.325 and -0.158 e.A^-3



Atomic coordinates and equivalent isotropic displacement parameters for **3c**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(01)	-0.16632(11)	-0.0089(2)	-0.0733(3)	0.0491(6)
C(02)	-0.10786(11)	-0.1015(2)	-0.0140(3)	0.0457(5)
C(03)	-0.04390(11)	-0.1048(2)	-0.1094(3)	0.0452(5)
C(04)	0.01249(11)	-0.2018(2)	-0.0416(3)	0.0436(5)
C(05)	0.07910(10)	-0.2129(2)	-0.1246(3)	0.0418(5)
C(06)	0.08998(11)	-0.1065(2)	-0.2931(3)	0.0486(5)
C(07)	0.13337(10)	-0.3229(2)	-0.0515(3)	0.0413(5)
C(08)	0.11897(10)	-0.4155(2)	0.1402(3)	0.0413(5)
C(09)	0.10495(13)	-0.3562(3)	0.3080(3)	0.0595(7)
C(10)	0.09057(15)	-0.4402(3)	0.4841(4)	0.0695(7)
C(11)	0.08963(13)	-0.5840(3)	0.4927(4)	0.0637(7)
C(12)	0.10394(15)	-0.6441(3)	0.3290(4)	0.0718(8)
C(13)	0.11906(14)	-0.5610(2)	0.1526(4)	0.0642(7)
C(14)	0.19798(12)	-0.3528(2)	-0.1430(3)	0.0521(6)
C(15)	0.22121(13)	-0.2836(3)	-0.3298(4)	0.0724(8)
C(16)	0.24996(14)	-0.4644(3)	-0.0596(4)	0.0665(7)
C(17)	-0.23021(11)	-0.0011(2)	0.0276(3)	0.0475(5)
C(18)	-0.24651(12)	-0.0985(3)	0.1977(3)	0.0586(6)
C(19)	-0.30898(13)	-0.0841(3)	0.2894(4)	0.0620(7)
C(20)	-0.33423(16)	-0.1817(4)	0.4671(5)	0.0883(10)
C(21)	-0.3491(4)	-0.0965(6)	0.6298(7)	0.210(3)
C(22)	-0.3974(2)	-0.2256(5)	0.4258(8)	0.167(2)
C(23)	-0.28373(19)	-0.3241(4)	0.5065(5)	0.1153(13)
C(24)	-0.28548(11)	0.1102(2)	-0.0371(3)	0.0548(6)
C(25)	-0.34697(12)	0.1244(3)	0.0607(4)	0.0604(6)
C(26)	-0.40967(13)	0.2379(3)	0.0190(5)	0.0821(9)
C(27)	-0.42756(19)	0.3271(4)	0.1863(6)	0.1212(14)
C(28)	-0.46715(16)	0.1635(4)	0.0089(6)	0.1200(14)
C(29)	-0.39690(17)	0.3379(4)	-0.1737(6)	0.1176(14)
N(01)	0.09459(11)	-0.0150(2)	-0.4221(3)	0.0759(7)
N(02)	0.24352(14)	-0.2345(4)	-0.4777(4)	0.1225(12)

N(03)	0.29389(13)	-0.5526(3)	-0.0035(4)	0.1042(10)
O(01)	-0.35894(8)	0.02794(19)	0.2249(3)	0.0684(5)
H(01)	-0.1627	0.0538	-0.1910	0.059
H(02)	-0.1119	-0.1676	0.1003	0.055
H(03)	-0.0385	-0.0393	-0.2235	0.054
H(04)	0.0052	-0.2668	0.0717	0.052
H(09)	0.1052	-0.2584	0.3025	0.071
H(10)	0.0815	-0.3994	0.5970	0.083
H(11)	0.0791	-0.6403	0.6114	0.076
H(12)	0.1036	-0.7420	0.3356	0.086
H(13)	0.1294	-0.6035	0.0409	0.077
H(18)	-0.2128	-0.1745	0.2468	0.070
H(21A)	-0.3085	-0.0716	0.6532	0.315
H(21B)	-0.3663	-0.1539	0.7450	0.315
H(21C)	-0.3821	-0.0090	0.5962	0.315
H(22A)	-0.3862	-0.2803	0.3205	0.250
H(22B)	-0.4311	-0.1397	0.3911	0.250
H(22C)	-0.4145	-0.2844	0.5398	0.250
H(23A)	-0.2765	-0.3729	0.3959	0.173
H(23B)	-0.3008	-0.3849	0.6184	0.173
H(23C)	-0.2419	-0.3051	0.5301	0.173
H(24)	-0.2786	0.1750	-0.1509	0.066
H(27A)	-0.4676	0.4006	0.1634	0.182
H(27B)	-0.3910	0.3725	0.1931	0.182
H(27C)	-0.4353	0.2636	0.3067	0.182
H(28A)	-0.5073	0.2360	-0.0166	0.180
H(28B)	-0.4751	0.1015	0.1304	0.180
H(28C)	-0.4552	0.1061	-0.0935	0.180
H(29A)	-0.4370	0.4106	-0.1989	0.176
H(29B)	-0.3849	0.2813	-0.2770	0.176
H(29C)	-0.3608	0.3845	-0.1663	0.176

Bond lengths [A] for 3c.

C(01)-C(02)	1.381(3)
C(01)-C(17)	1.391(3)
C(02)-C(03)	1.381(3)
C(03)-C(04)	1.384(3)
C(04)-C(05)	1.394(3)
C(05)-C(07)	1.423(3)
C(05)-C(06)	1.435(3)
C(06)-N(01)	1.144(3)
C(07)-C(14)	1.379(3)
C(07)-C(08)	1.498(3)
C(08)-C(09)	1.374(3)
C(08)-C(13)	1.377(3)
C(09)-C(10)	1.376(3)
C(10)-C(11)	1.368(3)
C(11)-C(12)	1.353(4)
C(12)-C(13)	1.378(3)
C(14)-C(15)	1.425(3)
C(14)-C(16)	1.425(4)
C(15)-N(02)	1.136(3)
C(16)-N(03)	1.141(3)
C(17)-C(18)	1.420(3)
C(17)-C(24)	1.424(3)
C(18)-C(19)	1.338(3)
C(19)-O(01)	1.357(3)
C(19)-C(20)	1.515(3)
C(20)-C(21)	1.490(6)
C(20)-C(23)	1.513(5)
C(20)-C(22)	1.529(5)
C(24)-C(25)	1.338(3)
C(25)-O(01)	1.365(3)
C(25)-C(26)	1.502(4)
C(26)-C(28)	1.526(4)
C(26)-C(29)	1.531(4)
C(26)-C(27)	1.540(5)

Bond angles [deg] for 3c.

C(02)-C(01)-C(17)	125.7(2)
C(01)-C(02)-C(03)	125.78(19)
C(02)-C(03)-C(04)	122.56(19)
C(03)-C(04)-C(05)	127.17(19)
C(04)-C(05)-C(07)	123.12(18)
C(04)-C(05)-C(06)	115.64(19)
C(07)-C(05)-C(06)	121.24(19)
N(01)-C(06)-C(05)	175.0(3)
C(14)-C(07)-C(05)	125.63(18)
C(14)-C(07)-C(08)	117.10(19)
C(05)-C(07)-C(08)	117.26(18)
C(09)-C(08)-C(13)	118.55(19)
C(09)-C(08)-C(07)	120.41(18)
C(13)-C(08)-C(07)	121.0(2)

C(08)-C(09)-C(10)	120.6(2)
C(11)-C(10)-C(09)	119.9(2)
C(12)-C(11)-C(10)	120.1(2)
C(11)-C(12)-C(13)	120.3(2)
C(08)-C(13)-C(12)	120.5(2)
C(07)-C(14)-C(15)	126.1(2)
C(07)-C(14)-C(16)	122.4(2)
C(15)-C(14)-C(16)	111.5(2)
N(02)-C(15)-C(14)	175.7(3)
N(03)-C(16)-C(14)	175.8(3)
C(01)-C(17)-C(18)	124.8(2)
C(01)-C(17)-C(24)	120.51(19)
C(18)-C(17)-C(24)	114.7(2)
C(19)-C(18)-C(17)	121.9(2)
C(18)-C(19)-O(01)	120.6(2)
C(18)-C(19)-C(20)	127.8(2)
O(01)-C(19)-C(20)	111.6(2)
C(21)-C(20)-C(23)	114.0(4)
C(21)-C(20)-C(19)	106.8(3)
C(23)-C(20)-C(19)	110.7(3)
C(21)-C(20)-C(22)	111.4(4)
C(23)-C(20)-C(22)	104.6(3)
C(19)-C(20)-C(22)	109.3(3)
C(25)-C(24)-C(17)	122.1(2)
C(24)-C(25)-O(01)	120.1(2)
C(24)-C(25)-C(26)	129.2(2)
O(01)-C(25)-C(26)	110.7(2)
C(25)-C(26)-C(28)	109.5(2)
C(25)-C(26)-C(29)	110.0(2)
C(28)-C(26)-C(29)	109.9(3)
C(25)-C(26)-C(27)	107.7(3)
C(28)-C(26)-C(27)	109.9(3)
C(29)-C(26)-C(27)	109.9(3)
C(19)-O(01)-C(25)	120.51(18)

Anisotropic displacement parameters for 3c.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(01)	0.0502(14)	0.0472(12)	0.0449(14)	-0.0005(10)	0.0014(11)	-0.0101(10)
C(02)	0.0500(13)	0.0438(12)	0.0406(13)	-0.0021(9)	-0.0007(10)	-0.0109(10)
C(03)	0.0480(13)	0.0438(11)	0.0416(13)	-0.0019(9)	-0.0033(10)	-0.0103(10)
C(04)	0.0506(13)	0.0410(11)	0.0385(13)	-0.0020(9)	-0.0041(10)	-0.0124(10)
C(05)	0.0484(12)	0.0410(11)	0.0348(13)	-0.0037(9)	0.0004(10)	-0.0122(10)

```
  C(06)       0.0475(13) 0.0514(13) 0.0418(14)-0.0025(11)-0.0001(11)-
0.0073(10)
  C(07)       0.0484(13) 0.0424(11) 0.0338(12)-0.0054(9) -0.0030(10)-
0.0121(10)
  C(08)       0.0446(12) 0.0403(11) 0.0370(13)-0.0015(9) -0.0031(10)-
0.0094(9)
  C(09)       0.0897(18) 0.0517(13) 0.0393(15)-0.0049(11)-0.0013(13)-
0.0246(13)
  C(10)       0.099(2)   0.0740(17) 0.0382(15)-0.0068(12)-0.0006(14)-
0.0293(15)
  C(11)       0.0719(16) 0.0677(16) 0.0455(16) 0.0133(13)-0.0041(13)-
0.0227(13)
  C(12)       0.104(2)   0.0492(14) 0.0619(19) 0.0024(13)-0.0004(16)-
0.0292(14)
  C(13)       0.096(2)   0.0472(14) 0.0506(16)-0.0087(11) 0.0007(14)-
0.0225(13)
  C(14)       0.0523(14) 0.0563(13) 0.0395(14) 0.0013(10) 0.0014(11)-
0.0062(11)
  C(15)       0.0531(15) 0.0859(19) 0.0573(19) 0.0093(14) 0.0085(13)
0.0012(13)
  C(16)       0.0567(16) 0.0790(18) 0.0465(16) 0.0063(13) 0.0070(13)-
0.0002(14)
  C(17)       0.0479(13) 0.0478(12) 0.0427(14)-0.0036(10) 0.0002(11)-
0.0083(10)
  C(18)       0.0529(15) 0.0610(14) 0.0501(16) 0.0072(11) 0.0026(12)-
0.0066(11)
  C(19)       0.0536(15) 0.0677(16) 0.0531(17) 0.0035(12) 0.0036(12)-
0.0063(13)
  C(20)       0.076(2)   0.101(2)   0.063(2)   0.0179(17) 0.0157(16)-
0.0089(17)
  C(21)       0.381(10)  0.172(5)   0.065(3)  -0.020(3)   0.081(4)  -
0.097(6)
  C(22)       0.106(3)   0.179(4)   0.190(5)   0.076(4)  -0.003(3)  -
0.072(3)
  C(23)       0.116(3)   0.108(3)   0.087(3)   0.039(2)   0.015(2)  -
0.015(2)
  C(24)       0.0508(14) 0.0549(13) 0.0499(15) 0.0045(10) 0.0016(12)-
0.0081(11)
  C(25)       0.0526(15) 0.0590(14) 0.0608(17) 0.0009(12) 0.0009(12)-
0.0070(11)
  C(26)       0.0496(16) 0.0800(19) 0.095(2)   0.0043(16) 0.0042(15)
0.0065(14)
  C(27)       0.092(3)   0.097(3)   0.144(4)  -0.020(2)   0.023(2)
0.0214(19)
  C(28)       0.060(2)   0.137(3)   0.149(4)   0.007(3)  -0.018(2)  -
0.013(2)
  C(29)       0.075(2)   0.107(3)   0.124(3)   0.038(2)  -0.004(2)
0.0224(18)
  N(01)       0.0779(15) 0.0784(15) 0.0532(14) 0.0185(12) 0.0027(12)-
0.0096(12)
  N(02)       0.0895(19) 0.143(3)   0.083(2)   0.0400(19) 0.0326(16)
0.0064(17)
  N(03)       0.0708(17) 0.124(2)   0.0762(19) 0.0224(16) 0.0053(14)
0.0231(16)
  O(01)       0.0534(10) 0.0736(11) 0.0623(12) 0.0042(9)  0.0130(8) -
0.0054(9)
```

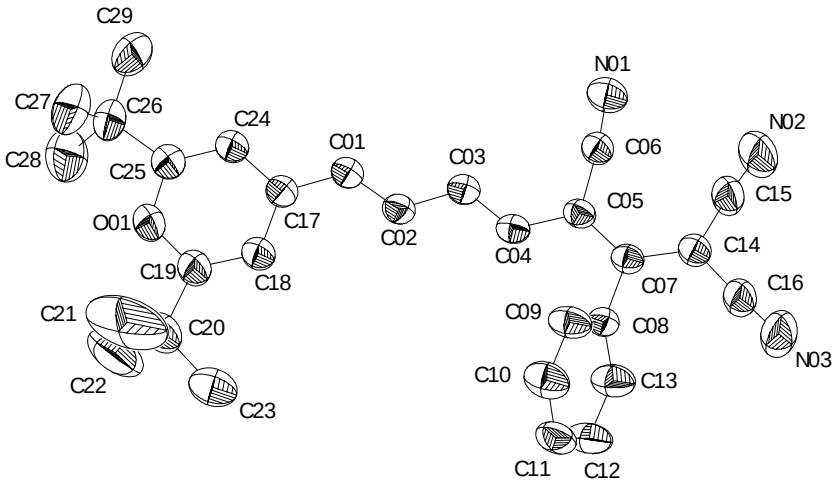


Figure S-71: ORTEP view of **3c**.

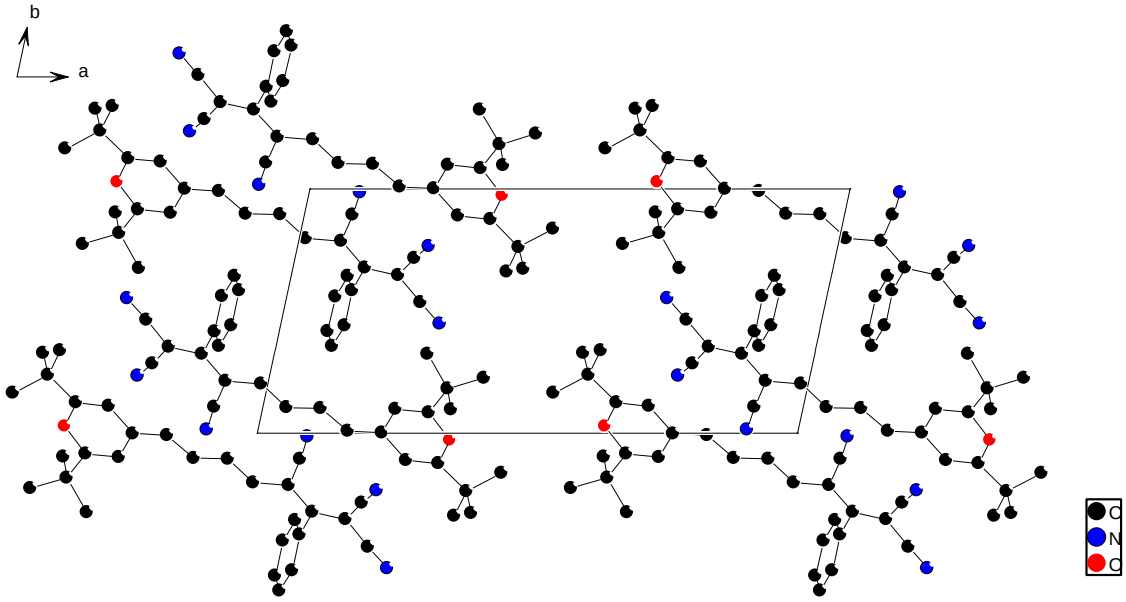


Figure S-72: Crystal packing of **3c** viewed along the [001] direction.

Computational procedures:

All theoretical calculations were performed by using the Gaussian 03[6] program. The molecular geometries were optimized using the B3P86[7] functional and the 6-31G*[8] basis set. The same model chemistry (B3P86/6-31G*) was used for TD-DFT calculations and the excited state dipole moments were calculated by using the one particle RhoCI density. Molecular hyperpolarizabilities at zero frequency were calculated by the Coupled Perturbed Hartree Fock method (CPHF) using the HF/6-31G* model. The default Gaussian 03 parameters were used in every case.

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

1'a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.683246	-1.148723	0.000122
2	8	0	-4.384882	-0.000086	0.000030
3	6	0	-2.334582	-1.204476	0.000114
4	1	0	-4.336564	-2.012052	0.000214
5	6	0	-3.683624	1.148438	-0.000083
6	6	0	-1.544950	0.000169	0.000005

[6] Gaussian 03, Revision B.05, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, V. G.; Montgomery, J. A., Vreven, Jr. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Pittsburgh PA, 2003.

[7] 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.

[8] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213-222.

7	1	0	-1.841426	-2.166658	0.000209
8	6	0	-2.334846	1.204510	-0.000101
9	1	0	-4.336772	2.011929	-0.000158
10	1	0	-1.841732	2.166742	-0.000199
11	6	0	-0.141289	0.000180	-0.000027
12	6	0	0.608464	-1.257518	0.000054
13	6	0	0.608578	1.257872	-0.000221
14	8	0	0.149964	-2.395379	-0.000226
15	8	0	0.150636	2.395876	0.000119
16	7	0	2.001913	-1.138119	0.000036
17	7	0	2.001988	1.137834	0.000023
18	6	0	2.750746	-0.000196	0.000209
19	1	0	2.505336	-2.017131	-0.000077
20	1	0	2.505658	2.016720	0.000002
21	16	0	4.407559	-0.000149	-0.000014

E(RB+HF-VWN+P86) = -1082.00911488 A.U.

1’b

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.776627	1.255628	0.000257
2	8	0	-5.675364	0.244494	0.000003
3	6	0	-3.443064	1.070425	0.000244
4	1	0	-5.269677	2.219364	0.000471
5	6	0	-5.189202	-1.018312	-0.000279
6	6	0	-2.879869	-0.258259	-0.000050
7	1	0	-2.810910	1.950278	0.000466
8	6	0	-3.873313	-1.302977	-0.000317
9	6	0	-1.530100	-0.568825	-0.000100
10	1	0	-5.987675	-1.749155	-0.000467
11	1	0	-3.563562	-2.342505	-0.000555
12	1	0	-1.240051	-1.613806	-0.000338
13	6	0	-0.506533	0.392785	0.000119
14	6	0	0.856327	0.181423	0.000113
15	1	0	-0.771935	1.449011	0.000347
16	6	0	1.702856	1.377844	0.000404
17	6	0	1.466252	-1.143867	-0.000212
18	8	0	1.298739	2.530938	-0.000551
19	8	0	0.879222	-2.217346	0.000397
20	7	0	3.079530	1.136102	0.000108
21	7	0	2.867186	-1.147483	0.000132
22	6	0	3.711215	-0.074366	0.000331
23	1	0	3.673462	1.956655	-0.000220
24	1	0	3.301751	-2.062574	0.000096
25	16	0	5.362072	-0.228830	-0.000208

E(RB+HF-VWN+P86) = -1159.66495729

1’c.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.020720	1.335092	-0.000099
2	8	0	7.006945	0.406500	-0.000100
3	6	0	4.709311	1.034272	-0.000055
4	1	0	6.426807	2.338588	-0.000137
5	6	0	6.629346	-0.895838	-0.000053
6	6	0	4.260799	-0.339350	-0.000005
7	1	0	4.003604	1.856309	-0.000059
8	6	0	5.344244	-1.293244	-0.000007
9	6	0	2.943754	-0.752111	0.000042
10	1	0	7.487737	-1.555161	-0.000058
11	6	0	1.811038	0.089081	0.000054
12	1	0	5.130065	-2.356795	0.000028
13	1	0	2.759677	-1.824818	0.000074
14	6	0	0.512635	-0.363150	0.000092
15	1	0	1.962816	1.168761	0.000017
16	1	0	0.297777	-1.426612	0.000119
17	6	0	-0.564590	0.546039	0.000082
18	6	0	-1.914977	0.274235	0.000135
19	1	0	-0.325316	1.609892	0.000053
20	6	0	-2.819321	1.428802	0.000201
21	6	0	-2.461155	-1.080068	0.000288
22	8	0	-2.473271	2.599880	0.000133
23	8	0	-1.823434	-2.123535	0.000094
24	7	0	-4.183121	1.119414	-0.000079
25	7	0	-3.860482	-1.150842	-0.000045
26	6	0	-4.755223	-0.119825	-0.000453
27	1	0	-4.815915	1.910359	0.000000
28	1	0	-4.250285	-2.085883	0.000032
29	16	0	-6.397072	-0.353814	-0.000097

E(RB+HF-VWN+P86) = -1237.32247070

1’d.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.291596	1.413973	0.000122
2	8	0	-8.328436	0.540754	0.000061
3	6	0	-5.999003	1.042492	0.000098
4	1	0	-7.642152	2.438227	0.000222
5	6	0	-8.020419	-0.781250	-0.000053

6	6	0	-5.623975	-0.354218	-0.000023
7	1	0	-5.250116	1.825528	0.000145
8	6	0	-6.759193	-1.247467	-0.000104
9	6	0	-4.332408	-0.836113	-0.000044
10	1	0	-8.913055	-1.393383	-0.000108
11	6	0	-3.151601	-0.059697	0.000032
12	1	0	-6.603940	-2.321331	-0.000198
13	1	0	-4.209300	-1.917935	-0.000174
14	6	0	-1.881836	-0.579049	0.000003
15	1	0	-3.243179	1.026402	0.000140
16	6	0	-0.719354	0.225320	-0.000014
17	1	0	-1.752330	-1.660645	-0.000045
18	6	0	0.567095	-0.257190	0.000006
19	1	0	-0.863074	1.307560	-0.000090
20	6	0	1.666591	0.626043	-0.000092
21	1	0	0.756709	-1.325421	0.000133
22	6	0	3.009836	0.321065	-0.000044
23	1	0	1.452626	1.695187	-0.000234
24	6	0	3.942408	1.453282	-0.000322
25	6	0	3.523269	-1.046280	0.000087
26	8	0	3.625368	2.632424	-0.000118
27	8	0	2.860970	-2.074195	-0.000328
28	7	0	5.298211	1.110545	0.000046
29	7	0	4.920652	-1.150806	0.000457
30	6	0	5.840045	-0.142003	0.000839
31	1	0	5.949941	1.885948	-0.000279
32	1	0	5.287467	-2.095141	0.000148
33	16	0	7.476000	-0.415529	-0.000190

E(RB+HF-VWN+P86) = -1314.98106228

2’a.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.635502	-1.409100	-0.031015
2	8	0	3.071398	-2.621296	-0.241528
3	6	0	2.930767	-0.267024	0.076086
4	1	0	4.713133	-1.484469	0.038631
5	6	0	1.729339	-2.665270	-0.363313
6	6	0	1.490875	-0.277400	-0.021485
7	1	0	3.442362	0.675159	0.235741
8	6	0	0.932173	-1.582373	-0.265613
9	1	0	1.382025	-3.673111	-0.553107
10	1	0	-0.134383	-1.718425	-0.389424
11	6	0	0.756984	0.892441	0.083051
12	6	0	1.362947	2.224372	0.121178
13	6	0	-0.659284	1.167469	0.021638
14	8	0	2.515206	2.600016	0.191923
15	7	0	-0.900830	2.447442	-0.011893

16	8	0	0.325954	3.121319	0.026908
17	6	0	-1.822577	0.259804	0.037153
18	6	0	-2.852432	0.438218	-0.892266
19	6	0	-1.948507	-0.736771	1.012952
20	6	0	-3.979347	-0.376631	-0.857034
21	6	0	-3.076831	-1.550011	1.045588
22	1	0	-2.758730	1.223034	-1.636071
23	1	0	-1.167956	-0.856959	1.759710
24	6	0	-4.092654	-1.374717	0.107853
25	1	0	-4.771587	-0.231058	-1.585794
26	1	0	-3.168250	-2.314027	1.812519
27	1	0	-4.973001	-2.010595	0.133995

E(RB+HF-VWN+P86) = -821.480667386

2’b. Z-isomer.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.987902	-2.160663	-0.210667
2	8	0	5.227761	-1.617981	-0.176471
3	6	0	2.853101	-1.440882	-0.141577
4	1	0	4.034123	-3.238525	-0.301396
5	6	0	5.309021	-0.268401	-0.069302
6	6	0	2.891137	-0.001261	-0.023235
7	1	0	1.912972	-1.978206	-0.182266
8	6	0	4.231799	0.533576	0.005377
9	6	0	1.795672	0.834997	0.056198
10	1	0	6.338980	0.063987	-0.053208
11	1	0	1.969049	1.904601	0.133163
12	1	0	4.383142	1.604483	0.088803
13	6	0	0.451161	0.409181	0.042366
14	6	0	-0.633901	1.246891	0.096309
15	1	0	0.239236	-0.656531	-0.028501
16	6	0	-0.595366	2.711500	0.087283
17	6	0	-2.041887	0.939601	0.049196
18	8	0	0.321717	3.502088	0.120973
19	7	0	-2.770664	2.018198	-0.005839
20	8	0	-1.906500	3.124965	0.006355
21	6	0	-2.695308	-0.377127	0.039763
22	6	0	-3.824393	-0.587387	-0.761098
23	6	0	-2.223030	-1.424569	0.840136
24	6	0	-4.460264	-1.822957	-0.767491
25	6	0	-2.860987	-2.661300	0.828989
26	1	0	-4.190208	0.230064	-1.374205
27	1	0	-1.377556	-1.257314	1.501375
28	6	0	-3.977740	-2.865003	0.022621
29	1	0	-5.334303	-1.974977	-1.394390
30	1	0	-2.491604	-3.463643	1.461609
31	1	0	-4.474488	-3.831081	0.013827

E(RB+HF-VWN+P86) = -899.137938877

2’b. E-isomer.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.814992	0.532035	0.035430
2	8	0	5.306163	-0.718324	-0.139059
3	6	0	3.501862	0.822332	0.073914
4	1	0	5.613135	1.256028	0.138809
5	6	0	4.406143	-1.721030	-0.280930
6	6	0	2.506557	-0.214847	-0.074291
7	1	0	3.218375	1.857487	0.221226
8	6	0	3.074834	-1.529426	-0.255734
9	6	0	1.138239	-0.028297	-0.052763
10	1	0	4.897638	-2.676120	-0.414888
11	1	0	0.517056	-0.910764	-0.171953
12	1	0	2.423633	-2.388375	-0.378907
13	6	0	0.506221	1.225355	0.078876
14	6	0	-0.829312	1.528846	0.096450
15	1	0	1.134820	2.114473	0.141925
16	6	0	-1.256796	2.932054	0.069788
17	6	0	-2.067152	0.791255	0.003136
18	8	0	-0.623411	3.959543	0.131828
19	7	0	-3.090706	1.591516	-0.100834
20	8	0	-2.626463	2.914420	-0.078735
21	6	0	-2.319071	-0.659529	0.033812
22	6	0	-3.240635	-1.224365	-0.854599
23	6	0	-1.694300	-1.478079	0.982265
24	6	0	-3.519562	-2.585787	-0.804766
25	6	0	-1.977144	-2.839477	1.030453
26	1	0	-3.732162	-0.582813	-1.578967
27	1	0	-1.004512	-1.038918	1.697614
28	6	0	-2.886461	-3.397287	0.134222
29	1	0	-4.233547	-3.014749	-1.502085
30	1	0	-1.494932	-3.463767	1.777592
31	1	0	-3.105364	-4.460732	0.171618

E(RB+HF-VWN+P86) = -899.134386648

2’c. Z-isomer.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	5.581206	-1.996106	-0.168542
2	8	0	6.777877	-1.359642	-0.145236
3	6	0	4.395060	-1.364755	-0.113484
4	1	0	5.709669	-3.068892	-0.237216
5	6	0	6.752818	-0.004636	-0.062408
6	6	0	4.320181	0.077055	-0.023456
7	1	0	3.498754	-1.972960	-0.140323
8	6	0	5.617414	0.712863	-0.003118
9	6	0	3.158718	0.816136	0.037292
10	1	0	7.753717	0.407186	-0.051277
11	1	0	3.261446	1.898035	0.098835
12	1	0	5.689704	1.793550	0.061310
13	6	0	1.841577	0.302594	0.025478
14	6	0	0.712212	1.078839	0.081540
15	1	0	1.705048	-0.777852	-0.032597
16	6	0	-0.583441	0.512019	0.062315
17	1	0	0.791412	2.161412	0.138207
18	6	0	-1.757844	1.217578	0.092730
19	1	0	-0.650981	-0.574593	0.002912
20	6	0	-1.887093	2.678083	0.070757
21	6	0	-3.121392	0.750989	0.031089
22	8	0	-1.067731	3.568424	0.108448
23	7	0	-3.967121	1.739406	-0.042061
24	8	0	-3.236221	2.937881	-0.028991
25	6	0	-3.621865	-0.631112	0.023102
26	6	0	-4.714689	-0.969734	-0.784189
27	6	0	-3.040441	-1.615877	0.830835
28	6	0	-5.208166	-2.268694	-0.788832
29	6	0	-3.535859	-2.916188	0.821429
30	1	0	-5.165286	-0.200985	-1.403826
31	1	0	-2.221987	-1.353674	1.494958
32	6	0	-4.617366	-3.246981	0.009237
33	1	0	-6.055028	-2.520144	-1.421070
34	1	0	-3.081920	-3.669824	1.458857
35	1	0	-5.002285	-4.262834	0.001239

E(RB+HF-VWN+P86) = -976.796034975

2’c. E-isomer.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.942185	-1.075180	0.043686
2	8	0	-6.744703	0.011557	-0.070343
3	6	0	-4.598586	-1.018096	0.041707
4	1	0	-6.523735	-1.983688	0.135267
5	6	0	-6.134350	1.217246	-0.193700
6	6	0	-3.905255	0.244862	-0.086080
7	1	0	-4.055128	-1.950355	0.138648
8	6	0	-4.798969	1.373620	-0.206148

9	6	0	-2.536933	0.408933	-0.097220
10	1	0	-6.857919	2.017728	-0.278969
11	1	0	-2.160666	1.425184	-0.202008
12	1	0	-4.395637	2.375588	-0.309390
13	6	0	-1.575235	-0.621345	0.014592
14	6	0	-0.217672	-0.424085	-0.000390
15	1	0	-1.923886	-1.648588	0.120706
16	6	0	0.683424	-1.509655	0.099289
17	1	0	0.169881	0.585053	-0.110400
18	6	0	2.051957	-1.521982	0.089637
19	1	0	0.241469	-2.506379	0.163569
20	6	0	2.771406	-2.801287	0.043796
21	6	0	3.101766	-0.535049	-0.013376
22	8	0	2.376997	-3.941405	0.104830
23	7	0	4.271408	-1.096683	-0.138469
24	8	0	4.103193	-2.487857	-0.123194
25	6	0	3.039507	0.935780	0.025195
26	6	0	3.822115	1.686361	-0.859298
27	6	0	2.256572	1.600541	0.976219
28	6	0	3.808705	3.075571	-0.803105
29	6	0	2.246007	2.990807	1.030015
30	1	0	4.437796	1.166085	-1.586040
31	1	0	1.675516	1.024172	1.690667
32	6	0	3.018137	3.731709	0.137960
33	1	0	4.416745	3.647967	-1.497905
34	1	0	1.641612	3.495895	1.778348
35	1	0	3.007741	4.817238	0.179761

E(RB+HF-VWN+P86) = -976.792395014

2’d. Z-isomer.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.031218	1.974585	-0.144547
2	8	0	-8.215544	1.313291	-0.123771
3	6	0	-5.832265	1.367792	-0.100311
4	1	0	-7.182095	3.045158	-0.201206
5	6	0	-8.160535	-0.042473	-0.054612
6	6	0	-5.725685	-0.073639	-0.025665
7	1	0	-4.949110	1.995217	-0.123196
8	6	0	-7.010221	-0.736078	-0.006799
9	6	0	-4.548749	-0.786792	0.023235
10	1	0	-9.152279	-0.475908	-0.043813
11	6	0	-3.240676	-0.246419	0.011404
12	1	0	-4.630419	-1.871405	0.075476
13	1	0	-7.060473	-1.818694	0.047121
14	6	0	-2.093552	-0.994340	0.058352
15	1	0	-3.126704	0.836513	-0.038720
16	6	0	-0.795295	-0.428987	0.043488

17	1	0	-2.172149	-2.079850	0.107933
18	6	0	0.370628	-1.148729	0.085671
19	1	0	-0.728535	0.659854	-0.006442
20	6	0	1.636721	-0.517428	0.062724
21	1	0	0.345631	-2.234249	0.134794
22	6	0	2.845305	-1.162859	0.083852
23	1	0	1.648218	0.571326	0.008470
24	6	0	3.048568	-2.615118	0.055276
25	6	0	4.183310	-0.627569	0.018624
26	8	0	2.275885	-3.546061	0.092474
27	7	0	5.077682	-1.571715	-0.061635
28	8	0	4.408862	-2.805724	-0.050534
29	6	0	4.613959	0.777866	0.013138
30	6	0	5.686039	1.172147	-0.796765
31	6	0	3.987148	1.730695	0.825157
32	6	0	6.114656	2.493888	-0.799689
33	6	0	4.417553	3.053956	0.817319
34	1	0	6.172029	0.428235	-1.419967
35	1	0	3.184649	1.427127	1.491074
36	6	0	5.478760	3.439831	0.002650
37	1	0	6.945907	2.788432	-1.434054
38	1	0	3.928525	3.782664	1.457744
39	1	0	5.812719	4.473572	-0.004126

E(RB+HF-VWN+P86) = -1054.45480653

2’c. E-isomer.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.203776	-1.228812	0.084073
2	8	0	-8.122899	-0.239129	-0.041344
3	6	0	-5.874989	-1.024481	0.070248
4	1	0	-7.681068	-2.194150	0.195238
5	6	0	-7.648265	1.024918	-0.187853
6	6	0	-5.324318	0.305002	-0.083488
7	1	0	-5.231599	-1.889618	0.178421
8	6	0	-6.338558	1.326638	-0.212497
9	6	0	-3.983043	0.616260	-0.111027
10	1	0	-8.455776	1.739782	-0.279857
11	6	0	-2.909743	-0.299571	-0.000168
12	1	0	-3.721925	1.666434	-0.232883
13	1	0	-6.049010	2.365336	-0.333854
14	6	0	-1.584874	0.048209	-0.035191
15	1	0	-3.141466	-1.357827	0.119341
16	6	0	-0.533630	-0.895044	0.070197
17	1	0	-1.317549	1.097954	-0.153668
18	6	0	0.803138	-0.592293	0.035695
19	1	0	-0.816902	-1.942863	0.184215
20	6	0	1.790128	-1.602796	0.118216
21	1	0	1.108189	0.444224	-0.080024

22	6	0	3.154523	-1.500795	0.081483
23	1	0	1.431396	-2.631946	0.186790
24	6	0	3.980324	-2.713205	0.010985
25	6	0	4.112922	-0.426731	-0.038402
26	8	0	3.687671	-3.883345	0.073740
27	7	0	5.323337	-0.884329	-0.194821
28	8	0	5.275877	-2.284992	-0.186032
29	6	0	3.923113	1.032522	0.017234
30	6	0	4.603115	1.857769	-0.885032
31	6	0	3.117418	1.615323	1.002506
32	6	0	4.466245	3.239625	-0.812177
33	6	0	2.984223	2.998324	1.073629
34	1	0	5.236864	1.401280	-1.638634
35	1	0	2.614439	0.981776	1.727680
36	6	0	3.654347	3.813385	0.163943
37	1	0	4.994736	3.870755	-1.521026
38	1	0	2.363377	3.440248	1.847979
39	1	0	3.547962	4.893160	0.218876

E(RB+HF-VWN+P86) = -1054.45112774

3’a.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.145002	-0.053374	-0.039184
2	8	0	-4.079150	-1.144581	-0.833665
3	6	0	-3.062847	0.639923	0.361811
4	6	0	-1.735062	0.241418	-0.035747
5	6	0	-1.711967	-0.912118	-0.899698
6	6	0	-2.855233	-1.533626	-1.249026
7	6	0	-0.609536	0.960264	0.356959
8	6	0	-0.828250	2.133281	1.134901
9	7	0	-1.058494	3.050786	1.815362
10	6	0	0.771339	0.579344	0.055009
11	6	0	1.700324	1.534207	-0.298342
12	6	0	3.100347	1.266359	-0.382175
13	7	0	4.248866	1.096110	-0.460601
14	6	0	1.331096	2.872115	-0.631017
15	7	0	1.059909	3.955941	-0.955719
16	6	0	1.164943	-0.836332	0.207957
17	6	0	0.694438	-1.571215	1.306933
18	6	0	1.062541	-2.899909	1.475463
19	6	0	1.888206	-3.521166	0.540025
20	6	0	2.349998	-2.804890	-0.561892
21	6	0	1.996829	-1.470475	-0.726688
22	1	0	-5.167338	0.183105	0.226126
23	1	0	-3.204140	1.508844	0.994719
24	1	0	0.055624	-1.084283	2.037419
25	1	0	-2.914164	-2.397785	-1.898239
26	1	0	-0.781950	-1.296425	-1.297022

27	1	0	0.706385	-3.451471	2.340519
28	1	0	2.171241	-4.561700	0.669823
29	1	0	2.989534	-3.284712	-1.296578
30	1	0	2.353055	-0.921617	-1.592462

E(RB+HF-VWN+P86) = -895.089945002

3a

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.680522	-0.507275	0.161629
2	8	0	3.740045	0.669089	-0.517094
3	6	0	2.500233	-1.098640	0.449433
4	6	0	1.247623	-0.510890	0.058639
5	6	0	1.376644	0.718955	-0.673293
6	6	0	2.589540	1.257684	-0.933147
7	6	0	0.032911	-1.141212	0.338591
8	6	0	0.098158	-2.410164	0.981715
9	7	0	0.207861	-3.417043	1.558511
10	6	0	-1.285539	-0.586707	0.044835
11	6	0	-2.306262	-1.394777	-0.412830
12	6	0	-3.665377	-0.964213	-0.487352
13	7	0	-4.785834	-0.658378	-0.563358
14	6	0	-2.080969	-2.726859	-0.871787
15	7	0	-1.927671	-3.798001	-1.299813
16	6	0	-1.535379	0.844167	0.319692
17	6	0	-1.044182	1.419034	1.501473
18	6	0	-1.281221	2.758098	1.785063
19	6	0	-1.993942	3.548559	0.885158
20	6	0	-2.474861	2.991109	-0.297444
21	6	0	-2.253199	1.647510	-0.577989
22	1	0	2.507494	-2.038999	0.988553
23	1	0	-0.492868	0.800473	2.203124
24	1	0	0.502612	1.235242	-1.046415
25	1	0	-0.911877	3.185370	2.712767
26	1	0	-2.175357	4.596511	1.105885
27	1	0	-3.028332	3.602137	-1.004197
28	1	0	-2.624102	1.221265	-1.504613
29	6	0	5.031385	-1.012933	0.518878
30	1	0	5.632115	-1.173700	-0.383123
31	1	0	5.563122	-0.284626	1.141099
32	1	0	4.955192	-1.954856	1.064269
33	6	0	2.849927	2.512618	-1.686217
34	1	0	1.911753	2.973340	-1.999472
35	1	0	3.403802	3.225144	-1.065136
36	1	0	3.459520	2.309549	-2.573638

E(RB+HF-VWN+P86) = -974.034501152 A.U.

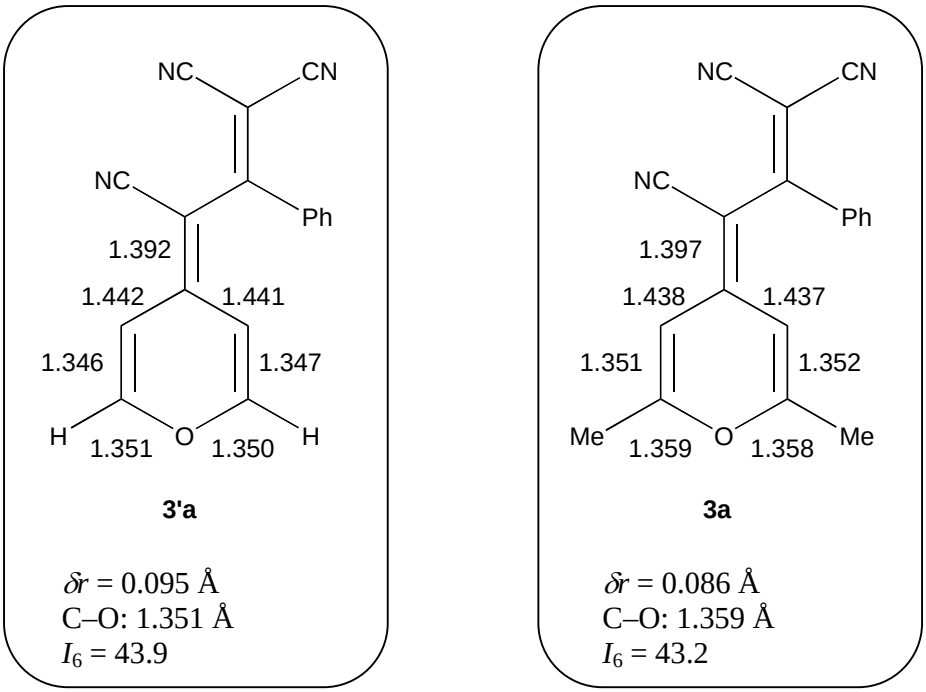


Figure S-73: DFT Calculated Geometries of **3a** and **3'a**: Selected Bond Distances (Å) and Structural Parameters (δr and I_6 are defined in the manuscript)

3'b.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.598837	1.391130	-0.667927
2	8	0	5.741448	0.696474	-0.465666
3	6	0	3.368433	0.879088	-0.476901
4	6	0	3.193433	-0.482463	-0.030790
5	6	0	4.436740	-1.184578	0.171362
6	6	0	5.622365	-0.586218	-0.047307
7	6	0	1.981954	-1.108545	0.198438
8	6	0	0.719777	-0.512371	0.027516
9	6	0	-0.499459	-1.138378	0.233212
10	6	0	-0.472932	-2.492743	0.684146
11	6	0	-1.756147	-0.440640	0.035795
12	6	0	-2.945622	-1.088496	-0.234381
13	6	0	-1.747139	1.038207	0.137933
14	6	0	-1.197339	1.664166	1.266330
15	6	0	-1.207347	3.049586	1.377394
16	6	0	-1.748412	3.828881	0.356521
17	6	0	-2.284821	3.216617	-0.773440

18	6	0	-2.290378	1.830260	-0.881233
19	6	0	-4.194666	-0.397115	-0.248710
20	7	0	-5.236607	0.121729	-0.262298
21	6	0	-3.044500	-2.473527	-0.560257
22	7	0	-3.183965	-3.583288	-0.881767
23	7	0	-0.351443	-3.570645	1.106616
24	1	0	4.805880	2.400491	-0.999986
25	1	0	2.519339	1.524215	-0.668745
26	1	0	4.428074	-2.216674	0.505167
27	1	0	6.591150	-1.050991	0.082585
28	1	0	2.009603	-2.142702	0.533392
29	1	0	0.670370	0.519291	-0.308163
30	1	0	-0.783315	1.055740	2.065069
31	1	0	-0.797424	3.521124	2.265829
32	1	0	-1.754279	4.911614	0.443291
33	1	0	-2.705338	3.818442	-1.573472
34	1	0	-2.708195	1.355927	-1.763705

E(RB+HF-VWN+P86) = -972.750143755

3’c.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.106355	1.505053	-0.647979
2	8	0	-7.256383	0.824868	-0.427904
3	6	0	-4.880355	0.980523	-0.468279
4	6	0	-4.712490	-0.381482	-0.015899
5	6	0	-5.963096	-1.068121	0.203386
6	6	0	-7.144160	-0.458404	-0.004015
7	6	0	-3.503542	-1.011689	0.200149
8	6	0	-2.225346	-0.442037	0.021730
9	6	0	-1.045785	-1.109264	0.249197
10	6	0	0.210242	-0.499857	0.053854
11	6	0	1.442791	-1.106330	0.229814
12	6	0	2.685183	-0.390467	0.005627
13	6	0	3.874251	-1.022334	-0.302852
14	6	0	5.115502	-0.318098	-0.342072
15	7	0	6.152260	0.210207	-0.376075
16	6	0	3.979244	-2.402462	-0.647054
17	7	0	4.122499	-3.506599	-0.985907
18	6	0	2.661032	1.086467	0.123495
19	6	0	2.126398	1.693730	1.269115
20	6	0	2.123869	3.077715	1.395693
21	6	0	2.636636	3.874185	0.373580
22	6	0	3.157220	3.280556	-0.773556
23	6	0	3.175603	1.895771	-0.897098
24	6	0	1.448981	-2.462113	0.678282
25	7	0	1.361866	-3.543182	1.101063
26	1	0	-6.305835	2.514635	-0.984000
27	1	0	-4.026276	1.614239	-0.675412

28	1	0	-5.963849	-2.098587	0.542811
29	1	0	-8.116042	-0.912307	0.140404
30	1	0	-3.538062	-2.045314	0.539487
31	1	0	-2.157517	0.591406	-0.318022
32	1	0	-1.075102	-2.143532	0.586564
33	1	0	0.217047	0.534727	-0.281488
34	1	0	1.733501	1.072065	2.068263
35	1	0	1.725145	3.534814	2.296665
36	1	0	2.631923	4.955919	0.472216
37	1	0	3.554697	3.895860	-1.575118
38	1	0	3.580118	1.436093	-1.793409

E(RB+HF-VWN+P86) = -1050.40852234

3’d.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-7.567053	1.611664	-0.627683
2	8	0	-8.723619	0.940285	-0.408434
3	6	0	-6.345414	1.075616	-0.455713
4	6	0	-6.186282	-0.291464	-0.012682
5	6	0	-7.443241	-0.968293	0.206043
6	6	0	-8.619535	-0.347613	0.006909
7	6	0	-1.248147	-0.467622	0.051985
8	6	0	-0.056381	-1.118409	0.259822
9	6	0	1.188177	-0.488339	0.056116
10	6	0	2.431680	-1.078569	0.211444
11	6	0	3.660743	-0.342844	-0.019824
12	6	0	4.855914	-0.954146	-0.346828
13	6	0	6.085876	-0.230880	-0.393069
14	7	0	7.114269	0.313126	-0.434179
15	6	0	4.978554	-2.329176	-0.705047
16	7	0	5.136239	-3.427850	-1.055168
17	6	0	3.616724	1.132535	0.111225
18	6	0	3.086983	1.722078	1.268272
19	6	0	3.065694	3.104728	1.406820
20	6	0	3.554626	3.917270	0.385695
21	6	0	4.070321	3.341151	-0.772486
22	6	0	4.107513	1.957888	-0.908191
23	6	0	2.463411	-2.438681	0.645625
24	7	0	2.398218	-3.524978	1.058856
25	1	0	-7.758678	2.625257	-0.956183
26	1	0	-5.486670	1.703545	-0.661459
27	1	0	-7.452329	-2.000961	0.538903
28	1	0	-9.594573	-0.794526	0.151914
29	1	0	-1.216628	0.571826	-0.279192
30	1	0	-0.066217	-2.156159	0.587504
31	1	0	1.175210	0.549313	-0.269091
32	1	0	2.712254	1.087922	2.066318
33	1	0	2.670447	3.548264	2.316054

34	1	0	3.534826	4.997955	0.493559
35	1	0	4.448955	3.969040	-1.573417
36	1	0	4.507995	1.511822	-1.813170
37	6	0	-2.522972	-1.048388	0.235392
38	1	0	-2.565999	-2.085809	0.565273
39	6	0	-3.697244	-0.372039	0.017701
40	1	0	-3.621153	0.663523	-0.313793
41	6	0	-4.982335	-0.931212	0.195059
42	1	0	-5.025237	-1.966888	0.528182

E(RB+HF-VWN+P86) = -1128.06746638

4’a.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.977653	-1.577400	0.624870
2	8	0	-3.995481	-0.698006	0.509248
3	6	0	-1.696899	-1.286356	0.326550
4	1	0	-3.323157	-2.535643	0.991417
5	6	0	-3.689932	0.551221	0.090503
6	6	0	-1.330863	0.029414	-0.140232
7	1	0	-0.947086	-2.056460	0.457687
8	6	0	-2.443112	0.945780	-0.225029
9	1	0	-4.569950	1.179673	0.044784
10	1	0	-2.281954	1.968966	-0.545412
11	6	0	-0.036875	0.428730	-0.438735
12	6	0	1.125690	-0.468768	-0.423821
13	6	0	2.318506	-0.132120	0.193919
14	6	0	3.425678	-1.010981	0.050438
15	7	0	4.274228	-1.792142	-0.118002
16	6	0	2.450778	1.006877	1.030889
17	7	0	2.579956	1.921647	1.738905
18	6	0	0.187948	1.784076	-0.802849
19	7	0	0.309974	2.892849	-1.139638
20	7	0	0.975299	-1.677159	-1.030197
21	1	0	0.317470	-1.738698	-1.794153
22	1	0	1.792729	-2.272982	-1.104816

E(RB+HF-VWN+P86) = -718.827734827

4’b.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.369256	-1.512414	0.520516

2	8	0	-5.403673	-0.651913	0.384516
3	6	0	-3.081938	-1.172075	0.323254
4	1	0	-4.712835	-2.497777	0.808698
5	6	0	-5.107626	0.623466	0.035446
6	6	0	-2.719365	0.173569	-0.056201
7	1	0	-2.331149	-1.939573	0.469275
8	6	0	-3.852962	1.057599	-0.182206
9	6	0	-1.437073	0.631191	-0.285035
10	1	0	-6.001162	1.229403	-0.041029
11	1	0	-3.701860	2.096068	-0.456861
12	1	0	-1.318771	1.680482	-0.544877
13	6	0	-0.267017	-0.150125	-0.200221
14	6	0	1.020944	0.318889	-0.360279
15	1	0	-0.357793	-1.207554	0.037766
16	6	0	2.164131	-0.587837	-0.306194
17	6	0	3.411509	-0.230277	0.187032
18	6	0	4.471233	-1.169846	0.077259
19	7	0	5.282283	-1.997681	-0.050449
20	6	0	3.657213	0.976422	0.892390
21	7	0	3.894485	1.942409	1.497359
22	6	0	1.228098	1.701629	-0.629751
23	7	0	1.311900	2.831342	-0.898190
24	7	0	1.932643	-1.863617	-0.725505
25	1	0	1.276953	-1.991174	-1.483063
26	1	0	2.719484	-2.502890	-0.724611

E(RB+HF-VWN+P86) = -796.486607933

4’c.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.665549	-1.543400	0.475046
2	8	0	-6.733280	-0.718178	0.361808
3	6	0	-4.391357	-1.146866	0.303683
4	1	0	-5.973532	-2.551960	0.719905
5	6	0	-6.481573	0.579956	0.059842
6	6	0	-4.075613	0.225771	-0.021120
7	1	0	-3.612566	-1.891073	0.420195
8	6	0	-5.242898	1.068677	-0.129370
9	6	0	-2.807288	0.731983	-0.215897
10	1	0	-7.396815	1.153964	-0.005714
11	6	0	-1.599904	0.004100	-0.133958
12	1	0	-5.131544	2.121278	-0.367432
13	1	0	-2.727469	1.791583	-0.451606
14	1	0	-1.649014	-1.059312	0.100930
15	6	0	-0.355232	0.548258	-0.328158
16	6	0	0.826292	-0.219716	-0.229723
17	1	0	-0.264454	1.608285	-0.557174
18	6	0	2.114758	0.256268	-0.352877

19	1	0	0.716714	-1.279130	-0.002161
20	6	0	3.261811	-0.644687	-0.280263
21	6	0	4.498560	-0.282082	0.237273
22	6	0	5.563770	-1.217079	0.144994
23	7	0	6.380435	-2.041354	0.029907
24	6	0	4.727007	0.922562	0.951519
25	7	0	4.952323	1.885885	1.565355
26	6	0	2.321194	1.642452	-0.606066
27	7	0	2.408230	2.774603	-0.862826
28	7	0	3.046908	-1.918523	-0.709357
29	1	0	2.390916	-2.053812	-1.464872
30	1	0	3.834860	-2.555846	-0.697638

E(RB+HF-VWN+P86) = -874.145305599

4’d.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.948265	-1.595659	0.455923
2	8	0	-8.042419	-0.803340	0.347033
3	6	0	-5.686361	-1.155492	0.304360
4	1	0	-7.225620	-2.618024	0.679238
5	6	0	-7.828411	0.508044	0.069613
6	6	0	-5.410730	0.232545	0.006358
7	1	0	-4.885107	-1.876589	0.414071
8	6	0	-6.604536	1.038915	-0.098918
9	6	0	-4.157504	0.779742	-0.168237
10	1	0	-8.760777	1.053873	0.004618
11	6	0	-2.926685	0.089338	-0.087787
12	1	0	-6.525577	2.098559	-0.318410
13	1	0	-4.109866	1.844999	-0.388205
14	6	0	-1.697949	0.672185	-0.265505
15	1	0	-2.943127	-0.978215	0.131692
16	6	0	-0.481523	-0.043940	-0.175924
17	1	0	-1.645882	1.738282	-0.483443
18	6	0	0.764834	0.504335	-0.341568
19	1	0	-0.549379	-1.110970	0.044226
20	6	0	1.945732	-0.263923	-0.235513
21	1	0	0.857968	1.567507	-0.554480
22	6	0	3.235574	0.214566	-0.334172
23	1	0	1.832868	-1.326122	-0.023491
24	6	0	4.382237	-0.686403	-0.259444
25	6	0	5.613924	-0.328804	0.274200
26	6	0	6.680561	-1.262000	0.181345
27	7	0	7.498966	-2.084360	0.064514
28	6	0	5.835351	0.867591	1.004213
29	7	0	6.055148	1.823350	1.631771
30	6	0	3.444944	1.604034	-0.566161
31	7	0	3.536175	2.739456	-0.806522
32	7	0	4.173100	-1.955479	-0.704387

33	1	0	3.522178	-2.084784	-1.465248
34	1	0	4.960779	-2.592995	-0.691156

E(RB+HF-VWN+P86) = -951.804328903

5'a. *s-cis*.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.796435	-1.545327	0.775532
2	6	0	-2.627811	-0.905190	0.572938
3	6	0	-2.594335	0.382227	-0.073252
4	6	0	-3.903133	0.892177	-0.401870
5	6	0	-5.016294	0.171508	-0.168113
6	1	0	-3.895494	-2.512176	1.251593
7	1	0	-1.726996	-1.388507	0.921820
8	1	0	-4.006127	1.865771	-0.869227
9	1	0	-6.024242	0.481369	-0.412328
10	6	0	-1.473819	1.157789	-0.316993
11	1	0	-1.681845	2.182587	-0.619447
12	8	0	-4.997995	-1.051325	0.404308
13	6	0	-0.099329	0.853669	-0.179383
14	6	0	0.902706	1.978814	0.012692
15	6	0	0.619560	-0.328777	-0.227107
16	8	0	2.175916	1.296863	0.120759
17	6	0	2.015606	-0.023438	-0.013144
18	6	0	0.117287	-1.595143	-0.604557
19	7	0	-0.357523	-2.602652	-0.944531
20	6	0	0.682910	2.736246	1.316753
21	1	0	1.484366	3.465822	1.462295
22	1	0	-0.274791	3.264183	1.289875
23	1	0	0.676860	2.047151	2.165527
24	6	0	0.994397	2.909848	-1.191948
25	1	0	0.074641	3.490974	-1.306061
26	1	0	1.825629	3.605866	-1.048716
27	1	0	1.167702	2.340088	-2.108731
28	6	0	3.119129	-0.841894	0.068065
29	6	0	4.403787	-0.264247	0.264327
30	7	0	5.457386	0.203708	0.424710
31	6	0	3.030436	-2.257023	-0.002882
32	7	0	3.001416	-3.420324	-0.039248

E(RB+HF-VWN+P86) = -933.488652484

5’a. *s-trans*.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.595650	-1.065832	-0.000324
2	6	0	-3.259605	-0.887233	-0.000069
3	6	0	-2.679542	0.435742	0.000096
4	6	0	-3.683329	1.478741	-0.000041
5	6	0	-4.999307	1.203274	-0.000317
6	1	0	-5.085101	-2.031642	-0.000441
7	1	0	-2.649935	-1.778179	0.000031
8	1	0	-3.375285	2.518979	0.000051
9	1	0	-5.792603	1.939272	-0.000472
10	6	0	-1.351064	0.818299	0.000423
11	1	0	-1.211611	1.897842	0.000604
12	8	0	-5.493187	-0.059548	-0.000459
13	6	0	-0.115029	0.125756	0.000275
14	6	0	0.203911	-1.359040	0.000260
15	6	0	1.099292	0.796357	0.000218
16	8	0	1.658716	-1.397803	0.000335
17	6	0	2.169779	-0.161954	0.000146
18	6	0	1.217444	2.206217	0.000213
19	7	0	1.202266	3.370124	0.000312
20	6	0	-0.211751	-2.073060	-1.283539
21	1	0	0.158913	-3.101573	-1.260899
22	1	0	-1.294944	-2.092844	-1.416116
23	1	0	0.225056	-1.565193	-2.147376
24	6	0	-0.211886	-2.073035	1.284040
25	1	0	-1.295100	-2.092850	1.416448
26	1	0	0.158801	-3.101545	1.261504
27	1	0	0.224780	-1.565120	2.147917
28	6	0	3.536608	0.000154	-0.000133
29	6	0	4.376464	-1.146948	-0.000348
30	7	0	5.065883	-2.084828	-0.000464
31	6	0	4.151336	1.279672	-0.000292
32	7	0	4.692820	2.310275	-0.000408

E(RB+HF-VWN+P86) = -933.484890956

5’b. *s-cis*.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.138824	1.732476	-0.000208
2	6	0	3.985361	1.038035	-0.000159
3	6	0	3.993789	-0.405987	0.000034
4	6	0	5.317394	-0.975840	0.000142

5	6	0	6.414714	-0.195121	0.000081
6	1	0	5.211633	2.812398	-0.000350
7	1	0	3.059785	1.603165	-0.000281
8	1	0	5.446903	-2.052963	0.000278
9	1	0	7.436286	-0.553130	0.000158
10	8	0	6.364096	1.155846	-0.000087
11	6	0	-0.915034	-1.009714	0.000016
12	6	0	-2.093188	-1.961534	0.000133
13	6	0	-1.429946	0.278419	-0.000140
14	8	0	-3.249192	-1.086757	-0.000071
15	6	0	-2.868064	0.195462	-0.000152
16	6	0	-0.660959	1.464194	-0.000387
17	7	0	0.065751	2.375004	-0.000665
18	6	0	-2.166515	-2.805306	1.267774
19	1	0	-3.092143	-3.387679	1.268535
20	1	0	-1.319409	-3.495709	1.317983
21	1	0	-2.151245	-2.167449	2.155437
22	6	0	-2.166435	-2.805779	-1.267192
23	1	0	-1.319380	-3.496270	-1.317045
24	1	0	-3.092107	-3.388081	-1.267825
25	1	0	-2.151025	-2.168265	-2.155099
26	6	0	-3.833233	1.178812	-0.000183
27	6	0	-5.206634	0.812284	-0.000436
28	7	0	-6.332898	0.517703	-0.000677
29	6	0	-3.511074	2.560796	0.000069
30	7	0	-3.283623	3.702863	0.001544
31	6	0	2.864982	-1.208092	0.000106
32	6	0	1.547479	-0.717431	0.000039
33	1	0	3.014260	-2.286524	0.000225
34	1	0	1.416012	0.358973	-0.000051
35	6	0	0.412577	-1.496004	0.000080
36	1	0	0.532362	-2.578197	0.000170

E(RB+HF-VWN+P86) = -1011.15484319

5’b. *s-trans*.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.786083	-1.317600	0.001234
2	6	0	4.502899	-0.912294	0.000704
3	6	0	4.165901	0.493036	-0.000087
4	6	0	5.322718	1.356721	-0.000261
5	6	0	6.571605	0.856868	0.000310
6	1	0	6.110042	-2.350604	0.001814
7	1	0	3.735142	-1.676853	0.000865
8	1	0	5.195352	2.434106	-0.000914
9	1	0	7.480442	1.444577	0.000187
10	8	0	6.842486	-0.471851	0.001135
11	6	0	-0.806085	0.186283	-0.000567
12	6	0	-1.063323	-1.306700	0.000169

13	6	0	-2.035852	0.818629	-0.001223
14	8	0	-2.514804	-1.398700	-0.000059
15	6	0	-3.070509	-0.181001	-0.000706
16	6	0	-2.194895	2.224498	-0.002744
17	7	0	-2.215823	3.388193	-0.004022
18	6	0	-0.593335	-2.005488	1.272312
19	1	0	-0.957243	-3.036706	1.274345
20	1	0	0.497785	-2.018479	1.334934
21	1	0	-0.983972	-1.494384	2.156065
22	6	0	-0.592911	-2.006602	-1.271279
23	1	0	0.498238	-2.020302	-1.333128
24	1	0	-0.957460	-3.037593	-1.272851
25	1	0	-0.982690	-1.495801	-2.155575
26	6	0	-4.442446	-0.068304	-0.000659
27	6	0	-5.241636	-1.243991	-0.001399
28	7	0	-5.898626	-2.204923	-0.001993
29	6	0	-5.101546	1.188922	0.000639
30	7	0	-5.677189	2.200849	0.009009
31	6	0	2.887800	1.013157	-0.000611
32	6	0	1.686287	0.270651	-0.000482
33	1	0	2.794696	2.097601	-0.001124
34	1	0	1.759246	-0.814246	0.000032
35	6	0	0.442575	0.850824	-0.000830
36	1	0	0.390450	1.938600	-0.001328

E(RB+HF-VWN+P86) = -1011.15097383

5’c. *s-cis.*

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	6.687896	1.829079	-0.000043
2	6	0	5.512532	1.174005	-0.000033
3	6	0	5.465900	-0.270167	0.000006
4	6	0	6.771922	-0.883887	0.000029
5	6	0	7.895162	-0.143084	0.000016
6	1	0	6.797569	2.905996	-0.000071
7	1	0	4.606065	1.767443	-0.000055
8	1	0	6.864232	-1.964934	0.000058
9	1	0	8.903439	-0.536720	0.000033
10	8	0	7.893979	1.212064	-0.000019
11	6	0	-1.914163	-0.960922	0.000004
12	6	0	-3.109958	-1.890638	0.000091
13	6	0	-2.402950	0.335812	-0.000086
14	8	0	-4.248932	-0.994154	-0.000005
15	6	0	-3.842823	0.280433	-0.000071
16	6	0	-1.617423	1.510888	-0.000263
17	7	0	-0.896167	2.425494	-0.000424
18	6	0	-3.200249	-2.733294	1.267558
19	1	0	-4.137303	-3.297130	1.267891
20	1	0	-2.367140	-3.440506	1.318000

21	1	0	-3.172475	-2.096084	2.155385
22	6	0	-3.200244	-2.733558	-1.267199
23	1	0	-2.367165	-3.440816	-1.317467
24	1	0	-4.137321	-3.297356	-1.267429
25	1	0	-3.172426	-2.096543	-2.155164
26	6	0	-4.790407	1.280913	-0.000094
27	6	0	-6.169749	0.936899	-0.000241
28	7	0	-7.300873	0.661441	-0.000384
29	6	0	-4.449678	2.658555	0.000029
30	7	0	-4.214934	3.799094	0.000853
31	6	0	4.314333	-1.032664	0.000021
32	6	0	0.567698	-0.746866	-0.000002
33	1	0	4.437060	-2.114498	0.000051
34	1	0	0.508882	0.339018	-0.000036
35	6	0	-0.597406	-1.477695	0.000020
36	1	0	-0.510345	-2.563217	0.000060
37	6	0	2.995331	-0.533608	0.000002
38	6	0	1.861393	-1.310254	0.000020
39	1	0	2.848399	0.545878	-0.000030
40	1	0	1.959265	-2.395705	0.000051

E(RB+HF-VWN+P86) = -1088.81208315

5’c. *s-trans.*

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	7.180003	-1.462715	0.001041
2	6	0	5.916873	-0.999862	0.000587
3	6	0	5.642920	0.419691	0.000045
4	6	0	6.838282	1.229915	0.000120
5	6	0	8.063234	0.674506	0.000602
6	1	0	7.456884	-2.509308	0.001621
7	1	0	5.114295	-1.727777	0.000667
8	1	0	6.760250	2.312082	-0.000128
9	1	0	8.997415	1.221071	0.000823
10	8	0	8.275189	-0.665602	0.000990
11	6	0	-1.785857	0.145543	-0.000790
12	6	0	-2.059342	-1.344412	0.000205
13	6	0	-3.008764	0.791757	-0.001179
14	8	0	-3.512245	-1.420030	-0.000092
15	6	0	-4.054110	-0.196455	-0.000645
16	6	0	-3.152981	2.199161	-0.002751
17	7	0	-3.163057	3.363025	-0.003427
18	6	0	-1.596557	-2.048046	1.272133
19	1	0	-1.972456	-3.074959	1.274485
20	1	0	-0.505679	-2.073565	1.333040
21	1	0	-1.980802	-1.532296	2.156033
22	6	0	-1.596146	-2.049565	-1.270904
23	1	0	-0.505233	-2.077344	-1.330169
24	1	0	-1.973918	-3.075801	-1.273045

25	1	0	-1.978165	-1.533688	-2.155662
26	6	0	-5.425077	-0.068628	-0.000480
27	6	0	-6.237245	-1.235306	-0.001053
28	7	0	-6.905419	-2.188540	-0.001462
29	6	0	-6.070925	1.195371	0.000492
30	7	0	-6.636709	2.212891	0.008799
31	6	0	4.388632	0.993630	-0.000479
32	6	0	0.706511	0.199498	-0.000747
33	1	0	4.343619	2.081386	-0.000941
34	1	0	0.781735	-0.886775	-0.000291
35	6	0	-0.529381	0.795073	-0.001159
36	1	0	-0.568008	1.883390	-0.001737
37	6	0	3.155643	0.304375	-0.000444
38	6	0	1.926773	0.914734	-0.000901
39	1	0	3.170147	-0.785623	-0.000012
40	1	0	1.877738	2.003034	-0.001376

E(RB+HF-VWN+P86) = -1088.81035655

5’d. *s-cis.*

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	8.124883	1.931624	-0.000185
2	6	0	6.946482	1.282917	-0.000099
3	6	0	6.890466	-0.161844	-0.000048
4	6	0	8.194570	-0.781769	-0.000099
5	6	0	9.321508	-0.047606	-0.000186
6	1	0	8.240063	3.008021	-0.000227
7	1	0	6.043026	1.881002	-0.000069
8	1	0	8.281320	-1.863345	-0.000069
9	1	0	10.327520	-0.446937	-0.000228
10	8	0	9.328912	1.309039	-0.000231
11	6	0	-2.944560	-0.925684	0.000088
12	6	0	-4.165298	-1.822329	-0.000007
13	6	0	-3.397611	0.384072	0.000015
14	8	0	-5.279290	-0.894825	-0.000166
15	6	0	-4.838222	0.368161	-0.000126
16	6	0	-2.580867	1.537605	0.000005
17	7	0	-1.837794	2.434523	-0.000018
18	6	0	-4.279325	-2.662425	1.267306
19	1	0	-5.231558	-3.200258	1.267092
20	1	0	-3.466005	-3.392291	1.318127
21	1	0	-4.234407	-2.026430	2.155301
22	6	0	-4.279056	-2.662534	-1.267271
23	1	0	-3.465762	-3.392446	-1.317827
24	1	0	-5.231316	-3.200319	-1.267233
25	1	0	-4.233895	-2.026626	-2.155316
26	6	0	-5.758699	1.393868	-0.000192
27	6	0	-7.146677	1.086588	-0.000485
28	7	0	-8.284775	0.841392	-0.000744

29	6	0	-5.382353	2.762185	0.000037
30	7	0	-5.119553	3.896593	0.000880
31	6	0	5.735967	-0.917091	0.000043
32	6	0	-0.455897	-0.782374	0.000379
33	1	0	5.854009	-1.999573	0.000074
34	1	0	-0.479326	0.304865	0.000235
35	6	0	-1.642588	-1.478045	0.000234
36	1	0	-1.585991	-2.565647	0.000213
37	6	0	4.415275	-0.416861	0.000103
38	6	0	3.285582	-1.196968	0.000193
39	1	0	4.269267	0.663023	0.000071
40	1	0	3.393362	-2.281408	0.000227
41	6	0	1.980065	-0.657306	0.000239
42	6	0	0.817968	-1.389959	0.000296
43	1	0	1.891989	0.430109	0.000273
44	1	0	0.875914	-2.478353	0.000278

E(RB+HF-VWN+P86) = -1166.47084124

5’d. *s-trans*.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.560749	-1.586823	-0.000225
2	6	0	-7.311921	-1.087344	-0.000134
3	6	0	-7.078663	0.339953	0.000058
4	6	0	-8.297900	1.114598	0.000137
5	6	0	-9.506029	0.524148	0.000035
6	1	0	-8.806815	-2.641087	-0.000369
7	1	0	-6.488229	-1.791340	-0.000209
8	1	0	-8.251652	2.198648	0.000283
9	1	0	-10.455557	1.043615	0.000086
10	8	0	-9.679889	-0.822133	-0.000148
11	6	0	2.805748	0.118302	-0.000106
12	6	0	3.080989	-1.371377	-0.000018
13	6	0	4.028295	0.766014	-0.000144
14	8	0	4.534240	-1.445137	0.000031
15	6	0	5.074464	-0.220935	-0.000037
16	6	0	4.171401	2.173446	-0.000220
17	7	0	4.181849	3.337341	-0.000204
18	6	0	2.619017	-2.076521	-1.271468
19	1	0	2.996633	-3.102819	-1.273278
20	1	0	1.528189	-2.104068	-1.331930
21	1	0	3.002088	-1.560624	-2.155778
22	6	0	2.618896	-2.076328	1.271494
23	1	0	1.528060	-2.103648	1.331959
24	1	0	2.996319	-3.102697	1.273410
25	1	0	3.002064	-1.560411	2.155751
26	6	0	6.445547	-0.091625	0.000011
27	6	0	7.258969	-1.257349	0.000102
28	7	0	7.928622	-2.209599	0.000208

29	6	0	7.090470	1.172791	-0.000034
30	7	0	7.657780	2.189530	0.000049
31	6	0	-5.841792	0.949049	0.000159
32	6	0	0.313514	0.168092	-0.000007
33	1	0	-5.828594	2.037867	0.000300
34	1	0	0.239472	-0.918146	0.000109
35	6	0	1.548697	0.765905	-0.000101
36	1	0	1.585443	1.854307	-0.000152
37	6	0	-4.587975	0.296668	0.000097
38	6	0	-3.378097	0.943348	0.000200
39	1	0	-4.568837	-0.793158	-0.000038
40	1	0	-3.364890	2.032968	0.000336
41	6	0	-2.135263	0.268402	0.000144
42	6	0	-0.907924	0.881108	0.000038
43	1	0	-2.163546	-0.822774	0.000192
44	1	0	-0.860892	1.969497	-0.000010

E(RB+HF-VWN+P86) = -1166.46963151

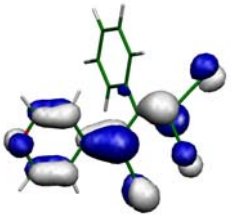
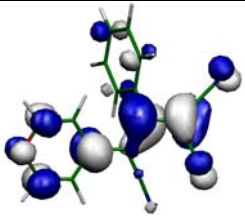
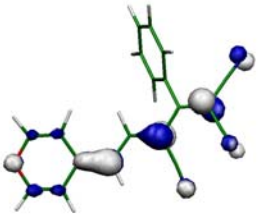
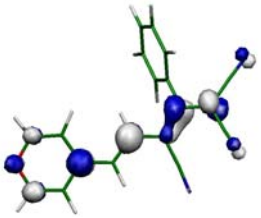
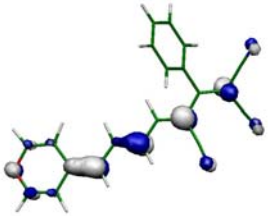
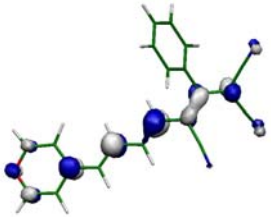
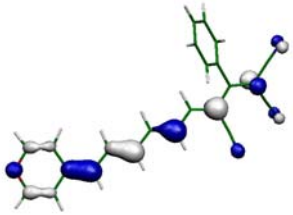
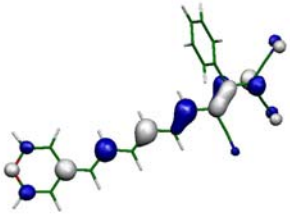
Compound	HOMO	LUMO
3'a	 -6.95 eV	 -3.62 eV
3'b	 -6.52 eV	 -3.74 eV
3'c	 -6.26 eV	 -3.79 eV
3'd	 -6.06 eV	 -3.82 eV

Figure S-74: Contour plots and energies calculated for the frontier orbitals of compounds **3'** using the B3P86/6-31G* model chemistry.

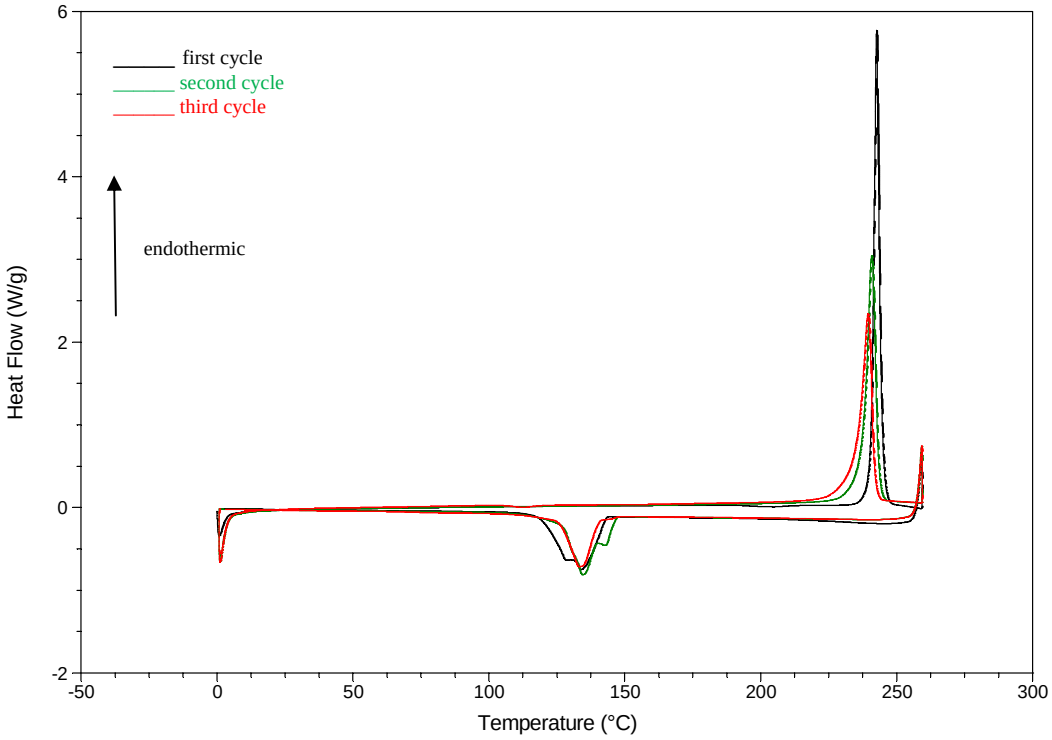
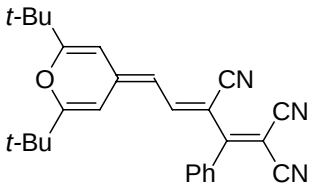


Figure S-75: DSC curves of compound **3b**.



3b

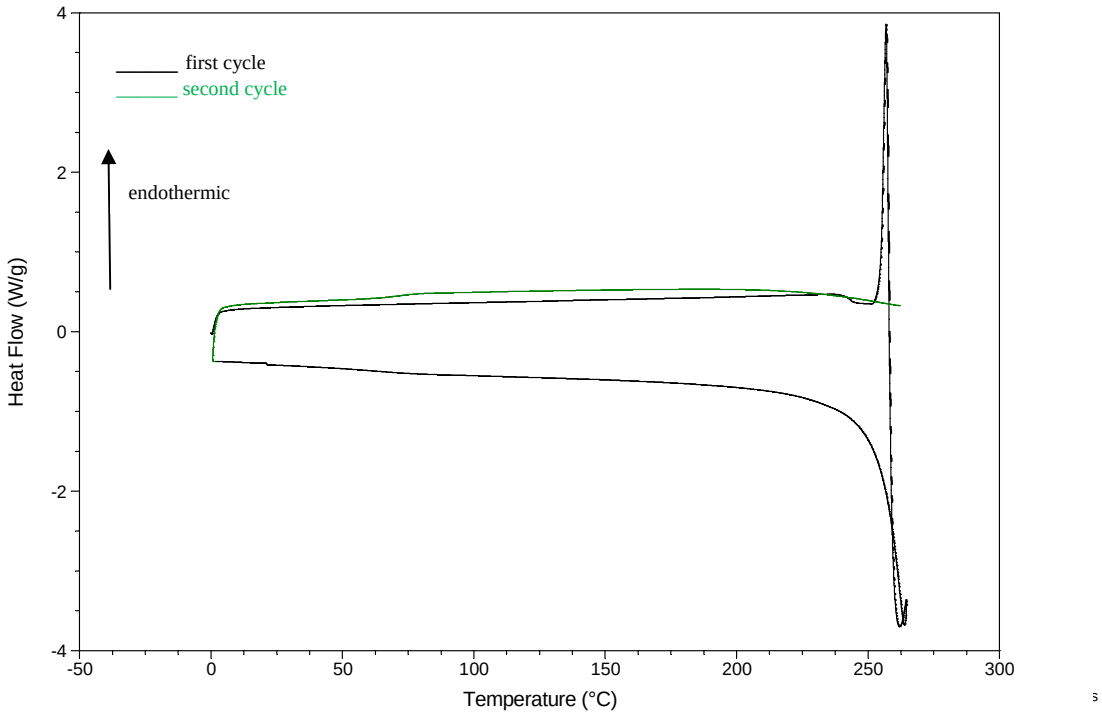
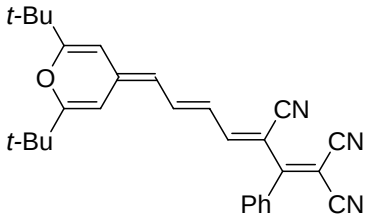


Figure S-76: DSC curves of compound **3c**.



3c

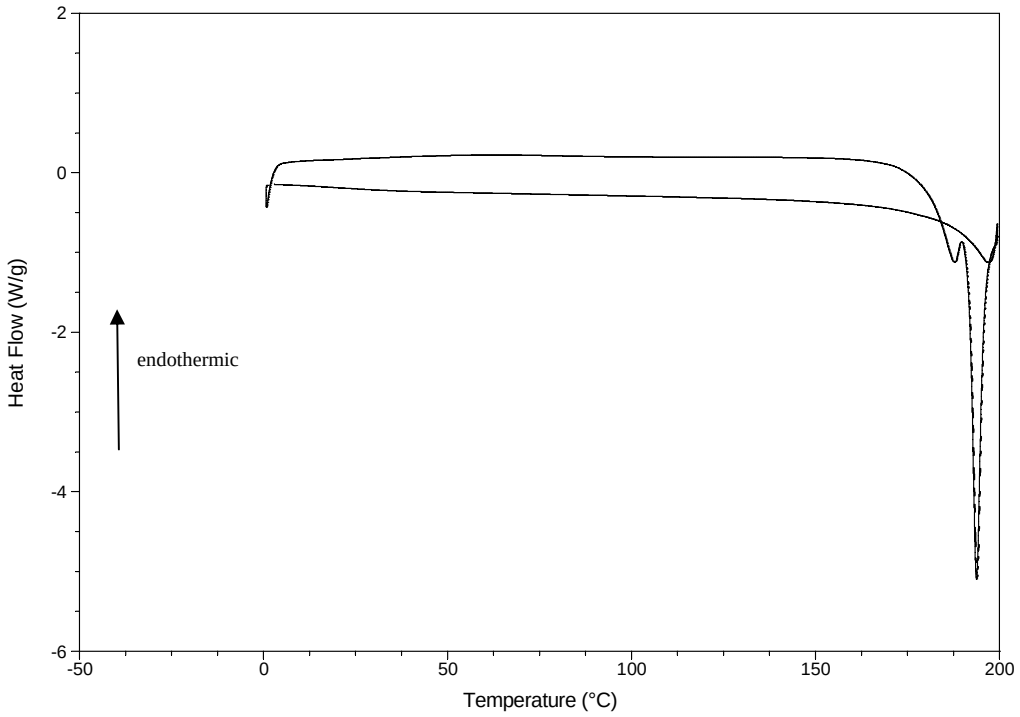
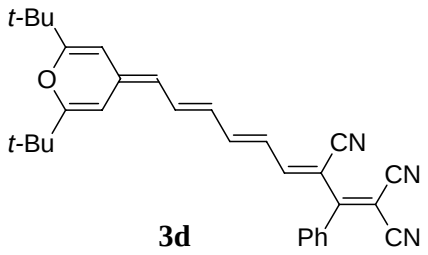


Figure S-77: DSC curve of compound **3d**.



3d