Electronic Supplementary Information

Alkylated Y-series acceptors for ternary organic solar cells with improved open-circuit voltage processed from non-halogenated solvents

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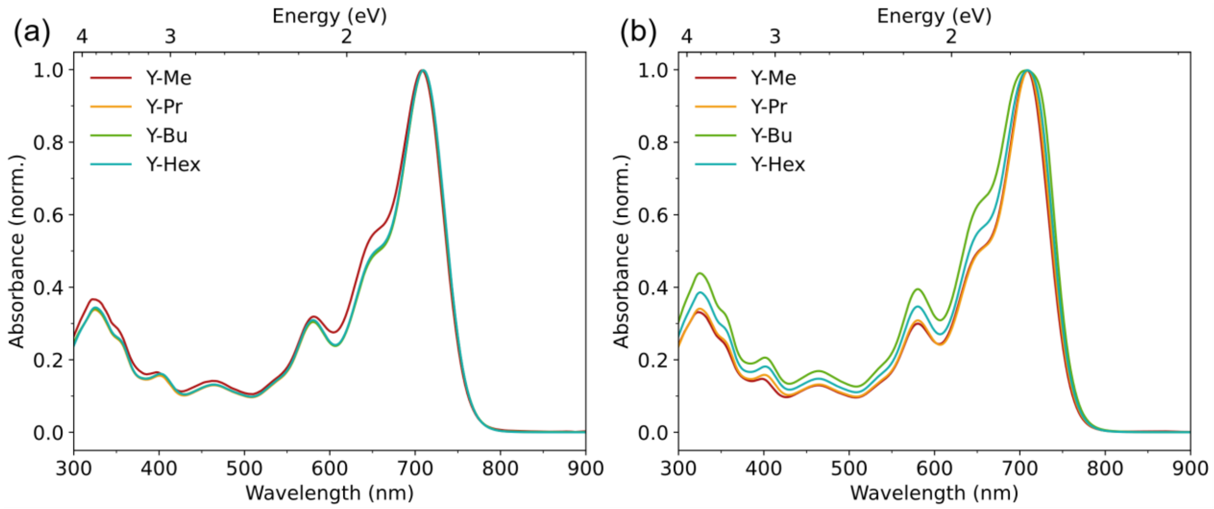


Fig. S1 UV-Vis absorption spectra of the acceptors Y-Me, Y-Pr, Y-Bu, Y-Hex in (a) *o*-xylene, and (b) chlorobenzene.

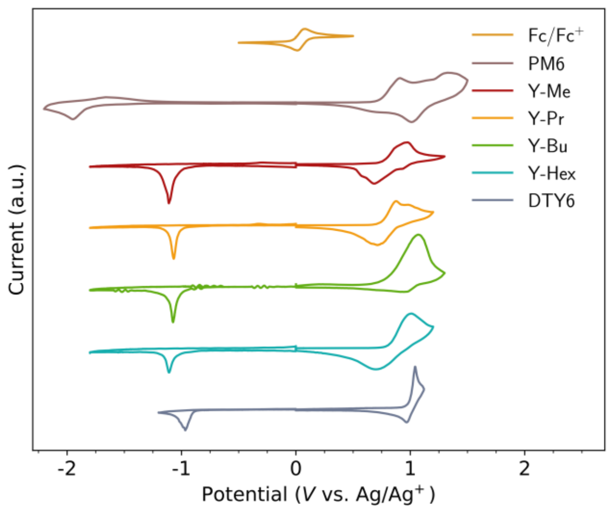


Fig. S2 Cyclic voltammograms of the absorber materials used for the fabrication of the ternary solar cells.

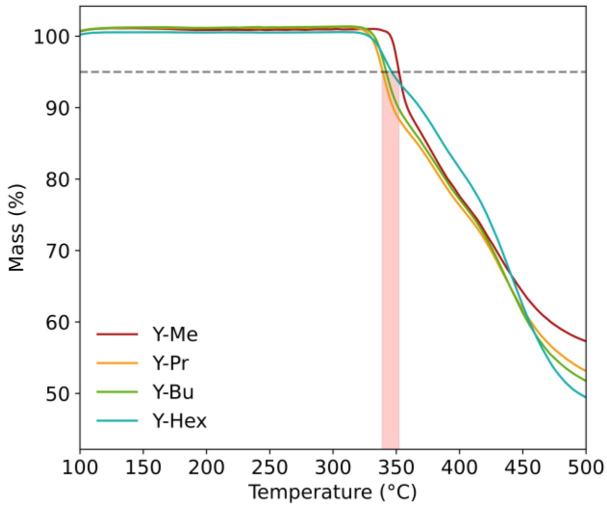


Fig. S3 TGA data of the acceptors Y-Me, Y-Pr, Y-Bu, and Y-Hex.

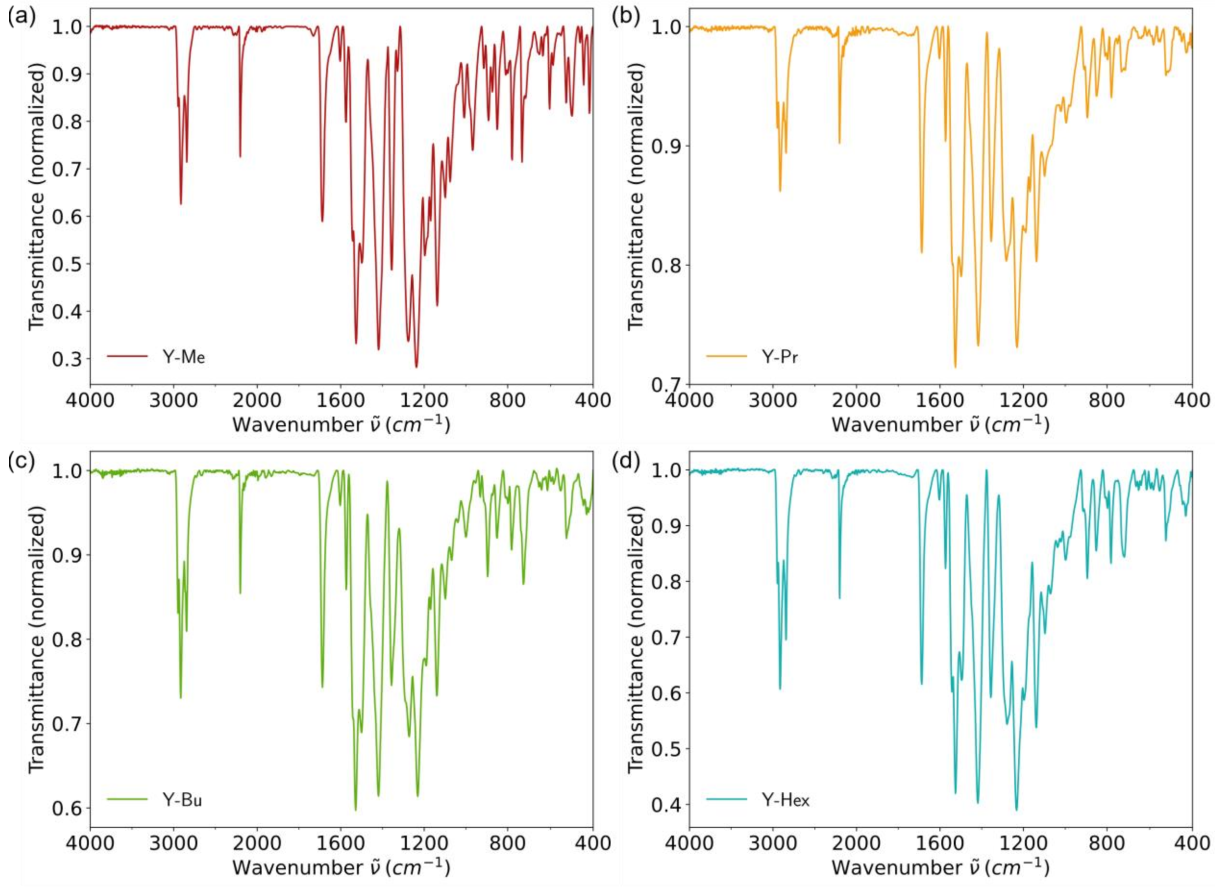


Fig. S4 ATR-FT-IR spectra of (a) Y-Me, (b) Y-Pr, (c) Y-Bu, and (d) Y-Hex.

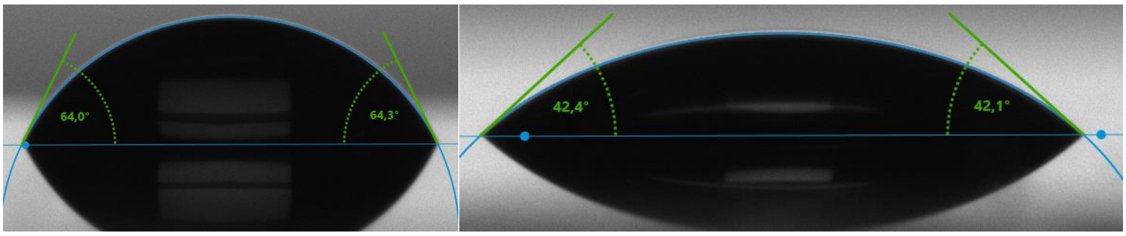


Fig. S5 Contact angle measurement of Y-Me with (left) ethylene glycol and (right) diiodomethane.

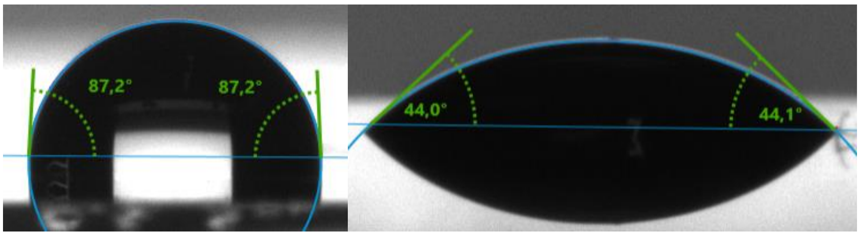


Fig. S6 Contact angle measurements of Y-Pr with (left) water and (right) diiodomethane.

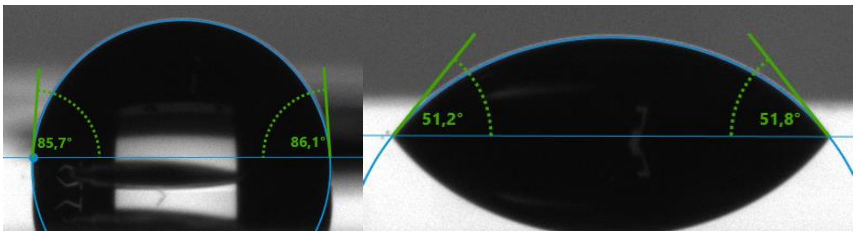


Fig. S7 Contact angle measurements of Y-Bu with (left) water and (right) diiodomethane.

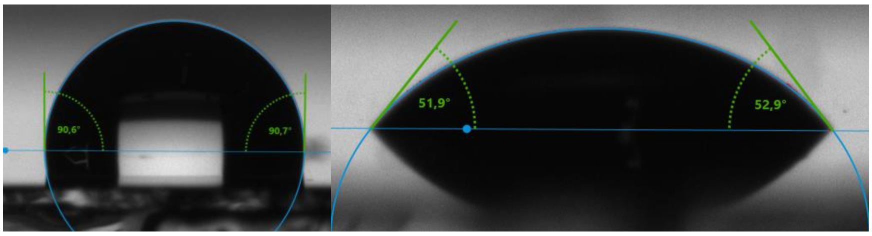


Fig. S8 Contact angle measurements of Y-Hex with (left) water and (right) diiodomethane.

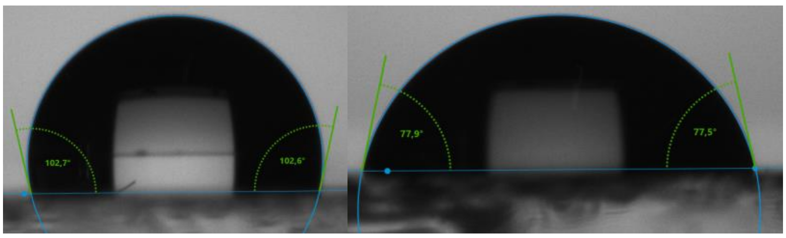


Fig. S9 Contact angle measurement of PM6 with (left) water and (right) ethylene glycol.

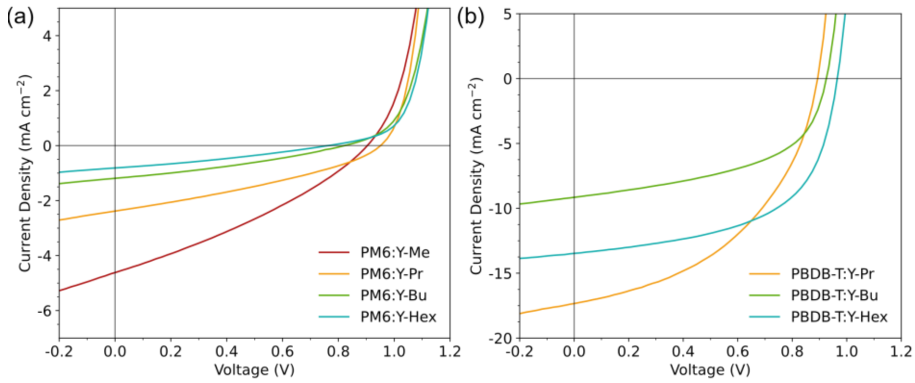


Fig. S10 *JV* curves of the binary OSCs (setup ITO/PEDOT:PSS/D:A/PNDIT-F3N-Br/Ag), processed from chloroform + 0.5 vol.% 1-chloronaphthalene with the donor polymer (a) PM6 and (b) PBDB-T.

Table S1 Photovoltaic data for binary OSCs plotted in **Fig. S10**

BHJ	D/A	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PM6:Y-Me	1/1.2	0.89	4.60	33	1.32
PM6:Y-Pr	1/1.2	0.95	2.37	33	0.76
PM6:Y-Bu	1/1.2	0.81	1.18	32	0.30
PM6:Y-Hex	1/1.2	0.77	0.81	30	0.19
PBDB-T:Y-Pr	1/1.2	0.89	17.32	46	7.20
PBDB-T:Y-Bu	1/1.2	0.93	9.14	51	4.37
PBDB-T:Y-Hex	1/1.2	0.97	13.47	57	7.41

Table S2 Photovoltaic data for the Y-Me based ternary OSCs with different weight content of Y-Me

Y-Me content (wt.%)[a]	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
10	0.85 ± 0.01	23.4 ± 0.7	67 ± 5	13.2 ± 1.5
15	0.87 ± 0.01	22.5 ± 0.4	72 ± 1	14.1 ± 0.2
20	0.85 ± 0.01	17.7 ± 0.8	76 ± 1	11.4 ± 0.5

[a] Relative amount of Y-Me respective to the total acceptor amount. The overall D/A ratio for all OSCs is 1/1.2.

Table S3 Series and shunt resistances for the ternary and binary systems

BHJ	R_s (Ω cm^2)	R_{sh} (Ω cm^2)
PM6:DTY6:Y-Me	1.08	606
PM6:DTY6:Y-Pr	1.68	690
PM6:DTY6:Y-Bu	1.30	889
PM6:DTY6:Y-Hex	1.22	494
PM6:DTY6	0.85	1469

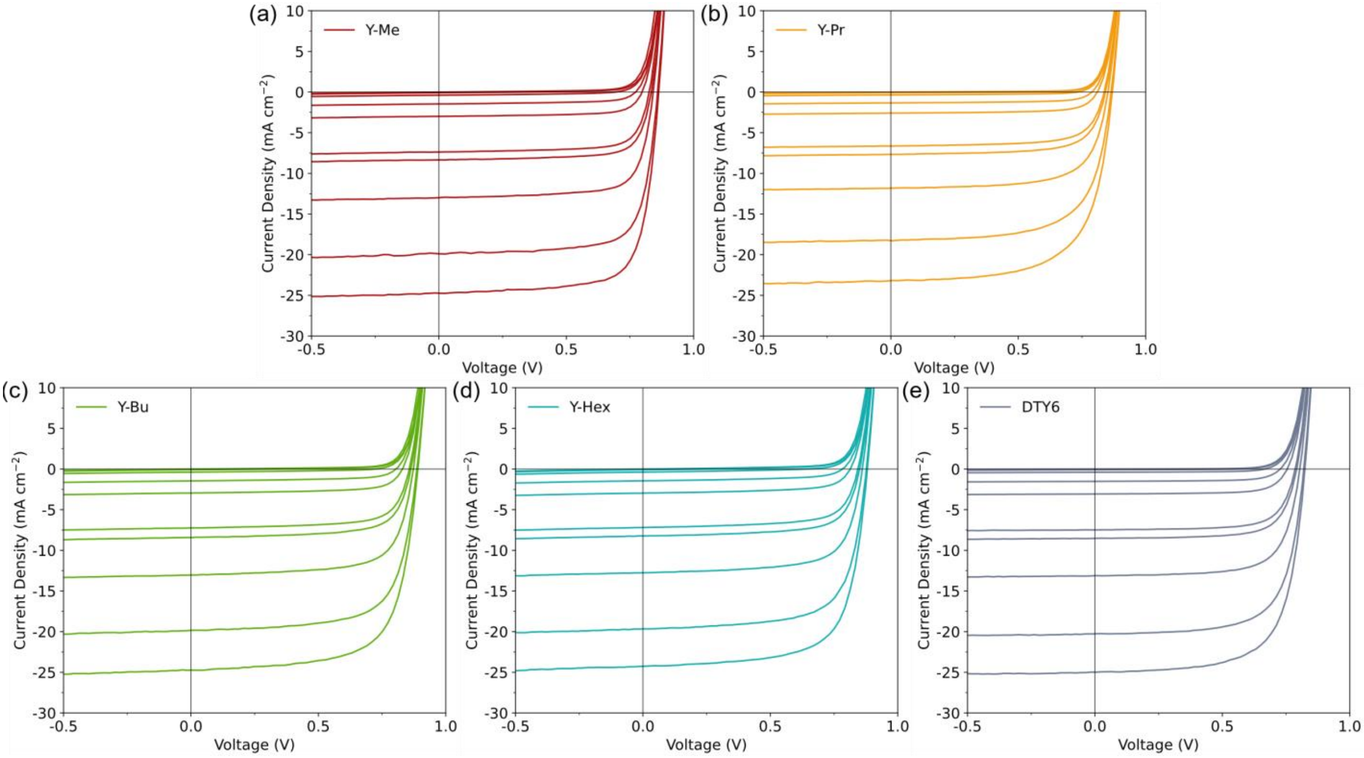


Fig. S11 *JV* curves of the light intensity dependence measurements for the respective ternary OSCs measured with different light filters. Curves of OSCs with the active layer PM6:DTY6:A, where A is (a) Y-Me, (b) Y-Pr, (c) Y-Bu, (d) Y-Hex, (e) none.

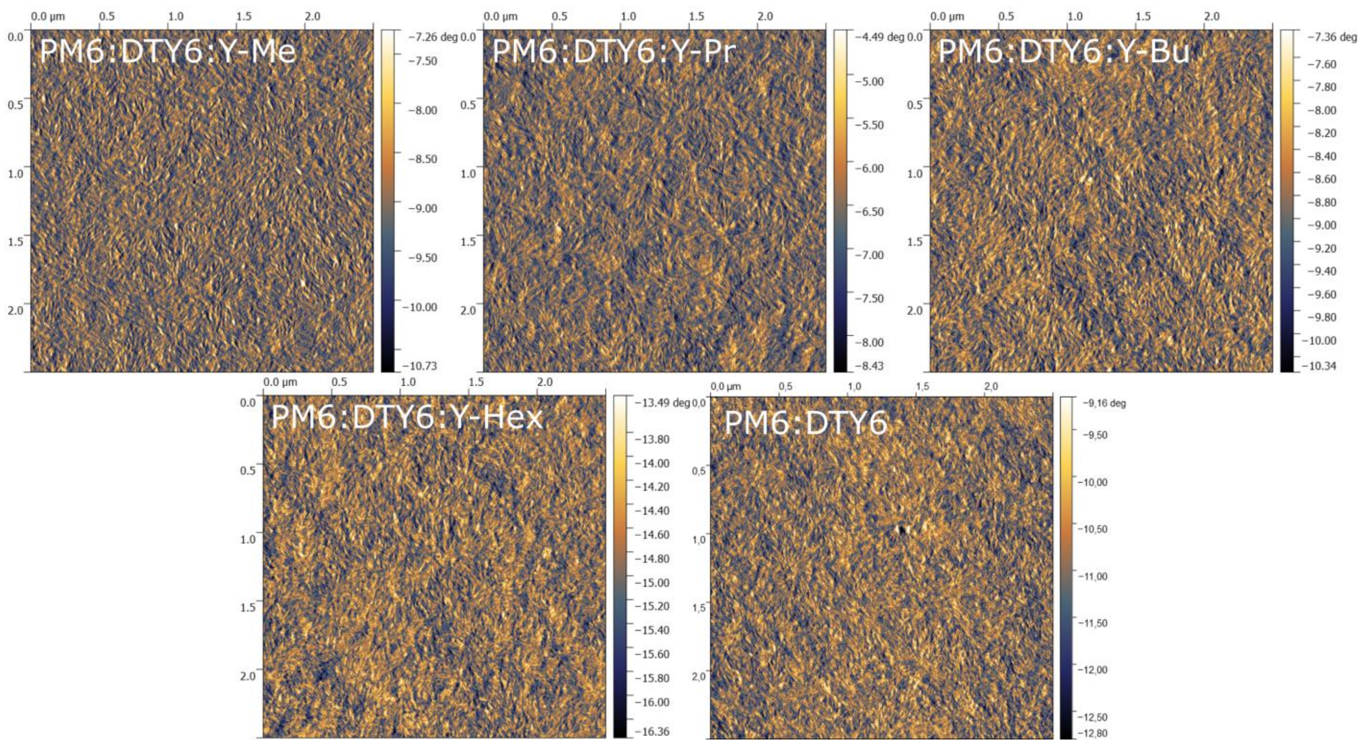


Fig. S12 AFM phase images (2.5 × 2.5 μm^2) of the active layers of the ternary and binary blends prepared on glass/ITO/PEDOT:PSS substrates.

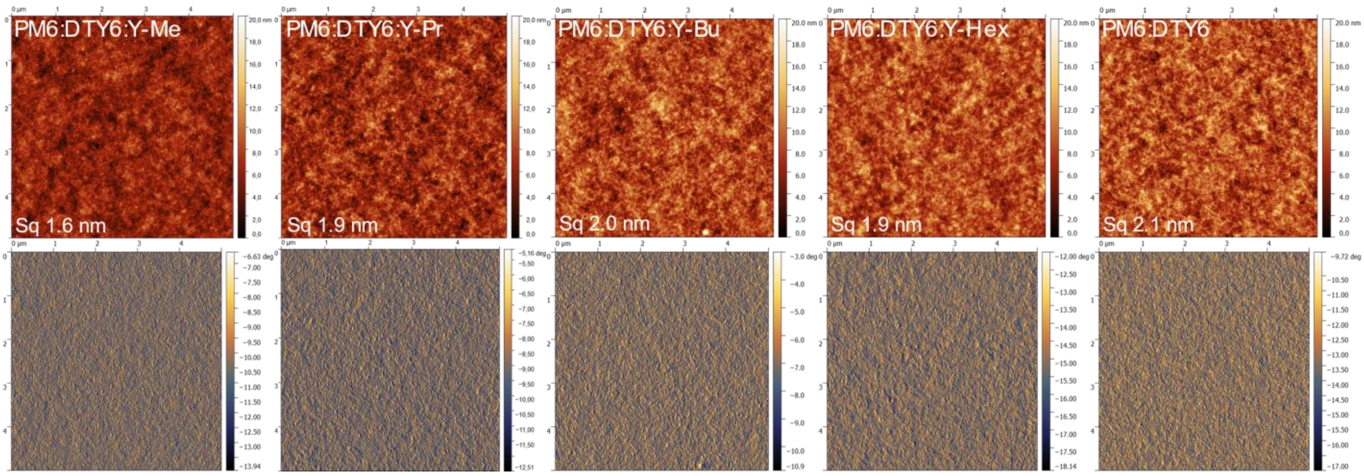


Fig. S13 AFM images ($5 \times 5\ \mu m^2$) of the active layers of the ternary and binary blends on top of ITO/PEDOT:PSS, with (top) height and (bottom) phase images.

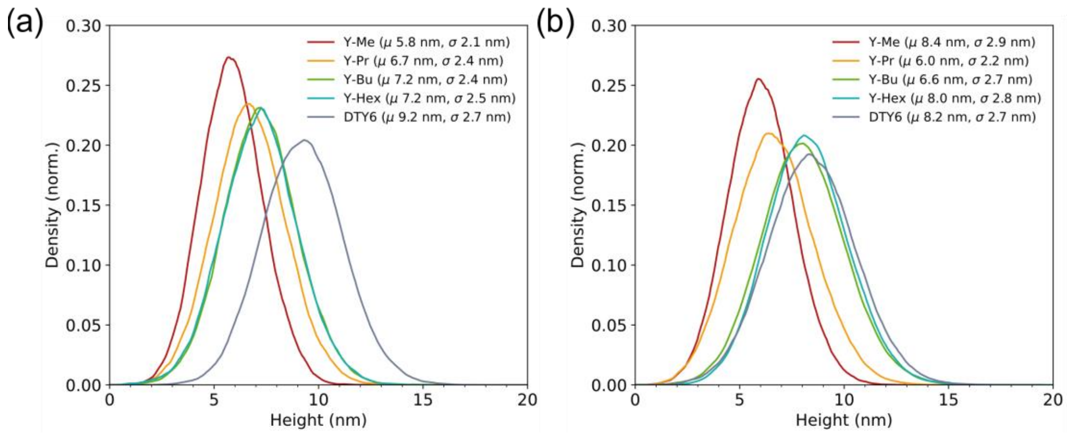


Fig. S14 Height distribution plots extracted from the (a) $2.5\times 2.5\ \mu m^2$ and (b) $5\times 5\ \mu m^2$ AFM images. Mean (μ) and standard deviation (σ) extracted from the gaussian curve fits.

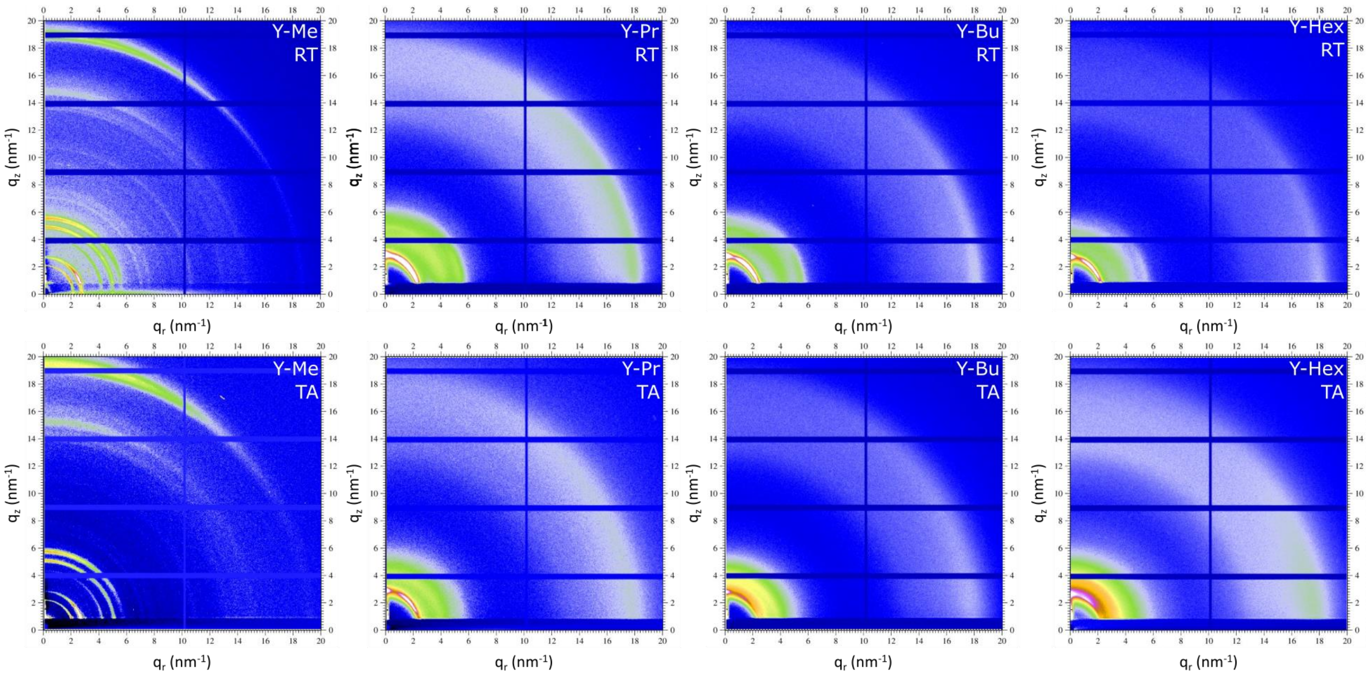


Fig. S15 2D GIWAXS images of pristine drop coated acceptor films without treatment (RT), and thermal annealing at 110 °C for 10 min (TA).

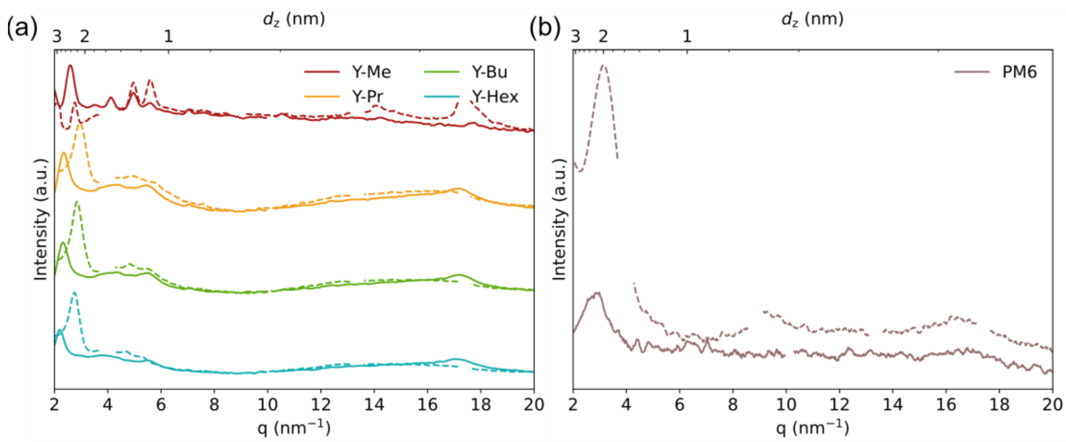


Fig. S16 GIWAXS line cuts in in-plane (solid) and out-of-plane (dashed) directions of drop coated acceptor films of (a) the non-annealed pristine acceptors, and (b) pristine PM6 after thermal annealing at 100 °C for 10 min.

Methods

General

Column chromatography was done using a Biotage "Selekt" automated flash chromatography system with purchased pre-filled columns "Sfär" from Biotage (spherical and irregular silica with particle size from 20 – 60 μm).

NMR spectra were recorded using a Bruker Avance III 300 MHz, a Varian Inova (400 MHz and 500 MHz), and a Jeol ECZR 400 MHz spectrometer. The spectra were processed with the software Jason (Jeol). All deuterated solvents were purchased from EurisoTop GmbH. The spectra were referenced to the TMS (default) or solvent signal.

Mass spectra were measured using a Micromass TofSpec 2E time-of-flight mass spectrometer from Waters and the appropriate software MassLynx Software V3.5 from Micromass/Waters. Matrices were dithranol or DCTB (*trans*-2-[3-(4-tertbutylphenyl)-2-methyl2-propenylidene]malononitrile). All spectra were calibrated with polyethylene glycol as external standard. Atmospheric pressure chemical ionization (APCI) mass spectra were recorded on an Advion ExpressionL CMS mass spectrometer with nitrogen as carrier gas and the included software Advion Mass Express. The samples were applied in solution onto a glass carrier and then directly inserted into the ionization chamber.

Thermogravimetry was done on a TGA8000 from Perkin Elmer in aluminium crucibles under helium atmosphere. The used scan range was from 30 to 550 °C with a scan rate of 10 °C min^{-1}.

UV-Vis spectra were recorded on a Shimadzu UV-1800 spectrometer, for both solution (0.01 mg ml^{-1} in chloroform, in 1 cm optical glass cuvettes from Hellma) and thin film (drop cast from 10 mg ml^{-1} chloroform solution) measurements.

Fluorescence spectra were measured on a FluoroLog 3 spectrofluorometer from Horiba Scientific Jobi Yvon together with a R2658 photomultiplier from Hamamtsu. The spectra were measured in solution (approx. 0.01 mg ml^{-1} in chloroform) from 680 – 1050 nm with at an excitation wavelength at 670 nm.

Infrared spectroscopy: FT-IR spectra were recorded on a Bruker ALPHA-p FT-IR spectrometer with the software OPUS 7.5. Measurements were done with solid powder samples in an attenuated total reflection (ATR) setup.

Cyclic voltammetry (CV) was done on a SP-50 single channel potentiostat from BioLogic and the corresponding software EC-Lab® (V11.31). Measurements were done in a three-electrode setup with a Pt disc working electrode (diameter 2 mm), a Pt wire counter electrode (diameter 0.5 mm) and a non-aqueous $Ag/AgNO_3$ reference electrode (0.5 mm Ag wire in a 0.1 M $AgNO_3$ solution in MeCN), with a 0.1 M tetra-butylammonium hexafluorophosphate ($TBAPF_6$) solution in acetonitrile as electrolyte. The respective material was drop coated onto the working electrode in a nitrogen filled glove box. To avoid interference from trapped charges, oxidation and reduction were measured separately with freshly prepared films and a scan speed of 50 mV s^{-1}. Fc/Fc^+ was used as external standard. The orbital energies were calculated using

$$E_{\mathrm{HOMO}} = -\left(E^{\mathrm{ox}}_{\mathrm{onset\ vs.Fc/Fc^+}} + 5.39\right)\ \mathrm{eV}$$

$$\mathrm{E}_{\mathrm{LUMO}} = -\left(\mathrm{E}^{\mathrm{red}}_{\mathrm{onset\ vs.Fc/Fc^+}} + 5.39\right)\ \mathrm{eV}$$

The Fermi energy level of NHE vs. vacuum was taken as 4.75 eV, whereas the redox potential of Fc/Fc^+ vs. NHE was taken as 0.64 V.[1,2]

Surface free energy (SFE) measurements were done on a Drop Shape Analysis System DSA100 from Krüss GmbH. The system is equipped with an IDS uEye UI306xCP-M video camera (IDS Imaging Development Systems GmbH). The used software was the Krüss Advance v1.8.0.4. The measurements were done with static contact angle measurement method using MilliQ water (H_2O) and diiodomethane (DIM) with a drop size of 2 µl and dispense rate of 2.67 µl s^{-1}. SFEs were calculated using the Owens-Wendt-Rabel-Kaelble (OWRK)[3] and Wu[4] methods. The Flory Huggins interaction parameter χ was calculated using

$$\chi_{A-B} = \left(\sqrt{A} - \sqrt{B}\right)^2$$

from the SFE values of the two respective components.

Solubility determination at room temperature was done by making saturated solutions of the respective materials. For that, 5 – 10 mg of the compound together with 0.20 – 0.40 ml of the respective solvent were put in a 4 ml glass vial topped with a screwcap with a PTFE/silicone septum. The mixture was stirred at RT for 2 h and then kept without stirring overnight at RT to equilibrate. All further handling was done through the vial septa to prevent solvent evaporation. On the next day, the saturated solution was filtered using a 0.45 µm PTFE syringe filter, into a new identical septum-capped vial. From that saturated solution, 20 µl were diluted in 10 ml $CHCl_3$ (a small solvent-to-$CHCl_3$ ratio should minimize errors from the presence of a second solvent) and a UV-Vis spectrum was recorded. By knowing the absorption coefficient of the respective compound in $CHCl_3$ (determined in advance), the saturation concentration (solubility) was calculated from Lambert-Beer's law.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted at an Anton Paar SAXSpoint 2.0 with a 50 W Cu-K_α X-ray source focused to a 0.3 mm^2 point source and a Dectris EIGER 2D pixel detector at a sample distance of 140 mm. The sample surface has been centered and adjusted with the GISAXS 2.0 sample stage to a grazing angle of 2° of the incidence X-rays. The patterns were averaged from six 5 min measurements, respectively. The analysis has been performed with software package SAXS Analysis. The compound films were drop-casted onto silicon substrates (grade: prime, thickness: 625 ± 20 µm) from Siegert Wafer and annealed at 100 °C for 10 min.

GIWAXS measurements were further done at the Austrian SAXS beamline 5.2L at the synchrotron ELETTRA (Trieste, Italy).[5] The setup uses a photon energy of 8 keV, a Dectris Pilatus3 1M detector at a sample distance of 294 mm and grazing angle of 1.1°. The angular calibration was carried out using silver behenate powder as standard (d-spacing of 58.38 Å). The 2D images were processed using the software IGOR Pro 7 and FIT2D. The 1D line-cuts were made with the software SAXSDOG.[6] For the measurements, the compound films were drop-casted onto silicon substrates (grade: prime, thickness: 625 ± 20 µm, from Siegert Wafer). As background, the 1D and 2D scattering patterns of an empty Si wafer were subtracted from the corresponding sample pattern.

Atomic force microscopy (AFM) images were acquired on a Tosca™ 400 atomic force microscope from Anton Paar, using silicon cantilevers (AP-ARROW-NCR from NanoWorld AG) in tapping mode (resonance frequency 285 kHz, force constant 42 N m^{-1}).

Profilometry measurements were done on a Bruker DektakXT stylus surface profiling system and a Vision 64 software (Bruker). The line scans were recorded with a 12.5 µm radius stylus tip, over a length of 1000 µm, with a stylus force of 3 mg and resolution of 0.33 µm pt^{-1}.

Solar Cells

Materials

The solar cell processing polymers PM6, PBDB-T, and PNDIT-F3N-Br were purchased from 1-Material. PEDOT:PSS was purchased from Heraeus (CLEVIOS™ P VP AI 4083).

Fabrication

Pre-patterned glass/ITO substrates ($15 \times 15 \times 1.1$ mm^3, 15 Ω sq^{-1}) were cleaned by wiping them with acetone using Kimwipes (Kimberly-Clark), then by sonication in a 2-propanol bath (40 °C, 60 min), followed by blow-drying in a nitrogen stream and finally oxygen plasma etching (99 W, 3 min, FEMTO, Diener Electronics).

For the conventional binary and ternary setups (ITO/PEDOT:PSS/BHJ/PNDIT-F3N-Br/Ag), a suspension of PEDOT:PSS in water was filtered through a 0.45 µm PTFE syringe filter, then spin-coated (50 µl with 3000 rpm and 2000 rpm s^{-1} for 40 s) onto freshly plasma-etched glass/ITO substrates, followed by thermal annealing at 150 °C for 15 min in ambient conditions. This gave an average film thickness of 30 nm. For the active layers, precursor solutions were prepared by dissolving the respective donors and acceptors in the respective solvent (*o*-xylene, chloroform + 0.5 vol.% 1-chloronaphthalene), in a D/A weight ratio of 1/1.2 and a total concentration of 14 – 18 mg ml^{-1}. The solutions were stirred overnight at RT before deposition. The active layers were applied with varying spin coating parameters (1000 - 5000 rpm), followed by thermal annealing at 100 °C for 10 min. The PNDIT-F3N-Br layer was spin coated from a 0.5 mg ml^{-1} methanol solution with 2000 rpm, 1500 rpm s^{-1} for 30 s. Lastly, an Ag electrode (100 nm, 0.1 – 2.0 Å s^{-1}) layer was applied by thermal evaporation at high vacuum ($< 1 \times 10^{-5}$ mbar, thickness monitor: Inficon SQM-160 rate/thickness monitor) through a shadow mask (3×3 mm^2).

Characterization

***J-V* curves** were recorded using a Keithley 2400 source meter connected to a LabView-based software. All measurements were done inside a nitrogen glove box. As light source, a Dedolight DLH400 lamp with a similar emission spectrum to AM1.5G was used at an intensity of 100 mW cm^{-2} (calibrated with a monocrystalline silicon WPVS reference solar cell from Fraunhofer ISE). The illumination area was defined with a shadow mask to be 2.65×2.65 mm^2. Scans were done from 1.50 V to -0.50 V (step width -0.02 V).

For the **light intensity dependence** measurements, various light filters were inserted between light source and solar cell. The filters were unmounted 25 mm absorptive neutral density filters from Thorlabs Inc. in various filter strengths (transmission values of 0.05%, 0.11%, 0.74%, 4.88%, 10.43%, 27.60%, 31.82%, 52.97% and 81.20%, respectively).

For the **J_{ph}-V_{eff} plots**, *JV* curves were recorded from +3 V to -3 V under illuminated and dark conditions. For processing, we followed a literature-known procedure.[7] J_{ph} is defined as the difference of the current density under illuminated (AM1.5G) conditions (J_{light}) and under dark conditions (J_{dark}) ($J_{ph} = J_{light} - J_{dark}$). V_{eff} is defined as the voltage where $J_{ph} = 0$ (V_0) subtracted by the applied voltage (V_{appl}) ($V_{eff} = V_0 – V_{appl}$).

From that plot, the exciton dissociation efficiency (η_{diss}) is calculated as the ratio of J_{ph} at short-circuit conditions to J_{ph} at V_{eff} = 2.0 V. Similarly, the charge collection efficiency (η_{cc}) is calculated as the ratio of J_{ph} at maximum-power-point conditions to J_{ph} at V_{eff} = 2.0 V.

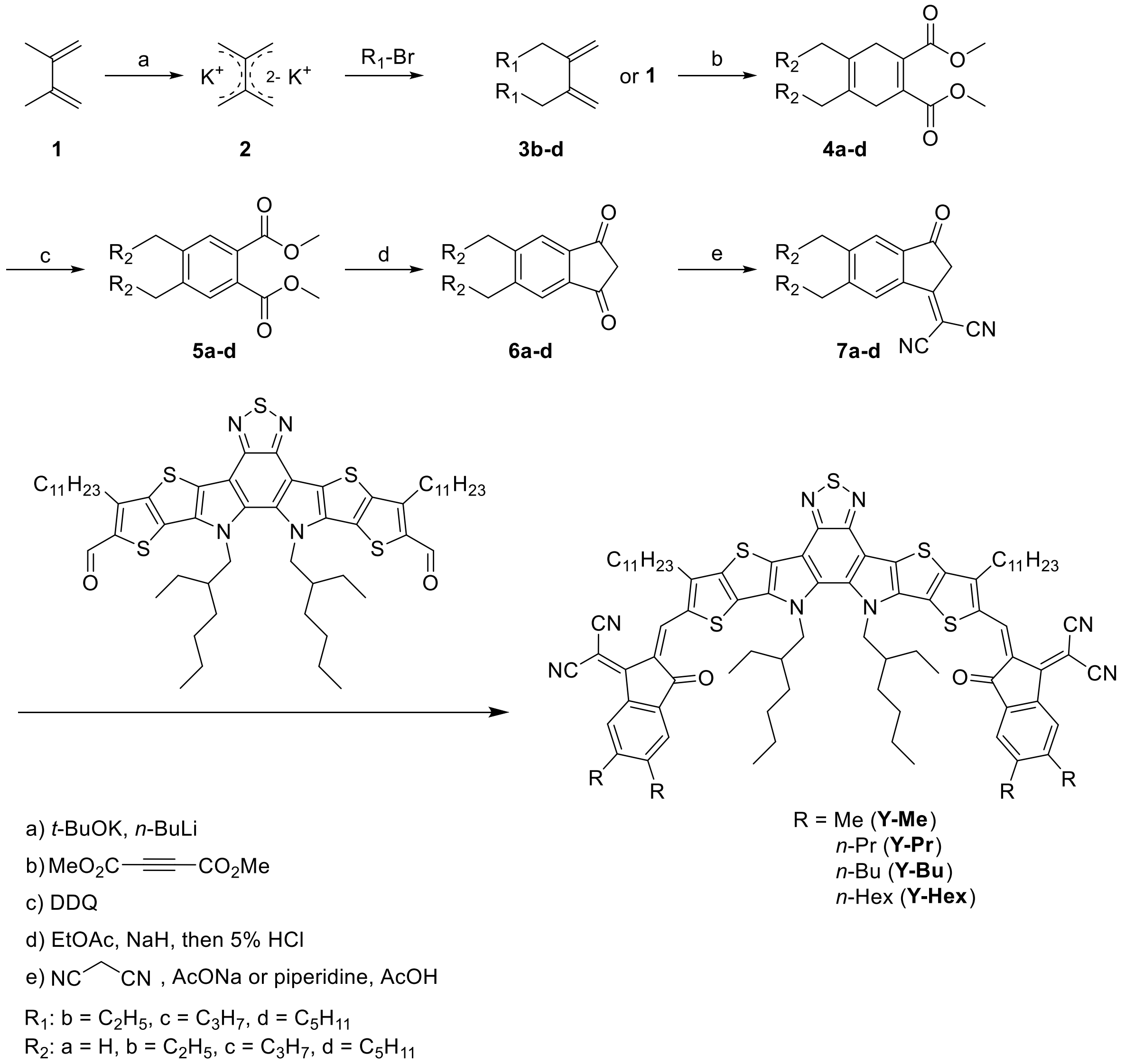
External quantum efficiency (EQE) spectra were measured with a Keithley 2400 source meter connected to a LabView-based software. Light source was a 75 W xenon lamp connected to a Multimode 4-AT monochromator from Amko. During measurement, the incident light beam was chopped at a frequency of 30 Hz. The setup calibration was done using a silicon photodiode (818-UV/DB, Newport Corporation). All spectra were recorded from 380 to 1000 nm with a 10 nm step width.

Synthesis

Materials

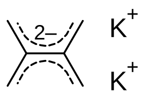
All chemicals were purchased from commercially available sources (Merck, Lumtec, abcr, VWR, Roth etc.) and used as received, unless otherwise stated. PPh_3 was recrystallized from EtOH before use. Anhydrous CH_2Cl_2 was prepared by distillation over P_4O_{10}. Anhydrous THF was prepared by running the solvent through an automated aluminium oxide column. Anhydrous DMF (99.8% purity grade) was purchased from Merck.

Procedures



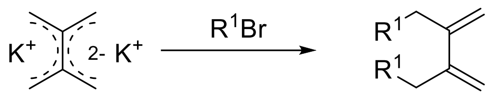
Scheme S1 Synthetic procedure for the novel acceptors.

*1,3-Butadiene dianion **(2)***



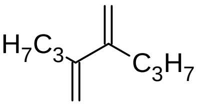
All experiments were performed using oven-dried glassware under Ar. 2 equiv. of sublimed potassium *tert*-butoxide were added to a round-bottom flask equipped with a stir bar. The flask was cooled in an ice bath and dry pentane (30 ml) was added, which resulted in a white suspension. 2 equiv. of a 2.5 M *n*-BuLi solution in hexane were added to the suspension, and stirring was continued for 10 min, yielding a Schlosser-Lochmann base. 1 equiv. of a 2,3-dimethyl-1,3-butadiene (**1**) solution in dry pentane was added to the cooled base within 30 min with efficient stirring. After evaporation of the solvent, a brownish solid was obtained. The product was used in alkylation reactions without further treatment, suspended in tetrahydrofuran at -78 °C.

Alkylated butadienes - General Procedure A



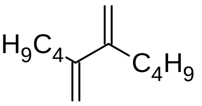
Using a wide-gauge plastic cannula, the thick suspension of dianion **2** in dry tetrahydrofuran (80 ml), kept at -78 °C, was transferred to a round-bottom flask, containing the haloalkane solution in dry tetrahydrofuran (80 ml), also cooled to -78 °C. When the mixture reached RT, pentane (70 ml) was added to the flask, and the mixture was washed with water (10 x 250 ml) and brine (1 x 250 ml) and dried over $MgSO_4$. The product was purified by vacuum distillation.

2,3-Dipropyl-1,3-butadiene ***(3b)***



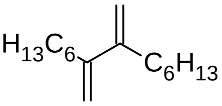
Following General Procedure A, dianion **2** (61.0 mmol) and 1-bromoethane (22.6 ml, 305 mmol) afforded **3b** (2.05 g, 25%) as a colorless oil (bp. 46 – 52 °C, 10 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.09 – 4.91 (m, 4 H), 2.23 (t, *J* = 7.3, 4 H), 1.55 – 1.41 (m, 4 H), 0.93 (t, *J* = 7.3 Hz, 6 H).

2,3-Dibutyl-1,3-butadiene ***(3c)***



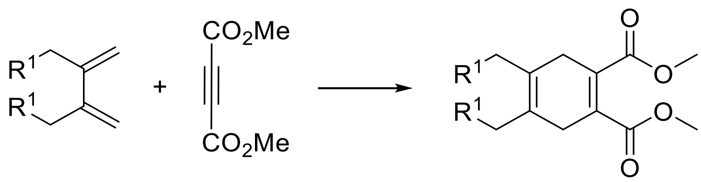
Following General Procedure A, dianion **2** (4.65 mmol) and 1-bromopropane (10.1 ml, 11.2 mmol) afforded **3c** (2.79 g, 36%) as a colorless oil (bp. 40 – 45 °C, 2 mmHg). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.09 – 5.04 (m, 2 H), 4.95 – 4.90 (m, 2 H), 2.31 – 2.18 (m, 4 H), 1.51 – 1.22 (m, 8 H), 0.92 (t, *J* = 7.0 Hz, 6 H).

2,3-Dihexyl-1,3-butadiene ***(3d)***



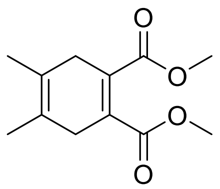
Following General Procedure A, dianion **2** (8.14 mmol) and 1-bromopentane (2.52 ml, 20.3 mmol) afforded **3d** (5.16 g, 24%) as a colorless oil (bp. 72 – 85 °C, 5×10^{-3} mmHg). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 5.11 – 4.85 (m, 4 H), 2.30 – 1.96 (m, 4 H), 1.52 – 1.18 (m, 16 H), 0.95 – 0.82 (m, 6 H).

Diels-Alder reaction - General Procedure B.



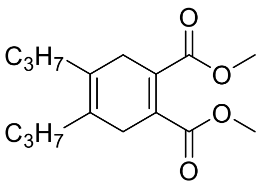
2,3-Dialkylbuta-1,3-diene (**1, 3b-d**) was added to dimethyl acetylenedicarboxylate. The solution was heated to 75 °C under Ar to initiate the reaction and the heating was stopped until the vigorous reaction subsided. The heating was resumed and the reaction was continued at 60 – 75 °C for 24 – 48 h. The compounds thus obtained were used for further synthesis without additional purification, assuming the yield to be quantitative, as evidenced by ^{1}H NMR spectra.

Dimethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate ***(4a)***



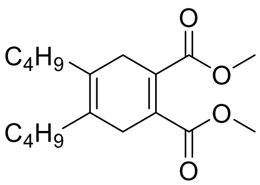
Following General Procedure B, 2,3-dimethylbuta-1,3-diene (**1**) (19.2 ml, 135 mmol) and dimethyl acetylenedicarboxylate (20.7 ml, 135 mmol) at 75 °C for 24 h afforded **4a** as a yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.70 (s, 6 H), 2.84 (s, 4 H), 1.58 (s, 6 H).

Dimethyl 4,5-dipropylcyclohexa-1,4-diene-1,2-dicarboxylate ***(4b)***



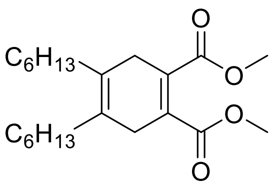
Following General Procedure B, 2,3-dipropylbuta-1,3-diene (**3b**) (3.86 g, 35.1 mmol) and dimethyl acetylenedicarboxylate (4.98 g, 35.1 mmol), heated at 75 °C for 24 h, afforded **4b** as a yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.79 (s, 6 H), 2.97 (s, 4 H), 2.10 – 1.99 (m, 4 H), 1.49 – 1.33 (m, 4 H), 0.91 (t, *J* = 7.3 Hz, 6 H).

Dimethyl 4,5-dibutylcyclohexa-1,4-diene-1,2-dicarboxylate ***(4c)***



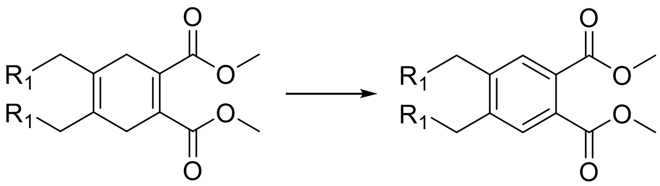
Following General Procedure B, 2,3-dibutylbuta-1,3-diene (**3c**) (2.79 g, 16.8 mmol)) and dimethyl acetylenedicarboxylate (2.38 g, 16.8 mmol), heated at 60 °C for 28 h, afforded **4c** as a yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.79 (s, 6 H), 2.97 (s, 4 H), 2.11 – 2.01 (m, 4 H), 1.41 – 1.23 (m, 8 H), 0.92 (t, *J* = 7.0 Hz, 6 H).

Dimethyl 4,5-dihexylcyclohexa-1,4-diene-1,2-dicarboxylate ***(4d)***



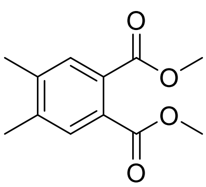
Following General Procedure B, 2,3-dihexylbuta-1,3-diene (**3d**) (3.37 g, 15.1 mmol) and dimethyl acetylenedicarboxylate (2.15 g, 15.1 mmol), heated at 75 °C for 48 h, afforded **4d** as a yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 3.79 (s, 6 H), 2.96 (s, 4 H), 2.10 – 2.00 (m, 4 H), 1.34 – 1.22 (m, 16 H), 0.90 (t, *J* = 6.6 Hz, 6 H).

Cyclohexadiene oxidation - General Procedure C



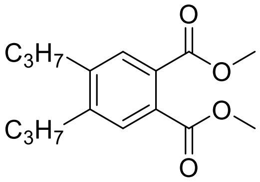
Dimethyl 4,5-dialkylcyclohexa-1,4-diene-1,2-dicarboxylate (**4a-d**) was dissolved in toluene. The solution was cooled to 0 °C, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was added slowly, then the reaction mixture was heated to 70 °C for 6 – 18 h, cooled and filtered through a pad of celite. The filtrate was evaporated and the product was purified by filtration through neutral alumina, using dichloromethane and petroleum ether mixture (1:1) as the solvent. The filtrate was evaporated to afford the product.

Dimethyl 4,5-dimethylphthalate ***(5a)***



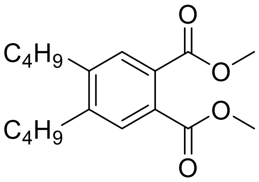
Following General Procedure C, dimethyl 4,5-dimethylcyclohexa-1,4-diene-1,2-dicarboxylate (**4a**) (30.0 g, 134 mmol), toluene (150 ml), and DDQ (33.7 g, 149 mmol), heated at 70 °C for 18 h, afforded **5a** (22.8 g, 77%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.50 (s, 2 H), 3.90 (s, 6 H), 2.33 (s, 6 H).

*Dimethyl 4,5-dipropylphthalate **(5b)***



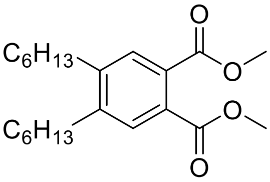
Following General Procedure C, dimethyl 4,5-dipropylcyclohexa-1,4-diene-1,2-dicarboxylate (**4b**) (9.62 g, 35.1 mmol), toluene (50 ml), and DDQ (9.15 g, 40.3 mmol), heated at 70 °C for 6 h, afforded **5b** (4.93 g, 52%) as a yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.51 (s, 2 H), 3.90 (s, 6 H), 2.70 – 2.59 (m, 4 H), 1.73 – 1.54 (m, 4 H), 1.00 (t, *J* = 7.3 Hz, 6 H).

*Dimethyl 4,5-dibutylphthalate **(5c)***



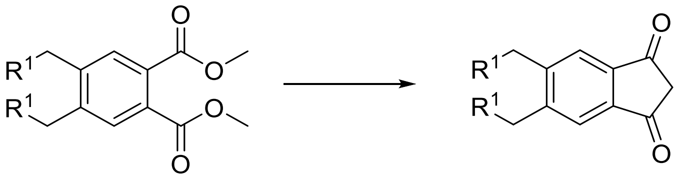
Following General Procedure C, dimethyl 4,5-dibutylcyclohexa-1,4-diene-1,2-dicarboxylate (**4c**) (5.17 g, 16.8 mmol), toluene (50 ml), and DDQ (4.19 g, 18.5 mmol), heated at 70 °C for 6 h, afforded **5c** (4.21 g, 82%) as a yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$) 7.51 (s, 2 H), 3.90 (s, 6 H), 2.70 – 2.34 (m, 4 H), 1.68 – 1.32 (m, 8 H), 0.96 (t, *J* = 7.2 Hz, 6 H).

*Dimethyl 4,5-dihexylphthalate **(5d)***



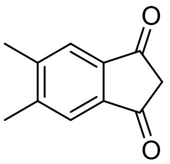
Following General Procedure C, dimethyl 4,5-dihexylcyclohexa-1,4-diene-1,2-dicarboxylate (**4d**) (7.15 g, 19.7 mmol), toluene (50 ml) and DDQ (5.15 g, 22.7 mmol), heated at 70 °C for 12 h, afforded **5d** (6.43 g, 90%) as a yellowish liquid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.50 (s, 2 H), 3.90 (s, 6 H), 2.70 – 2.57 (m, 4 H), 1.64 – 1.52 (m, 4 H), 1.46 – 1.22 (m, 12 H), 0.95 – 0.84 (m, 6 H).

Preparation of 1,3-indandiones – General Procedure E



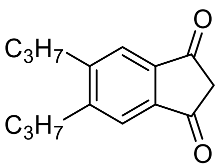
Phthalate **5a-d**, 60% sodium hydride and dry ethyl acetate were heated under Ar to 100 °C for 4 h. The reaction product was precipitated with petroleum ether (150 ml), filtered and introduced into 5% hydrochloric acid (200 ml), heated to 80 °C. The solution was stirred for 15 min, until the evolution of CO_2 ceased. The solution was cooled and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and evaporated.

*5,6-Dimethylindan-1,3-dione **(6a)***



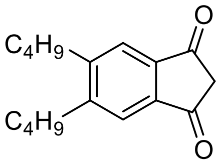
Following General Procedure E, dimethyl 4,5-dimethylphthalate (**5a**) (9.33 g, 42.0 mmol), 60% NaH (3.86 g, 96.6 mmol), and dry ethyl acetate (13.5 ml, 139 mmol) afforded **6a** (2.75 g, 38%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.74 (s, 2 H), 3.21 (s, 2 H), 2.46 (s, 6 H).

*5,6-Dipropylindan-1,3-dione **(6b)***



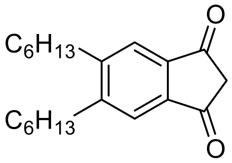
Following General Procedure E, dimethyl 4,5-dipropylphthalate (**5b**) (4.93 g, 17.7 mmol), 60% NaH (1.43 g, 35.4 mmol), and dry ethyl acetate (5.23 ml, 53.5 mmol) afforded, after flash column chromatography (25% EtOAc/hexane), **6b** (0.92 g, 23%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.72 (s, 2 H), 3.16 (s, 2 H), 2.77 – 2.67 (m, 4 H), 1.73-1.55 (m, 4 H), 1.00 (t, *J* = 7.3 Hz, 6 H).

*5,6-Dibutylindan-1,3-dione **(6c)***



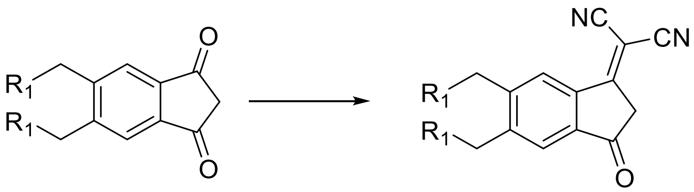
Following General Procedure E, dimethyl 4,5-dibutylphthalate (**5c**) (4.21 g, 13.7 mmol), 60% NaH (1.27 g, 31.6 mmol), and dry ethyl acetate (4.43 ml, 45.3 mmol) afforded, after flash column chromatography (20% EtOAc/hexane), **6c** (1.05 g, 30%) as a yellow solid. ^{1}H NMR (300 MHz, DMSO-d_6, δ) 7.76 (s, 2 H), 3.20 (s, 2 H), 2.82 – 2.74 (m, 4 H), 1.70-1.57 (m, 4 H), 1.52 – 1.37 (m, 4 H), 0.98 (t, J = 7.0 Hz, 6 H).

*5,6-Dihexylindan-1,3-dione **(6d)***



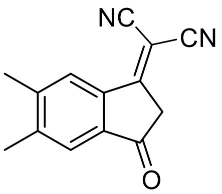
Following General Procedure E, dimethyl 4,5-dibutylphthalate (**5d**) (4.10 g, 11.3 mmol), 60% NaH (1.04 g, 26.0 mmol), and dry ethyl acetate (3.65 ml, 37.3 mmol) afforded **6d** (1.01 g, 28%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.76 (s, 2 H), 3.21 (s, 2 H), 2.83 – 2.68 (m, 4 H), 1.72 – 1.56 (m, 4 H), 1.45 – 1.30 (m, 12 H), 0.95 – 0.87 (m, 6 H).

Malononitrile addition to indan-1,3-dione – General Procedure F



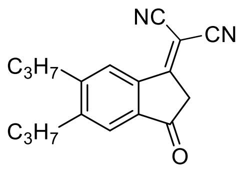
To a solution of indan-1,3-dione (**6a-d**) and malononitrile in anhydrous ethanol (50 ml), anhydrous sodium acetate was added with stirring, and stirring was continued for 40 min. The solution was poured into water (100 ml) and acidified with 5% hydrochloric acid to pH 1 – 2. The crude product was filtered.

*5,6-Dimethyl-3-(dicyanomethylidene)indan-1-one **(7a)***



Following General Procedure F, 5,6-dimethylindan-1,3-dione (**6a**) (2.75 g, 15.8 mmol), anhydrous sodium acetate (1.62 g, 40.5 mmol), and malononitrile (2.08 g, 31.6 mmol) afforded, after purification by recrystallization from acetonitrile, dissolution in dichloromethane, filtration through neutral alumina and evaporation, **7a** (1.78 g, 51%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.44 – 7.68 (m, 2 H), 3.68 (s, 2 H), 2.48 (s, 3 H), 2.46 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 194.74, 166.52, 146.92, 146.83, 140.76, 138.95, 126.32, 125.10, 112.46, 112.36, 77.47, 43.50, 21.22, 20.99. HRMS (m/z): $[M+H]^+$ calcd. $C_{14}H_{10}N_2O$: 223.0866. Found: 223.0862.

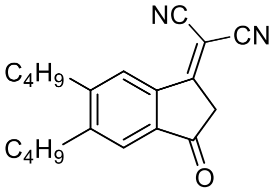
*5,6-Dipropyl-3-(dicyanomethylidene)indan-1-one **(7b)***



2-(3-oxo-5,6-dipropyl-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile

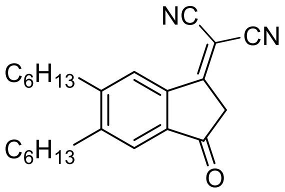
Following General Procedure F, 5,6-dipropylindan-1,3-dione (**6b**) (0.92 g, 4.0 mmol), anhydrous sodium acetate (0.44 g, 5.0 mmol), and malononitrile (0.53 g, 8.0 mmol) afforded, after purification by flash column chromatography (25% DCM/hexane), **7b** (0.88 g, 79%) as a yellowish solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.41 (s, 1 H), 7.76 (s, 1 H), 3.68 (s, 2 H), 2.84 – 2.72 (m, 4 H), 1.81 – 1.53 (m, 4 H), 1.09 – 1.00 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 194.84, 166.61, 150.65, 150.58, 143.91, 140.48, 138.60, 129.59, 125.93, 124.55, 112.52, 112.37, 77.46, 77.04, 76.62, 43.49, 35.41, 35.23, 34.52, 24.00, 23.66, 23.51, 14.09, 14.04. HRMS (m/z): $[M+H]^+$ calcd. $C_{18}H_{18}N_2O$: 279.1492. Found: 279.1494.

5,6-Dibutyl-3-(dicyanomethylidene)indan-1-one ***(7c)***



Following General Procedure F, 5,6-dibutylindan-1,3-dione (**6c**) (1.05 g, 4.06 mmol), anhydrous sodium acetate (0.43 g, 5.3 mmol), and malononitrile (0.54 g, 8.1 mmol) afforded, after purification by recrystallization from petroleum ether, **7c** (0.84 g, 68%) as yellowish crystals (mp. 83.6 – 84.3 °C). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.39 (s, 1 H), 7.75 (s, 1 H), 3.67 (s, 2 H), 2.86 – 2.71 (m, 4 H), 1.71 – 1.52 (m, 4 H), 1.51 – 1.30 (m, 4 H), 1.02 – 0.93 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 194.97, 166.72, 151.00, 150.89, 140.56, 138.70, 126.08, 124.67, 112.63, 112.50, 77.50, 43.59, 33.30, 33.09, 32.75, 32.64, 22.79, 22.75, 14.00, 13.96. HRMS (m/z): $[M+H]^+$ calcd. $C_{20}H_{22}N_2O$: 307.1816. Found: 307.1790.

5,6-Dihexyl-3-(dicyanomethylidene)indan-1-one ***(7d)***



Following General Procedure F, 5,6-dihexylindan-1,3-dione (**6d**) (1.01 g, 3.21 mmol), anhydrous sodium acetate (0.37 g, 4.2 mmol), and malononitrile (0.42 g, 6.4 mmol) afforded, after purification by flash column chromatography (25% EtOAc/hexane), **7d** (0.55 g, 55%) as orange crystals (mp 65.7 – 67.0 °C). ^{1}H NMR (300 MHz, $CDCl_3$, δ) 8.40 (s, 1 H), 7.76 (s, 1 H), 3.68 (s, 2 H), 2.85 – 2.71 (m, 4 H), 1.74 – 1.55 (m, 4 H), 1.49 – 1.28 (m, 12 H), 0.97 – 0.86 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, δ) 195.01, 166.72, 151.06, 150.97, 140.59, 138.72, 126.12, 124.70, 112.66, 112.53, 43.63, 33.64, 33.44, 31.72, 31.70, 30.72, 30.55, 29.39, 29.36, 22.71, 22.67, 14.18. HRMS (m/z): $[M+H]^-$ calcd. $C_{24}H_{30}N_2O$: 361.2285. Found: 361.2283.

General Knoevenagel procedure

A 3-neck round bottom flask with reflux condenser and nitrogen inlet was charged with the Y5-core (1.0 equiv.) and the respective end group (**7a-d**, 6.0 equiv.). The flask was flushed with nitrogen for 15 min, followed by addition of $CHCl_3$ (20-30 ml). After full dissolution, pyridine was added (immediate colour change) and the reaction mixture was refluxed overnight. After TLC indicated full conversion, the reaction mixture was concentrated to approx. half of its volume. Then at RT, 50-60 ml MeOH were added to precipitate the product. The solid was filtered and washed with MeOH. The crude solid was further purified by recrystallization. For that, the crude was dissolved in hot toluene (approx. 50 ml), followed by addition of the equal amount of MeOH as antisolvent. After 2-4 hours at RT, the solid was filtered and washed with toluene:MeOH 1:2, followed by vacuum drying. This gave the respective product as dark blue solid.

Compound ***Y-Me***

Y-Me was prepared according to the general Knoevenagel procedure (see above). Used amounts: Y5-core 205 mg (0.199 mmol), compound **7a** 265 mg (1.19 mmol), pyridine 1.00 ml (12.4 mmol). Yield 267 mg (93%) as dark blue solid.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 9.11 (s, 2 H), 8.47 (s, 2 H), 7.72 (s, 2 H), 4.77 (d, J = 8.3 Hz, 4 H), 3.23 (t, J = 7.6 Hz, 4 H), 2.47 (s, 12 H), 2.15 – 2.08 (m, 2 H), 1.94 – 1.83 (m, 4 H), 1.53 – 1.46 (m, 4 H), 1.41 – 1.34 (m, 4 H), 1.34 – 1.13 (m, 28 H), 1.08 – 0.92 (m, 12 H), 0.86 (t, J = 7.0 Hz, 6 H), 0.75 (t, J = 7.2 Hz, 6 H), 0.65 (t, J = 7.2 Hz, 6 H). HR-MS (MALDI-TOF) *m/z* for $C_{86}H_{98}N_8O_2S_5^+$ $[M]^+$: calcd. 1434.6416, found 1434.7921.

Compound ***Y-Pr***

Y-Pr was prepared according to the general Knoevenagel procedure (see above). Used amounts: Y5-core 205 mg (0.199 mmol), compound **7b** 332 mg (1.19 mmol), pyridine 1.00 ml (12.4 mmol). Yield 300 mg (97%) as dark blue solid.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 9.09 (s, 2(s, 2(s, 2 4.77 (d, *J* = 7.8 Hz, 4 H), 3.23 (t, *J* = 7.7 Hz, 4 H), 2.83 – 2.72 (m, 8 H), 2.20 – 2.11 (m, 2 H), 1.92 – 1.82 (m, 4 H), 1.79 – 1.68 (m, 8 H), 1.54 – 1.46 (m, 4 H), 1.40 – 1.33 (m, 4 H), 1.32 – 1.13 (m, 28 H), 1.13 – 0.89 (m, 24 H), 0.86 (t, *J* = 6.8 Hz, 6 H), 0.78 (t, *J* = 7.4 Hz, 6 H), 0.65 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ (ppm): 188.70, 161.23, 152.31, 149.30, 148.69, 147.40, 144.65, 138.06, 137.89, 135.08, 134.69, 134.43, 134.15, 133.22, 133.02, 129.10, 125.57, 123.80, 121.89, 115.53, 115.18, 113.36, 67.31, 55.60, 40.27, 35.60, 35.21, 31.92, 31.10, 29.79, 29.77, 29.74, 29.65, 29.63, 29.53, 29.50, 29.34, 27.57, 23.79, 23.53, 23.24, 22.82, 22.68, 14.14, 14.11, 13.70, 10.33. HR-MS (MALDI-TOF) *m/z* for $C_{94}H_{114}N_8O_2S_5^+$ $[M]^+$: calcd. 1546.7668, found 1546.7354.

Compound ***Y-Bu***

Y-Bu was prepared according to the general Knoevenagel procedure (see above). Used amounts: Y5-core 183 mg (0.178 mmol), compound **7c** 327 mg (1.07 mmol), pyridine 1.00 ml (12.4 mmol). Yield 260 mg (91%) as dark blue solid.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 9.09 (s, 2 H), 8.47 (s, 2 H), 7.76 (s, 2 H), 4.77 (d, *J* = 7.8 Hz, 4 H), 3.23 (t, *J* = 7.6 Hz, 4 H), 2.90 - 2.68 (m, 8 H), 2.21 - 2.09 (m 2 H), 1.94 - 1.80 (m, 4 H), 1.75 - 1.60 (m, 8 H), 1.53 - 1.42 (m, 12 H), 1.40 - 1.33 (m, 4 H), 1.33 - 1.12 (m, 30 H), 1.12 - 0.90 (m, 22 H), 0.86 (t, *J* = 7.2 Hz, 6 H), 0.78 (t, *J* = 7.2 Hz, 6 H), 0.65 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ (ppm): 188.73, 161.23, 152.28, 149.50, 148.90, 147.43, 144.64, 138.05, 137.89, 135.07, 134.66, 134.42, 134.40, 133.22, 133.00, 129.12, 125.65, 123.78, 121.91, 115.53, 115.18, 113.35, 67.34, 55.59, 40.27, 33.34, 32.89, 32.83, 32.61, 31.91, 31.09, 29.79, 29.76, 29.65, 29.63, 29.53, 29.50, 29.34, 27.58, 23.23, 22.82, 22.72, 22.68, 14.11, 13.98, 13.92, 13.70. HR-MS (MALDI-TOF) *m/z* for $C_{98}H_{122}N_8O_2S_5^+$ $[M]^+$: calcd. 1602.8295, found 1602.8362.

Compound ***Y-Hex***

Y-Hex was prepared according to the general Knoevenagel procedure (see above). Used amounts: Y5-core 171 mg (0.166 mmol), compound **7d** 362 mg (1.00 mmol), pyridine 1.00 ml (12.4 mmol). Yield 270 mg (95%) as dark blue solid.

^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ (ppm): 8.99 (s, 2 H), 8.38 (s, 2 H), 7.81 (s, 2 H), 4.82 (d, *J* = 8.2 Hz, 4 H), 3.34 - 3.02 (m, 4 H), 2.82 (t, *J* = 8.0 Hz, 4 H), 2.77 (t, *J* = 8.0 Hz, 4 H), 2.37 - 2.19 (m, 2 H), 1.90 - 1.78 (m, 4 H),1.87 - 1.70 (m, 4 H), 1.70 - 1.61 (m, 4 H), 1.54 - 1.42 (m, 12 H), 1.42 - 1.31 (m, 20 H), 1.31 - 0.99 (m, 40 H), 0.96 (t, *J* = 6.8 Hz, 6 H), 0.92 (t, *J* = 6.8 Hz, 6 H), 0.90 - 0.74 (m, 12 H), 0.74 - 0.61 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ (ppm): 188.67, 160.86, 152.18, 149.54, 149.02, 147.09, 144.63, 137.97, 135.03, 134.65, 134.20, 132.98, 128.80, 125.48, 123.77, 121.71, 115.49, 115.10, 113.40, 67.19, 55.65, 40.28, 33.70, 33.24, 31.91, 31.72, 31.65, 31.08, 30.63, 30.36, 29.79, 29.65, 29.62, 29.56, 29.54, 29.38, 29.33, 27.54, 27.47, 23.30, 23.25, 22.92, 22.67, 22.64, 22.61, 14.10, 14.07, 13.74, 10.51, 10.47. HR-MS (MALDI-TOF) *m/z* for $C_{106}H_{138}N_8O_2S_5^+$ $[M]^+$: calcd. 1714.9546, found 1714.9761.

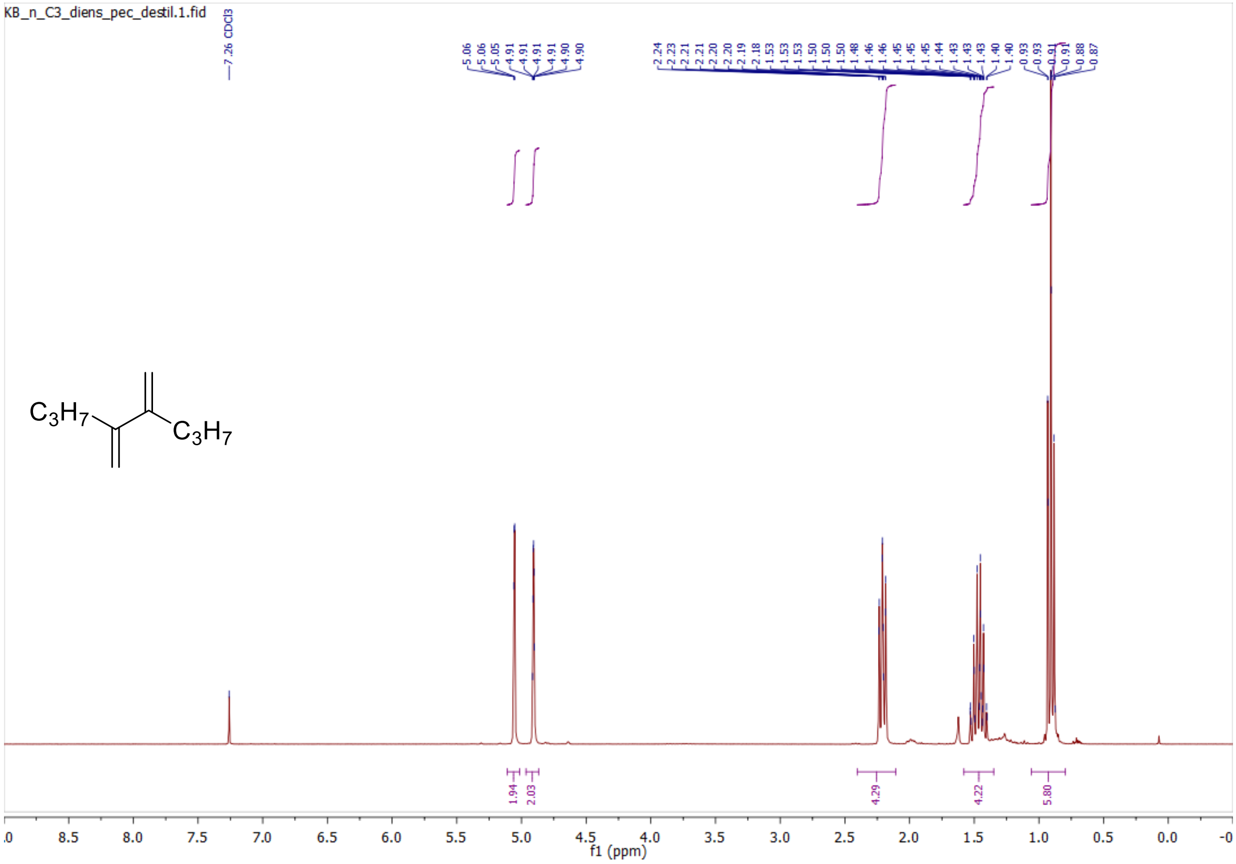


Fig. S17 [1]H NMR spectrum of compound **3b**.

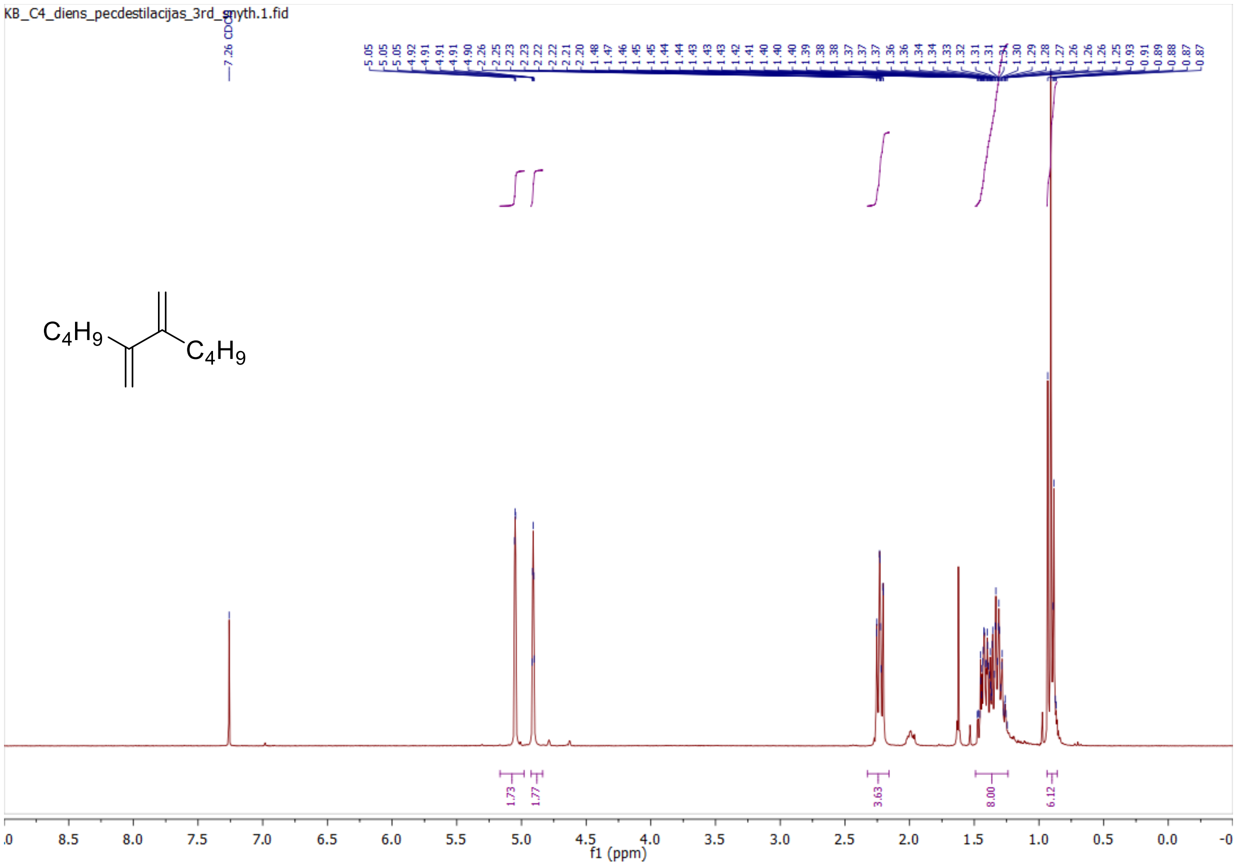


Fig. S18 [1]H NMR spectrum of compound **3c**.

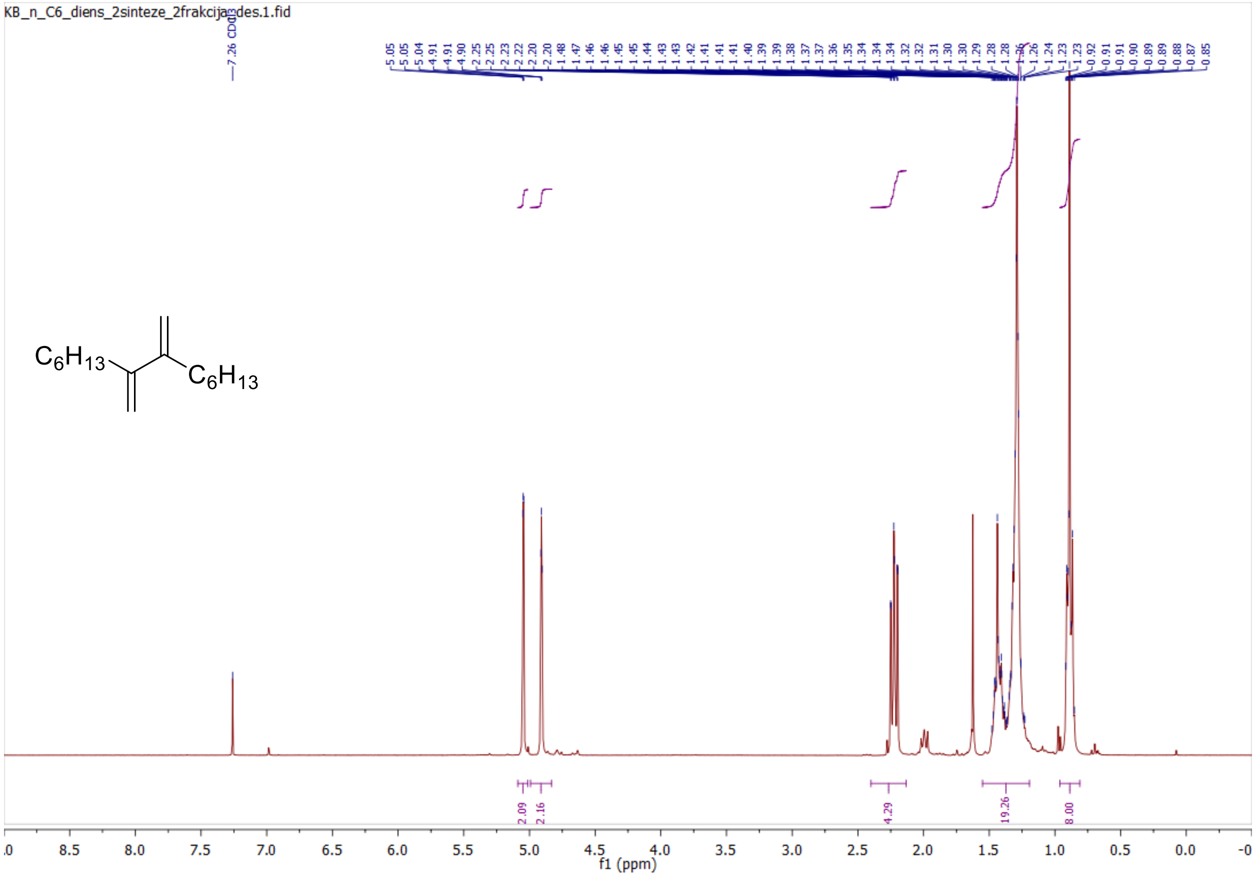


Fig. S19 ^{1}H NMR spectrum of compound **3d**.

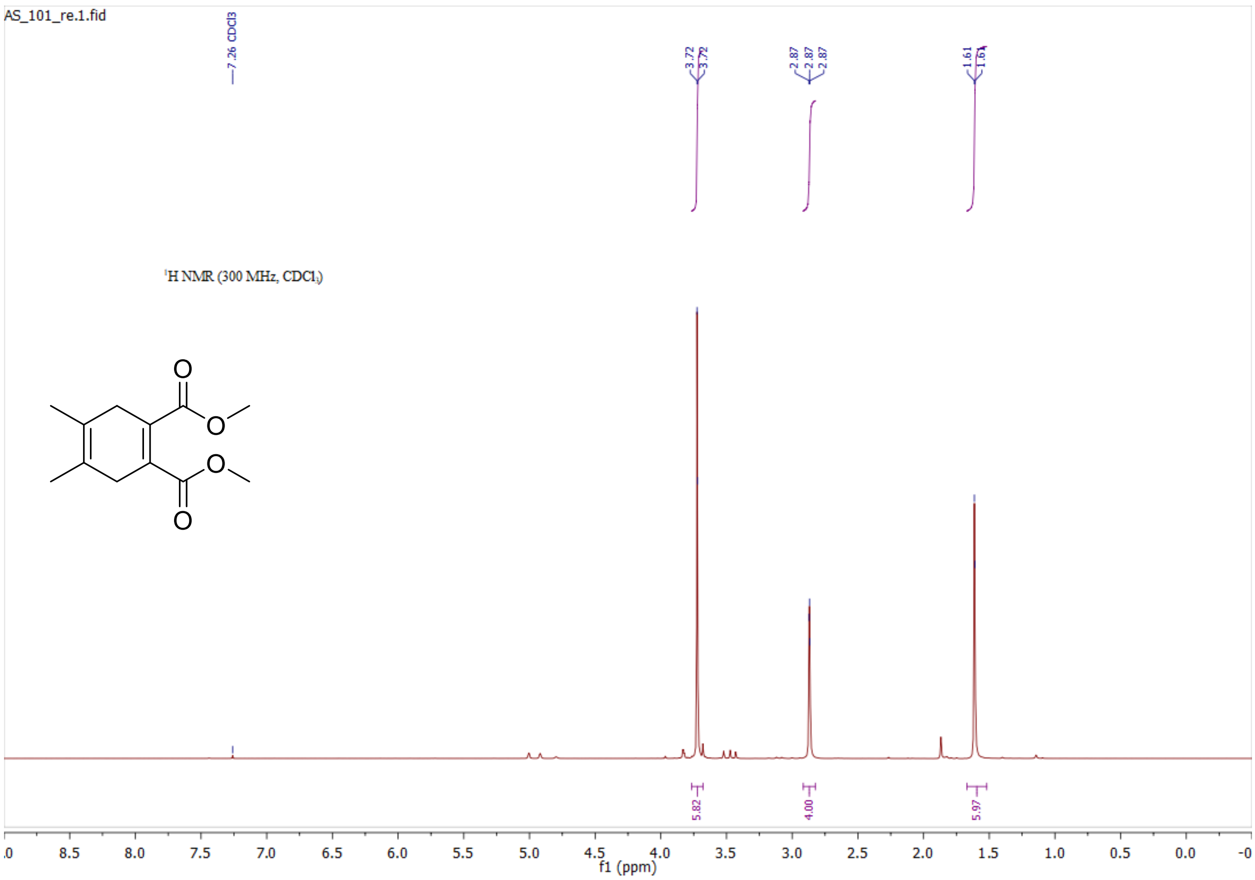


Fig. S20 ^{1}H NMR spectrum of compound **4a**.

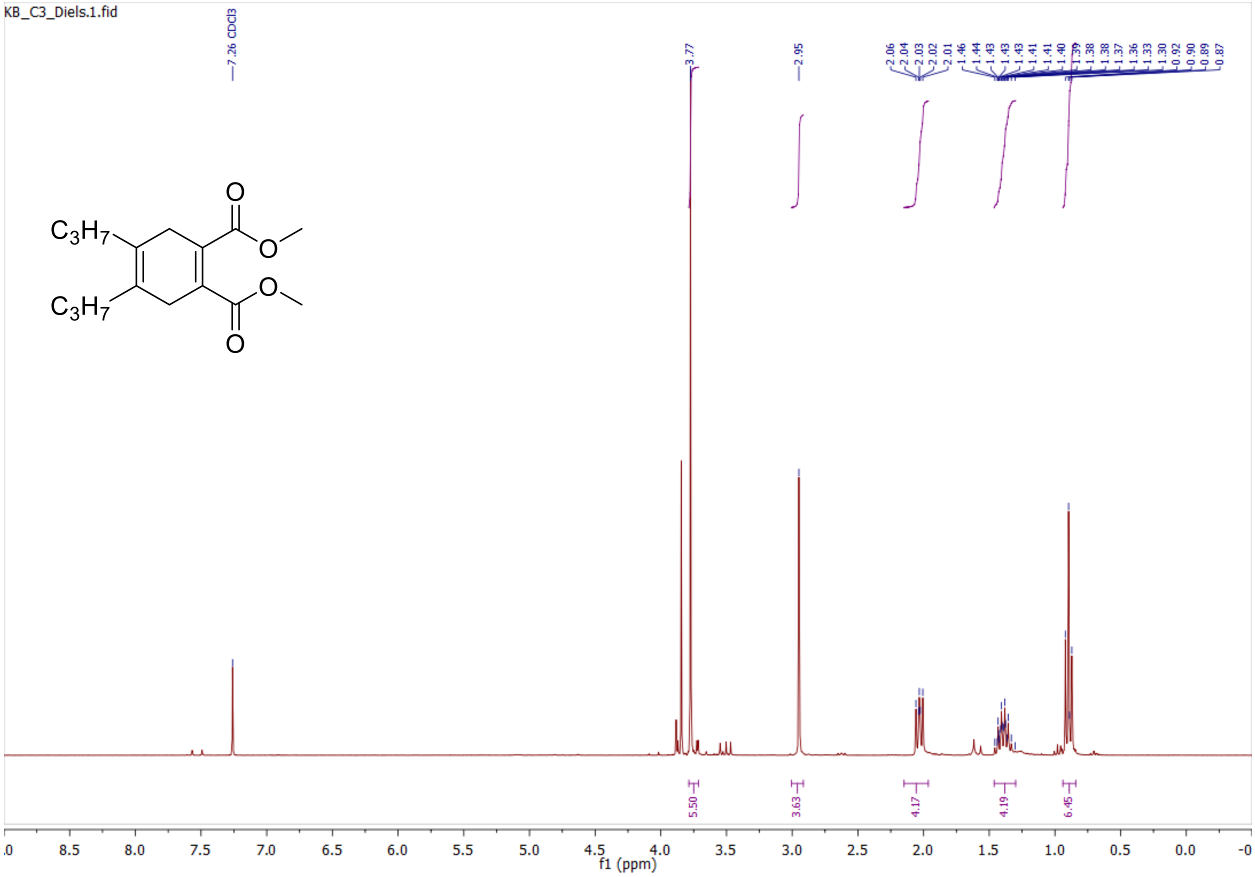


Fig. S21 [1]H NMR spectrum of compound **4b**.

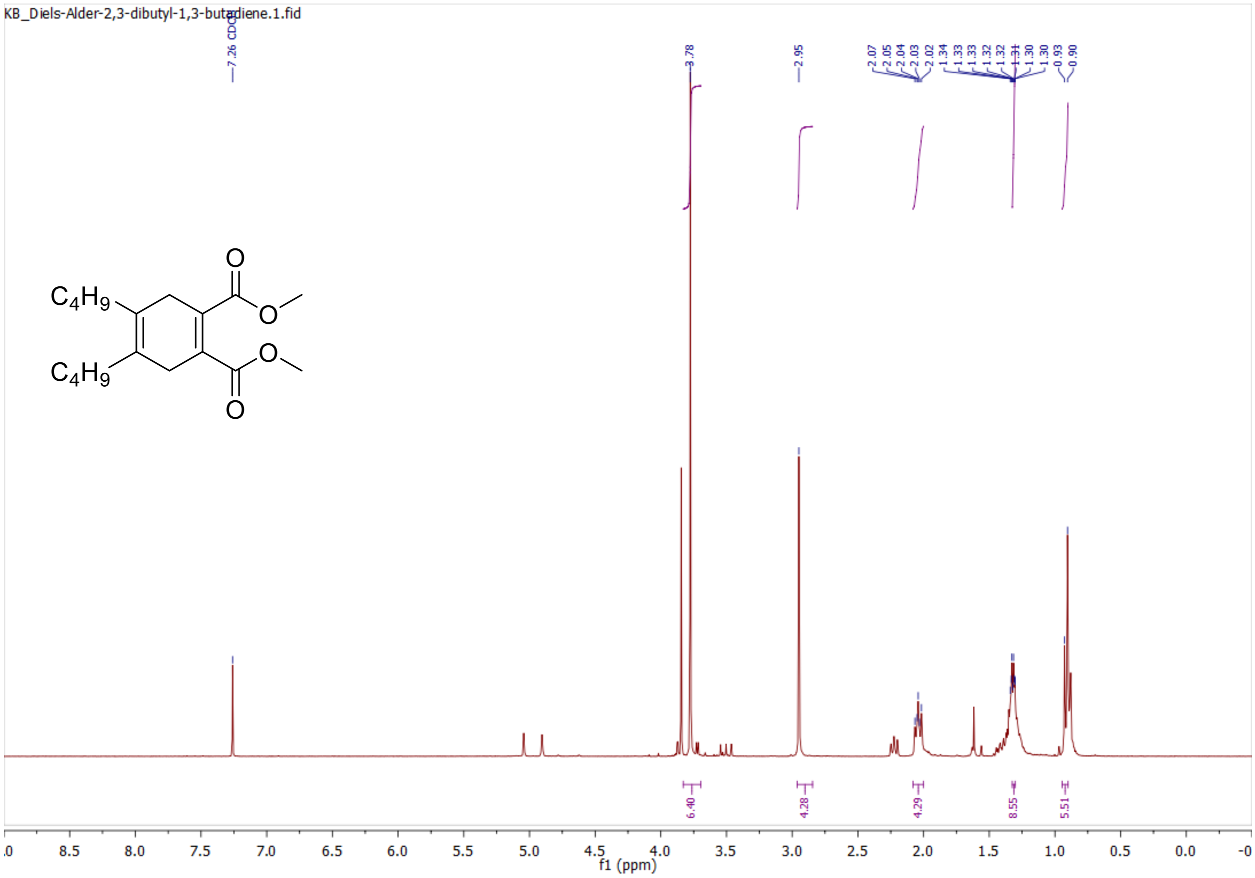


Fig. S22 [1]H NMR spectrum of compound **4c**.

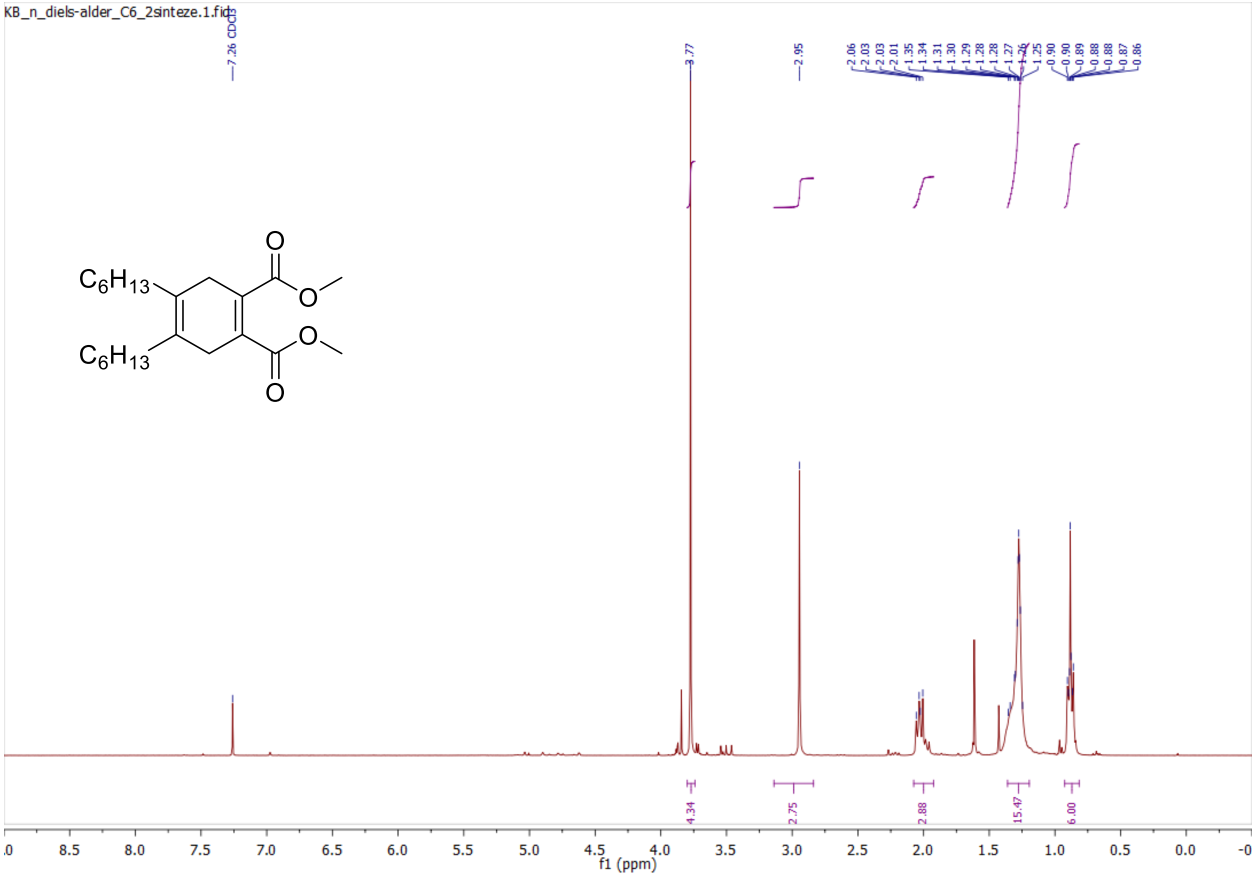


Fig. S23 ^{1}H NMR spectrum of compound **4d**.

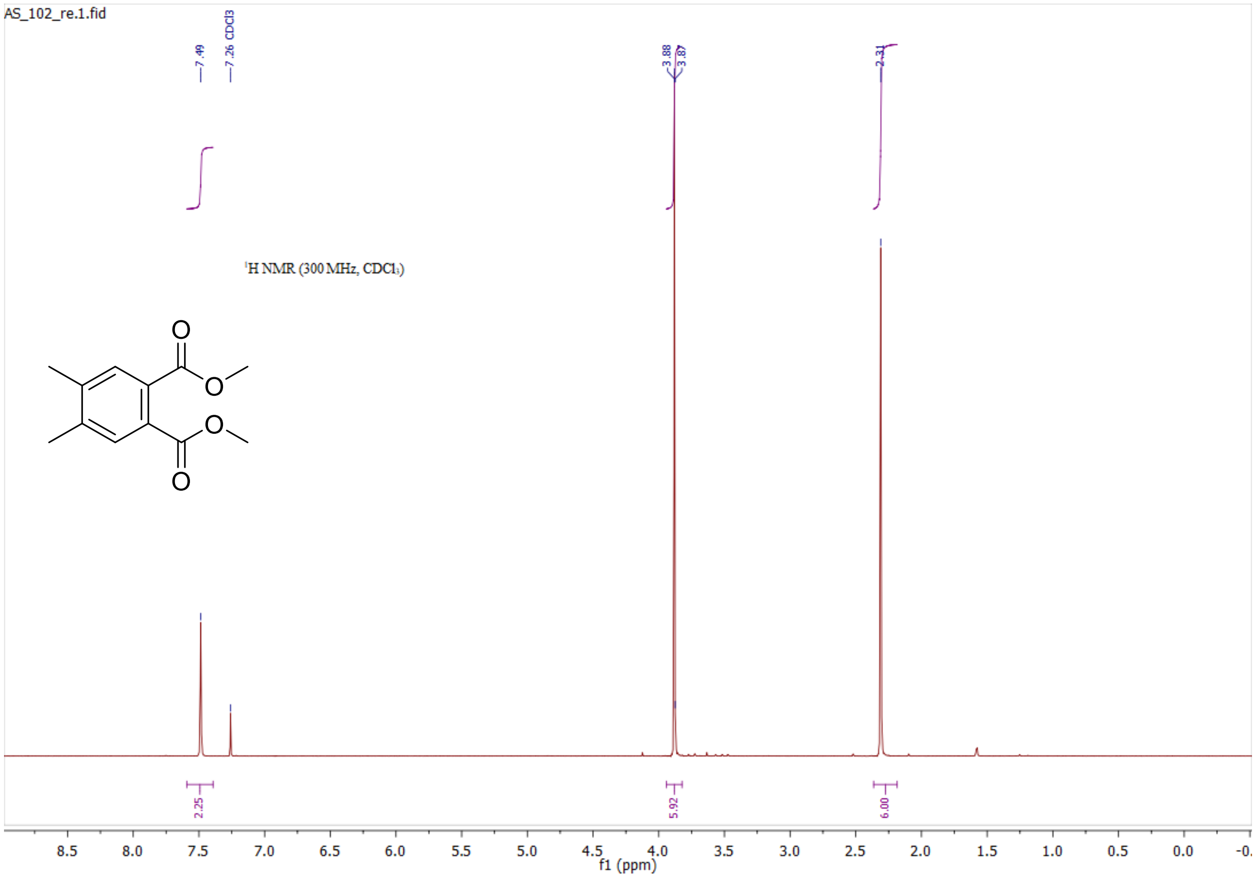


Fig. S24 ^{1}H NMR spectrum of compound **5a**.

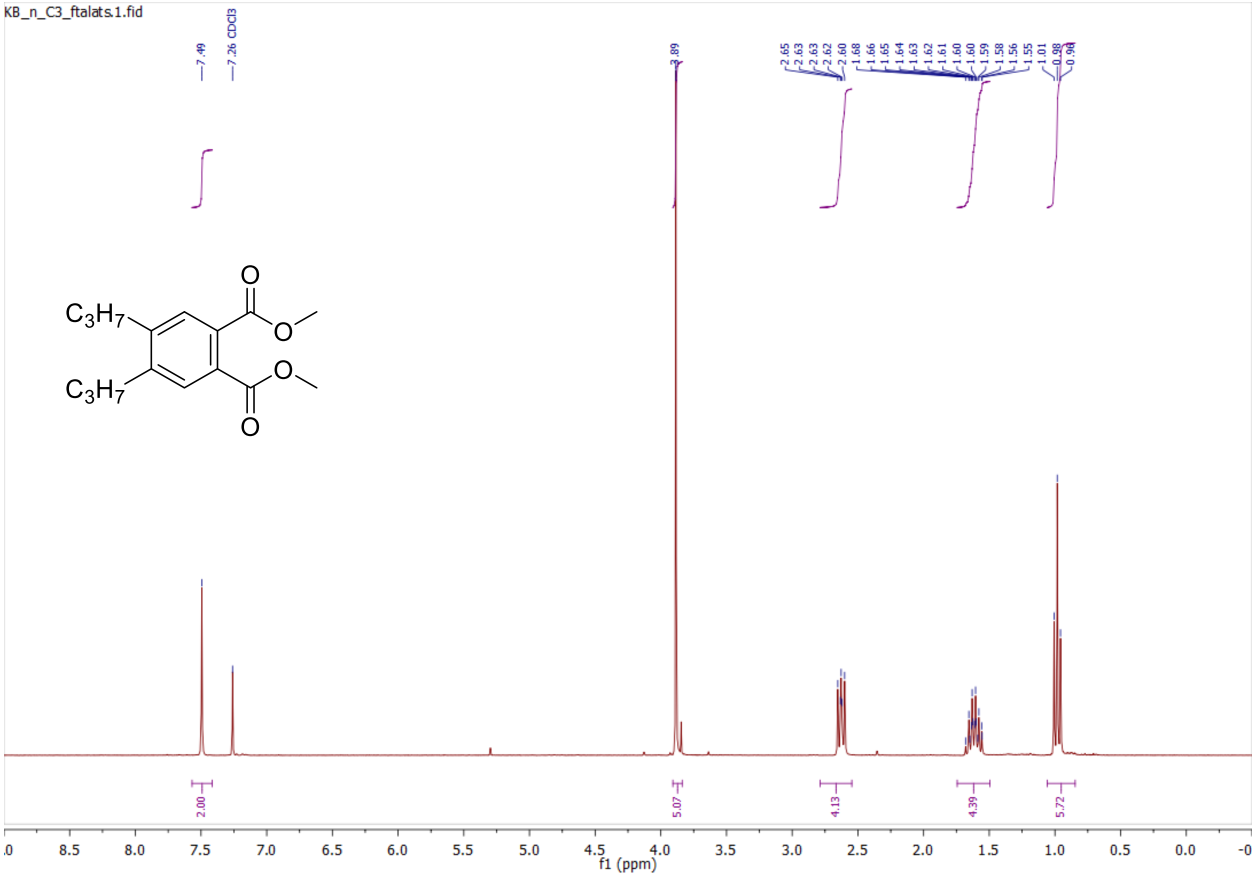


Fig. S25 ¹H NMR spectrum of compound **5b**.

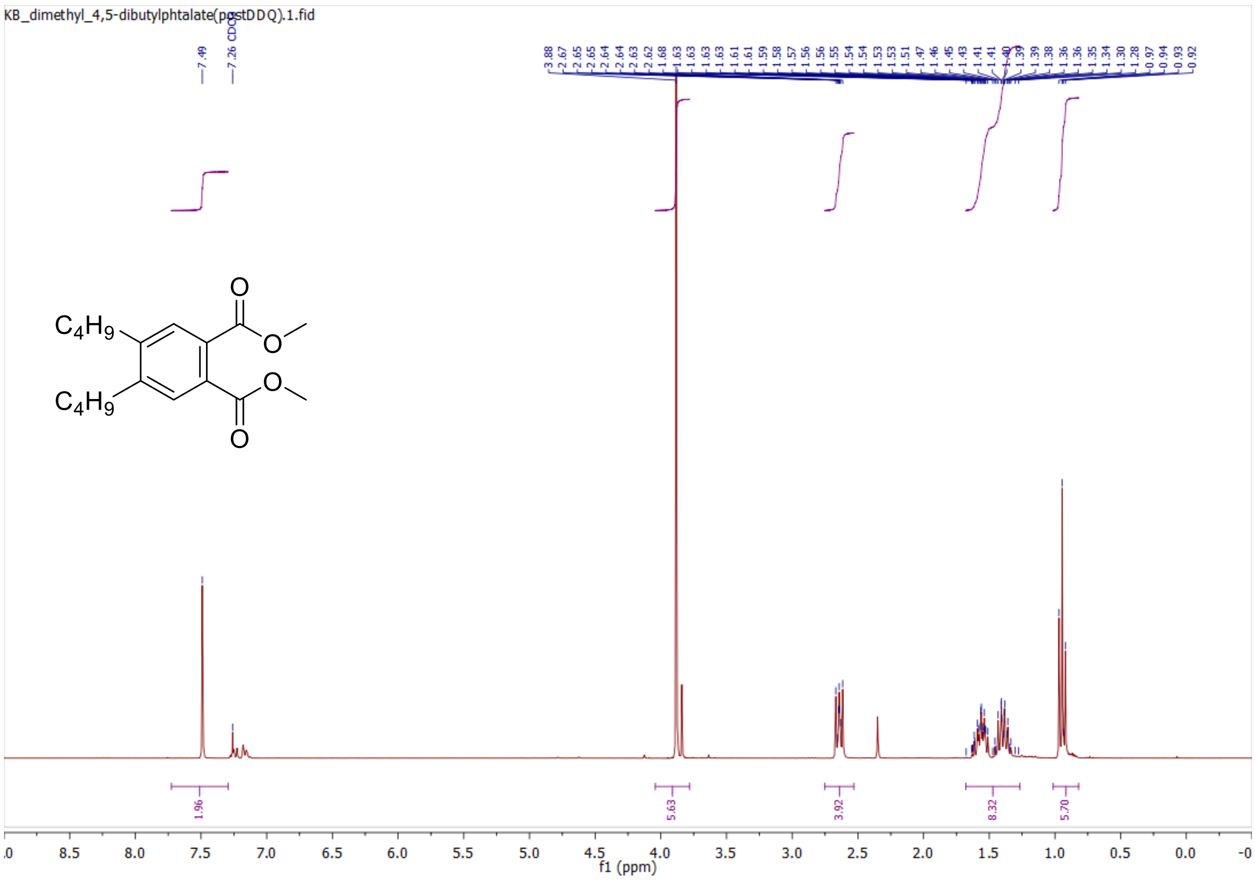


Fig. S26 ¹H NMR spectrum of compound **5c**.

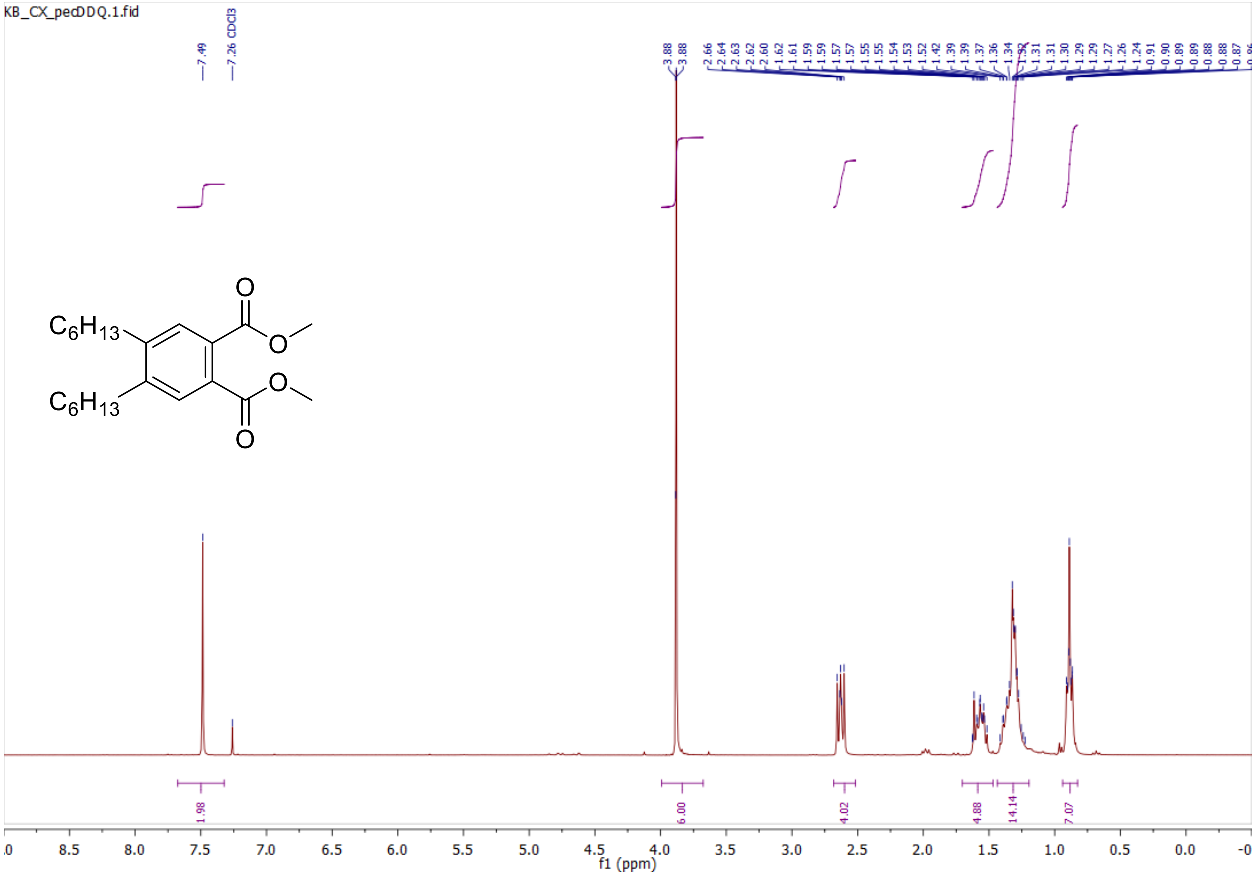


Fig. S27 [1]H NMR spectrum of compound **5d**.

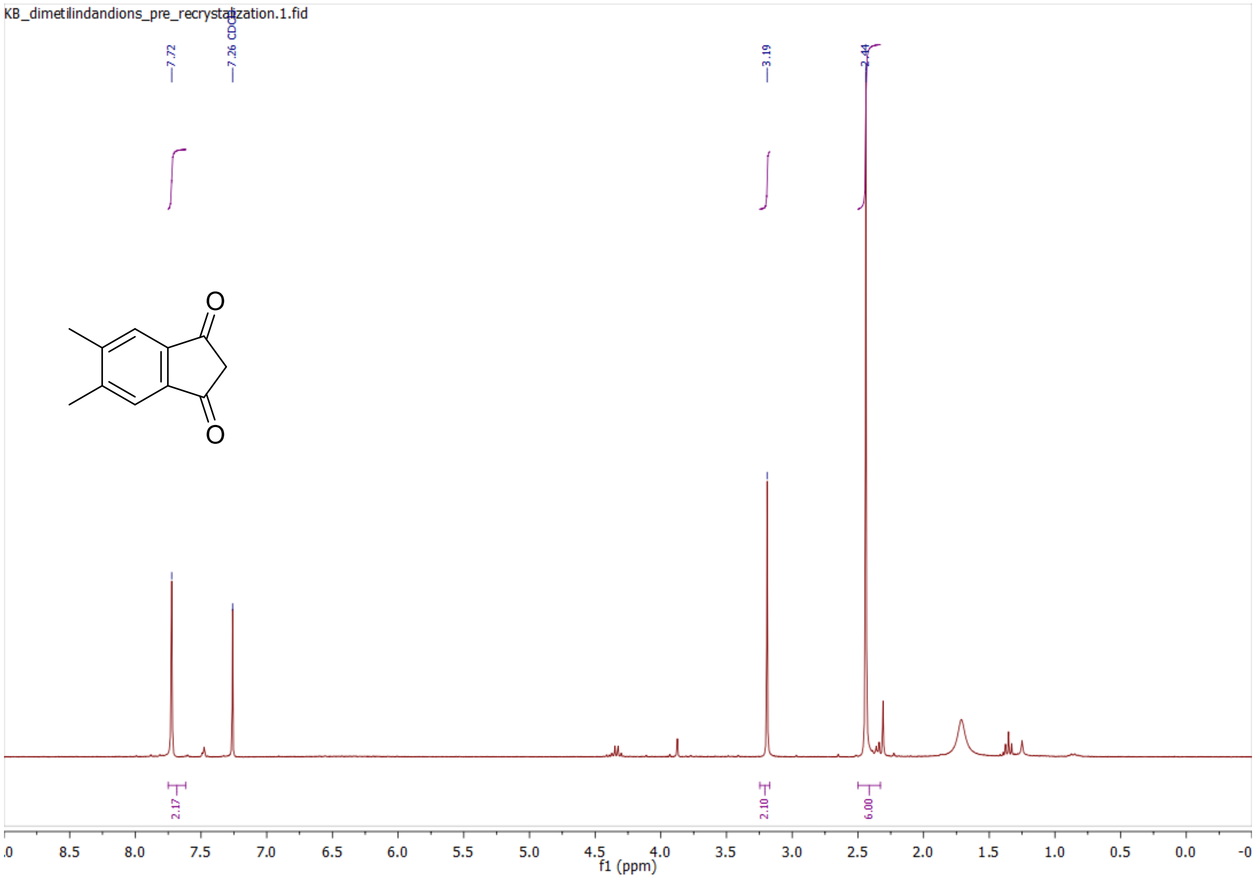


Fig. S28 [1]H NMR spectrum of compound **6a**.

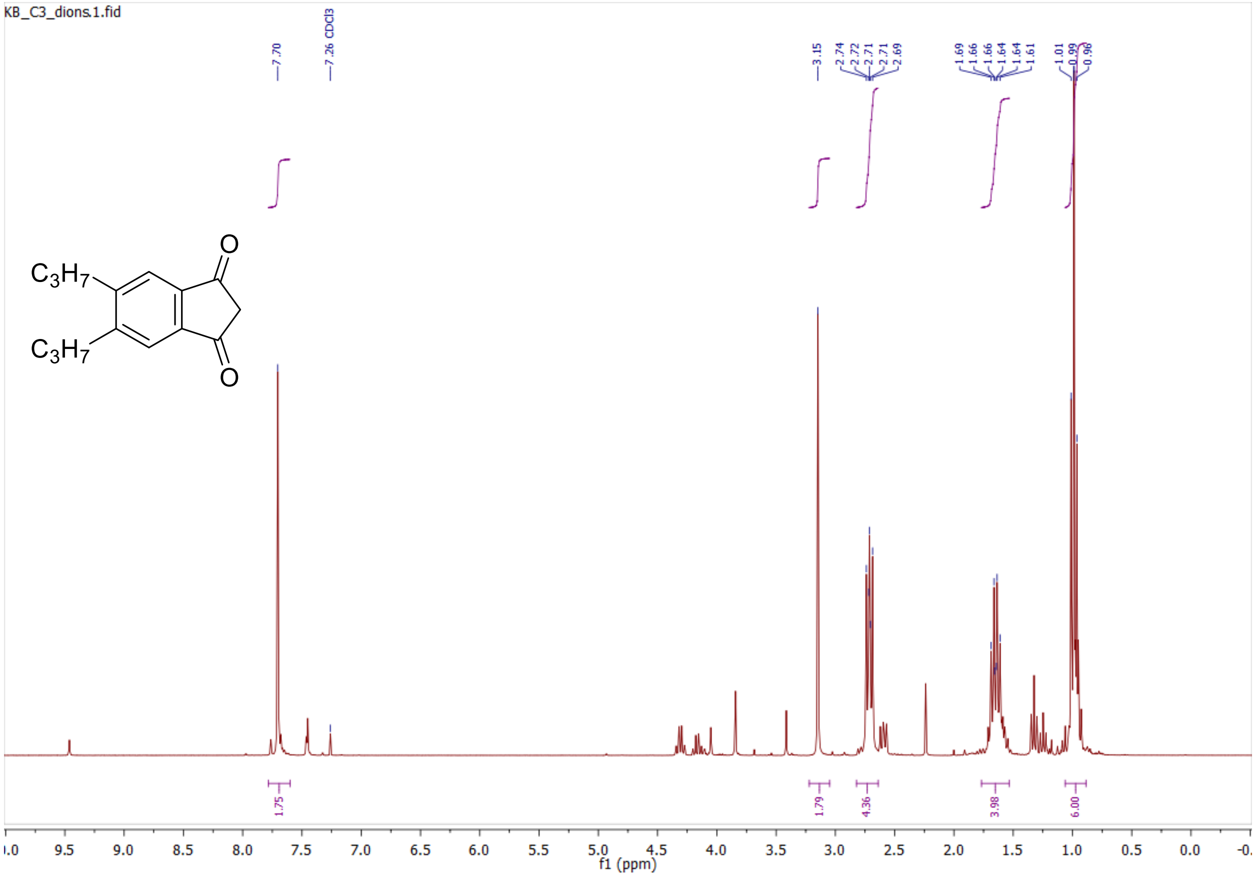


Fig. S29 [1]H NMR spectrum of compound **6b**.

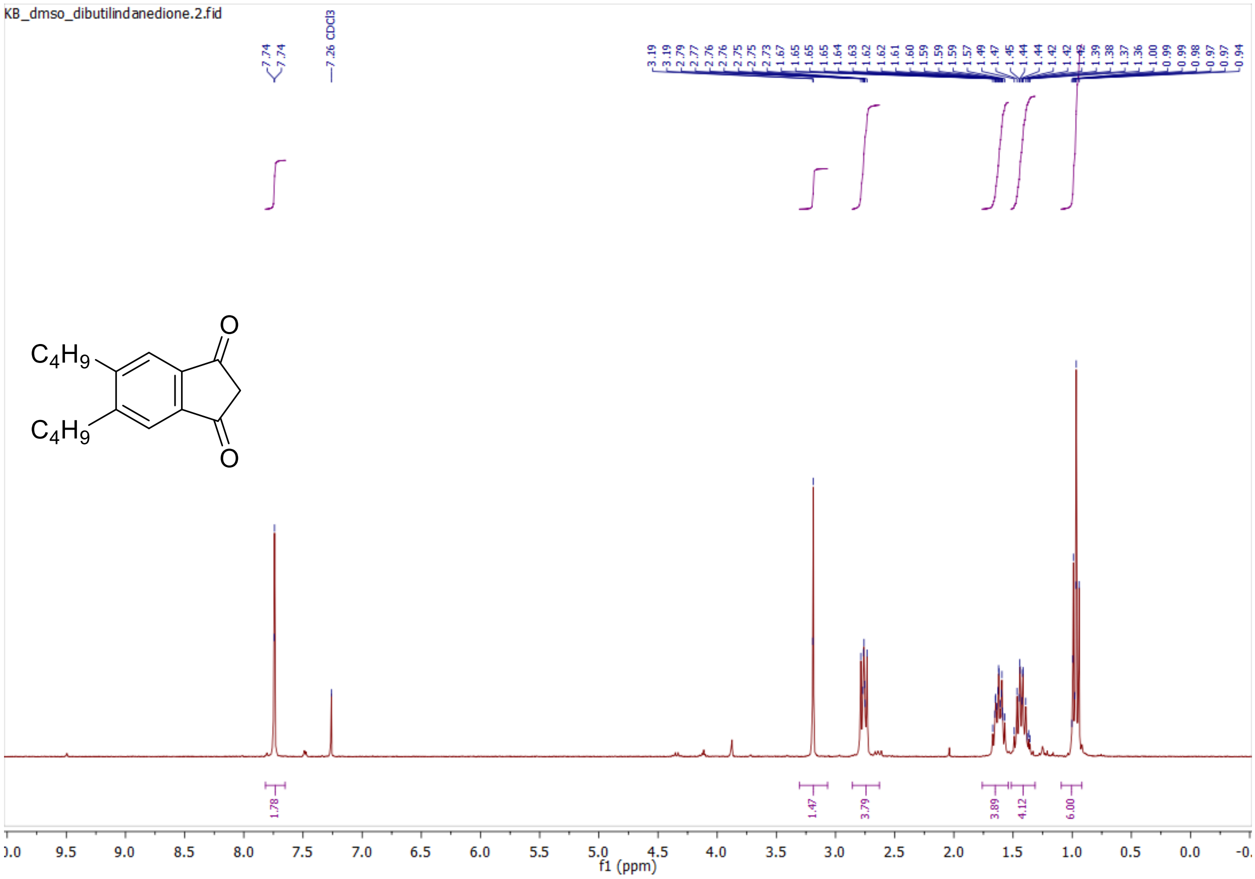


Fig. S30 [1]H NMR spectrum of compound **6c**.

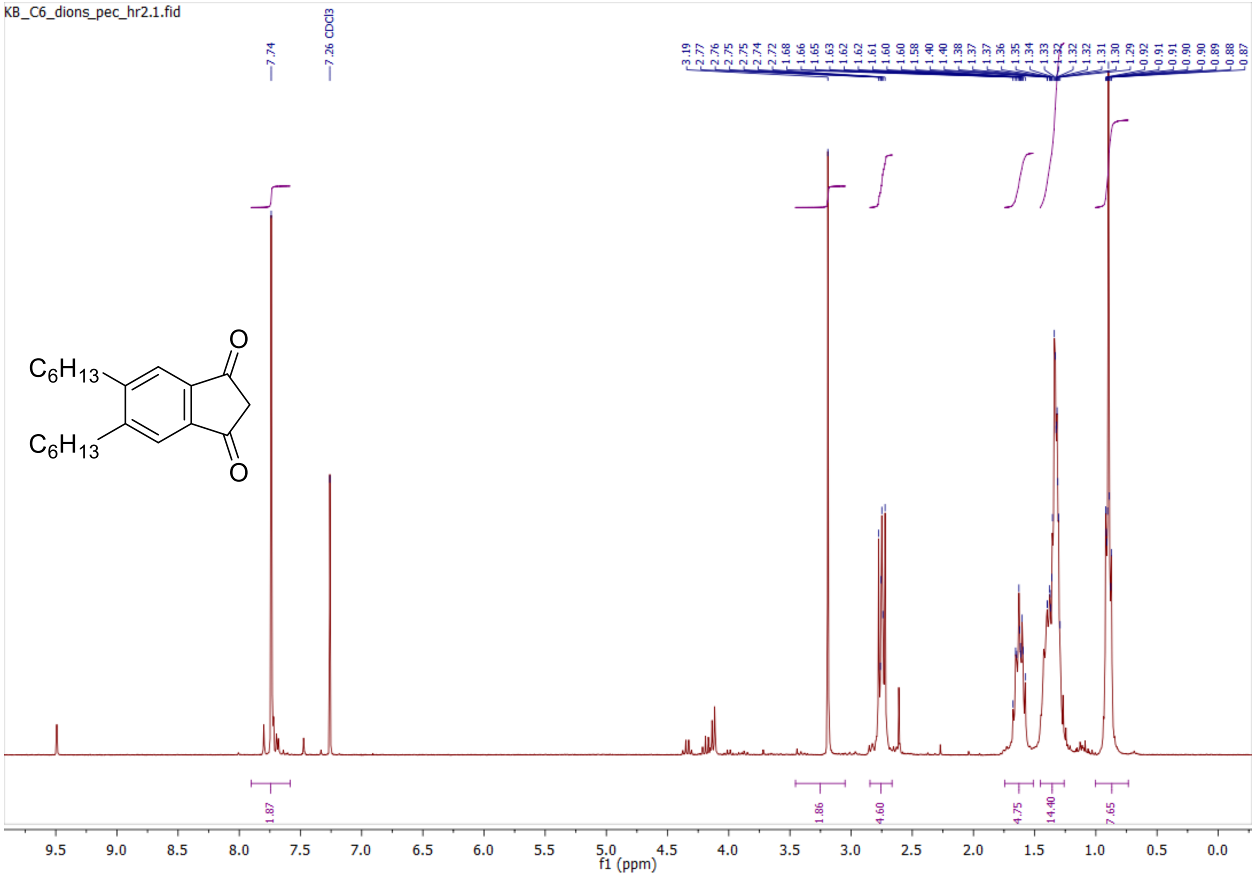


Fig. S31 ^{1}H NMR spectrum of compound **6d**.

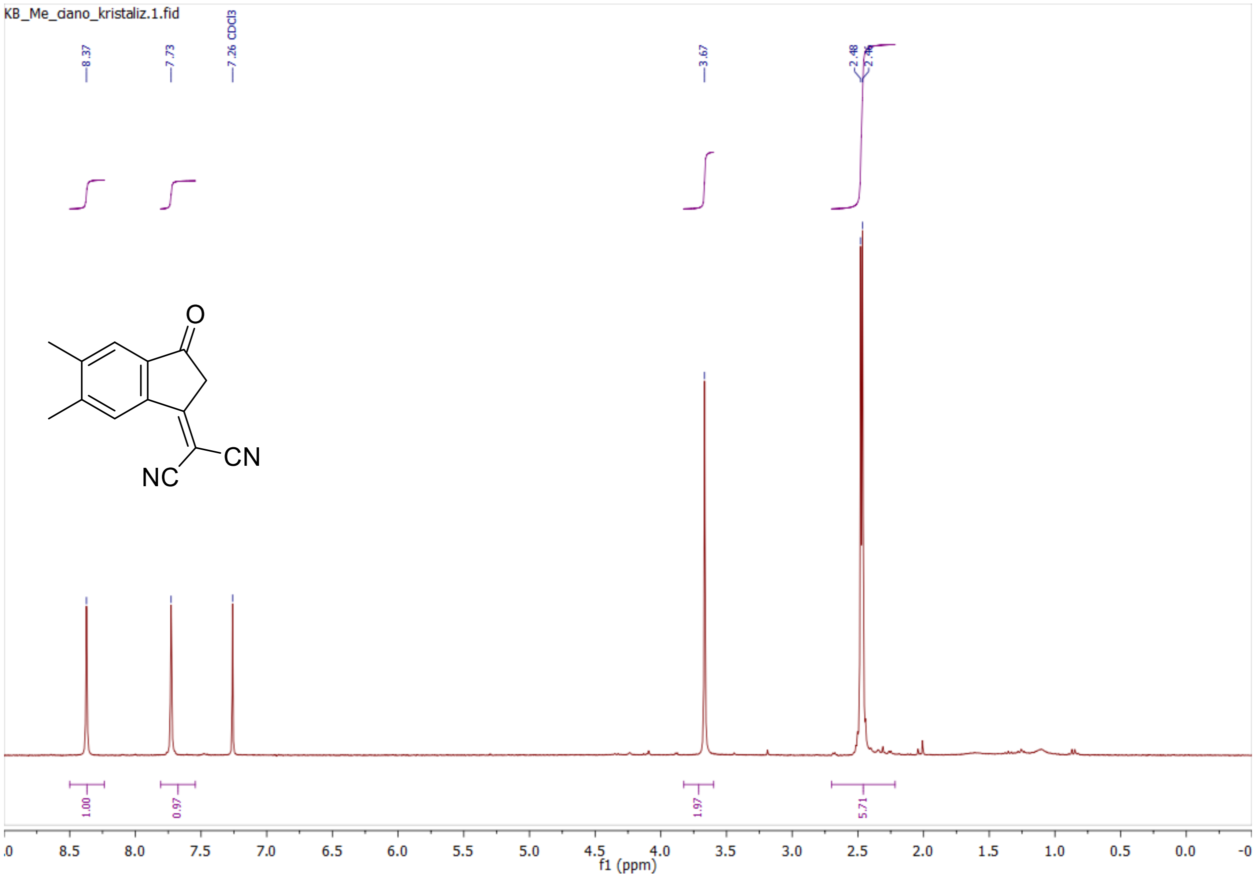


Fig. S32 ^{1}H NMR spectrum of compound **7a**.

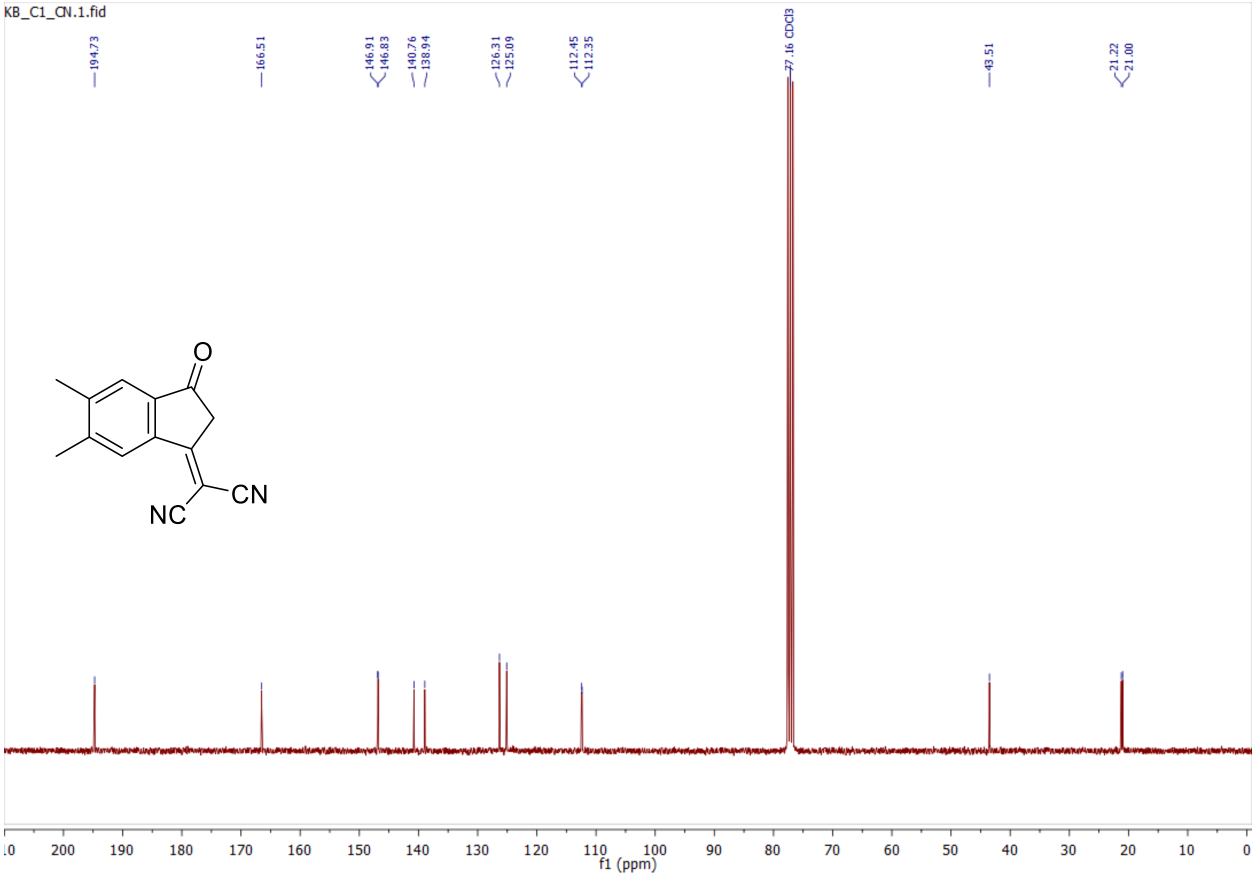


Fig. S33 ^{13}C NMR spectrum of compound **7a**.

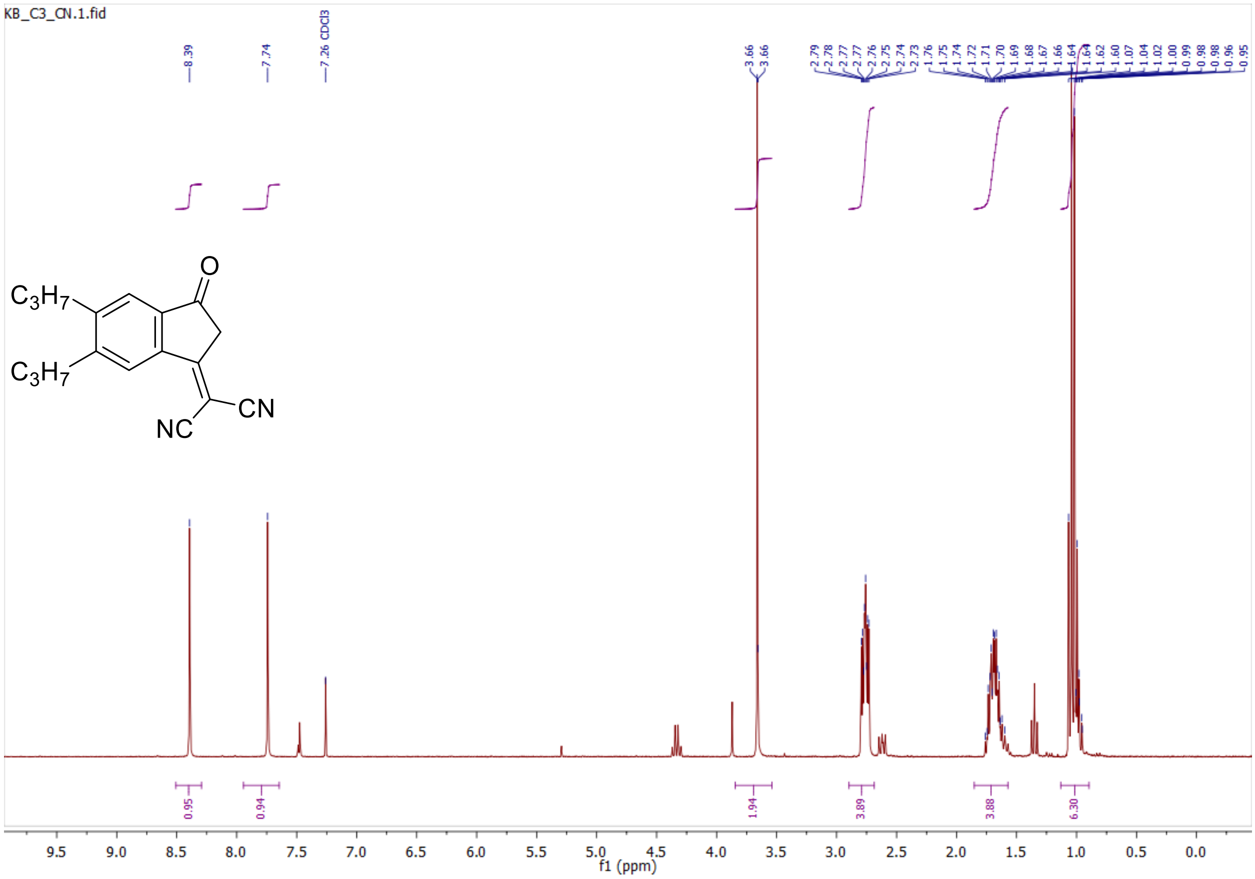


Fig. S34 ^{1}H NMR spectrum of compound **7b**.

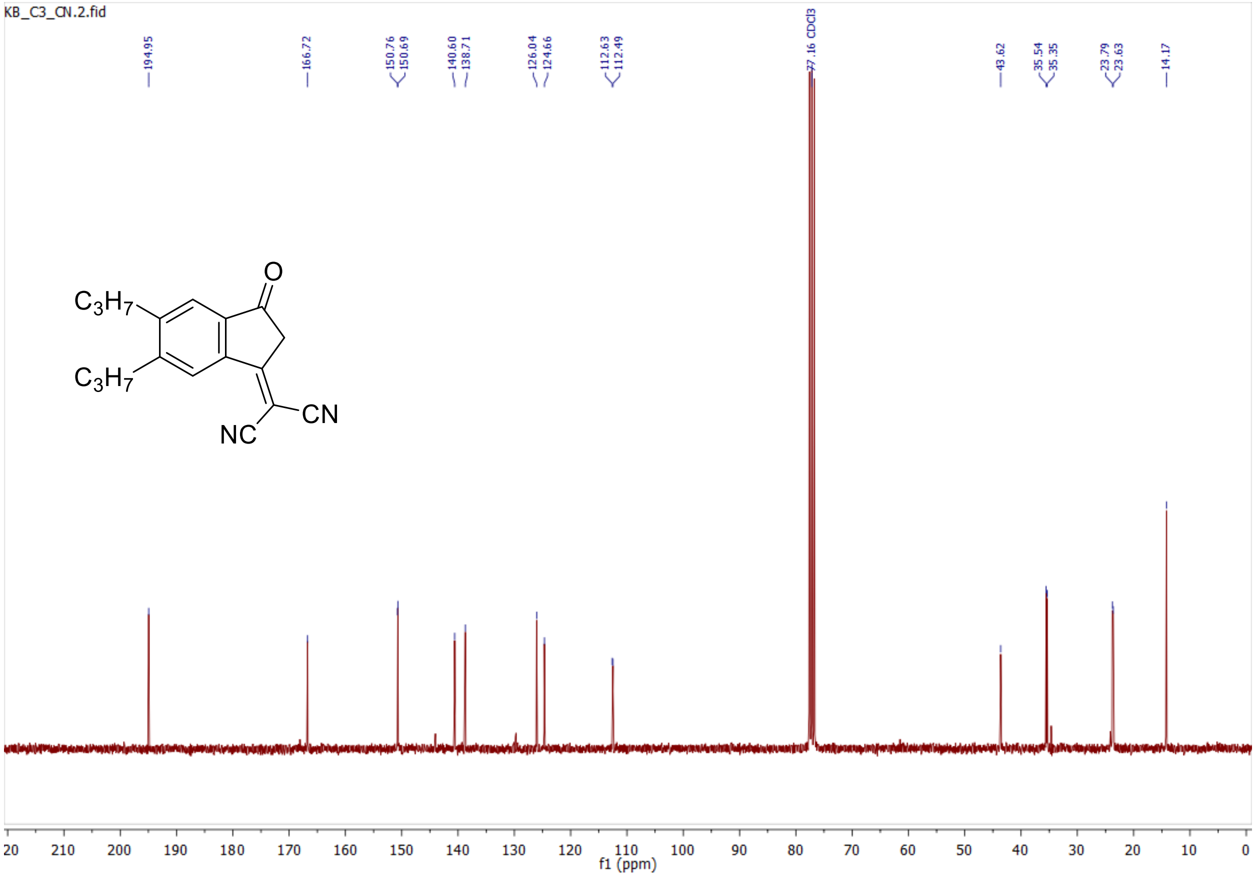


Fig. S35 ^{13}C NMR spectrum of compound **7b**.

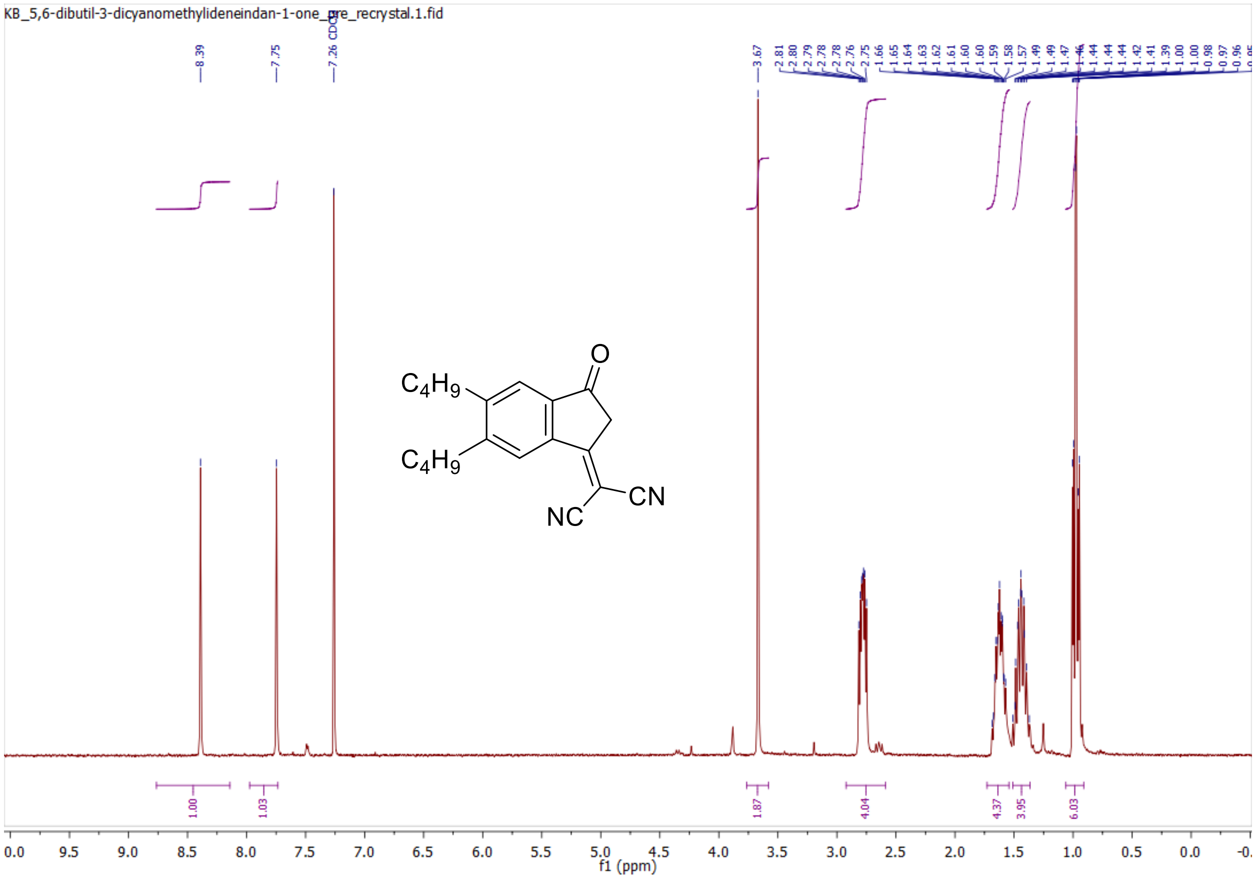


Fig. S36 ^{1}H NMR spectrum of compound **7c**.

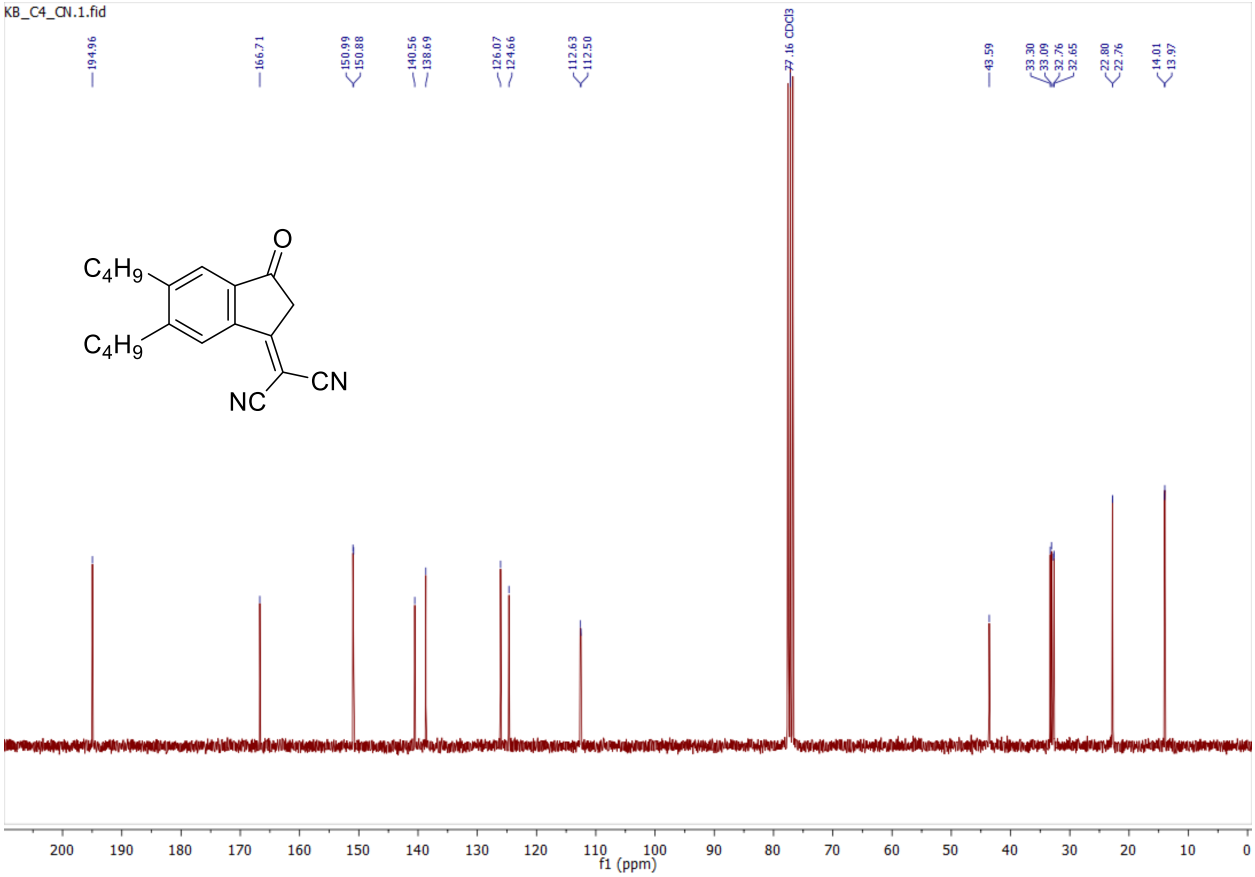


Fig. S37 ^{13}C NMR spectrum of compound **7c**.

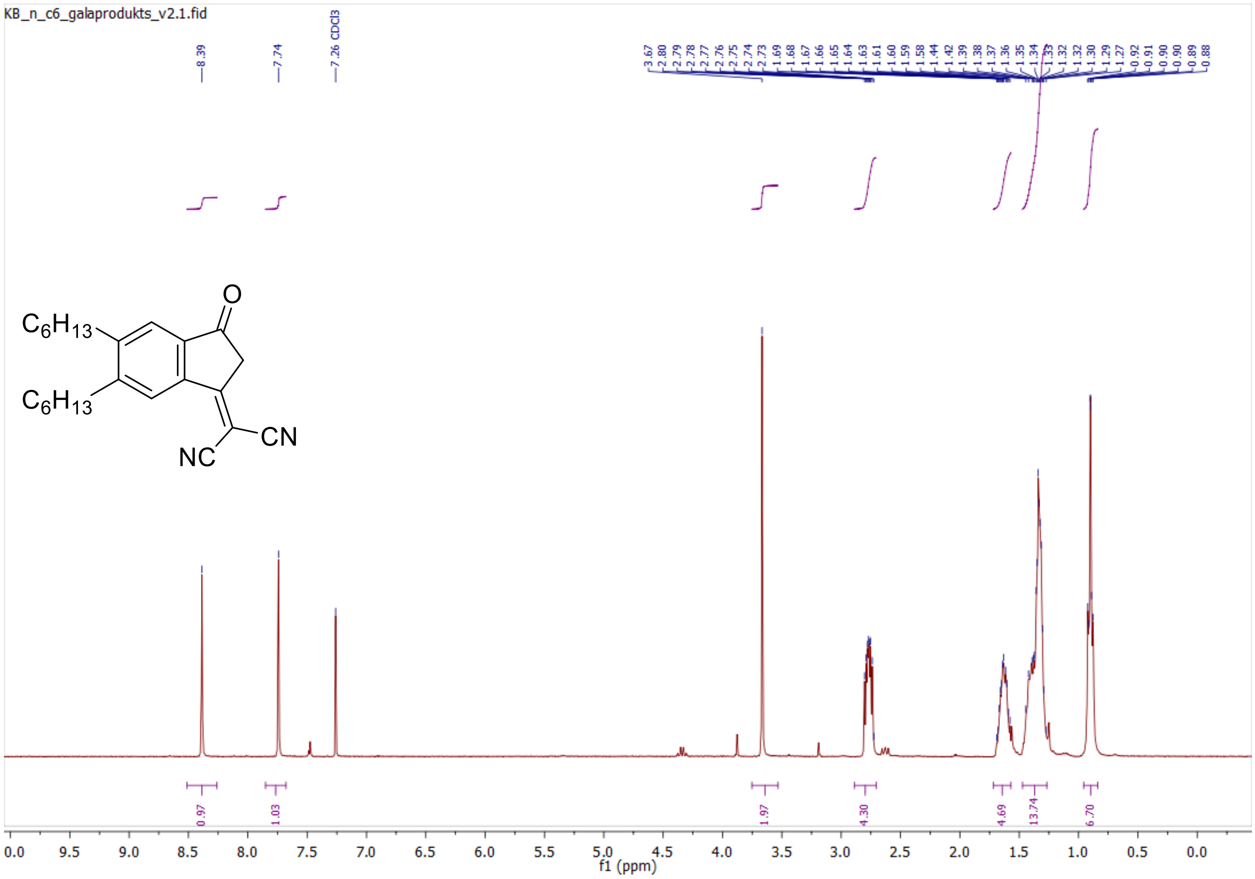


Fig. S38 ^{1}H NMR spectrum of compound **7d**.

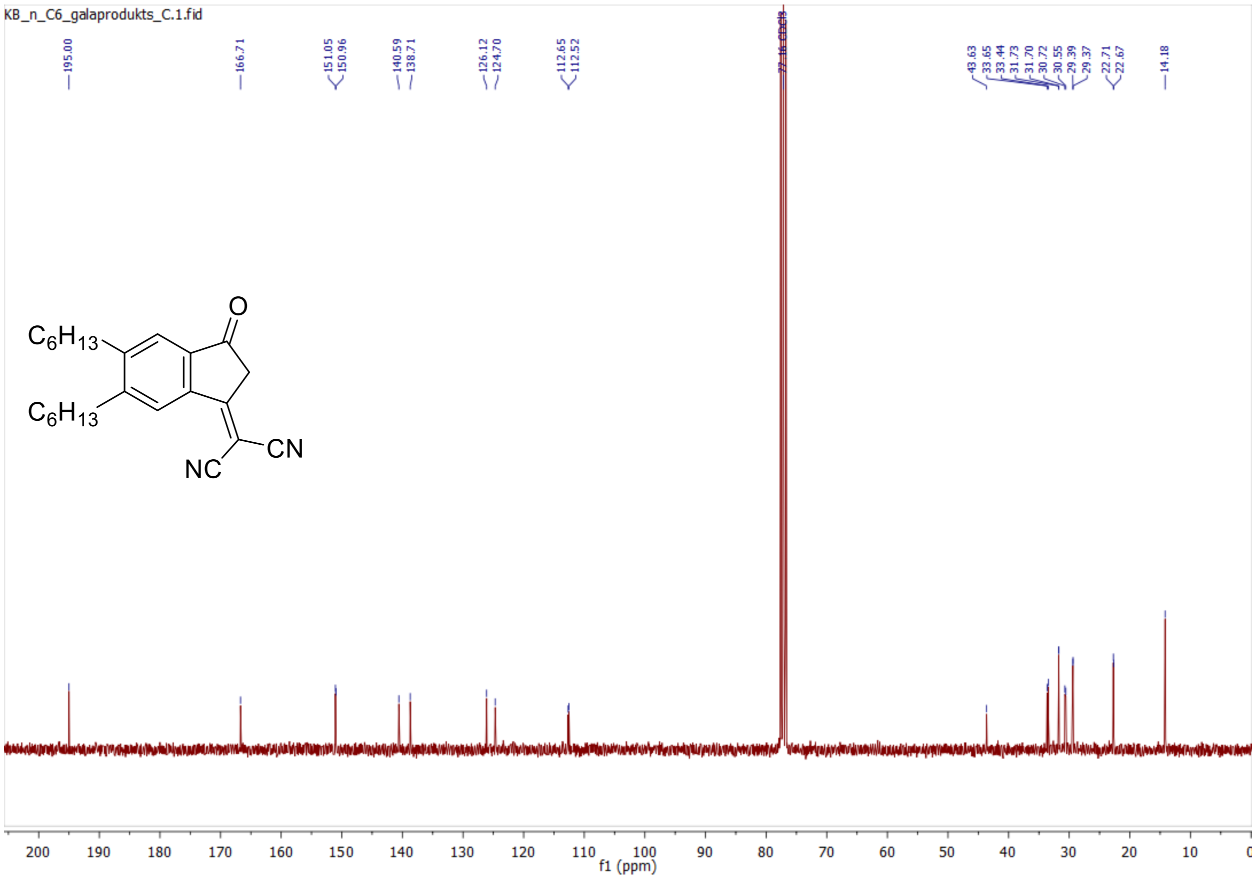


Fig. S39 ^{13}C NMR spectrum of compound **7d**.

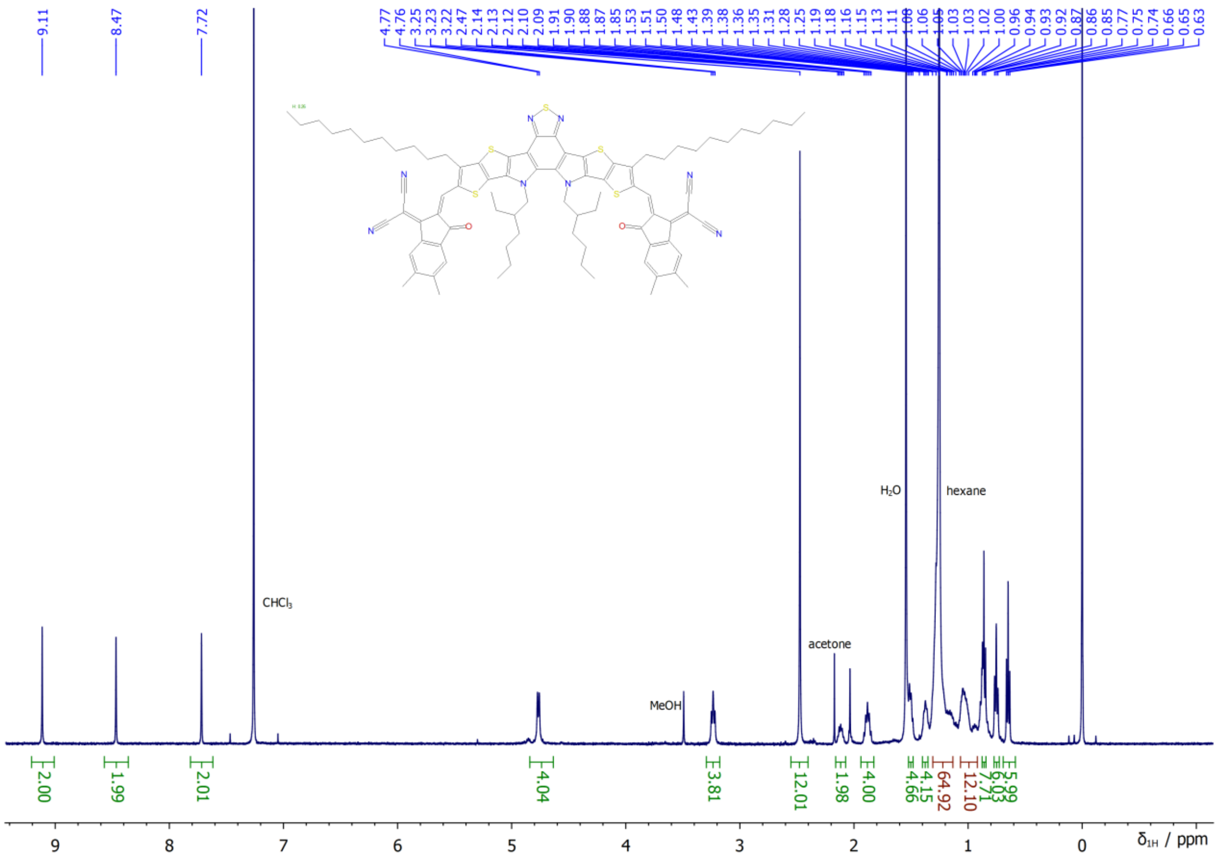


Fig. S40 ^{1}H NMR spectrum of compound **Y-Me**.

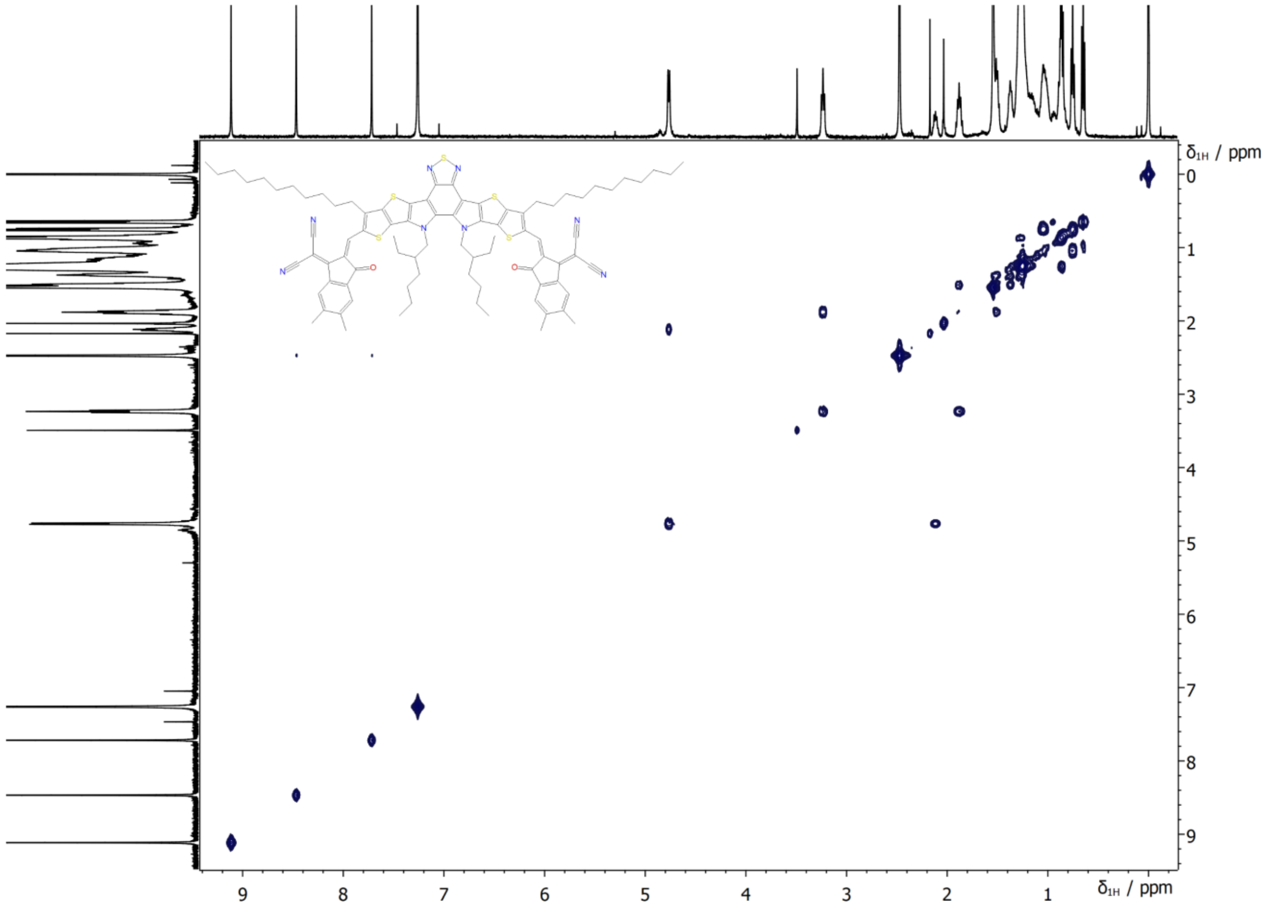


Fig. S41 COSY NMR spectrum of compound **Y-Me**.

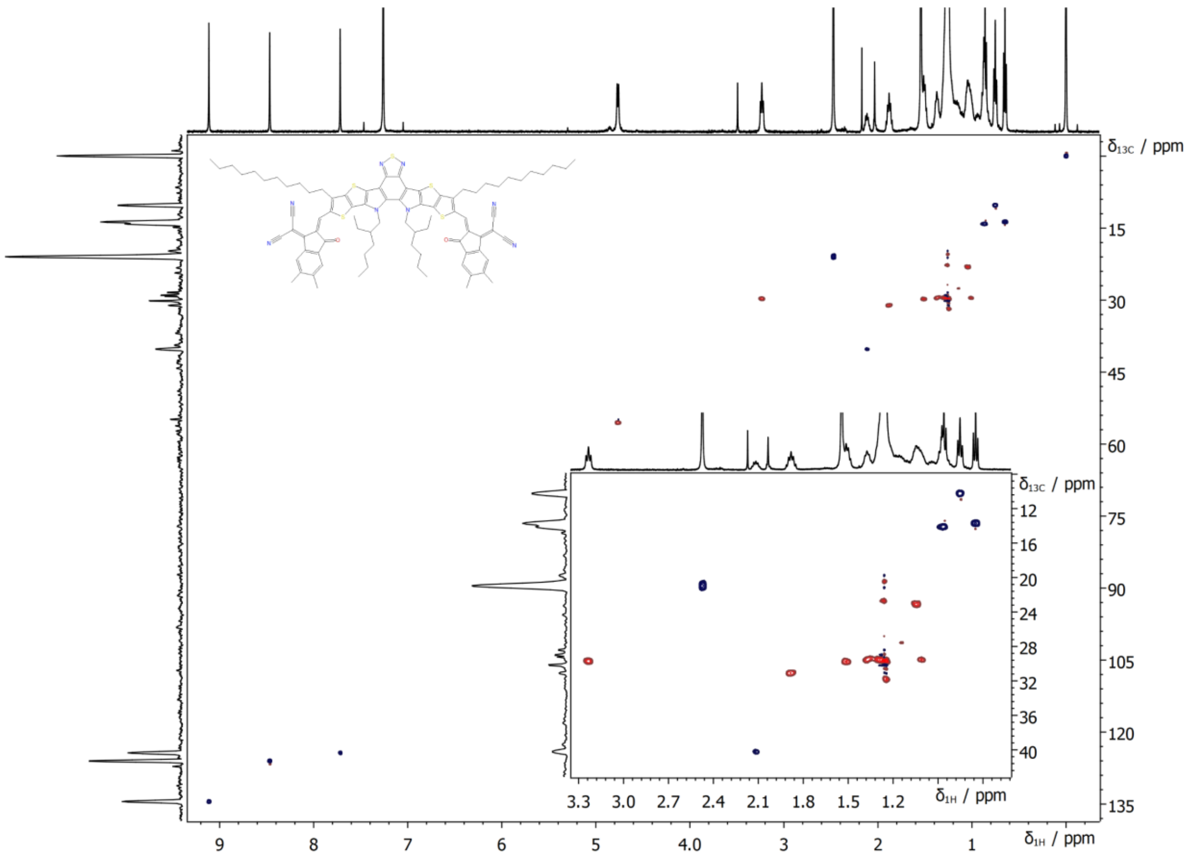


Fig. S42 HSQC NMR spectrum of compound **Y-Me**.

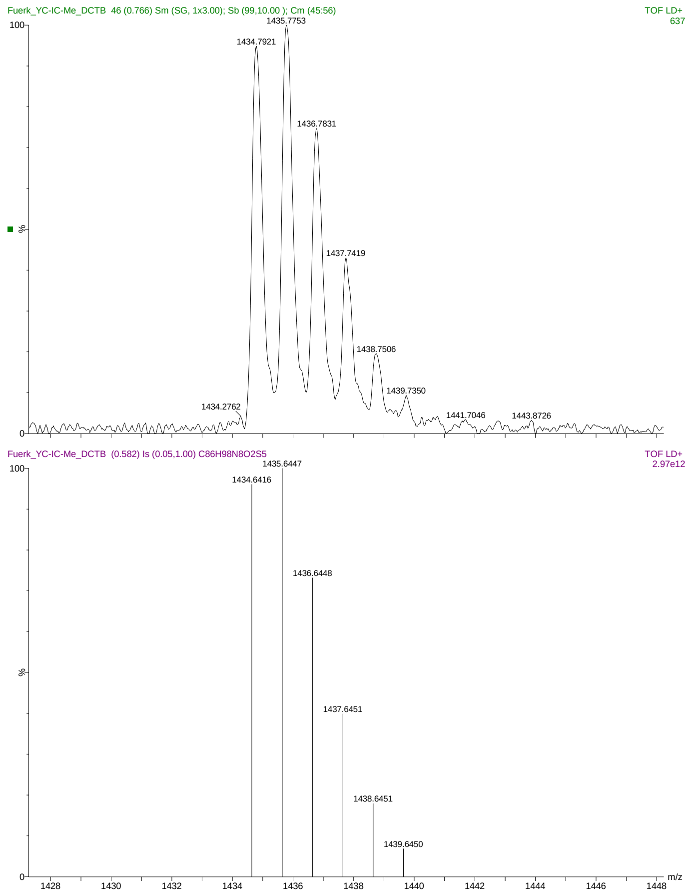


Fig. S43 HR-MS of compound **Y-Me**.

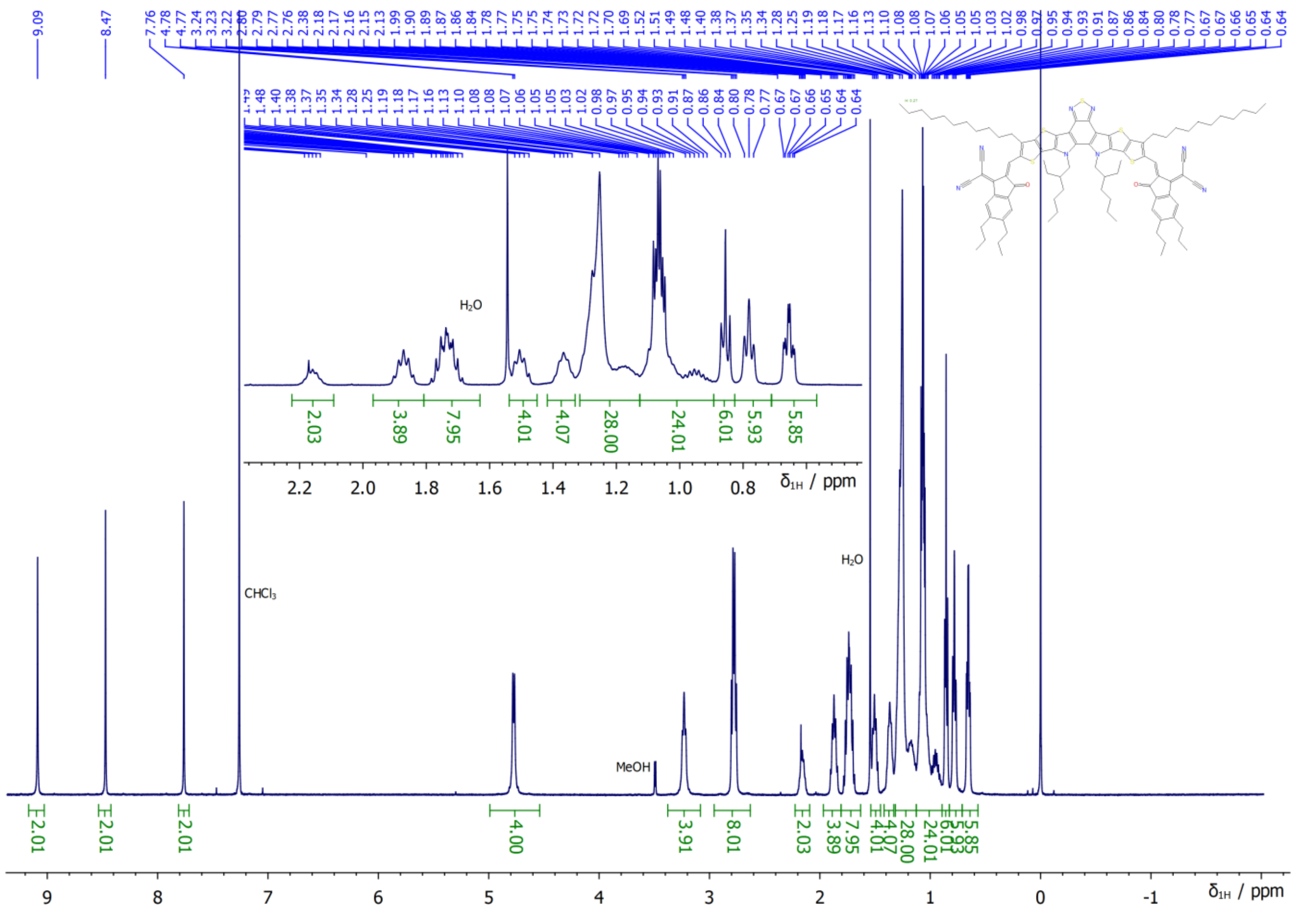


Fig. S44 ^{1}H NMR spectrum of compound **Y-Pr**.

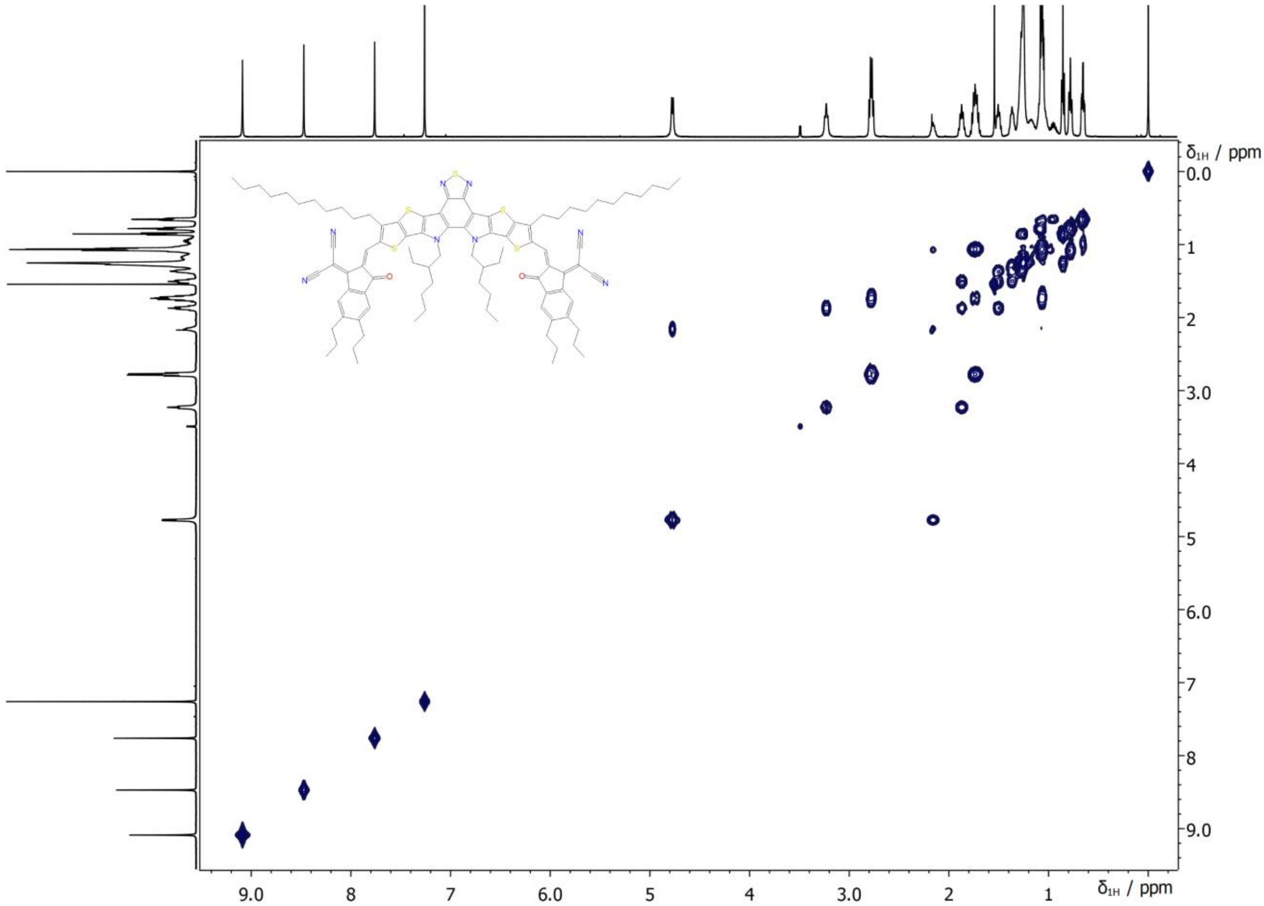


Fig. S45 COSY NMR spectrum of compound **Y-Pr**.

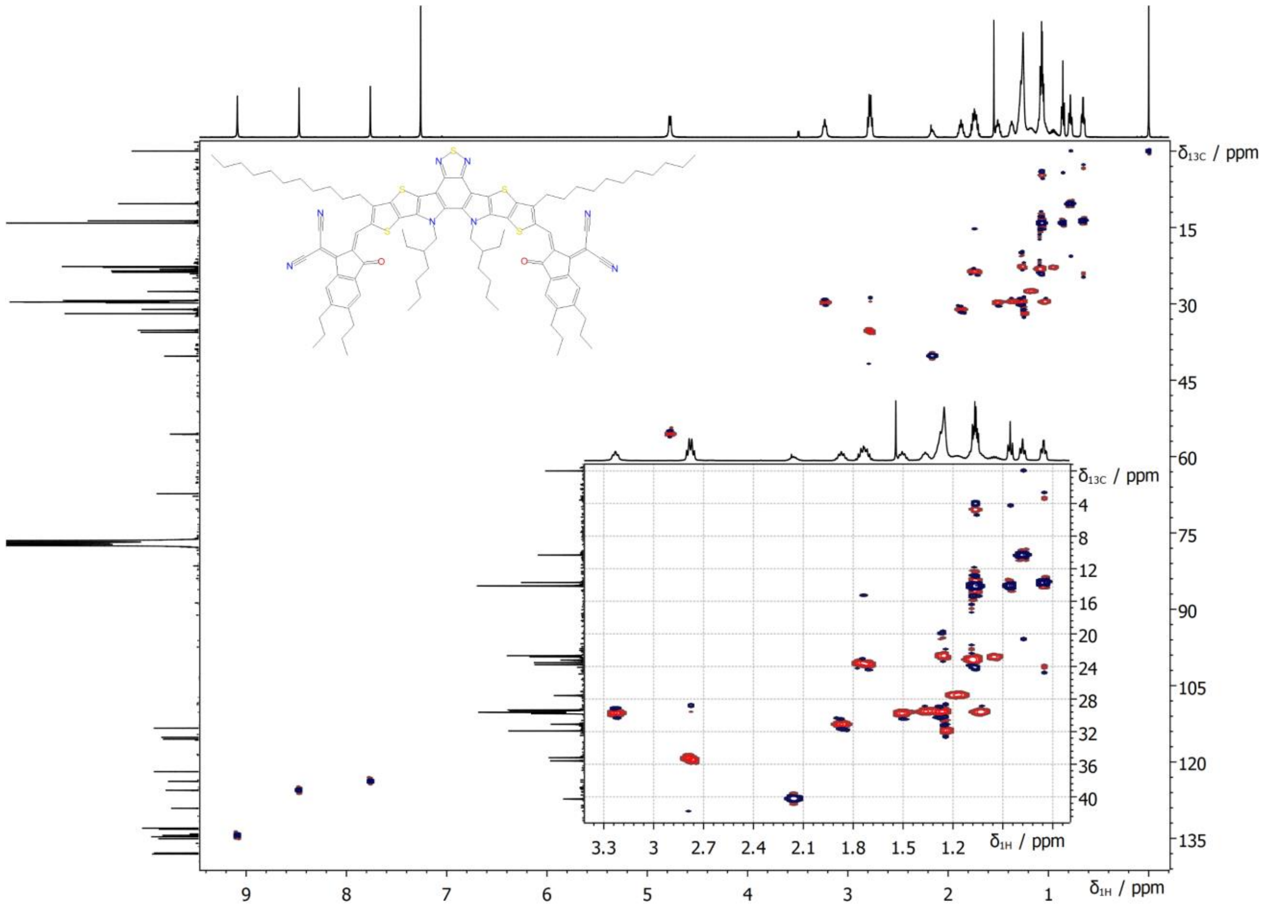


Fig. S46 HSQC NMR spectrum of compound **Y-Pr**.

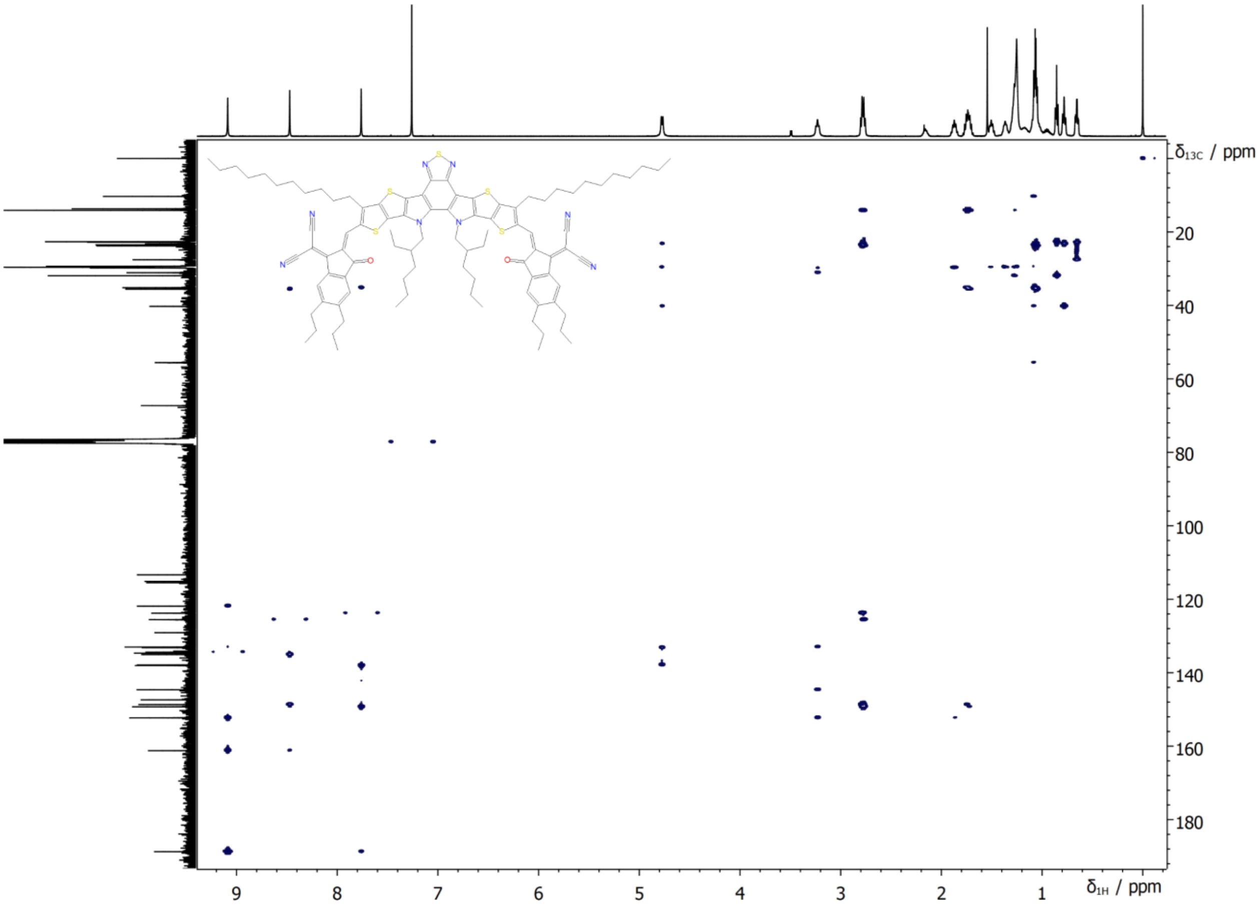


Fig. S47 HMBC NMR spectrum of compound **Y-Pr**.

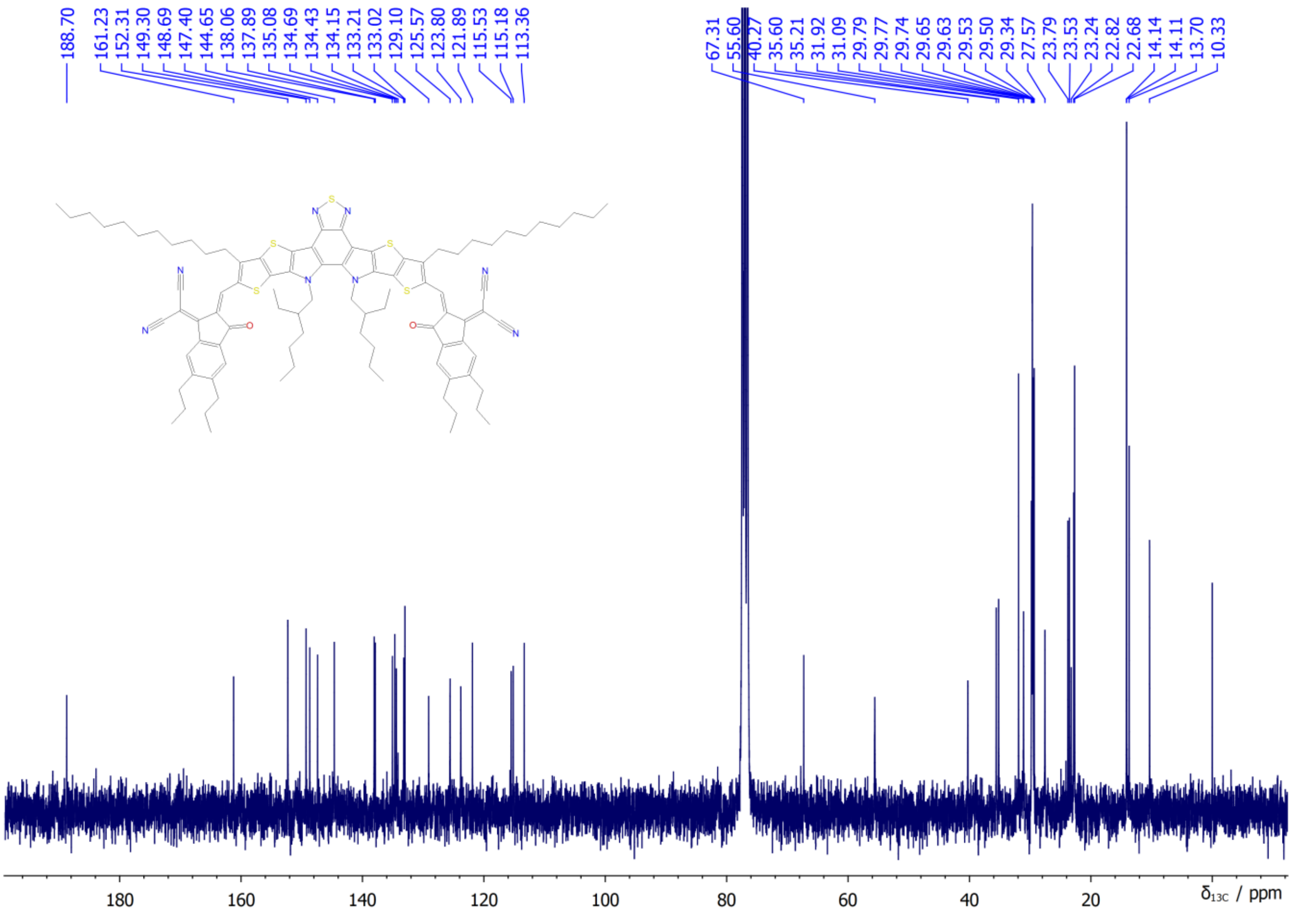


Fig. S48 ^{13}C NMR spectrum of compound **Y-Pr.**

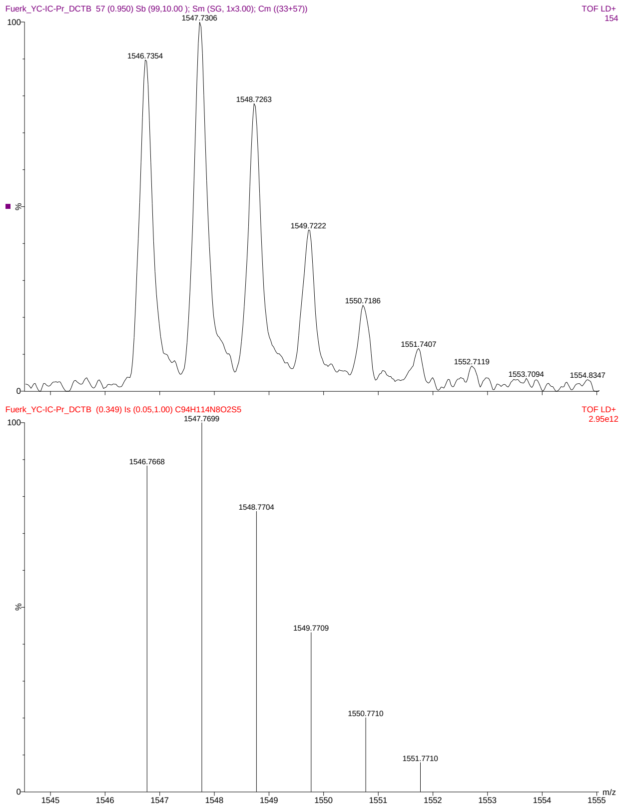


Fig. S49 HR-MS of compound **Y-Pr**.

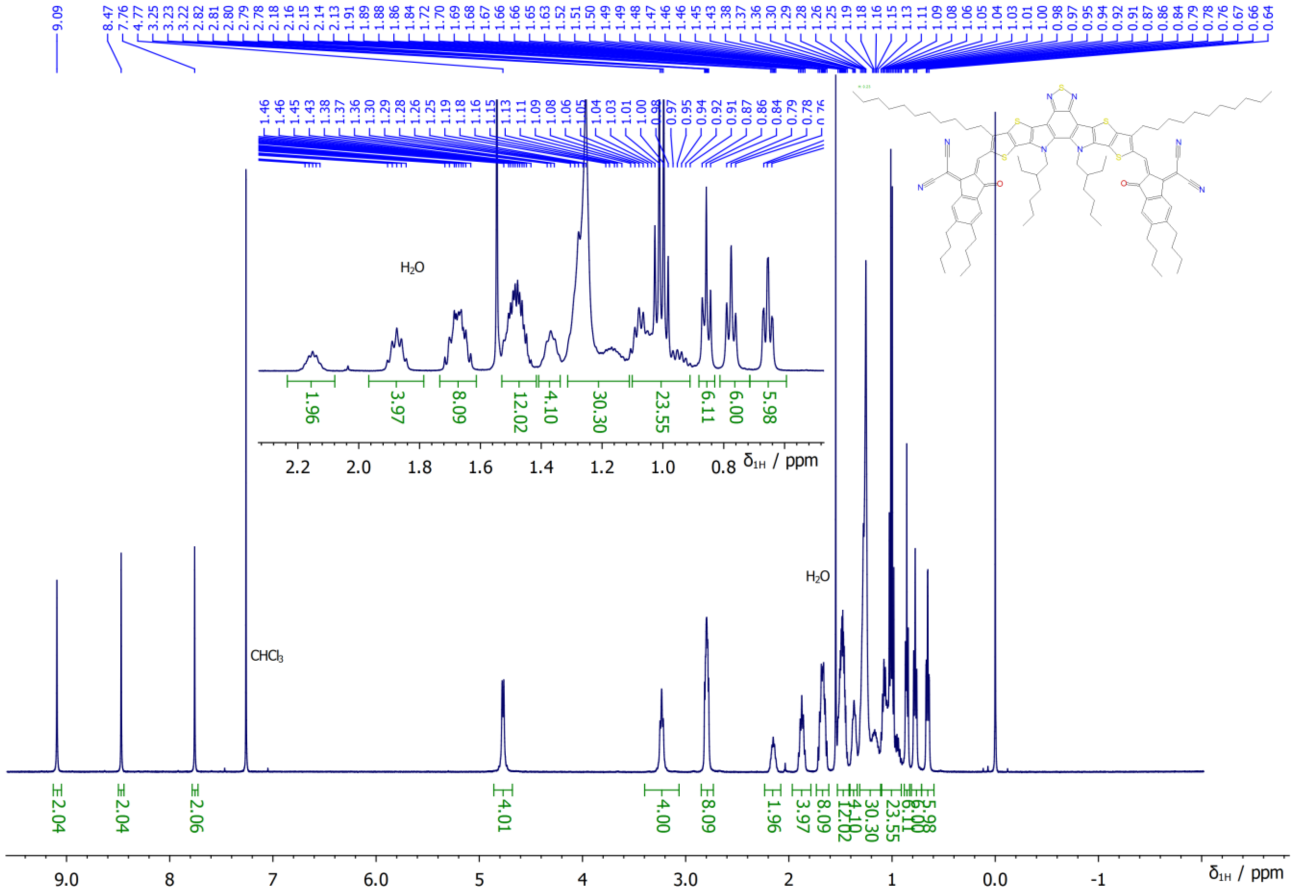


Fig. S50 ^{1}H NMR spectrum of compound **Y-Bu**.

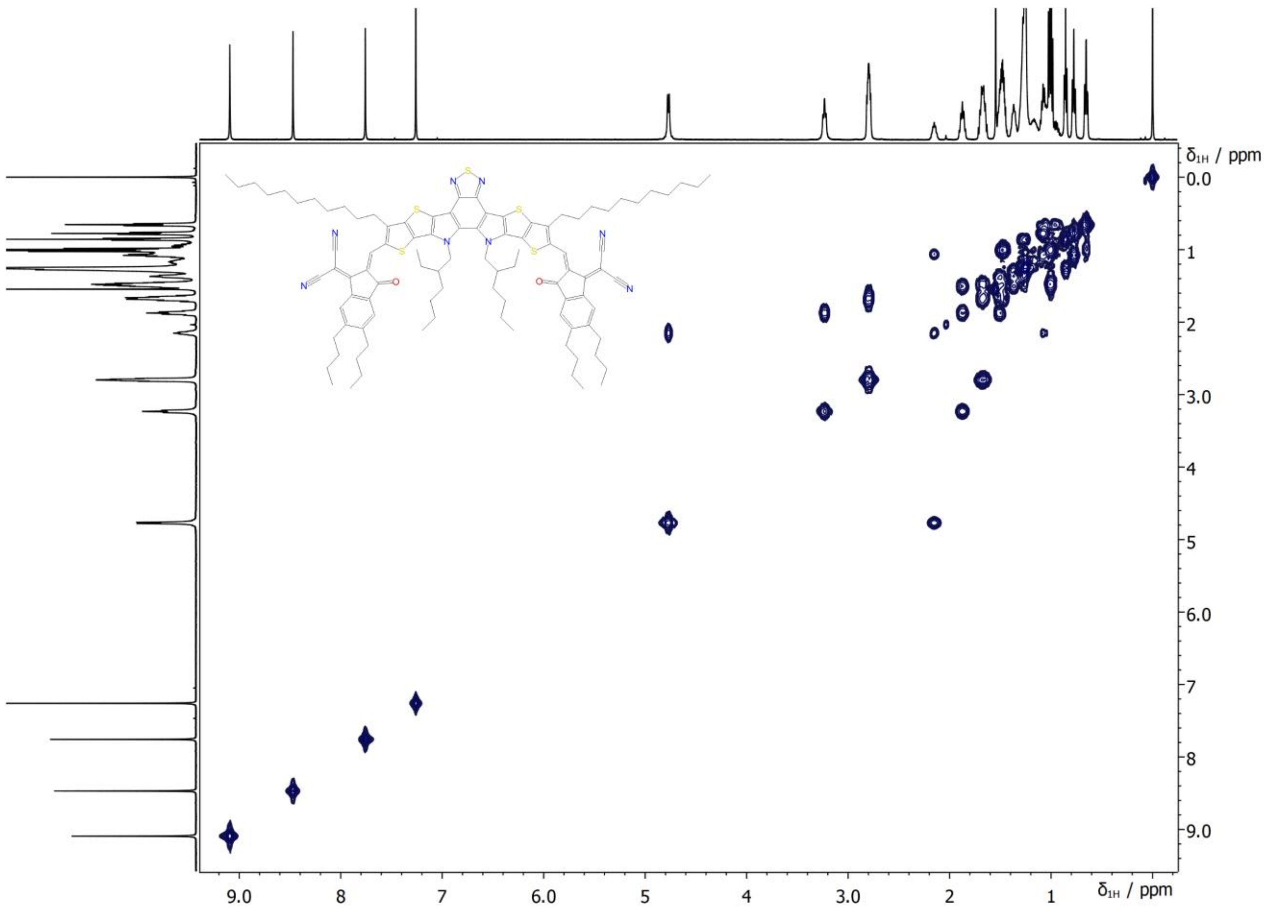


Fig. S51 COSY NMR spectrum of compound **Y-Bu**.

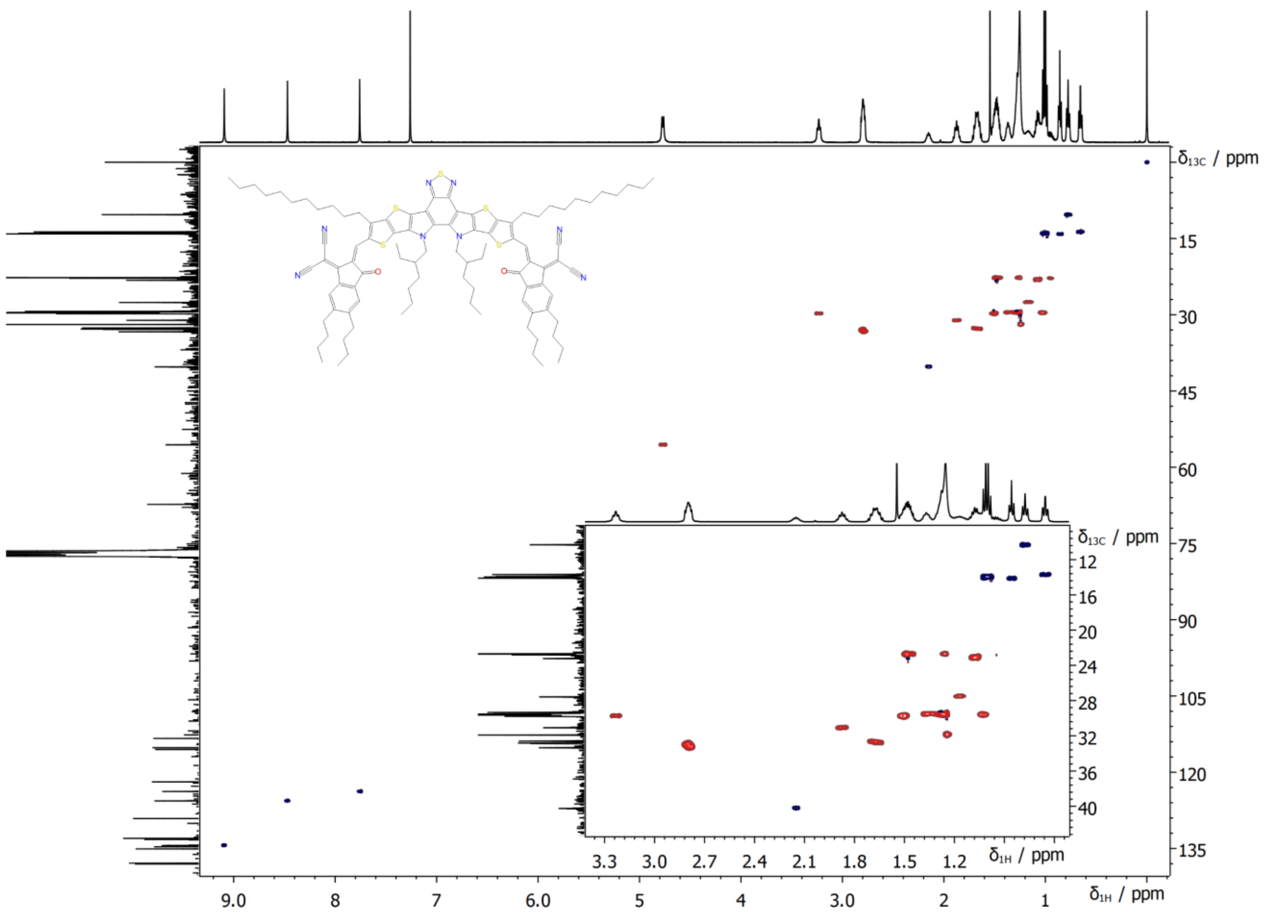


Fig. S52 HSQC NMR spectrum of compound **Y-Bu**.

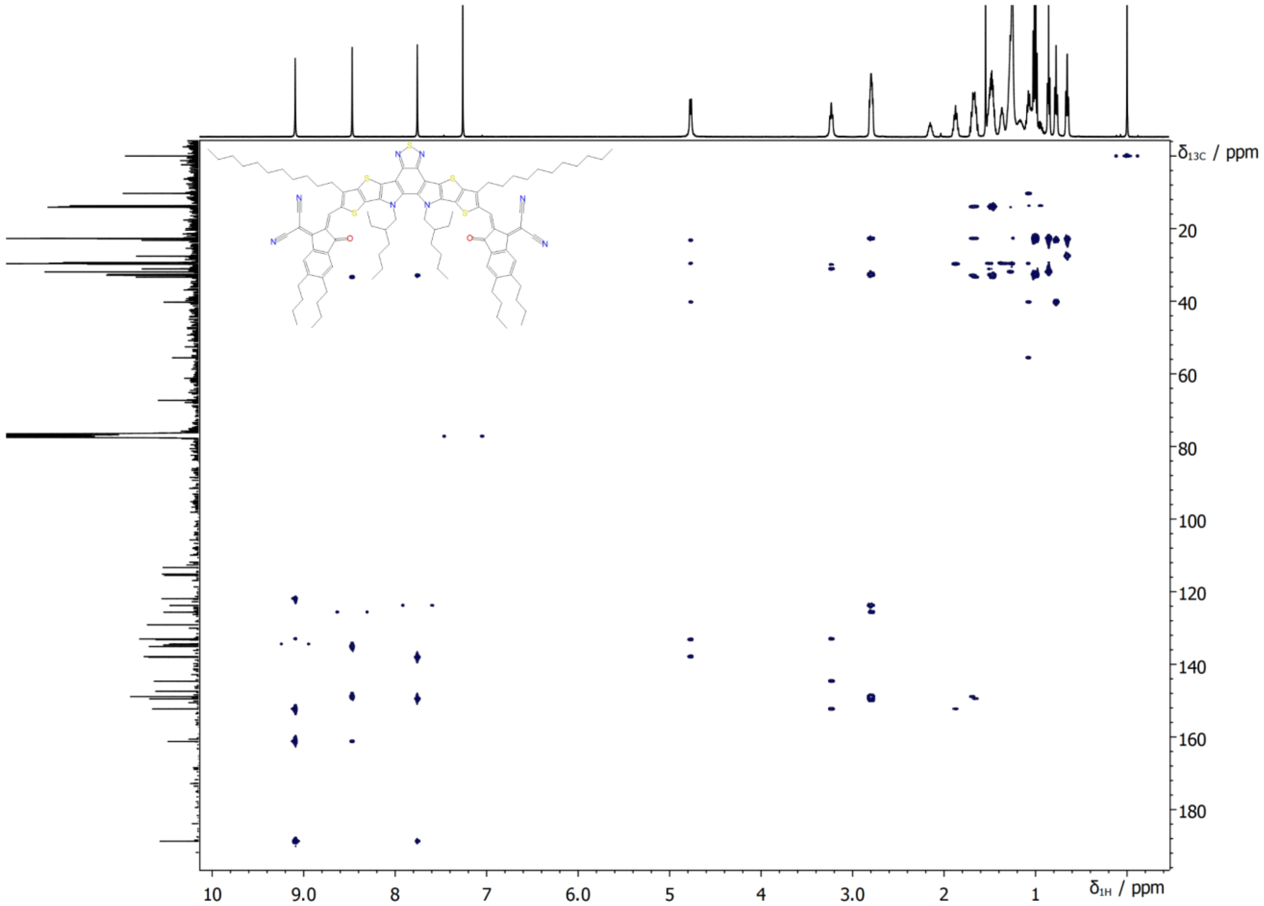


Fig. S53 HMBC NMR spectrum of compound **Y-Bu**.

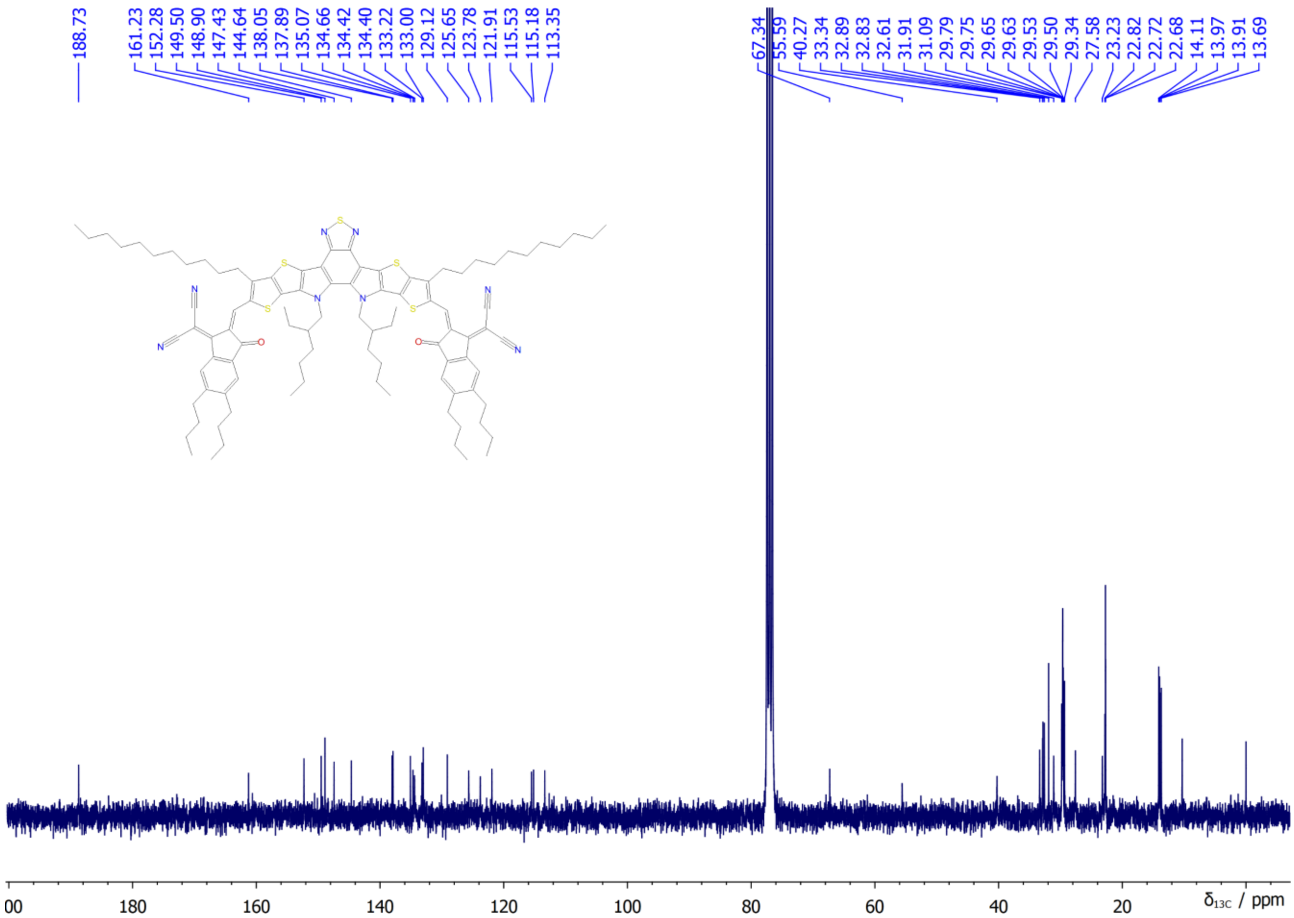


Fig. S54 ^{13}C NMR spectrum of compound **Y-Bu**.

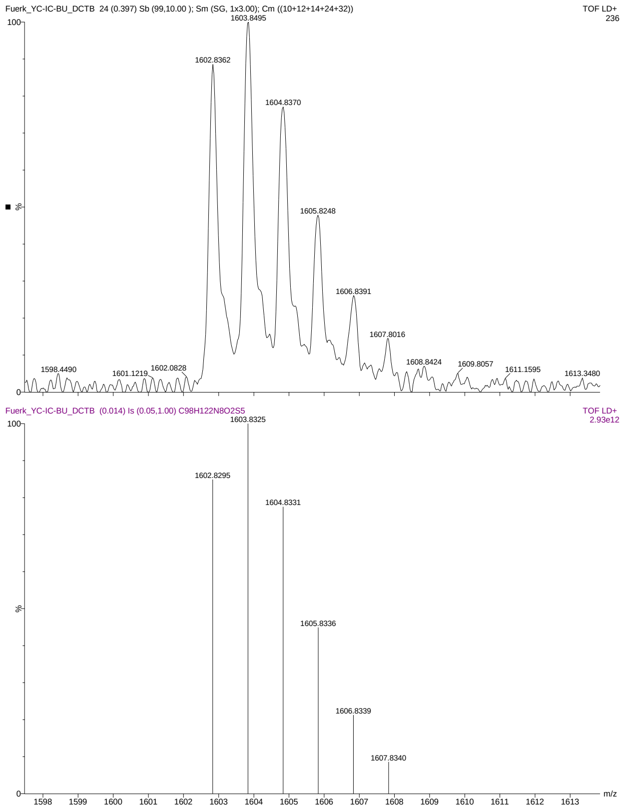


Fig. S55 HR-MS of compound **Y-Bu**.

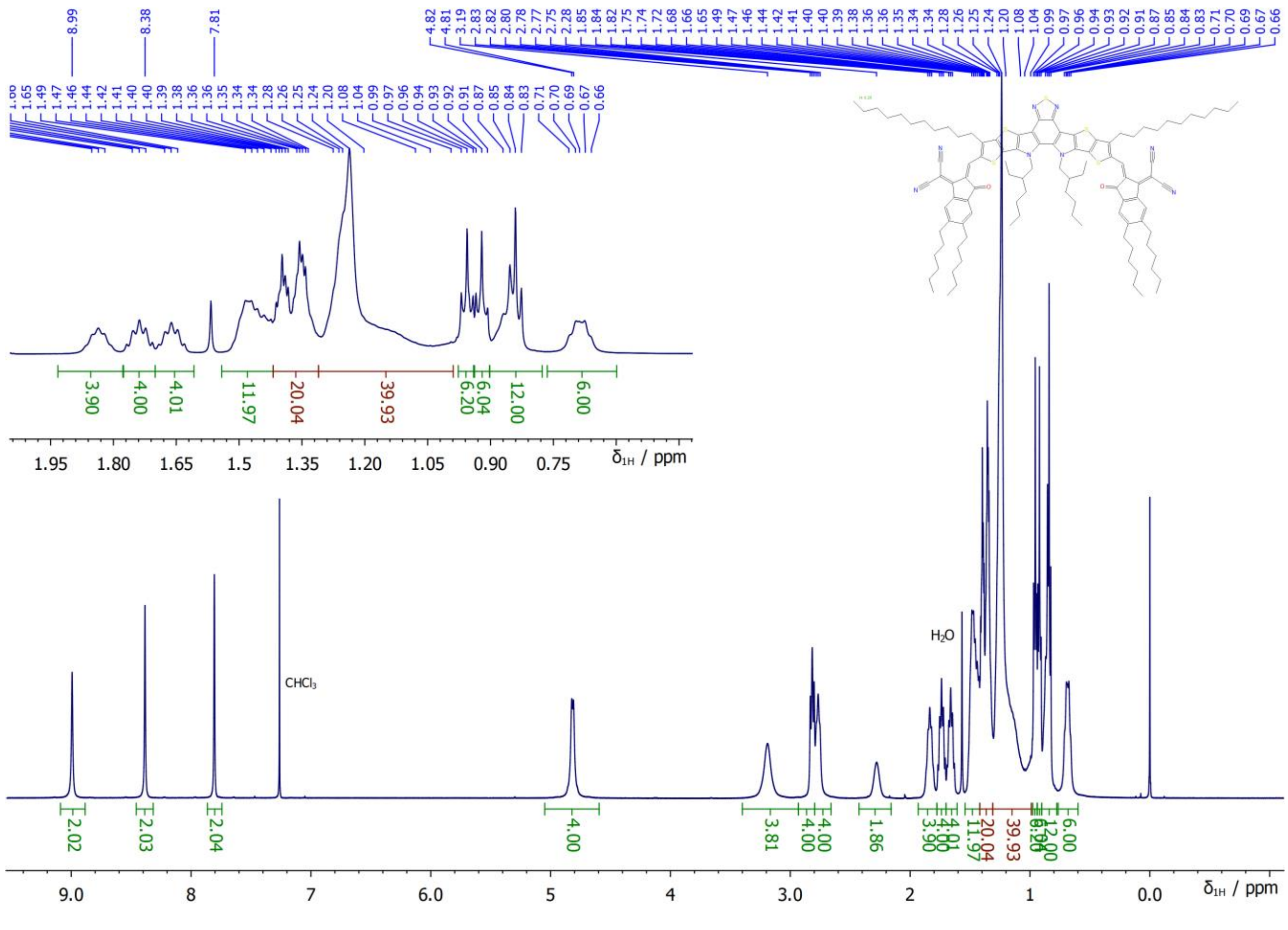


Fig. S56 ^{1}H NMR spectrum of compound **Y-Hex**.

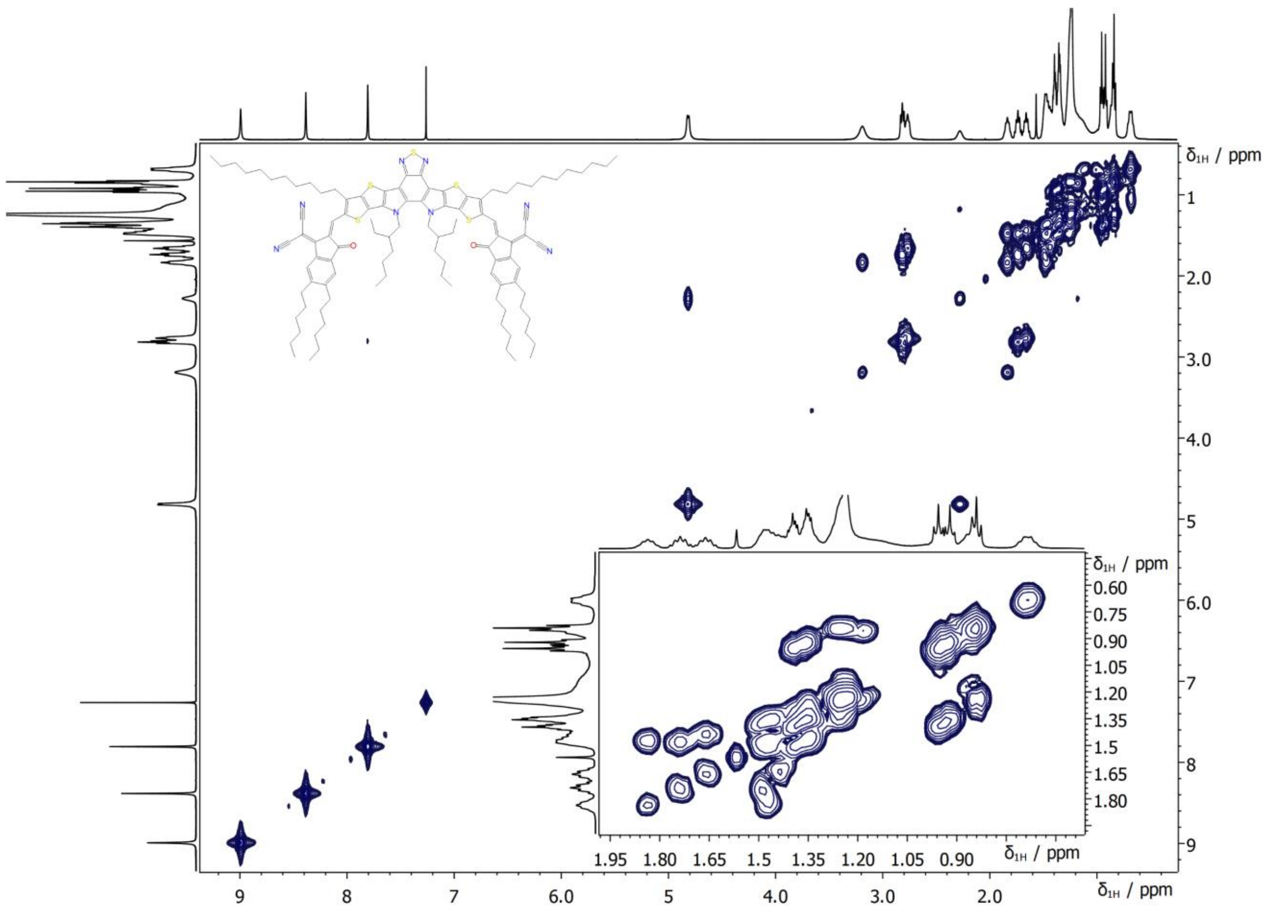


Fig. S57 COSY NMR spectrum of compound **Y-Hex**.

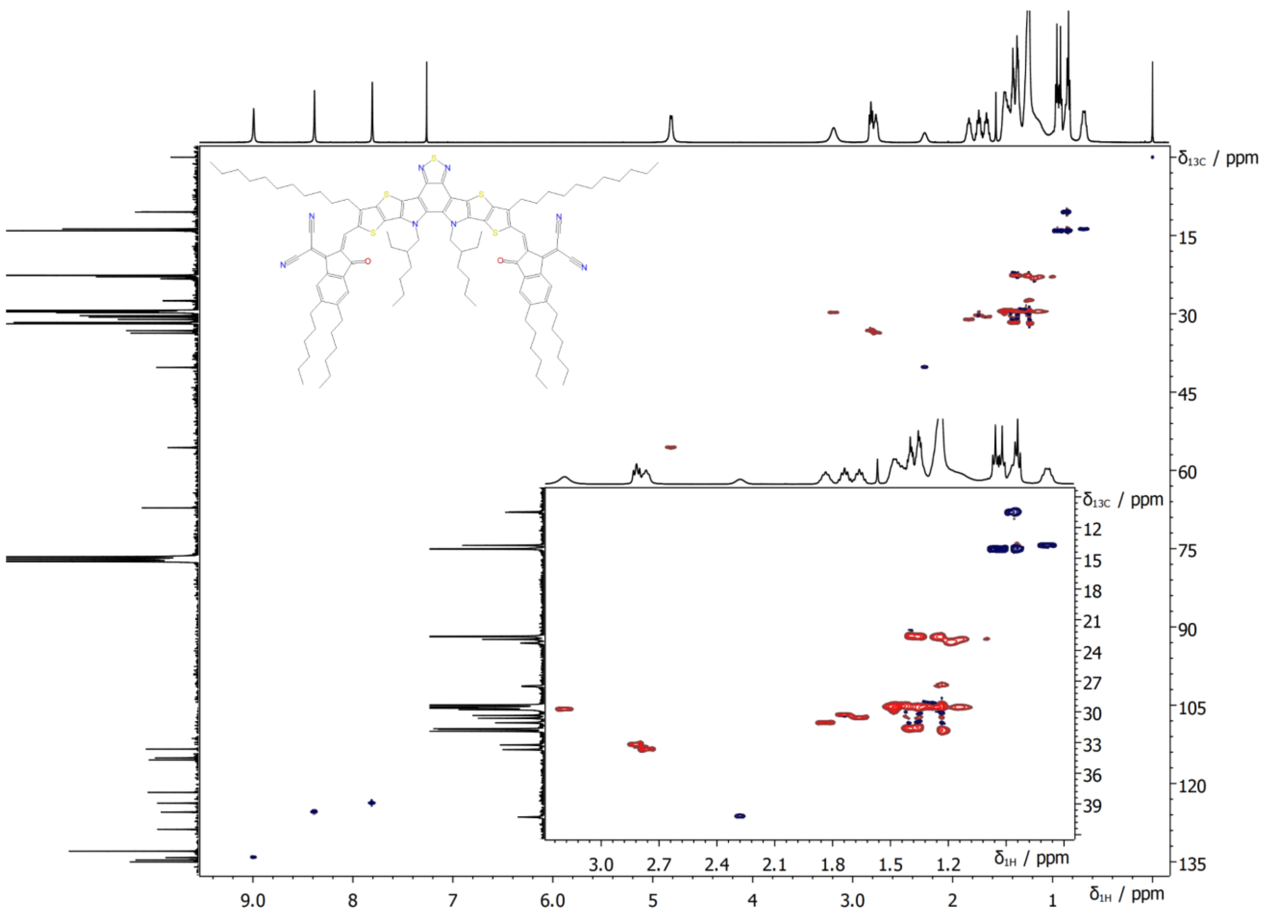


Fig. S58 HSQC NMR spectrum of compound **Y-Hex**.

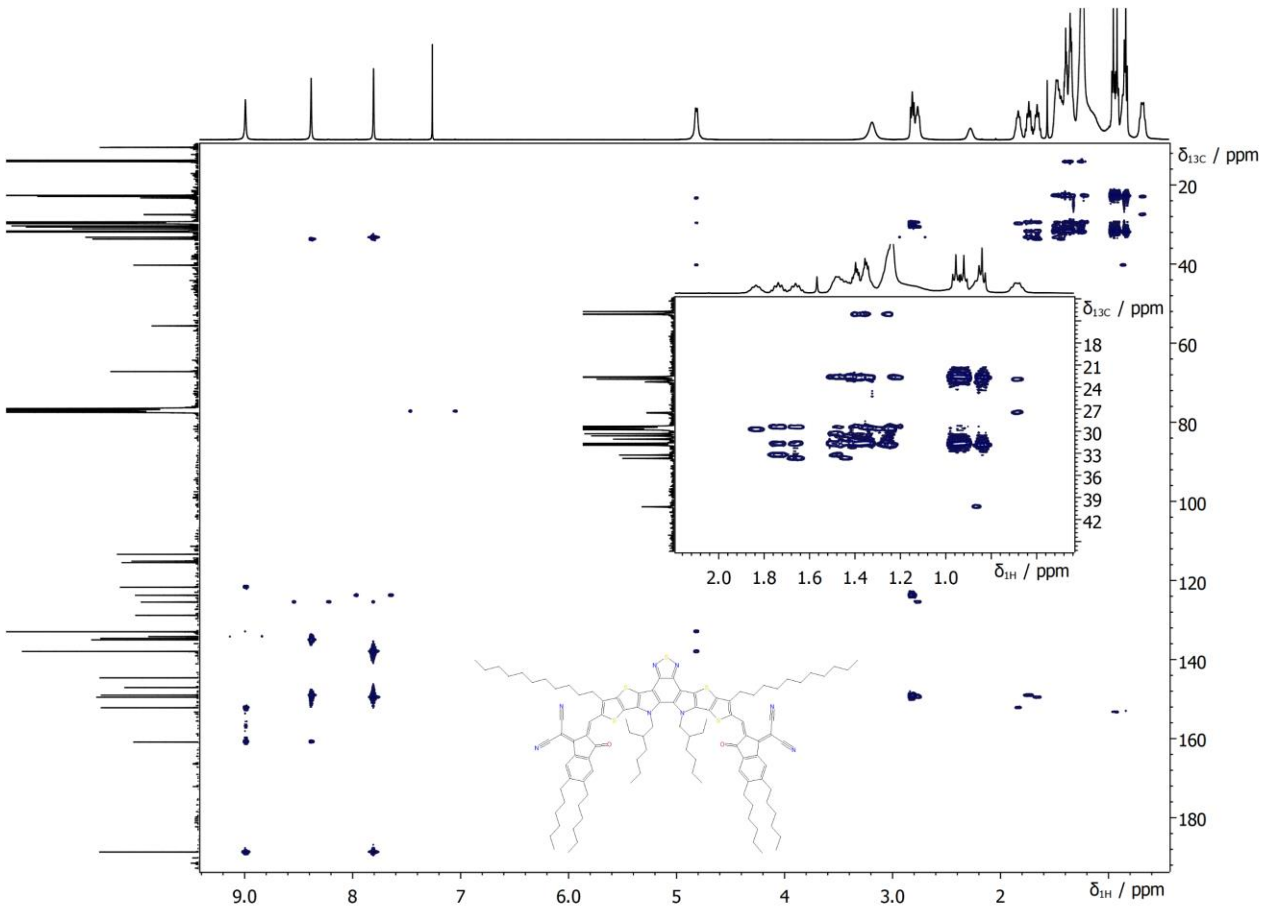


Fig. S59 HMBC NMR spectrum of compound **Y-Hex**.

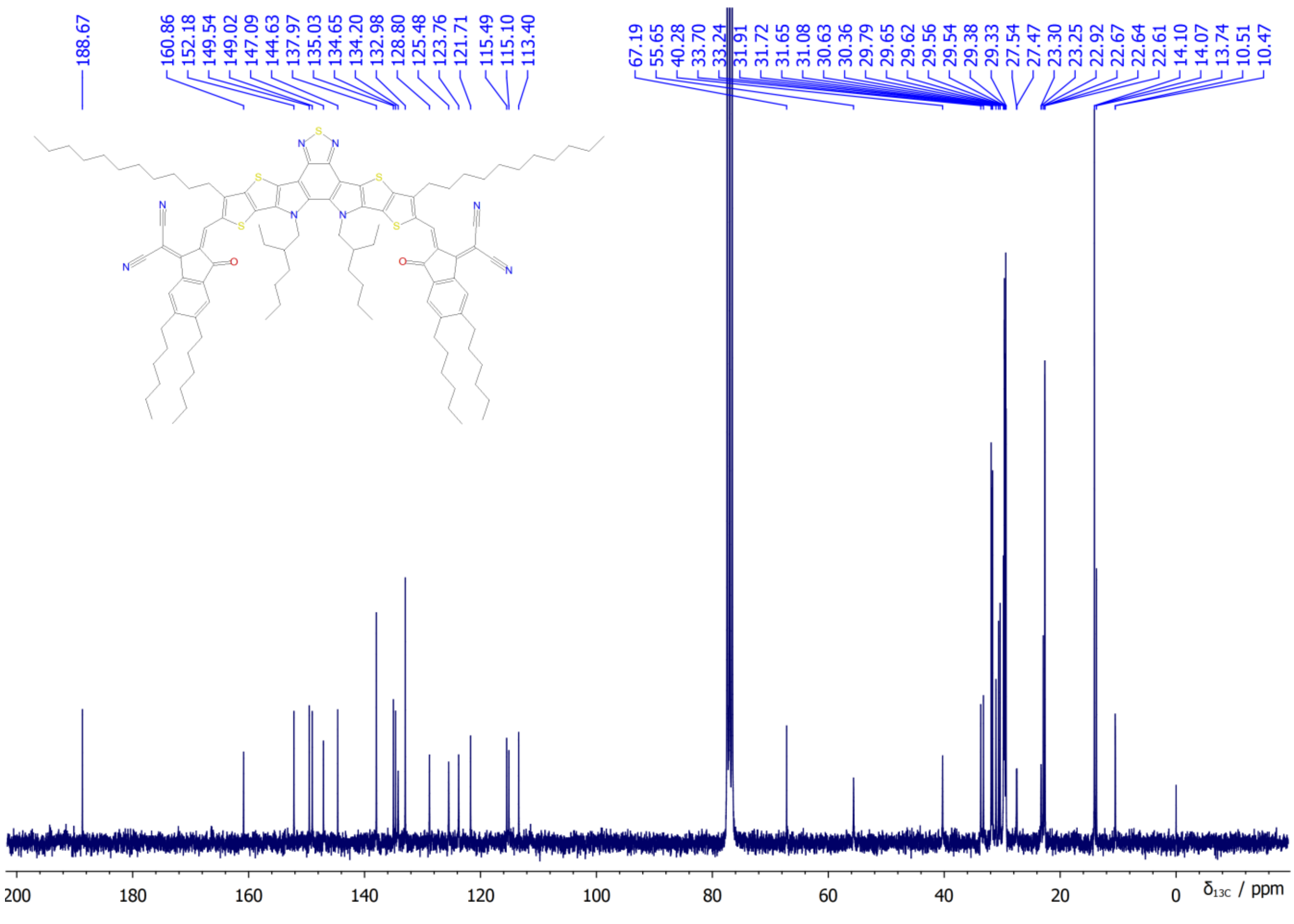


Fig. S60 ^{13}C NMR spectrum of compound **Y-Hex**.

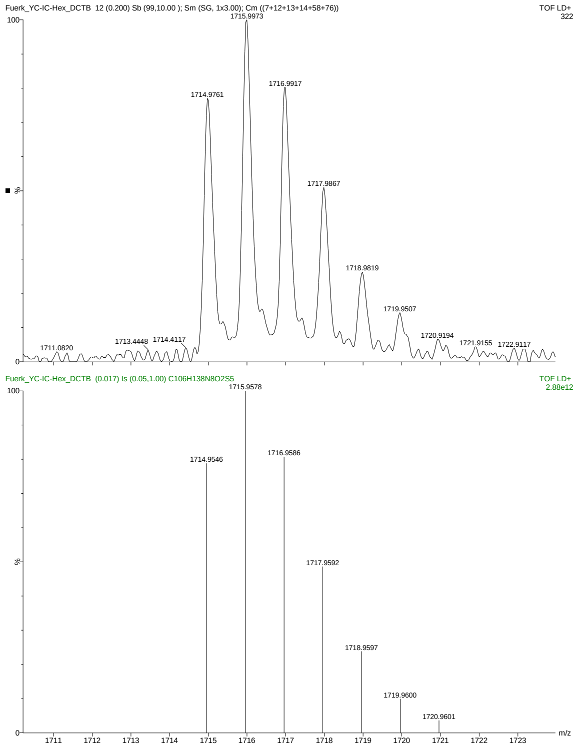


Fig. S61 HR-MS of compound **Y-Hex**.

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