Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Basic enemies of photochromism: irreversible transformation of fluorinated diarylethenes to polyenic enamines and enols

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Supporting Information

Content

List of Figures

List of Tables

(A) General Methods

All operations with air- and moisture-sensitive compounds were performed under nitrogen atmosphere using standard Schlenk techniques. The solvents for column chromatography were purified according to standard procedures. Malodinitrile was purchased from Merck. Amines and *n*-BuLi were purchased from Sigma-Aldrich. 5-Ethyl-2-thiophenecarboxaldehyde and 5-ethyl-2-furaldehyde were purchased from ABCR. Octafluorocyclopentene was purchased from TCI. Chemicals were used without further purification. Compounds C5F-T-Et-MN (**15**),[1] C5F-CHO (**6**)[,[2] C5H-CHO (**13**)[3] and C5F-yne (**18**)[4] were prepared according to known literature procedures.

Chromatography was performed on MN Kieselgel 60 M (silica gel, Macherey-Nagel, Germany). Elemental analyses were performed on a CHN-analyzer Heraeus (CHN-O-RAPID) by the Microanalysis laboratory of Konstanz University.

GC/MS was performed on an Agilent GC/MS 7890A/5975C instrument (EI, 70 eV). HRMS ESI/FT-ICR spectra were recorded on a Bruker APEX II FT/ICR instrument. FAB MS was performed on a Finnigan MAT 8200 instrument.

IR spectra were measured on a Perkin Elmer Spectrum 100 ATR spectrometer.

NMR spectra were recorded on a Bruker Avance DRX600 or a Bruker Avance 400. Trace impurities of protonated deuterated solvent were used as reference. ^{1}H NMR chemical shifts were referenced to residual protons in the NMR solvent ($CDCl_3$: δ = 7.26; CD_2Cl_2: δ = 5.32; CD_3CN: δ = 1.94; CD_3OD: δ = 3.31 ppm, acetone-d6: δ = 2.05 ppm). For ^{13}C NMR following values were used: $CDCl_3$: δ = 77.16; CD_2Cl_2: δ = 54.00; CD_3CN: δ = 1.32; CD_3OD: δ = 49.00 ppm; acetone-d6: δ = 206.68 ppm. Following abbreviations were used for NMR data: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), m (multiplet), br (broad), dd (doublet of doublets), dt (doublet of triplets), and tt (triplet of triplets). Structure assignments were done based on 2D-NMR (COSY, HSQC, HMBC, NOESY and HOESY) experiments.

Data collection for X-ray structure determination was performed at a STOE IPDS-II diffractometer equipped with a graphite monochromated radiation source (λ = 0.71073 Å), an image plate detection system and an Oxford Cryostream 700 with nitrogen as coolant gas. The selection, integration, and averaging procedure of the measured reflex intensities, the determination of the unit cell by a least-squares fit of the 2Θ values, data reduction, LP correction, and the space group determination were performed using the X-Area software package delivered with the diffractometer.[5] A semiempirical absorption correction method was performed after indexing of the crystal faces. The structures were solved by direct methods (SHELXS-97)[6] and refined by standard Fourier techniques against F square with a full-matrix least squares algorithm using SHELXL-2013 and the WinGX (2018.3)[7] software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined with a riding model. Graphical representations were prepared with ORTEP-III.[7] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1037923 (**C5F-Et-NPA**), CCDC 1037924 (7-T-Et-MN-pyrr (**8f**)), CCDC 894167 (C5F-MN (**7**)), CCDC 1946677 (**C5F-T-Et-NPA**), CCDC 1946676 (C5H-MN (**14**)) and CCDC 2016261 (C5F-yne (**18**)).

(B) Synthesis and Characterization

1) Synthesis of C5F-Et-MN **(12)**

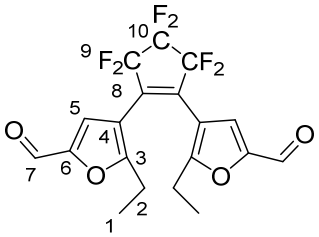
a) 4-Bromo-5-ethyl-2-furaldehyde: 5-Ethyl-2-furaldehyde (6.2 g, 50 mmol, 1.1 equiv.) was placed in a 250 mL two-necked flask equipped with a reflux condenser, magnetic stirring bar and a powder funnel and was cooled down to 0° C in an ice bath. $AlCl_3$ (14.7 g, 110 mmol, 2.4 equiv.) was added in three portions while stirring at low rpm values (alternatively a thick glass rod may be used for stirring). Then the powder funnel was replaced by a dropping funnel, and bromine (2.3 mL, 45 mmol, 1 equiv.) was added dropwise over 3 minutes. The resulting dark viscous mixture was left overnight in the ice bath, allowing it to warm up to rt. The flask was then cooled down in an ice bath, and crushed ice (100 g) was added in small portions to the reaction mixture avoiding overheating. The resulting heterogeneous mixture was extracted with Et_2O (3x100 mL), the combined organic phase were dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The dark oily residue was dissolved in *n*-hexane (300 mL) at 50° C, and the orange solution containing black suspended particles was filtered hot through a paper filter. After removing the hexane 5.3 g of brown oil remained, which solidified upon standing. The desired 4-bromo-5-ethyl-2-furaldehyde was obtained in 52% yield as brown solid and was used for the next step without further purification. MS (EI, 70 eV) for $C_7H_7BrO_2$: 202 [M (^{79}Br)], 204 [M (^{81}Br)].

b) 2-(4-Bromo-5-ethylfuran-2-yl)-5,5-dimethyl-1,3-dioxane: Acetal protection of 4-bromo-5-ethylfuran-2-carbaldehyde was done as described in ref [8] for its methyl analogue. Isolated as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 (s, 3H; CH_3 (C10)), 1.19 (t, $^3J_{HH}$ = 7.6 Hz, 3H; CH_3 (C1)), 1.23 (s, 3H; CH_3 (C11)), 2.64 (q, $^3J_{HH}$ = 7.6 Hz, 2H; CH_2 (C2)), 3.57 (d, $^2J_{HH}$ = 11.2 Hz, 2H; CH_2 (C8)), 3.72 (d, $^2J_{HH}$ = 11.2 Hz, 2H; CH_2 (C8)), 5.37 (s, 1H; CH (C7)), 6.40 ppm (s, 1H; CH (C5); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.35 (C1), 19.95 (C2), 22.06 (C10), 23.14 (C11), 30.61 (C9), 77.64 (C8), 95.95 (C4), 96.04 (C7), 111.48 (C5), 149.54 (C6), 154.30 ppm (C3); MS (EI, 70 eV) for $C_{12}H_{17}BrO_3$: 288 [M (^{79}Br)], 290 [M (^{81}Br)].

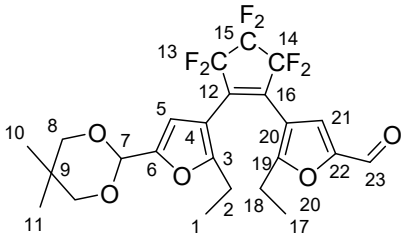
c) 2,2'-((Hexafluorocyclopent-1-ene-1,2-diyl)bis(5-ethylfuran-4,2-diyl))bis(5,5-dimethyl-1,3-dioxane) C5F-Et-NPA: 2-(4-Bromo-5-ethylfuran-2-yl)-5,5-dimethyl-1,3-dioxane (1.46 g, 5.05 mmol, 1 equiv.) was dissolved in dry THF (50 mL) at -78° C. *n*BuLi (1.6 M, 3.47 mL, 5.56 mmol, 1.1 equiv.) was added dropwise at -78° C and the mixture was kept at that temperature for another 30 min. Octafluorocyclopentene (0.33 mL, 2.52 mmol, 0.5 equiv.) was added dropwise, and the reaction mixture was left to warm up to rt overnight. After quenching with brine (10 mL), THF was removed *in vacuo*, water (50 mL) was added and the mixture was extracted with diethyl ether (5x50 mL). Combined organic phases were dried over $MgSO_4$ and the volatiles were evaporated. The resulting brown oil was purified by column chromatography on silica gel using n-hexane/EtOAc 4/1 mixture as eluent. The title compound was isolated in 54% yield as yellow oil (0.81 g, 1.36 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.76 (s, 6H; CH_3 (C10)), 0.94 (t, $^3J_{HH}$ = 7.5 Hz, 6H; CH_3 (C1)), 1.24 (s, 6H; CH_3 (C11)), 2.26 (q, $^3J_{HH}$ = 7.5 Hz, 4H; CH_2 (C2)), 3.56 (d, $^2J_{HH}$ = 11.0 Hz, 4H; CH_2 (C8)), 3.72 (d, $^2J_{HH}$ = 11.0 Hz, 4H; CH_2 (C8)), 5.38 (s, 2H; CH (C7)), 6.44 ppm (s, 2H; CH (C5)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.58 (C1), 21.08 (C2), 22.02 (C10), 23.13 (C11), 30.60 (C9), 77.63 (C8), 95.90 (C7), 108.17 (C5),

108.51 (C4), 111.07 (m, C14), 116.01 (m, C13), 133.30 (m, C12), 150.81 (C6), 157.59 ppm (C3); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.63 (t, *J* = 5.2 Hz, 4F), -131.82 ppm (p, *J* = 5.2 Hz; 2F); IR: υ = 2951, 2850, 1263, 1101 cm^{-1}; MS (EI, 70 eV): 592 [M]; HRMS (ESI) calcd for $C_{29}H_{34}F_6O_6$: 593.2332 [M+H], found: 593.2323; elemental analysis calcd (%) for $C_{29}H_{34}F_6O_6$: C 58.78, H 5.78; found: C 58.77, H 6.09.

d) 4,4'-(Hexafluorocyclopent-1-ene-1,2-diyl)bis(5-ethylfuran-2-carbaldehyde) (C5F-Et-CHO **(11)): C5F-Et-NPA** (1 g, 1.69 mmol) was dissolved in a THF/acetone mixture (30 mL each) and cooled to 10° C. Conc. HCl (15 ml) was slowly added while maintaining the temperature between 10 – 15 °C. After complete addition, the solution was stirred at rt and monitored by TLC. After complete deprotection the organic solvents were removed *in vacuo* and the residue was brought to pH = 9 by adding aqueous $NaHCO_3$. After extraction with diethyl ether (3 x 50 mL) the combined organic fractions were dried over $MgSO_4$ and the solvent was removed *in vacuo*. The oily residue was purified by column chromatography on silica gel using n-hexane/EtOAc 2/1 mixture as eluent, thus giving 87% (0.62 g, 1.47 mmol) of C5F-Et-CHO (**11**) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.04 (t, $^3J_{HH}$ = 7.5 Hz, 6H; CH_3 (C1)), 2.34 (q, $^3J_{HH}$ = 7.5 Hz, 4H; CH_2 (C2)), 7.21 (s, 2H; CH (C5)), 9.58 ppm (s, 2H; CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.24 (C1), 21.54 (C2), 110.52 (C4), 110.74 (m, C10), 115.81 (m, C9), 120.83 (C5), 133.57 (m, C8), 152.42 (C6), 163.34 (C3) 177.15 ppm (CHO); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.74 (t, *J* = 5.0 Hz, 4F), -131.64 ppm (p, *J* = 4.8 Hz; 2F); IR: υ = 2984, 2848, 1682 (C=O), 1110 cm^{-1}; MS (EI, 70 eV): 420 [M]; HRMS (ESI) calcd for $C_{19}H_{14}F_6O_4$: 421.0869 [M+H], found: 421.0933; elemental analysis calcd (%) for $C_{19}H_{14}F_6O_4$: C 54.30, H 3.36; found: C 54.26, H 3.94.



e) 4-(2-(5-(5,5-Dimethyl-1,3-dioxan-2-yl)-2-ethylfuran-3-yl)-3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)-5-ethylfuran-2-carbaldehyde was isolated as byproduct from several batches of deprotection of **C5F-Et-NPA**. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.78 (s, 3H; CH_3 (C10)), 0.97 (t, $^3J_{HH}$ = 7.5 Hz, 3H; CH_3 (C1)), 1.05 (t, $^3J_{HH}$ = 7.5 Hz, 3H; CH_3 (C17)), 1.24 (s, 3H; CH_3 (C11)), 2.27 (q, $^3J_{HH}$ = 7.5 Hz, 2H; CH_2 (C2)), 2.38 (q, $^3J_{HH}$ = 7.5 Hz, 2H; CH_2 (C18)), 3.58 (d, $^2J_{HH}$ = 10.2 Hz, 2H; CH_2 (C8)), 3.73 (d, $^2J_{HH}$ = 11.3 Hz, 2H; CH_2 (C8)), 5.39 (s, 1H; CH (C7)), 6.43 (s, 1H; CH (C5)), 7.24 (s, 1H; CH (C21)), 9.57 ppm (s, 1H; CHO); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.11 (C17), 11.56 (C1), 21.07 (C2), 21.41 (C18), 21.91 (C10), 23.03 (C11), 30.52 (C9), 77.57 (C8), 95.67 (C7), 107.72 (C5), 108.08 (C4), 110.83 (m, C15), 110.99 (C20), 114.51 (m, C13, C14), 121.74 (C21), 131.17 (m, C16), 135.47 (m, C12), 151.36 (C6), 152.07 (C22), 157.59 (C3), 163.55 (C19), 177.04 ppm (CHO); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.51 (t, *J* = 4.4 Hz, 2F), -110.87 (t, *J* = 4.3 Hz, 2F), -131.76 ppm (p, *J* = 5.1 Hz; 2F); IR: υ = 2960, 2851, 1686 (C=O), 1276, 1103 cm^{-1}; MS (EI, 70 eV): 506 [M]; HRMS (ESI) calcd for $C_{24}H_{24}F_6O_5$: 507.1600 [M+H], found: 507.1523.



f) 2,2'-(((Hexafluorocyclopent-1-ene-1,2-diyl)bis(5-ethylfuran-4,2-diyl))bis(methanylylidene))malodinitrile (C5F-Et-MN **(12)):** Dialdehyde **11** (0.46 g, 1.1 mmol) and malodinitrile (0.24 g, 3.6 mmol, 3.3 equiv.) were dissolved in dry benzene (25 mL). Pyridine (0.1 mL) was added and the reaction mixture was stirred overnight at rt. Benzene was removed *in vacuo* and the remaining brownish solid was purified by column chromatography on silica using *n*-hexane/EtOAc 1/4 mixture as eluent. C5F-Et-MN (**12**) was isolated in 91% (0.52 g) as yellow oil which solidified after sonication in $CHCl_3$/*n*-hexane 1/5 mixture to a yellowish solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.16 (t, $^3J_{HH}$ = 7.5 Hz, 6H; CH_3 (C1)), 2.46 (q, $^3J_{HH}$ = 7.5 Hz, 4H; CH_2 (C2)), 7.21 (s, 2H; CH (C5)), 7.41 ppm (s, 2H; CH (C7)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.07 (C1), 21.87 (C2), 79.91 (C8), 112.09 (C4), 112.36 (C10), 113.41 (C9), 115.63 (m, C12), 122.42 (C5), 133.60 (m, C11), 141.76 (C7), 147.70 (C6), 164.84 ppm (C3); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.45 (t, *J* = 4.9 Hz, 4F), -131.52 ppm (p, *J* = 4.8 Hz; 2F); IR: υ = 2924, 2231 (CN), 1608, 1109 cm^{-1}; HRMS (ESI, pos. mode) calcd for $C_{25}H_{14}F_6N_4O_2$: 517.1093 [M+H], found: 517.1056; HRMS (ESI, neg. mode) calcd for $C_{25}H_{14}F_6N_4O_2$: 515.0937 [M-H], found: 515.1018.

2,2'-(((Hexafluorocyclopent-1-ene-1,2-diyl)bis(5-methylfuran-4,2-diyl))bis(methanylylidene))malodinitrile (5F-MN **(7)):** C5F-CHO (**6**) (50 mg, 0.127 mmol, 1 equiv.) and malodinitrile (18.5 mg, 0.28 mmol, 2.2 equiv.) were dissolved in dry benzene (8 mL). Pyridine (0.05 mL) was added and the reaction mixture was stirred overnight at rt. A white precipitate was filtered off and washed with *n*-hexane. C5F-MN (**7**) was isolated in 92 % (57 mg) yield as white solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 2.27 (s, 6H; CH_3 (C1)), 7.27 (s, 2H; CH (C4)), 7.43 ppm (s, 2H; CH (C6)); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 14.34 (C1), 79.87 (C7), 110.61 (m, C12), 112.24 (C9), 113.13 (C3), 113.27 (C8), 115.59 (tt, $^1J_{CF}$ = 258.1, $^2J_{CF}$ = 24.4 Hz; C11), 122.19 (C4), 133.60 (t, $^2J_{CF}$ = 24.9 Hz; C10), 141.81 (C6), 147.62 (C5), 160.35 ppm (C2); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -109.99 (t, *J* = 4.9 Hz, 4F), -131.47 ppm (p, *J* = 5.0 Hz; 2F); IR: υ = 2225 (CN) cm^{-1}; MS (FAB, add. NaI): 489 [M+H], 511 [M+Na]; HRMS (ESI) calcd for $C_{23}H_{10}F_6N_4O_2$: 489.0781 [M+H], found: 489.0774; elemental analysis calcd (%) for $C_{23}H_{10}F_6N_4O_2$: C 56.57, H 2.06, N 11.47; found: C 56.39, H 2.47, N 11.66.

2,2'-((cyclopent-1-ene-1,2-diylbis(5-methylfuran-4,2-diyl))bis(methanylylidene))dimalononitrile (C5H-MN **(14):** C5H-CHO (**13**) (100 mg, 0.35 mmol) and malononitrile (49 mg, 0.74 mmol) were dissolved in dry benzene (10 mL). Pyridine (0.05 mL) was added and the reaction mixture was stirred overnight at rt. Benzene was removed *in vacuo* and the remaining brownish solid was purified by column chromatography using *n*-hexane/EtOAc 1/3 mixture as eluent to give a oil which solidified after sonification in $CHCl_3$/*n*-hexane 1/5 mixture. (C5H-MN **(14)** was isolated in 68% (91 mg) yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.09 (p, $^3J_{HH}$ = 7.6 Hz, 2H; CH_2 (C12)), 2.19 (s, 6H; CH_3 (C1)), 2.77 (t, $^3J_{HH}$ = 7.5 Hz, 4H; CH_2 (C11)), 7.11 (s, 2H; CH (C4)), 7.33 ppm (s, 2H; CH (C6)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.18 (C1), 22.64 (C12), 37.96 (C11), 75.85 (C7), 113.04 (C9), 114.20 (C8), 123.06 (C3), 124.34 (C4), 131.13 (C10), 142.13 (C6), 146.64 (C5), 157.85 ppm (C2); IR: υ =

2930, 2847, 2223 (CN), 1607, 1568, 1494, 1118 cm^{-1}; HRMS (ESI, neg. mode) calcd for $C_{23}H_{16}N_4O_2$: 379.1190 [M-H], found: 379.1222.

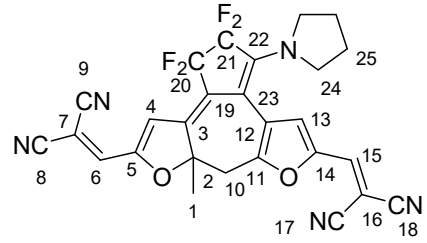
1,2-Bis(5-ethynyl-2-methylfuran-3-yl)cyclopent-1-ene (C5H-YNE **(19)):** C5H-CHO (**6**) (10 mg, 0.035 mmol) was dissolved in methanol (3 mL) at rt. Dimethyl 1-diazo-2-oxopropylphosphonate (16.2 mg, 0.084 mmol) and potassium carbonate (19 mg, 0.140 mmol) were added and the mixture was stirred overnight. Volatiles were removed *in vacuo*, water (2 mL) was added and the mixture was extracted with dichloromethane (2 x 5 mL). Combined organic phases were dried over $MgSO_4$ and the volatiles were evaporated. Resulting orange-colored oil was purified by column chromatography on silica gel using n-hexane/dichloromethane 2/1 mixture as eluent. C5H-YNE (**19**) was isolated in 71 % yield (7 mg) as colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 6H; CH_3 (C1)), 2.00 (p, $^3J_{HH}$ = 7.5 Hz, 2H; CH_2 (C10)), 2.68 (t, $^3J_{HH}$ = 7.5 Hz, 4H; CH_2 (C9)), 3.39 (s, 2H; CH (C7)), 6.45 ppm (s, 2H; CH (C4)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.59 (C1), 22.61 (C10), 37.97 (C9), 74.31 (C6), 81.85 (C7), 117.72 (C4), 118.87 (C3), 130.13 (C8), 133.96 (C5), 150.20 ppm (C2); IR: υ = 3311, 2954, 2921, 2851, 2097, 1529 cm^{-1}; MS (EI): 276 [M]; HRMS (EI) calcd for $C_{19}H_{16}O_2$: 276.1150 [M], found: 276.1153.

General procedure: Reaction of bis(dicyanovinyl) DAEs with secondary amines

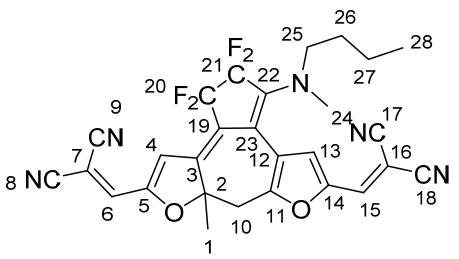
C5F-MN (**7**) (50 mg, 0.1 mmol, 1 equiv.) was dissolved in dry benzene (7 mL), and amine (1.27 mmol, 10 equiv.) was added. The reaction mixture turned magenta (greenish-blue when dicyclohexylamine was used). After stirring overnight at r. t. volatiles were removed *in vacuo* and the oily residue was subjected to column chromatography (*n*-hexane/EtOAc 3/1, then 1/1 (then methanol for dicyclohexyl derivative)). Corresponding magenta (green for dicyclohexyl derivative) fraction containing tetrafluoro product was separated from the mixture of unidentifiable yellow- to brown-colored degradation products of DAE. Immobile polar dark residue on top of column contained mainly the corresponding amine hydrofluoride.

2,2'-((1,1,2,2-Tetrafluoro-7a-methyl-3-(piperidin-1-yl)-1,2,7,7a-tetrahydroazuleno[5,4-b:7,8-b']difuran-5,9-diyl)bis(methanylylidene))malodinitrile (7-MN-pip (**8a**))**:** According to general procedure **8a** was obtained as dark-magenta solid (19 mg, 35%) besides 11 mg (22%) starting material **7**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (s, 3H; CH_3), 1.68 (m, 4H; CH_2 (C25 and C26)), 1.79 (m, 2H; CH_2 (C25)), 3.23 (m, 2H; NCH_2), 3.33 (d, $^2J_{HH}$ = 15.0 Hz, 1H; CH_2 (C10)), 3.43 (m, 2H; NCH_2), 3.72 (d, $^2J_{HH}$ = 14.9 Hz, 1H; CH_2 (C10)), 6.71 (t, J_{HF} = 2.3 Hz, 1H; CH (C4)), 7.07 (s, 1H; CH (C6)), 7.56 (s, 1H; CH (C15)), 7.67 ppm (s, 1H; CH (C13)); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 23.53 (C26), 26.21 (C25), 26.71 (C1), 39.29 (C10), 51.81 (C24), 78.55 (C16), 81.52 (C7), 87.88 (C2), 109.81 (m, C23), 112.52 (C9), 112.93 (C17), 113.40 (C18), 114.35 (C8), 118.33 (C12), 120.34 (C4), 121.74 (C13), 136.80 (C3), 141.10 (C6), 143.11 (C15), 143.97 (m, C22), 146.75 (C14), 153.56 (C5), 155.73 ppm (C11) (signals of C19, C20 and C21 were not identified); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -105.35 (d, J = 252.6 Hz, 1F), -106.96 (d, J = 250.0 Hz, 1F), -118.53 (d, J = 252.9 Hz, 1F), -119.31 ppm (d, J = 249.9 Hz, 1F); IR: υ = 3107, 2943, 2859, 2225 (CN), 1607, 1506, 1275 cm^{-1}; MS (FAB): 534 [M+H]; HRMS (ESI) calcd for $C_{28}H_{19}F_4N_5O_2$: 533.1475, found: 533.1522 (neg. mode).

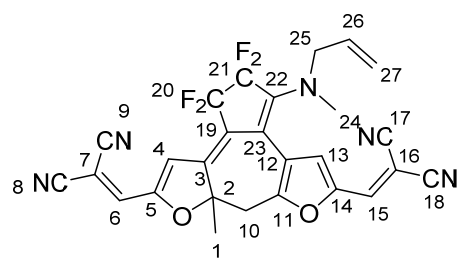
2,2'-((1,1,2,2-Tetrafluoro-7a-methyl-3-(pyrrolidin-1-yl)-1,2,7,7a-tetrahydroazuleno[5,4-b:7,8-b']difuran-5,9-diyl)bis(methanylylidene))malodinitrile (7-MN-pyrr (**8b**)**):** According to general procedure **8b** was obtained as dark-magenta solid (46 mg, 88%) besides trace amounts of starting material **7**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (s, 3H; CH_3), 1.91 (m, 2H; CH_2 (C25)), 2.10 (m, 2H; CH_2 (C25)), 3.29 (m, 2H; NCH_2), 3.32 (d, $^{2}J_{HH}$ = 14.8 Hz, 1H; CH_2 (C10)), 3.72 (m, 2H; NCH_2), 3.73 (d, $^{2}J_{HH}$ = 14.7 Hz, 1H; CH_2 (C10)), 6.72 (t, J_{HF} = 2.4 Hz, 1H; CH (C4)), 7.06 (s, 1H; CH (C6)), 7.43 (s, 1H; CH (C13)), 7.57 ppm (s, 1H; CH (C15)); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.68 (C25), 26.67 (C1), 39.28 (C10), 51.74 (C24), 78.25 (C16), 80.92 (C7), 87.92 (C2), 107.94 (m, C23), 112.62 (C9), 112.97 (C17), 113.43 (C18), 114.47 (C8), 118.43 (C12), 120.77 (C4), 122.71 (C13), 124.25 (t, $^{2}J_{CF}$ = 21.4 Hz; C19), 135.34 (C3), 141.11 (C6), 142.23 (t, $^{2}J_{CF}$ = 21.3 Hz; C22), 143.16 (C15), 146.43 (C14), 153.11 (C5), 155.94 ppm (C11); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -107.37 (d, *J* = 252.5 Hz, 1F), -108.34 (d, *J* = 256.7 Hz, 1F), -115.24 (d, *J* = 256.7 Hz, 1F), -115.45 ppm (d, *J* = 254.3 Hz, 1F); correlations confirmed by NOESY (C13-H and C24-H) and HOESY (F and C4-H; F and C24-H) data; IR: υ = 3120, 2926, 2222 (CN), 1617, 1595 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{17}F_4N_5O_2$: 520.1391 [M+H], found: 520.1388.



2,2'-((3-(Butyl(methyl)amino)-1,1,2,2-tetrafluoro-7a-methyl-1,2,7,7a-tetrahydroazuleno [5,4-b:7,8-b']difuran-5,9-diyl)bis(methanylylidene))malodinitrile (7-MN-mebu (**8c**)**):** According to general procedure **8c** was obtained as dark-magenta solid (24 mg, 44%) besides 13 mg (27%) starting material **7**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H; CH_3 (C28)), 1.22 (s, 3H; CH_3), 1.31 (m, 2H; CH_2 (C27)), 1.65 (m, 2H; CH_2 (C26)), 3.02 (s, 3H; NCH_3), 3.20 (m, 1H; CH_2 (C25)), 3.33 (d, $^{2}J_{HH}$ = 14.9 Hz, 1H; CH_2 (C10)), 3.51 (m, 1H; CH_2 (C25)), 3.73 (d, $^{2}J_{HH}$ = 14.9 Hz, 1H; CH_2 (C10)), 6.71 (t, J_{HF} = 2.3 Hz, 1H; CH (C4), 7.07 (s, 1H; CH (C6)), 7.54 (s, 1H; CH (C13)), 7.58 ppm (s, 1H; CH (C15)); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.72 (C28), 19.89 (C27), 26.65 (C1), 30.22 (C26), 39.27 (C10), 40.91 (C24), 54.48 (C25), 78.61 (C16), 81.52 (C7), 87.87 (C2), 109.58 (C23), 112.50 (C9), 112.92 (C17), 113.34 (C18), 114.33 (C8), 118.17 (C12), 120.36 (C4), 121.88 (C13), 123.41 (t, $^{2}J_{CF}$ = 20.4 Hz; C19), 136.57 (C3), 141.13 (C6), 143.20 (C15), 144.61 (t, $^{2}J_{CF}$ = 21.3 Hz; C22), 146.74 (C14), 153.54 (C5), 155.74 ppm (C11); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -105.41 (d, *J* = 253.3 Hz, 1F), -106.94 (d, *J* = 250.0 Hz, 1F), -118.35 (d, *J* = 252.8 Hz, 1F), -119.13 ppm (d, *J* = 250.1 Hz, 1F); correlations confirmed by ROESY (C13-H and C24-H) and HOESY (F and C4-H; F and C25-H, C24-H) data; IR: υ = 2928, 2222 (CN), 1617, 1499 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{21}F_4N_5O_2$: 536.1710 [M+H], found: 536.1918.

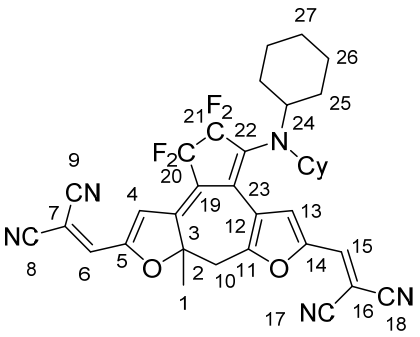


2,2'-((3-(Allyl(methyl)amino)-1,1,2,2-tetrafluoro-7a-methyl-1,2,7,7a-tetrahydroazuleno [5,4-b:7,8-b']difuran-5,9-diyl)bis(methanylylidene))malodinitrile (7-MN-meall (**8d**)**):** According to general procedure **8d** was obtained as dark-violet amorphous mass (11 mg, 21%) besides 7 mg (14%) starting material **7**. ^{1}H NMR (600 MHz, CD_3CN): δ = 1.20 (s, 3H; CH_3), 2.93 (s, 3H; NCH_3), 3.41 (d, $^{2}J_{HH}$ = 14.8 Hz, 1H; CH_2 (C10)), 3.57 (d, $^{2}J_{HH}$ = 14.8 Hz, 1H; CH_2 (C10)), 3.80 (dd, $^{2}J_{HH}$ = 15.0, J_{HH}(allyl) = 7 Hz, 1H;

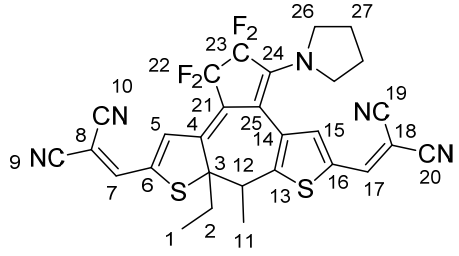


CH_2 (allyl)), 3.99 (dd, $^2J_{HH}$ = 15.0, J_{HH}(allyl) = 6 Hz, 1H; CH_2 (allyl)), 5.29 (m, 2H; HCH (C27)), 5.85 (m, 1H; CH (C26)), 6.81 (s, 1H; CH (C4)), 7.39 (s, 1H; CH (C6)), 7.41 (s, 1H; CH (C13)), 7.76 ppm (s, 1H; CH (C15)); ^{13}C NMR (150 MHz, CD_3CN): δ = 26.67 (C1), 39.62 (C10), 40.18 (C24), 57.70 (C25), 78.12 (C16), 81.44 (C7), 88.76 (C2), 112.60 (from HMBC data) (C23), 113.79 (C9), 114.03 (C17), 115.13 (C18), 115.57 (C8), 118.60 (overlaps with solvent peak) (C12), 120.38 (C27), 120.99 (C4), 123.35 (m, C19), 125.19 (C13), 133.68 (C26), 138.24 (C3), 143.43 (C6), 143.80 (m, C22), 144.39 (C15), 147.85 (C14), 155.01 (C5), 157.17 ppm (C11); ^{19}F NMR (376 MHz, CD_3CN): δ = -106.11 (d, J = 253.7 Hz, 1F), -107.92 (d, J = 250.9 Hz, 1F), -119.11 ppm (m, 2F); correlations confirmed by NOESY (C13-H and C24-H, C25-H, C-26-H) data; IR: υ = 2226 (CN), 1615, 1508 cm^{-1}; MS (FAB): 519 [M]; MS (ESI) for $C_{27}H_{17}F_4N_5O_2$: 520 [M+H].

2,2'-((3-(Dicyclohexylamino)-1,1,2,2-tetrafluoro-7a-methyl-2,7,7a-tetrahydroazuleno [5,4-b:7,8-b']difuran-5,9-diyl)bis(methanylylidene))malodinitrile (7-MN-cy (**8e**))**:** According to general procedure **8e** was obtained as greenish-blue solid (41 mg, 65%) besides trace amounts of starting material **7**. ^{1}H NMR (400 MHz, CD_3CN): δ = 1.10 (s, 3H; CH_3), 1.18 (m, 2H; CH_2), 1.31 (m, 8H; CH_2), 1.65 (m, 2H; CH_2), 1.82 (m, 4H; CH_2), 2.01 (m, 4H; CH_2), 3.18 (m, 2H; NCH), 3.31 (d, $^2J_{HH}$ = 14.5 Hz, 1H; CH_2 (C10)), 3.55 (d, $^2J_{HH}$ = 14.5 Hz, 1H; CH_2 (C10)), 6.83 (t, J_{HF} = 2.5 Hz, 1H; CH (C4), 7.23 (s, 1H; CH (C6)), 7.62 (s, 1H; CH (C13)), 7.74 ppm (s, 1H; CH (C15)); ^{13}C NMR (150 MHz, CD_3CN): δ = 25.00 (C26), 25.63 (C27), 26.84 (C1), 30.05 (C25), 40.52 (C10), 55.12 (C24), 77.00 (C16), 77.02 (C7), 88.83 (C2), 113.20 (m, C23), 114.14 (C17), 114.72 (C9), 115.40 (C18), 116.52 (C8), 119.34 (C12), 122.99 (C4), 125.16 (m, C19), 127.34 (C13), 133.66 (C3), 140.14 (m, C22), 141.38 (C6), 144.13 (C15), 146.47 (C14), 153.54 (C5), 156.93 ppm (C11); ^{19}F NMR (376 MHz, CD_3CN): δ = -107.83 (d, J = 251.5 Hz, 1F), -108.20 (d, J = 251.8 Hz, 1F), -117.97 (d, J = 251.9 Hz, 1F), -118.16 ppm (d, J = 251.4 Hz, 1F); IR: υ = 2943, 2193 (CN), 1674 cm^{-1}; MS (ESI) for $C_{35}H_{31}F_4N_5O_2$: 629 [M].



2,2'-((7a-Ethyl-1,1,2,2-tetrafluoro-7-methyl-3-(pyrrolidin-1-yl)-1,2,7,7a-tetrahydroazuleno [5,4-b:7,8-b']dithiophene-5,9-diyl)bis(methanylylidene))malodinitrile (7-T-Et-MN-pyrr (**8f**))**:** C5F-T-Et-MN (**15**) (40 mg, 0.073 mmol, 1 equiv.) was dissolved in dry benzene (10 mL). Pyrrolidine (0.05 mL) was added and the reaction mixture was stirred overnight at rt. Benzene was removed *in vacuo* and the remaining dark-green oil was filtered through a short column with silica gel using CH_2Cl_2/*n*-hexane 1/1 to remove unchanged starting material (9 mg, 22%) then 5/1 as eluent. Intensively colored green-blue fraction containing product was obtained, the volatiles were evaporated, and 17 mg (40%) of **8f** were obtained as dark-green crystals. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.82 (m, 3H; CH_3 (C1)), 0.88 (m, 1H; CH_2 (C2)), 1.65 (m, 1H; CH_2 (C2)), 1.79 (d, $^3J_{HH}$ = 7.0 Hz, 3H; CH_3 (C11)), 1.87 (m, 2H; CH_2 (C27)), 2.08 (m, 2H; CH_2 (C27)), 3.19 (m, 2H; CH_2 (C26)), 3.66 ((m, 2H; CH_2 (C26)), 3.92 (q, $^3J_{HH}$ = 7.0 Hz, 1H; CH (C12)), 7.21 (dd, J_{HF} = 4.4, 1.5 Hz, 1H; CH (C5)), 7.45 (s, 1H; CH (C7)), 7.61 (s, 1H; CH (C15)), 7.79 ppm (s, 1H; CH (C17)); ^{13}C NMR (150 MHz, CD_2Cl_2): δ = 8.66 (C1), 18.76 (C11), 25.97 (C27), 33.06 (C2), 44.57 (C12), 52.58 (C26), 73.17 (C3), 79.00 (C18), 79.89 (C8), 112.18 (m, C25), 113.58 (C10), 113.71 (C19), 114.32 (C20), 115.24



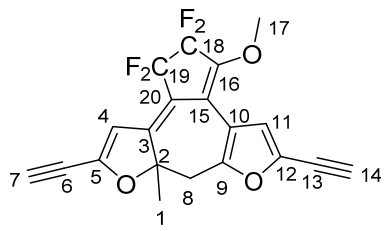
(C9), 115.58 (m, CF_2), 116.05 (tt, $^1J_{CF}$ = 259.1, $^2J_{CF}$ = 23.6 Hz; CF_2), 131.41 (C16), 132.12 (C14), 133.03 (m, C21), 136.42 (C6), 136.87 (C4), 138.65 (C15), 142.18 (C5), 143.20 (t, $^2J_{CF}$ = 21.1 Hz; C24), 150.58 (C7), 150.94 (C17), 157.53 ppm (C13); ^{19}F NMR (376 MHz, CD_2Cl_2): δ = -104.83 (d, *J* = 253.4 Hz, 1F), -109.61 (d, *J* = 256.8 Hz, 1F), -112.75 (d, *J* = 253.4 Hz, 1F), -114.77 ppm (d, *J* = 256.7 Hz; 1F); IR: υ = 2971, 2216 (CN), 1574, 1439 cm^{-1}; MS (MALDI-TOF): 579 [M]; HRMS (ESI) calcd for $C_{29}H_{21}F_4N_5S_2$: 580.1253 [M+H], found: 580.1242.

2,2'-((3-(Dicyanomethyl)-1,1,2,2-tetrafluoro-7a-methyl-1,2,7,7a-tetrahydroazuleno[5,4-b:7,8-b']difuran-5,9-diyl)bis(methanylylidene))malodinitrile (7-MN-MN (**8g**))**:** C5F-CHO (**6**) (50 mg, 0.127 mmol) and malodinitrile (19 mg, 0.28 mmol) were dissolved in dry benzene (10 mL). DIPEA (0.05 mL, 0.29 mmol) was added and the reaction mixture was stirred for 3 h at rt. Benzene was removed *in vacuo* and the remaining greenish solid was purified by column chromatography using *n*-hexane/EtOAc 1/1 as eluent. A small amount of C5F-MN (**7**) was isolated (3 mg, 4%), whereas a green-colored fraction remained at the column start. Subsequent addition of methanol eluted a polar deep-green fraction. Volatiles were removed, and 7-MN-MN (**8g**) was obtained as dark-blue solid (6 mg, 9%). ^{1}H NMR (600 MHz, CD_3CN): δ = 1.10 (s, 3H; CH_3), 3.31 (d, $^2J_{HH}$ = 14.5 Hz, 1H; CH_2 (C10)), 3.55 (d, $^2J_{HH}$ = 14.5 Hz, 1H; CH_2 (C10)), 6.84 (t, J_{HF} = 2.3 Hz, 1H; CH (C4), 7.23 (s, 1H; CH (C6)), 7.61 (s, 1H; CH (C13)), 7.74 ppm (s, 1H; CH (C15)); ^{13}C NMR (150 MHz, CD_3CN): δ = 26.83 (C1), 40.49 (C10), 76.95 (C16), 76.98 (C7), 88.82 (C2), 105.98 (C24), 113.21 (m, C23), 114.15 (C17), 114.72 (C9), 115.40 (C18), 116.52 (C8), 119.30 (C12), 120.44 (C25), 123.00 (C4), 125.12 (m, C19), 127.36 (C13), 133.65 (C3), 140.11 (m, C22), 141.39 (C6), 144.15 (C15), 146.45 (C14), 153.53 (C5), 156.94 ppm (C11); ^{19}F NMR (376 MHz, CD_3CN): δ = -107.84 (d, *J* = 251.6 Hz, 1F), -108.23 (d, *J* = 251.7 Hz, 1F), -118.01 (d, *J* = 251.6 Hz, 1F), -118.18 ppm (d, *J* = 251.7 Hz; 1F); IR: υ = 2193 (CN) cm^{-1}; HRMS (ESI, neg. mode) calcd for $C_{26}H_{10}F_4N_6O_2$: 513.0729 [M-H], found: 513.0740.

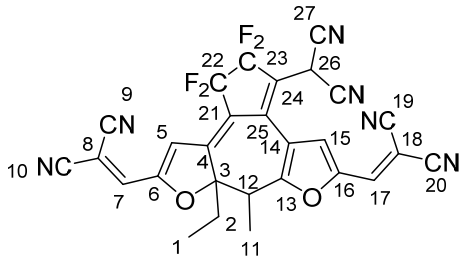
(2Z,2'Z)-3,3'-(1,1,2,2-Tetrafluoro-3-methoxy-7a-methyl-1,2,7,7a-tetrahydroazuleno[5,4-b:7,8-b']difuran-5,9-diyl)bis(2-(pyridin-4-yl)acrylonitrile) (7-MN-4PyOMe (**17**))**:** C5F-CHO (**6**) (0.1 g, 0.25 mmol) and pyridine-4-acetonitrile hydrochloride (0.08 g, 0.5 mmol) were dissolved in dry MeOH (10 mL). After the addition of K_2CO_3 (0.176 g, 1.27 mmol), the reaction mixture was stirred for 48 h at rt. After addition of diethyl ether (50 mL) the obtained mixture was washed consecutively with water (30 mL), aqueous K_2CO_3 (30 mL) and again with water (30 mL). The organic fraction was dried over $MgSO_4$, and the volatiles were removed in vacuo. The dark residue was purified by column chromatography on SiO_2 (*n*-hexane/EtOAc 1:1) giving C5F-4Py (**16**) (0.12 g, 77%) [Fully characterized in ref. 2]. Further elution with EtOAc provided 7-MN-4PyOMe (**17**) as byproduct in form of an orange solid (11 mg, 7%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.49 (s, 3H; CH_3 (C1)), 3.46 (d, $^2J_{HH}$ = 15.8 Hz, 1H; CH_2 (C12)), 3.76 (d, $^2J_{HH}$ = 15.8 Hz, 1H; CH_2 (C12)), 4.21 (s, 3H; OMe), 6.59 (br, 1H; CH (C4)), 7.21 (s, 1H; CH (C6)), 7.55 (s, 1H; CH (C17)), 7.56 (m, 4H; CH (C9 and C21)), 7.95 (s, 1H; CH (C15)), 8.72 ppm (m, 4H; CH (C10 and C22); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 26.42 (C1), 38.64 (C12), 58.86 (C28), 87.88 (C2), 105.86 (C18), 111.90 (C7), 113.67 (C4), 115.80 (C11), 115.83 (C14), 116.51 (C19), 116.67 (m, C27), 117.27 (m, C23), 118.38 (C15), 119.78 (C9/C21), 120.15 (C9/C21), 129.08

(C6), 129.78 (C17), 141.06 (C8), 141.40 (C20), 143.27 (C3), 146.39 (t, $^2J_{CF}$ = 22 Hz; C24), 148.50 (C16), 150.37 (C10/C22), 150.72 (C10/C22), 153.69 (C13), 157.32 ppm (C5); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -107.70 (d, *J* = 260 Hz, 1F), -109.82 (d, *J* = 250 Hz, 1F), -114.41 (d, *J* = 260 Hz, 1F), -115.13 ppm (d, *J* = 250 Hz; 1F); MS (FAB): 584 [M]; HRMS (ESI) calcd for $C_{32}H_{20}F_4N_4O_3$: 585.1544 [M+H], found: 585.1556.

5,9-Diethynyl-1,1,2,2-tetrafluoro-3-methoxy-7a-methyl-1,2,7,7a-tetrahydroazuleno[5,4-b:7,8-b']difuran (7-yne-OMe (**20**))**:** Dimethyldiazomethylphosphonate (235 mg, 1.22 mmol, 2.4 equiv.) was added to a Schlenk flask containing C5F-CHO (**6**) (200 mg, 0.51 mmol) and potassium carbonate (281 mg, 2.04 mmol, 4 equiv.) in dry methanol (20 mL). The reaction mixture was stirred for 90 min. MeOH was removed *in vacuo*, and the remaining brown oil was purified by column chromatography (*n*-hexane/EtOAc 10/1). 73 mg (37%) of pure C5F-yne (**18**)[4] and 14 mg (7 %) of yellow oil containing unstable 7-yne-OMe (**20**) were separated from the darkening mixture of oligomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.35 (s, 3H; CH_3), 3.25 (d, $^2J_{HH}$ = 15.9 Hz, 1H; CH_2 (C8)), 3.41 (d, $^2J_{HH}$ = 15.9 Hz, 1H; CH_2 (C8)), 3.43 (s, 1H; *sp*CH), 3.43 (s, 1H; *sp*CH), 4.08 (s, 3H; OMe), 6.32 (t, J_{HF} = 2.1 Hz, 1H; CH (C4), 7.23 ppm (s, 1H; CH (C11)); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 25.88 (C1), 38.19 (C8), 58.47 (OMe), 73.27 (C13), 74.47 (C6), 82.73 (C14), 84.84 (C7), 86.52 (C2), 110.46 (C4), 113.32 (t, $^2J_{CF}$ = 22.1 Hz; C20), 113.43 (C10), 115.33 (m, CF_2), 116.01 (CF_2), 117.25 (m, C15), 117.37 (C11), 135.20 (C12), 143.98 (t, J_{CF} = 2.7 Hz; C3), 144.42 (t, $^2J_{CF}$ = 20.3 Hz; C16), 144.50 (C5), 151.03 ppm (C9); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -107.38 (d, *J* = 258.2 Hz, 1F), -110.21 (d, *J* = 248.6 Hz, 1F), -114.80 (d, *J* = 258.7 Hz, 1F), -115.64 ppm (d, *J* = 248.8 Hz, 1F); MS (EI, 70 eV) for $C_{20}H_{12}F_4O_3$: 376 [M].



2,2'-((3-(Dicyanomethyl)-7a-ethyl-1,1,2,2-tetrafluoro-7-methyl-1,2,7,7a-tetrahydroazuleno [5,4-b:7,8-b']difuran-5,9-diyl)bis(methanylylidene))malodinitrile (7-Et-MN-MN (**8h**))**:** C5F-Et-MN (**12**) (50 mg, 0.1 mmol) and malodinitrile (13.5 mg, 0.2 mmol) were dissolved in dry dioxane (5 mL). Diisopropylethylamine (0.1 mL) was added, and the reaction mixture turned blue and changed to green within several seconds. After stirring overnight at r. t. the volatiles were removed *in vacuo*, and the resulting dark-green oil was purified by column chromatography (*n*-hexane/EtOAc 1/1 to remove the starting materials (14 mg, 27%), then MeOH to elute 16 mg (29%) of 7-Et-MN-MN (**8h**) as green solid. ^{1}H NMR (400 MHz, CD_3OD): δ = 0.68 (m, 3H; CH_3 (C1)), 0.69 (m, 1H; CH_2), 1.75 (d, $^3J_{HH}$ = 7.0 Hz, 3H; CH_3 (C11)), 1.85 (m, 1H; CH_2), 3.48 (q, $^3J_{HH}$ = 7.0 Hz, 1H; CH (C12)), 6.97 (t, J_{HF} = 2.1 Hz, 1H; CH (C5)), 7.43 (s, 1H; CH (C7)), 7.59 (s, 1H; CH (C15)), 7.93 ppm (s, 1H; CH (C17)); ^{13}C NMR (150 MHz, CD_3OD): δ = 7.51 (C1), 10.87 (C11), 29.81 (C2), 45.62 (C12), 76.71 (C18), 77.42 (C8), 94.26 (C3), 114.32 (C19), 114.56 (m, C25), 114.84 (C10), 115.51 (C20), 116.38 (C9), 118.70 (C14), 121.31 (C27), 124.40 (C5), 126.45 (m, C21), 127.74 (C15), 134.11 (C4), 140.41 (m, C24), 141.23 (C7), 144.73 (C17), 146.80 (C16), 154.80 (C6), 161.05 ppm (C13); ^{19}F NMR (376 MHz, CD_3OD): δ = -108.70 (d, *J* = 251.8 Hz, 1F), -108.93 (d, *J* = 253.2 Hz, 1F), -118.72 (d, *J* = 251.9 Hz, 1F), -118.88 ppm (d, *J* = 252.8 Hz; 1F); IR: υ = 2197 (CN) cm^{-1}; MS (MALDI-TOF, neg. mode): 541 [M-H]; HRMS (ESI, neg. mode) calcd for $C_{28}H_{14}F_4N_6O_2$: 541.1031 [M-H], found: 541.1078.



8a-Ethyl-1,1,2,2-tetrafluoro-3-hydroxy-8-methyl-5a,10a-bisphenylethynyl-1,2,8,8a-tetrahydroazuleno[5,4-b:7,8-b']dibenzothiophene 7,7,9,9-tetraoxide (7-BTSO2Et-PhCC-OH (**22**)**):** Diiodo DAE **21** (44 mg, 0.054 mmol), phenyl acetylene (22 mg, 0.20 mmol, 0.023 ml) and triethylamine (0.1 ml, 0.72 mmol) were dissolved in THF (5 ml), and the solution was degassed. $Pd(amphos)_2Cl_2$ (7.6 mg, 0.011 mmol) and CuI (1 mg, 0.005 mmol) were added, and the reaction mixture was stirred overnight under nitrogen at 50ºC. Volatiles were removed in vacuo, and the remaining brown oil was purified by column chromatography on silica gel using dichloromethane, EtOAc and EtOAc/acetone 10:1 subsequently as eluents. The only isolated product was enol 7-BTSO2Et-PhCC-OH (**22**) (21 mg, 52%); none of the starting material diiodo DAE **21** was recovered. ^{1}H NMR (600 MHz, acetone-*d6*): δ = 0.59 (t, $^3J_{HH}$ = 7.5 Hz, 3H; CH_3 (C1)), 1.93 (d, $^3J_{HH}$ = 7.2 Hz, 3H; CH_3 (C17)), 2.19 (dq, $^2J_{HH}$ = 14.9, $^3J_{HH}$ = 7.4 Hz, 1H; CH_2 (C2)), 2.36 (dq, $^2J_{HH}$ = 15.2, $^3J_{HH}$ = 7.6 Hz, 1H; CH_2 (C2)), 3.87 (q, $^3J_{HH}$ = 7.2 Hz, 1H; CH (C18)), 7.44 (m, 6H; CH (C15, C16, C31 and C32)), 7.61 (m, 4H; CH (C14 and C30), 7.69 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.6 Hz, 1H; CH (C7)), 7.70 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 1.6 Hz, 1H; CH (C23)), 7.71 (d, $^4J_{HH}$ = 1.6 Hz, 1H; CH (C9)), 7.76 (d, $^4J_{HH}$ = 1.5 Hz, 1H; CH (C25)), 7.80 (dd, $^3J_{HH}$ = 8.3, J_{HF} = 4.9 Hz, 1H; CH (C6)), 7.83 ppm (d, $^3J_{HH}$ = 8.0 Hz, 1H; CH (C22)); ^{13}C NMR (150 MHz, acetone-*d6*): δ = 10.00 (C17), 11.61 (C1), 28.29 (C2), 37.66 (C18), 78.90 (C3), 88,78 (C27), 88.92 (C11), 91.66 and 92.59 (C12 and C28), 103.42 (C37), 111.45 (C4), 121.99 (C8), 122.69 (C25), 123.49 and 123.66 (C13 and C29), 124.23 (C9), 124.72 (C24), 127.64 (m, C6), 128.57 (C22), 129.48 and 129.50 (C15 and C31), 129.62 and 129.80 (C16 and C32), 131.83 (C21), 132.44 and 132.52 (C14 and C30), 134.34 (br, C19), 135.89 (t, $^2J_{CF}$ = 20 Hz; C33), 135.99 (C7), 136.18 (C23), 136.90 (C10), 138.52 (C20), 139.42 (C26), 140.77 (C5), 172.34 ppm (t, $^2J_{CF}$ = 21 Hz; C36); signals of C34 and C35 mix with noise background; ^{19}F NMR (376 MHz, acetone-*d6*): δ = -94.80 (d, *J* = 242 Hz, 1F), -117.87 (d, *J* = 262 Hz, 1F), -124.32 (d, *J* = 242 Hz, 1F), -134.29 ppm (d, *J* = 262 Hz, 1F); IR: υ = 3490 (br), 2965, 1549, 1285 cm^{-1}; HRMS (ESI, neg. mode) calcd for $C_{41}H_{26}F_4O_5S_2$ [M-H]: 737.1074, found: 737.1100.

1,1,2,2,3-pentafluoro-7a-methyl-5,9-bis((E)-4-(methylthio)styryl)-1,2,7,7a-tetrahydroazuleno[5,4-b:7,8-b']difuran (7-4SMe (**23**)**):** 4-Methylthiobenzyltriphenylphosphonium bromide (670 mg, 1.4 mmol) was suspended in dry methanol (50 ml) containing MeONa (170 mg, 3.1 mmol). After stirring for 15 min, C5F-CHO (**6**) (250 mg, 0.64 mmol) was added, and the reaction mixture was stirred overnight at r.t. The reaction mixture was neutralized with aqueous ammonium chloride and concentrated in vacuo. The oily residue was mixed with dichloromethane (150 ml) and water (50 ml). Organic phase was separated, dried over $MgSO_4$, and the volatiles were removed. The remaining dark-blue solid was collected to provide DAE C5F-4SMe (**24**) (170 mg, 41%). The greenish residue in the flask was dissolved in dichloromethane and filtered through a short column filled with silica with dichloromethane as eluent. 7-4-SMe (**23**) was collected in milligram quantities from several batches of C5F-4-SMe (**24**) synthesis as greenish solid.[2] ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.47 (s, 3H; CH_3 (C1)), 2.51 (broad s, 6H; CH_3 (C12 and C24)), 3.40 (d, $^2J_{HH}$ = 15.7 Hz, 1H; CH_2 (C13)), 3.52 (d, $^2J_{HH}$ = 15.8 Hz, 1H; CH_2 (C13)), 6.08 (br, 1H; CH (C4)), 6.68 (d, $^3J_{HH}$ = 16.0

Hz, 1H; CH (C6)), 6.74 (d, J_{HF} = 2.7 Hz, 1H; CH (C16)), 6.82 (d, $^3J_{HH}$ = 16.2 Hz, 1H; CH (C18)), 7.05 (d, $^3J_{HH}$ = 16.2 Hz, 1H; CH (C19)), 7.15 (d, $^3J_{HH}$ = 15.8 Hz, 1H; CH (C7)), 7.24 (d, $^3J_{HH}$ = 8.3 Hz, 2H; CH (C10)), 7.25 (d, $^3J_{HH}$ = 8.3 Hz, 2H; CH (C22)), 7.41 (d, $^3J_{HH}$ = 8.3 Hz, 2H; CH (C21)), 7.42 ppm (d, $^3J_{HH}$ = 8.3 Hz, 2H; CH (C9)); carbon shift values were assigned using data from HSQC and HMBC spectra: δ = 15.5 (C12 and C24), 26.3 (C1), 37.9 (C13), 86.5 (C2), 103.3 (C4), 108.3 (C16), 112.3 (C15), 114.9 (C18), 115.1 (C6), 126.2 (C10), 126.8 (C21), 127.2 (C22), 127.6 (C9), 128.3 (C19), 132.3 (C8), 133.3 (C20), 135.1 (C7), 138.5 (C23), 140.2 (C11), 150.6 (C3), 150.7 (C14), 152.9 (C17), 163.4 ppm (C5); ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.66 (d, J = 248 Hz, 1F), -114.51 (dd, J = 253, 16.8 Hz, 1F), -116.11 (d, J = 248 Hz, 1F), -122.31 (dd, J = 253, 13.6 Hz, 1F), -145.05 ppm (dd, J = 16.7, 13.6 Hz; 1F); MS (FAB): 612 [M+].

(C) Crystallographic Data

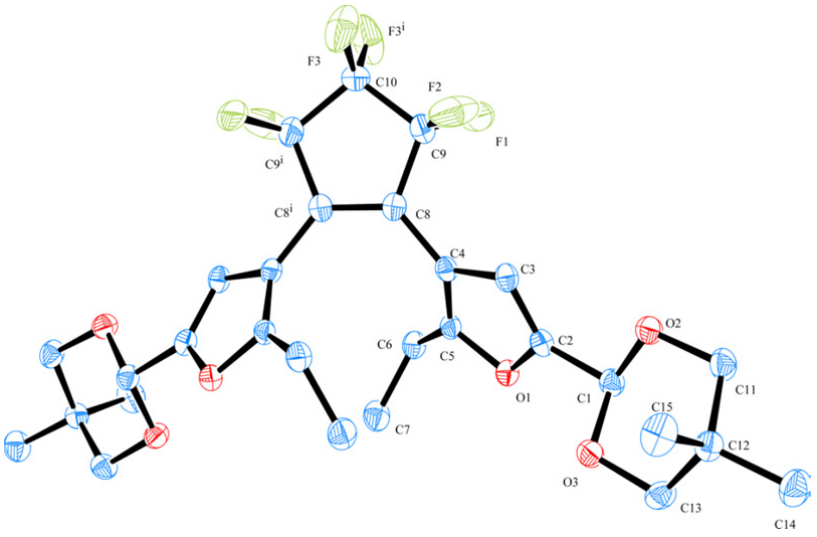


Figure S1. ORTEP of **C5F-Et-NPA** with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.

Table S1. Crystal data and structure refinement parameters for **C5F-Et-NPA**

	C5F-Et-NPA (CCDC 1037923)	
Empirical formula	$C_{29}H_{34}F_6O_6$	
Formula weight	592.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 21.3540(16) Å	α= 90°
	b = 12.3394(10) Å	β= 101.844(6)°
	c = 10.9586(8) Å	γ = 90°
Volume	2826.1(4) Å^3	
Z	4	
Density (calculated)	1.393 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	1240	
Crystal size	0.400 x 0.400 x 0.400 mm^3	
Theta range for data collection	1.917 to 25.767°.	
Index ranges	-25<=h<=25, -15<=k<=14, -13<=l<=13	
Reflections collected	17707	
Independent reflections	2669 [R(int) = 0.1355]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Integration	
Max. and min. transmission	0.9829 and 0.9680	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2669 / 0 / 186	
Goodness-of-fit on F^2	0.953	
Final R indices [I>2sigma(I)]	R_1 = 0.0551, wR_2 = 0.1111	
R indices (all data)	R_1 = 0.0975, wR_2 = 0.1255	
Largest diff. peak and hole	0.201 and -0.384 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **C5F-Et-NPA**.

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

	x	y	z	U(eq)
C(1)	1871(1)	6781(2)	575(2)	22(1)
C(2)	1403(1)	7329(2)	-429(2)	20(1)
C(3)	1084(1)	8269(2)	-448(2)	20(1)
C(4)	715(1)	8393(2)	-1693(2)	19(1)
C(5)	847(1)	7522(2)	-2356(2)	20(1)
C(6)	681(1)	7211(2)	-3697(2)	23(1)
C(7)	342(1)	6126(2)	-3985(3)	30(1)
C(8)	298(1)	9313(2)	-2148(2)	21(1)
C(9)	526(1)	10437(2)	-1819(3)	31(1)
C(10)	0	11200(3)	-2500	24(1)
C(11)	2480(1)	7092(2)	2569(2)	28(1)
C(12)	2232(1)	6053(2)	3056(2)	23(1)
C(13)	2034(1)	5309(2)	1940(2)	26(1)
C(14)	2779(1)	5532(3)	3994(3)	33(1)
C(15)	1661(1)	6294(3)	3658(3)	35(1)
F(1)	1088(1)	10649(2)	-2157(3)	72(1)
F(2)	635(1)	10618(2)	-576(2)	70(1)
F(3)	-216(1)	11838(2)	-1703(2)	59(1)
O(1)	1269(1)	6849(1)	-1588(2)	21(1)
O(2)	2026(1)	7540(1)	1542(2)	25(1)
O(3)	1592(1)	5835(2)	946(2)	25(1)

Table S3. Bond lengths [Å] and angles [°] for **C5F-Et-NPA**

C(1)-O(2)	1.402(3)	C(5)-C(6)	1.489(3)	C(10)-C(9)#1	1.536(4)
C(1)-O(3)	1.409(3)	C(6)-C(7)	1.525(4)	C(11)-O(2)	1.437(3)
C(1)-C(2)	1.489(3)	C(8)-C(8)#1	1.347(5)	C(11)-C(12)	1.524(4)
C(2)-C(3)	1.343(4)	C(8)-C(9)	1.490(4)	C(12)-C(13)	1.518(4)
C(2)-O(1)	1.377(3)	C(9)-F(2)	1.352(3)	C(12)-C(15)	1.530(4)
C(3)-C(4)	1.437(3)	C(9)-F(1)	1.353(3)	C(12)-C(14)	1.531(4)
C(4)-C(5)	1.359(3)	C(9)-C(10)	1.536(4)	C(13)-O(3)	1.440(3)
C(4)-C(8)	1.465(3)	C(10)-F(3)	1.327(3)		
C(5)-O(1)	1.378(3)	C(10)-F(3)#1	1.327(3)		

O(2)-C(1)-O(3)	112.55(19)	F(2)-C(9)-C(10)	110.2(2)
O(2)-C(1)-C(2)	105.9(2)	F(1)-C(9)-C(10)	110.5(2)
O(3)-C(1)-C(2)	109.22(19)	C(8)-C(9)-C(10)	106.5(2)
C(3)-C(2)-O(1)	110.4(2)	F(3)-C(10)-F(3)#1	107.2(3)
C(3)-C(2)-C(1)	131.7(2)	F(3)-C(10)-C(9)	111.24(13)
O(1)-C(2)-C(1)	117.9(2)	F(3)#1-C(10)-C(9)	111.41(14)
C(2)-C(3)-C(4)	106.5(2)	F(3)-C(10)-C(9)#1	111.41(14)
C(5)-C(4)-C(3)	106.8(2)	F(3)#1-C(10)-C(9)#1	111.24(13)
C(5)-C(4)-C(8)	127.5(2)	C(9)-C(10)-C(9)#1	104.4(3)
C(3)-C(4)-C(8)	125.6(2)	O(2)-C(11)-C(12)	111.8(2)
C(4)-C(5)-O(1)	109.4(2)	C(13)-C(12)-C(11)	106.6(2)
C(4)-C(5)-C(6)	134.3(2)	C(13)-C(12)-C(15)	110.5(2)
O(1)-C(5)-C(6)	116.1(2)	C(11)-C(12)-C(15)	110.6(2)
C(5)-C(6)-C(7)	115.9(2)	C(13)-C(12)-C(14)	109.6(2)
C(8)#1-C(8)-C(4)	129.17(13)	C(11)-C(12)-C(14)	108.4(2)
C(8)#1-C(8)-C(9)	111.23(14)	C(15)-C(12)-C(14)	111.0(2)
C(4)-C(8)-C(9)	119.6(2)	O(3)-C(13)-C(12)	111.6(2)
F(2)-C(9)-F(1)	105.4(2)	C(2)-O(1)-C(5)	106.85(19)
F(2)-C(9)-C(8)	112.2(2)	C(1)-O(2)-C(11)	110.6(2)
F(1)-C(9)-C(8)	112.2(2)	C(1)-O(3)-C(13)	109.96(18)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z-1/2

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **C5F-Et-NPA**.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^*2U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U11	U22	U33	U23	U13	U12
C(1)	19(1)	24(1)	23(1)	1(1)	5(1)	-1(1)
C(2)	18(1)	25(1)	18(1)	-1(1)	4(1)	-3(1)
C(3)	17(1)	26(2)	18(1)	-2(1)	4(1)	-1(1)
C(4)	15(1)	22(1)	20(1)	1(1)	5(1)	-3(1)
C(5)	15(1)	21(1)	22(1)	2(1)	3(1)	-1(1)
C(6)	21(1)	29(2)	20(1)	0(1)	4(1)	1(1)
C(7)	28(1)	34(2)	28(2)	-11(1)	1(1)	2(1)
C(8)	19(1)	27(2)	18(1)	0(1)	6(1)	1(1)
C(9)	23(1)	30(2)	37(2)	-6(1)	-1(1)	-2(1)
C(10)	27(2)	22(2)	24(2)	0	7(2)	0
C(11)	25(1)	32(2)	24(1)	4(1)	-2(1)	-4(1)
C(12)	22(1)	27(2)	21(1)	4(1)	5(1)	0(1)
C(13)	28(1)	24(2)	26(1)	7(1)	7(1)	2(1)
C(14)	31(1)	39(2)	26(2)	7(1)	1(1)	2(1)
C(15)	34(2)	49(2)	25(2)	3(1)	12(1)	6(1)
F(1)	21(1)	30(1)	168(2)	4(1)	27(1)	-4(1)
F(2)	115(2)	32(1)	40(1)	-14(1)	-38(1)	19(1)
F(3)	42(1)	81(2)	48(1)	-36(1)	-5(1)	28(1)
O(1)	18(1)	23(1)	20(1)	-1(1)	4(1)	1(1)
O(2)	27(1)	24(1)	21(1)	2(1)	-2(1)	-2(1)
O(3)	25(1)	24(1)	24(1)	4(1)	0(1)	-4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **C5F-Et-NPA**.

	x	y	z	U(eq)
H(1)	2256	6591	265	26
H(3)	1099	8745	214	24
H(6A)	1073	7194	-4016	28
H(6B)	411	7773	-4147	28
H(7A)	256	6002	-4869	46
H(7B)	-53	6136	-3697	46
H(7C)	610	5556	-3571	46
H(11A)	2570	7620	3238	33
H(11B)	2877	6939	2303	33
H(13A)	2411	5087	1639	31
H(13B)	1835	4664	2195	31
H(14A)	2903	6003	4699	50
H(14B)	3138	5416	3606	50
H(14C)	2639	4851	4266	50
H(15A)	1793	6768	4358	53
H(15B)	1502	5629	3934	53
H(15C)	1329	6637	3059	53

Table S6. Torsion angles [°] for **C5F-Et-NPA**.

O(2)-C(1)-C(2)-C(3)	-10.0(3)	F(1)-C(9)-C(10)-F(3)	-116.3(2)
O(3)-C(1)-C(2)-C(3)	111.4(3)	C(8)-C(9)-C(10)-F(3)	121.6(2)
O(2)-C(1)-C(2)-O(1)	166.99(18)	F(2)-C(9)-C(10)-F(3)#1	119.3(3)
O(3)-C(1)-C(2)-O(1)	-71.6(3)	F(1)-C(9)-C(10)-F(3)#1	3.3(3)
O(1)-C(2)-C(3)-C(4)	0.8(3)	C(8)-C(9)-C(10)-F(3)#1	-118.8(2)
C(1)-C(2)-C(3)-C(4)	178.0(2)	F(2)-C(9)-C(10)-C(9)#1	-120.5(2)
C(2)-C(3)-C(4)-C(5)	-1.3(3)	F(1)-C(9)-C(10)-C(9)#1	123.4(2)
C(2)-C(3)-C(4)-C(8)	-179.1(2)	C(8)-C(9)-C(10)-C(9)#1	1.35(11)
C(3)-C(4)-C(5)-O(1)	1.2(2)	O(2)-C(11)-C(12)-C(13)	52.9(3)
C(8)-C(4)-C(5)-O(1)	179.0(2)	O(2)-C(11)-C(12)-C(15)	-67.2(3)
C(3)-C(4)-C(5)-C(6)	-172.8(2)	O(2)-C(11)-C(12)-C(14)	170.9(2)
C(8)-C(4)-C(5)-C(6)	5.0(4)	C(11)-C(12)-C(13)-O(3)	-53.7(3)
C(4)-C(5)-C(6)-C(7)	-123.8(3)	C(15)-C(12)-C(13)-O(3)	66.6(3)
O(1)-C(5)-C(6)-C(7)	62.5(3)	C(14)-C(12)-C(13)-O(3)	-170.9(2)
C(5)-C(4)-C(8)-C(8)#1	47.6(5)	C(3)-C(2)-O(1)-C(5)	-0.1(2)
C(3)-C(4)-C(8)-C(8)#1	-135.0(3)	C(1)-C(2)-O(1)-C(5)	-177.7(2)
C(5)-C(4)-C(8)-C(9)	-133.1(3)	C(4)-C(5)-O(1)-C(2)	-0.8(2)
C(3)-C(4)-C(8)-C(9)	44.3(3)	C(6)-C(5)-O(1)-C(2)	174.52(19)
C(8)#1-C(8)-C(9)-F(2)	116.7(3)	O(3)-C(1)-O(2)-C(11)	60.7(2)
C(4)-C(8)-C(9)-F(2)	-62.8(3)	C(2)-C(1)-O(2)-C(11)	179.97(18)
C(8)#1-C(8)-C(9)-F(1)	-125.0(3)	C(12)-C(11)-O(2)-C(1)	-57.0(3)
C(4)-C(8)-C(9)-F(1)	55.6(3)	O(2)-C(1)-O(3)-C(13)	-61.2(2)
C(8)#1-C(8)-C(9)-C(10)	-4.0(3)	C(2)-C(1)-O(3)-C(13)	-178.6(2)
C(4)-C(8)-C(9)-C(10)	176.60(18)	C(12)-C(13)-O(3)-C(1)	58.4(2)
F(2)-C(9)-C(10)-F(3)	-0.2(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z-1/2

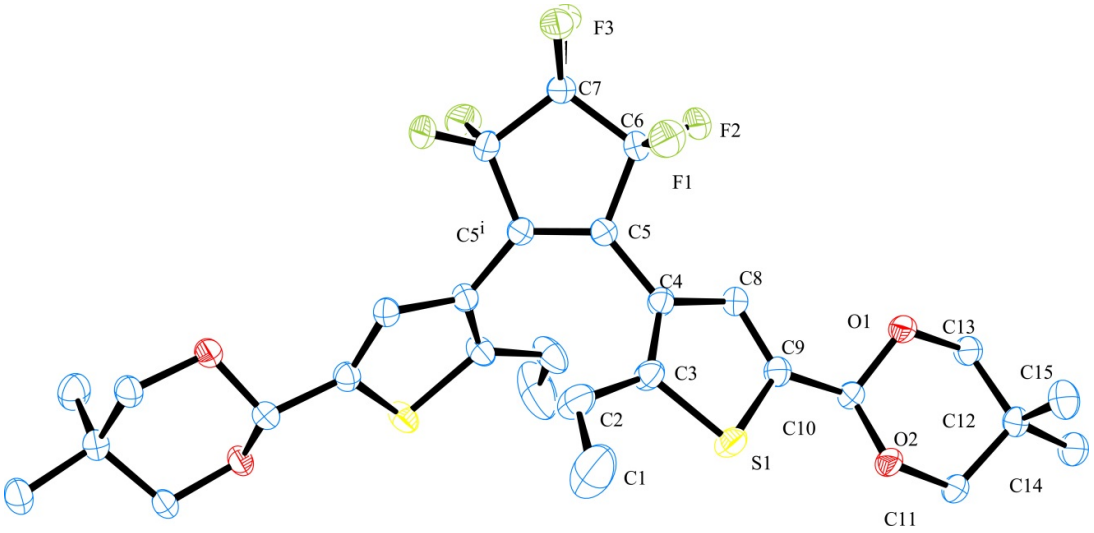


Figure S2. ORTEP of **C5F-T-Et-NPA** with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.

Table S7. Crystal data and structure refinement parameters for **C5F-T-Et-NPA**

	C5F-T-Et-NPA (CCDC 1946677)
Empirical formula	$C_{29}\,H_{34}\,F_6\,O_4\,S_2$
Formula weight	624.68
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P b c n
Unit cell dimensions	a = 25.3473(19) Å α= 90°
	b = 11.0250(8) Å β= 90°
	c = 10.6805(11) Å γ = 90°
Volume	2984.7(4) $Å^3$
Z	4
Density (calculated)	1.390 Mg/m^3
Absorption coefficient	0.25 mm^{-1}
F(000)	1304
Crystal size	0.480 x 0.433 x 0.390 mm^3
Theta range for data collection	1.607 to 26.830°.
Index ranges	-31<=h<=32, -13<=k<=13, -13<=l<=13
Reflections collected	41581
Independent reflections	3180 [R(int) = 0.0881]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Integration
Max. and min. transmission	0.9345 and 0.8507
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3180 / 0 / 217
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R_1 = 0. 0414, wR_2 = 0.1106
R indices (all data)	R_1 = 0. 0482, wR_2 = 0.1145
Largest diff. peak and hole	1.091 and -0.464 $e.Å^{-3}$

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **C5F-T-Et-NPA**.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4340(1)	8890(3)	5104(3)	73(1)
C(2)	4609(1)	8117(2)	4176(2)	39(1)
C(3)	4327(1)	7895(2)	2963(2)	26(1)
C(4)	4380(1)	6947(2)	2136(2)	22(1)
C(5)	4745(1)	5929(2)	2313(2)	22(1)
C(6)	4552(1)	4663(2)	2107(2)	42(1)
C(7)	5000	3834(2)	2500	24(1)
C(8)	4036(1)	7052(2)	1076(2)	22(1)
C(9)	3736(1)	8070(2)	1108(2)	23(1)
C(10)	3364(1)	8541(2)	135(2)	23(1)
C(11)	2690(1)	9931(2)	-222(2)	25(1)
C(12)	2363(1)	8966(2)	-890(2)	25(1)
C(13)	2748(1)	8012(2)	-1376(2)	26(1)
C(14)	2080(1)	9559(2)	-1995(2)	33(1)
C(15)	1964(1)	8396(2)	6(2)	35(1)
O(1)	3083(1)	7565(1)	-384(1)	25(1)
O(2)	3030(1)	9399(1)	707(1)	25(1)
S(1)	3858(1)	8908(1)	2436(1)	27(1)
F(1)	4169(1)	4422(2)	3212(3)	38(1)
F(2)	4283(1)	4394(2)	1204(3)	37(1)
F(3)	5092(1)	2842(3)	1824(3)	35(1)
F(4)	4084(1)	4409(2)	2297(3)	37(1)
F(5)	4578(2)	4513(2)	652(3)	35(1)
F(6)	5196(1)	3456(4)	1371(3)	37(1)

Table S9. Bond lengths [Å] and angles [°] for **C5F-T-Et-NPA**.

C(1)-C(2)	1.475(3)	C(6)-C(7)	1.517(2)	C(9)-S(1)	1.7209(17)
C(2)-C(3)	1.500(2)	C(6)-F(1)	1.551(4)	C(10)-O(1)	1.404(2)
C(3)-C(4)	1.376(2)	C(6)-F(5)	1.564(4)	C(10)-O(2)	1.408(2)
C(3)-S(1)	1.7254(17)	C(7)-F(3)#1	1.331(3)	C(11)-O(2)	1.4405(19)
C(4)-C(8)	1.434(2)	C(7)-F(3)	1.331(3)	C(11)-C(12)	1.525(2)
C(4)-C(5)	1.466(2)	C(7)-F(6)	1.369(3)	C(12)-C(13)	1.525(2)
C(5)-C(5)#1	1.355(3)	C(7)-F(6)#1	1.369(3)	C(12)-C(15)	1.527(2)
C(5)-C(6)	1.495(2)	C(7)-C(6)#1	1.517(2)	C(12)-C(14)	1.528(2)
C(6)-F(2)	1.217(3)	C(8)-C(9)	1.355(2)	C(13)-O(1)	1.445(2)
C(6)-F(4)	1.234(3)	C(9)-C(10)	1.496(2)	F(3)-F(3)#1	1.516(7)

C(1)-C(2)-C(3)	116.94(18)	F(6)#1-C(7)-C(6)	98.94(18)
C(4)-C(3)-C(2)	129.16(16)	F(3)#1-C(7)-C(6)#1	118.40(14)
C(4)-C(3)-S(1)	110.48(13)	F(3)-C(7)-C(6)#1	120.97(16)
C(2)-C(3)-S(1)	120.36(13)	F(6)-C(7)-C(6)#1	98.94(18)
C(3)-C(4)-C(8)	112.67(15)	F(6)#1-C(7)-C(6)#1	102.22(17)
C(3)-C(4)-C(5)	124.11(15)	C(6)-C(7)-C(6)#1	105.9(2)
C(8)-C(4)-C(5)	123.23(15)	C(9)-C(8)-C(4)	112.88(15)
C(5)#1-C(5)-C(4)	129.82(9)	C(8)-C(9)-C(10)	128.55(15)
C(5)#1-C(5)-C(6)	110.85(10)	C(8)-C(9)-S(1)	111.39(13)
C(4)-C(5)-C(6)	119.31(14)	C(10)-C(9)-S(1)	119.94(12)
F(2)-C(6)-C(5)	121.8(2)	O(1)-C(10)-O(2)	112.41(13)
F(4)-C(6)-C(5)	120.1(2)	O(1)-C(10)-C(9)	109.12(13)
F(2)-C(6)-C(7)	119.5(2)	O(2)-C(10)-C(9)	108.09(13)
F(4)-C(6)-C(7)	122.4(2)	O(2)-C(11)-C(12)	111.27(13)
C(5)-C(6)-C(7)	106.06(15)	C(13)-C(12)-C(11)	107.04(14)
F(2)-C(6)-F(1)	102.2(2)	C(13)-C(12)-C(15)	110.69(15)
C(5)-C(6)-F(1)	104.63(19)	C(11)-C(12)-C(15)	110.67(15)
C(7)-C(6)-F(1)	98.86(18)	C(13)-C(12)-C(14)	109.41(15)
F(4)-C(6)-F(5)	100.4(2)	C(11)-C(12)-C(14)	108.48(14)
C(5)-C(6)-F(5)	103.37(19)	C(15)-C(12)-C(14)	110.45(15)
C(7)-C(6)-F(5)	100.30(17)	O(1)-C(13)-C(12)	111.22(14)
F(3)#1-C(7)-F(3)	69.4(4)	C(10)-O(1)-C(13)	108.99(12)
F(6)-C(7)-F(6)#1	144.5(4)	C(10)-O(2)-C(11)	109.58(12)
F(3)#1-C(7)-C(6)	120.96(16)	C(9)-S(1)-C(3)	92.57(8)
F(3)-C(7)-C(6)	118.40(14)	C(7)-F(3)-F(3)#1	55.29(19)
F(6)-C(7)-C(6)	102.22(17)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **C5F-T-Et-NPA**.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	76(2)	93(2)	50(2)	-34(2)	-27(1)	42(2)
C(2)	52(1)	37(1)	27(1)	-9(1)	-15(1)	18(1)
C(3)	29(1)	26(1)	24(1)	0(1)	-4(1)	7(1)
C(4)	21(1)	23(1)	22(1)	1(1)	-2(1)	1(1)
C(5)	22(1)	21(1)	22(1)	-1(1)	-2(1)	0(1)
C(6)	24(1)	24(1)	78(2)	-4(1)	-19(1)	-1(1)
C(7)	25(1)	21(1)	26(1)	0	-3(1)	0
C(8)	19(1)	23(1)	22(1)	0(1)	-1(1)	0(1)
C(9)	22(1)	25(1)	21(1)	1(1)	-1(1)	0(1)
C(10)	22(1)	21(1)	25(1)	1(1)	-2(1)	2(1)
C(11)	24(1)	23(1)	28(1)	2(1)	-7(1)	4(1)
C(12)	22(1)	26(1)	26(1)	1(1)	-5(1)	1(1)
C(13)	28(1)	26(1)	24(1)	-1(1)	-7(1)	2(1)
C(14)	33(1)	34(1)	32(1)	0(1)	-12(1)	4(1)
C(15)	26(1)	42(1)	37(1)	2(1)	1(1)	-5(1)
O(1)	26(1)	22(1)	26(1)	-1(1)	-6(1)	2(1)
O(2)	25(1)	24(1)	26(1)	-2(1)	-7(1)	6(1)
S(1)	32(1)	26(1)	24(1)	-2(1)	-5(1)	10(1)
F(1)	24(1)	34(1)	55(2)	8(1)	12(1)	-3(1)
F(2)	37(2)	28(1)	44(2)	-4(1)	-24(2)	-1(1)
F(3)	36(1)	23(1)	47(2)	-12(1)	-12(1)	6(1)
F(4)	18(1)	30(1)	64(3)	2(1)	-2(1)	-3(1)
F(5)	51(2)	28(1)	26(1)	-6(1)	-16(1)	6(1)
F(6)	35(1)	44(2)	32(1)	-15(1)	-3(1)	6(1)

Table S11. Torsion angles [°] for **C5F-T-Et-NPA**.

C(1)-C(2)-C(3)-C(4)	-155.8(3)	F(4)-C(6)-C(7)-F(6)#1	-39.2(4)
C(1)-C(2)-C(3)-S(1)	24.0(3)	C(5)-C(6)-C(7)-F(6)#1	104.1(2)
C(2)-C(3)-C(4)-C(8)	179.58(19)	F(1)-C(6)-C(7)-F(6)#1	-4.1(3)
S(1)-C(3)-C(4)-C(8)	-0.20(19)	F(5)-C(6)-C(7)-F(6)#1	-148.7(3)
C(2)-C(3)-C(4)-C(5)	0.1(3)	F(2)-C(6)-C(7)-C(6)#1	140.9(3)
S(1)-C(3)-C(4)-C(5)	-179.68(13)	F(4)-C(6)-C(7)-C(6)#1	-144.7(3)
C(3)-C(4)-C(5)-C(5)#1	-44.3(3)	C(5)-C(6)-C(7)-C(6)#1	-1.47(9)
C(8)-C(4)-C(5)-C(5)#1	136.2(2)	F(1)-C(6)-C(7)-C(6)#1	-109.58(18)
C(3)-C(4)-C(5)-C(6)	133.5(2)	F(5)-C(6)-C(7)-C(6)#1	105.80(19)
C(8)-C(4)-C(5)-C(6)	-45.9(3)	C(3)-C(4)-C(8)-C(9)	0.8(2)
C(5)#1-C(5)-C(6)-F(2)	-137.0(3)	C(5)-C(4)-C(8)-C(9)	-179.74(15)
C(4)-C(5)-C(6)-F(2)	44.7(4)	C(4)-C(8)-C(9)-C(10)	174.86(16)
C(5)#1-C(5)-C(6)-F(4)	148.6(3)	C(4)-C(8)-C(9)-S(1)	-0.99(18)
C(4)-C(5)-C(6)-F(4)	-29.7(4)	C(8)-C(9)-C(10)-O(1)	40.2(2)
C(5)#1-C(5)-C(6)-C(7)	4.3(3)	S(1)-C(9)-C(10)-O(1)	-144.22(12)
C(4)-C(5)-C(6)-C(7)	-173.97(14)	C(8)-C(9)-C(10)-O(2)	162.76(16)
C(5)#1-C(5)-C(6)-F(1)	108.2(2)	S(1)-C(9)-C(10)-O(2)	-21.69(18)
C(4)-C(5)-C(6)-F(1)	-70.0(2)	O(2)-C(11)-C(12)-C(13)	-52.98(18)
C(5)#1-C(5)-C(6)-F(5)	-100.8(2)	O(2)-C(11)-C(12)-C(15)	67.73(18)
C(4)-C(5)-C(6)-F(5)	81.0(2)	O(2)-C(11)-C(12)-C(14)	-170.95(14)
F(2)-C(6)-C(7)-F(3)#1	-80.6(4)	C(11)-C(12)-C(13)-O(1)	53.57(18)
F(4)-C(6)-C(7)-F(3)#1	-6.3(4)	C(15)-C(12)-C(13)-O(1)	-67.12(18)
C(5)-C(6)-C(7)-F(3)#1	137.0(2)	C(14)-C(12)-C(13)-O(1)	170.93(14)
F(1)-C(6)-C(7)-F(3)#1	28.8(3)	O(2)-C(10)-O(1)-C(13)	63.62(17)
F(5)-C(6)-C(7)-F(3)#1	-115.8(3)	C(9)-C(10)-O(1)-C(13)	-176.48(13)
F(2)-C(6)-C(7)-F(3)	1.2(3)	C(12)-C(13)-O(1)-C(10)	-58.88(17)
F(4)-C(6)-C(7)-F(3)	75.6(3)	O(1)-C(10)-O(2)-C(11)	-63.32(17)
C(5)-C(6)-C(7)-F(3)	-141.2(3)	C(9)-C(10)-O(2)-C(11)	176.18(13)
F(1)-C(6)-C(7)-F(3)	110.7(2)	C(12)-C(11)-O(2)-C(10)	57.83(18)
F(5)-C(6)-C(7)-F(3)	-33.9(3)	C(8)-C(9)-S(1)-C(3)	0.75(14)
F(2)-C(6)-C(7)-F(6)	37.8(3)	C(10)-C(9)-S(1)-C(3)	-175.51(14)
F(4)-C(6)-C(7)-F(6)	112.1(3)	C(4)-C(3)-S(1)-C(9)	-0.30(14)
C(5)-C(6)-C(7)-F(6)	-104.6(2)	C(2)-C(3)-S(1)-C(9)	179.89(17)
F(1)-C(6)-C(7)-F(6)	147.3(2)	F(6)-C(7)-F(3)-F(3)#1	172.9(3)
F(5)-C(6)-C(7)-F(6)	2.7(2)	F(6)#1-C(7)-F(3)-F(3)#1	-4.5(2)
F(2)-C(6)-C(7)-F(6)#1	-113.5(3)	C(6)-C(7)-F(3)-F(3)#1	-114.95(19)
		C(6)#1-C(7)-F(3)-F(3)#1	111.5(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,y,-z+1/2

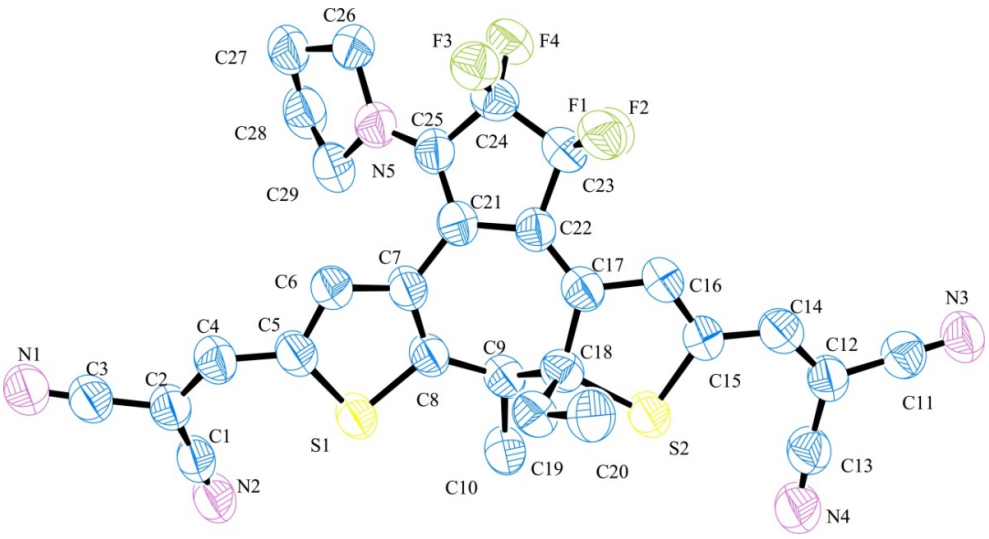


Figure S3. ORTEP of 7-T-Et-MN-pyrr (**8f**) with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.

Table S12. Crystal data and structure refinement parameters for 7-T-Et-MN-pyrr (**8f**)

	7-T-Et-MN-pyrr (**8f**) (CCDC 1037924)
Empirical formula	$C_{29}H_{21}F_4N_5S_2$
Formula weight	579.63
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P* -1
Unit cell dimensions	a = 6.3781(16) Å α= 92.61(2)° b = 13.826(4) Å β= 91.07(2)° c = 15.124(4) Å γ = 96.54(2)°
Volume	1323.2(6) $Å^3$
Z	2
Density (calculated)	1.455 Mg/m^3
Absorption coefficient	0.259 mm^{-1}
F(000)	596
Crystal size	0.400 x 0.253 x 0.150 mm^3
Theta range for data collection	1.484 to 26.290°.
Index ranges	-7<=h<=7, -16<=k<=17, -18<=l<=18
Reflections collected	14778
Independent reflections	5138 [R(int) = 0.1195]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Integration
Max. and min. transmission	0.9585 and 0.6354
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5138 / 0 / 363
Goodness-of-fit on F^2	0.846
Final R indices [I>2sigma(I)]	R_1 = 0.0559, wR_2 = 0.1127
R indices (all data)	R_1 = 0.1733, wR_2 = 0.1487
Largest diff. peak and hole	0.264 and -0.220 e.$Å^{-3}$

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 7-T-Et-MN-pyrr (**8f**).

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	10727(10)	8912(4)	4063(3)	74(1)
C(2)	8592(8)	9117(3)	4194(3)	68(1)
C(3)	7900(8)	9889(4)	3697(3)	77(1)
C(4)	7301(8)	8706(3)	4816(3)	71(1)
C(5)	7730(8)	7986(3)	5449(3)	71(1)
C(6)	6568(7)	7889(3)	6210(3)	65(1)
C(7)	7418(8)	7269(3)	6808(3)	65(1)
C(8)	9093(7)	6840(3)	6464(3)	64(1)
C(9)	10221(7)	6074(3)	6875(3)	66(1)
C(18)	8664(7)	5147(3)	7047(3)	63(1)
C(17)	7267(7)	5315(3)	7848(3)	66(1)
C(16)	7240(8)	4521(3)	8431(3)	69(1)
C(15)	8682(8)	3891(3)	8286(3)	66(1)
C(14)	9020(8)	3174(3)	8904(3)	70(1)
C(12)	10494(8)	2545(3)	8925(3)	71(1)
C(13)	12027(9)	2433(4)	8253(3)	79(1)
C(11)	10558(8)	1920(4)	9675(3)	73(1)
C(22)	6393(7)	6140(3)	8071(3)	62(1)
C(21)	6502(7)	7072(3)	7685(3)	63(1)
C(25)	5696(8)	7775(4)	8218(3)	66(1)
C(24)	4441(8)	7259(4)	8936(3)	70(1)
C(23)	5137(8)	6224(4)	8910(3)	68(1)
C(29)	7715(8)	9305(3)	7773(3)	79(1)
C(28)	7975(10)	10259(4)	8285(3)	92(2)
C(27)	5751(11)	10410(4)	8504(3)	95(2)
C(26)	4751(9)	9402(3)	8742(3)	86(2)
C(10)	12158(7)	5840(3)	6343(3)	74(1)
C(19)	7359(7)	4796(3)	6203(3)	67(1)
C(20)	5815(8)	3878(3)	6274(3)	76(1)
F(4)	4709(4)	7689(2)	9756(2)	76(1)
F(3)	2322(5)	7210(2)	8755(2)	79(1)
F(1)	3451(5)	5542(2)	8955(2)	79(1)
F(2)	6342(4)	6144(2)	9654(2)	80(1)
N(2)	12441(8)	8781(3)	3962(3)	90(1)
N(1)	7389(7)	10540(3)	3328(3)	86(1)
N(4)	13220(8)	2293(3)	7729(3)	105(2)
N(3)	10605(7)	1427(3)	10260(3)	85(1)
N(5)	5920(6)	8739(3)	8201(2)	71(1)
S(1)	9736(2)	7262(1)	5430(1)	70(1)
S(2)	10234(2)	4152(1)	7361(1)	72(1)

Table S14. Bond lengths [Å] and angles [°] for 7-T-Et-MN-pyrr (**8f**)

C(1)-N(2)	1.140(6)	C(18)-C(19)	1.539(6)	C(21)-C(25)	1.384(6)
C(1)-C(2)	1.437(7)	C(18)-C(17)	1.541(6)	C(25)-N(5)	1.325(5)
C(2)-C(4)	1.362(6)	C(18)-S(2)	1.864(4)	C(25)-C(24)	1.517(6)
C(2)-C(3)	1.438(7)	C(17)-C(22)	1.358(6)	C(24)-F(4)	1.349(5)
C(3)-N(1)	1.155(5)	C(17)-C(16)	1.438(6)	C(24)-F(3)	1.367(5)
C(4)-C(5)	1.457(6)	C(16)-C(15)	1.351(6)	C(24)-C(23)	1.545(6)
C(5)-C(6)	1.384(5)	C(15)-C(14)	1.425(6)	C(23)-F(1)	1.352(5)
C(5)-S(1)	1.712(5)	C(15)-S(2)	1.756(4)	C(23)-F(2)	1.367(5)
C(6)-C(7)	1.416(6)	C(14)-C(12)	1.352(6)	C(29)-N(5)	1.487(6)
C(7)-C(8)	1.379(6)	C(12)-C(13)	1.439(7)	C(29)-C(28)	1.489(6)
C(7)-C(21)	1.483(6)	C(12)-C(11)	1.459(6)	C(28)-C(27)	1.498(7)
C(8)-C(9)	1.496(6)	C(13)-N(4)	1.135(5)	C(27)-C(26)	1.527(7)
C(8)-S(1)	1.734(4)	C(11)-N(3)	1.143(5)	C(26)-N(5)	1.476(5)
C(9)-C(10)	1.544(6)	C(22)-C(21)	1.433(6)	C(19)-C(20)	1.525(6)
C(9)-C(18)	1.565(6)	C(22)-C(23)	1.521(6)		

N(2)-C(1)-C(2)	177.8(6)	C(15)-C(16)-C(17)	116.5(4)
C(4)-C(2)-C(1)	124.4(4)	C(16)-C(15)-C(14)	121.1(4)
C(4)-C(2)-C(3)	118.9(4)	C(16)-C(15)-S(2)	113.3(3)
C(1)-C(2)-C(3)	116.3(4)	C(14)-C(15)-S(2)	125.2(4)
N(1)-C(3)-C(2)	176.8(6)	C(12)-C(14)-C(15)	130.2(4)
C(2)-C(4)-C(5)	128.7(4)	C(14)-C(12)-C(13)	124.8(4)
C(6)-C(5)-C(4)	120.3(4)	C(14)-C(12)-C(11)	118.8(4)
C(6)-C(5)-S(1)	112.0(3)	C(13)-C(12)-C(11)	116.4(4)
C(4)-C(5)-S(1)	127.4(3)	N(4)-C(13)-C(12)	176.3(5)
C(5)-C(6)-C(7)	112.2(4)	N(3)-C(11)-C(12)	179.8(6)
C(8)-C(7)-C(6)	112.6(4)	C(17)-C(22)-C(21)	132.4(4)
C(8)-C(7)-C(21)	124.6(4)	C(17)-C(22)-C(23)	121.2(4)
C(6)-C(7)-C(21)	122.7(4)	C(21)-C(22)-C(23)	106.3(4)
C(7)-C(8)-C(9)	126.9(4)	C(25)-C(21)-C(22)	113.4(4)
C(7)-C(8)-S(1)	111.3(3)	C(25)-C(21)-C(7)	123.2(4)
C(9)-C(8)-S(1)	121.8(3)	C(22)-C(21)-C(7)	123.4(4)
C(8)-C(9)-C(10)	112.2(3)	N(5)-C(25)-C(21)	131.4(4)
C(8)-C(9)-C(18)	111.2(4)	N(5)-C(25)-C(24)	120.8(4)
C(10)-C(9)-C(18)	112.9(4)	C(21)-C(25)-C(24)	107.8(4)
C(19)-C(18)-C(17)	112.5(4)	F(4)-C(24)-F(3)	104.9(4)
C(19)-C(18)-C(9)	110.7(3)	F(4)-C(24)-C(25)	115.5(4)
C(17)-C(18)-C(9)	111.7(3)	F(3)-C(24)-C(25)	110.8(4)
C(19)-C(18)-S(2)	108.0(3)	F(4)-C(24)-C(23)	111.2(4)
C(17)-C(18)-S(2)	105.1(3)	F(3)-C(24)-C(23)	110.1(4)
C(9)-C(18)-S(2)	108.6(3)	C(25)-C(24)-C(23)	104.5(4)
C(22)-C(17)-C(16)	121.9(4)	F(1)-C(23)-F(2)	105.9(4)
C(22)-C(17)-C(18)	126.8(4)	F(1)-C(23)-C(22)	114.4(4)
C(16)-C(17)-C(18)	110.7(4)	F(2)-C(23)-C(22)	112.0(4)

F(1)-C(23)-C(24)	110.9(4)	C(20)-C(19)-C(18)	116.1(4)
F(2)-C(23)-C(24)	107.9(4)	C(25)-N(5)-C(26)	125.7(4)
C(22)-C(23)-C(24)	105.7(4)	C(25)-N(5)-C(29)	123.2(4)
N(5)-C(29)-C(28)	103.9(4)	C(26)-N(5)-C(29)	109.9(4)
C(29)-C(28)-C(27)	102.9(5)	C(5)-S(1)-C(8)	91.6(2)
C(28)-C(27)-C(26)	104.0(4)	C(15)-S(2)-C(18)	92.3(2)
N(5)-C(26)-C(27)	103.0(4)		

Symmetry transformations used to generate equivalent atoms:

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 7-T-Et-MN-pyrr (**8f**).

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	81(4)	77(3)	66(3)	24(2)	8(3)	16(3)
C(2)	68(4)	75(3)	63(3)	14(2)	2(3)	11(3)
C(3)	70(4)	93(4)	70(3)	19(3)	6(3)	15(3)
C(4)	68(3)	83(3)	64(3)	16(2)	-2(2)	10(3)
C(5)	78(4)	76(3)	59(3)	14(2)	6(3)	8(3)
C(6)	67(3)	66(3)	63(3)	9(2)	6(2)	9(2)
C(7)	68(3)	68(3)	60(3)	16(2)	5(2)	9(3)
C(8)	65(3)	72(3)	55(2)	12(2)	3(2)	10(3)
C(9)	64(3)	75(3)	58(2)	10(2)	3(2)	8(3)
C(18)	62(3)	65(3)	60(3)	3(2)	4(2)	0(2)
C(17)	66(3)	73(3)	59(3)	9(2)	2(2)	8(3)
C(16)	78(4)	70(3)	59(3)	14(2)	10(2)	7(3)
C(15)	72(3)	65(3)	62(3)	12(2)	6(2)	7(3)
C(14)	75(4)	70(3)	62(3)	3(2)	4(2)	-1(3)
C(12)	76(4)	71(3)	69(3)	16(2)	6(3)	13(3)
C(13)	76(4)	83(4)	82(3)	19(3)	8(3)	20(3)
C(11)	67(3)	79(3)	74(3)	10(3)	-2(3)	12(3)
C(22)	61(3)	64(3)	61(3)	11(2)	2(2)	10(2)
C(21)	65(3)	66(3)	59(3)	8(2)	-2(2)	7(2)
C(25)	76(3)	62(3)	62(3)	10(2)	-2(2)	11(3)
C(24)	62(4)	85(4)	61(3)	2(3)	1(2)	9(3)
C(23)	67(4)	80(4)	58(3)	11(2)	6(3)	3(3)
C(29)	92(4)	76(3)	67(3)	15(3)	-2(3)	1(3)
C(28)	128(6)	76(4)	70(3)	9(3)	-10(3)	4(3)
C(27)	152(6)	78(4)	59(3)	9(3)	0(3)	31(4)
C(26)	122(5)	74(3)	68(3)	8(3)	10(3)	34(3)
C(10)	67(3)	79(3)	77(3)	21(2)	2(3)	8(3)
C(19)	69(3)	72(3)	58(3)	5(2)	0(2)	3(3)
C(20)	73(4)	78(3)	76(3)	7(2)	-4(3)	8(3)
F(4)	87(2)	86(2)	54(1)	5(1)	6(1)	5(2)
F(3)	76(2)	86(2)	78(2)	10(1)	8(2)	14(2)
F(1)	77(2)	80(2)	78(2)	13(1)	17(1)	0(2)
F(2)	93(2)	88(2)	60(2)	15(1)	-1(1)	15(2)
N(2)	86(4)	110(3)	82(3)	35(2)	16(3)	23(3)
N(1)	88(3)	98(3)	77(3)	20(2)	5(2)	19(3)
N(4)	110(4)	106(4)	111(3)	38(3)	39(3)	43(3)
N(3)	94(4)	87(3)	77(3)	24(2)	3(2)	16(3)
N(5)	82(3)	69(3)	62(2)	7(2)	-2(2)	13(2)
S(1)	71(1)	79(1)	62(1)	18(1)	7(1)	10(1)
S(2)	74(1)	78(1)	65(1)	16(1)	8(1)	12(1)

Table S16. Torsion angles [°] for 7-T-Et-MN-pyrr (**8f**).

C(1)-C(2)-C(4)-C(5)	-1.5(8)	C(6)-C(7)-C(21)-C(25)	-38.3(7)
C(3)-C(2)-C(4)-C(5)	-173.9(5)	C(8)-C(7)-C(21)-C(22)	-33.7(7)
C(2)-C(4)-C(5)-C(6)	158.2(5)	C(6)-C(7)-C(21)-C(22)	142.7(5)
C(2)-C(4)-C(5)-S(1)	-15.6(8)	C(22)-C(21)-C(25)-N(5)	162.9(5)
C(4)-C(5)-C(6)-C(7)	-170.6(4)	C(7)-C(21)-C(25)-N(5)	-16.2(8)
S(1)-C(5)-C(6)-C(7)	4.2(5)	C(22)-C(21)-C(25)-C(24)	-14.5(5)
C(5)-C(6)-C(7)-C(8)	-5.3(6)	C(7)-C(21)-C(25)-C(24)	166.4(4)
C(5)-C(6)-C(7)-C(21)	178.0(4)	N(5)-C(25)-C(24)-F(4)	-39.9(6)
C(6)-C(7)-C(8)-C(9)	-173.5(4)	C(21)-C(25)-C(24)-F(4)	137.9(4)
C(21)-C(7)-C(8)-C(9)	3.2(8)	N(5)-C(25)-C(24)-F(3)	79.1(5)
C(6)-C(7)-C(8)-S(1)	4.0(5)	C(21)-C(25)-C(24)-F(3)	-103.1(4)
C(21)-C(7)-C(8)-S(1)	-179.3(4)	N(5)-C(25)-C(24)-C(23)	-162.4(4)
C(7)-C(8)-C(9)-C(10)	-174.4(4)	C(21)-C(25)-C(24)-C(23)	15.4(5)
S(1)-C(8)-C(9)-C(10)	8.4(6)	C(17)-C(22)-C(23)-F(1)	-58.5(6)
C(7)-C(8)-C(9)-C(18)	58.0(6)	C(21)-C(22)-C(23)-F(1)	125.4(4)
S(1)-C(8)-C(9)-C(18)	-119.2(4)	C(17)-C(22)-C(23)-F(2)	62.0(6)
C(8)-C(9)-C(18)-C(19)	51.4(4)	C(21)-C(22)-C(23)-F(2)	-114.1(4)
C(10)-C(9)-C(18)-C(19)	-75.8(4)	C(17)-C(22)-C(23)-C(24)	179.2(4)
C(8)-C(9)-C(18)-C(17)	-74.8(4)	C(21)-C(22)-C(23)-C(24)	3.1(5)
C(10)-C(9)-C(18)-C(17)	158.0(4)	F(4)-C(24)-C(23)-F(1)	99.3(4)
C(8)-C(9)-C(18)-S(2)	169.8(3)	F(3)-C(24)-C(23)-F(1)	-16.5(5)
C(10)-C(9)-C(18)-S(2)	42.5(4)	C(25)-C(24)-C(23)-F(1)	-135.5(4)
C(19)-C(18)-C(17)-C(22)	-86.2(5)	F(4)-C(24)-C(23)-F(2)	-16.3(5)
C(9)-C(18)-C(17)-C(22)	38.9(6)	F(3)-C(24)-C(23)-F(2)	-132.0(4)
S(2)-C(18)-C(17)-C(22)	156.6(4)	C(25)-C(24)-C(23)-F(2)	109.0(4)
C(19)-C(18)-C(17)-C(16)	102.6(4)	F(4)-C(24)-C(23)-C(22)	-136.3(4)
C(9)-C(18)-C(17)-C(16)	-132.3(4)	F(3)-C(24)-C(23)-C(22)	108.0(4)
S(2)-C(18)-C(17)-C(16)	-14.6(4)	C(25)-C(24)-C(23)-C(22)	-11.0(5)
C(22)-C(17)-C(16)-C(15)	-159.6(5)	N(5)-C(29)-C(28)-C(27)	-35.1(5)
C(18)-C(17)-C(16)-C(15)	12.1(6)	C(29)-C(28)-C(27)-C(26)	40.7(5)
C(17)-C(16)-C(15)-C(14)	169.9(4)	C(28)-C(27)-C(26)-N(5)	-29.9(5)
C(17)-C(16)-C(15)-S(2)	-2.9(6)	C(17)-C(18)-C(19)-C(20)	-55.9(5)
C(16)-C(15)-C(14)-C(12)	-173.2(5)	C(9)-C(18)-C(19)-C(20)	178.4(4)
S(2)-C(15)-C(14)-C(12)	-1.3(8)	S(2)-C(18)-C(19)-C(20)	59.6(4)
C(15)-C(14)-C(12)-C(13)	-4.1(9)	C(21)-C(25)-N(5)-C(26)	171.8(5)
C(15)-C(14)-C(12)-C(11)	176.3(5)	C(24)-C(25)-N(5)-C(26)	-11.0(7)
C(16)-C(17)-C(22)-C(21)	168.5(5)	C(21)-C(25)-N(5)-C(29)	-21.9(7)
C(18)-C(17)-C(22)-C(21)	-1.8(8)	C(24)-C(25)-N(5)-C(29)	155.2(4)
C(16)-C(17)-C(22)-C(23)	-6.5(7)	C(27)-C(26)-N(5)-C(25)	175.9(4)
C(18)-C(17)-C(22)-C(23)	-176.8(4)	C(27)-C(26)-N(5)-C(29)	8.1(5)
C(17)-C(22)-C(21)-C(25)	-168.4(5)	C(28)-C(29)-N(5)-C(25)	-151.4(4)
C(23)-C(22)-C(21)-C(25)	7.1(5)	C(28)-C(29)-N(5)-C(26)	16.8(5)
C(17)-C(22)-C(21)-C(7)	10.7(8)	C(6)-C(5)-S(1)-C(8)	-1.6(4)
C(23)-C(22)-C(21)-C(7)	-173.8(4)	C(4)-C(5)-S(1)-C(8)	172.7(5)
C(8)-C(7)-C(21)-C(25)	145.3(5)	C(7)-C(8)-S(1)-C(5)	-1.4(4)

C(9)-C(8)-S(1)-C(5)	176.2(4)	C(19)-C(18)-S(2)-C(15)	-109.0(3)
C(16)-C(15)-S(2)-C(18)	-5.5(4)	C(17)-C(18)-S(2)-C(15)	11.3(3)
C(14)-C(15)-S(2)-C(18)	-178.0(4)	C(9)-C(18)-S(2)-C(15)	131.0(3)

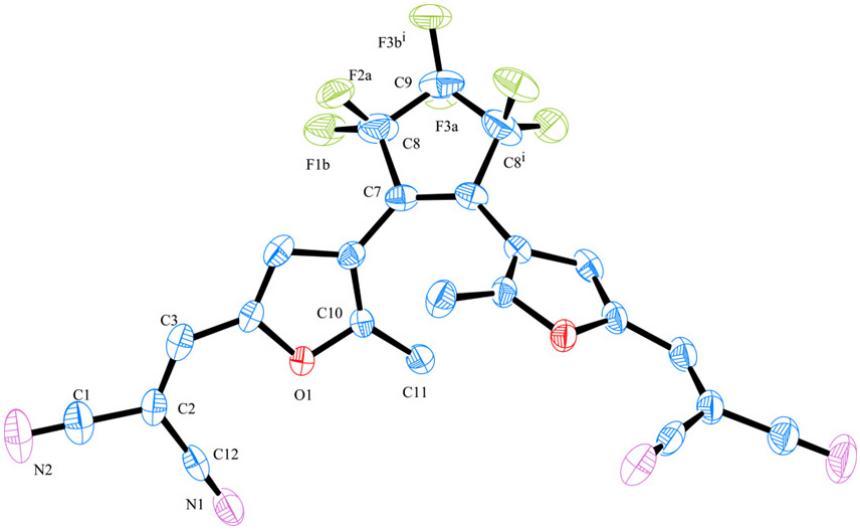


Figure S4. ORTEP of C5F-MN (**7**) with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.

Table S17. Crystal data and structure refinement parameters for C5F-MN (**7**)

	C5F-MN (**7**) (CCDC 894167)
Empirical formula	C_{23} H_{10} F6 N_4 O_2
Formula weight	488.35
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C* 2/c
Unit cell dimensions	a = 21.890(4) Å α= 90°
	b = 9.2771(15) Å β= 99.344(12)°
	c = 10.6726(14) Å γ = 90°
Volume	2138.6(6) Å^3
Z	4
Density (calculated)	1.517 Mg/m^3
Absorption coefficient	0.135 mm^{-1}
F(000)	984
Crystal size	0.400 x 0.267 x 0.100 mm^3
Theta range for data collection	1.89 to 26.82°.
Index ranges	27<=h<=27, -11<=k<=11, -13<=l<=12
Reflections collected	14031
Independent reflections	2275 [R(int) = 0.2274]
Completeness to theta = 26.82°	99.2 %
Absorption correction	Integration
Max. and min. transmission	0.9871 and 0.9315
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2275 / 0 / 188
Goodness-of-fit on F^2	0. 985
Final R indices [I>2sigma(I)]	R_1 = 0.0589, wR_2 = 0.1048
R indices (all data)	R_1 = 0.1270, wR_2 = 0.1219
Largest diff. peak and hole	0.209 and -0.202 e.Å^{-3}

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C5F-MN (**7**).
U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1A)	952(2)	10897(4)	3393(6)	55(2)
F(2A)	468(3)	10723(5)	701(5)	49(1)
F(3A)	325(2)	12008(7)	3674(4)	58(2)
F(1B)	1112(2)	10820(4)	2484(7)	58(2)
F(2B)	731(3)	10907(5)	1341(7)	53(1)
F(3B)	72(3)	12724(5)	3219(5)	62(2)
O(1)	1257(1)	5829(2)	2657(2)	33(1)
N(1)	2070(1)	2981(3)	3212(2)	49(1)
N(2)	3089(1)	3788(3)	94(3)	69(1)
C(1)	2707(1)	4157(3)	637(3)	48(1)
C(2)	2231(1)	4609(3)	1335(3)	36(1)
C(3)	1914(1)	5836(3)	1028(3)	37(1)
C(4)	1445(1)	6494(3)	1625(2)	32(1)
C(5)	1130(1)	7736(3)	1364(2)	35(1)
C(6)	711(1)	7866(2)	2252(2)	29(1)
C(7)	291(1)	9064(2)	2368(2)	32(1)
C(8)	505(1)	10574(3)	2197(4)	58(1)
C(9)	0	11550(4)	2500	51(1)
C(10)	812(1)	6686(3)	3030(2)	30(1)
C(11)	572(1)	6215(3)	4176(3)	41(1)
C(12)	2139(1)	3708(3)	2376(3)	37(1)

Table S19. Bond lengths [Å] and angles [°] for C5F-MN (**7**).

F(1A)-C(8)	1.507(5)	O(1)-C(4)	1.383(3)	C(6)-C(10)	1.370(3)
F(2A)-C(8)	1.592(7)	N(1)-C(12)	1.148(3)	C(6)-C(7)	1.461(3)
F(3A)-C(9)	1.403(4)	N(2)-C(1)	1.144(4)	C(7)-C(7)#1	1.348(5)
F(1B)-C(8)	1.334(4)	C(1)-C(2)	1.438(4)	C(7)-C(8)	1.498(4)
F(1B)-F(2B)	1.363(12)	C(2)-C(3)	1.346(4)	C(8)-C(9)	1.504(4)
F(2B)-C(8)	1.150(6)	C(2)-C(12)	1.430(4)	C(9)-F(3B)#1	1.327(5)
F(3B)-C(9)	1.327(5)	C(3)-C(4)	1.430(4)	C(9)-F(3A)#1	1.403(4)
F(3B)-F(3B)#1	1.516(11)	C(4)-C(5)	1.348(3)	C(9)-C(8)#1	1.504(4)
O(1)-C(10)	1.366(3)	C(5)-C(6)	1.427(3)	C(10)-C(11)	1.474(4)

C(8)-F(1B)-F(2B)	50.4(3)	F(2B)-C(8)-F(1A)	108.3(6)
C(8)-F(2B)-F(1B)	63.5(5)	C(7)-C(8)-F(1A)	104.8(3)
C(9)-F(3B)-F(3B)#1	55.2(3)	C(9)-C(8)-F(1A)	95.6(3)
C(10)-O(1)-C(4)	106.92(18)	F(1B)-C(8)-F(2A)	95.8(5)
N(2)-C(1)-C(2)	179.2(4)	C(7)-C(8)-F(2A)	103.7(3)
C(3)-C(2)-C(12)	123.5(2)	C(9)-C(8)-F(2A)	104.2(3)
C(3)-C(2)-C(1)	120.6(3)	F(1A)-C(8)-F(2A)	138.8(5)
C(12)-C(2)-C(1)	115.9(2)	F(3B)-C(9)-F(3B)#1	69.6(6)
C(2)-C(3)-C(4)	129.2(2)	F(3B)#1-C(9)-F(3A)	105.2(6)
C(5)-C(4)-O(1)	109.7(2)	F(3B)-C(9)-F(3A)#1	105.2(6)
C(5)-C(4)-C(3)	130.7(2)	F(3A)-C(9)-F(3A)#1	144.7(6)
O(1)-C(4)-C(3)	119.5(2)	F(3B)-C(9)-C(8)#1	113.1(2)
C(4)-C(5)-C(6)	107.3(2)	F(3B)#1-C(9)-C(8)#1	126.6(3)
C(10)-C(6)-C(5)	106.2(2)	F(3A)-C(9)-C(8)#1	105.9(2)
C(10)-C(6)-C(7)	126.7(2)	F(3A)#1-C(9)-C(8)#1	95.2(3)
C(5)-C(6)-C(7)	127.0(2)	F(3B)-C(9)-C(8)	126.6(3)
C(7)#1-C(7)-C(6)	130.33(13)	F(3B)#1-C(9)-C(8)	113.0(2)
C(7)#1-C(7)-C(8)	110.52(16)	F(3A)-C(9)-C(8)	95.2(3)
C(6)-C(7)-C(8)	119.1(2)	F(3A)#1-C(9)-C(8)	105.9(2)
F(2B)-C(8)-F(1B)	66.1(6)	C(8)#1-C(9)-C(8)	106.0(3)
F(2B)-C(8)-C(7)	122.1(4)	O(1)-C(10)-C(6)	109.9(2)
F(1B)-C(8)-C(7)	116.9(3)	O(1)-C(10)-C(11)	115.8(2)
F(2B)-C(8)-C(9)	115.8(3)	C(6)-C(10)-C(11)	134.2(2)
F(1B)-C(8)-C(9)	126.0(3)	N(1)-C(12)-C(2)	179.5(3)
C(7)-C(8)-C(9)	106.3(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+1/2

Table S20. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for C5F-MN (**7**).

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1A)	52(2)	45(2)	59(4)	2(2)	-15(2)	-17(2)
F(2A)	72(3)	36(2)	42(3)	10(2)	21(2)	0(2)
F(3A)	75(3)	49(3)	46(2)	-13(2)	3(2)	-18(2)
F(1B)	46(2)	37(2)	84(5)	7(2)	-4(2)	-14(2)
F(2B)	68(3)	37(2)	60(4)	10(2)	28(3)	-4(2)
F(3B)	89(3)	32(2)	67(3)	-18(2)	27(3)	-17(2)
O(1)	30(1)	34(1)	37(1)	3(1)	14(1)	2(1)
N(1)	47(1)	54(2)	48(2)	-2(1)	16(1)	17(1)
N(2)	48(2)	95(2)	72(2)	-26(2)	32(2)	-3(1)
C(1)	37(2)	60(2)	48(2)	-18(2)	13(1)	-7(1)
C(2)	29(1)	46(2)	34(2)	-9(1)	11(1)	-7(1)
C(3)	33(1)	47(2)	31(1)	-5(1)	11(1)	-11(1)
C(4)	30(1)	38(1)	31(1)	2(1)	12(1)	-7(1)
C(5)	33(1)	41(1)	32(1)	6(1)	6(1)	-11(1)
C(6)	26(1)	28(1)	32(1)	0(1)	4(1)	-6(1)
C(7)	35(1)	27(1)	31(1)	3(1)	-2(1)	-2(1)
C(8)	41(2)	36(2)	93(3)	14(2)	-1(2)	-7(1)
C(9)	84(3)	28(2)	37(2)	0	3(2)	0
C(10)	23(1)	32(1)	35(1)	1(1)	7(1)	2(1)
C(11)	43(2)	40(2)	44(2)	10(1)	18(1)	11(1)
C(12)	30(1)	44(2)	39(2)	-12(1)	9(1)	9(1)

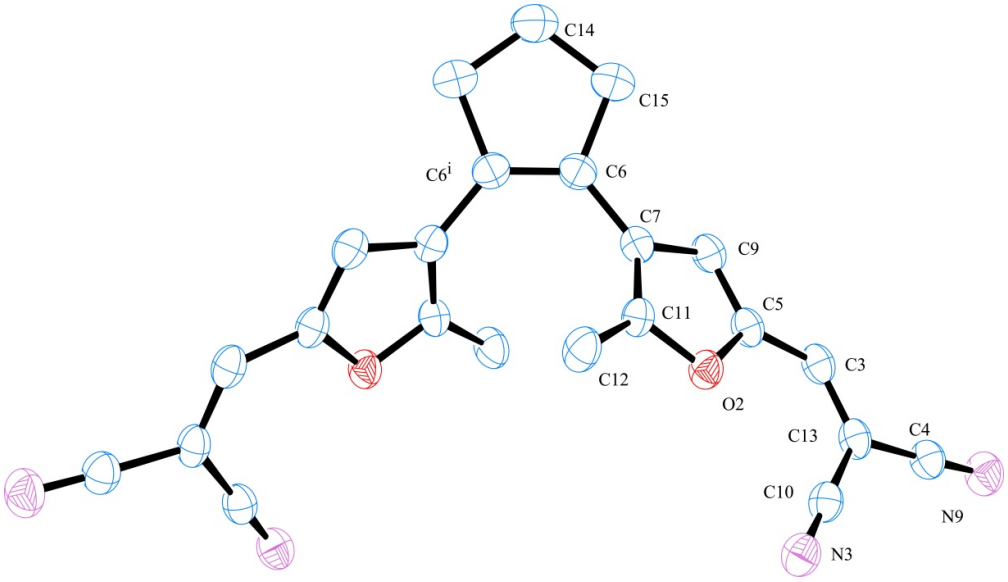


Figure S5. ORTEP of C5H-MN (**14**) with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.

Table S21. Crystal data and structure refinement parameters for C5H-MN (**14**)

	C5H-MN (**14**) (CCDC 1946676)
Empirical formula	$C_{23}\ H_{16}\ N_4\ O_2$
Formula weight	380.40
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 21.831(3) Å α= 90°
	b = 9.0389(8) Å β= 101.746(10)°
	c = 10.1044(13) Å γ = 90°
Volume	1952.2(4) $Å^3$
Z	4
Density (calculated)	1.294 Mg/m^3
Absorption coefficient	0.086 mm^{-1}
F(000)	792
Crystal size	0.900 x 0.800 x 0.750 mm^3
Theta range for data collection	1.906 to 26.171°.
Index ranges	-26<=h<=26, -11<=k<=11, -12<=l<=12
Reflections collected	11920
Independent reflections	1960 [R(int) = 0.2671]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Integration
Max. and min. transmission	0.9794 and 0.9430
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1960 / 0 / 133
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R_1 = 0. 0559, wR_2 = 0.1328
R indices (all data)	R_1 = 0. 0901, wR_2 = 0.1425
Largest diff. peak and hole	0.293 and -0.204 $e.Å^{-3}$

Table S22. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for C5H-MN (**14**).
U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	1238(1)	944(2)	7697(1)	34(1)
N(3)	1938(1)	-2181(2)	8039(2)	40(1)
C(3)	1902(1)	1015(2)	6044(2)	35(1)
C(4)	2683(1)	-710(2)	5602(2)	37(1)
C(5)	1437(1)	1666(2)	6654(2)	33(1)
C(6)	294(1)	4346(2)	7396(2)	34(1)
C(7)	709(1)	3091(2)	7302(2)	32(1)
N(9)	3078(1)	-999(2)	5050(2)	47(1)
C(9)	1130(1)	2972(2)	6400(2)	35(1)
C(10)	2054(1)	-1346(2)	7271(2)	34(1)
C(11)	800(1)	1838(2)	8081(2)	32(1)
C(12)	550(1)	1304(2)	9255(2)	41(1)
C(13)	2193(1)	-306(2)	6302(2)	34(1)
C(14)	0	6876(4)	7500	55(1)
C(15)	529(1)	5898(2)	7264(3)	51(1)

Table S23. Bond lengths [Å] and angles [°] for C5H-MN (**14**).

O(2)-C(11)	1.368(2)	C(4)-C(13)	1.445(3)	C(7)-C(9)	1.425(3)
O(2)-C(5)	1.382(2)	C(5)-C(9)	1.356(3)	C(10)-C(13)	1.434(3)
N(3)-C(10)	1.147(3)	C(6)-C(6)#1	1.343(4)	C(11)-C(12)	1.483(3)
C(3)-C(13)	1.353(3)	C(6)-C(7)	1.466(3)	C(14)-C(15)	1.512(3)
C(3)-C(5)	1.418(3)	C(6)-C(15)	1.509(3)	C(14)-C(15)#1	1.512(3)
C(4)-N(9)	1.148(3)	C(7)-C(11)	1.370(3)		

C(11)-O(2)-C(5)	106.53(15)	C(9)-C(7)-C(6)	125.92(17)
C(13)-C(3)-C(5)	129.15(18)	C(5)-C(9)-C(7)	107.68(17)
N(9)-C(4)-C(13)	178.4(2)	N(3)-C(10)-C(13)	179.5(2)
C(9)-C(5)-O(2)	109.54(17)	O(2)-C(11)-C(7)	110.69(16)
C(9)-C(5)-C(3)	130.46(17)	O(2)-C(11)-C(12)	115.26(16)
O(2)-C(5)-C(3)	119.99(17)	C(7)-C(11)-C(12)	133.98(18)
C(6)#1-C(6)-C(7)	129.22(11)	C(3)-C(13)-C(10)	123.67(17)
C(6)#1-C(6)-C(15)	111.52(12)	C(3)-C(13)-C(4)	119.61(18)
C(7)-C(6)-C(15)	119.25(18)	C(10)-C(13)-C(4)	116.71(18)
C(11)-C(7)-C(9)	105.54(17)	C(15)-C(14)-C(15)#1	108.4(3)
C(11)-C(7)-C(6)	128.47(18)	C(6)-C(15)-C(14)	104.23(19)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+3/2

Table S24. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C5H-MN (**14**).

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	33(1)	39(1)	33(1)	4(1)	14(1)	2(1)
N(3)	41(1)	46(1)	37(1)	-2(1)	14(1)	4(1)
C(3)	32(1)	45(1)	29(1)	-1(1)	10(1)	-6(1)
C(4)	37(1)	42(1)	34(1)	-2(1)	11(1)	-2(1)
C(5)	32(1)	40(1)	29(1)	2(1)	12(1)	-5(1)
C(6)	36(1)	34(1)	33(1)	2(1)	7(1)	-2(1)
C(7)	30(1)	35(1)	33(1)	-1(1)	7(1)	-4(1)
N(9)	45(1)	56(1)	45(1)	-6(1)	22(1)	-1(1)
C(9)	33(1)	40(1)	33(1)	3(1)	10(1)	-5(1)
C(10)	32(1)	42(1)	30(1)	-5(1)	9(1)	2(1)
C(11)	29(1)	38(1)	33(1)	-1(1)	11(1)	2(1)
C(12)	41(1)	48(1)	38(1)	8(1)	18(1)	8(1)
C(13)	31(1)	45(1)	28(1)	-4(1)	12(1)	-4(1)
C(14)	62(2)	36(2)	72(2)	0	24(2)	0
C(15)	52(1)	36(1)	68(2)	4(1)	18(1)	-3(1)

Table S25. Torsion angles [°] for C5H-MN (**14**).

C(11)-O(2)-C(5)-C(9)	0.1(2)
C(11)-O(2)-C(5)-C(3)	179.37(17)
C(13)-C(3)-C(5)-C(9)	-178.6(2)
C(13)-C(3)-C(5)-O(2)	2.3(3)
C(6)#1-C(6)-C(7)-C(11)	-41.8(4)
C(15)-C(6)-C(7)-C(11)	137.4(2)
C(6)#1-C(6)-C(7)-C(9)	141.7(3)
C(15)-C(6)-C(7)-C(9)	-39.1(3)
O(2)-C(5)-C(9)-C(7)	-0.9(2)
C(3)-C(5)-C(9)-C(7)	179.92(19)
C(11)-C(7)-C(9)-C(5)	1.3(2)
C(6)-C(7)-C(9)-C(5)	178.52(18)
C(5)-O(2)-C(11)-C(7)	0.8(2)
C(5)-O(2)-C(11)-C(12)	-176.55(17)
C(9)-C(7)-C(11)-O(2)	-1.3(2)
C(6)-C(7)-C(11)-O(2)	-178.41(18)
C(9)-C(7)-C(11)-C(12)	175.4(2)
C(6)-C(7)-C(11)-C(12)	-1.7(4)
C(5)-C(3)-C(13)-C(10)	2.0(3)
C(5)-C(3)-C(13)-C(4)	-176.44(19)
C(6)#1-C(6)-C(15)-C(14)	2.9(3)
C(7)-C(6)-C(15)-C(14)	-176.45(15)
C(15)#1-C(14)-C(15)-C(6)	-0.97(10)

Symmetry transformations used to generate equivalent atoms: #1 -x,y,-z+3/2

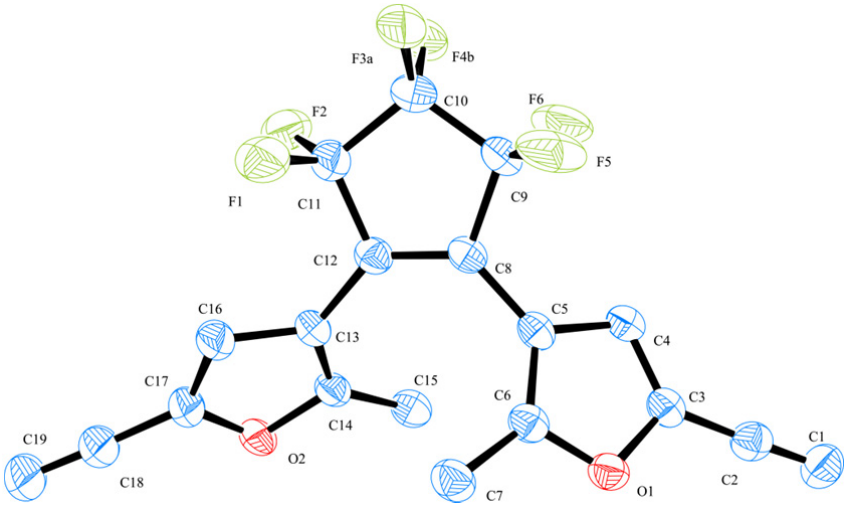


Figure S6. ORTEP of C5F-yne (**18**) with ellipsoids drawn at the 50% level and hydrogen atoms omitted for clarity.

Table S26. Crystal data and structure refinement parameters for C5F-yne (**18**)

	C5F- yne (**18**) (CCDC 2016261)
Empirical formula	$C_{19}\,H_{10}\,F_6\,O_2$
Formula weight	384.27
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.1470(10) Å α= 81.952(12)° b = 8.3925(12) Å β= 87.947(12)° c = 14.495(2) Å γ = 78.899(12)°
Volume	844.7(2) $Å^3$
Z	2
Density (calculated)	1.511 Mg/m^3
Absorption coefficient	0.142 mm^{-1}
F(000)	388
Crystal size	0.900 x 0.667 x 0.200 mm^3
Theta range for data collection	1.419 to 24.716°.
Index ranges	-8<=h<=8, -9<=k<=9, -16<=l<=17
Reflections collected	9373
Independent reflections	2841 [R(int) = 0.0674]
Completeness to theta = 25.242°	93.1 %
Absorption correction	Integration
Max. and min. transmission	0.9788 and 0.9412
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2841 / 0 / 265
Goodness-of-fit on F^2	0.920
Final R indices [I>2sigma(I)]	R_1 = 0. 0386, wR_2 = 0.0882
R indices (all data)	R_1 = 0. 0644, wR_2 = 0.0961
Largest diff. peak and hole	0.183 and -0.197 $e.Å^{-3}$

Table S27. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C5F- yne (**18**).

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	10134(2)	7066(2)	4555(1)	57(1)
F(2)	7898(2)	9044(2)	4024(1)	52(1)
F(5)	13805(2)	8707(2)	2730(1)	67(1)
F(6)	11635(2)	10670(2)	2164(1)	66(1)
O(1)	12323(2)	6120(2)	199(1)	34(1)
O(2)	5930(2)	5368(2)	2315(1)	35(1)
C(1)	13350(3)	8518(3)	-1841(2)	44(1)
C(2)	12896(3)	8147(3)	-1060(2)	36(1)
C(3)	12362(3)	7752(2)	-114(1)	31(1)
C(4)	11890(3)	8645(3)	588(1)	30(1)
C(5)	11494(2)	7554(2)	1388(1)	28(1)
C(6)	11798(3)	6031(3)	1116(1)	32(1)
C(7)	11707(3)	4375(3)	1594(2)	39(1)
C(8)	10938(3)	7997(2)	2313(1)	28(1)
C(9)	11906(3)	9199(3)	2696(1)	33(1)
C(10)	11073(4)	9377(4)	3657(2)	58(1)
C(11)	9638(3)	8214(3)	3812(1)	38(1)
C(12)	9633(3)	7491(3)	2923(1)	31(1)
C(13)	8237(3)	6457(2)	2840(1)	31(1)
C(14)	7191(3)	6399(2)	2079(1)	31(1)
C(15)	7070(3)	7233(3)	1112(1)	36(1)
C(16)	7557(3)	5410(3)	3593(2)	38(1)
C(17)	6184(3)	4783(3)	3247(1)	38(1)
C(18)	5005(3)	3691(3)	3666(2)	48(1)
C(19)	4059(4)	2784(4)	4043(2)	66(1)
F(3A)	12067(14)	9454(11)	4314(3)	52(2)
F(4A)	10730(20)	10639(17)	3956(10)	85(4)
F(3B)	12765(12)	8440(30)	4262(4)	104(4)
F(4B)	9830(11)	11069(5)	3525(6)	51(2)

Table S28. Bond lengths [Å] and angles [°] for C5F- yne (**18**).

F(1)-C(11)	1.350(3)	C(4)-C(5)	1.429(3)	C(10)-F(3B)	1.538(10)
F(2)-C(11)	1.351(2)	C(5)-C(6)	1.365(3)	C(11)-C(12)	1.498(3)
F(5)-C(9)	1.341(2)	C(5)-C(8)	1.463(3)	C(12)-C(13)	1.462(3)
F(6)-C(9)	1.345(2)	C(6)-C(7)	1.476(3)	C(13)-C(14)	1.367(3)
O(1)-C(6)	1.364(2)	C(8)-C(12)	1.349(3)	C(13)-C(16)	1.434(3)
O(1)-C(3)	1.386(2)	C(8)-C(9)	1.502(3)	C(14)-C(15)	1.474(3)
O(2)-C(14)	1.369(2)	C(9)-C(10)	1.511(3)	C(16)-C(17)	1.341(3)
O(2)-C(17)	1.377(2)	C(10)-F(4A)	1.179(8)	C(17)-C(18)	1.422(3)
C(1)-C(2)	1.182(3)	C(10)-F(3A)	1.225(6)	C(18)-C(19)	1.179(3)
C(2)-C(3)	1.421(3)	C(10)-F(4B)	1.514(6)	F(3A)-F(4A)	1.30(3)
C(3)-C(4)	1.343(3)	C(10)-C(11)	1.537(3)		

C(6)-O(1)-C(3)	106.84(15)	F(3A)-C(10)-C(11)	117.9(3)
C(14)-O(2)-C(17)	107.00(15)	C(9)-C(10)-C(11)	105.42(18)
C(1)-C(2)-C(3)	178.1(2)	F(4B)-C(10)-C(11)	103.9(3)
C(4)-C(3)-O(1)	109.62(17)	C(9)-C(10)-F(3B)	100.4(5)
C(4)-C(3)-C(2)	133.3(2)	F(4B)-C(10)-F(3B)	138.0(11)
O(1)-C(3)-C(2)	117.11(17)	C(11)-C(10)-F(3B)	102.7(5)
C(3)-C(4)-C(5)	107.39(18)	F(1)-C(11)-F(2)	105.32(17)
C(6)-C(5)-C(4)	106.09(17)	F(1)-C(11)-C(12)	112.69(18)
C(6)-C(5)-C(8)	127.66(18)	F(2)-C(11)-C(12)	112.22(16)
C(4)-C(5)-C(8)	126.22(18)	F(1)-C(11)-C(10)	110.53(19)
O(1)-C(6)-C(5)	110.04(17)	F(2)-C(11)-C(10)	110.2(2)
O(1)-C(6)-C(7)	115.67(17)	C(12)-C(11)-C(10)	105.91(17)
C(5)-C(6)-C(7)	134.28(18)	C(8)-C(12)-C(13)	131.35(18)
C(12)-C(8)-C(5)	130.20(18)	C(8)-C(12)-C(11)	111.01(17)
C(12)-C(8)-C(9)	110.97(17)	C(13)-C(12)-C(11)	117.59(16)
C(5)-C(8)-C(9)	118.83(16)	C(14)-C(13)-C(16)	106.31(17)
F(5)-C(9)-F(6)	104.70(18)	C(14)-C(13)-C(12)	128.10(18)
F(5)-C(9)-C(8)	112.21(16)	C(16)-C(13)-C(12)	125.31(17)
F(6)-C(9)-C(8)	112.58(17)	C(13)-C(14)-O(2)	109.59(17)
F(5)-C(9)-C(10)	111.03(19)	C(13)-C(14)-C(15)	134.86(18)
F(6)-C(9)-C(10)	109.82(19)	O(2)-C(14)-C(15)	115.47(16)
C(8)-C(9)-C(10)	106.57(16)	C(17)-C(16)-C(13)	106.90(18)
F(4A)-C(10)-F(3A)	65.6(14)	C(16)-C(17)-O(2)	110.19(18)
F(4A)-C(10)-C(9)	123.1(6)	C(16)-C(17)-C(18)	132.0(2)
F(3A)-C(10)-C(9)	121.8(4)	O(2)-C(17)-C(18)	117.78(18)
C(9)-C(10)-F(4B)	103.1(3)	C(19)-C(18)-C(17)	177.6(3)
F(4A)-C(10)-C(11)	119.5(4)	C(10)-F(3A)-F(4A)	55.5(7)
		C(10)-F(4A)-F(3A)	58.9(9)

Table S29. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C5F- yne (**18**).

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	83(1)	54(1)	37(1)	-3(1)	-17(1)	-21(1)
F(2)	50(1)	59(1)	52(1)	-25(1)	6(1)	-13(1)
F(5)	28(1)	70(1)	117(1)	-56(1)	-3(1)	-13(1)
F(6)	116(1)	30(1)	58(1)	-5(1)	-16(1)	-28(1)
O(1)	33(1)	28(1)	40(1)	-8(1)	1(1)	-6(1)
O(2)	30(1)	38(1)	42(1)	-9(1)	1(1)	-18(1)
C(1)	46(1)	42(1)	40(1)	-6(1)	6(1)	-3(1)
C(2)	32(1)	34(1)	41(1)	-8(1)	-1(1)	-3(1)
C(3)	27(1)	28(1)	38(1)	-2(1)	-3(1)	-5(1)
C(4)	26(1)	25(1)	37(1)	-4(1)	-3(1)	-5(1)
C(5)	22(1)	27(1)	35(1)	-1(1)	-4(1)	-6(1)
C(6)	27(1)	30(1)	38(1)	-5(1)	-2(1)	-6(1)
C(7)	40(1)	28(1)	48(1)	-4(1)	2(1)	-6(1)
C(8)	26(1)	26(1)	33(1)	-3(1)	-6(1)	-6(1)
C(9)	30(1)	27(1)	44(1)	-5(1)	-1(1)	-9(1)
C(10)	72(2)	76(2)	44(1)	-25(1)	6(1)	-49(2)
C(11)	40(1)	41(1)	34(1)	-5(1)	-1(1)	-14(1)
C(12)	30(1)	31(1)	32(1)	-4(1)	-3(1)	-9(1)
C(13)	30(1)	30(1)	33(1)	-4(1)	1(1)	-11(1)
C(14)	27(1)	28(1)	39(1)	-8(1)	3(1)	-9(1)
C(15)	31(1)	38(1)	40(1)	-6(1)	-6(1)	-10(1)
C(16)	44(1)	42(1)	33(1)	-5(1)	-1(1)	-19(1)
C(17)	41(1)	42(1)	36(1)	-6(1)	5(1)	-19(1)
C(18)	54(1)	54(2)	44(1)	-13(1)	8(1)	-28(1)
C(19)	83(2)	79(2)	54(2)	-21(1)	22(1)	-55(2)
F(3A)	56(4)	72(4)	40(2)	-10(2)	-10(2)	-36(3)
F(4A)	104(7)	89(6)	95(6)	-64(6)	54(6)	-70(6)
F(3B)	54(3)	205(12)	57(2)	18(4)	-24(2)	-59(5)
F(4B)	62(3)	29(2)	68(3)	-19(2)	22(3)	-13(2)

Table S30. Torsion angles [°] for C5F- yne (**18**).

C(6)-O(1)-C(3)-C(4)	0.4(2)	F(3A)-C(10)-C(11)-F(2)	95.6(6)
C(6)-O(1)-C(3)-C(2)	179.40(16)	C(9)-C(10)-C(11)-F(2)	-124.4(2)
O(1)-C(3)-C(4)-C(5)	-1.0(2)	F(4B)-C(10)-C(11)-F(2)	-16.3(4)
C(2)-C(3)-C(4)-C(5)	-179.8(2)	F(3B)-C(10)-C(11)-F(2)	130.9(6)
C(3)-C(4)-C(5)-C(6)	1.2(2)	F(4A)-C(10)-C(11)-C(12)	141.0(12)
C(3)-C(4)-C(5)-C(8)	179.46(17)	F(3A)-C(10)-C(11)-C(12)	-142.7(6)
C(3)-O(1)-C(6)-C(5)	0.4(2)	C(9)-C(10)-C(11)-C(12)	-2.8(3)
C(3)-O(1)-C(6)-C(7)	-178.77(16)	F(4B)-C(10)-C(11)-C(12)	105.3(4)
C(4)-C(5)-C(6)-O(1)	-1.0(2)	F(3B)-C(10)-C(11)-C(12)	-107.5(6)
C(8)-C(5)-C(6)-O(1)	-179.18(16)	C(5)-C(8)-C(12)-C(13)	-6.0(4)
C(4)-C(5)-C(6)-C(7)	177.9(2)	C(9)-C(8)-C(12)-C(13)	174.0(2)
C(8)-C(5)-C(6)-C(7)	-0.2(4)	C(5)-C(8)-C(12)-C(11)	176.81(19)
C(6)-C(5)-C(8)-C(12)	-42.9(3)	C(9)-C(8)-C(12)-C(11)	-3.2(2)
C(4)-C(5)-C(8)-C(12)	139.3(2)	F(1)-C(11)-C(12)-C(8)	-117.2(2)
C(6)-C(5)-C(8)-C(9)	137.1(2)	F(2)-C(11)-C(12)-C(8)	124.13(19)
C(4)-C(5)-C(8)-C(9)	-40.7(3)	C(10)-C(11)-C(12)-C(8)	3.8(3)
C(12)-C(8)-C(9)-F(5)	123.0(2)	F(1)-C(11)-C(12)-C(13)	65.2(2)
C(5)-C(8)-C(9)-F(5)	-57.0(2)	F(2)-C(11)-C(12)-C(13)	-53.5(2)
C(12)-C(8)-C(9)-F(6)	-119.21(19)	C(10)-C(11)-C(12)-C(13)	-173.8(2)
C(5)-C(8)-C(9)-F(6)	60.8(2)	C(8)-C(12)-C(13)-C(14)	-37.2(4)
C(12)-C(8)-C(9)-C(10)	1.2(2)	C(11)-C(12)-C(13)-C(14)	139.9(2)
C(5)-C(8)-C(9)-C(10)	-178.75(19)	C(8)-C(12)-C(13)-C(16)	149.8(2)
F(5)-C(9)-C(10)-F(4A)	96.5(11)	C(11)-C(12)-C(13)-C(16)	-33.2(3)
F(6)-C(9)-C(10)-F(4A)	-18.8(11)	C(16)-C(13)-C(14)-O(2)	-0.7(2)
C(8)-C(9)-C(10)-F(4A)	-141.0(11)	C(12)-C(13)-C(14)-O(2)	-174.81(18)
F(5)-C(9)-C(10)-F(3A)	16.6(6)	C(16)-C(13)-C(14)-C(15)	175.8(2)
F(6)-C(9)-C(10)-F(3A)	-98.7(6)	C(12)-C(13)-C(14)-C(15)	1.7(4)
C(8)-C(9)-C(10)-F(3A)	139.1(5)	C(17)-O(2)-C(14)-C(13)	0.6(2)
F(5)-C(9)-C(10)-F(4B)	129.9(4)	C(17)-O(2)-C(14)-C(15)	-176.72(17)
F(6)-C(9)-C(10)-F(4B)	14.6(4)	C(14)-C(13)-C(16)-C(17)	0.6(2)
C(8)-C(9)-C(10)-F(4B)	-107.6(4)	C(12)-C(13)-C(16)-C(17)	174.9(2)
F(5)-C(9)-C(10)-C(11)	-121.4(2)	C(13)-C(16)-C(17)-O(2)	-0.3(2)
F(6)-C(9)-C(10)-C(11)	123.3(2)	C(13)-C(16)-C(17)-C(18)	-179.5(2)
C(8)-C(9)-C(10)-C(11)	1.1(3)	C(14)-O(2)-C(17)-C(16)	-0.2(2)
F(5)-C(9)-C(10)-F(3B)	-15.0(7)	C(14)-O(2)-C(17)-C(18)	179.15(19)
F(6)-C(9)-C(10)-F(3B)	-130.3(7)	C(9)-C(10)-F(3A)-F(4A)	115.2(4)
C(8)-C(9)-C(10)-F(3B)	107.5(6)	F(4B)-C(10)-F(3A)-F(4A)	1.3(4)
F(4A)-C(10)-C(11)-F(1)	-96.7(12)	C(11)-C(10)-F(3A)-F(4A)	-111.8(5)
F(3A)-C(10)-C(11)-F(1)	-20.4(7)	F(3B)-C(10)-F(3A)-F(4A)	175.9(7)
C(9)-C(10)-C(11)-F(1)	119.5(2)	C(9)-C(10)-F(4A)-F(3A)	-113.3(6)
F(4B)-C(10)-C(11)-F(1)	-132.4(4)	F(4B)-C(10)-F(4A)-F(3A)	-177.9(6)
F(3B)-C(10)-C(11)-F(1)	14.9(6)	C(11)-C(10)-F(4A)-F(3A)	109.6(7)
F(4A)-C(10)-C(11)-F(2)	19.4(12)	F(3B)-C(10)-F(4A)-F(3A)	-2.4(4)

(D) Plots of one- and two dimensional NMR Spectra

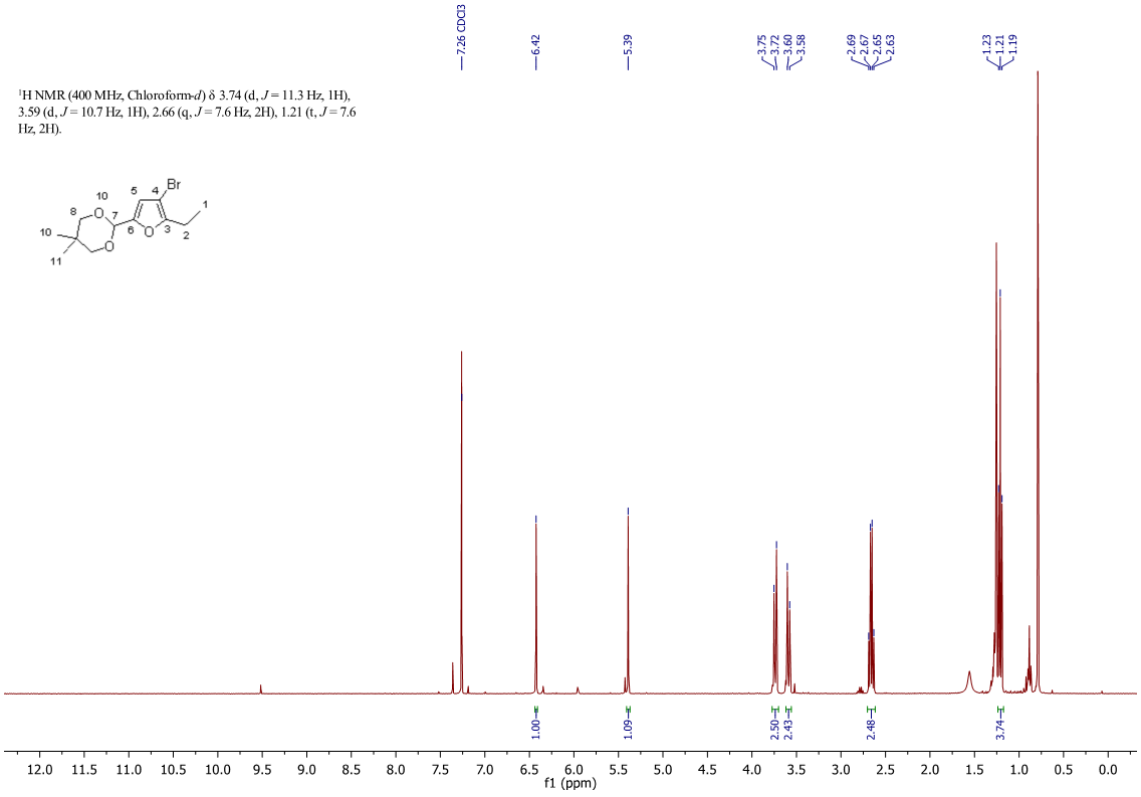


Figure S7. ^{1}H NMR spectrum of 2-(4-bromo-5-ethylfuran-2-yl)-5,5-dimethyl-1,3-dioxane in $CDCl_3$.

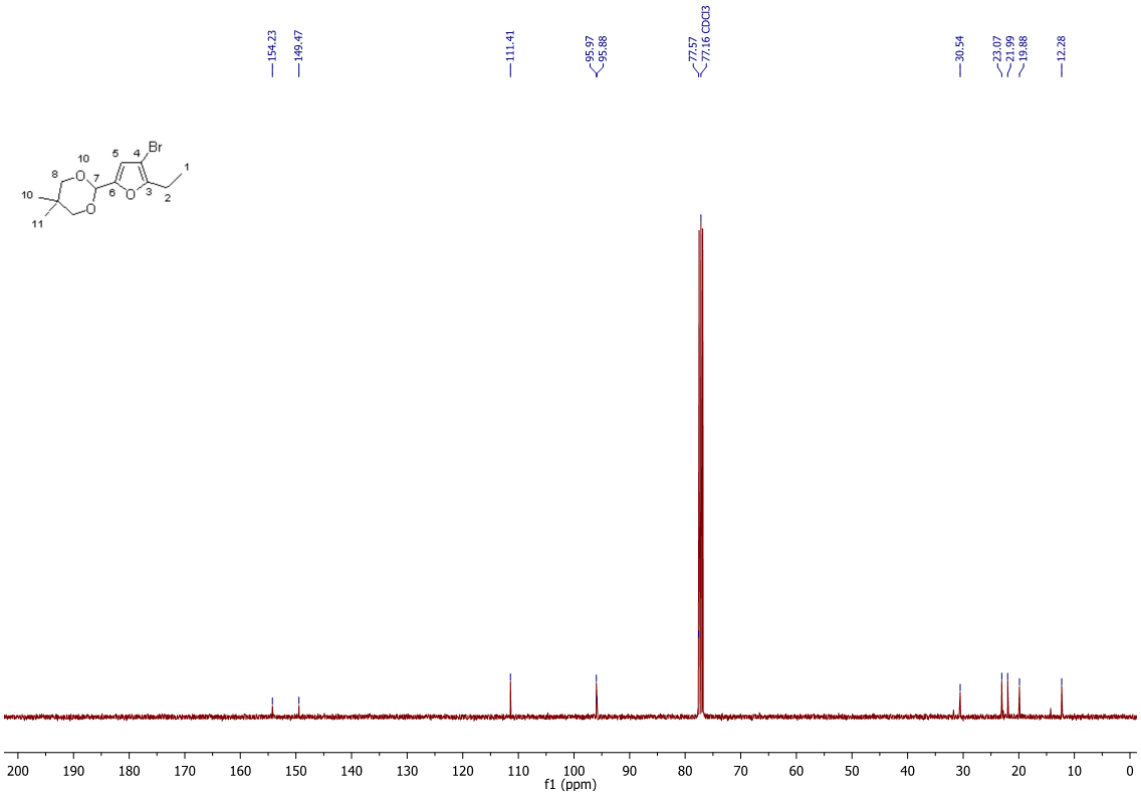


Figure S8. ^{13}C NMR spectrum of 2-(4-bromo-5-ethylfuran-2-yl)-5,5-dimethyl-1,3-dioxane in $CDCl_3$.

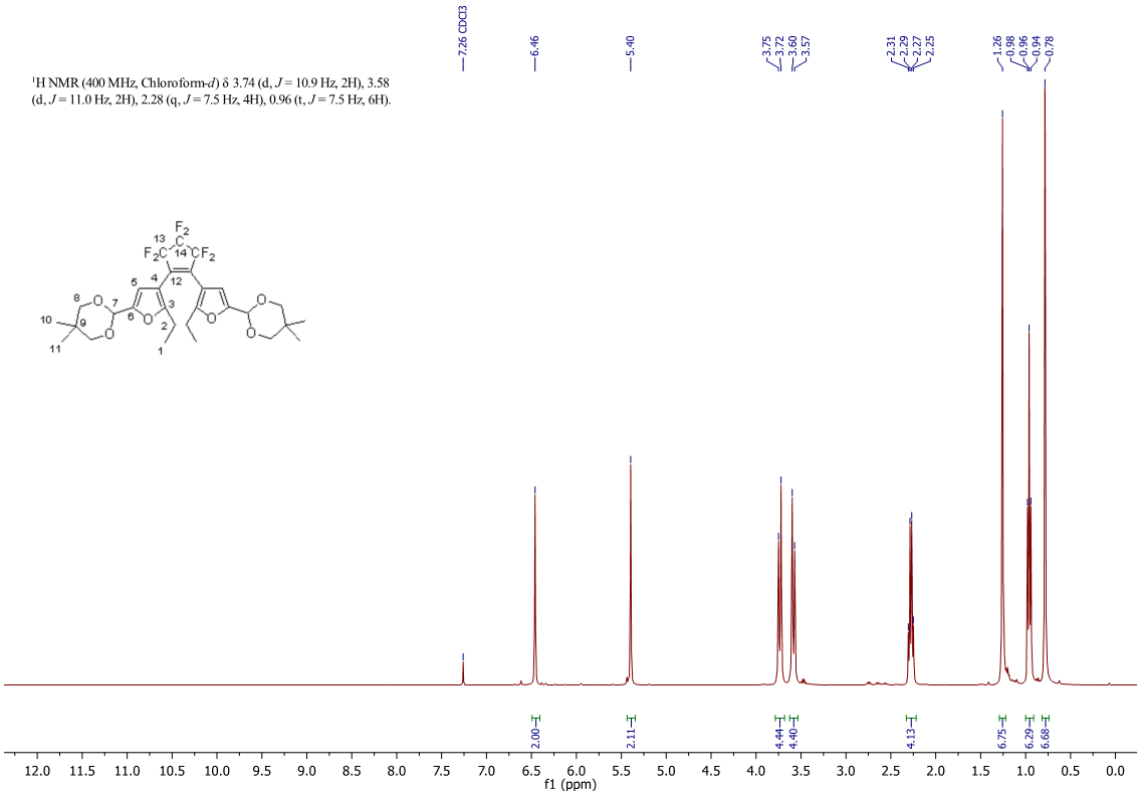


Figure S9. ^{1}H NMR spectrum of **C5F-Et-NPA** in $CDCl_3$.

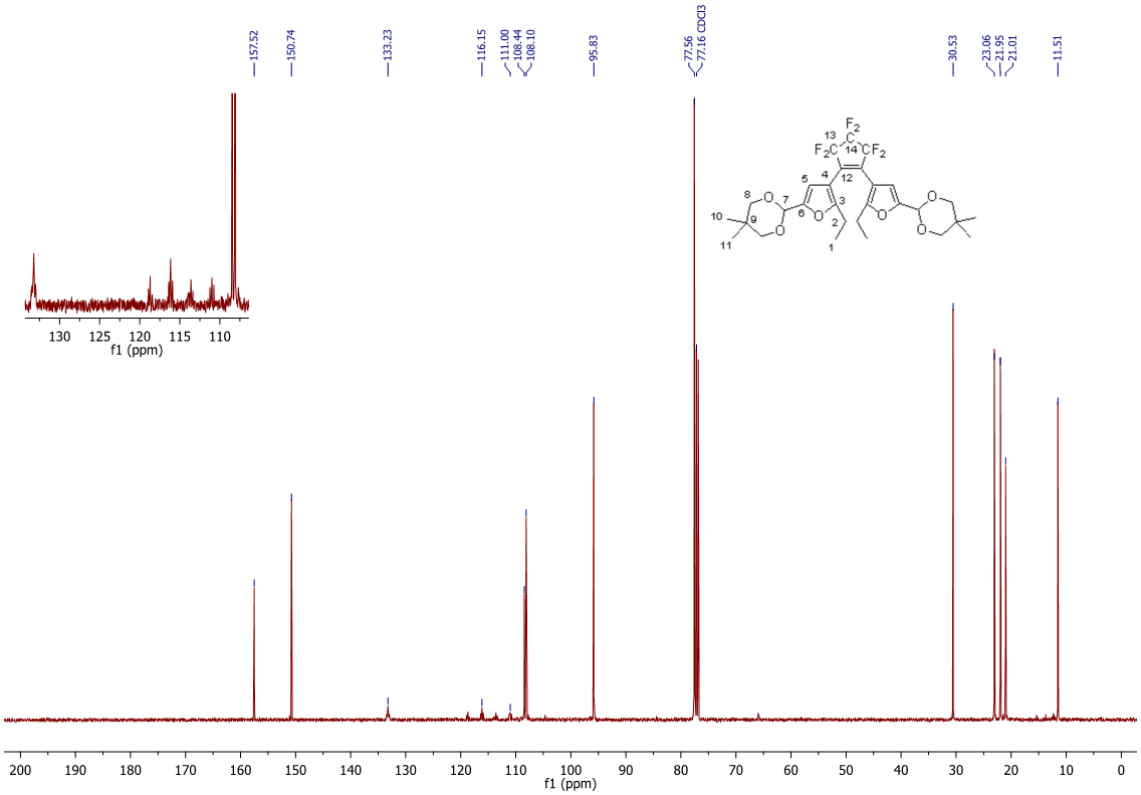


Figure S10. ^{13}C NMR spectrum of **C5F-Et-NPA** in $CDCl_3$.

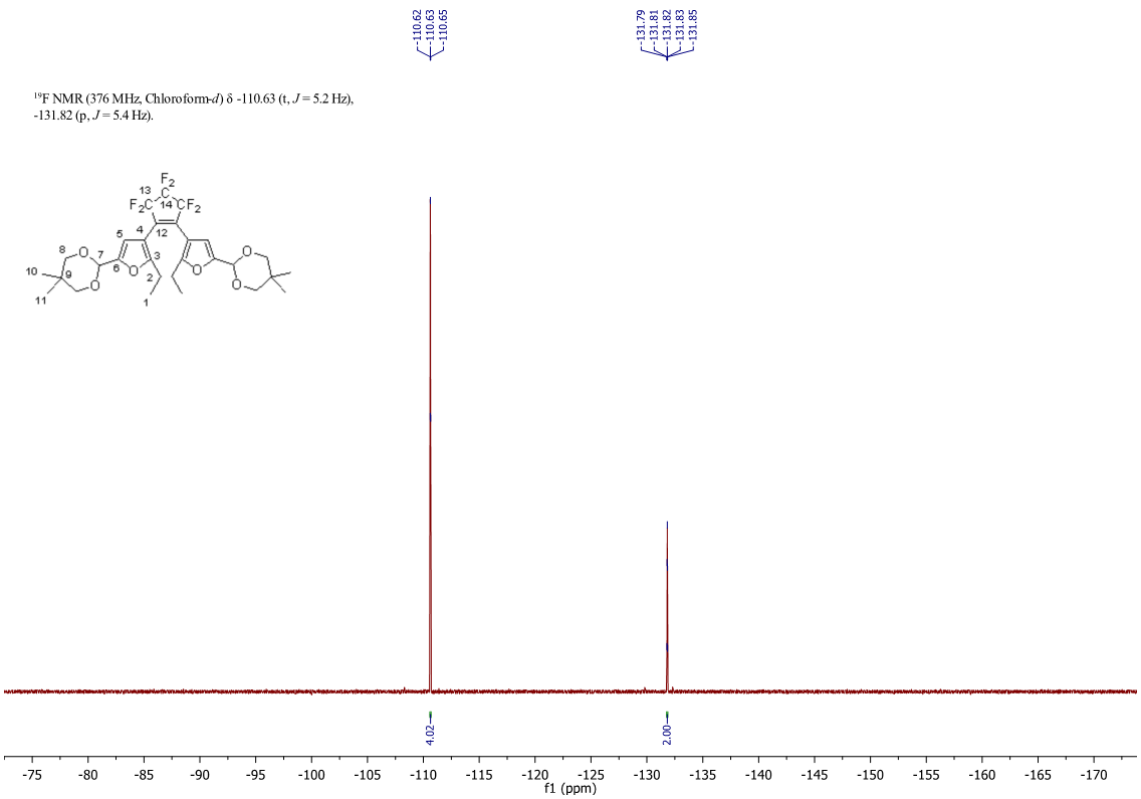


Figure S11. ^{19}F NMR spectrum of **C5F-Et-NPA** in $CDCl_3$.

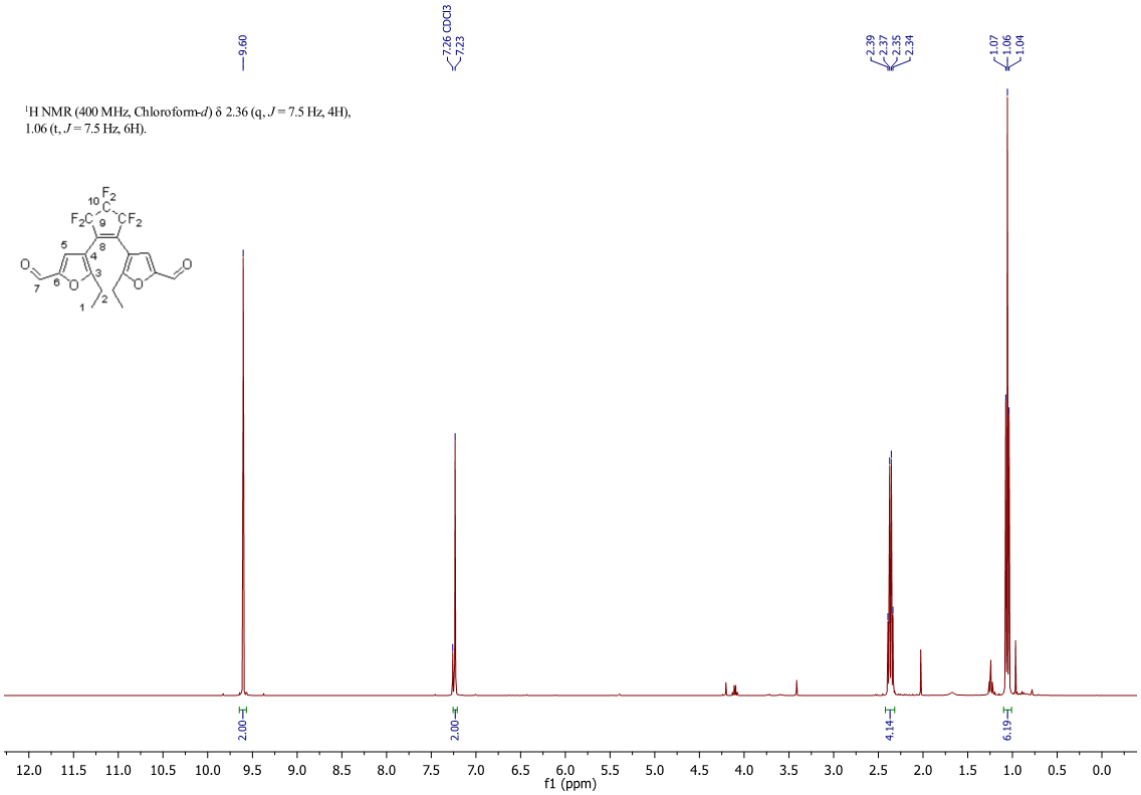


Figure S12. ^{1}H NMR spectrum of C5F-Et-CHO (**11**) in $CDCl_3$.

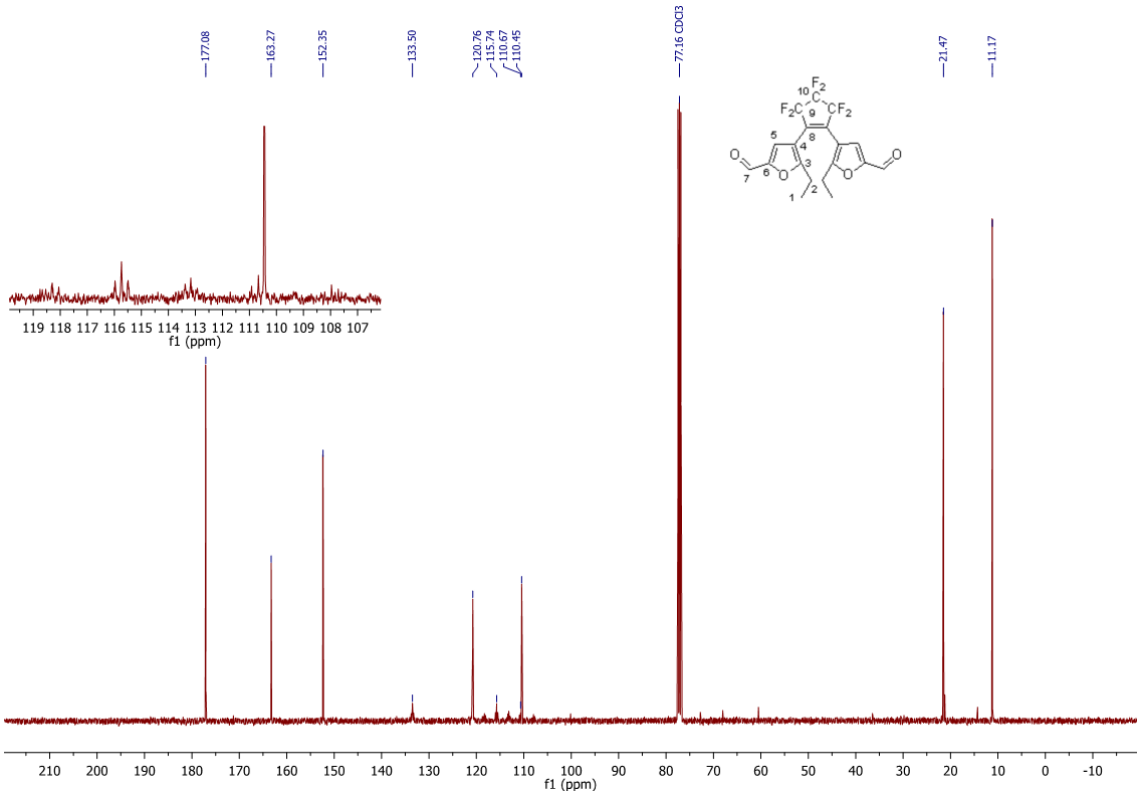


Figure S13. ^{13}C NMR spectrum of C5F-Et-CHO (**11**) in $CDCl_3$.

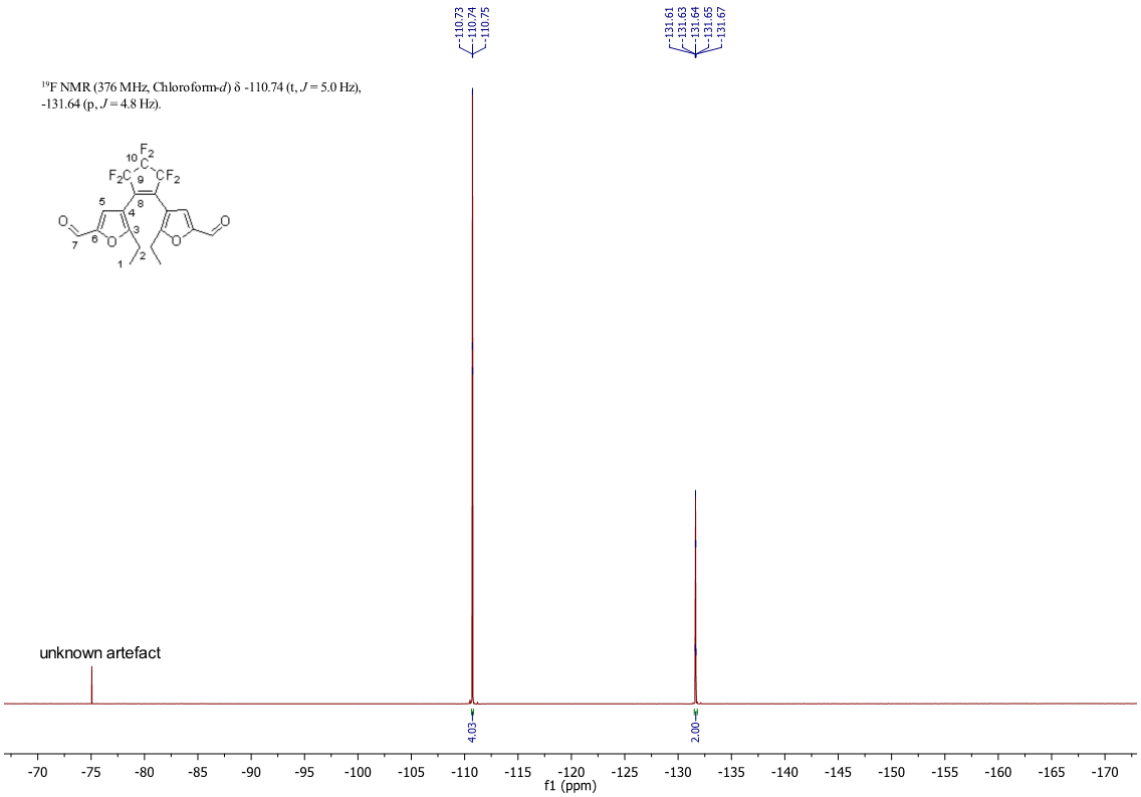


Figure S14. ^{19}F NMR spectrum of C5F-Et-CHO (**11**) in $CDCl_3$.

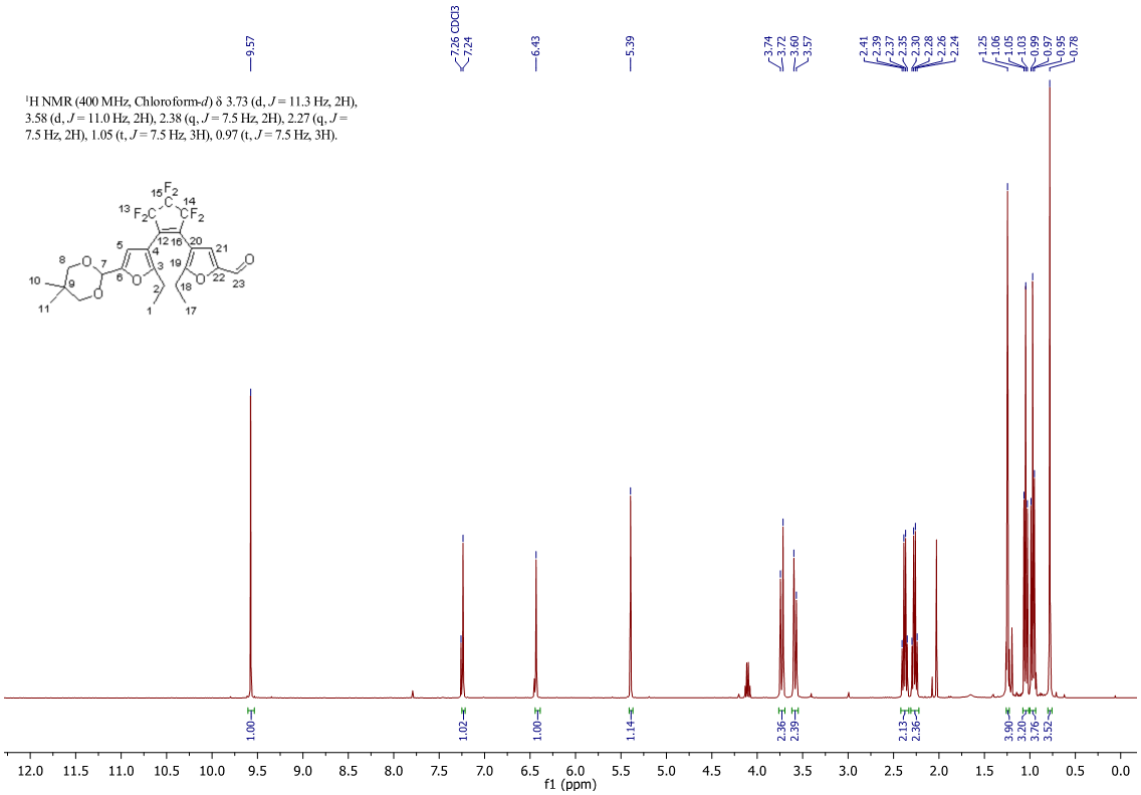


Figure S15. ^{1}H NMR spectrum of **C5F-Et-NPA-CHO** in $CDCl_3$.

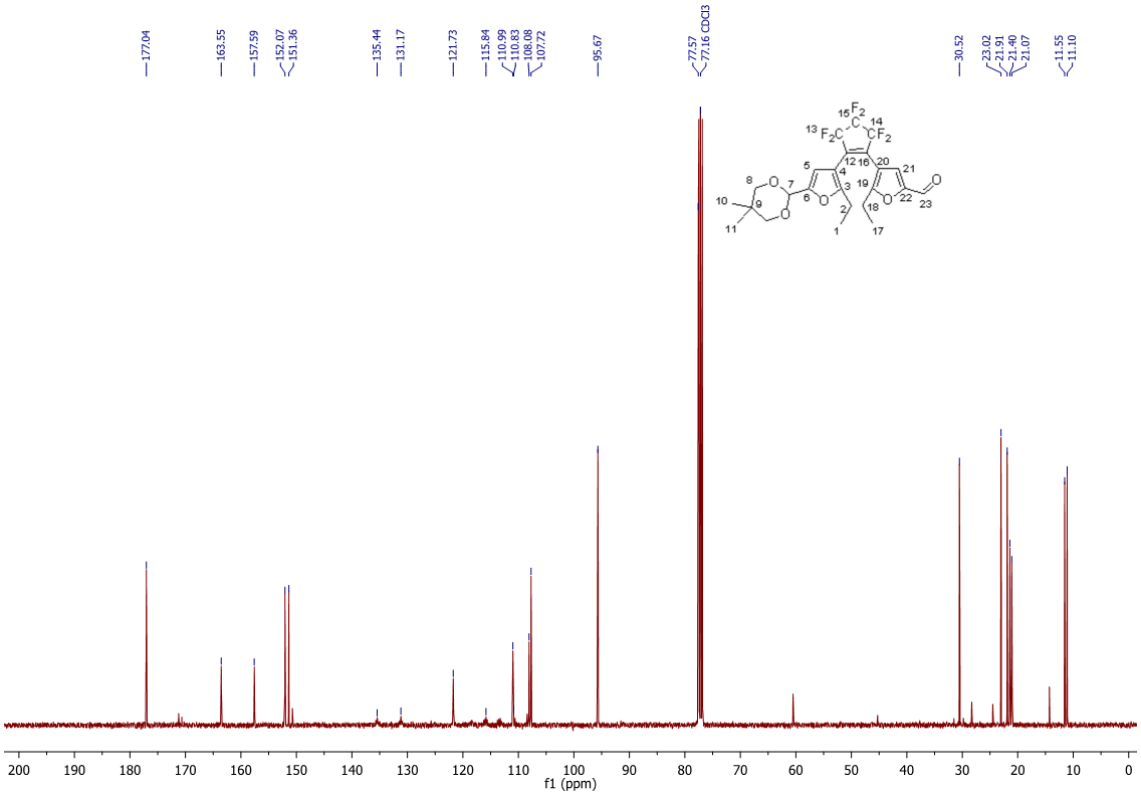


Figure S16. ^{13}C NMR spectrum of **C5F-Et-NPA-CHO** in $CDCl_3$.

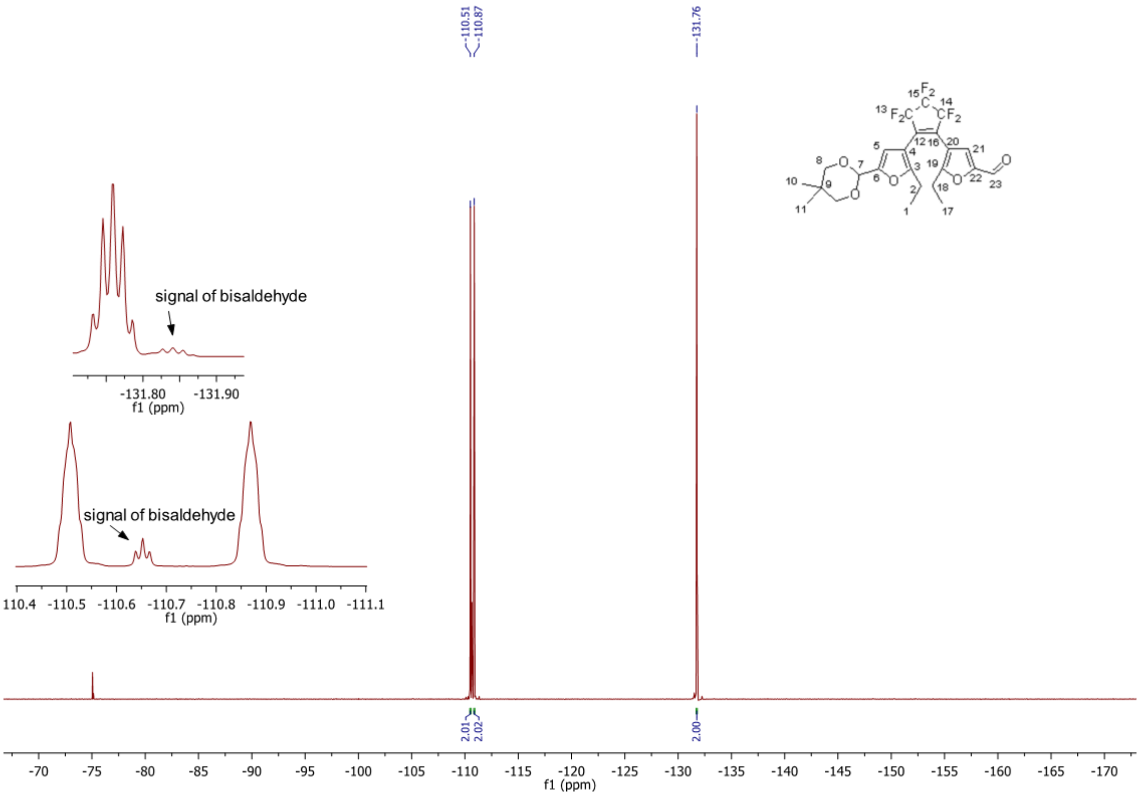


Figure S17. ^{19}F NMR spectrum of **C5F-Et-NPA-CHO** in $CDCl_3$.

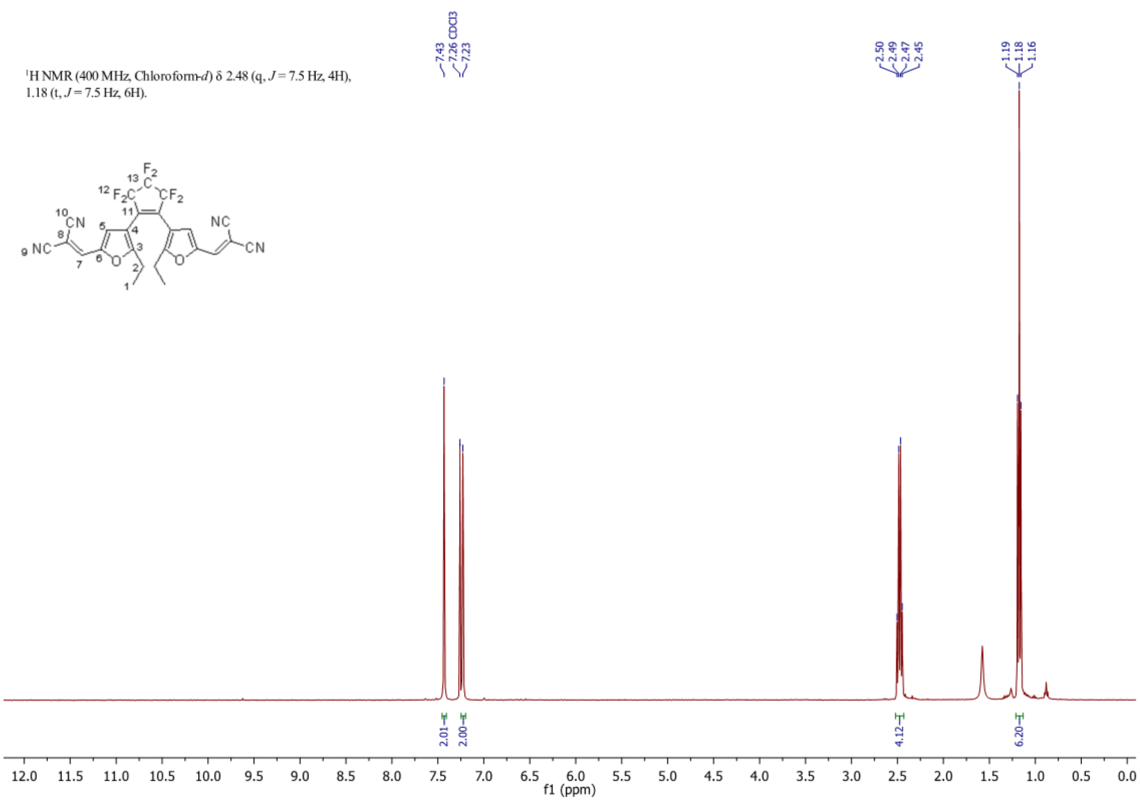


Figure S18. ^{1}H NMR spectrum of C5F-Et-MN (**12**) in $CDCl_3$.

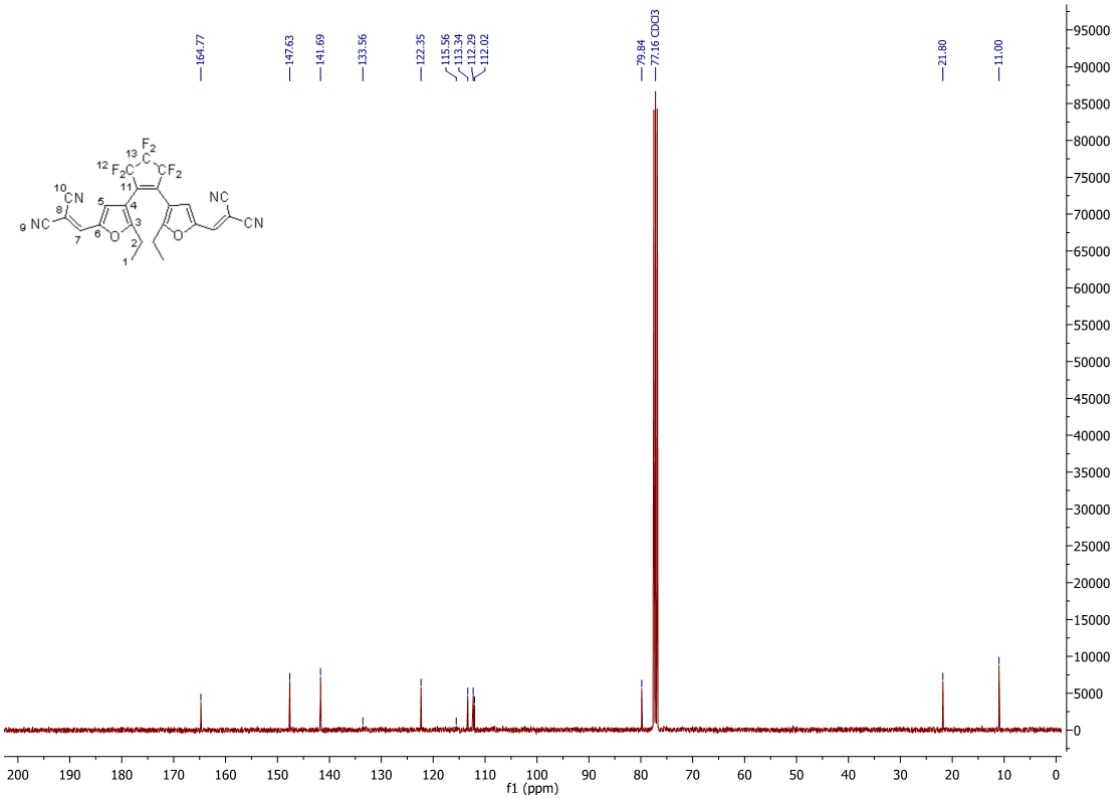
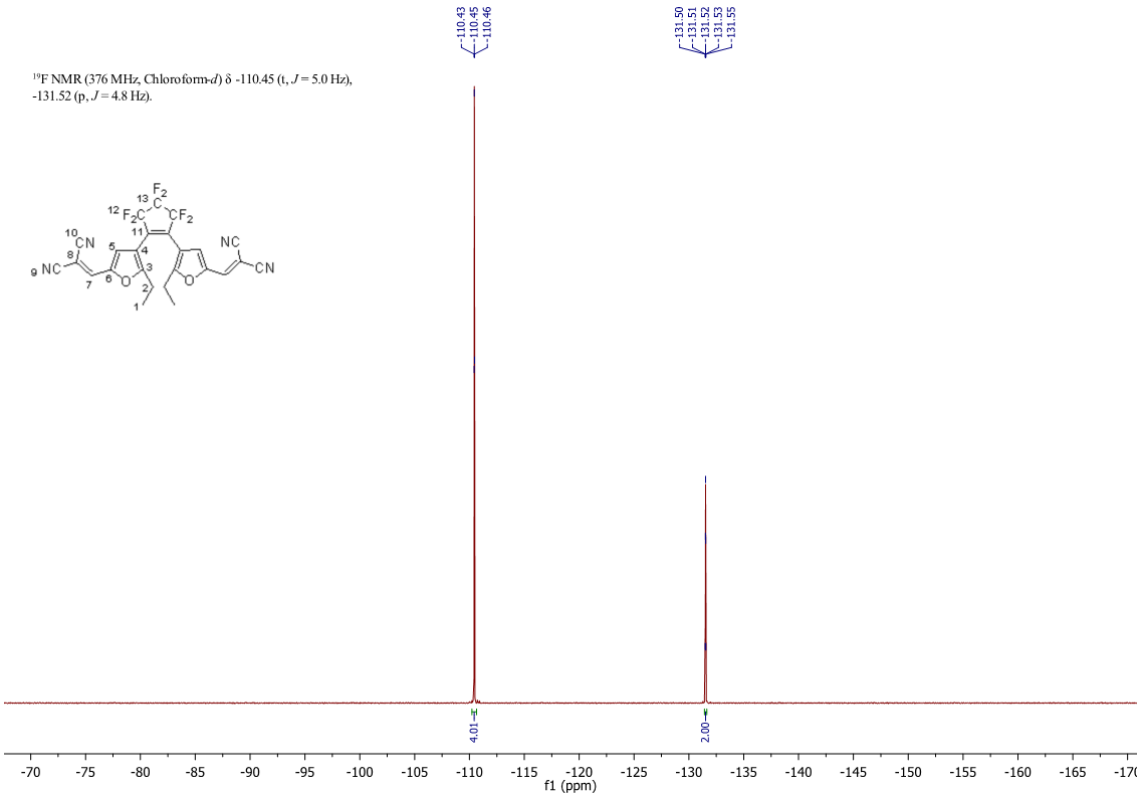


Figure S19. ^{13}C NMR spectrum of C5F-Et-MN (**12**) in $CDCl_3$.



^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.45 (t, *J* = 5.0 Hz), -131.52 (p, *J* = 4.8 Hz).

Figure S20. ^{19}F NMR spectrum of C5F-Et-MN (**12**) in $CDCl_3$.

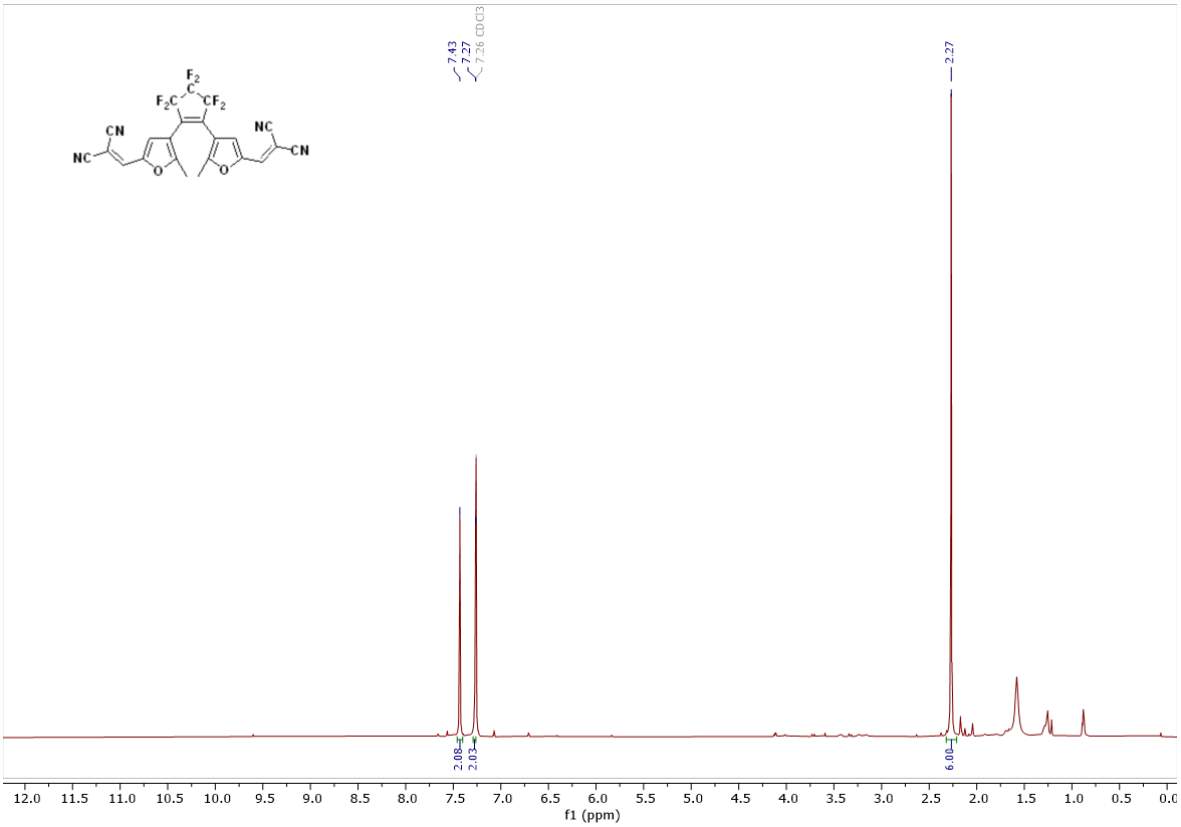


Figure S21. ^{1}H NMR spectrum of C5F-MN (**7**) in $CDCl_3$.

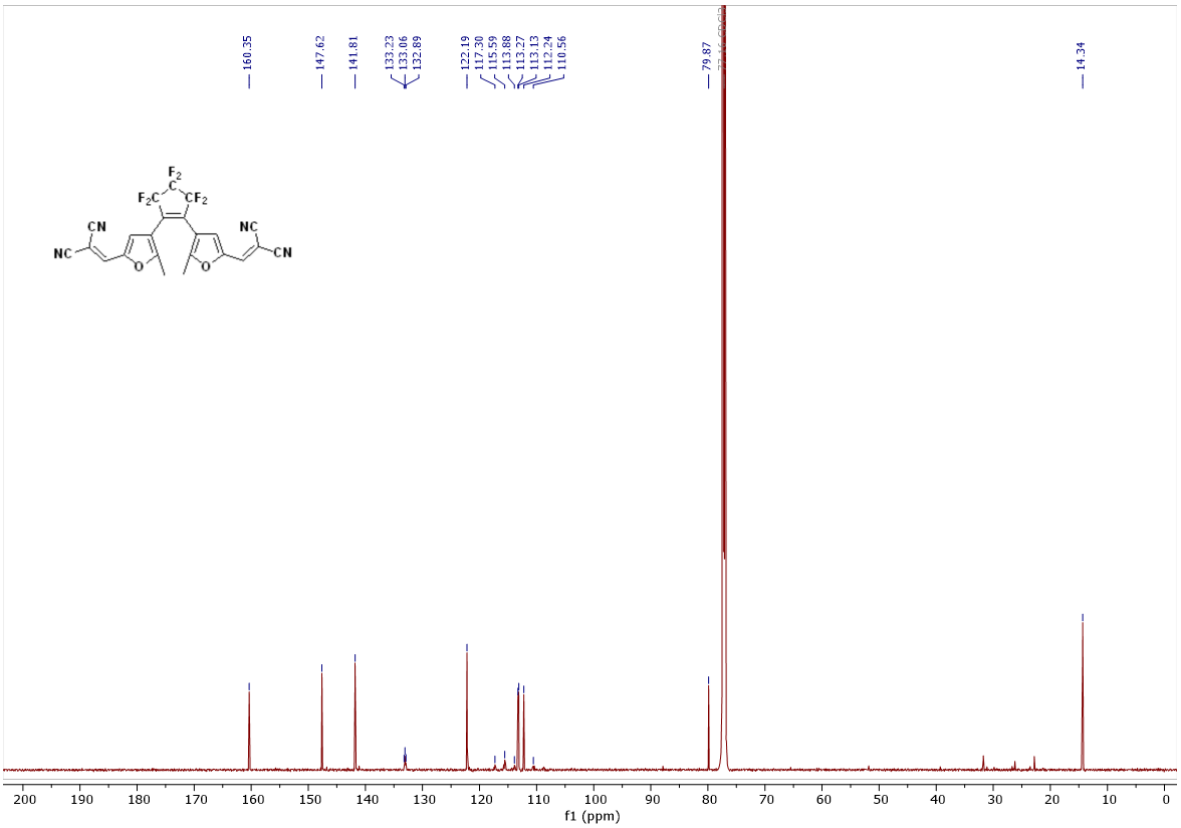


Figure S22. ^{13}C NMR spectrum of C5F-MN (**7**) in $CDCl_3$.

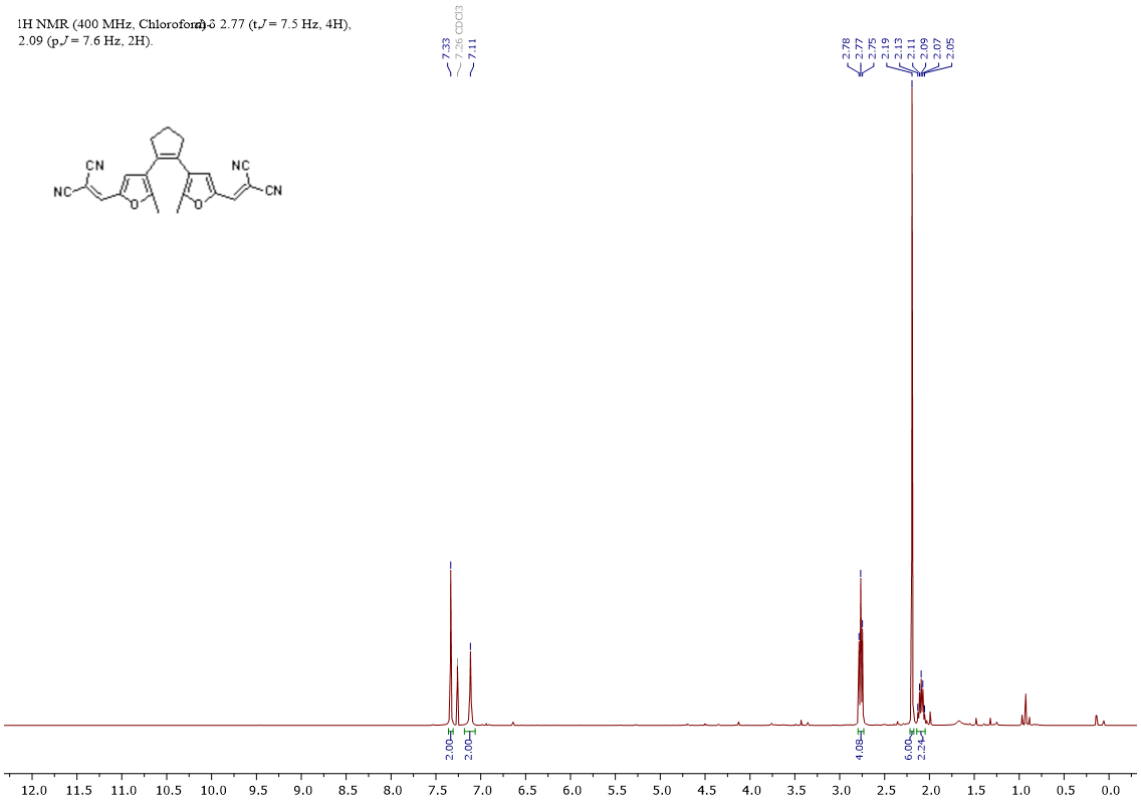


Figure S23. ^{1}H NMR spectrum of C5H-MN (**14**) in $CDCl_3$.

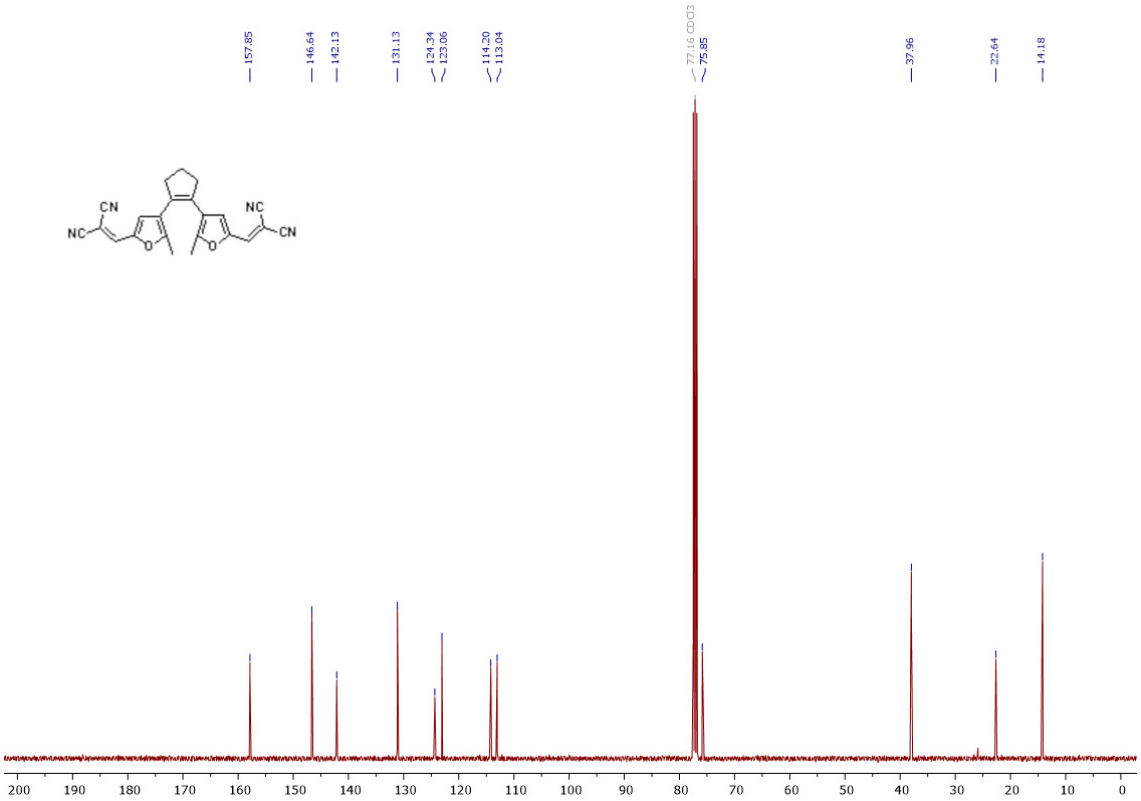


Figure S24. ^{13}C NMR spectrum of C5H-MN (**14**) in $CDCl_3$.

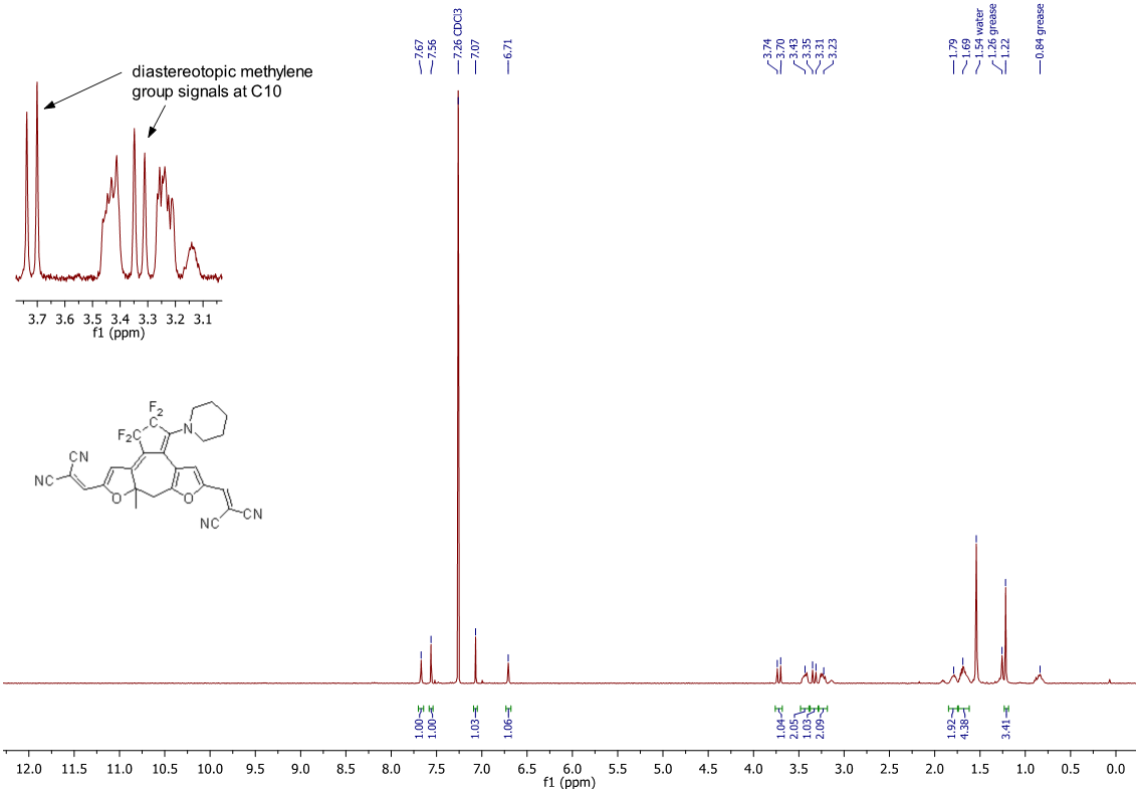


Figure S25. ^{1}H NMR spectrum of 7-MN-pip (**8a**) in $CDCl_3$.

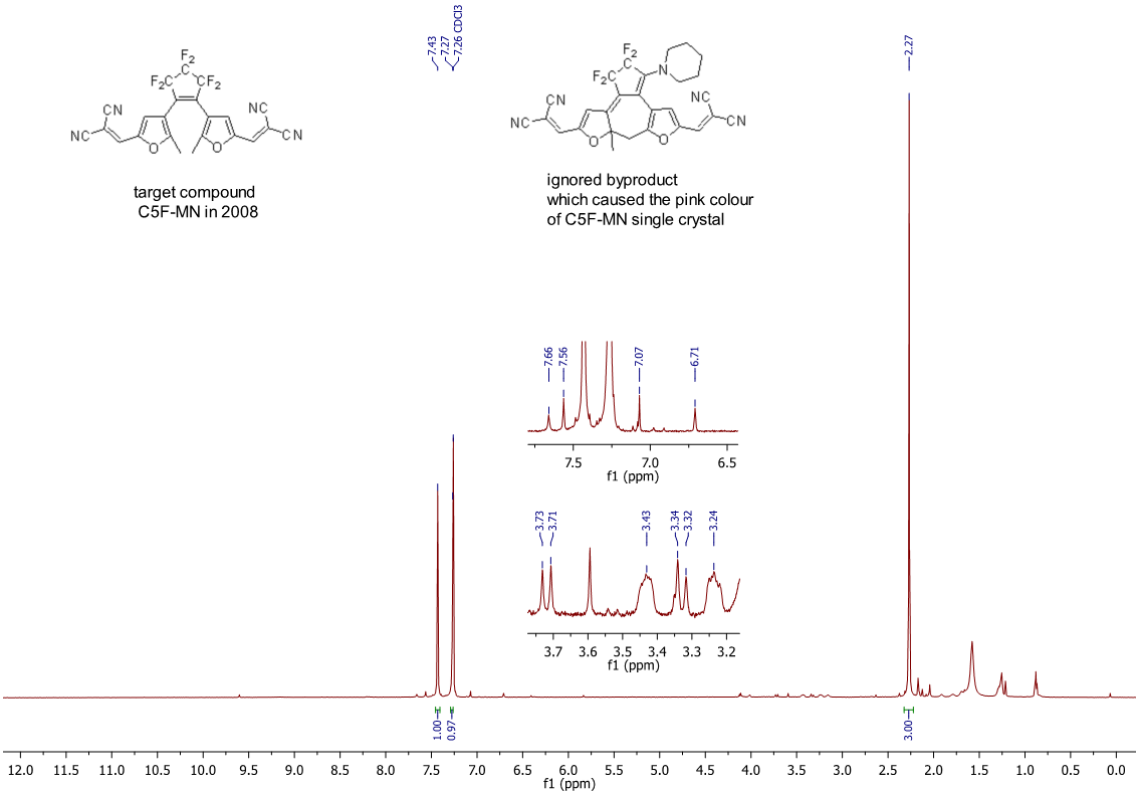


Figure S26. ^{1}H NMR spectrum of C5F-MN (**7**) in $CDCl_3$ contaminated with trace amounts of byproduct 7-MN-pip (**8a**) from ref [2].

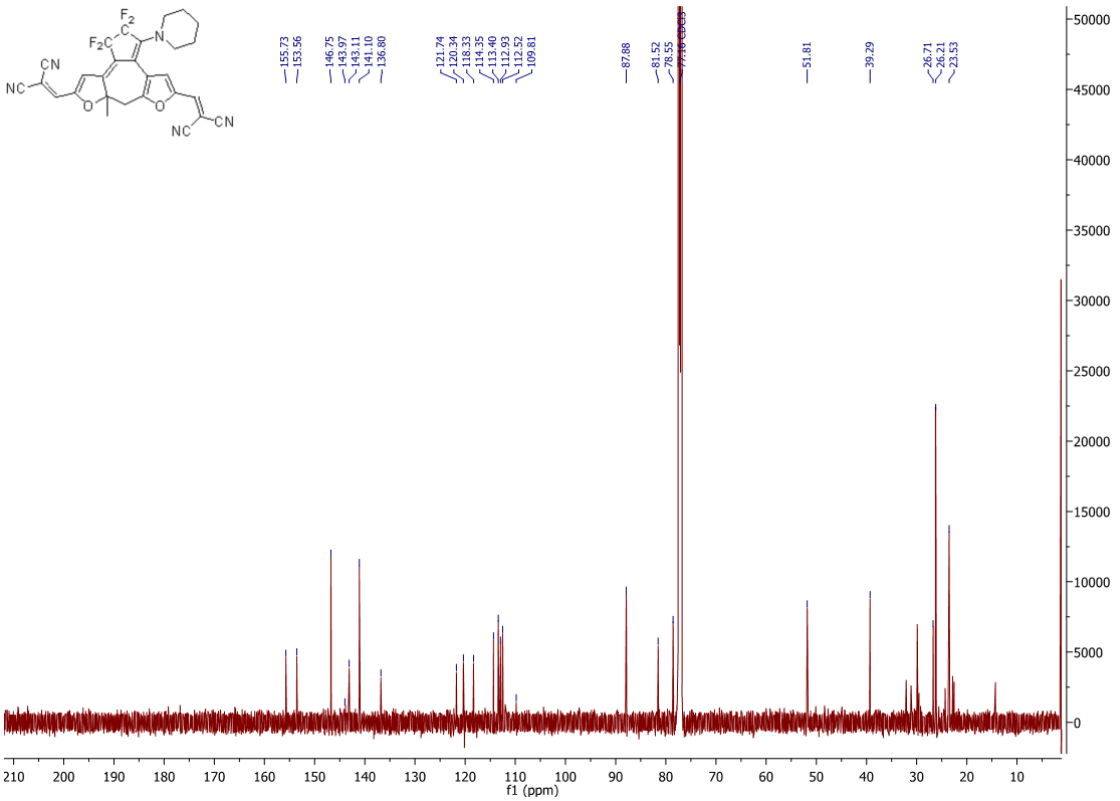


Figure S27. ^{13}C NMR spectrum of 7-MN-pip (**8a**) in $CDCl_3$.

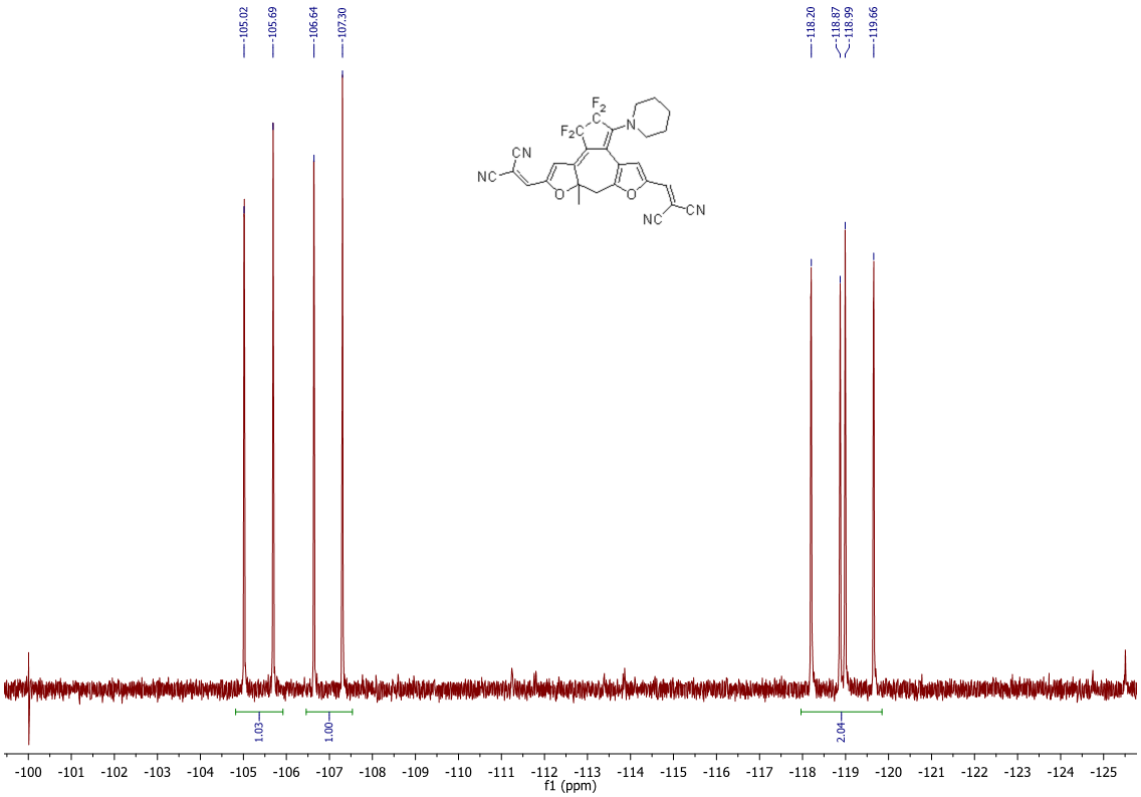


Figure S28. ^{19}F NMR spectrum of 7-MN-pip (**8a**) in $CDCl_3$.

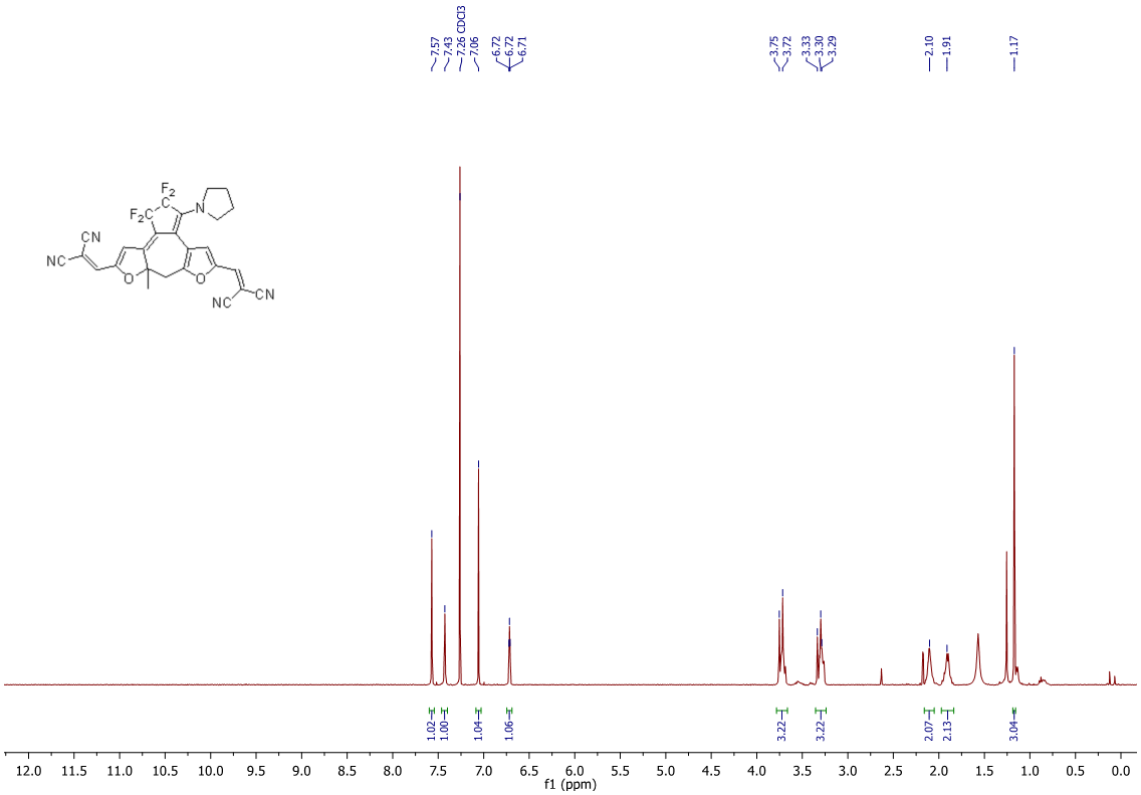


Figure S29. ^{1}H NMR spectrum of 7-MN-pyrr (**8b**) in $CDCl_3$.

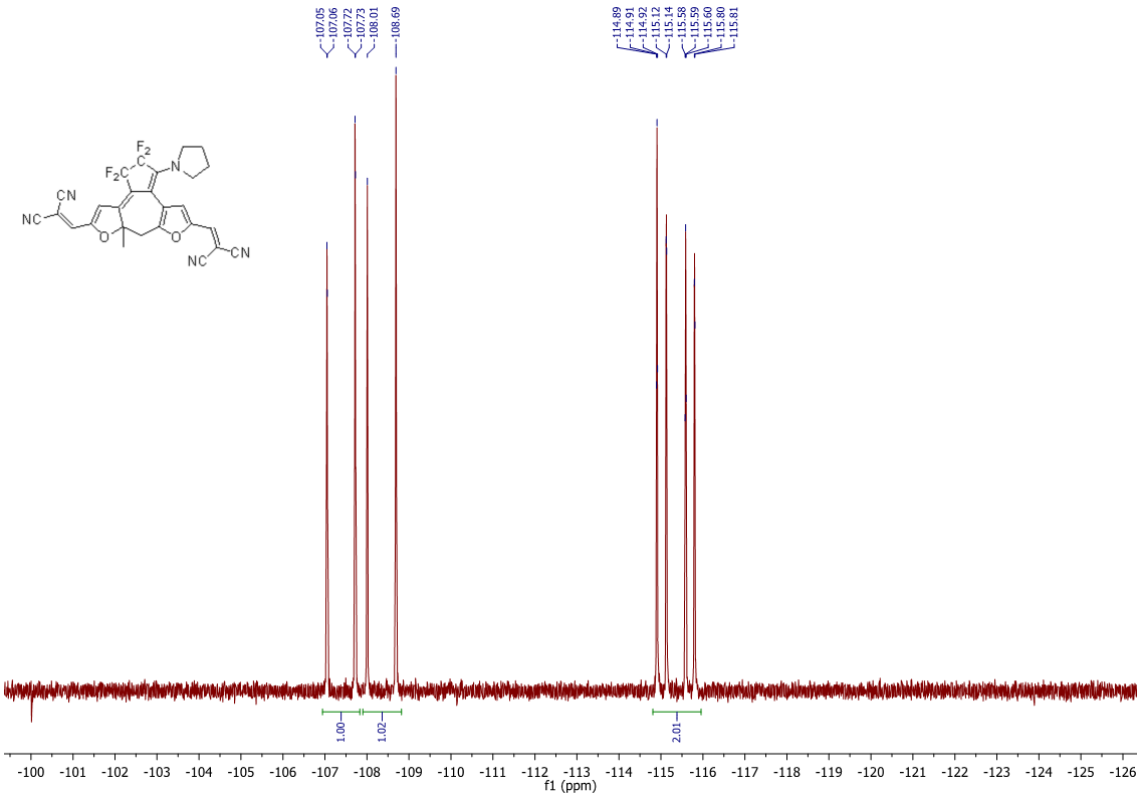


Figure S30. ^{19}F NMR spectrum of 7-MN-pyrr (**8b**) in $CDCl_3$.

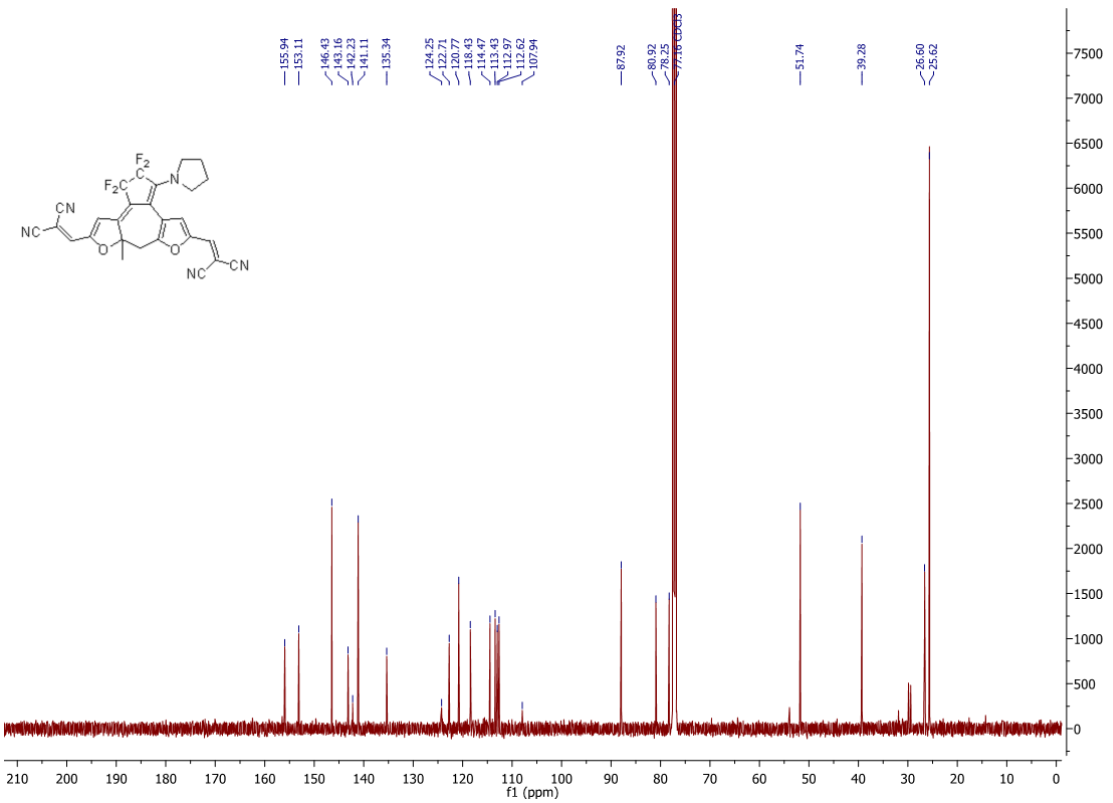


Figure S31. ^{13}C NMR spectrum of 7-MN-pyrr (**8b**) in $CDCl_3$.

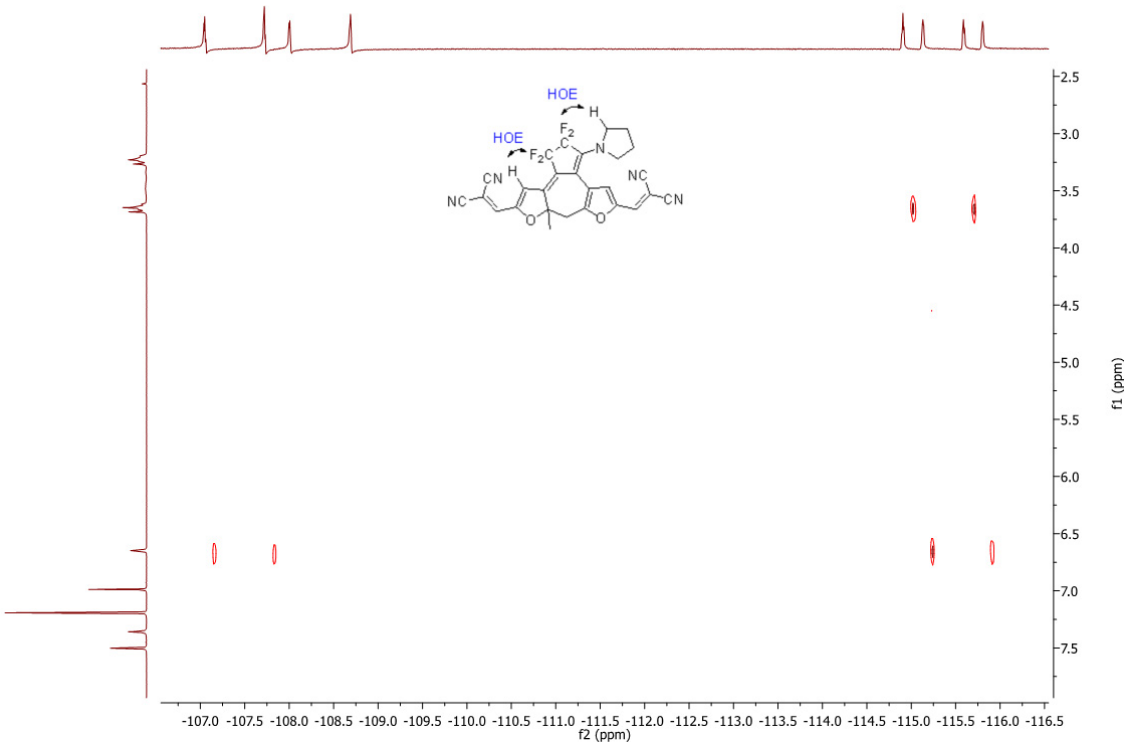


Figure S32. {^{1}H,^{19}F}-HOESY spectrum of 7-MN-pyrr (**8b**) in $CDCl_3$.

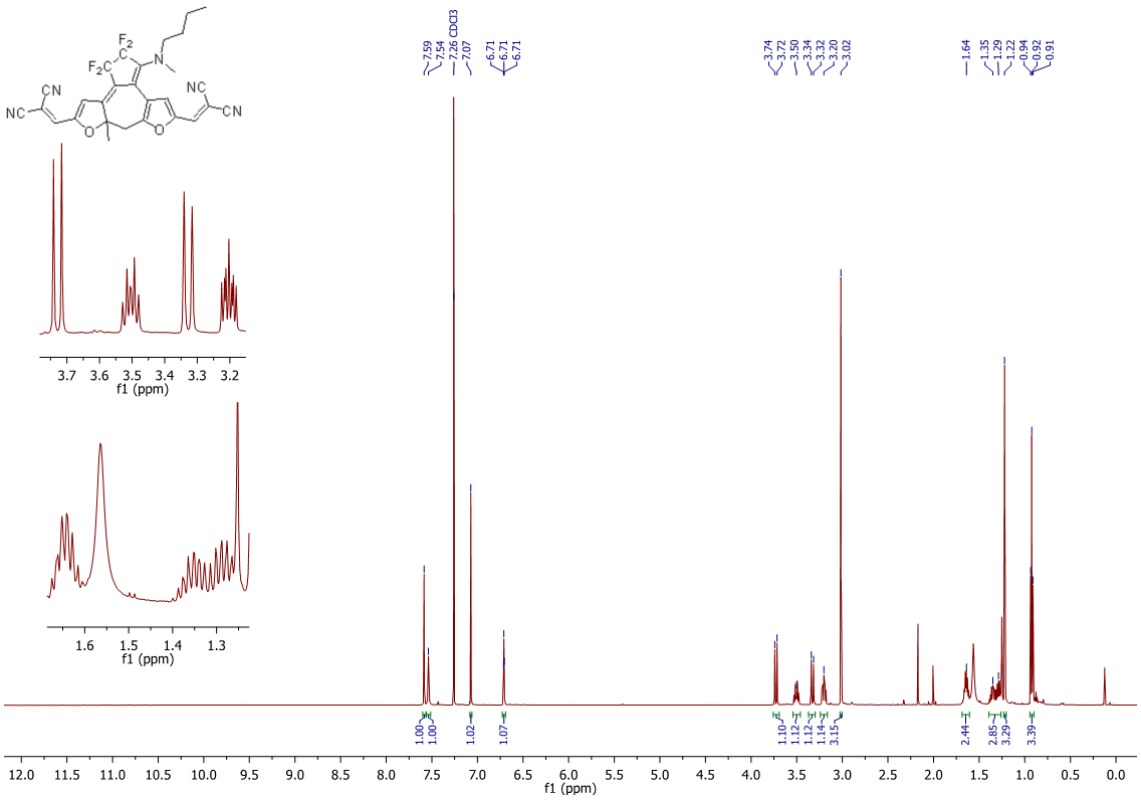


Figure S33. ^{1}H NMR spectrum of 7-MN-mebu (**8c**) in $CDCl_3$.

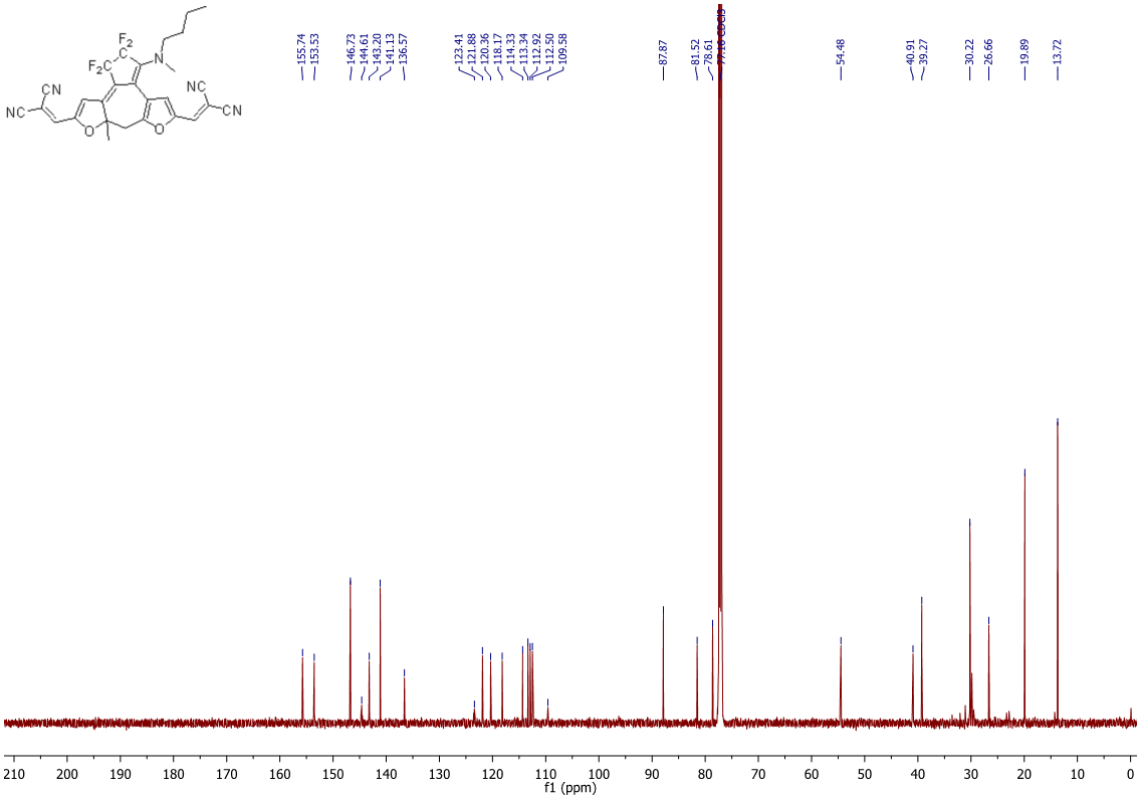


Figure S34. ^{13}C NMR spectrum of 7-MN-mebu (**8c**) in $CDCl_3$.

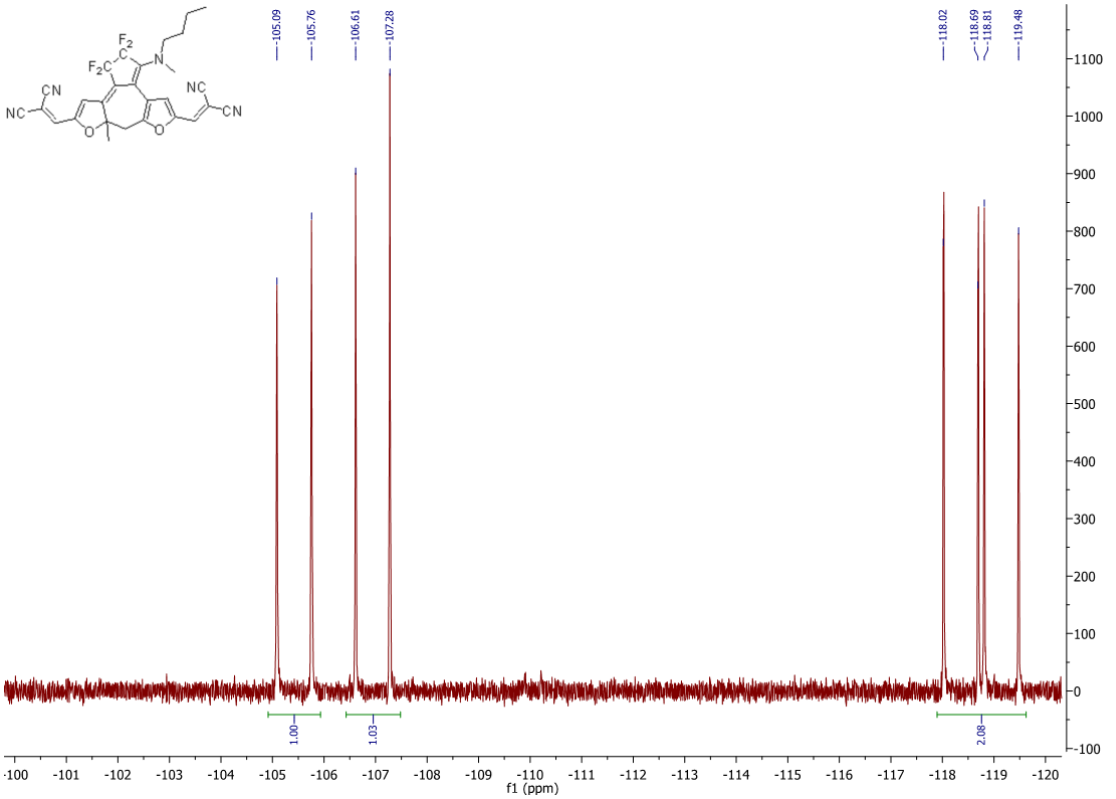


Figure S35. ^{19}F NMR spectrum of 7-MN-mebu (**8c**) in $CDCl_3$.

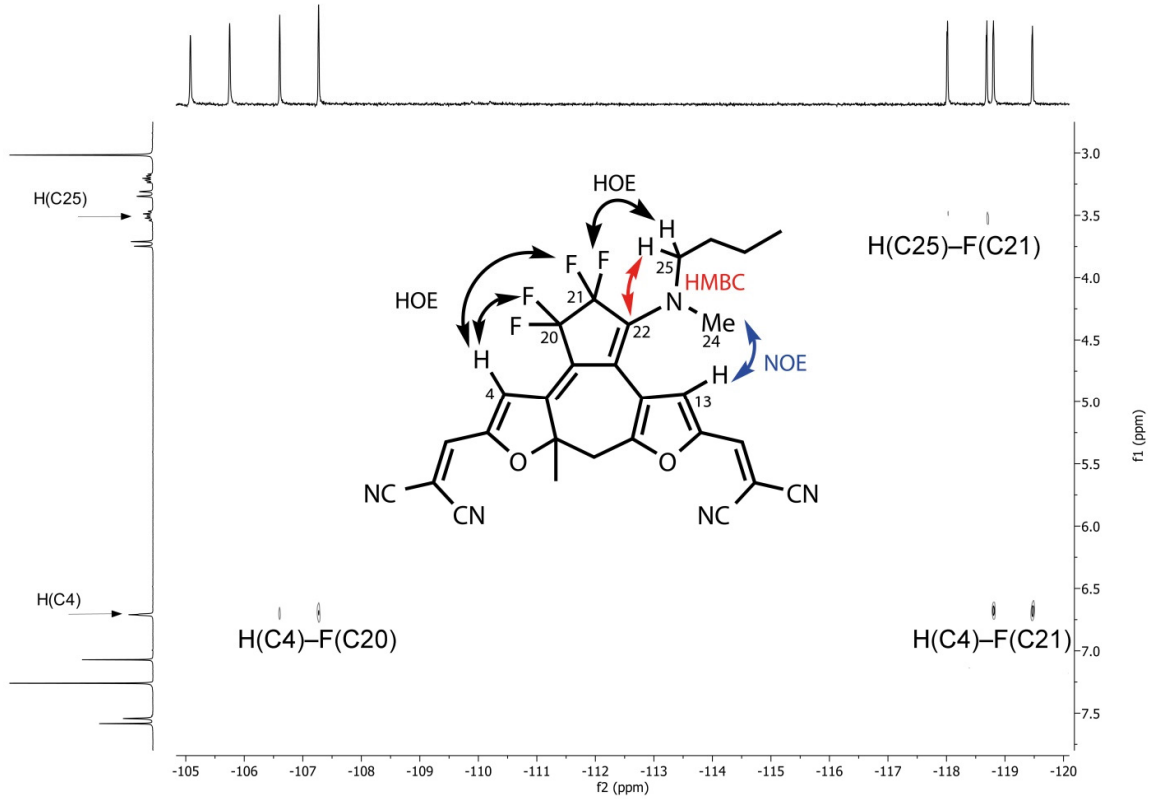


Figure S36. {^{1}H,^{19}F}-HOESY spectrum of 7-MN-mebu (**8c**) in $CDCl_3$. Inset shows coupling of protons and fluorine atoms of the tetrafluorocyclopentene moiety.

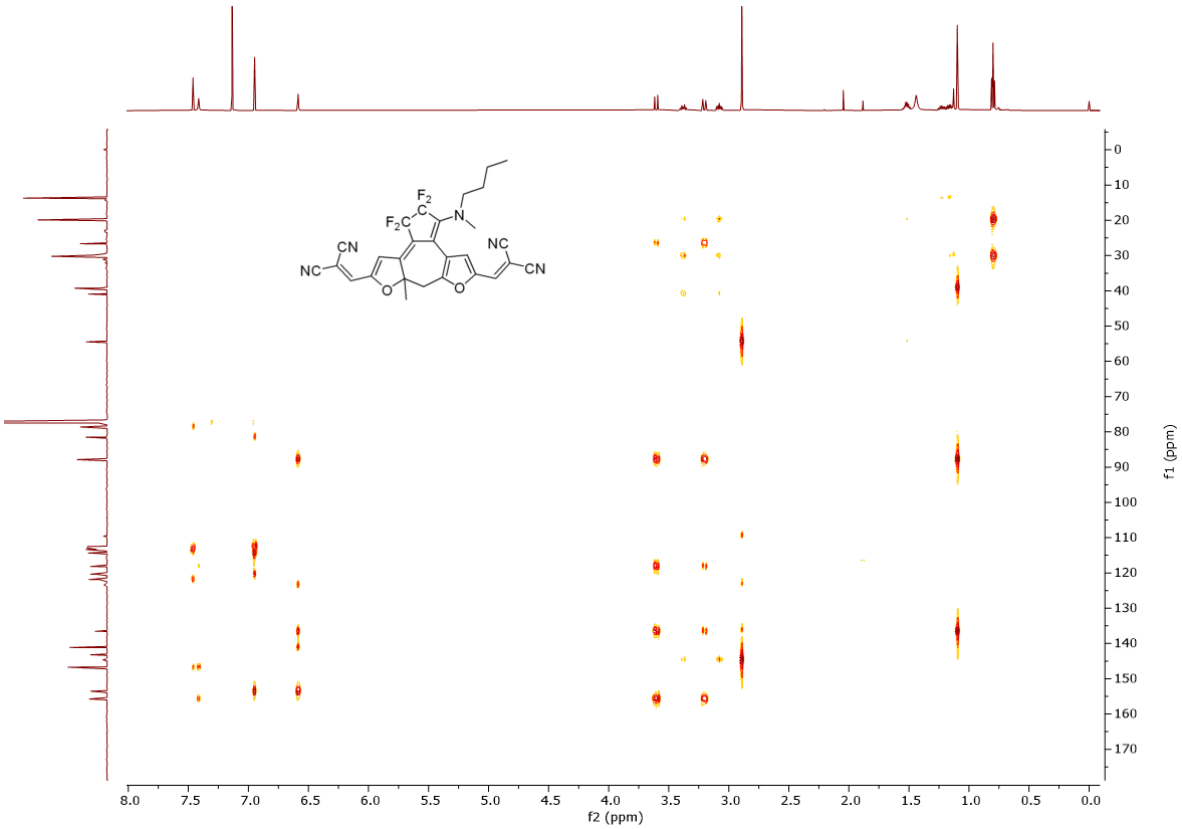


Figure S37. HMBC spectrum of 7-MN-mebu (**8c**) in $CDCl_3$.

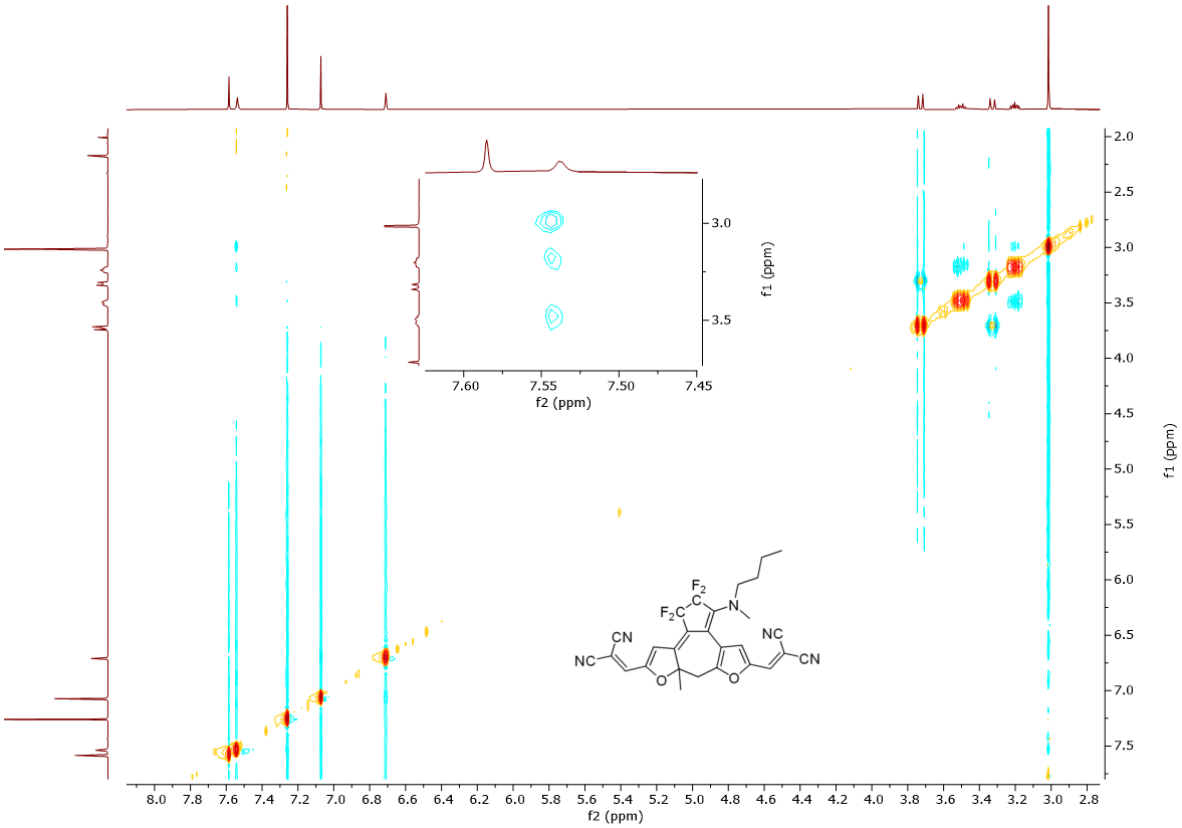


Figure S38. NOESY spectrum of 7-MN-mebu (**8c**) in $CDCl_3$.

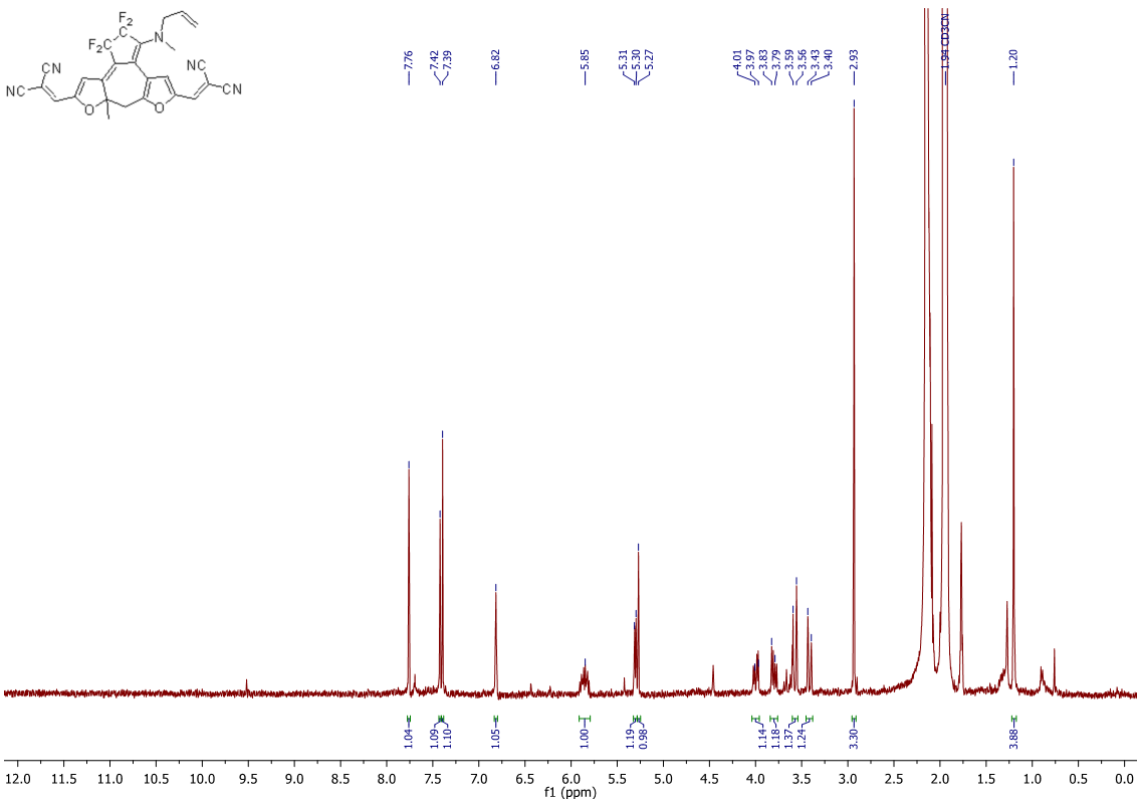


Figure S39. ^{1}H NMR spectrum of 7-MN-meall (**8d**) in $CDCl_3$.

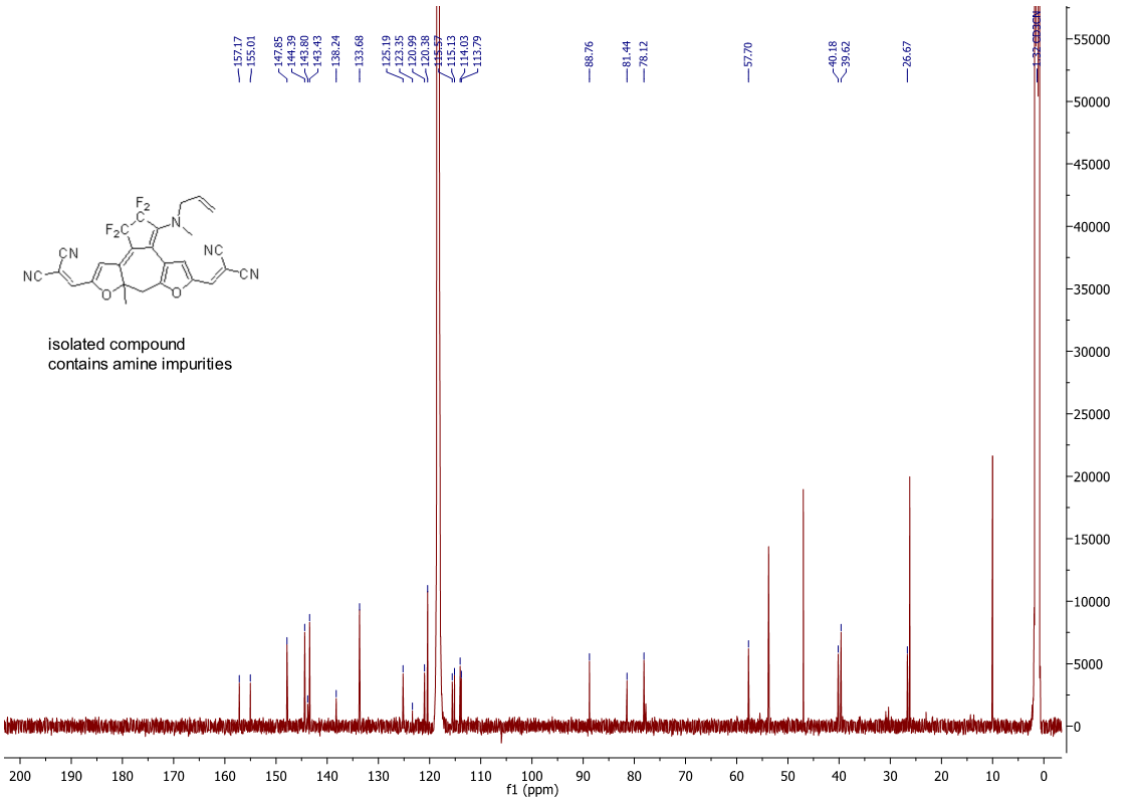


Figure S40. ^{13}C NMR spectrum of 7-MN-meall (**8d**) in $CDCl_3$.

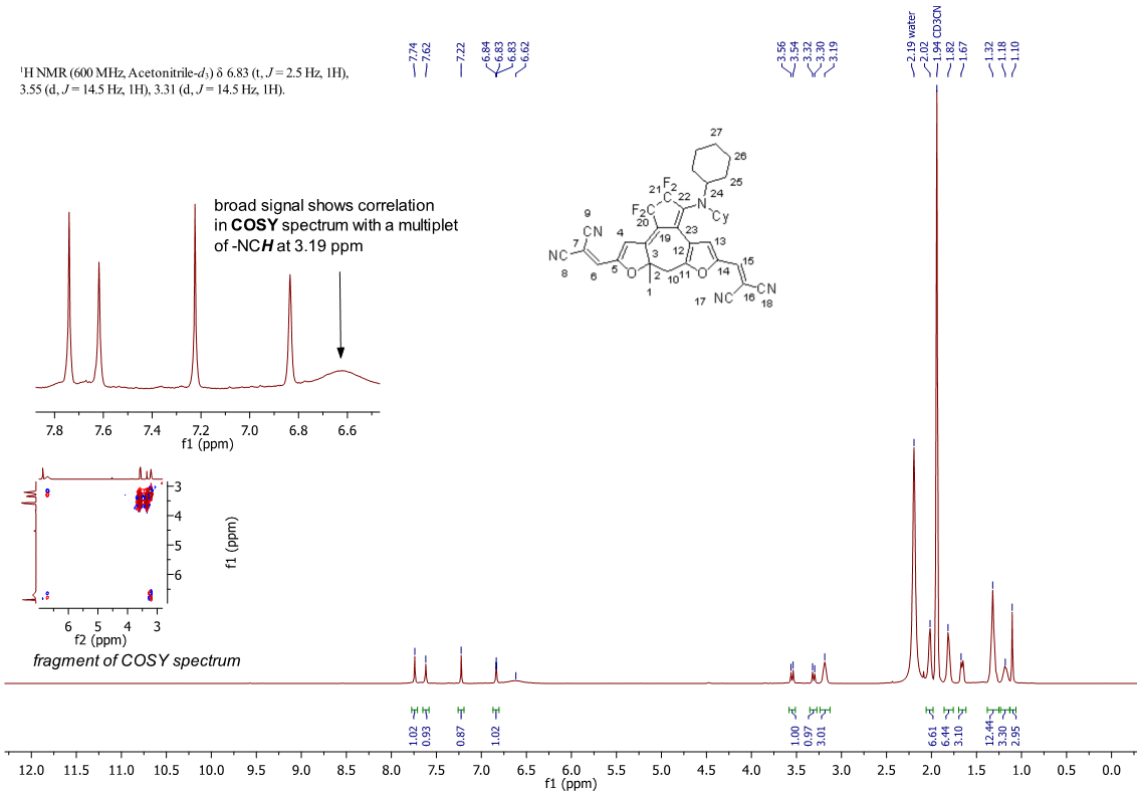


Figure S41. ^{1}H NMR spectrum of 7-MN-cy (**8e**) in CD_3CN.

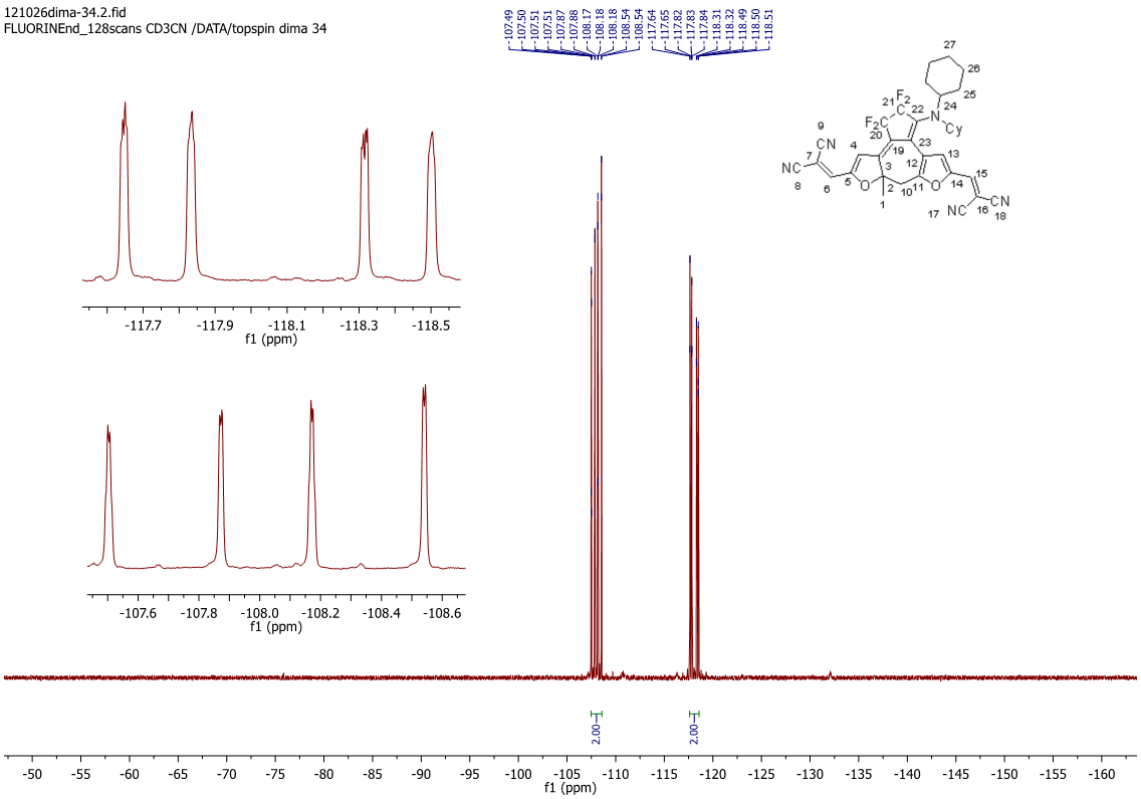


Figure S42. ^{19}F NMR spectrum of 7-MN-cy (**8e**) in CD_3CN.

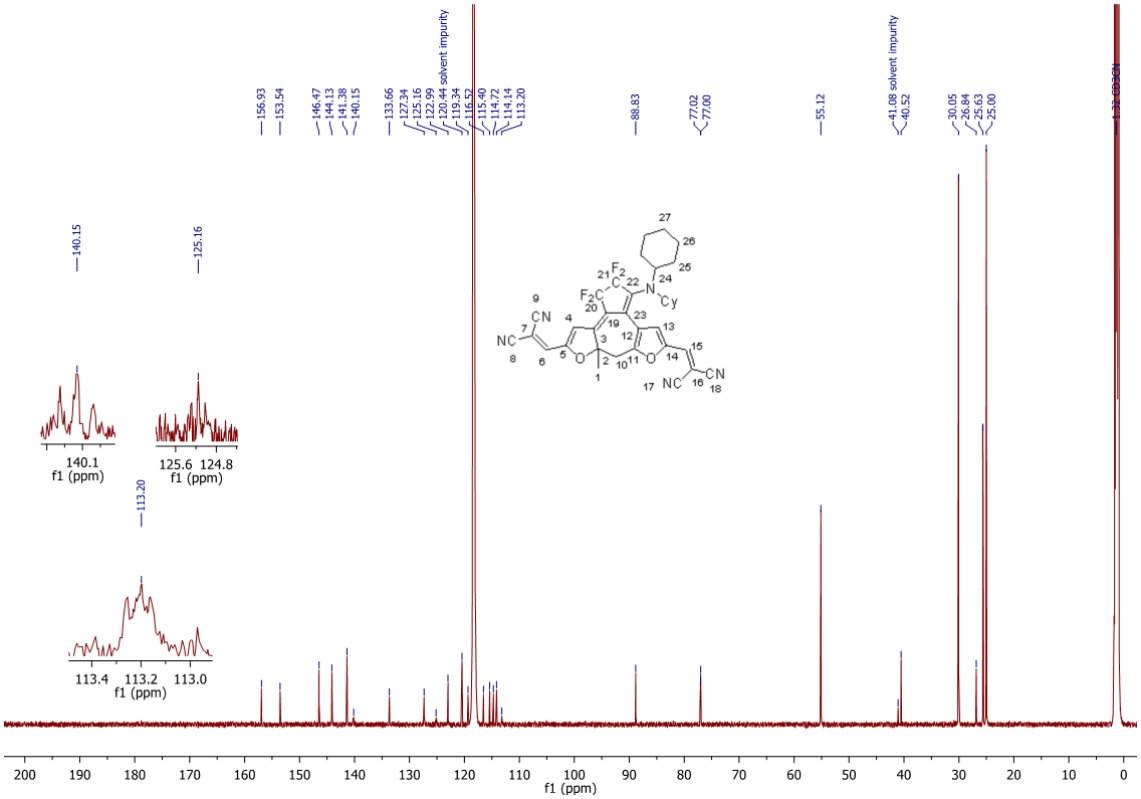


Figure S43. ^{13}C NMR spectrum of 7-MN-cy (**8e**) in CD_3CN.

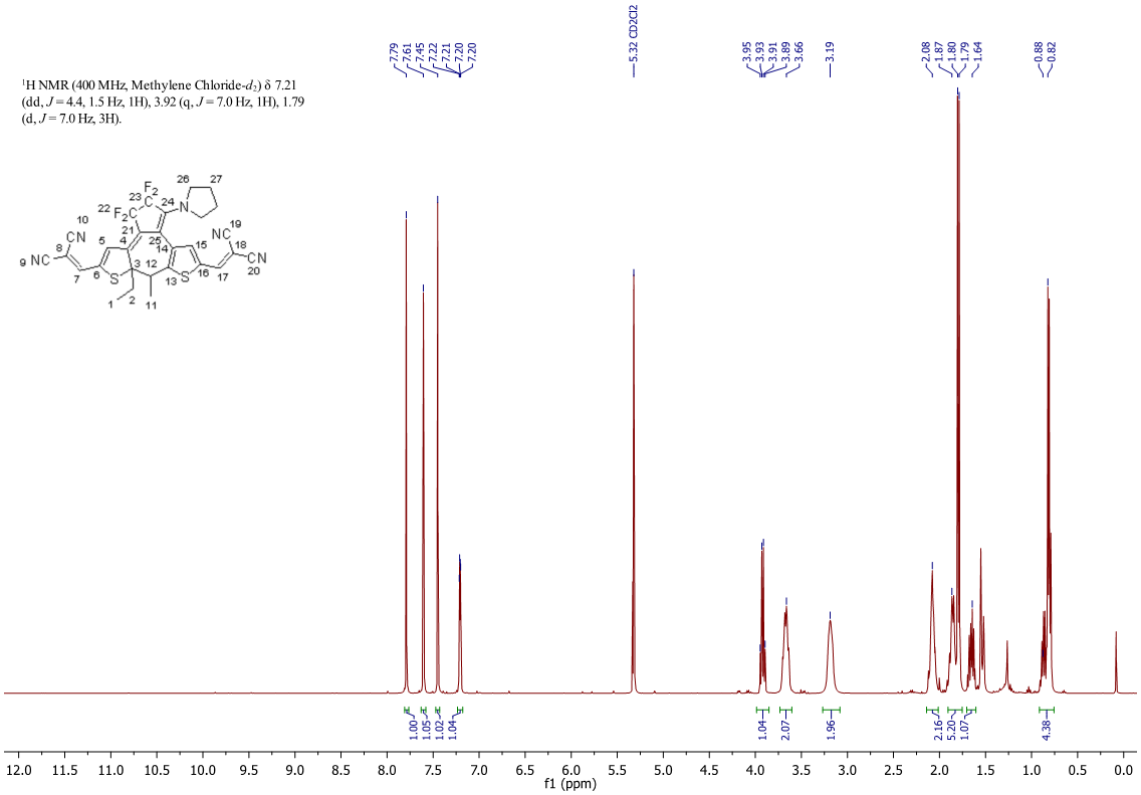


Figure S44. ^{1}H NMR spectrum of 7-T-Et-MN-pyrr (**8f**) in CD_2Cl_2.

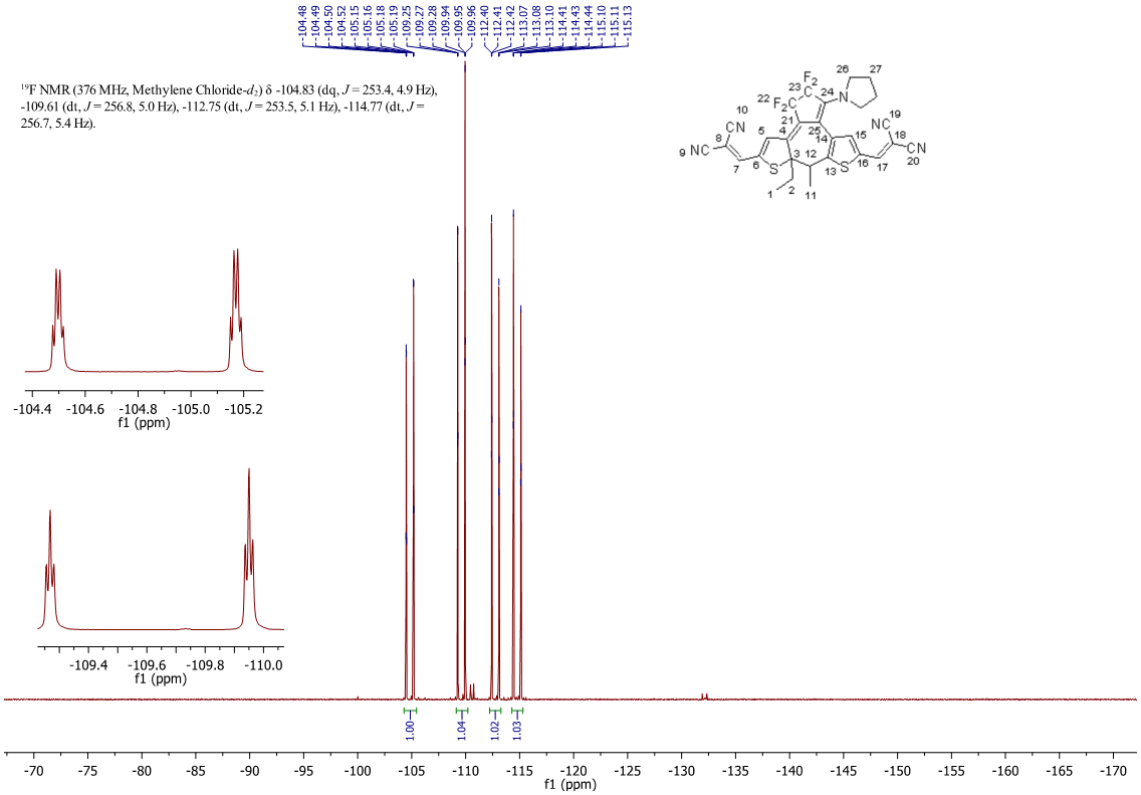


Figure S45. ^{19}F NMR spectrum of 7-T-Et-MN-pyrr (**8f**) in CD_2Cl_2.

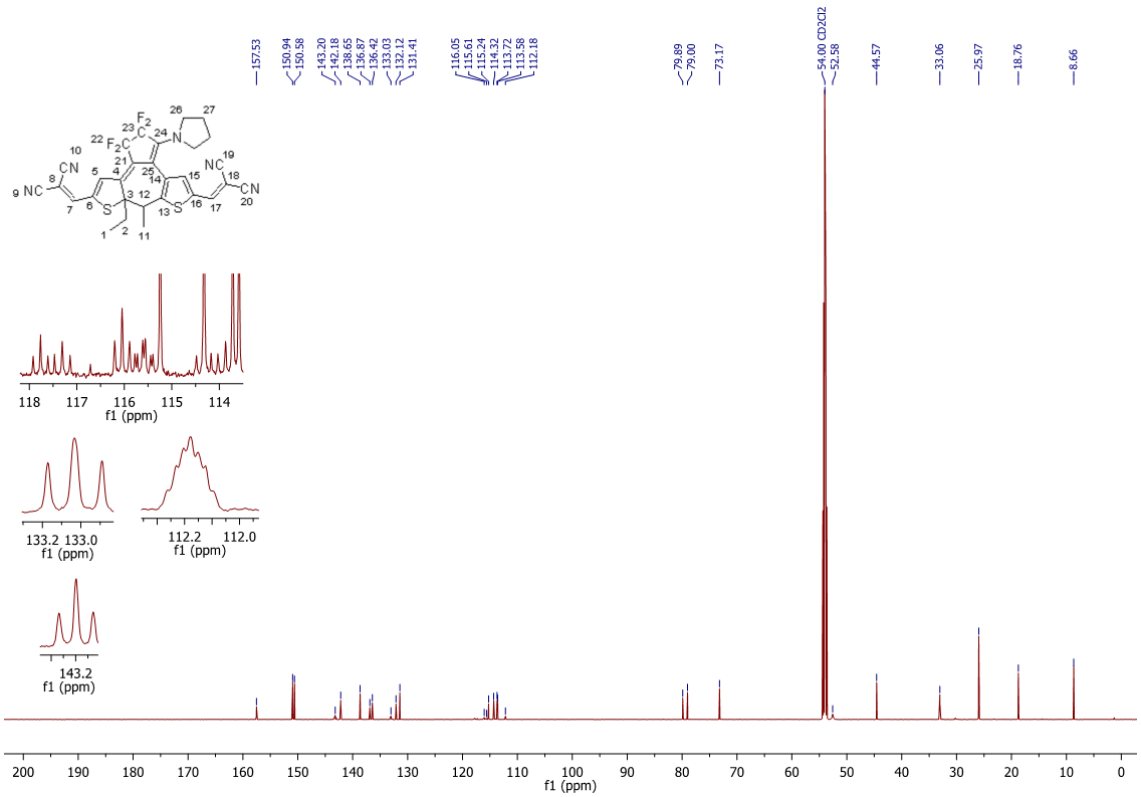


Figure S46. ^{13}C NMR spectrum of 7-T-Et-MN-pyrr (**8f**) in CD_2Cl_2.

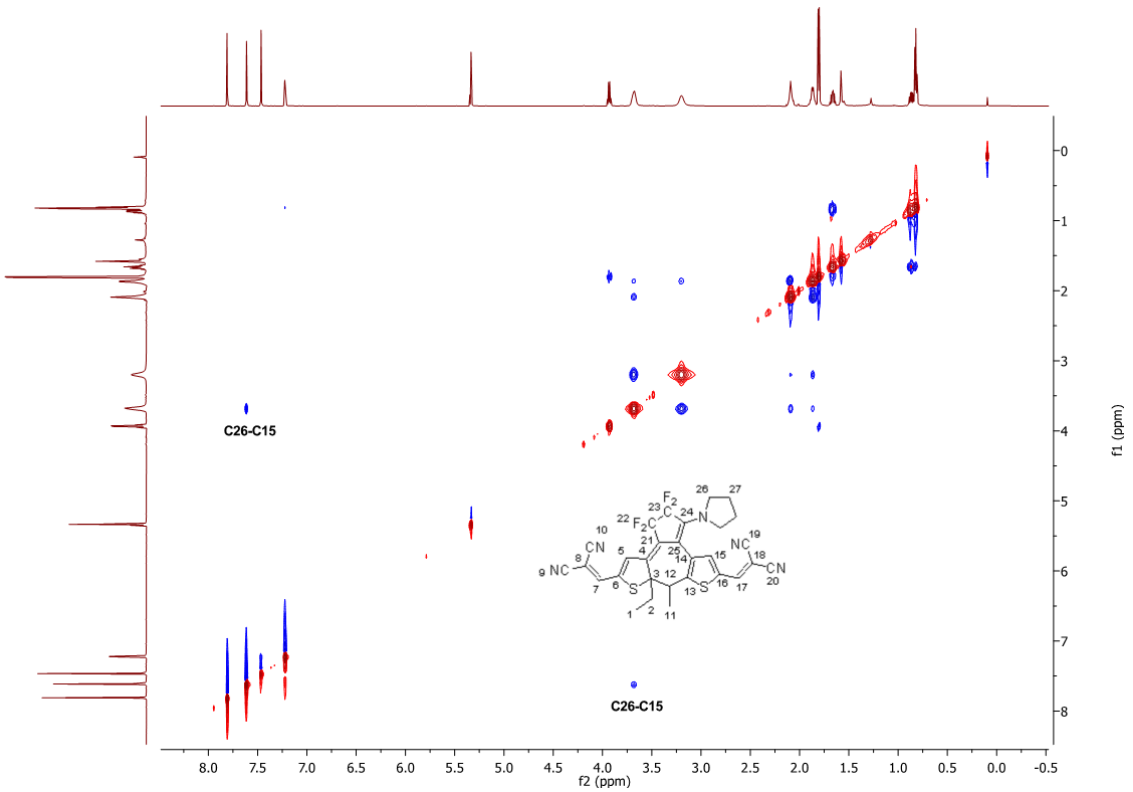


Figure S47. NOESY spectrum of 7-T-Et-MN-pyrr (**8f**) in CD_2Cl_2.

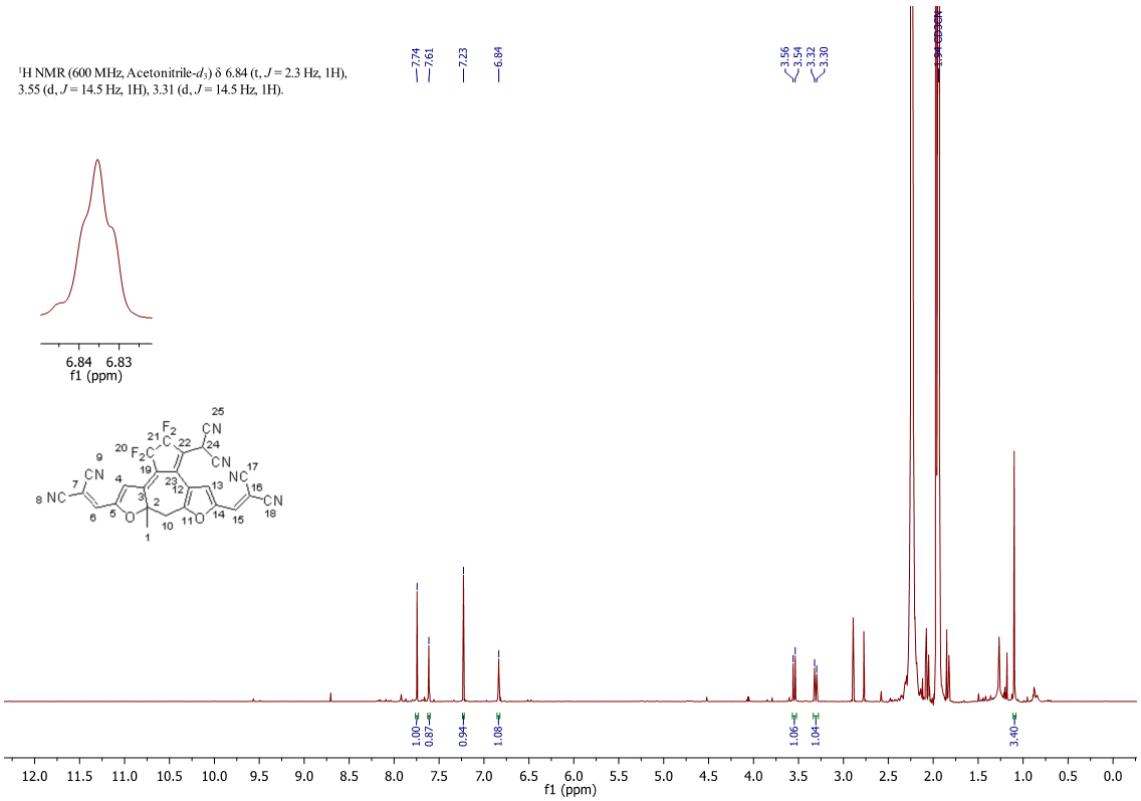


Figure S48. ^{1}H NMR spectrum of 7-MN-MN (**8g**) in CD_3CN.

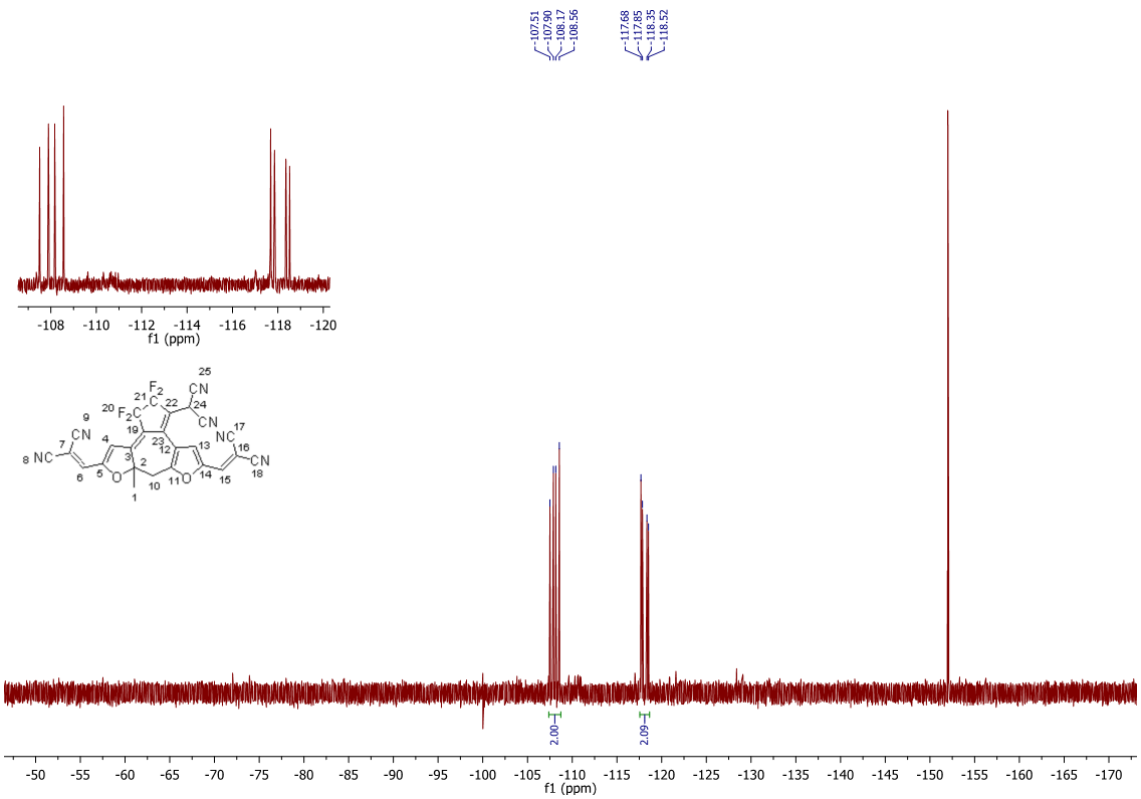


Figure S49. ^{19}F NMR spectrum of 7-MN-MN (**8g**) in CD_3CN.

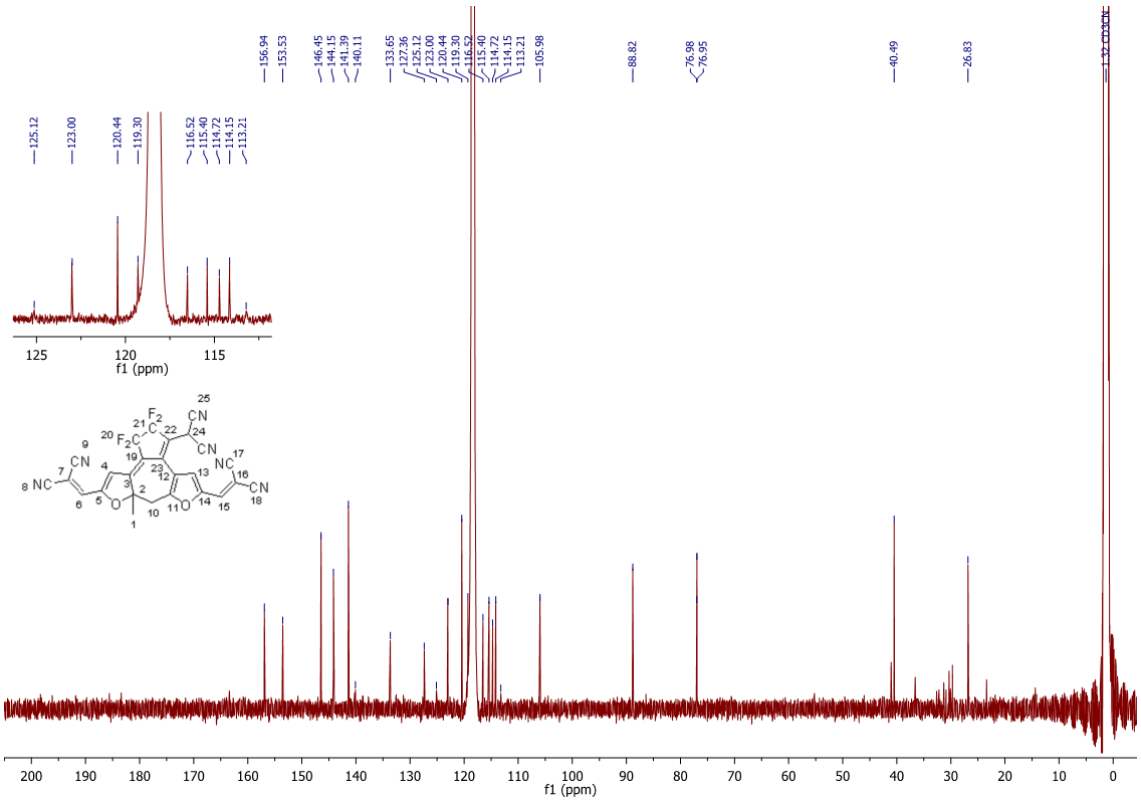


Figure S50. ^{13}C NMR spectrum of 7-MN-MN (**8g**) in CD_3CN.

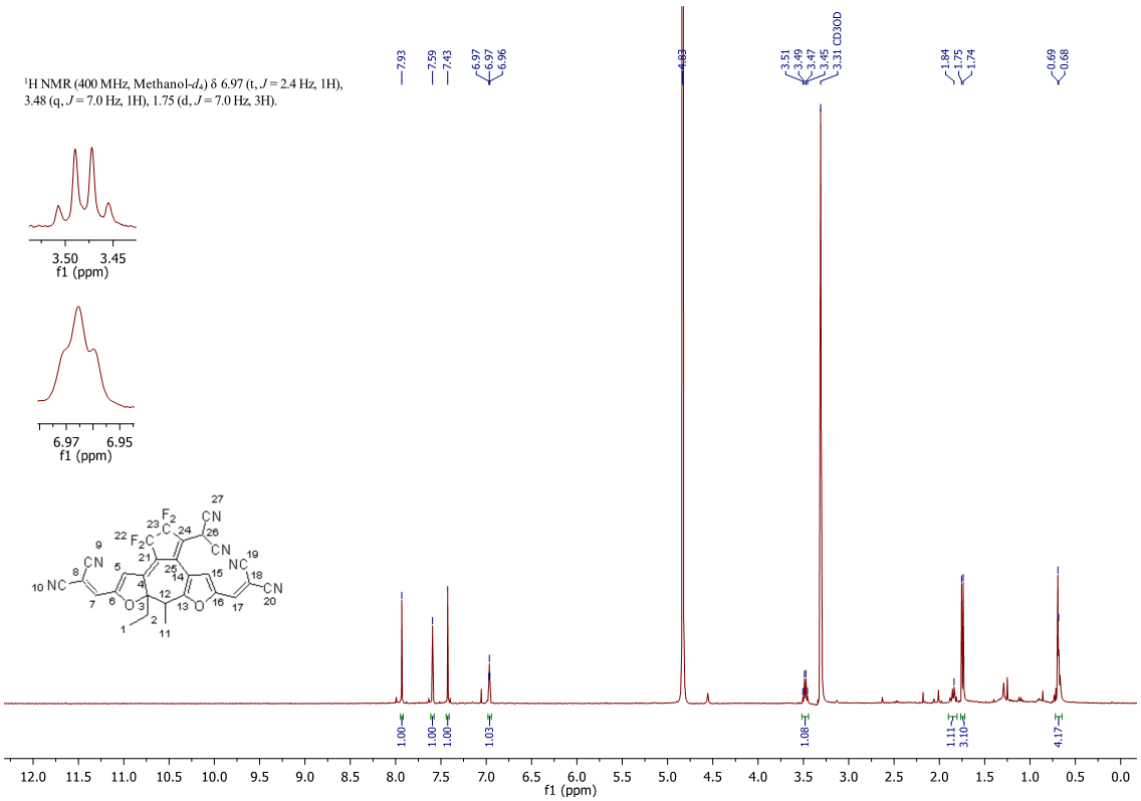


Figure S51. ^{1}H NMR spectrum of 7-Et-MN-MN (**8h**) in CD_3OD.

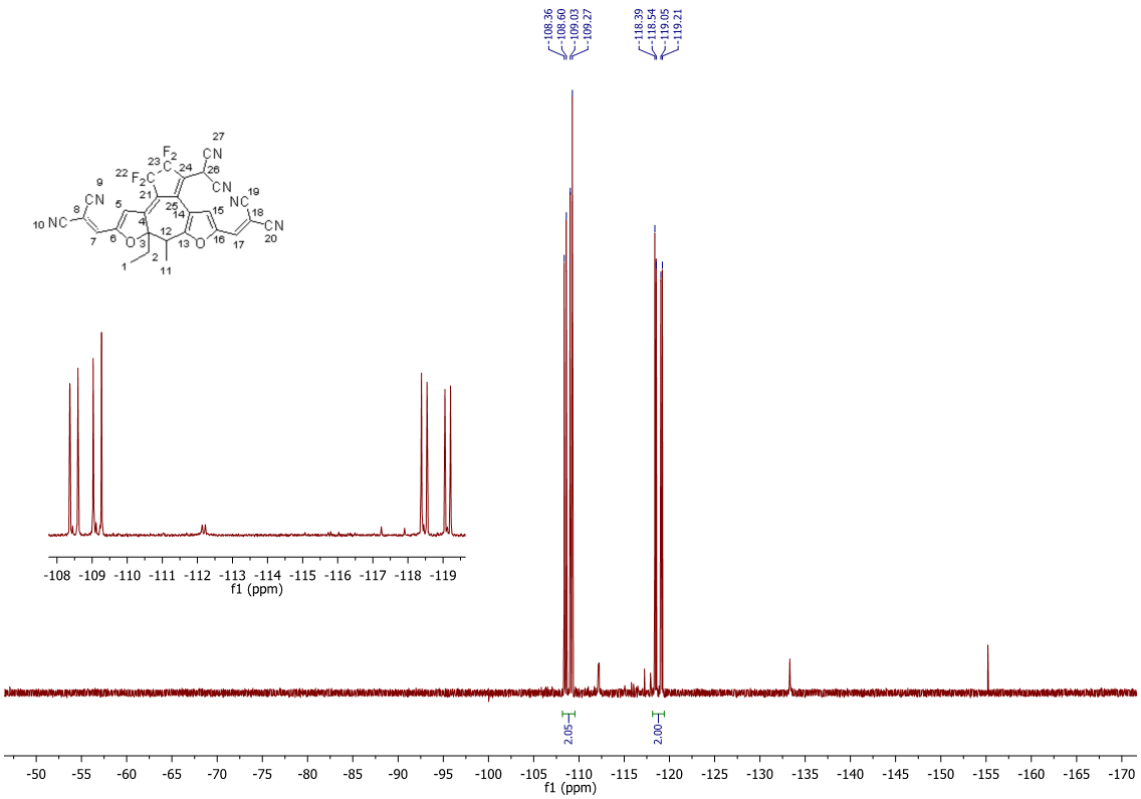


Figure S52. ^{19}F NMR spectrum of 7-Et-MN-MN (**8h**) in CD_3OD.

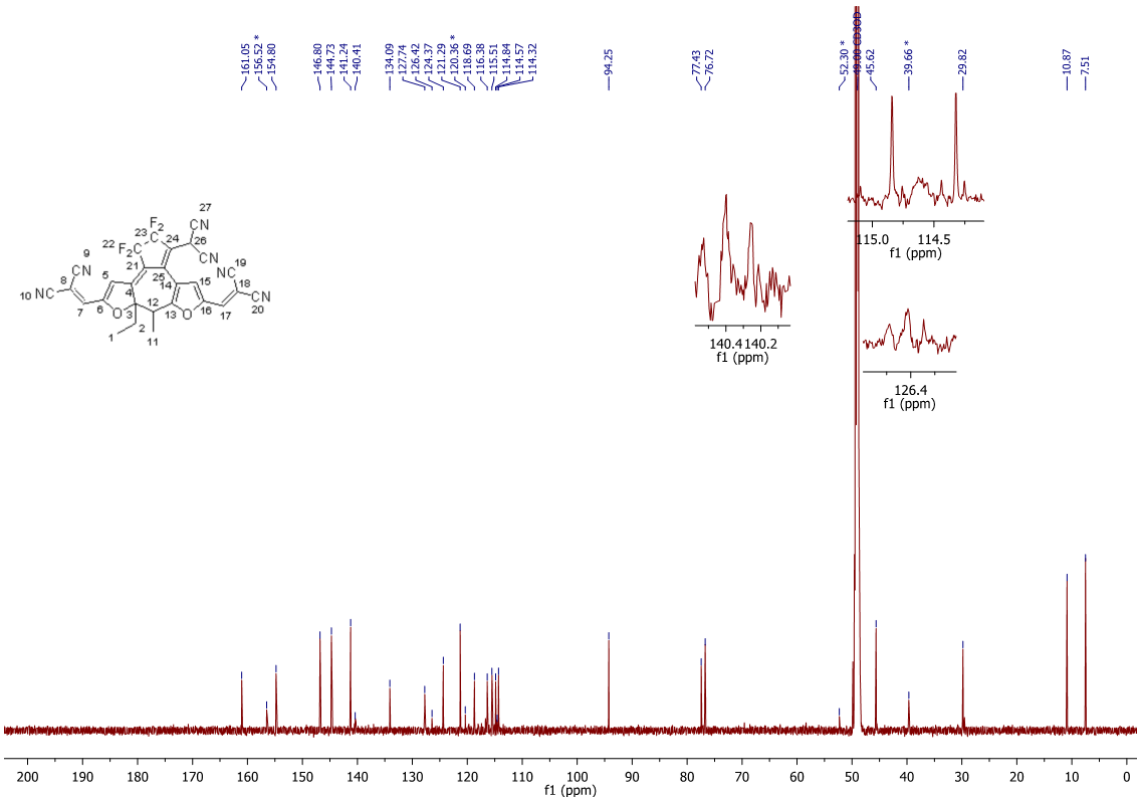


Figure S53. ^{13}C NMR spectrum of 7-Et-MN-MN (**8h**) inCD_3OD.

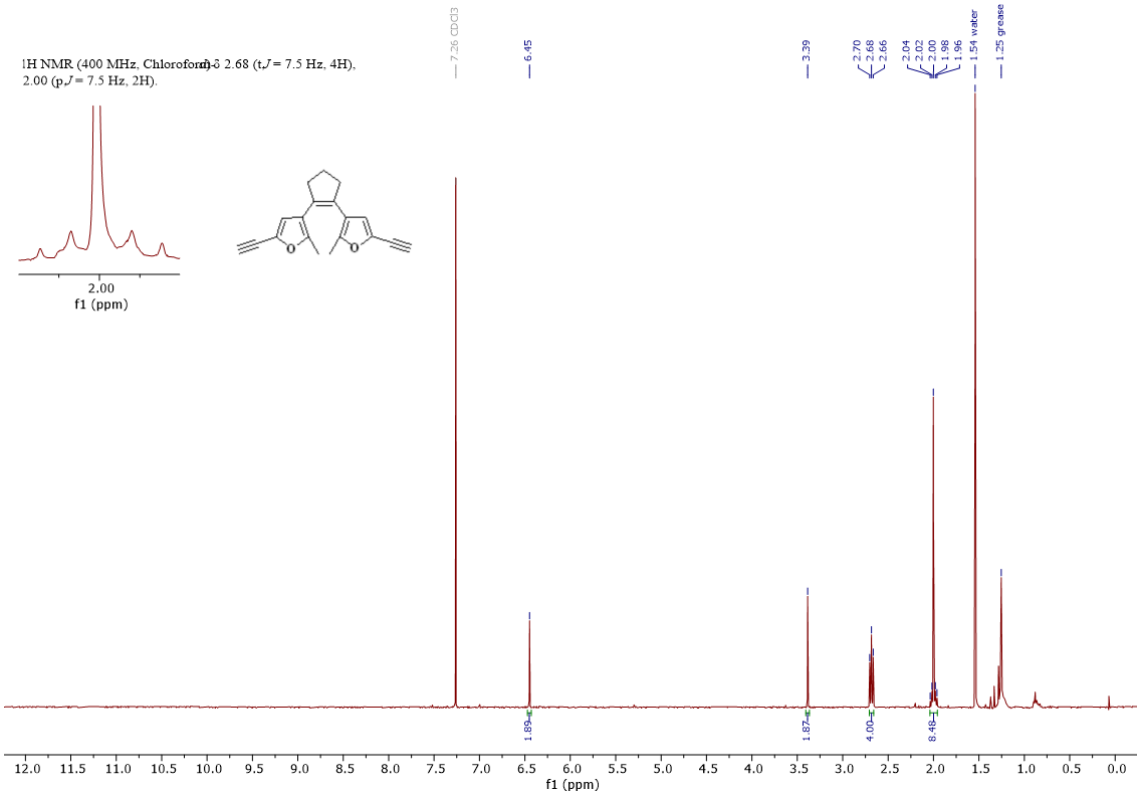


Figure S54. ^{1}H NMR spectrum of C5H-yne (**19**) in $CDCl_3$.

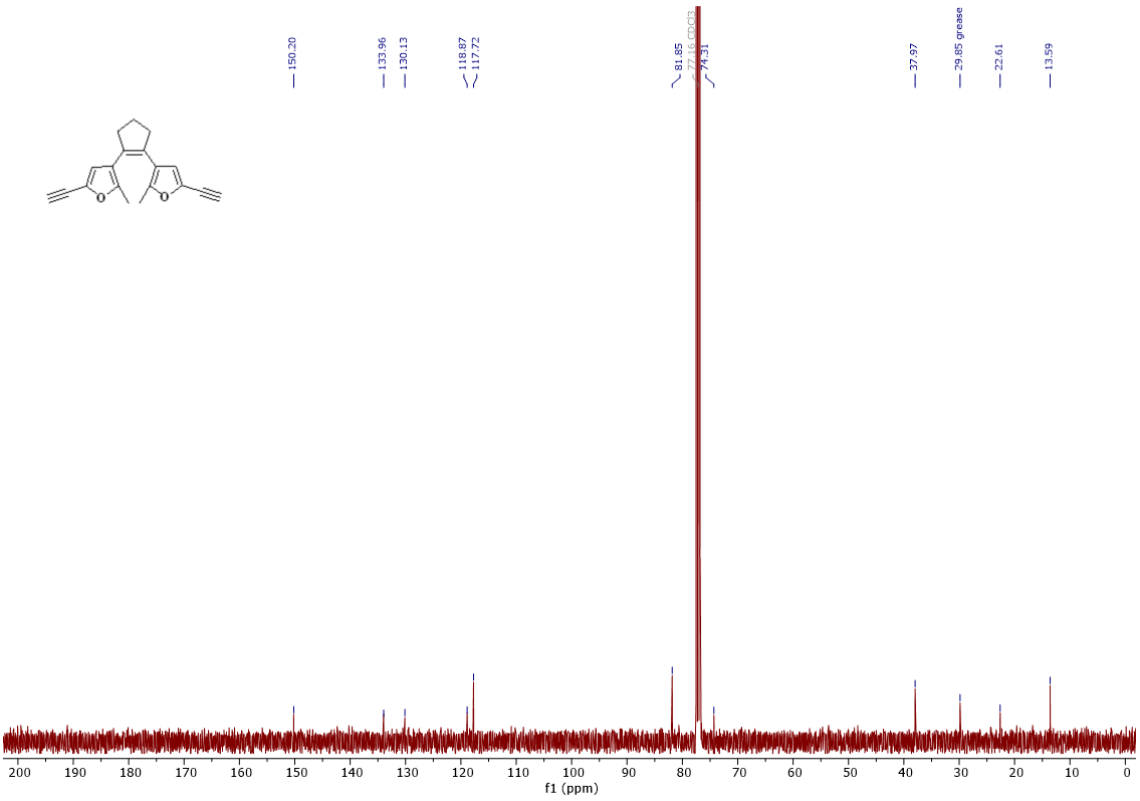
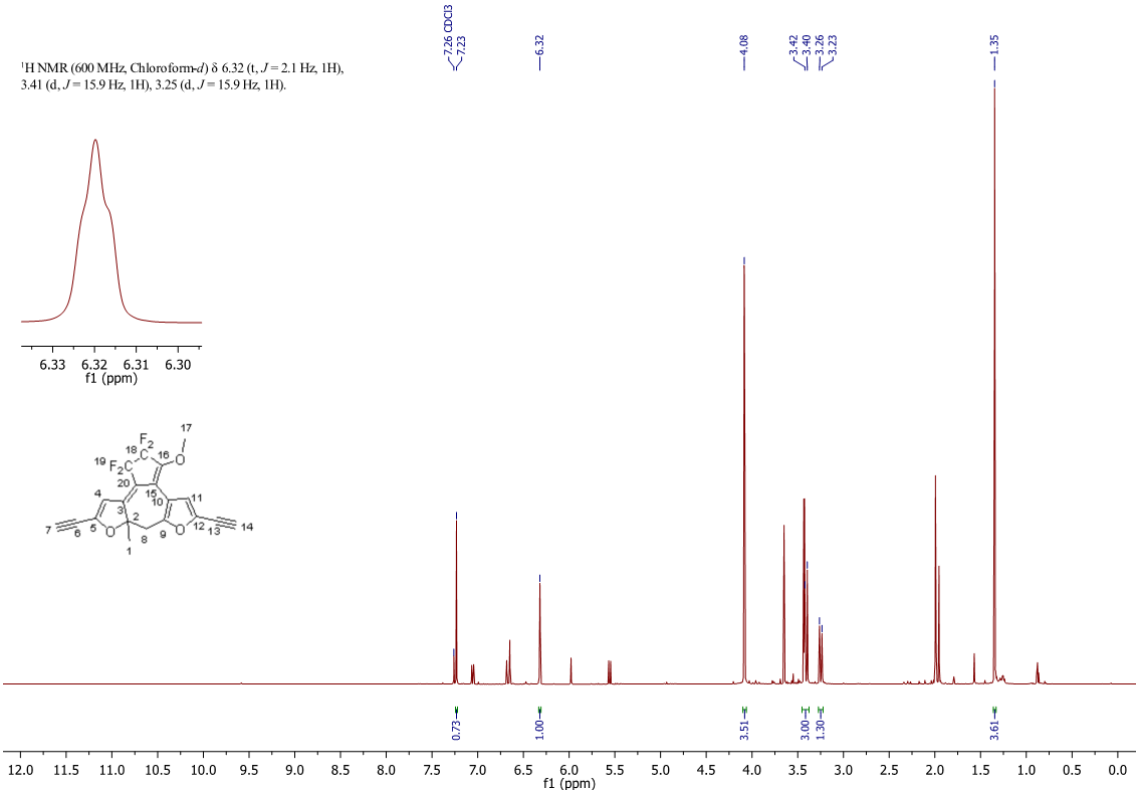


Figure S55. ^{13}C NMR spectrum of C5H-yne (**19**) in $CDCl_3$.



^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.32 (t, *J* = 2.1 Hz, 1H), 3.41 (d, *J* = 15.9 Hz, 1H), 3.25 (d, *J* = 15.9 Hz, 1H).

Figure S56. ^{1}H NMR spectrum of 7-yne-OMe (**20**) in $CDCl_3$ (only signals corresponding to **20** are marked).

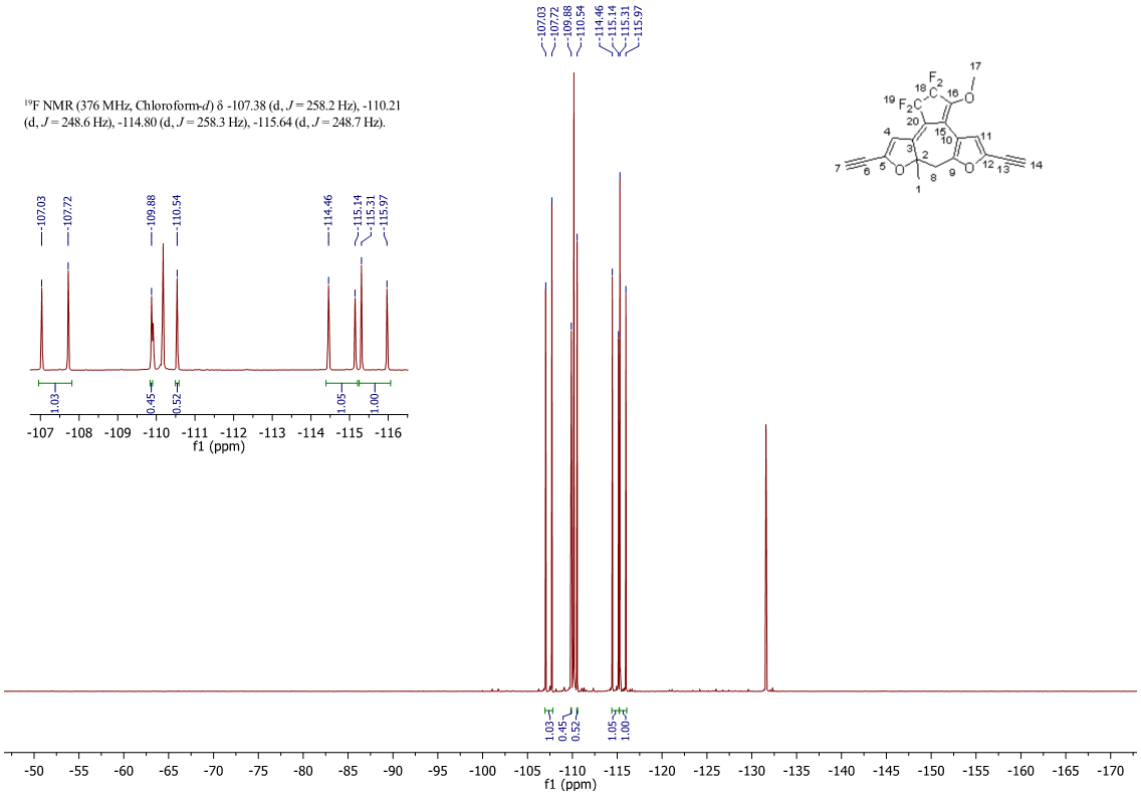


Figure S57. ^{19}F NMR spectrum of 7-yne-OMe (**20**) in $CDCl_3$ (only signals corresponding to **20** are marked).

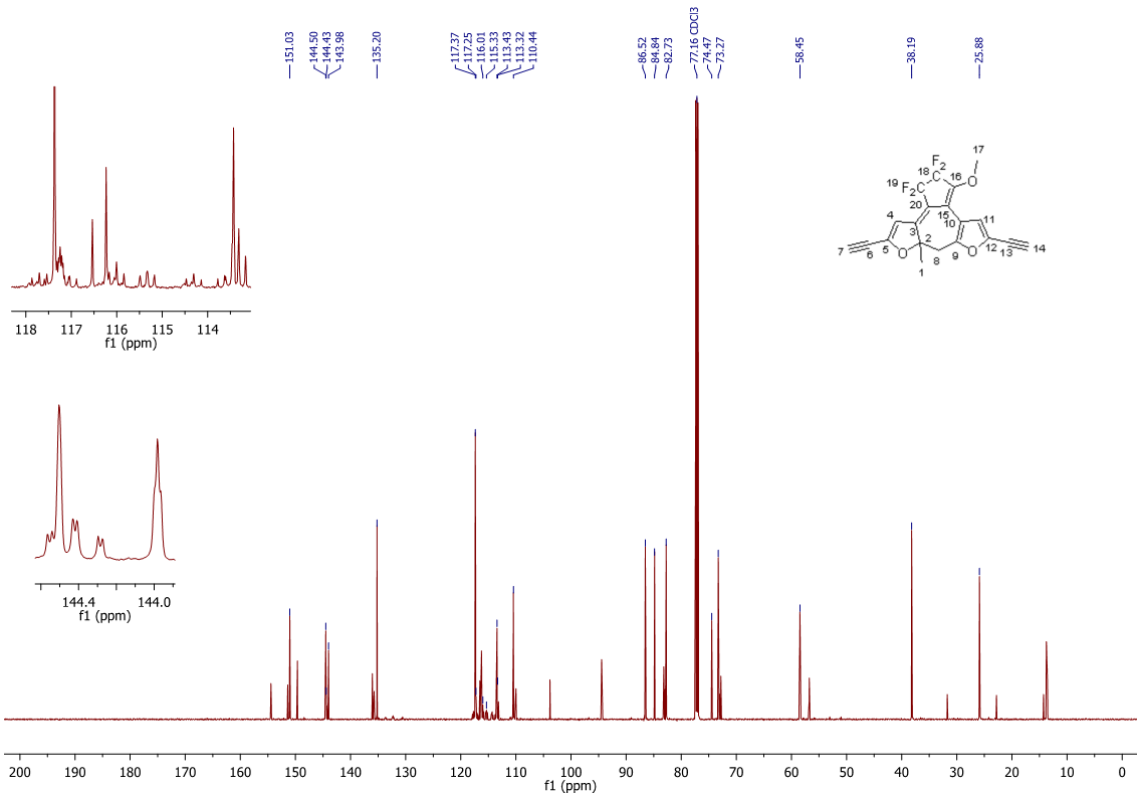


Figure S58. ^{13}C NMR spectrum of 7-yne-OMe (**20**) in $CDCl_3$ (only signals corresponding to **20** are marked).

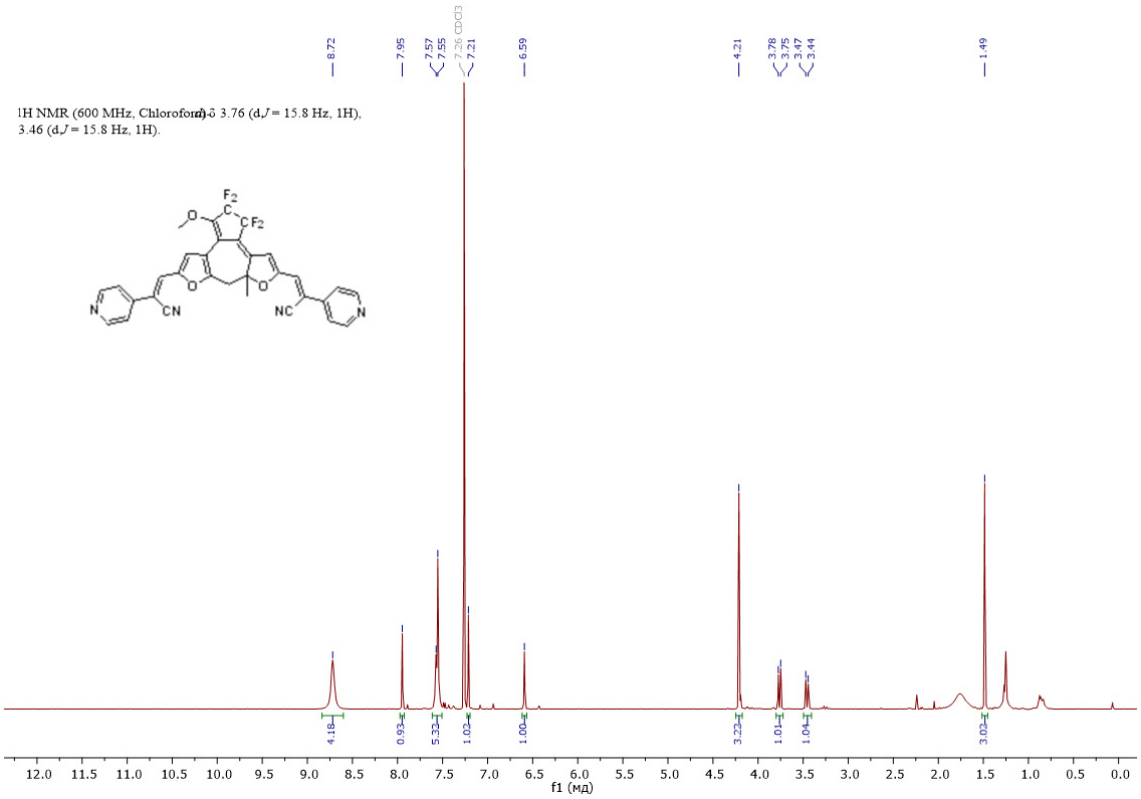


Figure S59. ^{1}H NMR spectrum of 7-MN-4PyOMe (**17**) in $CDCl_3$.

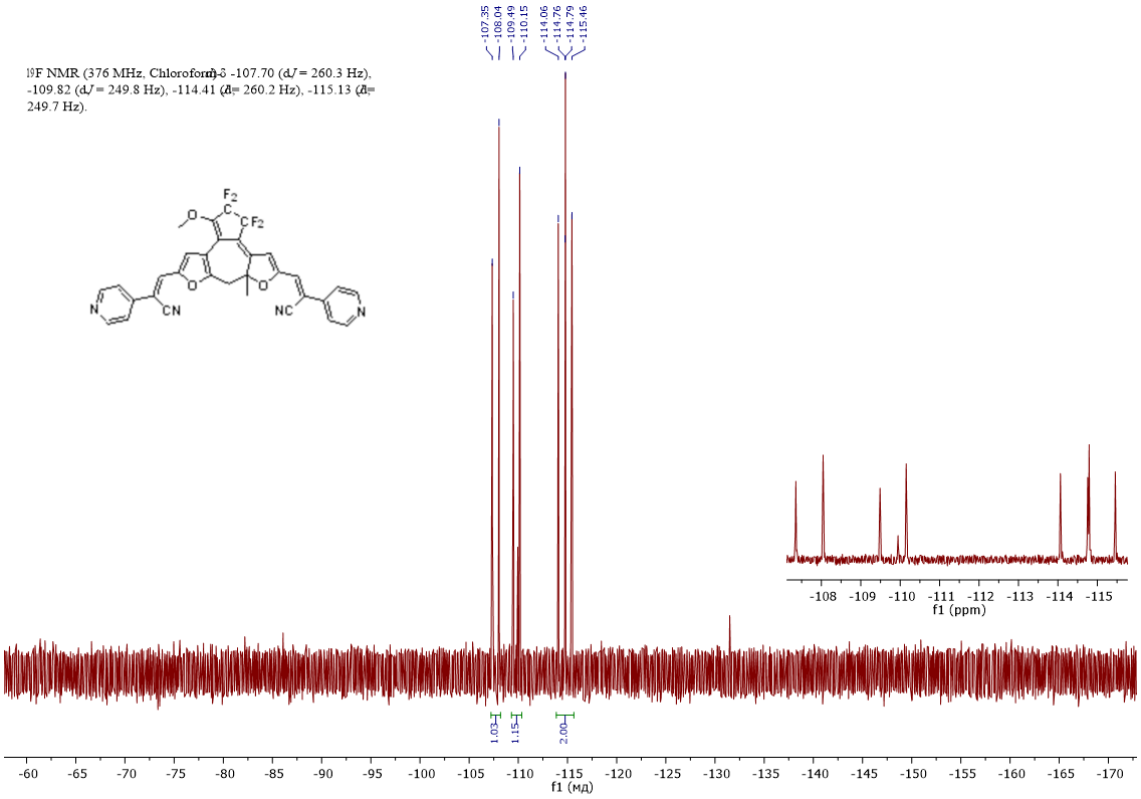


Figure S60. ^{19}F NMR spectrum of 7-MN-4PyOMe (**17**) in $CDCl_3$.

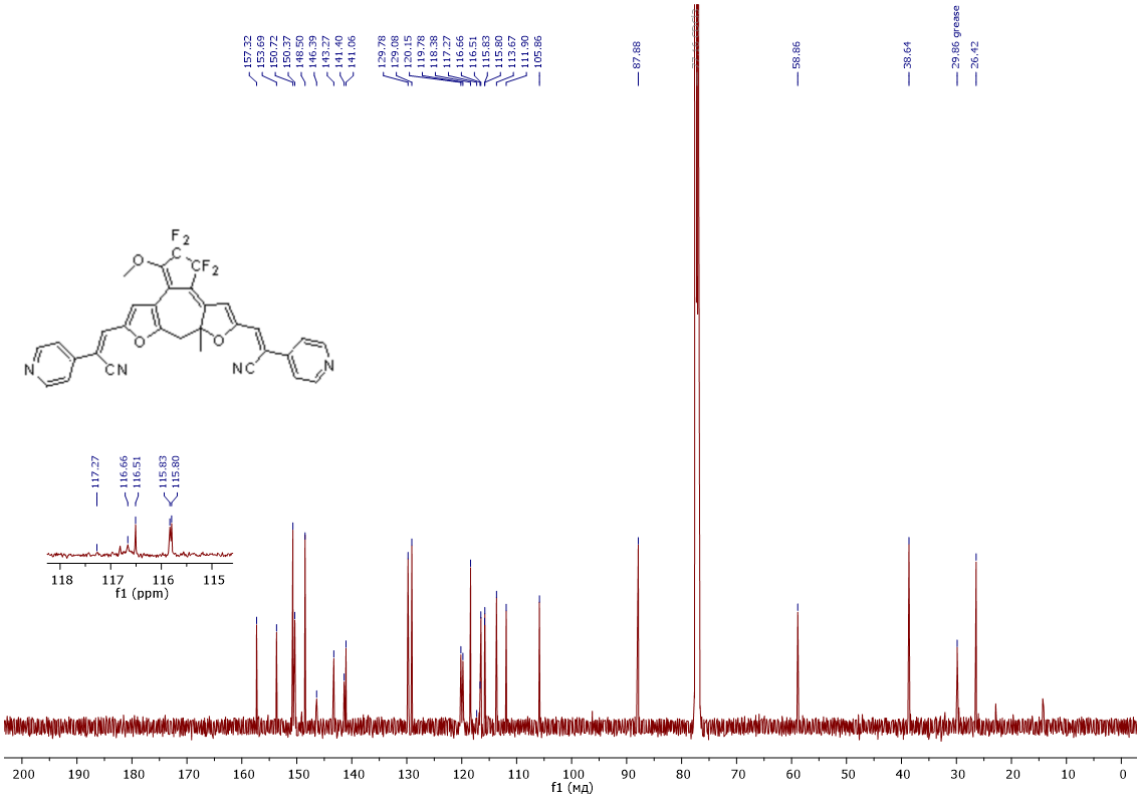


Figure S61. ^{13}C NMR spectrum of 7-MN-4PyOMe (**17**) in $CDCl_3$.

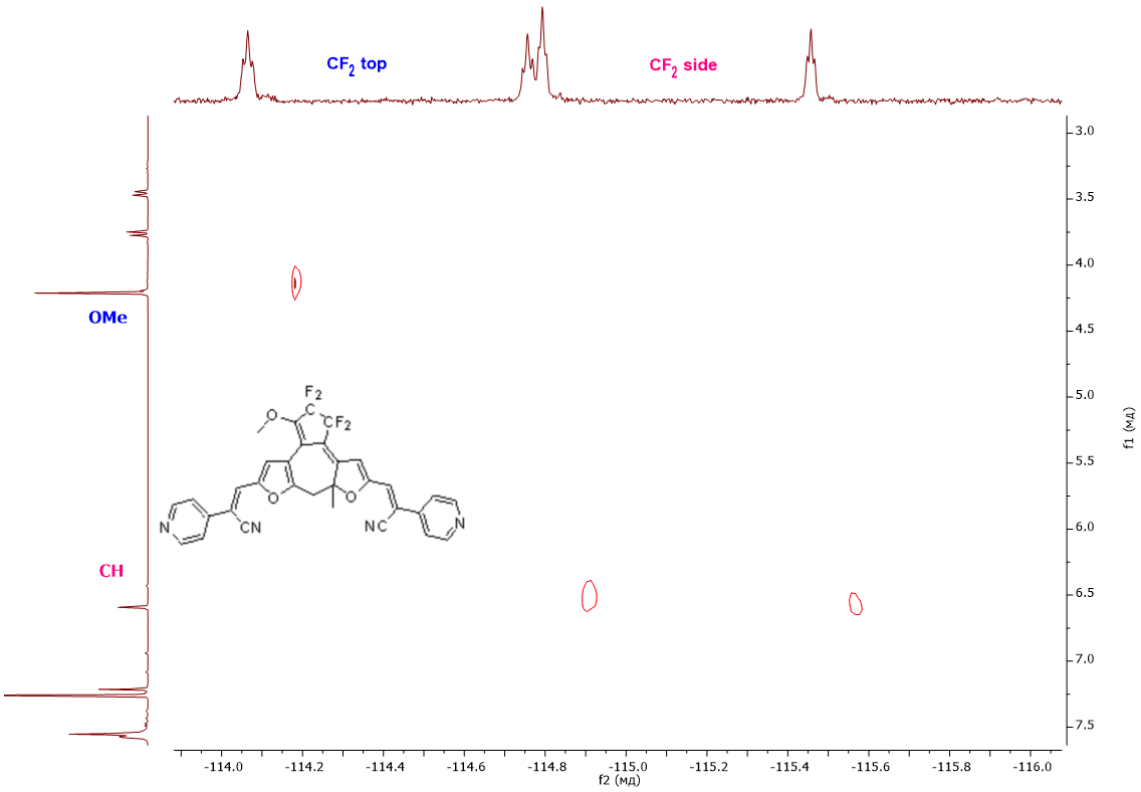


Figure S62. {^{1}H,^{19}F}-HOESY spectrum of 7-MN-4PyOMe (**17**) in $CDCl_3$.

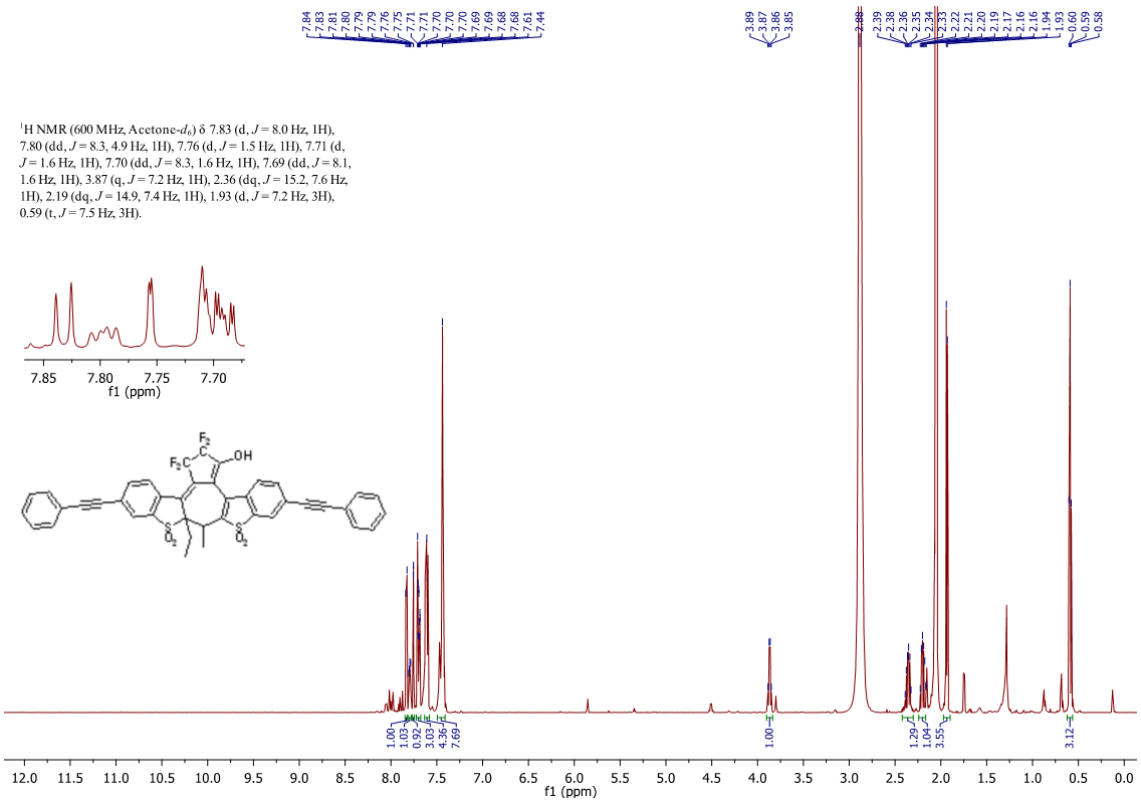


Figure S63. [1]H NMR spectrum of 7-BTSO2Et-PhCC-OH (**22**) in acetone-d6.

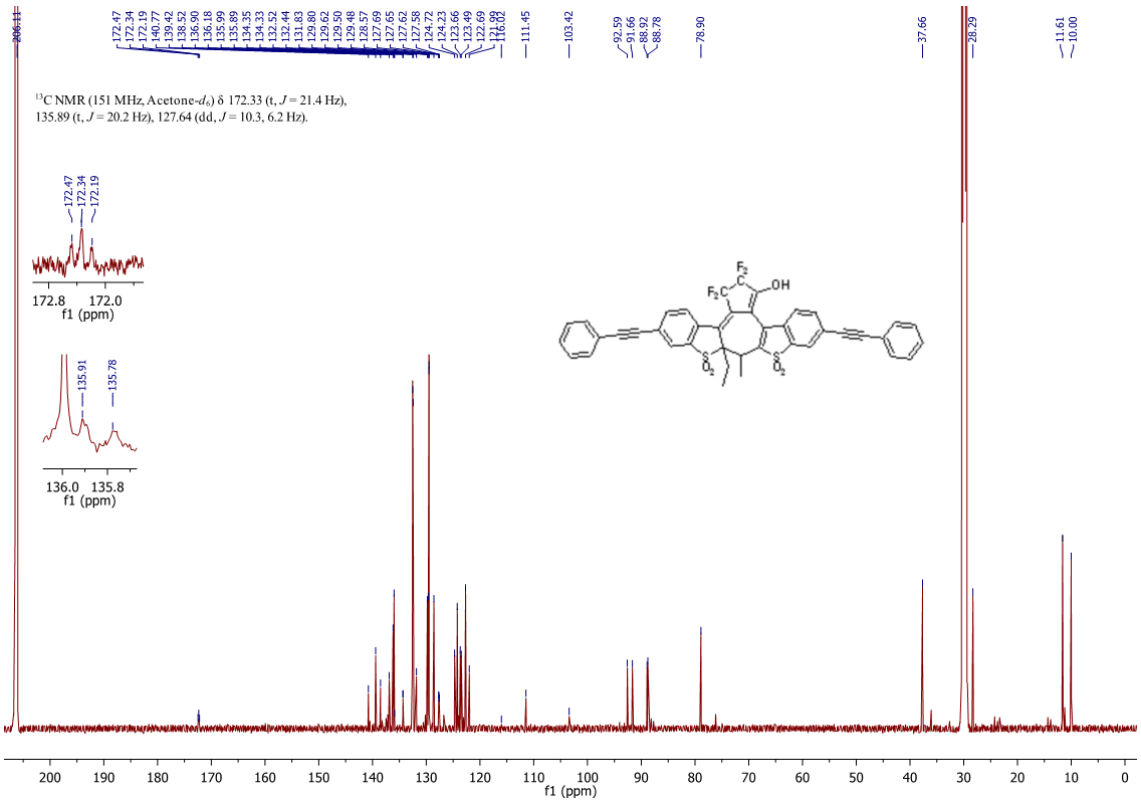


Figure S64. [13]C NMR spectrum of 7-BTSO2Et-PhCC-OH (**22**) in acetone-d6.

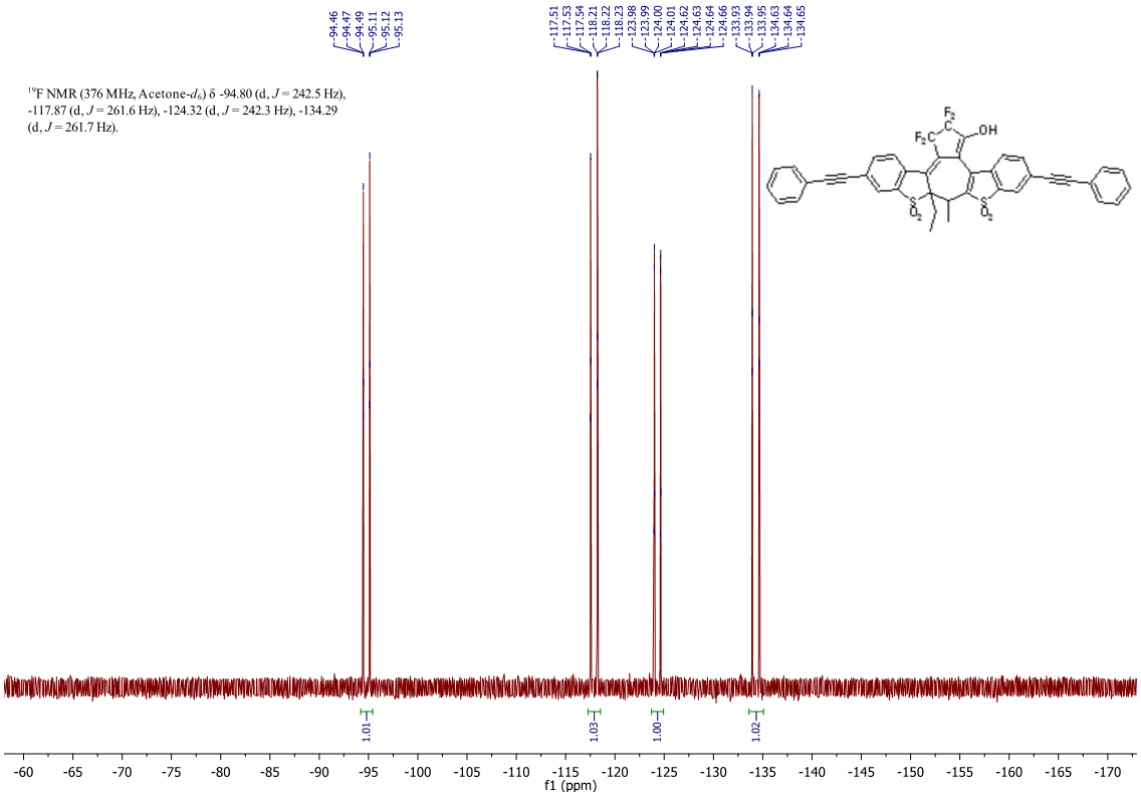


Figure S65. ^{19}F NMR spectrum of 7-BTSO2Et-PhCC-OH (**22**) in acetone-d6.

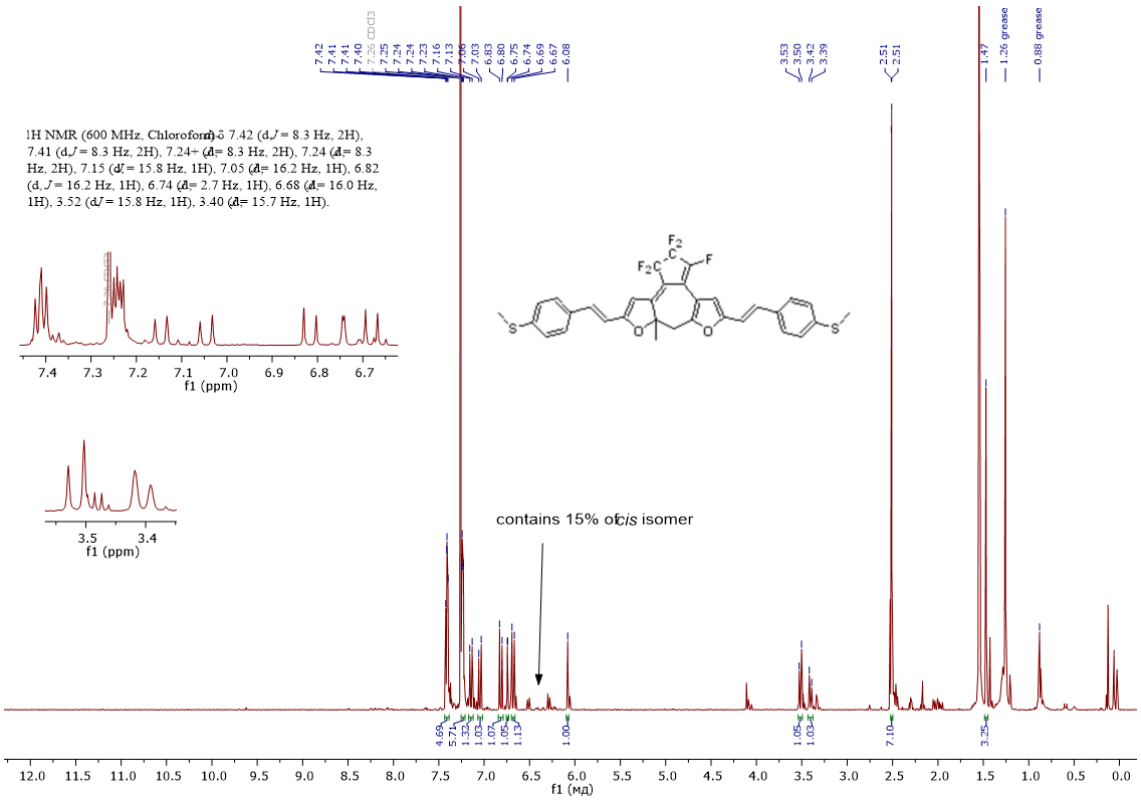


Figure S66. ^{1}H NMR spectrum of 7-4SMe (**23**) in $CDCl_3$.

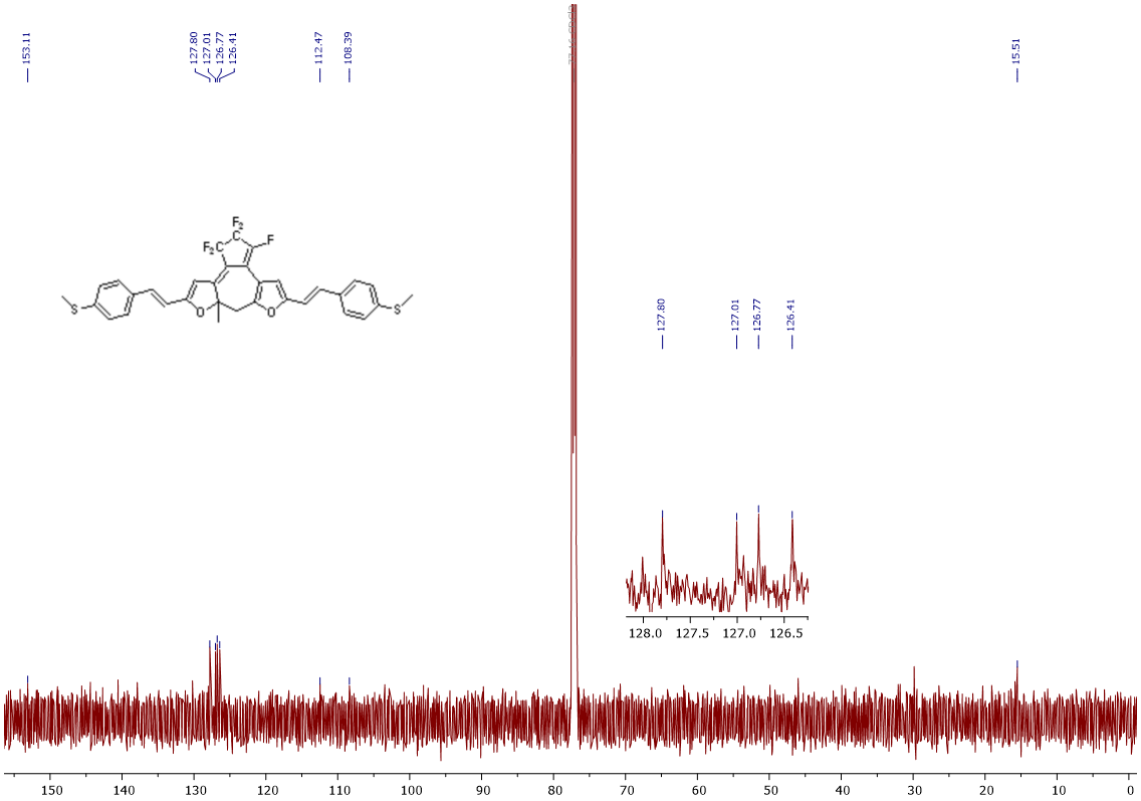


Figure S67. ^{13}C NMR spectrum of 7-4SMe (**23**) in $CDCl_3$.

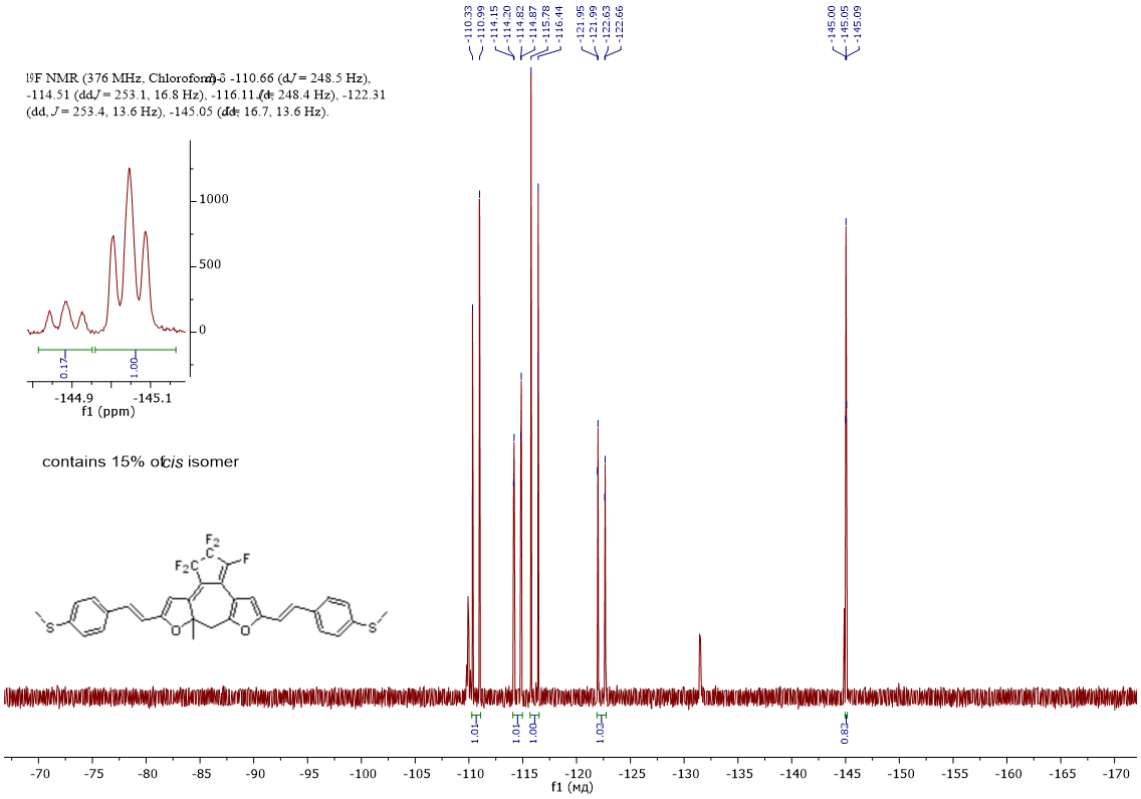


Figure S68. ^{19}F NMR spectrum of 7-4SMe (**23**) in $CDCl_3$.

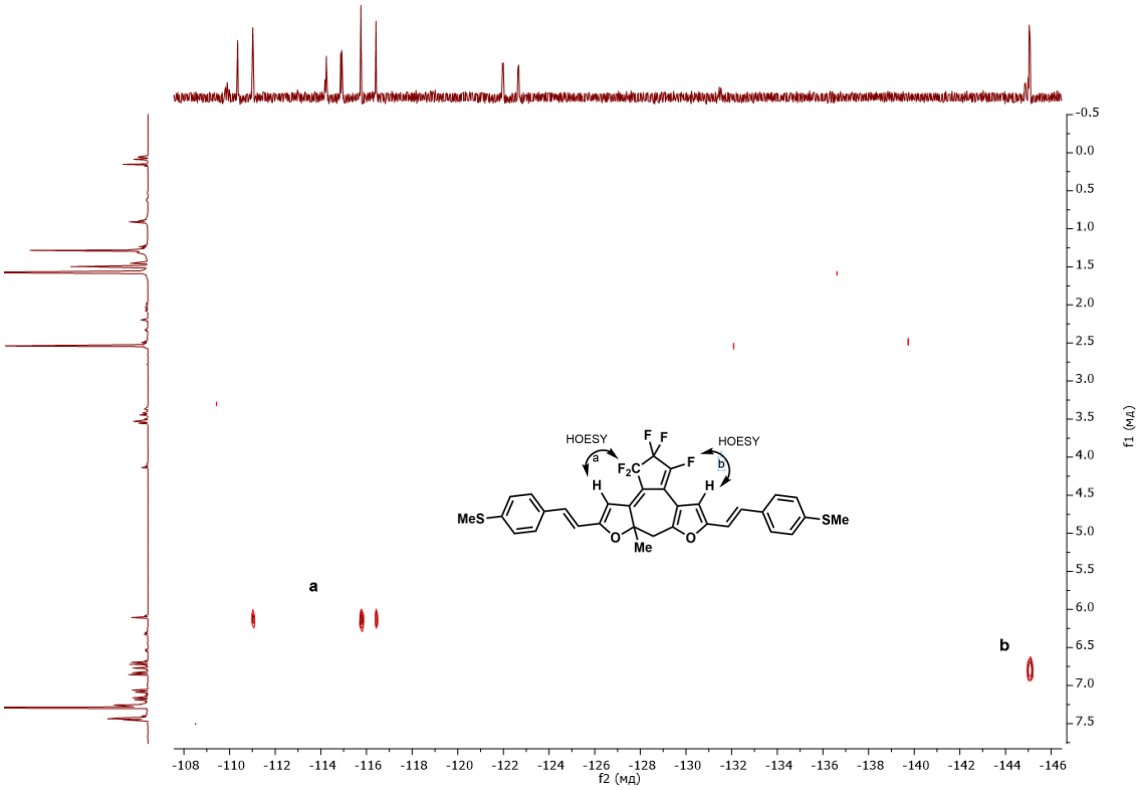


Figure S69. {^{1}H,^{19}F}-HOESY spectrum of 7-4SMe (**23**) in $CDCl_3$.

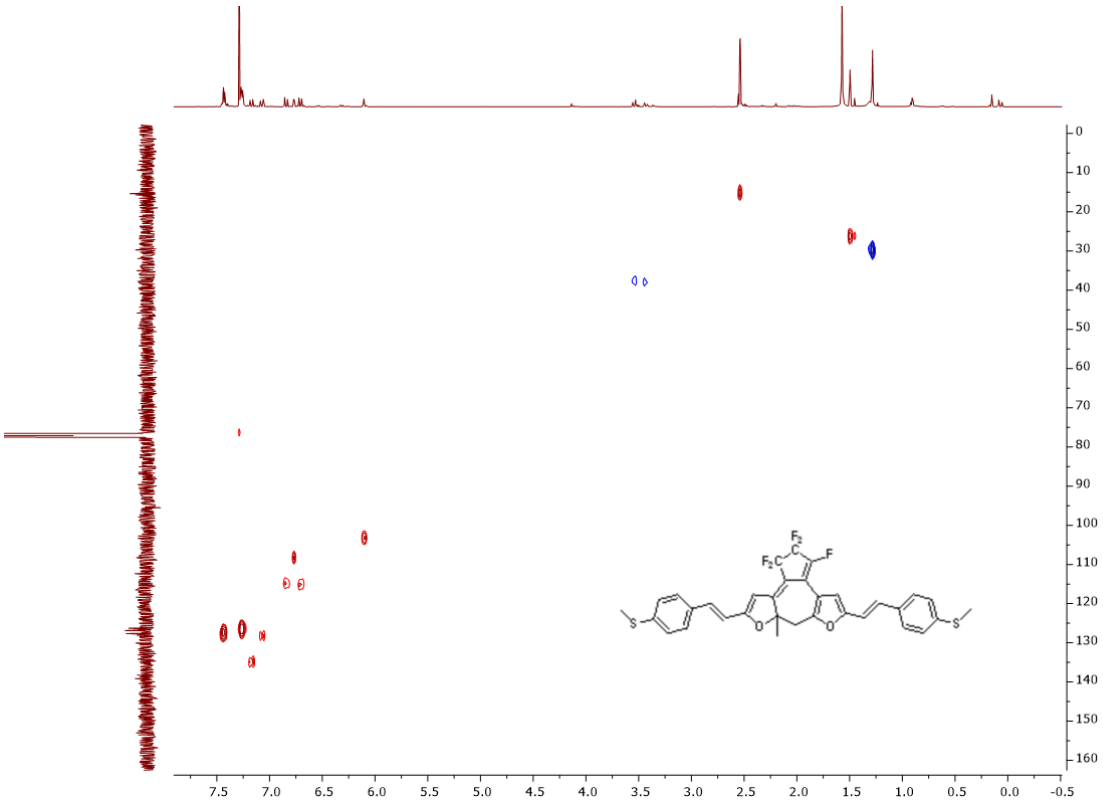


Figure S70. HSQC spectrum of 7-4SMe (**23**) in $CDCl_3$.

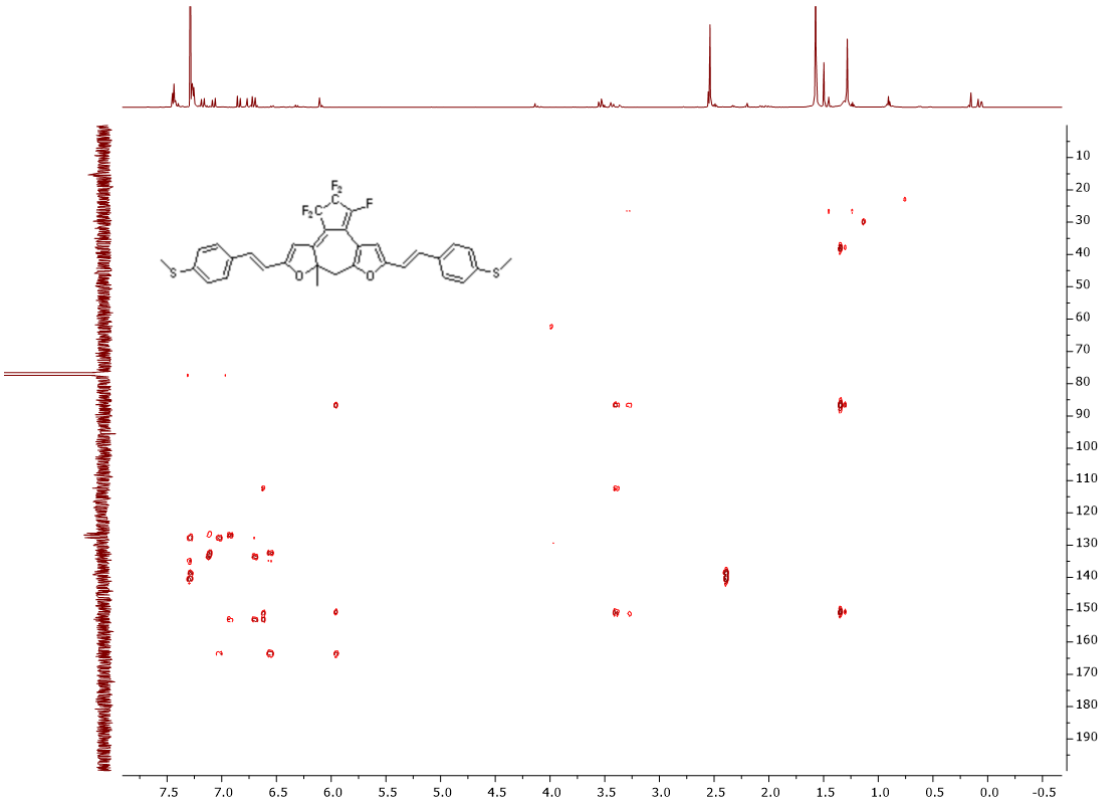


Figure S71. HMBC spectrum of 7-4SMe (**23**) in $CDCl_3$.

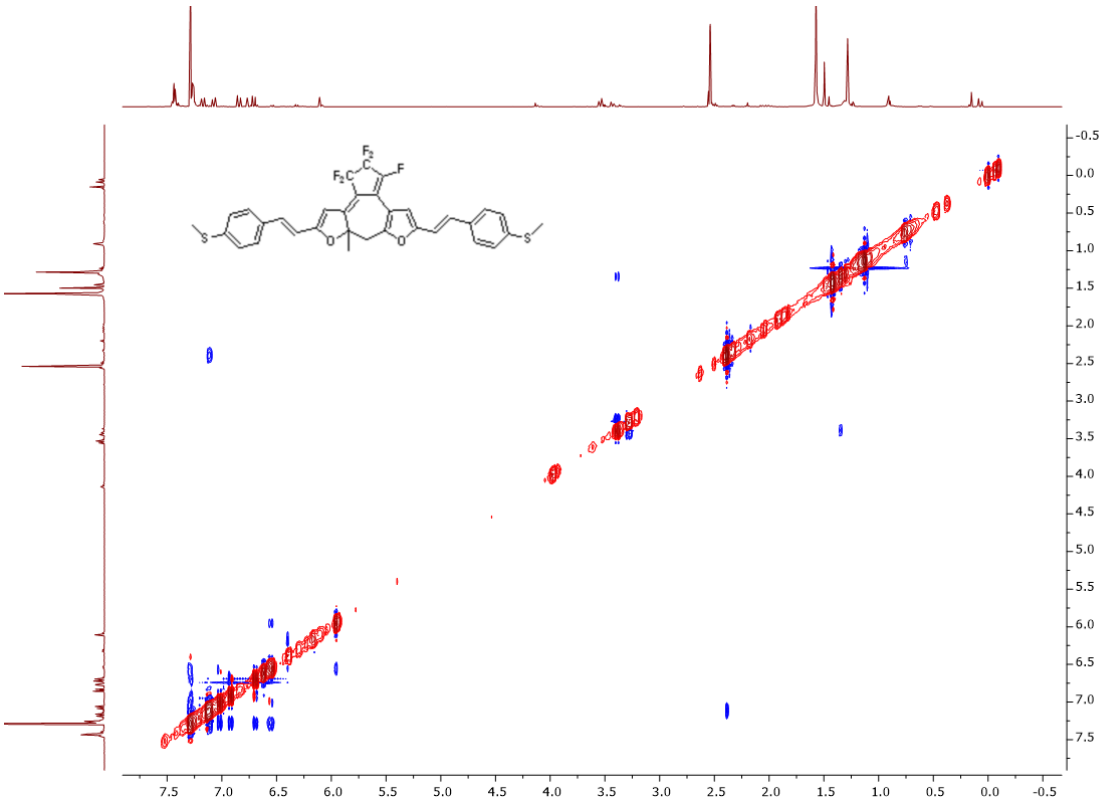


Figure S72. NOESY spectrum of 7-4SMe (**23**) in $CDCl_3$.

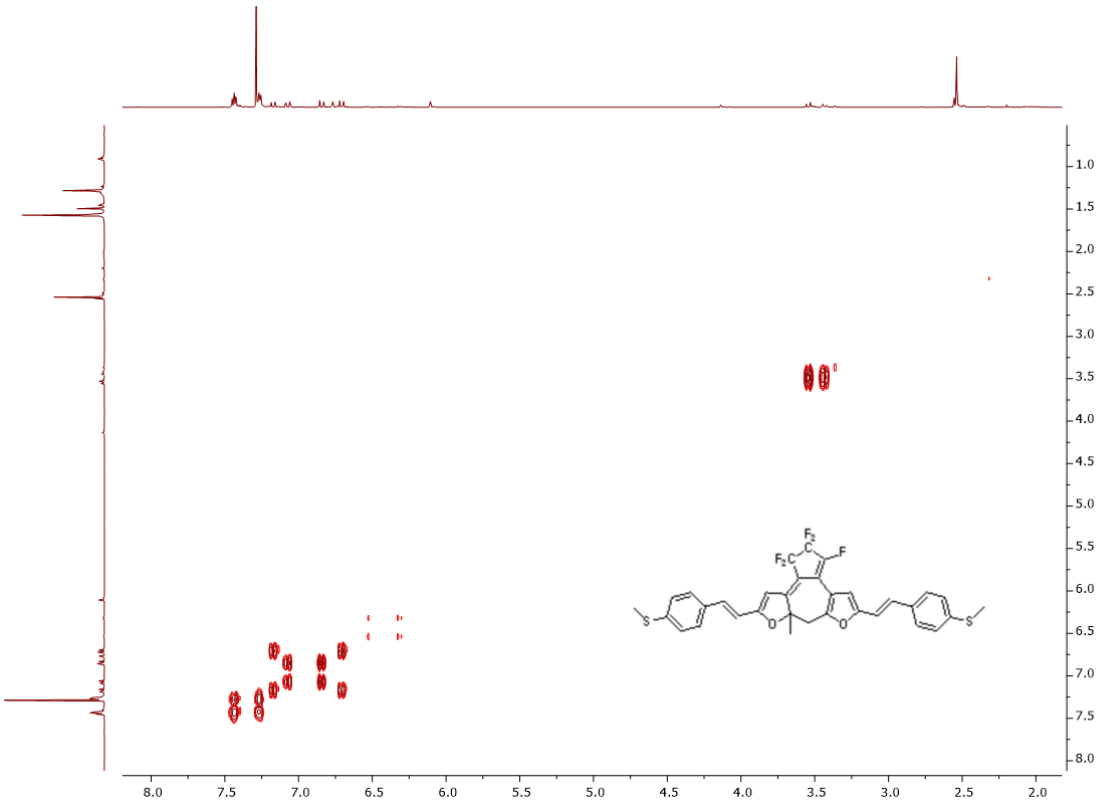


Figure S73. COSY spectrum of 7-4SMe (**23**) in $CDCl_3$.

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