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Novel 2-alkoxy- and 2-alkylthio-substituted pyrimidines containing 2-(1-methyl-1*H*-pyrrol-2-yl)vinyl moieties: optical and electrochemical properties

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Materials and methods

^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury plus-300 (300 MHz) and Bruker AvanceNeo III HD (400 MHz) spectrophotometers in $CDCl_3$ using hexamethyldisiloxane (0.055 ppm) as the internal standard. NMR data are reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *quint* = quintet, *m* = multiplet, *dd* = double doublet), integration, and coupling constants (Hz). Signals of pyrrole ring protons are denoted as *Pyr*, pyrimidine ring protons – as *Pyrim*. The elemental analysis was carried out using CHNS-932 LECO Corp analyzer.

UV–VIS absorption spectra were recorded in 10 × 10 × 45 mm cuvettes on a Shimadzu UV-2600 spectrophotometer for THF solutions of compounds with concentration of solutions from 1×10^{-5} to 5×10^{-5} mol L^{-1}. Emission spectra were recorded using a Shimadzu RF-5301 PC spectrofluorophotometer: the excitation wavelength was specified from the absorbance spectra, cuvette dimensions were 10 × 10 × 45 mm, solvent was THF, concentration of solutions was 2×10^{-5}mol L^{-1}.

CV measurements were carried out using a ZRA Interface 1000 potentiostat/galvanostat equipped with a standard three-electrode cell with an ITO working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode in 0.1 mol dm^{-3} solution of $Et_4N^+ClO^-_4$ in the acetonitrile–dichloromethane (9 : 1) mixture as supporting electrolyte at the potential scan rate (V_{scan}) of –100 mV s^{-1} and ambient conditions.

The films of pyrimidines **7**–**10** were prepared under inert atmosphere in the glovebox system from chlorobenzene solutions of samples (5 mg per 1 ml) on a quartz glass plate by spin-coating technique.

Purity of compounds was monitored by thin-layer chromatography (TLC): Sorbfil plates, visualization by UV light (365 nm) or iodine vapours. The mixtures were separated and the target products purified by column chromatography on silica gel (Lancaster, Silica Gel 60, 0.060–0.2 mm).

The solvents were dried according to the standard operating procedures and distilled before use. *N*-methylpyrrol-2-carbaldehyde, 1-bromohexane and bromoethane were purchased from Alfa Aesar.

Synthesis

*2-Hydroxy-4,6-dimethylpyrimidine hydrochloride (**1**).* This synthesis was performend according to the known procedure[S1,S2] with slight modifications. The refluxing solution of urea (12.0 g, 0.20 mol) and acetylacetone (20.0 g, 20.3 ml, 0.20 mol) in ethanol (100 ml) was treated with HCl (cc, 27 ml) under stirring. The resulting reaction mixture was then refluxed for 24 h and cooled down; the resulting precipitate of 4,6-dimethyl-2-hydroxypyrimidine hydrochloride **1** was isolated by filtration and subsequent washing with cold ethanol and diethyl ether to give a target compound **1** as white needles, m.p. > 265 °C (decomp.), in the yield of 75%.

*2-Mercapto-4,6-dimethylpyrimidine hydrochloride (**2**).* This synthesis was performend according to the known procedure[S3,S4] with slight modifications. Suspension of thiourea (7.6 g, 0.1 mol) and acetylacetone (12.3 ml, 12 g, 0.12 mol) in ethanol (250 ml) was treated with HCl (25 ml), then heated under reflux for 2–3 h, and cooled down. The resulting residue was filtered off to give the pyrimidine **2** as yellow needles, m.p. 190–195°C, in the yield of 80%.

*General procedure for preparation of compounds **3** and **5**.*
Suspension of 2-hydroxy-4,6-dimethylpyrimidine hydrochloride **1** or 2-mercapto-4,6-dimethylpyrimidine hydrochloride **2** (0.023 mol) and NaOH (0.23 mol) in DMSO (50 ml) was treated with alkyl bromide (0.045 mol) and stirred for 48 h at room temperature, then poured into the cold water, and extracted with CH_2Cl_2. The combined organic layers were carefully washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated to give the residues of compounds **3** and **5**.

*2-Ethoxy-4,6-dimethylpyrimidine (**3**)*, a colorless gradually hardening oil (yield 85%), ^{1}H NMR (300 MHz, $CDC1_3$), δ: 1.40 (t, 3H, *J* 6.9 Hz, $OCH_2\underline{CH_3}$), 2.40 (s, 6H, $2CH_3$), 4.40 (q, 2H, *J* 6.9 Hz, $OC\underline{H_2}CH_3$), 6.63 (*s*, 1H, Pyrim). Lit. data[S5,S6]
*2-Ethylthio-4,6-dimethylpyrimidine (**5**),* a yellow gradually hardening oil, yield 60%.^{1}H NMR (300 MHz, $CDCl_3$), *δ*: 1.4 (t, 3H, *J* 7.0 Hz, CH_3), 2.37 (s, 6H, $2CH_3$), 3.24 (t, 2H, *J* 7.0 Hz, SCH_2), 7.24 (1H, s, Pyrim).

*General procedure for preparation of compounds **4** and **6**.* The mixture of 2-hydroxy-4,6-dimethylpyrimidine hydrochloride **1** or 2-mercapto-4,6-dimethylpyrimidine hydrochloride **2** (0.010 mol), alkylbromide (0.015 mol) and K_2CO_3 (0.10 mol) in dry DMF (100 ml) was heated

under reflux for 6 h, then cooled down, poured into cold water, and extracted with CH_2Cl_2. The combined organic layers were carefully washed with water, dried under Na_2SO_4. The solvent was then removed by vacuum evaporation to give the residues of target compounds **4** and **6**.

*2-Hexyloxy-4,6-dimethylpyrimidine(**4**)*, a colorless gradually hardening oil (yield 94%); m.p.:~ 42 °C,. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.92 (t, 3H, *J* 6.9 Hz, CH_3), 1.32–1.51 (m, 6H, 3 CH_2), 1.80 (pent, 2H, *J* ≈ 7 Hz, $\underline{CH_2}CH_2O$), 2.39 (s, 6H, $2CH_3$), 4.32 (t, 2H, *J* 6.9 Hz, CH_2O), 6.64 (s, 1H, Pyrim).

*2-Hexylthio-4,6-dimethylpyrimidine (**6**)*, a red gradually hardening oil, yield 60%.^{1}H NMR (300 MHz, $CDCl_3$), *δ*: 0.89 (t, 3H, *J* 6.6 Hz, CH_3), 1.35 (m, 4H, $2CH_2$), 1.51 (m, 2H, $SCH_2CH_2\underline{CH_2}C$), 1.81 (m, 2H, $SCH_2\underline{CH_2}C$), 2.37 (s, 6H, $2CH_3$), 3.24 (t, 2H, *J* 4.8 Hz, SCH_2), 7.24 (s, 1H, Pyrim,).

*General procedure for preparation of compounds **7–10**.* A mixture of corresponding 2-alkoxy- or 2-alkylthiopyrimidines **3**–**6** (1 mmol) and 1-methyl-1*H*-pyrrole-2-carbaldehyde (0.22 g, 0.22 ml, 2 mmol) was heated under reflux for 8 h in 5M aqueous solution of NaOH in presence of catalytic amount of Aliquat 336, then cooled down, poured into cold water, and extracted with CH_2Cl_2. The combined organic layers were carefully washed with water and dried over Na_2SO_4. The solvent was then removed by vacuum evaporation to give the residues of target compounds **7**–**10**, which were isolated and purified by column chromatography on silica gel (eluent was CH_2Cl_2).

*2-Ethoxy-4,6-bis[(E)-2-(1-methyl-1H-pyrrol-2-yl)ethenyl]pyrimidine (**7**)*, a yellow solid, (60% yield); m.p.: 153–154 ºC. ^{1}H ($CDCl_3$, 400 MHz), *δ*: 7.89, 7.85 (d, 2H, *J* 15.40 Hz, 2CH=), 6.76, 6.72 (d, 2H, *J* 15.64 Hz, 2CH=), 6.74 (t, 2H, *J* 1.96 Hz, Pyr), 6.70 (s, 1H, Pyrim), 6.68 (dd, 2H, J_1 4.89 Hz, J_2 1.47 Hz, Pyr), 6.21 (m, 2H, Pyr), 4.56 (q, 2H, *J* 7.08 Hz, $OC\underline{H_2}CH_3$), 3.78 (s, 6H, N–CH_3), 1.51 (dd, 3H, J_1 7.08 Hz, J_2 6.11 Hz, $OCH_2C\underline{H_3}$).^{13}C NMR (100 MHz, $CDCl_3$), *δ*: 164.61, 130.52, 125.23, 123.94, 121.28, 110.34, 109.58, 108.61, 62.33, 33.82, 14.12. Found (%): C 71.60; H 6.57; N 16.64. $C_{20}H_{22}N_4O$. Calculated (%): C 71.83; H 6.63; N 16.75. UV−VIS (THF, λ_{max}^{abs}/nm (ε, M^{-1} dm^{-3}): 242 (6 600), 315 (9 100), 408 (29 415).

*2-Hexyloxy-4,6-bis[(E)-2-(1-methyl-1H-pyrrol-2-yl)ethenyl]pyrimidine (**8**)*, a yellow solid (0.25 g; 65% yield); m.p.: 95–96 ºC. ^{1}H ($CDCl_3$, 300 MHz), *δ*: 7.87, 7.82 (d, 2H, *J* 15.30 Hz, 2CH=), 6.66–6.74 (m, 7H, 1H Pyrim, 2H 2CH=, 4H Pyr), 6.18 (dd, 2H, J_1 6.23 Hz, J_2 2.57 Hz, Pyr), 4.45 (t, 2H, J_1 6.97 Hz, $OC\underline{H_2}CH_2CH_2CH_2CH_2CH_3$), 3.75 (s, 6H, N–$CH_3$), 1.87 (quint, 2H, *J*

6.97 Hz, $OCH_2C\underline{H}_2CH_2CH_2CH_2CH_3$), 1.51 (m, 2H, $OCH_2CH_2C\underline{H}_2CH_2CH_2CH_3$), 1.36 (m, 2H, $OCH_2CH_2CH_2C\underline{H}_2CH_2CH_3$), 1.25 (m, 2H, $OCH_2CH_2CH_2CH_2C\underline{H}_2CH_3$), 0.90 (t, 3H, *J* 6.97 Hz, $OCH_2CH_2CH_2CH_2CH_2C\underline{H}_3$). ^{13}C NMR (75 MHz, $CDCl_3$), *δ*: 164.90, 130.87, 125.70, 124.35, 121.58, 110.68, 109.98, 109.03, 67.17, 34.26, 31.64, 28.97, 25.76, 22.58, 14.00. Found (%): C 73.63; H 7.57; N 14.13. $C_{24}H_{30}N_4O$. Calculated (%): C 73.81; H 7.74; N 14.35. UV−VIS (THF, λ_{max}^{abs}/nm (ε, M^{-1} dm^{-3}): 243 (7 6420, 316 (11 475), 410 (41 529).

*2-Ethylthio-4,6-bis[(E)-2-(1-methyl-1H-pyrrol-2-yl)ethenyl]pyrimidine (**9**)*, a yellow solid (0.22 g; 62% yield); m.p.: 123–124 ºC. ^{1}H ($CDCl_3$, 400 MHz), *δ*: 7.86, 7.83 (d, 2H, *J* 15.40 Hz, 2CH=), 6.73 (t, 2H, *J* 1.71 Hz, Pyr), 6.72, 6.69 (d, 2H, *J* 15.40 Hz, 2CH=), 6.68–6.66 (m, 3H, 1H, Pyrim, 2H, Pyr), 6.21 (t, 2H, *J* 1.96 Hz, Pyr), 3.76 (s, 6H, N–CH_3), 3.26 (q, 2H, *J* 7.34 Hz, $SC\underline{H}_2CH_3$), 1.49 (t, 3H, *J* 7.34 Hz, $SCH_2C\underline{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$), *δ*: 170.51, 162.50, 130.48, 125.25, 124.04, 121.10, 111.25, 109.55, 108.64, 33.73, 24.83, 14.16. Found (%): C 68.35; H 6.63; N 15.77; S 9.09. $C_{20}H_{22}N_4S$. Calculated (%): C 68.54; H 6.33; N 15.99; S 9.15. UV−VIS (THF, λ_{max}^{abs}/nm (ε, M^{-1} dm^{-3}): 254 (9 730), 295 (6 410), 414 (21 570).

*2-Hexylthio-4,6-bis[(E)-2-(1-methyl-1H-pyrrol-2-yl)ethenyl]pyrimidine (**10**)*, a yellow solid (0.28 g; 68% yield); m.p.: 128–130 ºC. ^{1}H ($CDCl_3$, 300 MHz), *δ*: 7.84, 7.79 (d, 2H, *J* 15.3 Hz, 2CH=), 6.65–6.72 (m, 7H, 1H Pyrim, 2H 2CH=, 4H Pyr), 6.18 (t, 2H, *J* 2.57 Hz, Pyr), 3.21 (t, 2H, *J* 6.97 Hz, $SC\underline{H}_2C\underline{H}_2CH_2CH_2CH_2CH_3$), 3.37 (s, 6H, N-$CH_3$), 1.81 (quint, 2H, *J* 6.97 Hz, $SCH_2C\underline{H}_2CH_2CH_2CH_2CH_3$), 1.47 (quint, 2H, *J* 6.97 Hz, $SCH_2CH_2C\underline{H}_2CH_2CH_2CH_3$), 1.29–1.32 (m, 4H, $SCH_2CH_2CH_2C\underline{H}_2C\underline{H}_2CH_3$), 0.87 (t, 3H, *J* 6.97 Hz, $SCH_2CH_2CH_2CH_2CH_2C\underline{H}_3$,). ^{13}C NMR (75 MHz, $CDCl_3$), *δ*: 162.81, 130.90, 125.82, 124.53, 121.39, 111.84, 110.06, 109.13, 34.25, 31.49, 30.98, 29.65, 28.94, 22.63, 14.01. Found (%): C 70.65; H 7.84; N 13.57; S 7.84. $C_{24}H_{30}N_4S$. Calculated (%): C 70.90; H 7.44; N 13.78; S 7.89. UV−VIS (THF, λ_{max}^{abs}/nm (ε, M^{-1} dm^{-3}): 255 (11 890), 300 (8 370), 415 (31 320).

^{1}H and ^{13}C-NMR spectra of pyrimidines 7–10

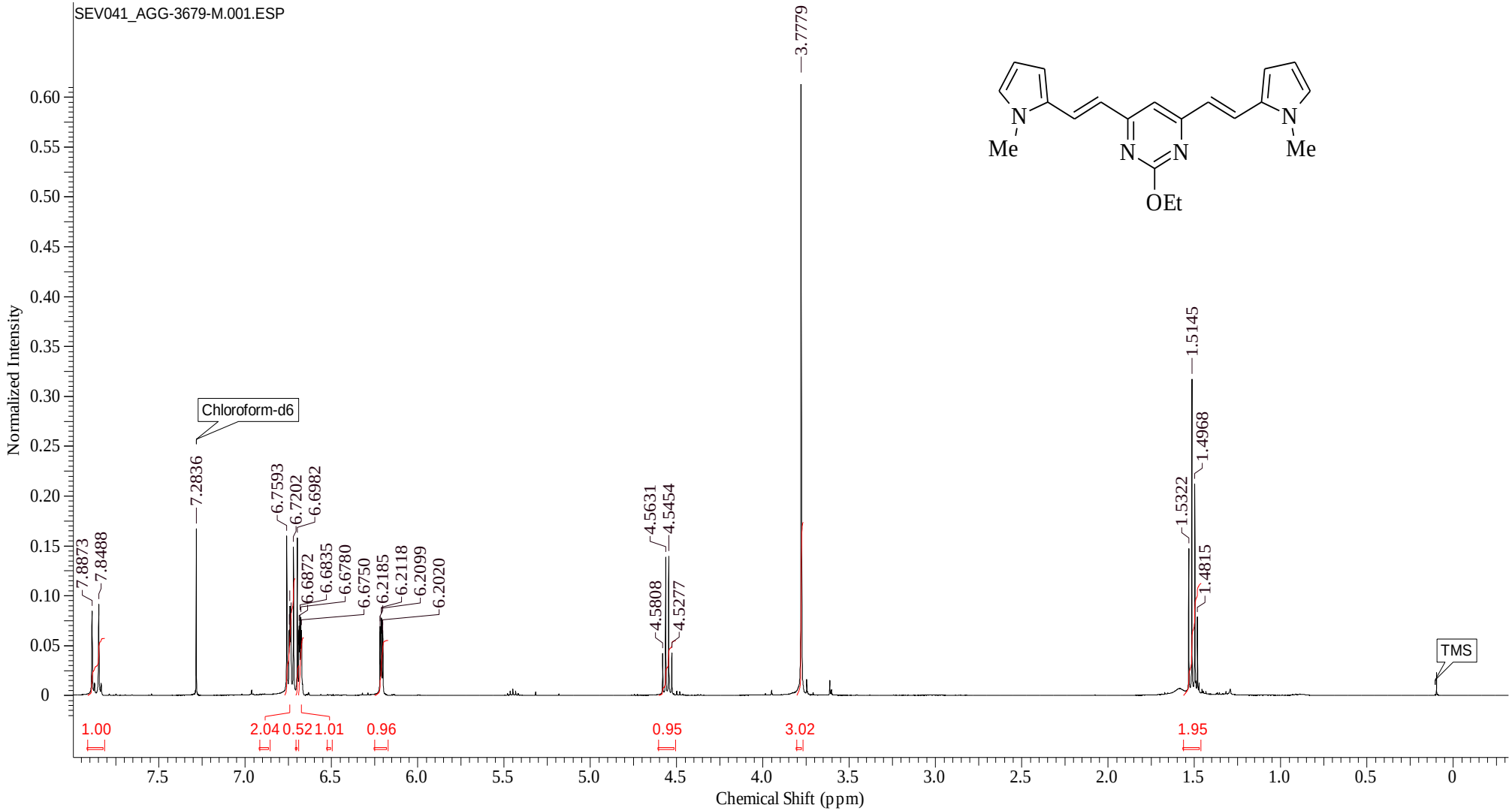

Figure S1 ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of **7**.

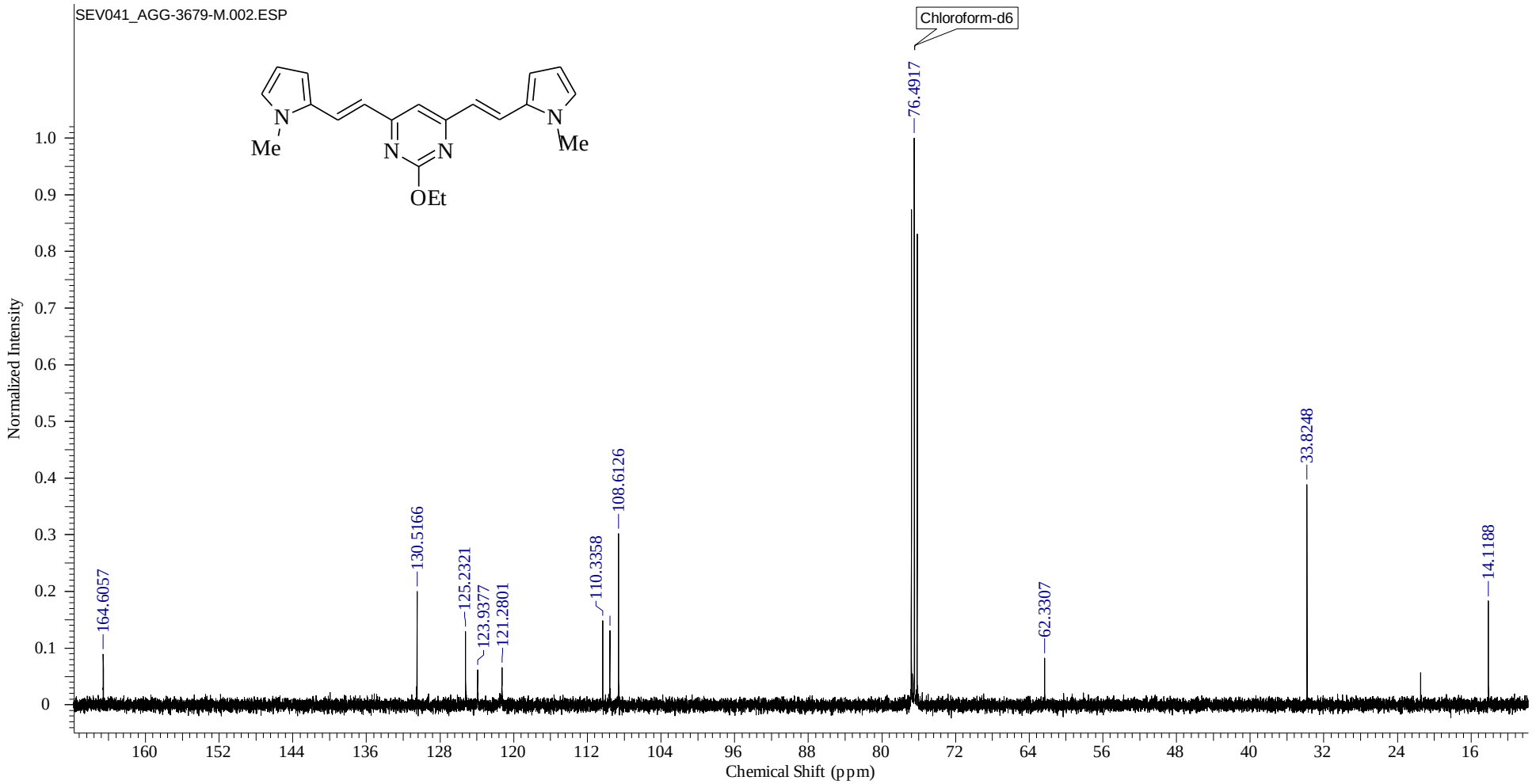

Figure S2 ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **7**.

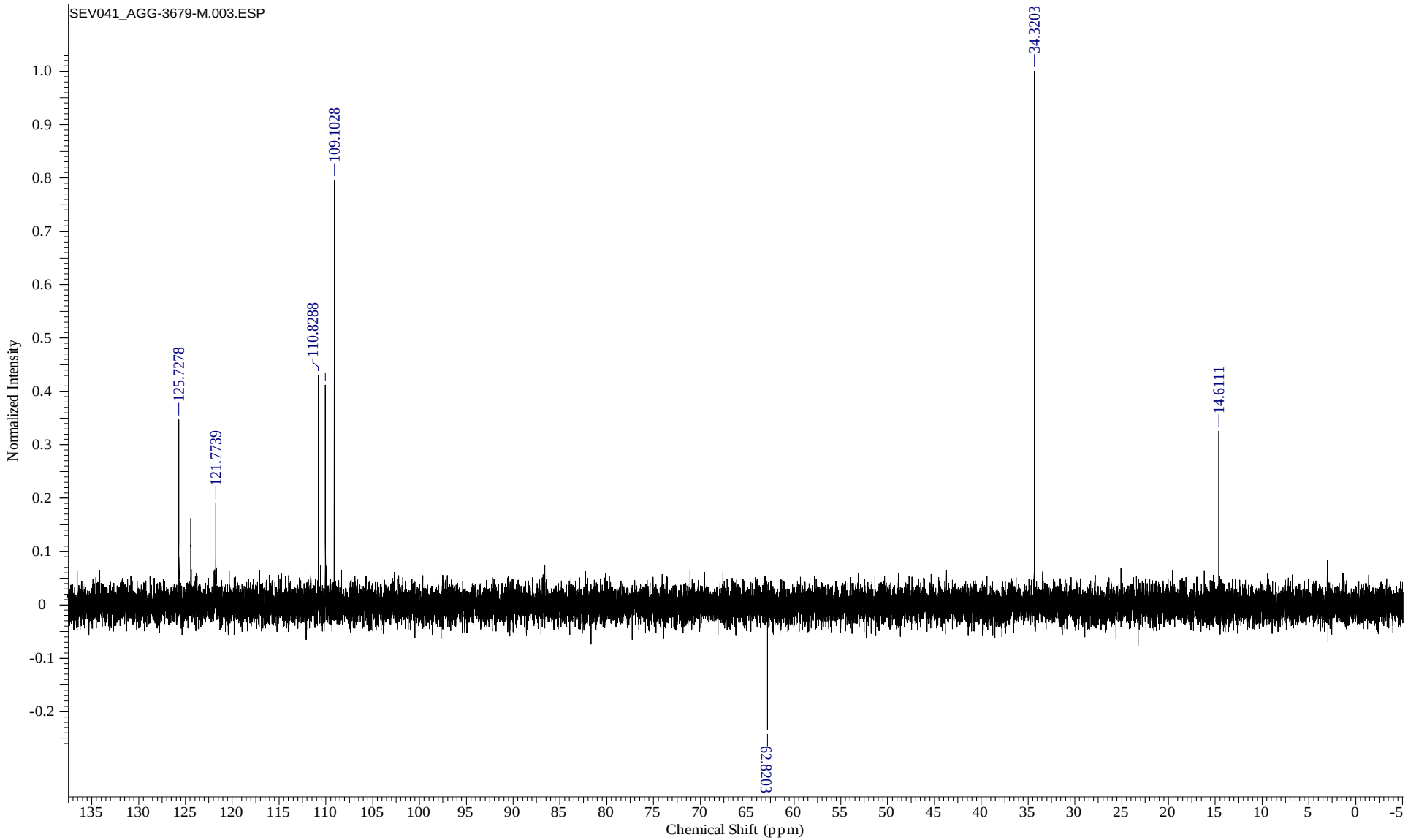

Figure S3 ^{13}C NMR DEPT ($CDCl_3$, 100 MHz) spectrum of **7**.

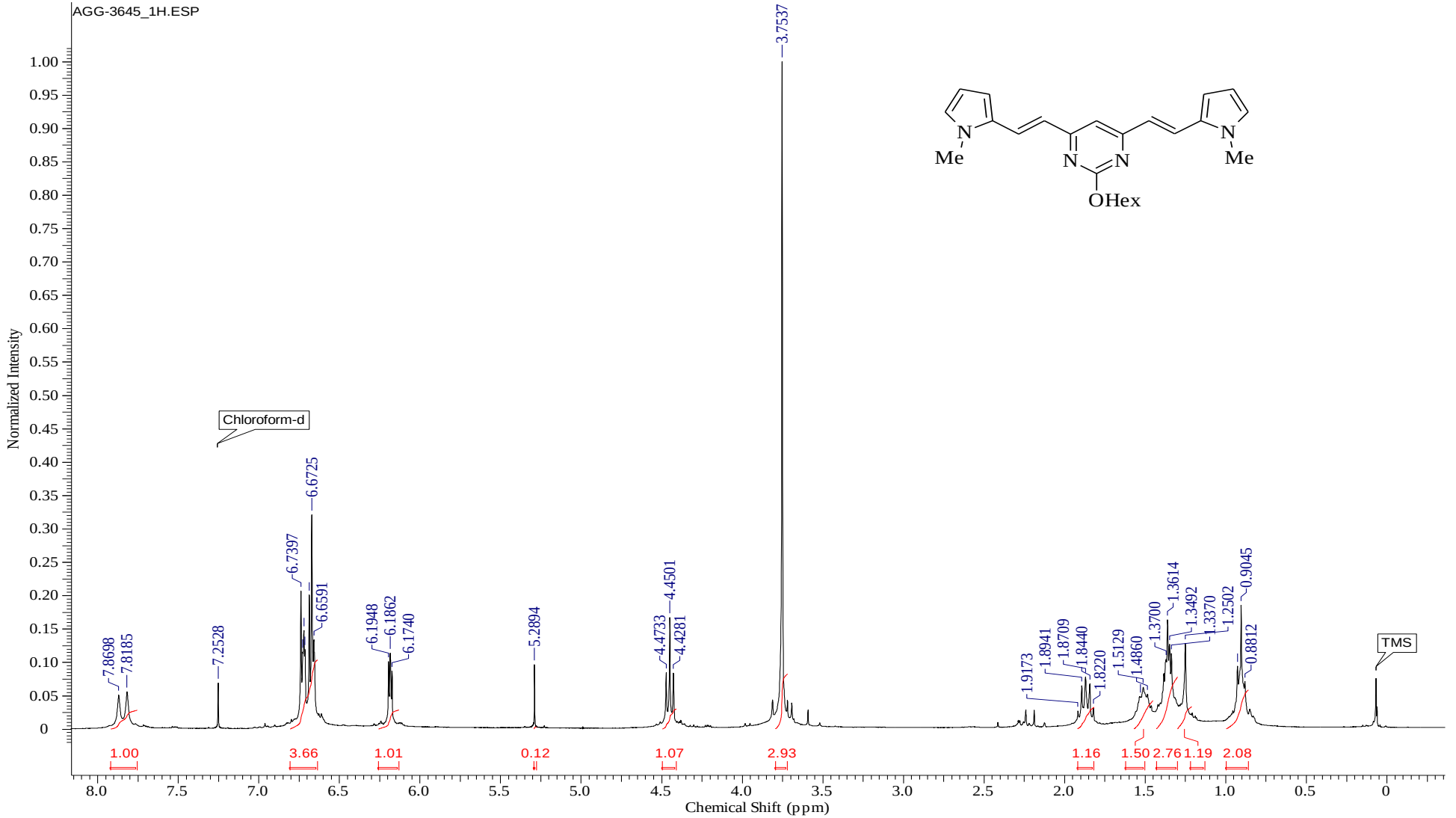

Figure S4 ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **8**.

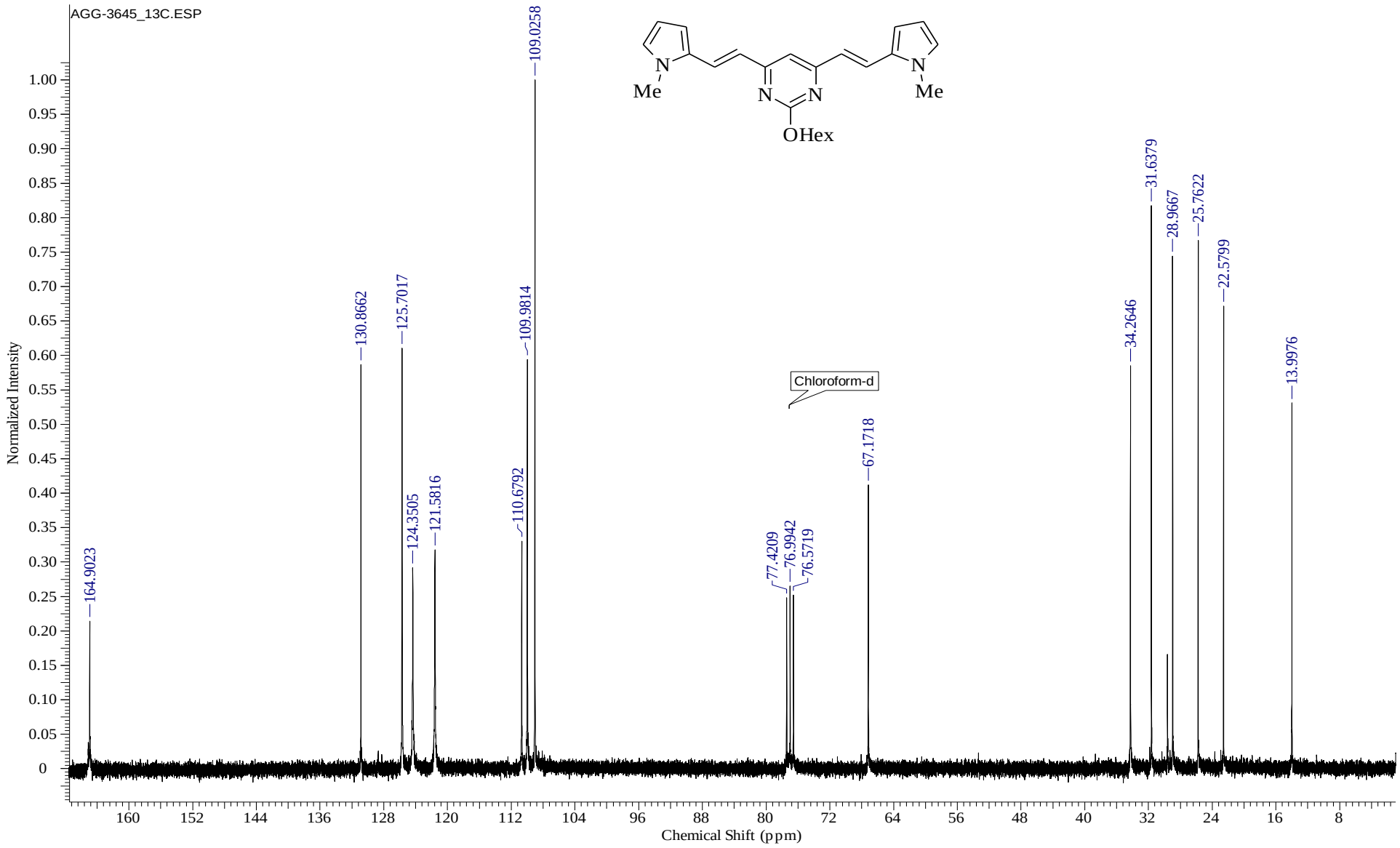

Figure S5 ^{13}C NMR ($CDCl_3$, 75 MHz)spectrum of **8**.

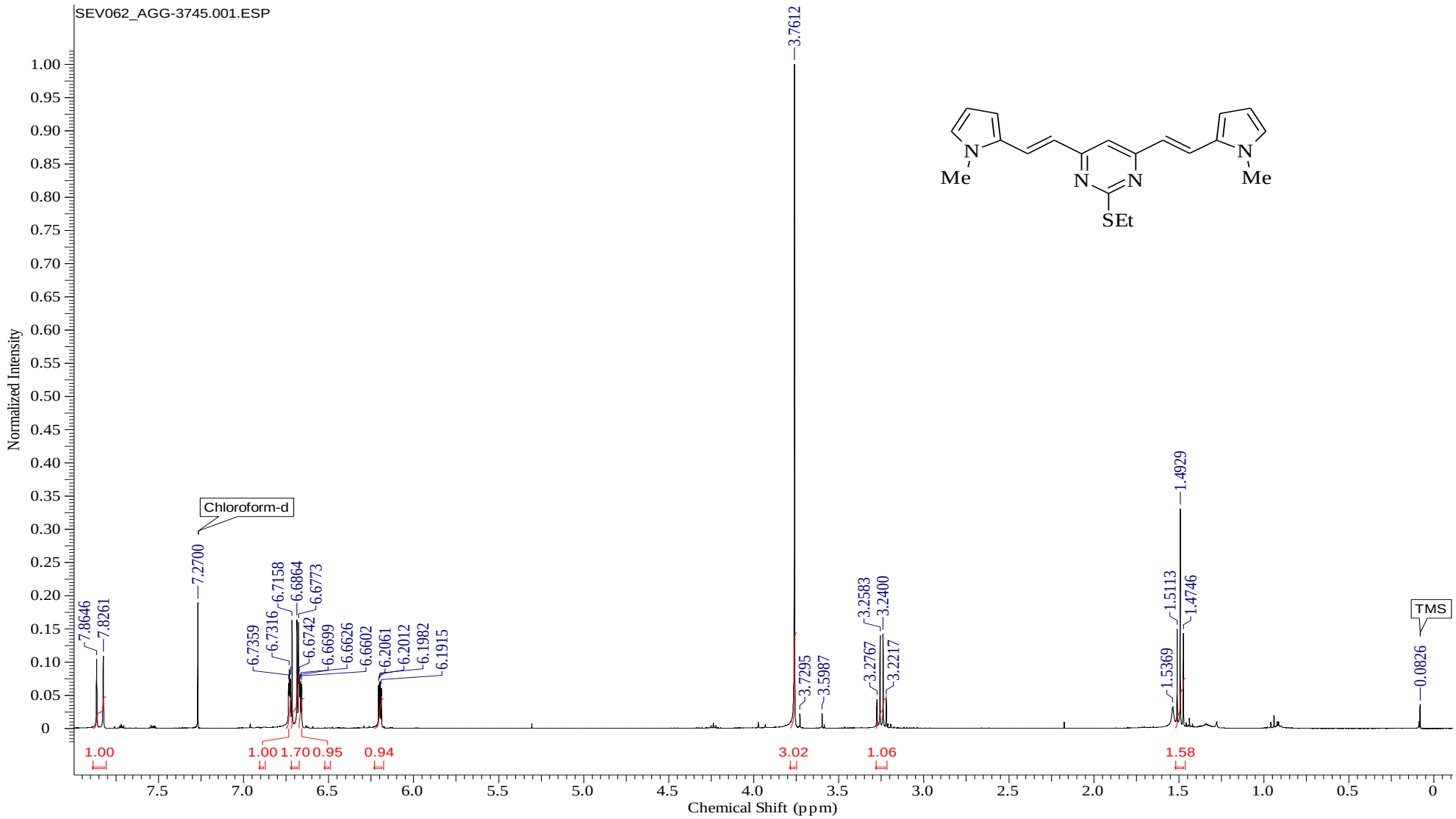

Figure S6 ^{1}H NMR ($CDCl_3$, 400 MHz)spectrum of **9**.

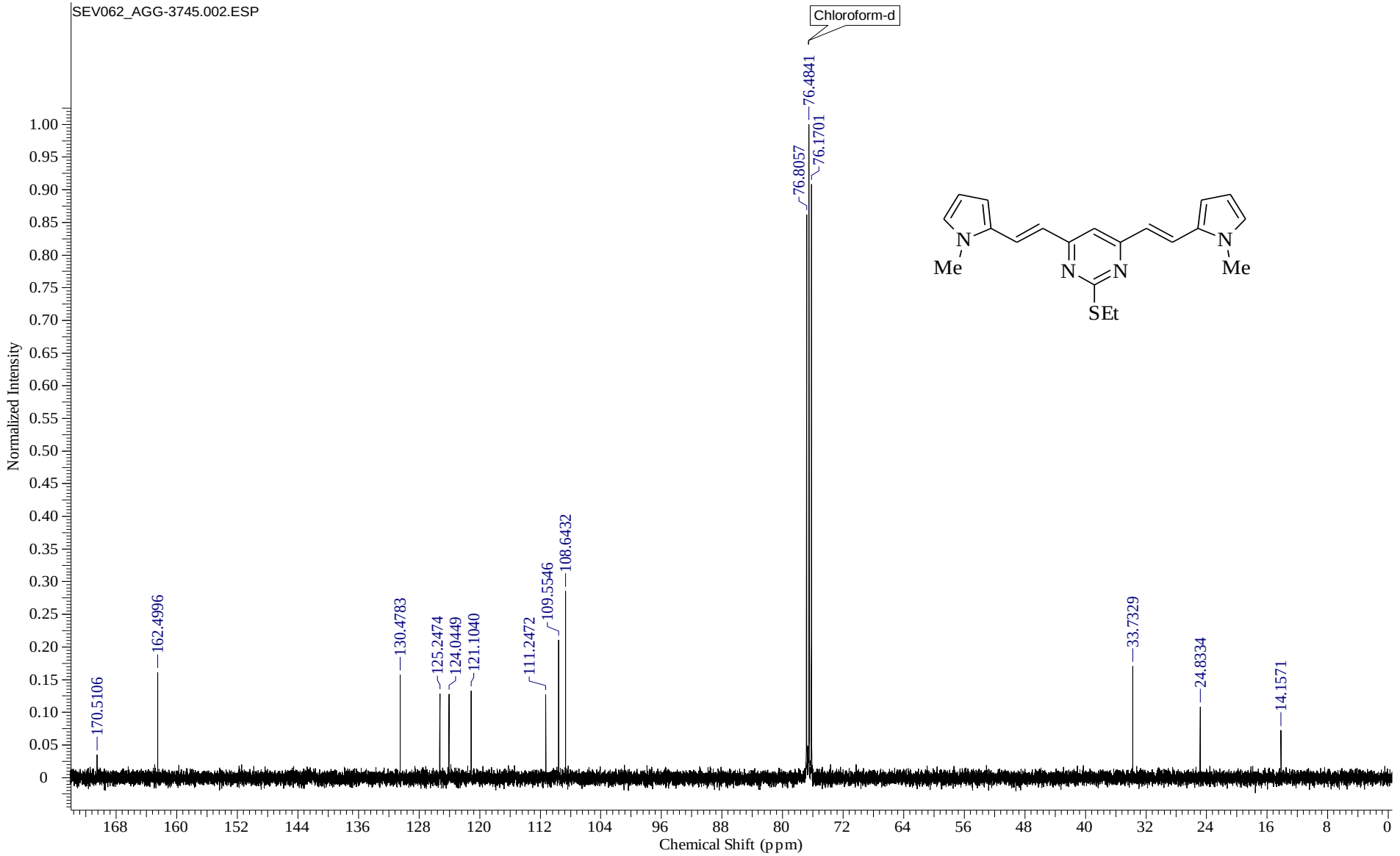

Figure S7. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of **9**.

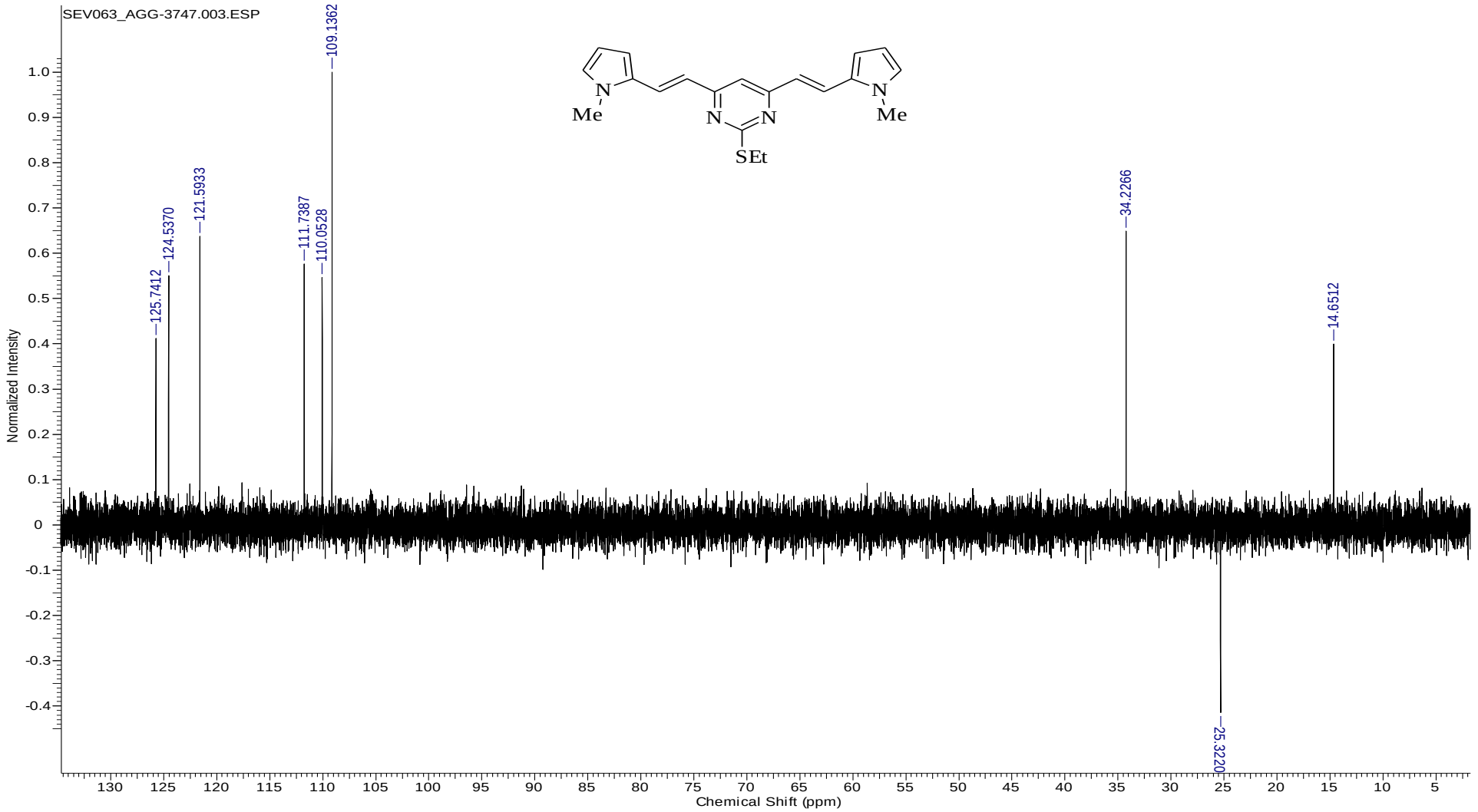

Figure S8 ^{13}C NMR DEPT ($CDCl_3$, 100 MHz) spectrum of **9**.

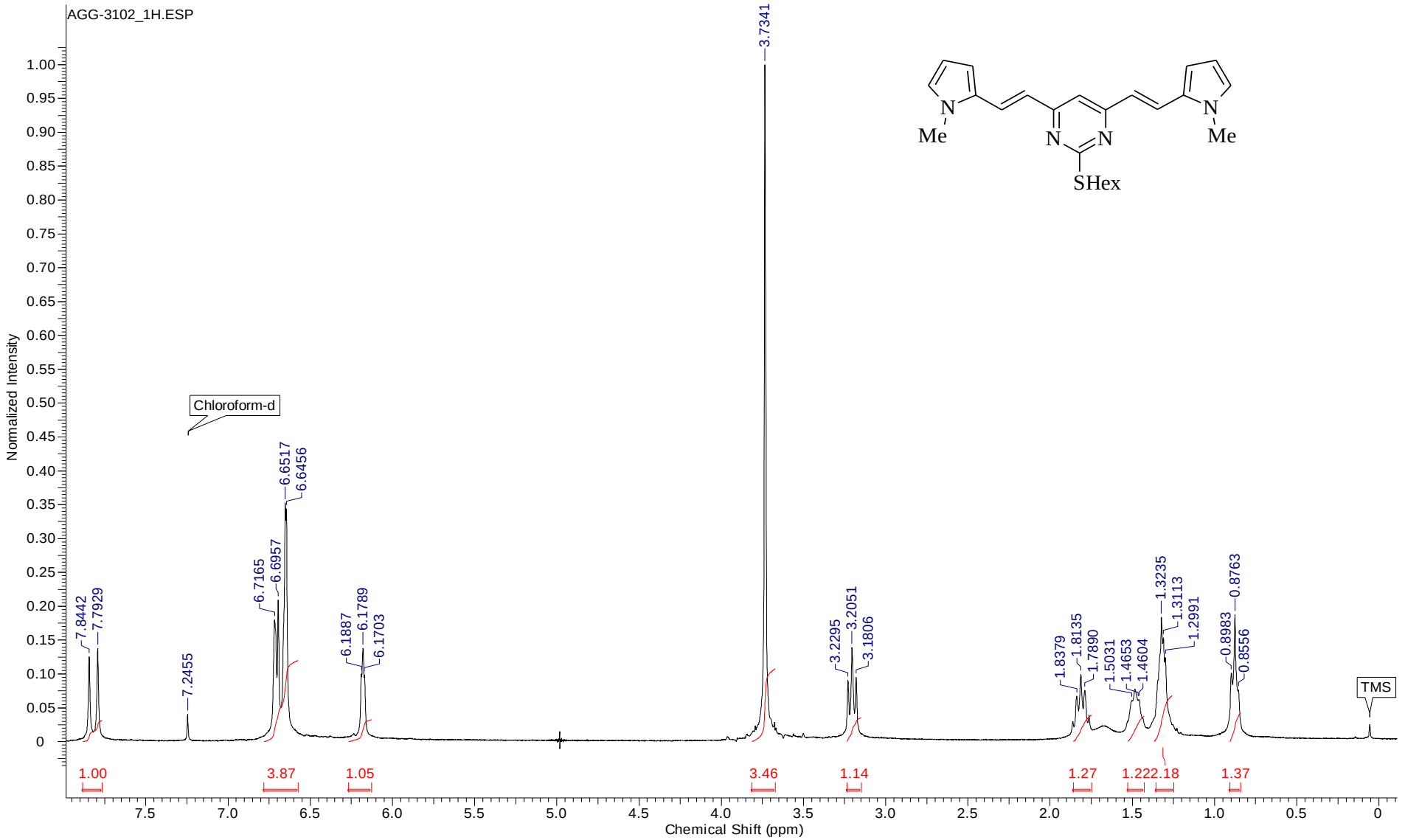

Figure S9 ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **10**.

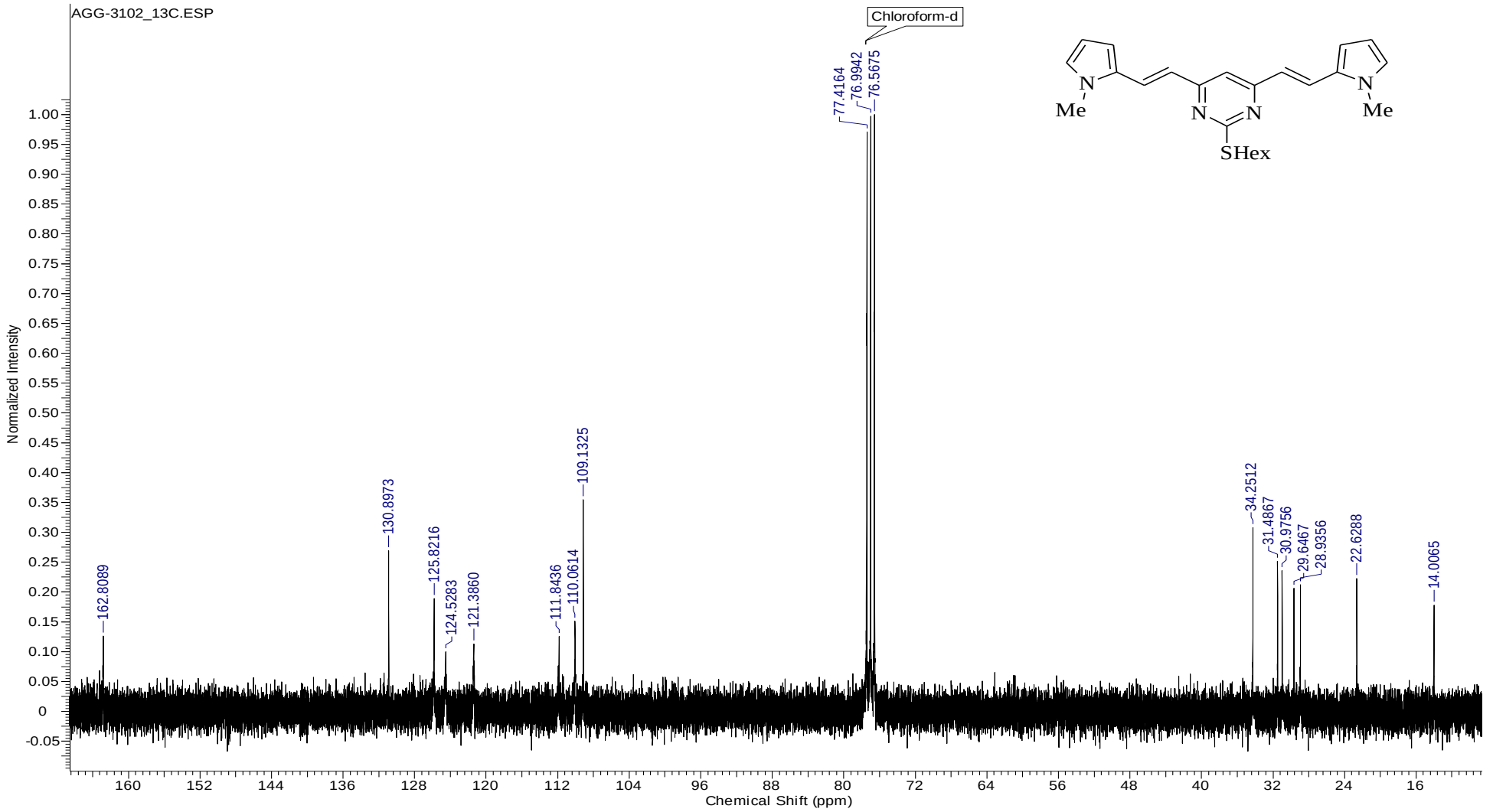

Figure S10 ^{13}C NMR ($CDCl_3$, 75 MHz) spectrum of **10**.

Single crystal X-ray analysis of compound 10

The unit cell parameters and X-ray diffraction intensities were carried out using an Xcalibur Ruby diffractometer. The empirical absorption was corrected by multi-scan method using SCALE3 ABSPACK algorithm (CrysAlisPro, Agilent Technologies, Version 1.171.37.33, release 27-03-2014 CrysAlis171 .NET). The structure was solved by direct method and refined by the full-matrix least-squares method in the anisotropic approximation for all non-hydrogen atoms using the SHELXS-97 and SHELXL-97 program packages.[S7] Hydrogen atoms were located from the Fourier synthesis of the electron density and refined using a riding model. The restraints (DFIX, SAME, SIMU, DELU) were used in refinement of disordered alkyl chain. The crystals for XRD experiments were prepared by crystallization from EtOH.

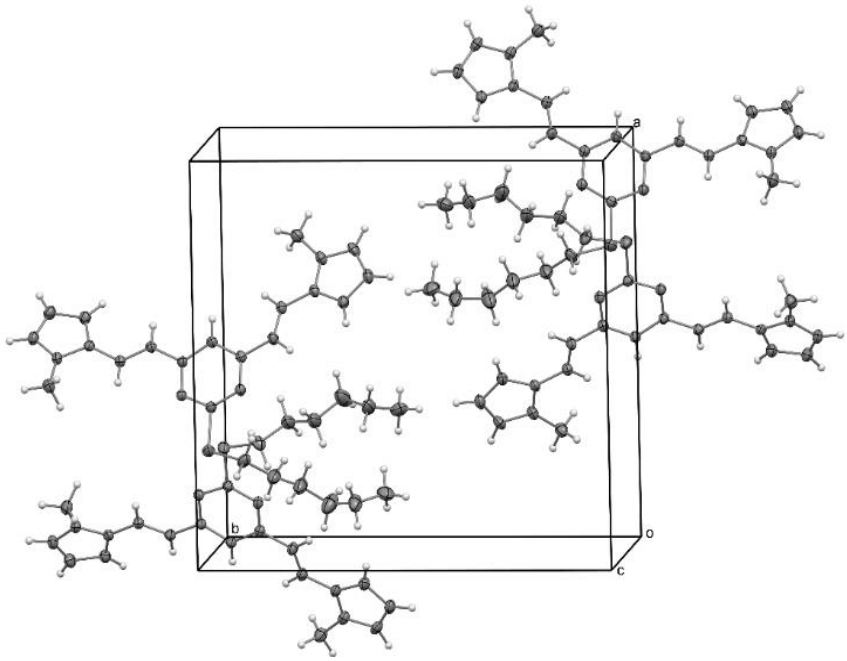

Figure S11 The crystal packing structures of compound **10**.

Cyclic voltammetry measurements

The CV measurements were carried out for MeCN/CH_2Cl_2 (9 : 1) solutions containing Et_4NClO_4 (c = 10^{-3} mol dm^{-3}) as a supporting electrolyte in a three-electrode cell (RE – Ag|AgCl; SE – Pt wire; WE – ITO-covered glass plate). The redox potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc+).

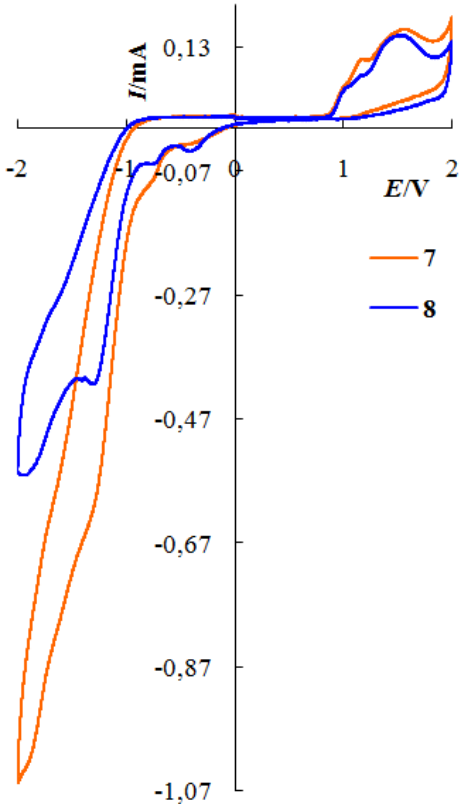

Figure S12 Cyclic voltammograms of pyrimidines **7** (orange) and **8** (blue) measured at a scan rate of 100 mV s^{-1} in CH_3CN : CH_2Cl_2 (9 : 1, v : v) (0.1 mol dm^{-3} of $Et_4N^+ClO^-_4$) at RT.

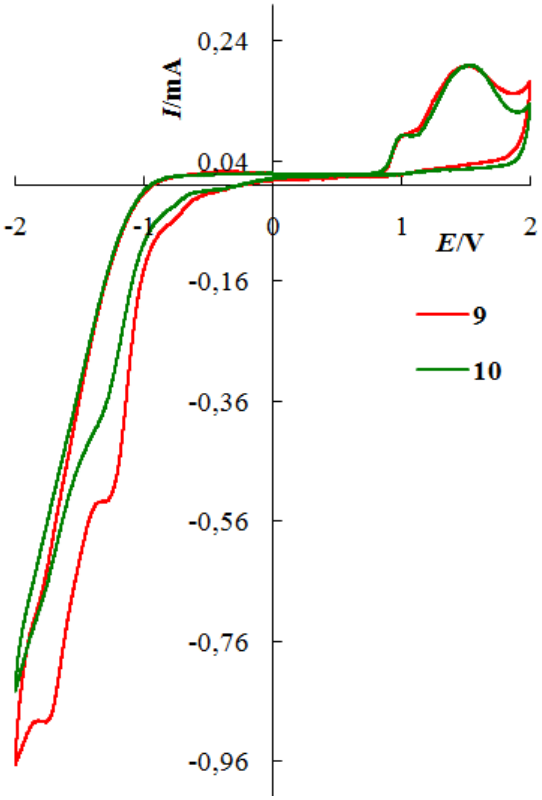

Figure S13 Cyclic voltammograms of pyrimidines **9** (red) and **10** (green) measured at a scan rate of 100 mV s^{-1} in CH_3CN : CH_2Cl_2 (9 : 1, v : v) (0.1 mol dm^{-3} of $Et_4N^+ClO^-_4$) at RT.

Electronic Absorption and Emission spectra

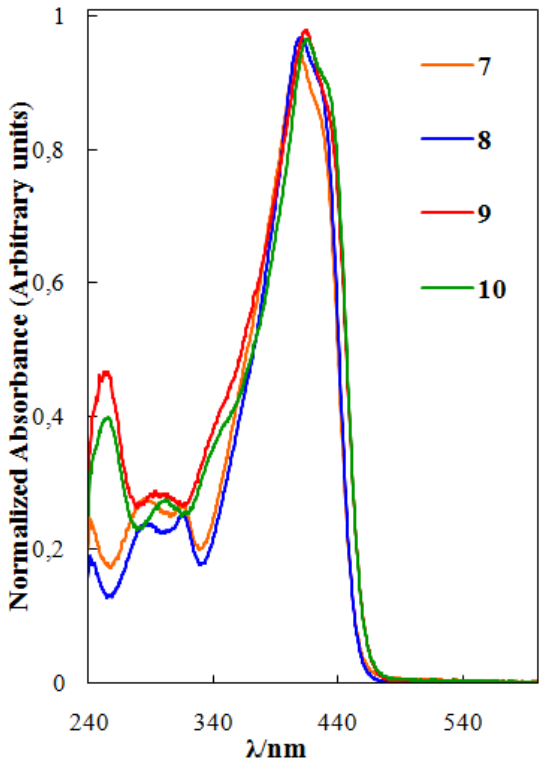

Figure S14 Normalized electronic absorption spectra of THF solution (2×10^{-5} mol dm^{-3}) of compounds **7** (orange), **8** (blue), **9** (red), and **10** (green).

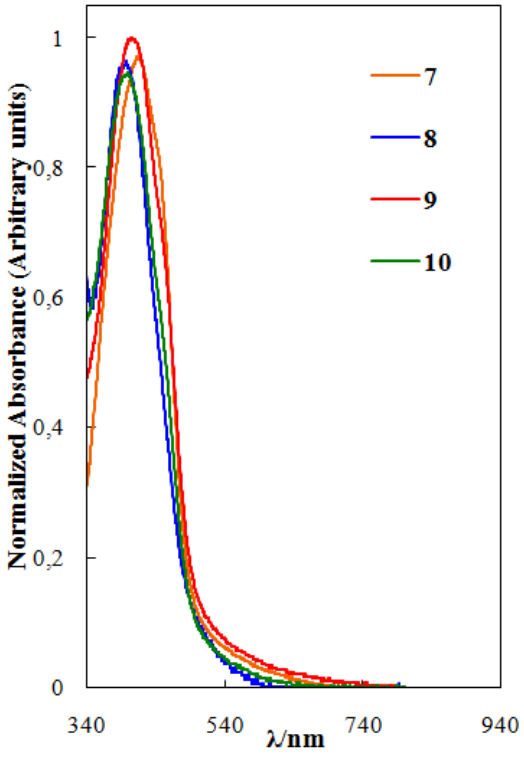

Figure S15 Normalized electronic absorption spectra of films, prepared from compounds **7** (orange), **8** (blue), **9** (red), and **10** (green).

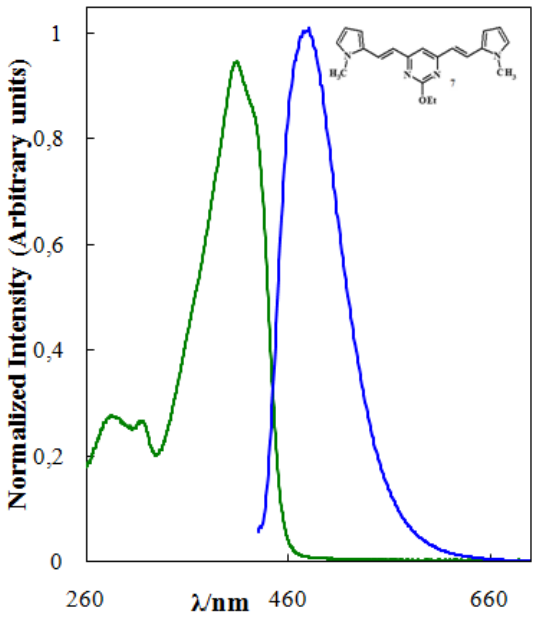

Figure S16 Normalized electronic absorption (green) and emission (blue, λ_{ex} = 435 nm) spectra of THF solution of compound **7**.

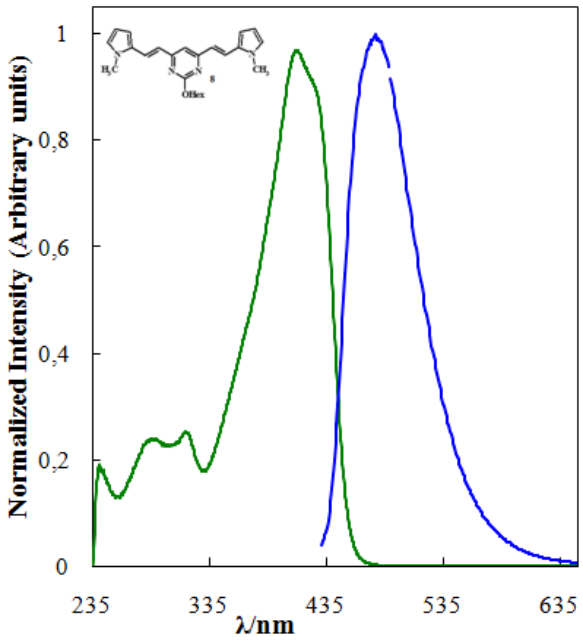

Figure S17 Normalized electronic absorption (green) and emission (blue, λ_{ex} = 435 nm) spectra of THF solution of compound **8**.

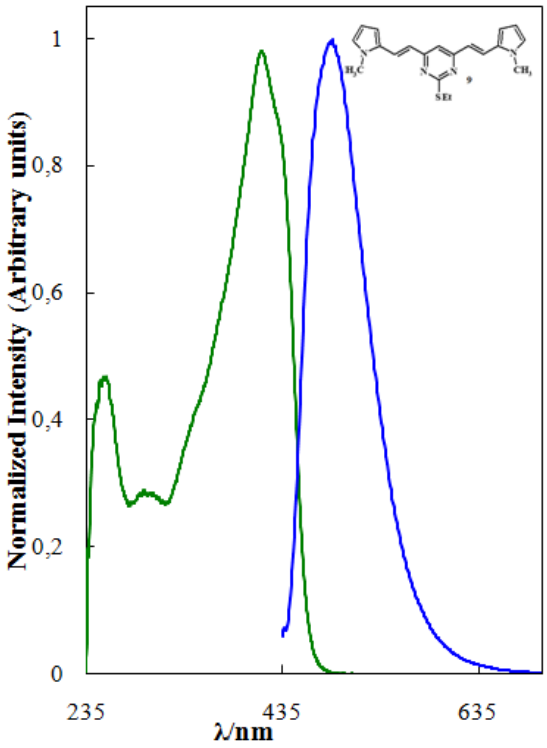

Figure S18 Normalized electronic absorption (green) and emission (blue, λ_{ex} = 435 nm) spectra of THF solution of compound **9.**

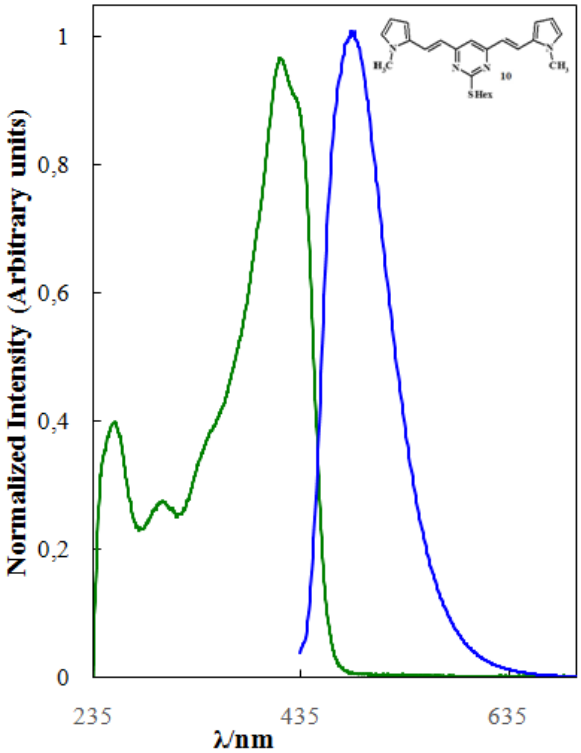

Figure S19 Normalized electronic absorption (green) and emission (blue, λ_{ex} = 435 nm) spectra of THF solution of compound **10.**

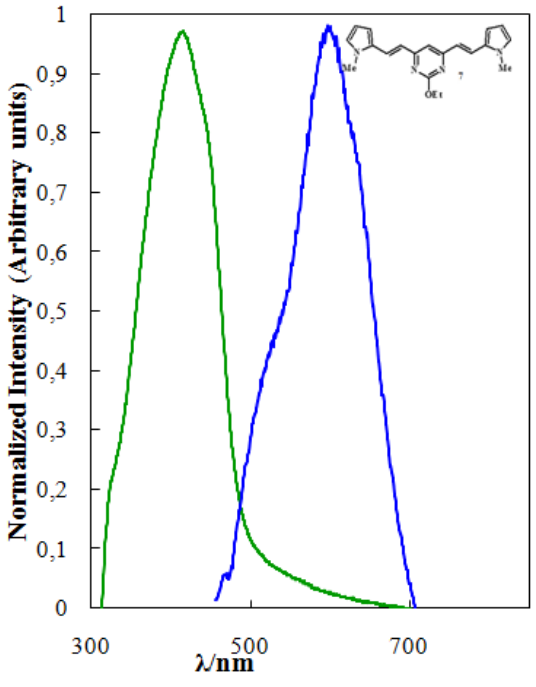

Figure S20 Normalized electronic absorption (green) and emission (blue, λ_{ex} = 435 nm) spectra of thin film of compound **7**.

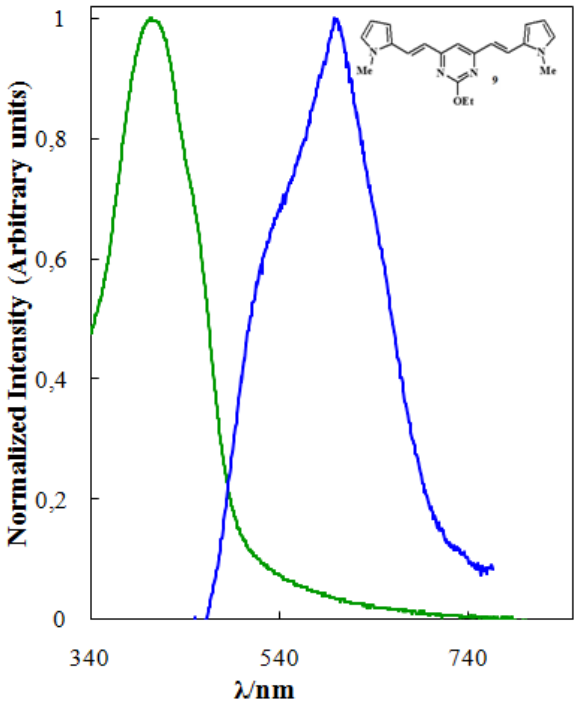

Figure S21. Normalized electronic absorption (green) and emission (blue, λ_{ex} = 400 nm) spectra of thin film of compound **9**.

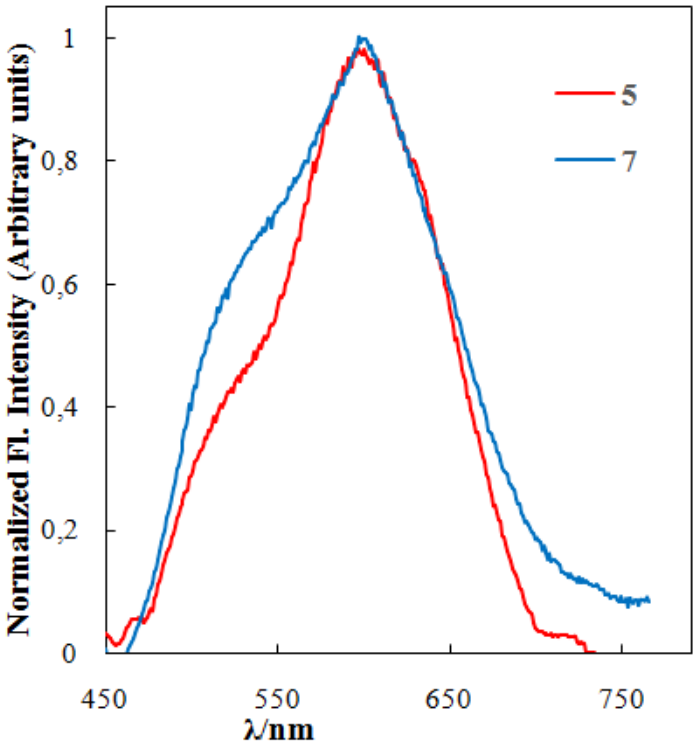

Figure S22 Emission spectra of films prepared from compounds **5** (red) and **7** (blue).

Table S1 UV–VIS and photoluminescence data for THF solutions and films of divinylpyrimidines **7–10**.

Comp		λ_{max}^{abs}/nm (ε, $M^{-1}*L^{-1}$)	λ_{onset}/nm	E_g^{opt}/eV[a]	λ_{max}^{emi}/nm	Δυ/cm^{-1}[b]	Φ_F[c]
7	solution	243 (6 540) 285 (8 240) 316 (9 090) 410 (29 790)	465	2.67	480	3 557	0.084
	film	416	500	2.48	600	7 372	-
8	solution	243 (6 930) 288 (10 310) 316 (11 500) 411 (40 620)	462	2.68	472	3 144	0.086
	film	395	520	2.38	-	-	-
9	solution	253 (9 700) 418 (21 570)	475	2.61	489	3 474	0.075
	film	409	511	2.43	602	7 838	-
10	solution	255 (11 890) 300 (8 370) 415 (31 320)	470	2.64	477	3 132	0.082
	film	398	535	2.32	-	-	-
4,6-di[2-(1-methyl-1*H*-pyrrol-2-yl)vinyl]-pyrimidine[S2]	THF DCM	318 406 289 (95 200) 408 (29 700)	-	-	485 496	4 349	0,14

[a] $E_g^{opt} = 1240/\lambda_{onset}$, wherein λ_{onset} is the long wavelength absorption edge;

[b] Stokes shift $\Delta\upsilon = 1/\lambda_{max}^{abs} - 1/\lambda_{max}^{emi}$;

[c] Fluorescence quantum yields were determined relative to 3-aminophtalimide in EtOH as the standard ($\Phi_F = 0.6$)[S8]

Quantum Chemical Calculation

All calculations where performed using a Firefly program,[S9] which is partially based on the GAMESS (US) source code on the PSU-Kepler supercomputer. The geometries of all structures were initially optimized at the PBE0-D3/def2-TZVP level of theory. All electronic properties obtained at the PBE0-D3/def2-TZVPD (HOMO/LUMO energies) and TDDFT-PBE0-D3/def2-TZVPD (vertical excitation) levels.

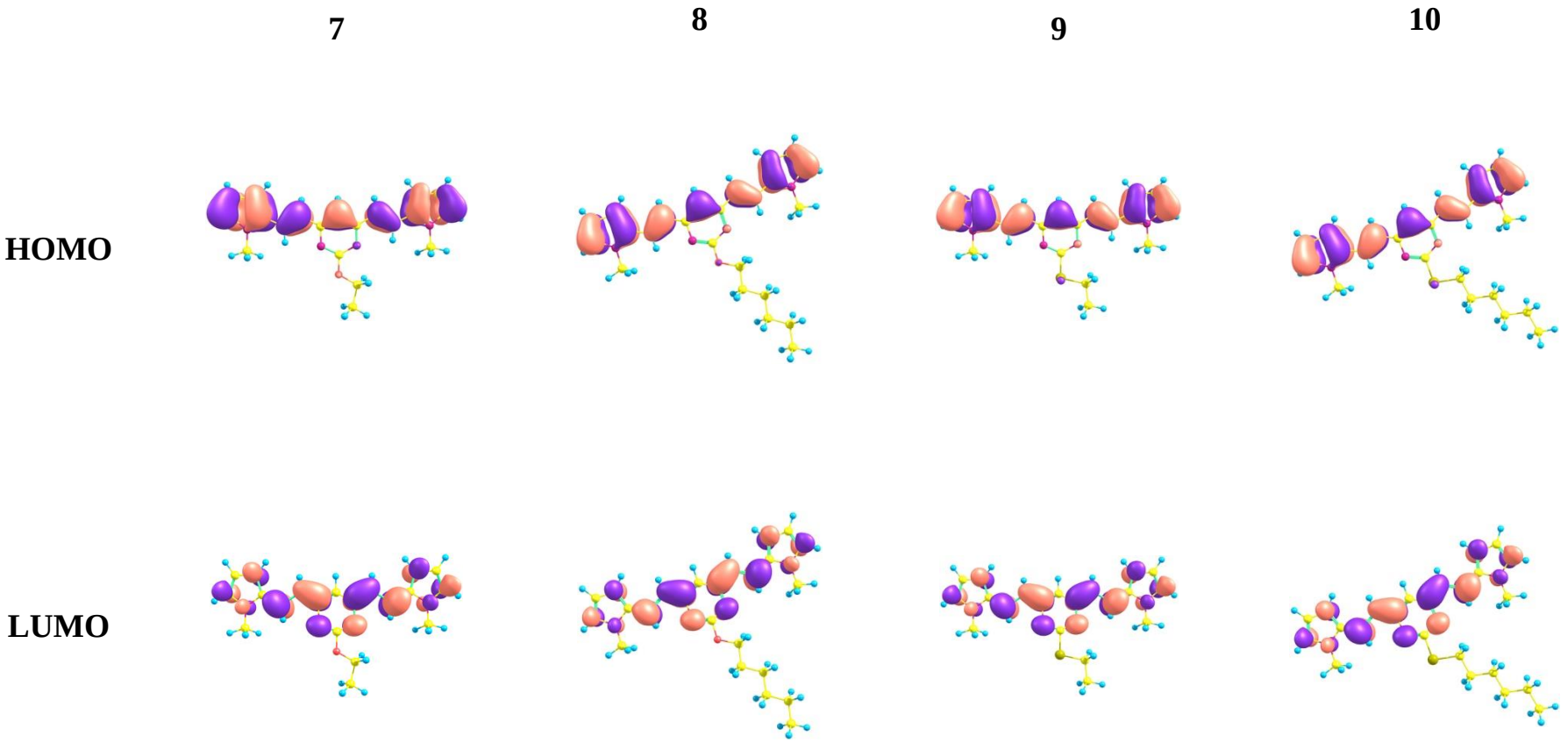

Figure S23 Frontier molecular orbitals of pyrimidines **7–10**.

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