Anthradithiophene-Based Organic Semiconductors through Regiodirected Double Annulations

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1. General experimental

All commercially available reagents and solvents were purchased from Sigma-Aldrich, Fluorochem and Alfa Aesar. They were all used as received. 2,5-Dibromoterephthalaldehyde **1**[1] and compound **7** were synthesized according to literature.[2] Flash chromatography was carried out using Merck silica gel 60 (pore size 60 Å, 270-400 Mesh). ^{1}H and ^{13}C NMR spectra were recorded from solutions in deuterated solvents on 300 Bruker or 400 Jeol spectrometers with the residual solvent as the internal standard. Mass spectra of pure compounds were recorded using an Electron Spray Ionization Agilent Technologies mass spectrometer, Direct Exposure Probe mass spectrometer, GC-MS ThermoScientific spectrometer and a Bruker Autoflex MALDI-TOF in positive reflectron mode with or without trans-2-(3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene)malononitrile (DCTB) as the matrix. The spectra were recorded also without the matrix, giving in most cases equivalent results due to the direct formation of the radical cation of the relevant species. The UV-Vis spectroscopic studies were recorded using JASCO V-550 spectrophotometer. The photoluminescence experiments and lifetime experiments were recorded using Horiba Fluorolog®-3 Model FL3-22iHR. Cyclic voltammetry experiments were carried out using a Epsilon-Eclipse potentiostat with a polished glassy carbon working electrode, platinum counter electrode, silver pseudo-reference electrode, and tetrabutylammonium hexofluorophosphate (recrystallized three times from EtOH) as a supporting electrolyte. Sample concentrations were between 0.2 and 1.0 mM in CH_2Cl_2. All electrochemical measurements were referenced to the Fc/Fc$^+$ redox couple. Band gaps were estimated using the onset of the initial oxidation and reduction events, and E_{HOMO} and E_{LUMO} were estimated given an E_{HOMO} of 4.80 eV for ferrocene. In all figures the first scan is shown, which is similar to subsequent scans.[3] Theoretical energy calculations were performed with density functional theory (DFT) calculations using the DFT/B3LYP framework with the DZP basis set. Solubilizing alkyl groups were replaced with methyl groups in small molecules **9** and **10** for simplicity.

Hole mobility measurements. Hole-only devices were prepared for the investigation of mobility of positive charge carriers. The devices had the sandwiched structure ITO/PEDOT:PSS/PDTIDTBT/MoO3/Au, where ITO is indium tin oxide and PEDOT:PSS is poly(3,4-ethylenedioxythiophene)/polystyrene sulphonic acid (CLEVIOS P VP AI 4083, H.C. Starck). ITO-coated glass substrates were first cleaned in detergent and water, then ultrasonicated in acetone and isopropyl alcohol for 15 min each. The layer of PEDOT:PSS (~ 40 nm) was spin-coated at 4000 rpm onto the ITO-glass substrates, and baked in an oven at 120°C for 10 min. The small molecule layer was deposited by spin-coating (280 rpm) from a chloroform solution (40 g·L^{-1}) to a thickness of 600 nm. The MoO$_3$ layer (5 nm) and the Au top electrode (100 nm) were thermally evaporated at a base pressure of 4×10^{-6} mbar through a shadow mask defining a device active area of 8 mm^2. The electrical characterization of hole-only devices was carried out at room temperature in an Ar-filled glove-box. *J-V* characteristics were taken using a digital source meter (Keithley model 2400) and Impedance Spectroscopy measurements were performed using an Agilent 4294A impedance analyzer. The impedance measurements were done in the frequency range 40 Hz–1 MHz, with an amplitude of the harmonic voltage modulation of 20 mV. The DC bias was varied in the range 0 V–30 V. AFM images were acquired on films with a thickness comparable to that used for the devices (Figure S9).

The transit time of charge carriers τ can be inferred from the peak frequency of the negative differential subsceptance or from the peak frequency of the imaginary part of impedance (*ImZ*).[4] Figure S7 shows the frequency dependence of *ImZ*, at various values of the dc bias, for a hole-only device based on small molecule **9**, indicating that clear peaks were observed, shifting toward higher frequencies as the dc voltage was increased. The transit time of charge carriers was obtained from the peak frequency through $\tau = k\tau_{\mathrm{p}}$, where τ_{p} is the time constant corresponding to the peak frequency of *ImZ* and k a constant dependent on the dispersion degree. The value of 0.44 was assumed for k, which has been reported for a moderate degree of dispersion.[5] The values of hole mobility μ was calculated

by using the well-known expression $\mu = d/(E\,\tau)$, where d is the film thickness. As shown in Figure S7, the hole mobility of spin-coated small molecule **9** exhibits an almost field-independent behavior, suggesting a low energetic disorder.[6] The mean value of the data shown in Figure 5 is 2.45×10^{-5} $cm^2\cdot V^{-1}\cdot s^{-1}$, a remarkable value for the bulk mobility of a low-molecular weight and spin-coated compound.

Given the rough independence on field, the hole mobility was also extracted from the current-density *versus* voltage (*J-V*) characteristic of the hole-only device made of small molecule **9**. In figure S8, J is reported as a function of square V, showing the excellent linear behavior expected for the space-charge-limited current in an one-carrier only device, as predicted by the Mott-Gurney low:[7]

$$J = \frac{9}{8}\varepsilon\varepsilon_0\mu\frac{V^2}{d^3}$$

where ε and ε_0 are the relative dielectric constant and the permittivity in vacuum, respectively. By plotting J as a function of V^2, the slope of the line is strictly correlated with mobility. A value of 2.38×10^{-5} $cm^2\cdot V^{-1}\cdot s^{-1}$ was calculated by assuming $\varepsilon = 3$, in excellent agreement with the mean hole mobility obtained with impedance spectroscopy.

X-ray diffraction (XRD) investigation. XRD investigation was conducted on films (600 nm thick) of compound **9** spin-coated from a chloroform solution onto a glass substrate. XRD patterns were collected in Bragg-Brentano geometry by means of a Malvern Panalytical MRD system equipped with a copper source ($\lambda = 0.15418$ nm). Each step of $0.05°$ 2-theta was investigated for 80 s with a multi-channel solid-state detector, in the range $2° - 60°$. The contribution of the glass support was subtracted before plotting the data.

2. Synthesis of New Compounds

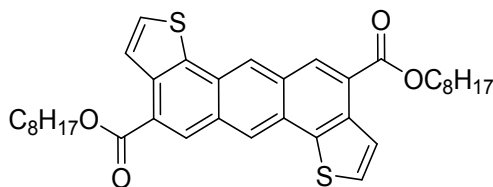**Anthra[1,2-*b*:5,6-*b′*]dithiophene-4,10-dicarboxylic acid (3a)**
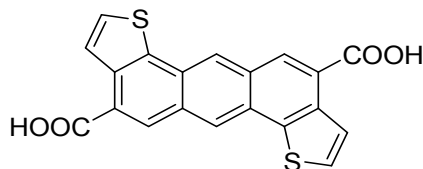
A three-necked flask equipped with condenser and mechanical stirring was charged in argon atmosphere with 3-thiopheneacetic acid (28.4 g, 0.2 mol, 2 eq), Pd(OAc)$_2$ (2.25 g, 0.01 mol, 0.01 eq), PPh$_3$ (5.25 g, 0.02 mol, 0.1 eq), K$_2$CO$_3$ (55.3 g, 0.4 mol, 4 eq) and dry DMAc (2 L). The reaction mixture was warmed to 110 °C and 2,5-dibromoterephthalaldehyde **1** (29.2 g, 0.1 mol, 1 eq) was added portionwise in 10 min under inert atmosphere. The reaction mixture was kept at the same temperature under stirring for 24 h, and then the reaction solvent was removed under reduced pressure. The dark crude reaction mixture was dissolved in distilled water (1 L) and HCl conc (50 mL) was added dropwise until full acidity (pH = 1). The precipitate was filtered under reduced pressure and washed with MeOH (500 mL). The dark powder was purified by Soxhlet extraction with acetone for 24 h to give **3a** as a black powder (26.9 g, 81%). ^{1}H NMR (300 MHz, DMSO-d_6) δ: 13.37 (s, 2H), 9.19 (s, 2H), 8.90 (s, 2H), 8.31 (d, J = 5.4 Hz, 2H), 8.01 (d, J = 5.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 167.9, 138.7, 134.8, 131.1, 130.1, 128.2, 127.6, 126.4, 125.8, 125.0. ESI-MS: 377 [M −1]⁻. Anal. calcd. for C$_{20}$H$_{10}$O$_4$S$_2$: C 63.5; H 2.7; found: C 63.7; H 2.9.

General procedure for the alkylation of compound 3a. *Synthesis of compound* **3b**. 9-(bromomethyl)nonadecane (36.1 g, 100 mmol, 2 eq) was added to a solution of compound **3a** (18.9 g, 50 mmol, 1 eq), Bu$_4$NI (3.69 g, 10 mmol, 0.2 eq), K$_2$CO$_3$ (13.82 g, 100 mmol, 2 eq) in dry DMAc (500 mL) under inert atmosphere and then stirred at 130 °C for 48 h. After removal of solvent under reduced pressure, the crude reaction mixture was dissolved in hexane:AcOEt (98:2) and filtered

through a short silica gel path (4 cm). The organic solvent was removed under reduced pressure, the crude reaction mixture was dissolved in CHCl$_3$ and precipitated in EtOH and ^{i}PrOH (twice) to give **3b** as a yellow powder (23.9 g, 51%).
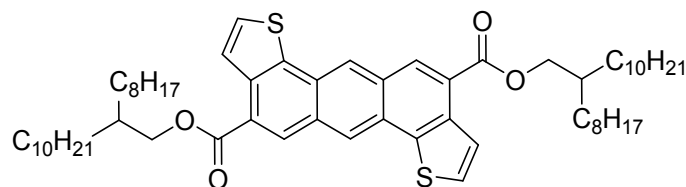

Bis(2-octyldodecyl) anthra[1,2-b:5,6-b']dithiophene-4,10-dicarboxylate (**3b**). Yellow powder (51%). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.79 (s, 2H), 8.69 (s, 2H), 8.36 (d, J = 5.3 Hz, 2H), 7.63 (d, J = 5.3 Hz, 2H), 4.39 (d, J = 5.1 Hz, 4H), 1.92 (s, 2H), 1.57 – 1.13 (m, 64H), 0.95 – 0.75 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 166.6, 139.1, 134.6, 130.9, 130.0, 128.6, 126.6, 125.7, 125.2, 124.6, 77.2, 76.7, 76.3, 67.8, 37.3, 31.6, 31.4, 29.8, 29.4, 29.4, 29.3, 29.1, 26.6, 22.4, 13.8. DEP-MS *m/z* (%): 938 [*M*]$^+$ (100). Anal. calcd. for C$_{60}$H$_{90}$O$_4$S$_2$: C 76.7; H 9.7; found: C 76.8; H 9.7.

Bis(n-octyl) anthra[1,2-b:5,6-b']dithiophene-4,10-dicarboxylate (**3c**). Yellow powder (48%). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.77 (s, 2H), 8.69 (s, 2H), 8.34 (d, J = 5.3 Hz, 2H), 7.62 (d, J = 5.3 Hz, 2H), 4.46 (t, J = 6.7 Hz, 4H), 1.89 (t, J = 6.9 Hz, 4H), 1.57 – 1.19 (m, 20H), 0.97 – 0.84 (m, 6H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 166.6, 139.1, 134.6, 130.9, 130.0, 128.6, 126.6, 125.7, 125.2, 124.6, 65.7, 32.0, 29.5, 29.4, 29.0, 26.3, 22.9, 14.3. DEP-MS *m/z* (%): 602 [*M*]$^+$ (10). Anal. calcd. for C$_{36}$H$_{42}$O$_4$S$_2$: C 71.7; H 7.0; found: C 71.9; H 7.1.
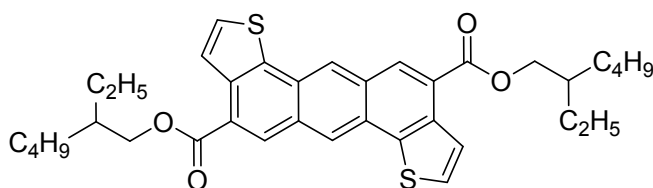
Bis(2-etylhexyl) anthra[1,2-b:5,6-b']dithiophene-4,10-dicarboxylate (**3d**). Yellow powder (32%). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.77 (s, 2H), 8.69 (s, 2H), 8.34 (d, J = 5.3 Hz, 2H), 7.62 (d, J = 5.3 Hz, 2H), 4.39 (d, J = 5.1 Hz, 4H), 1.92 (s, 2H), 1.57 – 1.13 (m, 16H), 0.95–0.75 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 165.6, 139.1, 133.9, 131.0, 130.3, 128.6, 126.6, 125.8, 125.2, 124.3, 65.6, 32.1, 29.5, 29.4, 29.1, 26.3, 22.9, 14.5. DEP-MS m/z (%): 602 [M]$^+$ (100). Anal. calcd. for C$_{36}$H$_{42}$O$_4$S$_2$: C 71.7; H 7.0; found: C 71.5; H 7.1.

Bis(2-ethylhexyl) 2,8-dibromoanthra[1,2-b:5,6-b']dithiophene-4,10-dicarboxylate (4).
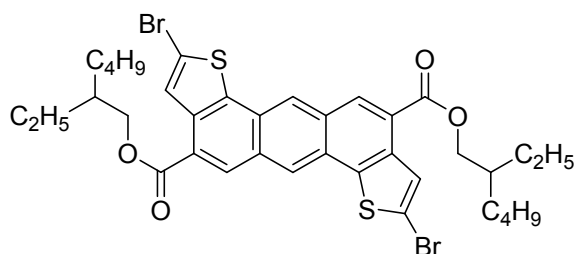
N-Bromosuccinimide (71 mg, 0.4 mmol, 4 eq) was added to a solution of compound **3d** (60 mg, 0.1 mmol, 1 eq) in a mixture of CHCl$_3$ and AcOH (8:2, 1 mL) under inert atmosphere. The reaction mixture was kept under stirring at room temperature for 24 h. After removal of the solvent under reduced pressure, the crude reaction mixture was dissolved in hexane:AcOEt (98:2) and filtered through a short silica gel path (4 cm). The organic solvent was removed under reduced pressure to give **4** as a yellow powder (18 mg, 25%). ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.63 (s, 2H), 8.57 (s, 2H), 8.34 (s, 2H), 4.43 (d, J = 5.1 Hz, 4H), 1.92 (s, 2H), 1.57 – 1.13 (m, 16H), 0.95 – 0.75 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 165.6, 139.1, 133.9, 131.0, 130.3, 128.6, 126.6, 125.8, 125.2, 124.3, 65.6, 32.1, 29.5, 29.4, 29.1, 26.3, 22.9, 14.5. DEP-MS m/z (%): 760 [M]$^+$ (100). Anal. calcd. for C$_{36}$H$_{40}$Br$_2$O$_4$S$_2$: C 56.9, H 5.3; found: C 56.8; H 5.4.

Bis(2-octyldodecyl) 2,8-bis(tributylstannyl)anthra[1,2-*b*:5,6-*b′*]dithiophene-4,10-dicarboxylate (5)
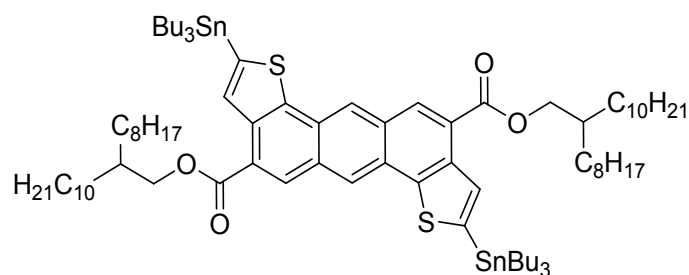
A solution of compound **3b** (1 g, 1.06 mmol, 1eq) in dry THF (25 mL) under argon was cooled to -78 °C. After 15 min, a solution of LDA (1 M in hexane, 4.26 mL, 4.26 mmol, 4 eq) was added dropwise and kept for 2h at the same temperature, then Bu_3SnCl (722 µL, 2.66 mmol, 2.5 eq) was added in one portion. The reaction mixture was kept at -78°C for 30 min, and then it was warmed to room temperature and stirred overnight. The reaction mixture was quenched with H_2O (20 mL), most of the organic solvent was removed under reduced pressure, and the aqueous phase extracted with Et_2O (3 x 20 mL). the combined organic phase was dried (Na_2SO_4). After removal of the solvent under reduced pressure, the reaction mixture was purified by flash chromatography on neutral alumina (*n*-hexane as the eluent) affording **5** as a pale yellow oil (1.31 g, 81%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.91 (s, 2H), 8.73 (s, 2H), 8.41 (s, 2H), 4.44 (d, *J* = 5.1 Hz, 4H), 1.92 (s, 2H), 1.57 – 1.13 (m, 16H), 0.95 – 0.75 (m, 12H). ^{13}C NMR (75 MHz, CDCl$_3$) δ: 167.7, 149.8, 145.0, 139.7, 136.4, 135.0, 131.3, 130.4, 128.9, 125.5, 65.6, 32.1, 29.5, 29.4, 29.1, 26.3, 22.9, 14.5. APCI-MS *m/z* (%): 1518 [*M*]$^+$ (100).

bis(2-octyldodecyl) 2-(tributylstannyl)anthra[1,2-*b*:5,6-*b′*]dithiophene-4,10-dicarboxylate (6).
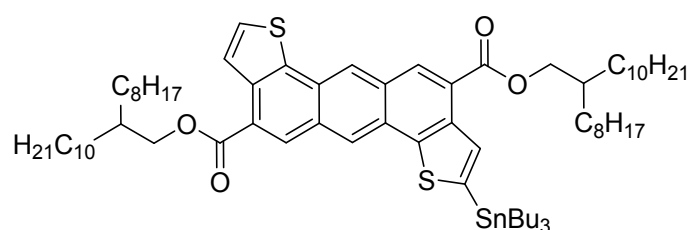
A solution of compound **5d** (1 g, 1.06 mmol, 1eq) in dry THF (25 mL) under argon atmosphere was cooled to -78°C. After 15 min LDA (1 M in hexane, 1.59 mL, 1.59 mmol, 1.5 eq) was added dropwise and kept for 2h at the same temperature, then Bu$_4$SnCl (288 µL, 1.59 mmol, 1.5 eq) was added in one portion. The reaction mixture was kept at -78°C for 30 min, and then it was warmed to room temperature and stirred overnight. The reaction mixture was quenched with H$_2$O (20 mL), most of the organic solvent was removed under reduced pressure, and the aqueous phase extracted with Et$_2$O (3 x 20 mL). the combined organic phase was dried (Na$_2$SO$_4$). After removal of the solvent under reduced pressure, the reaction mixture was purified by flash chromatography on neutral alumina (*n*-hexane as the eluent) affording pure compound **6** as a pale yellow oil (627 mg, 48%).^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.90 (s, 1H), 8.75 (s, 1H), 8.72 (s, 1H), 8.43 (s, 1H), 8.38 (d, *J* = 5.4 Hz, 1H), 7.64 (d, *J* = 5.4 Hz, 1H), 4.40 (t, *J* = 5.2 Hz, 4H), 1.96 – 1.87 (m, 2H), 1.73 – 1.19 (m, 76H), 0.94 (t, *J* = 7.3 Hz, 9H), 0.94 – 0.77 (m, 12H). ^{13}C NMR (101 MHz, CDCl$_3$) δ: 167.1, 166.8, 144.4, 139.3, 139.2, 134.5, 134.4, 131.0, 130.6, 130.1, 129.9, 128.5, 126.6, 125.7, 125.5, 125.2, 125.1, 124.5, 68.3, 37.7, 34.4, 32.0, 31.7, 31.7, 30.5, 30.2, 30.1, 29.8, 29.6, 29.5, 29.2, 27.4, 27.0, 27.0, 22.8, 14.2, 13.8, 11.2.

bis(2-octyldodecyl) 2,8-bis(4-(((2-octyldodecyl)oxy)carbonyl)naphtho[1,2-b]thiophen-2-yl)anthra[1,2-b:5,6-b']dithiophene-4,10-dicarboxylate (9).
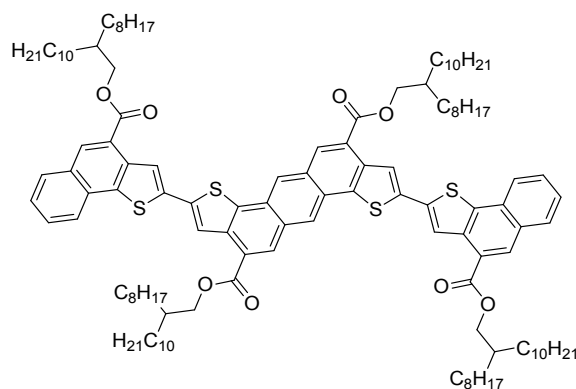
A solution of compound **5** (303 mg, 0.2 mmol, 1 eq), 2-octyldodecyl 2-bromonaphtho[1,2-b]thiophene-4-carboxylate **7** (235 mg, 0.4 mmol, 2 eq) in dry toluene (2 mL)was degassed for 5 min

under argon atmosphere. Pd(PPh$_3$)$_4$ (4.62 mg, 4 μmol, 0.02 eq) was added in one portion, and the solution was further degassed for 10 min. The reaction mixture was heated at reflux under stirring for 24 h. The reaction solvent was removed under reduced pressure and the reaction mixture was purified by flash chromatography (SiO$_2$; petroleum ether:CH$_2$Cl$_2$ 8:2), to obtain compound **9** as a dark yellow solid (277 mg, 71%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.40 (s, 2H), 8.28 (s, 2H), 8.20 (s, 2H), 8.18 (s, 2H), 8.13 (s, 2H), 7.74 (d, J = 8.0 Hz, 4H), 7.62 (d, J = 8.0 Hz, 4H), 7.39 (t, J = 7.4 Hz, 4H), 7.25 (t, J = 7.4 Hz, 4H), 4.52 (d, J = 5.0 Hz, 4H), 4.44 (d, J = 5.4 Hz, 4H), 2.12 – 2.02 (m, 2H), 1.98 (d, J = 5.3 Hz, 2H), 1.66 – 1.13 (m, 128H), 0.82 (dd, J = 12.9, 6.0 Hz, 24H). ^{13}C NMR (101 MHz, CDCl$_3$) δ: 166.3, 166.1, 138.3, 138.2, 137.2, 137.1, 135.7, 134.7, 131.0, 130.4, 130.1, 129.5, 129.4, 128.6, 127.3, 125.8, 124.4, 124.2, 123.7, 123.3, 123.2, 123.0, 68.5, 68.2, 37.8, 32.1, 32.1, 32.1, 31.9, 31.8, 30.4, 30.0, 29.9, 29.9, 29.8, 29.6, 29.5 27.2, 22.8, 22.8, 14.2. MALDI-TOF: m/z [M]$^+$ = 1953.25; calcd. for C$_{126}$H$_{182}$O$_8$S$_4$: 1953.28.

tetrakis(2-octyldodecyl) 2,2'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(anthra[1,2-b:5,6-b']dithiophene-4,10-dicarboxylate) (10).
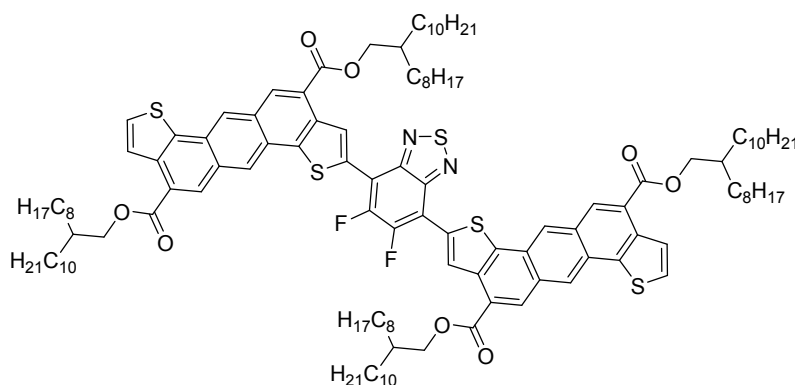
A solution of compound **6** (303 mg, 0.2 mmol, 1 eq), 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole **8** (235 mg, 0.4 mmol, 2 eq) in dry toluene (2 mL) was degassed for 5 min under argon atmosphere. Pd(PPh$_3$)$_4$ (4.62 mg, 4 μmol, 0.02 eq) was added in one portion, and the solution was further degassed for 10 min. The reaction mixture was heated at reflux under

stirring for 24 h. The reaction solvent was removed under reduced pressure and the reaction mixture was purified by flash chromatography (SiO$_2$; petroleum ether:CH$_2$Cl$_2$ 8:2), to obtain compound **10** as a dark red solid (277 mg, 76%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.77 (s, 0H), 8.33 − 8.17 (m, 0H), 8.07 (s, 0H), 7.81 (d, J = 22.4 Hz, 0H), 7.33 (d, J = 5.1 Hz, 0H), 4.53 (d, J = 5.5 Hz, 0H), 4.26 (d, J = 4.3 Hz, 0H), 2.11 (d, J = 5.6 Hz, 0H), 1.97 − 1.79 (m, 0H), 1.80 − 1.09 (m, 8H), 0.98 − 0.75 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ: 165.73, 138.39, 133.98, 133.26, 130.74, 130.50, 129.41, 129.27, 129.05, 128.98, 127.70, 126.48, 126.39, 124.96, 124.35, 124.07, 123.75, 123.42, 68.58, 37.79, 37.58, 32.14, 31.67, 31.50, 30.46, 30.27, 30.02, 29.90, 29.67, 29.56, 29.54, 29.47, 27.11, 26.92, 22.85, 14.25. MALDI-TOF: m/z [M]$^{•+}$ = 2045.09; calcd. for C$_{126}$H$_{182}$O$_8$S$_4$: 2045.22.

3. Additional Tables and Figures

Table S1. Optimization for the formation of ester derivatives **3**

Entry	Compound	Reaction conditions	Yield [%]
1	**3c**	$C_8H_{17}Br$, K_2CO_3, DMAc, 70 °C	8
2	**3c**	$C_8H_{17}Br$, KOH, H_2O, 100 °C	0
3	**3c**	(a) oxalyl chloride in DMF, 100°C, then (b) $C_8H_{17}OH$ Et_3N, $CHCl_3$, 40°C	0
4	**3c**	(a) $SOCl_2$ toluene, at reflux, then (b) $C_8H_{17}OH$, Et_3N, THF, 60°C	24
5	**3c**	$C_8H_{17}Br$ (2 eq), K_2CO_3 (3 eq), Bu_4NBr (3 eq), DMAc, 130°C	48
6	**3d**	1-bromo-2-ethylhexane (2 eq), K_2CO_3 (3 eq), Bu_4NBr (3 eq), DMAc, 130°C (one pot)	41
7	**3b**	9-(bromomethyl)nonadecane, K_2CO_3 (3 eq), Bu_4NBr (3 eq), DMAc, 130°C (one pot)	41
8	**3b**	9-(bromomethyl)nonadecane, K_2CO_3 (3 eq), Bu_4NBr (3 eq), DMAc, 130°C (from isolated **3a**)	51

Table S2. *E* factor calculations for compounds **3a** and **3b**.
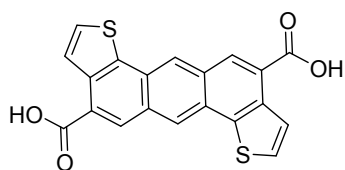
	Amount (g)	Waste (g)
2,5-dibromoterephthalaldehyde	29.19	5.55
3-thiopheneacetic acid	28.43	5.40
Pd(OAc)$_2$	2.25	2.25
PPh$_3$	5.25	5.25
K$_2$CO$_3$	55.28	55.28
DMAc	8.71	0
HCl	14.58	0
Total	**143.69**	**73.73**

Total waste = 73.73 g; Compound obtained = 26,87 g
E-factor = 2.74
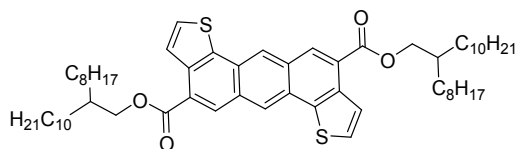
	Amount (g)	Waste (g)
Compound **3a**	18.92	9.27
9-(bromomethyl)nonadecane	36.14	17.71
K$_2$CO$_3$	27.64	27.64
DMAc	8.71	0
Silica gel	80.00	80
Hexane	131.00	131
Ethyl acetate	18.04	18.04
iPrOH	157.20	157.20
Total	**477.65**	**440.85**

Total waste = 440.85 g; Compound obtained = 24,42 g
E-factor = 18.1

Table S3. Bromination experiments on esters **3**

Entry	Starting ADT	Reaction condition	Yield
1	**3b**	NBS, CHCl$_3$, rt	0
2	**3b**	NBS, DMF, 100°C	0
3	**3b**	NBS, CHCl$_3$:AcOH 8:2, rt	0
4	**3b**	Br$_2$, CHCl$_3$, rt	0
5	**3b**	Br$_2$, DMF, rt	0
6	**3c**	NBS, CHCl$_3$:AcOH 8:2, rt	0
7	**3d**	NBS, DMF, 100°C	0
8	**3d**	NBS, CHCl$_3$:AcOH 8:2, rt	25
9	**3d**	NBS, CHCl$_3$:AcOH 1:1, rt	0
10	**3a**	Br$_2$, NaOH, H$_2$O, reflux	0
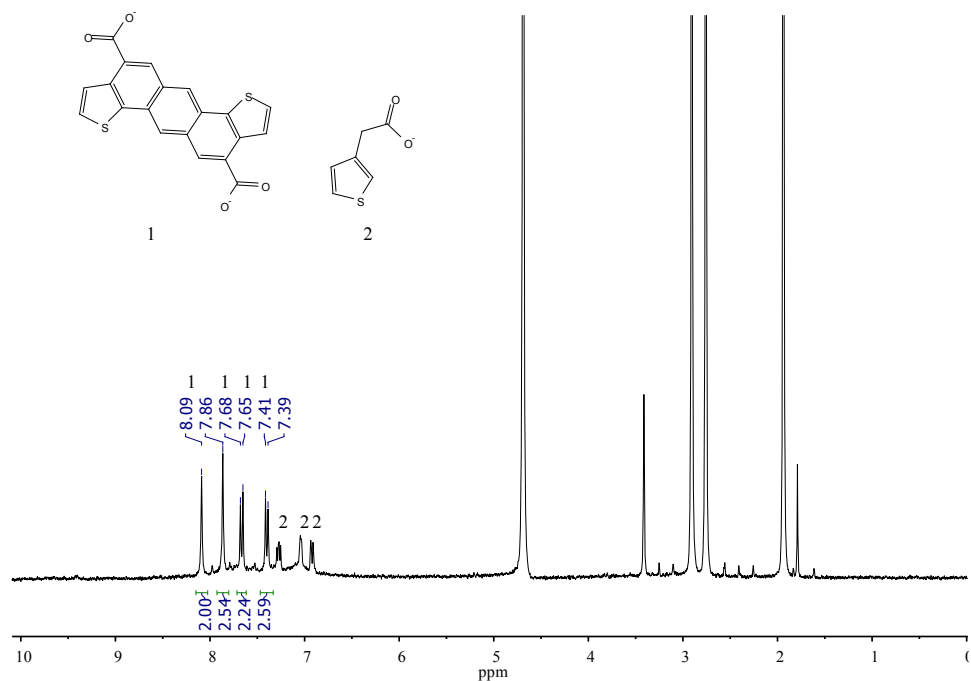
Figure S1. [^1]H NMR spectra (D$_2$O, 400 MHz, 298 K) of the crude reaction mixture for the preparation of compound **3a**, performed in the presence of Pd(OAc)$_2$ as the catalyst (10%), DMAc, 130°C, without the use of added phosphines. The crude reaction mixture was obtained removing the reaction solvent (DMAc) under reduced pressure.
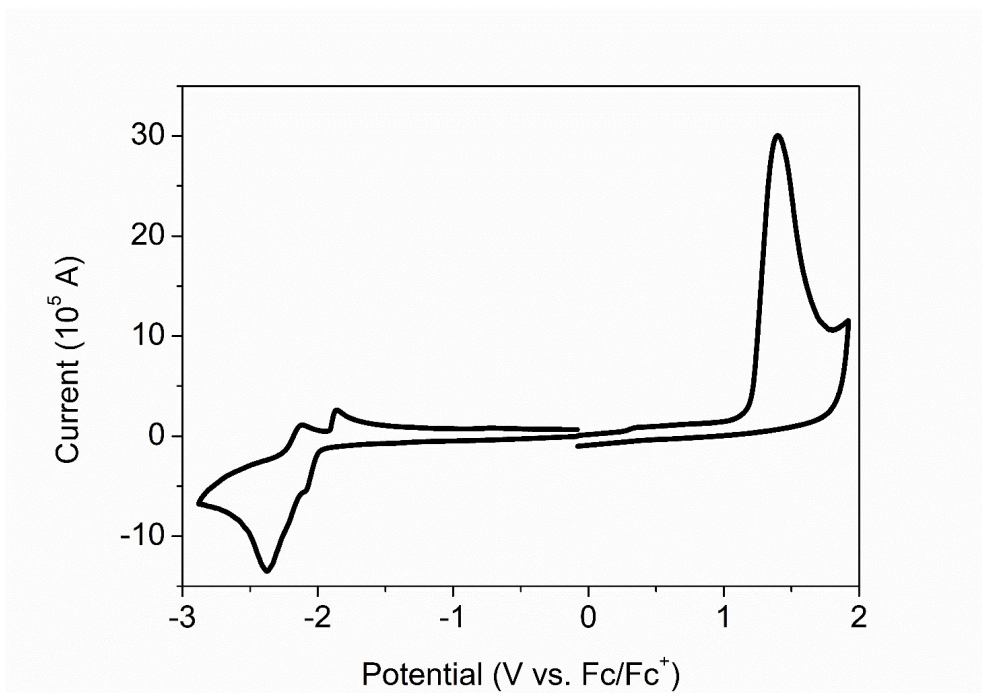
Figure S2. Cyclic voltammogram of compound **3b**.
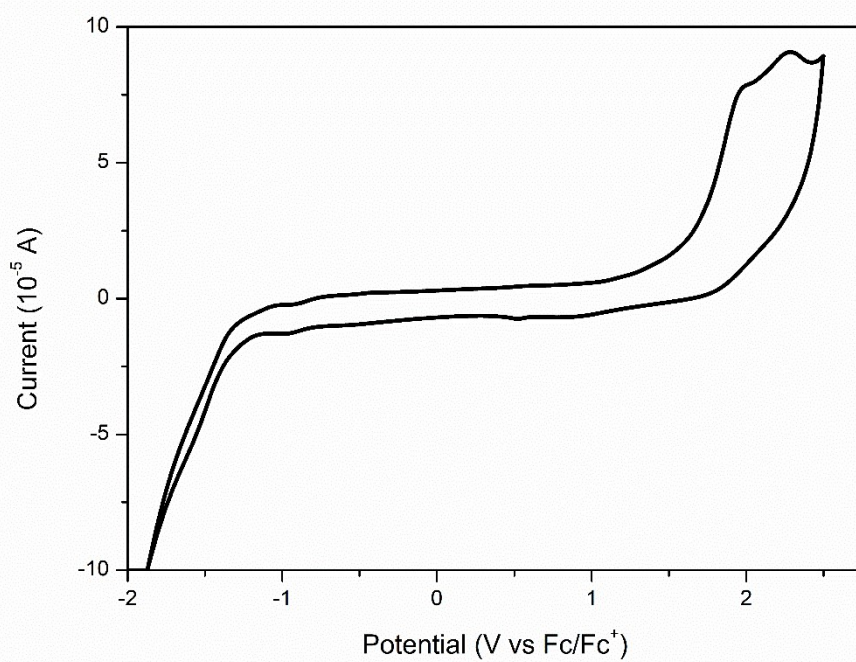
Figure S3. Cyclic voltammogram of compound **9**.
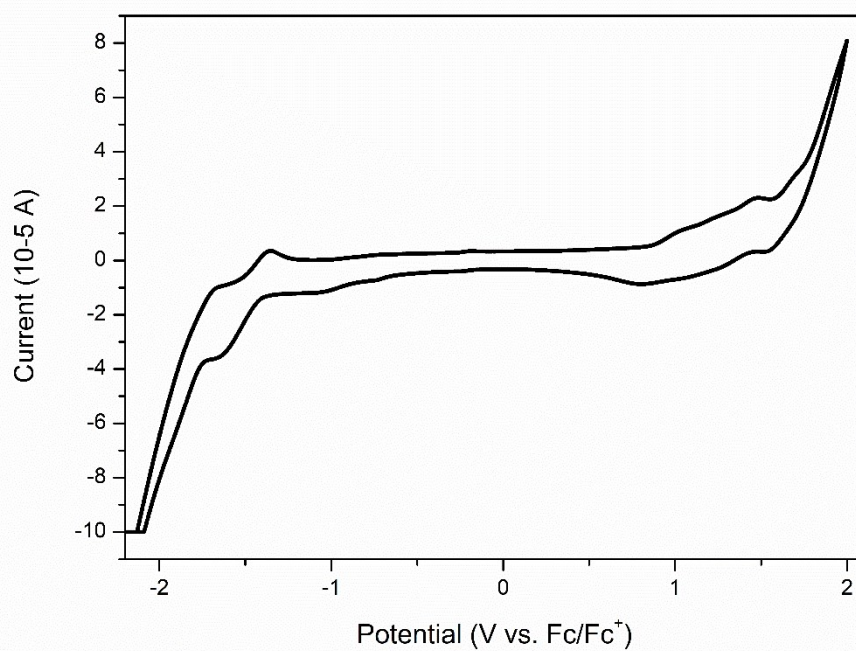
Figure S4. Cyclic voltammogram of compound **10**.
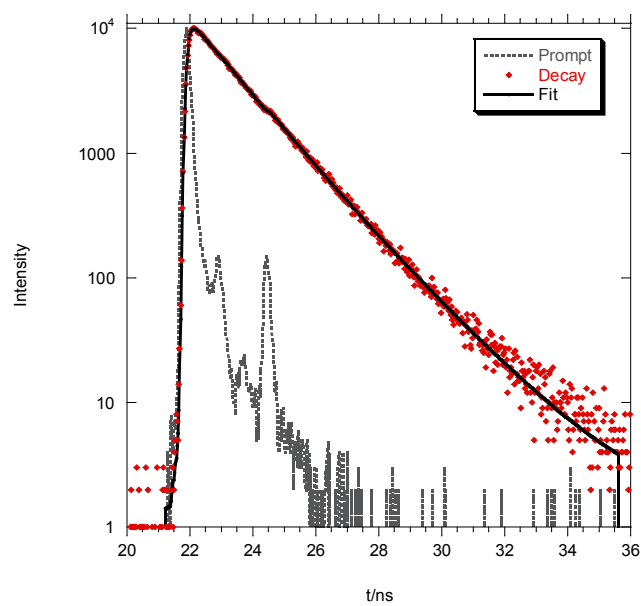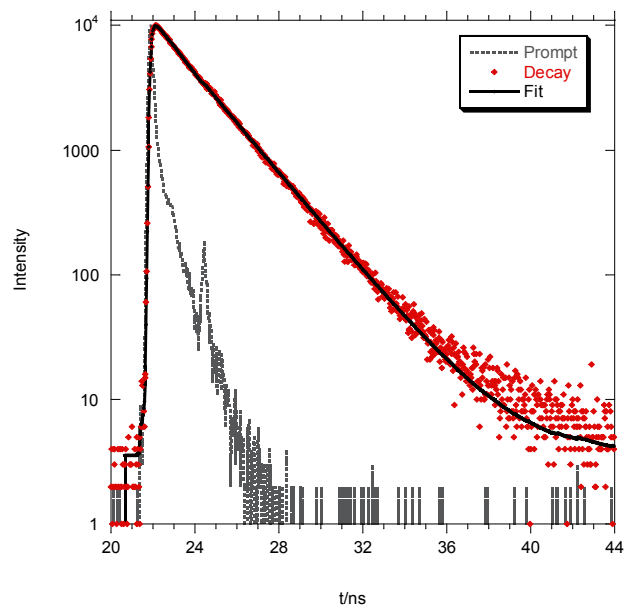
Figure S5. PL decay (λ_{ex}=407 nm) in chloroform of compounds **9** (top, λ_{em}@560nm) and **10** (bottom, λ_{em}@590nm). Bi-exponential fit (black lines) for **9** (0.60 ns (0.43), 2.20 ns (0.57), X^2= 1.402641) and **10** (1.16ns (0.66), 1.79ns (0.34), X^2= 1.177968)
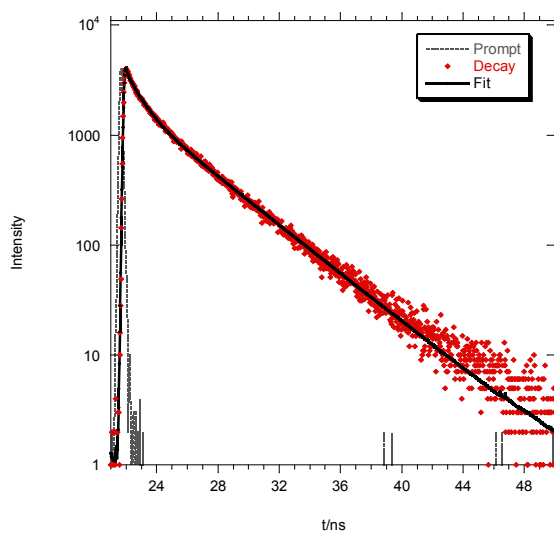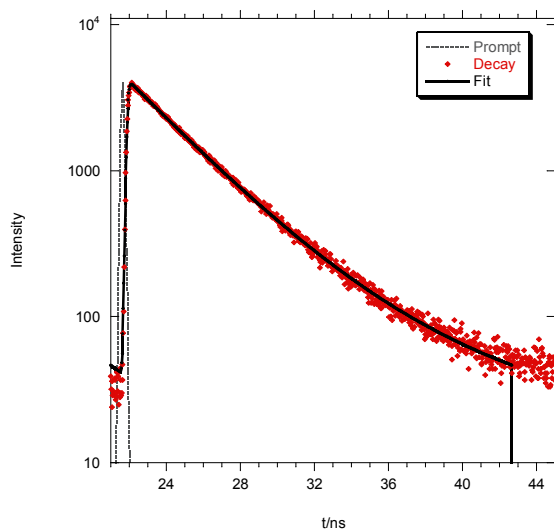
Figure S6. PL decay (λ_{ex}=407 nm) in film cast of compounds **9** (top, λ_{em}@766nm) and **10** (bottom, λ_{em}@725nm). Bi-exponential fit (black lines) for **9** (3.28 ns (0.93), 8.60 ns (0.07), X^2= 2.125197) and Three-exponential fit (black line) for **10** (0.95ns (0.01), 3.94ns (0.00), 0.002ns (0.99), X^2= 1.423133)
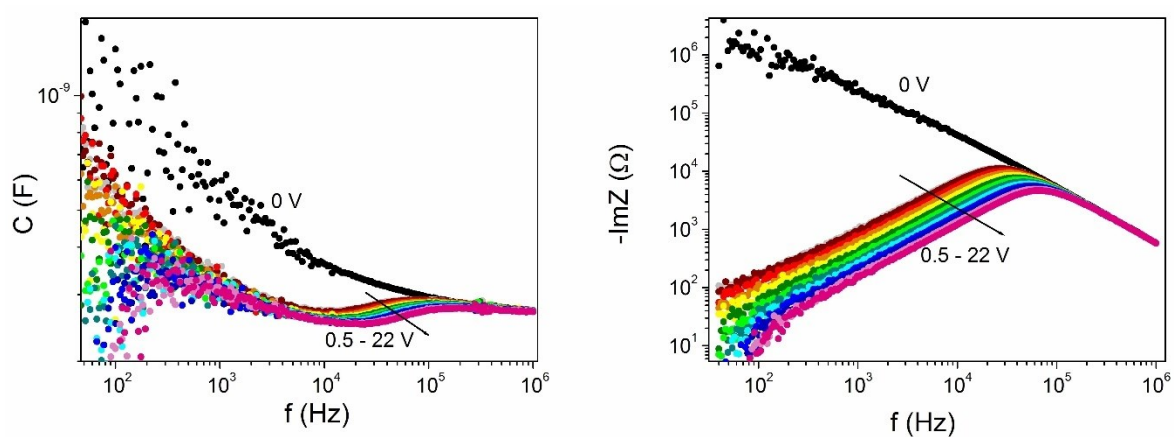
Figure S7. Variation of the capacitance (left) and of the imaginary part of impedance (right) with frequency and for various values of the dc bias for a hole-only device made of small molecule **9** (600 nm thick films).
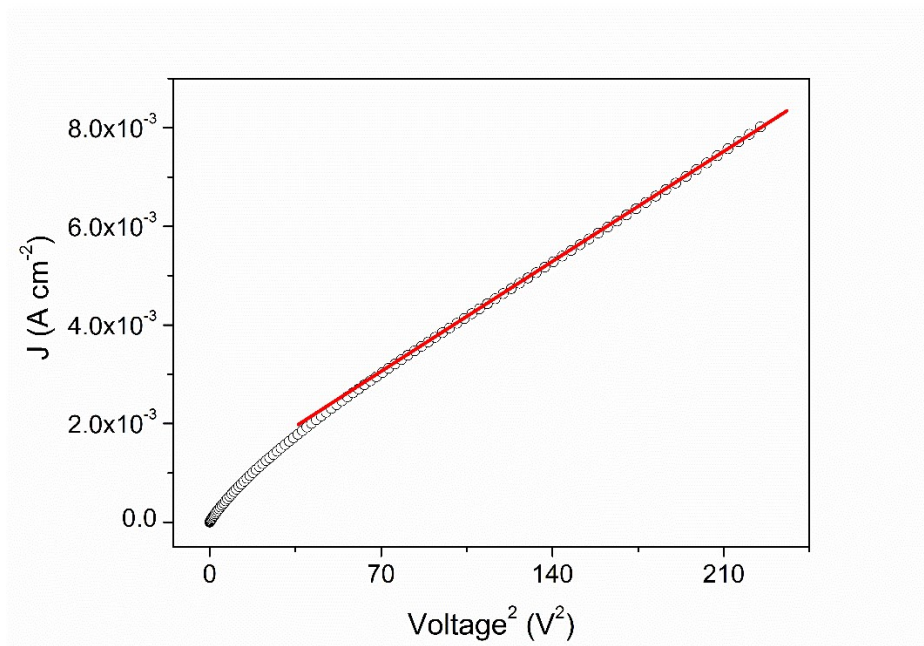
Figure S8. Current-density versus square voltage for a hole-only device made of small molecule **9** (600 nm thick film). The red line indicates the linear fit to the experimental data.
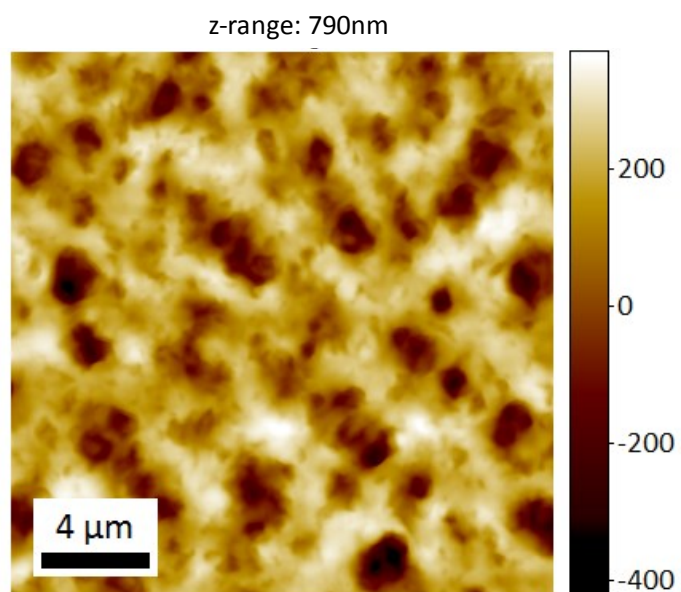
Figure S9. AFM image of a film (600 nm thick) of small molecule **9**. Root-mean-square roughness of 120 nm.

Spectra of New Compounds

Compound **3a**

^{1}H NMR (300 MHz, DMSO-d$_6$)

^{13}C NMR (101 MHz, DMSO-d$_6$)

167.88

138.68
134.81
131.05
130.09
128.24
127.64
126.44
125.78
124.98

ppm

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
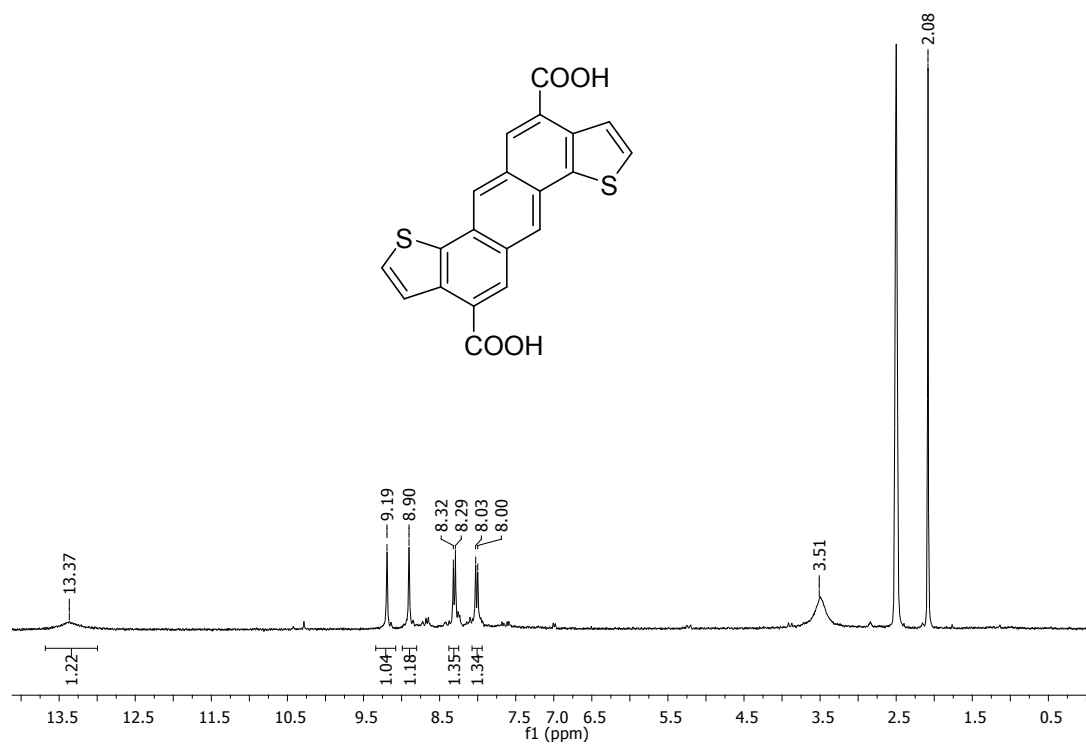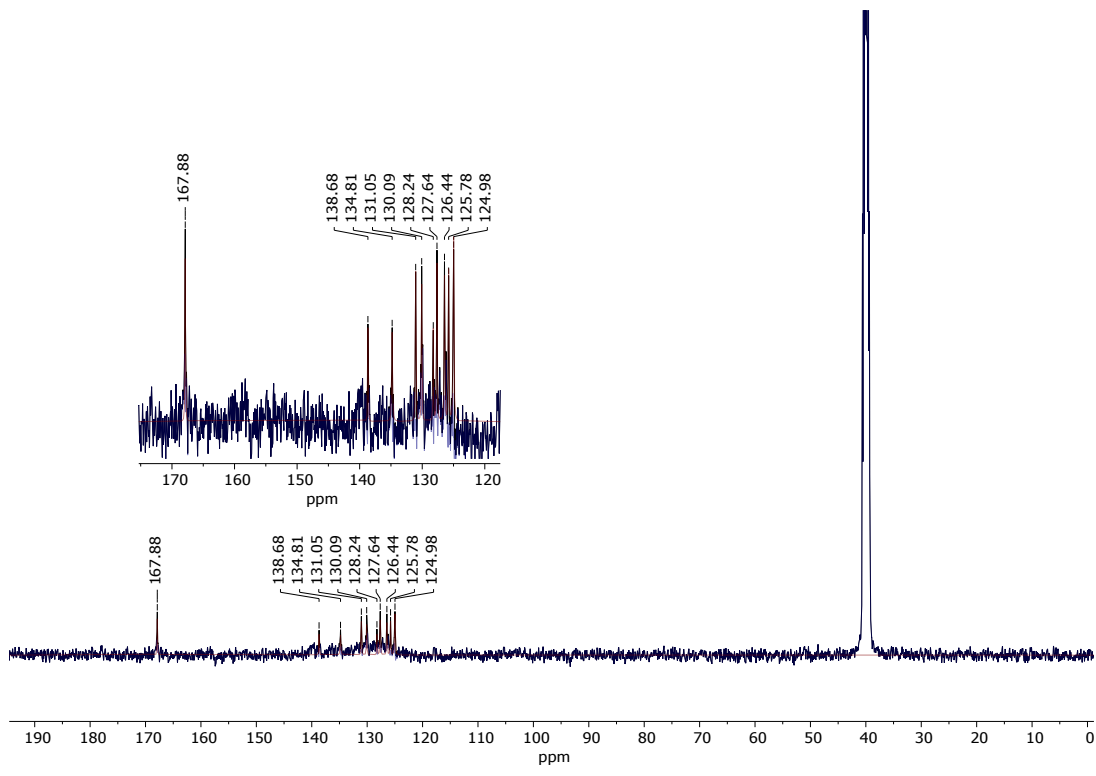
Compound **3b**

¹H NMR (300 MHz, CDCl₃)
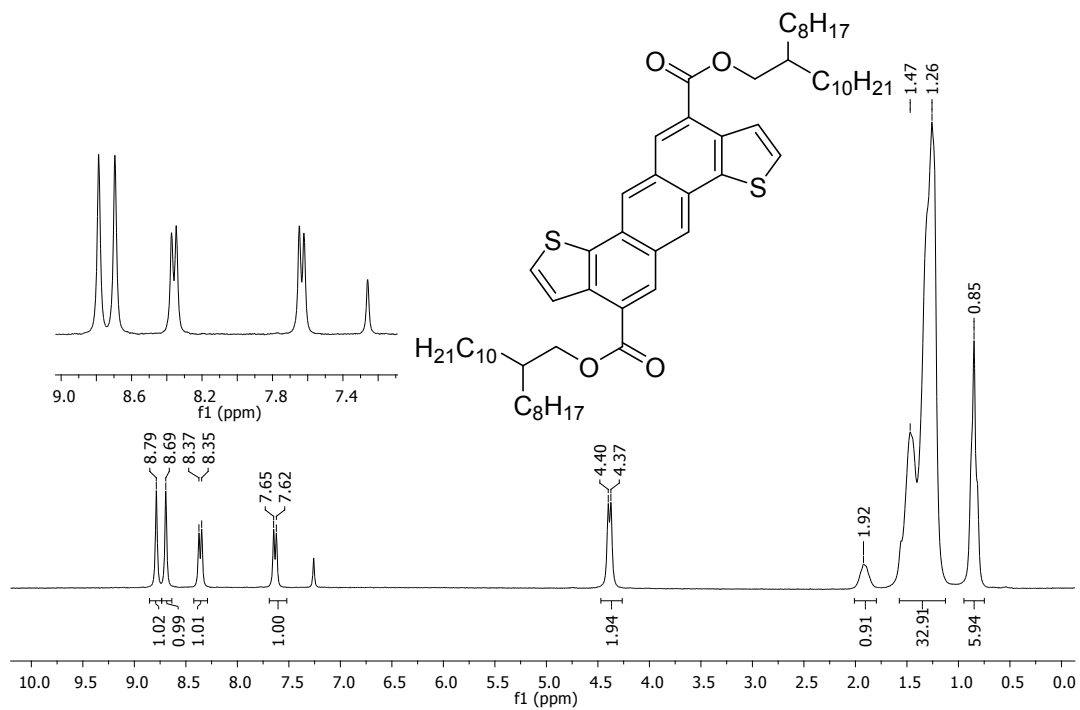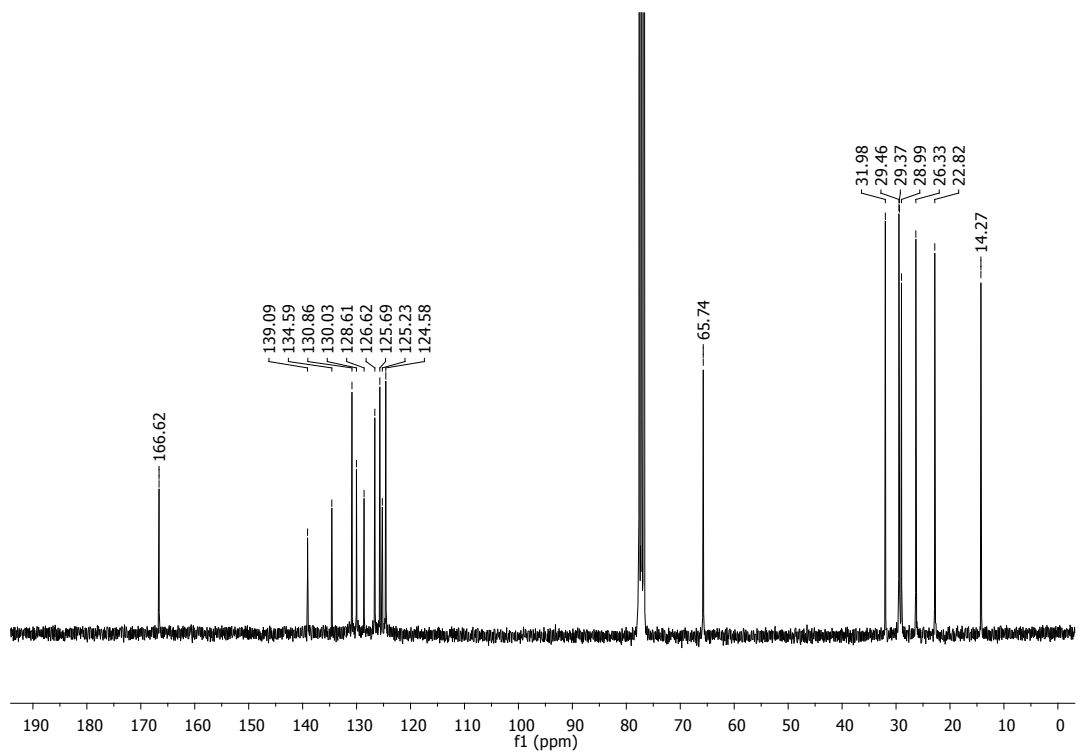
¹³C NMR (101 MHz, CDCl₃)

ESI-MS
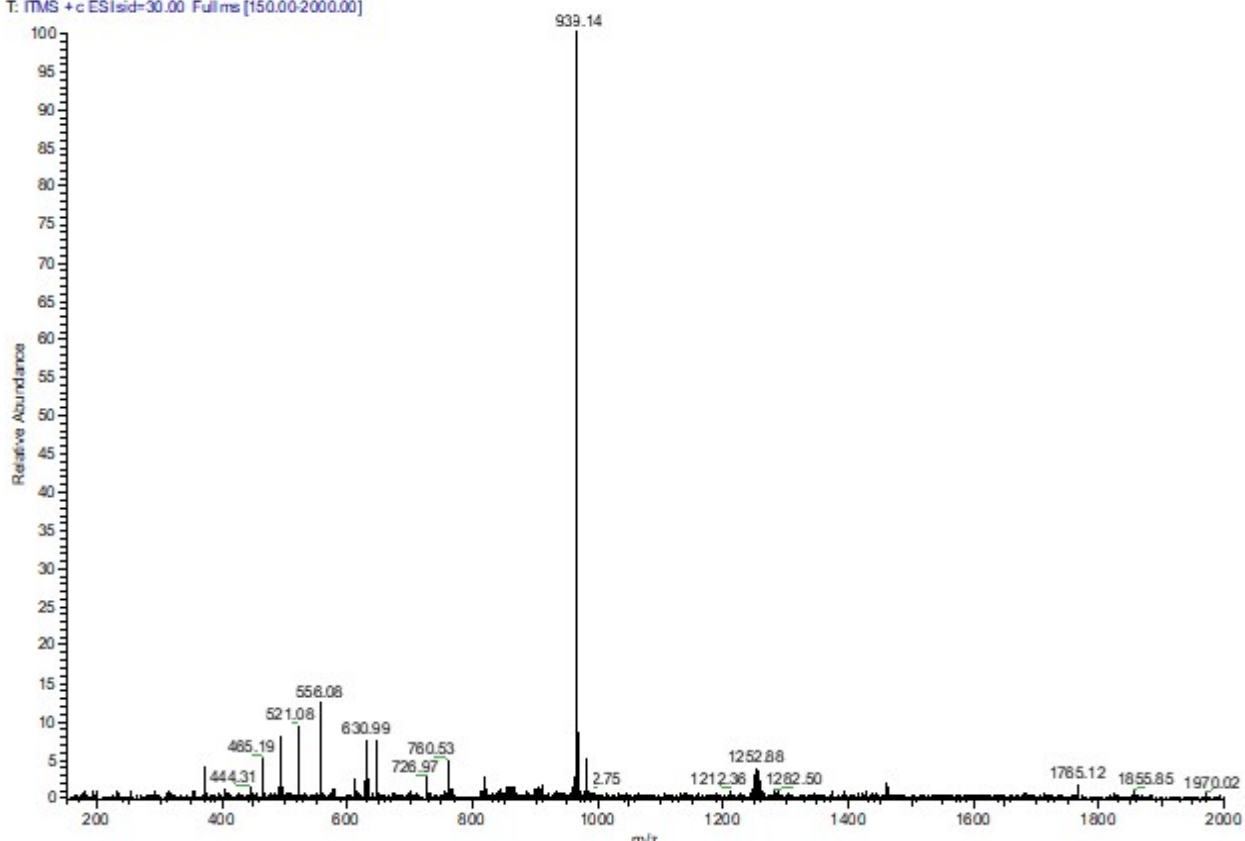
Compound **3c**

¹H NMR (300 MHz, CDCl₃)
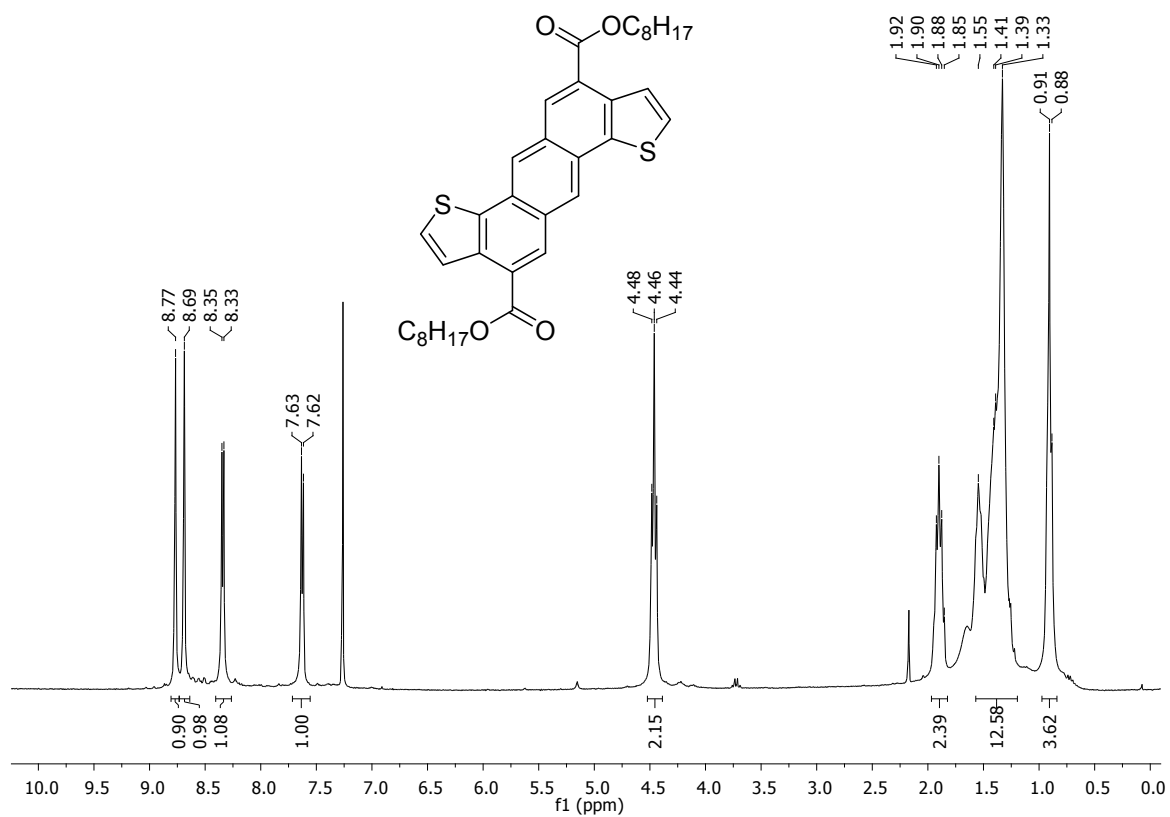
¹³C NMR (101 MHz, CDCl₃)
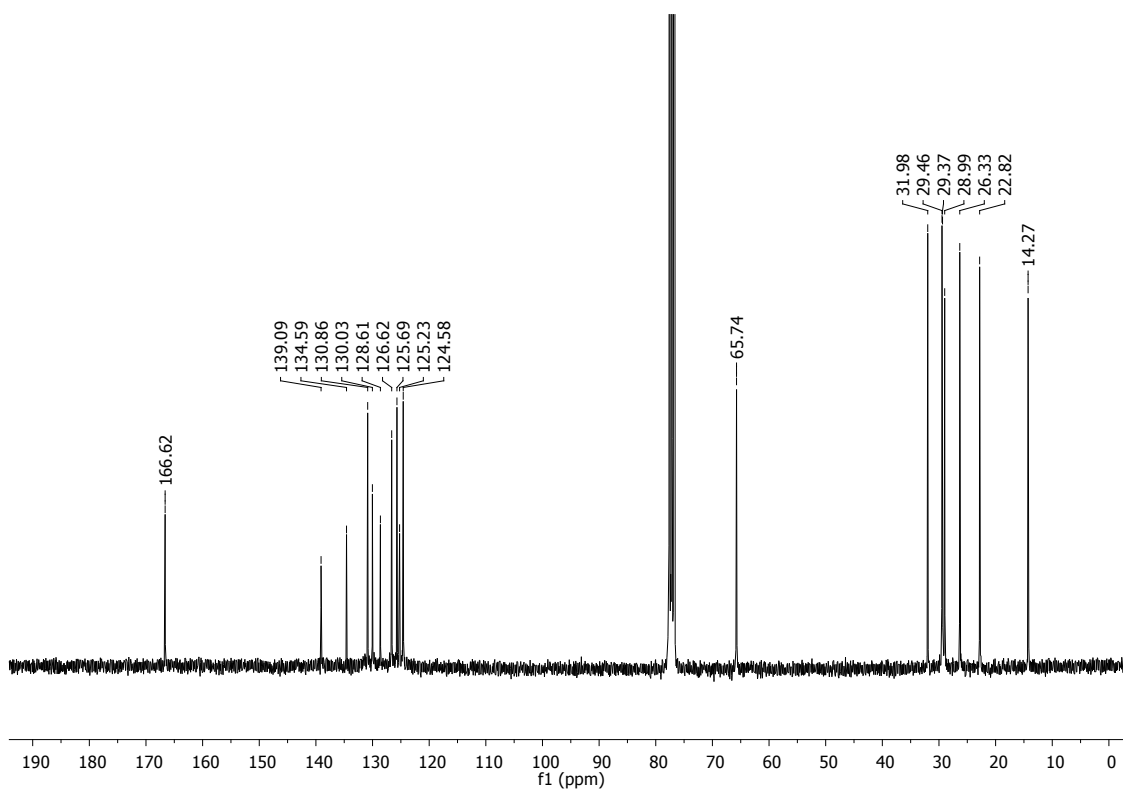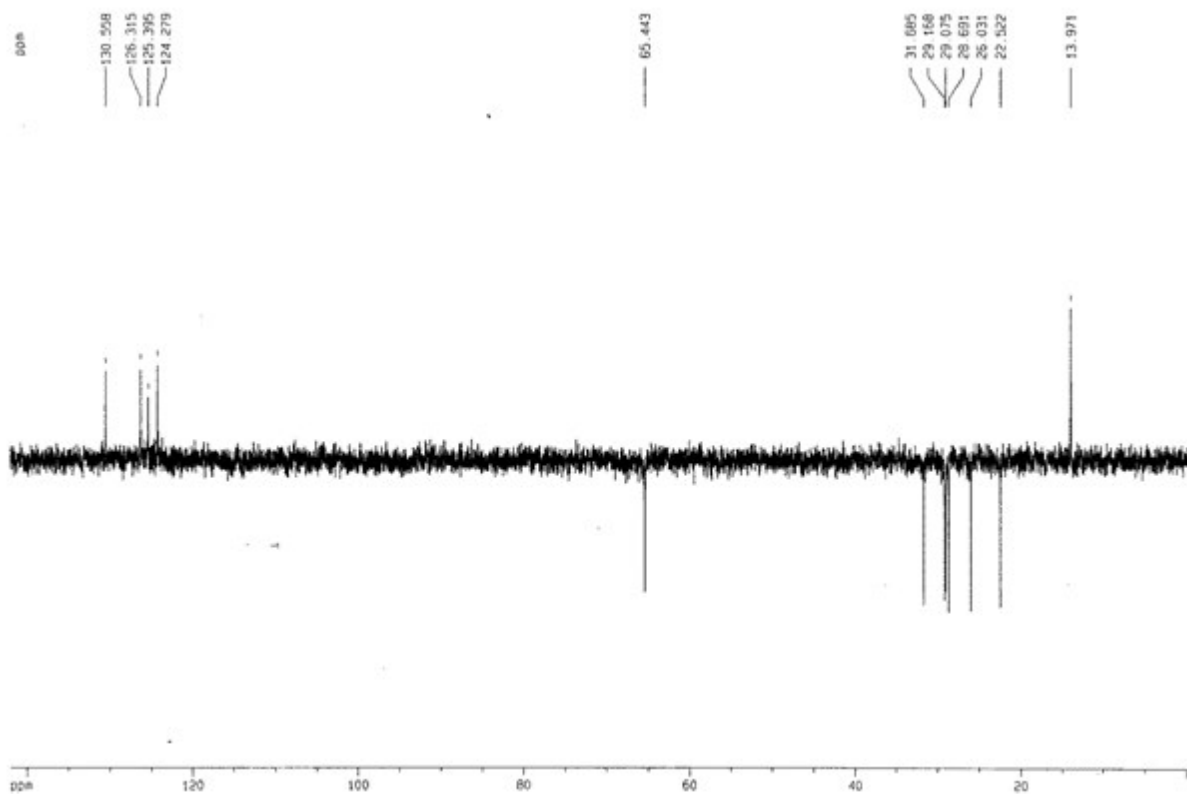
DEPT

DEP-MS

pasini20 #54 RT: 0.72 AV: 1 SB: 20 0.58-0.67 , 0.89-1.03 NL: 4.70E7
T: + c Full ms [50.00-1000.00]
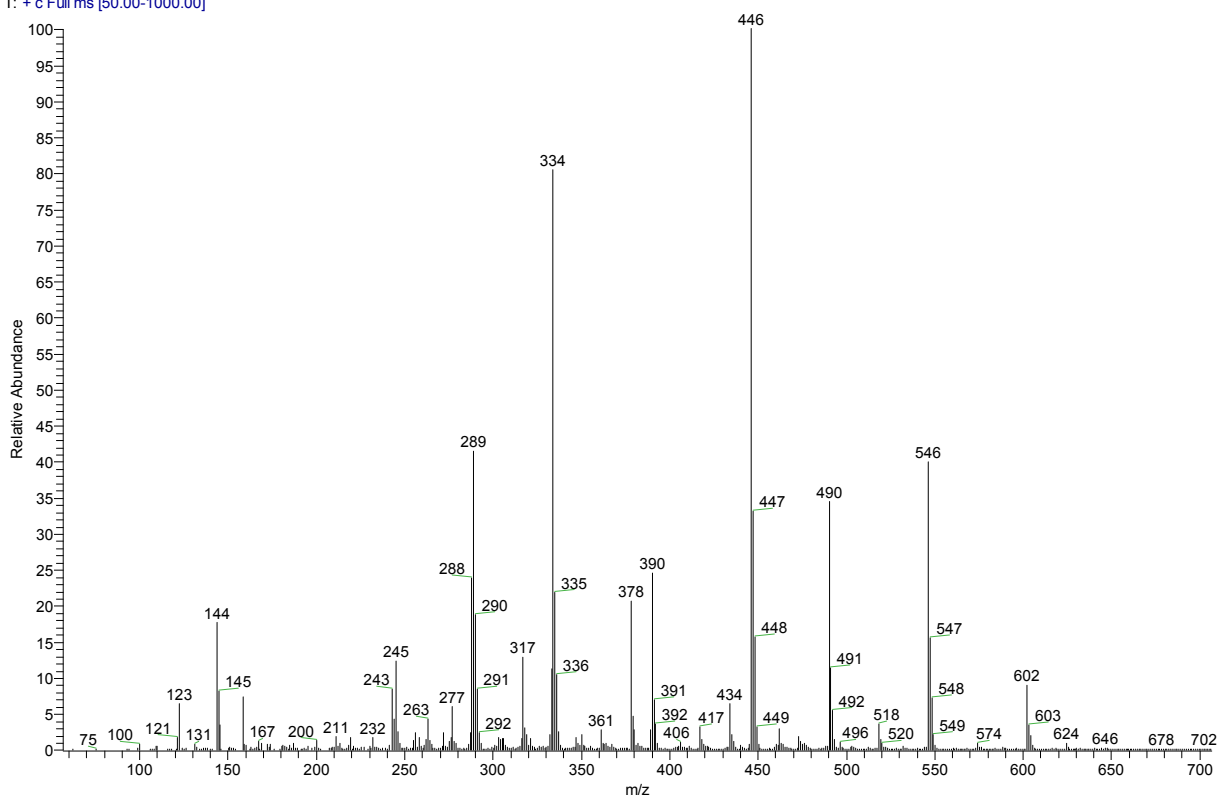
Compound **3d**

^{1}H NMR (300 MHz, CDCl₃)4

^{13}C NMR (101 MHz, CDCl₃)

DEPT
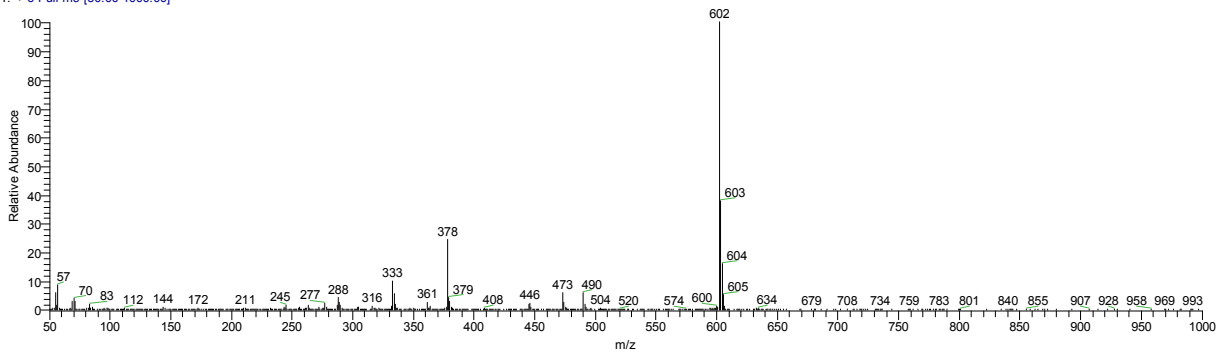
DEP-MS

Compound **4**

¹H NMR (300 MHz, CDCl₃)
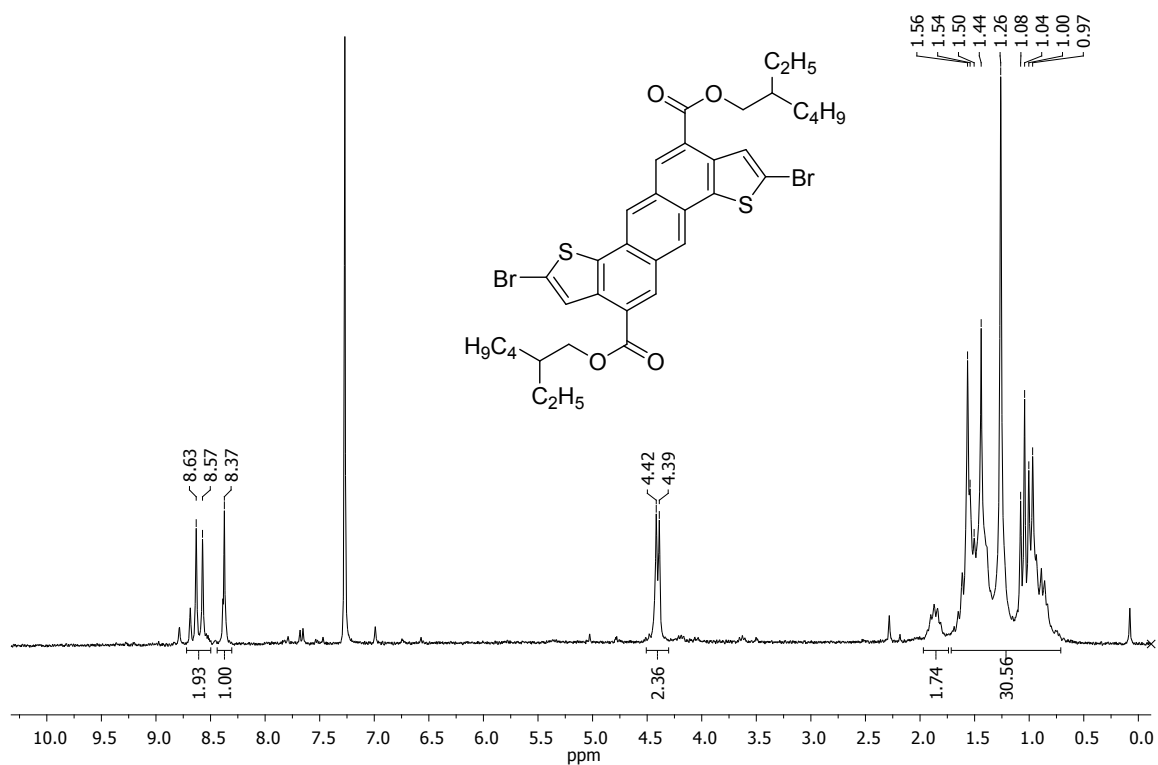
¹³C NMR (101 MHz, CDCl₃)
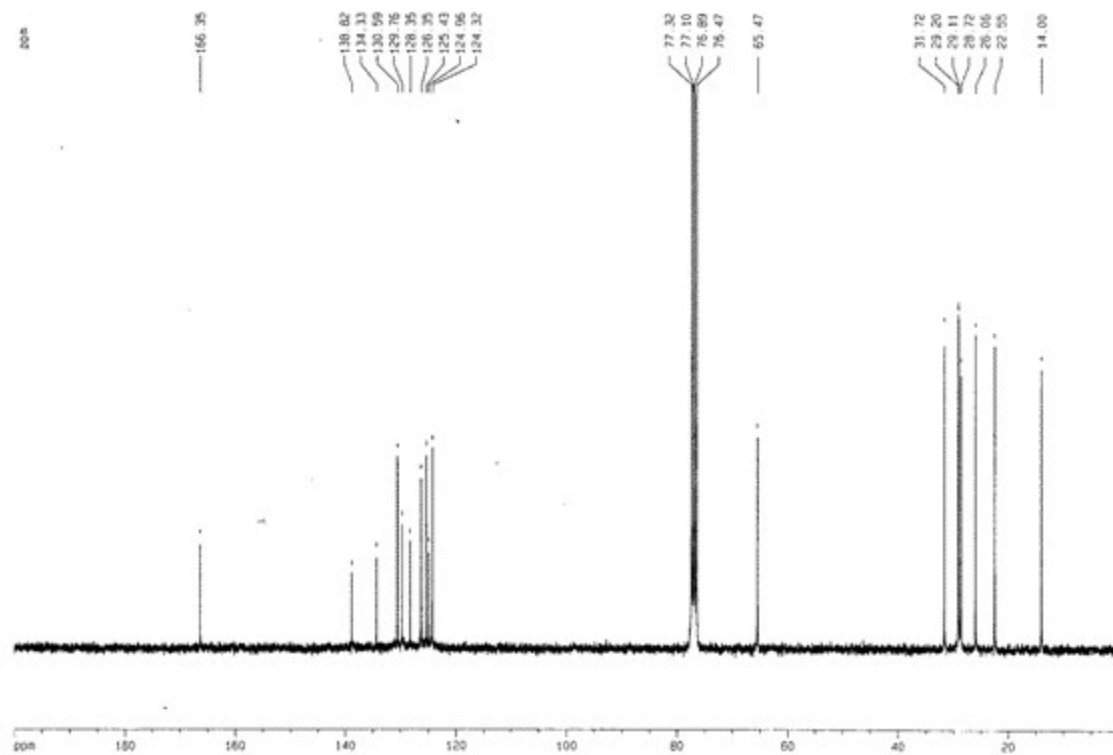
DEP-MS

RT: 0.00 - 2.82

NL:
3.29E8
TIC MS
pasini24_17
0607120158

pasini24_170607120158 #53 RT: 0.71 AV: 1 SB: 68 0.11-0.57 , 0.81-1.20 NL: 3.21E7
T: + c Full ms [50.00-1000.00]
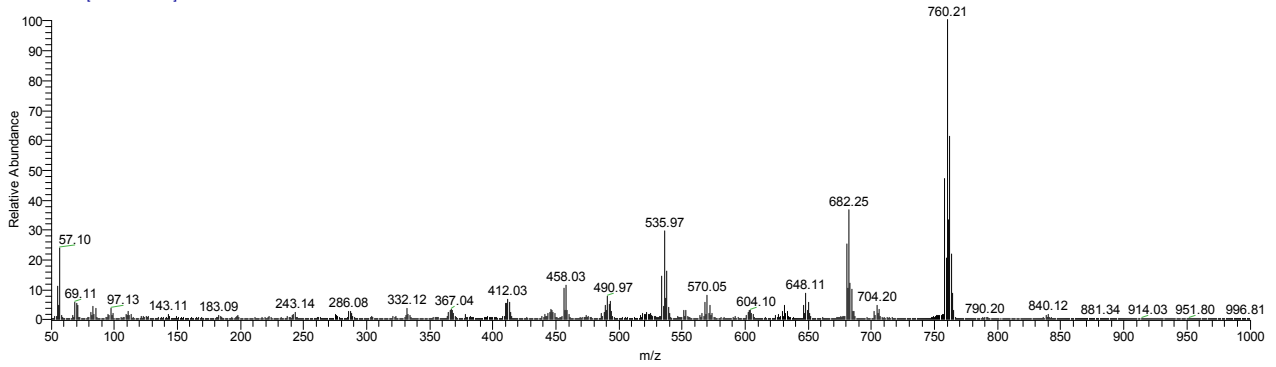
pasini24_170607120158 #53 RT: 0.71 AV: 1 SB: 80 0.20-0.66 , 0.80-1.34 NL: 3.21E7
T: + c Full ms [50.00-1000.00]

S30
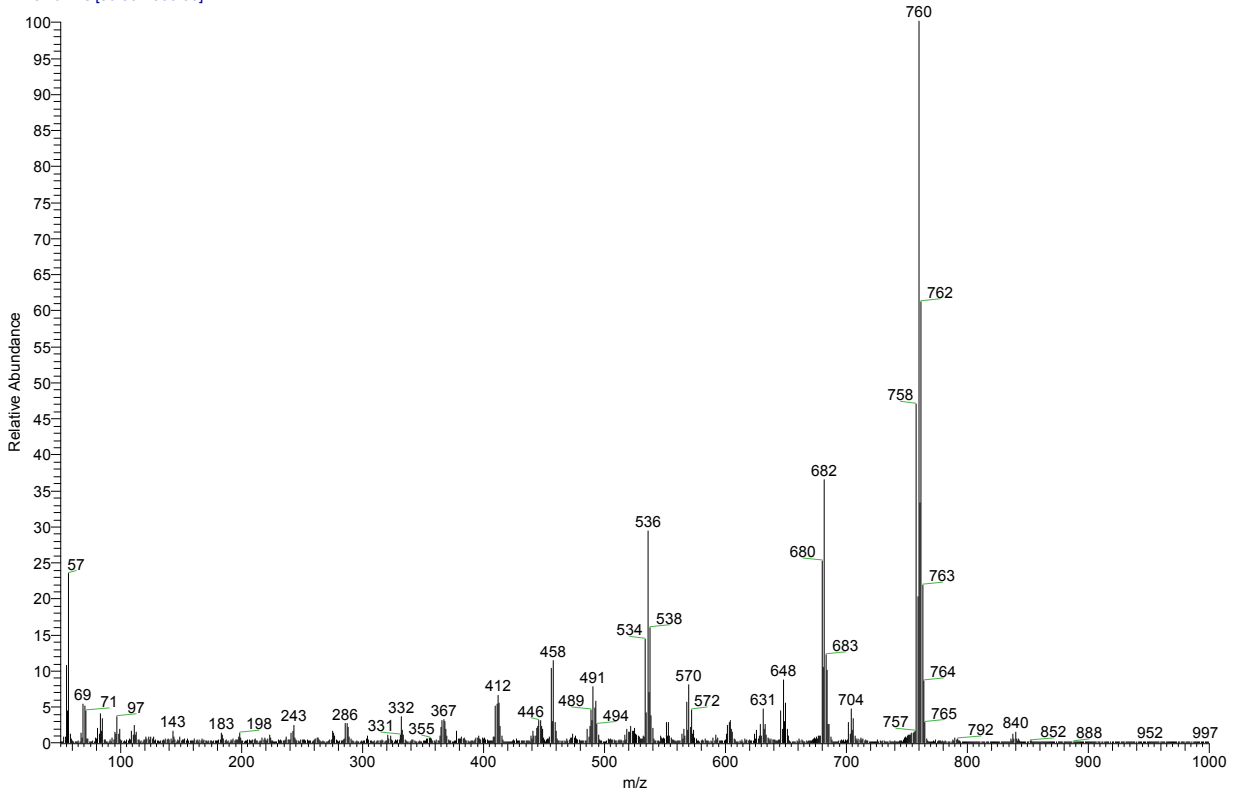
Compound **5**

¹H NMR (300 MHz, CDCl₃)
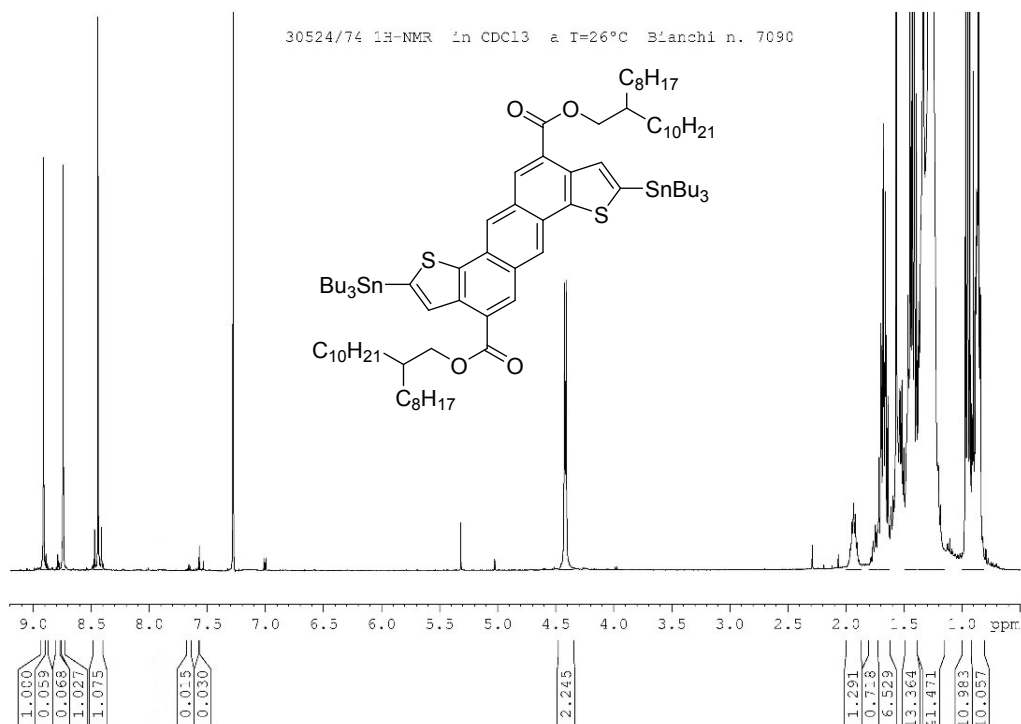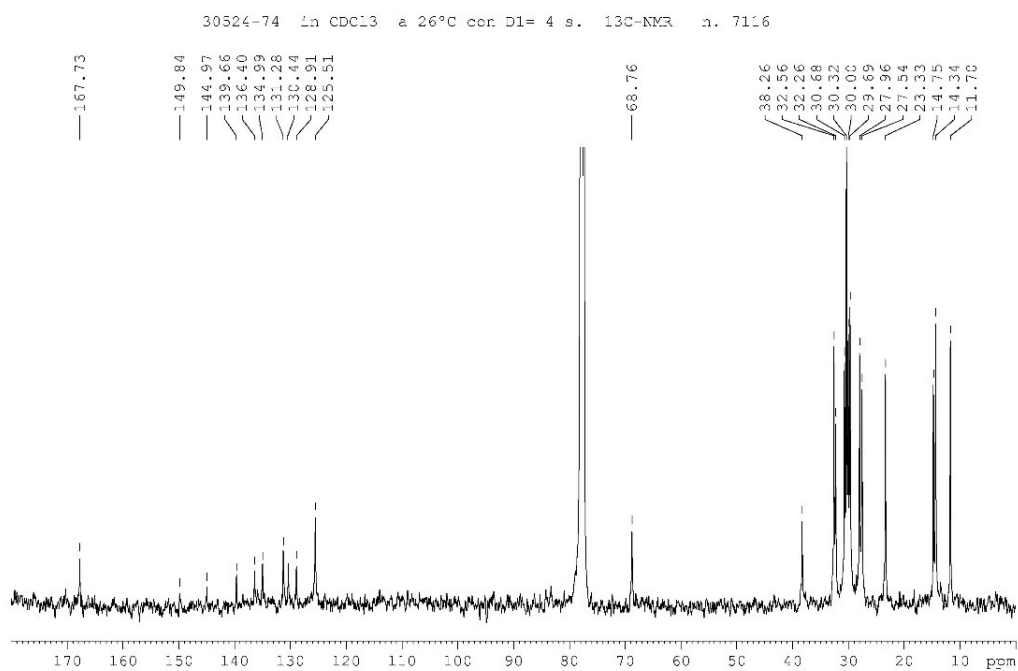
¹³C NMR (101 MHz, CDCl₃)

APCI FTICR MS

S32
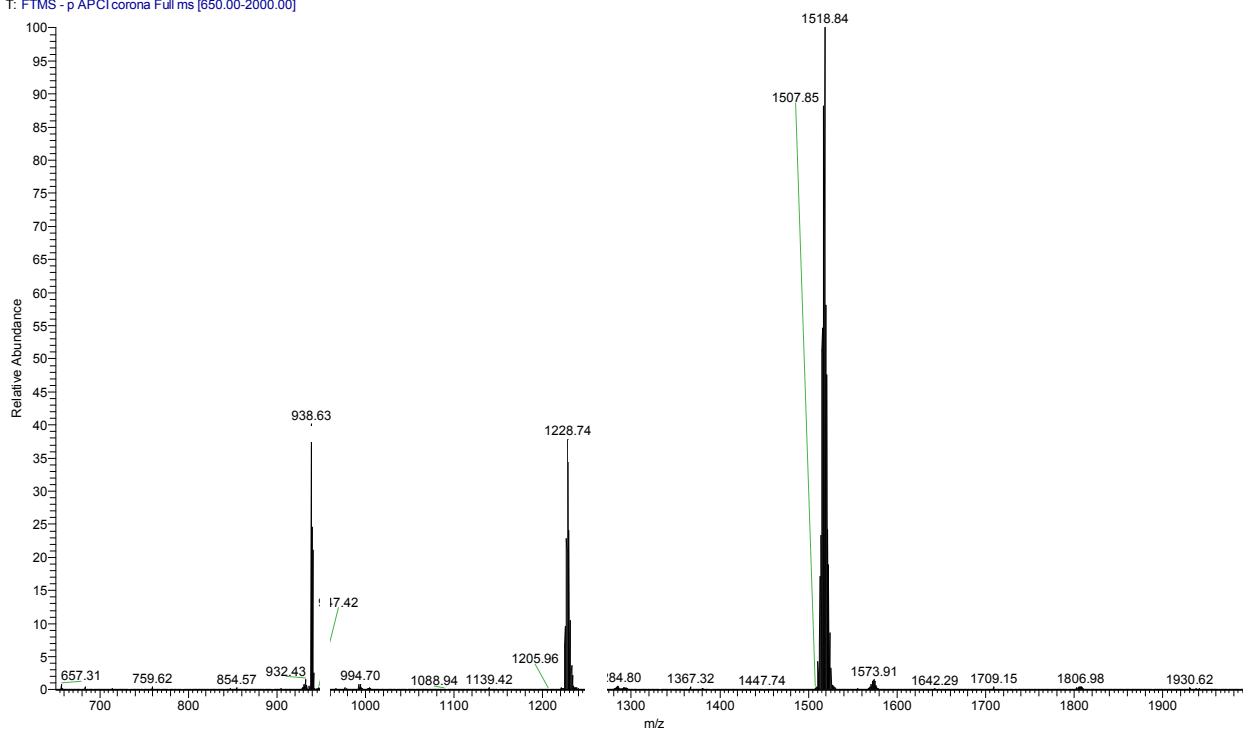
Compound **6**

¹H NMR (300 MHz, CDCl₃)
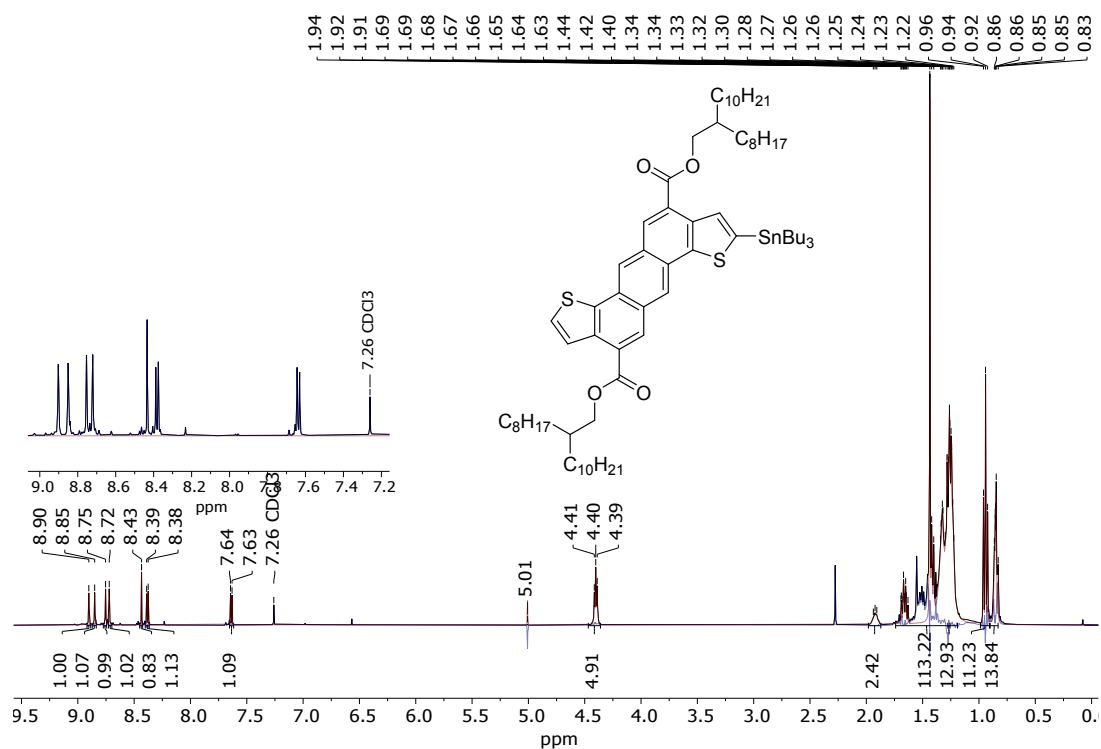
¹³C NMR (101 MHz, CDCl₃)
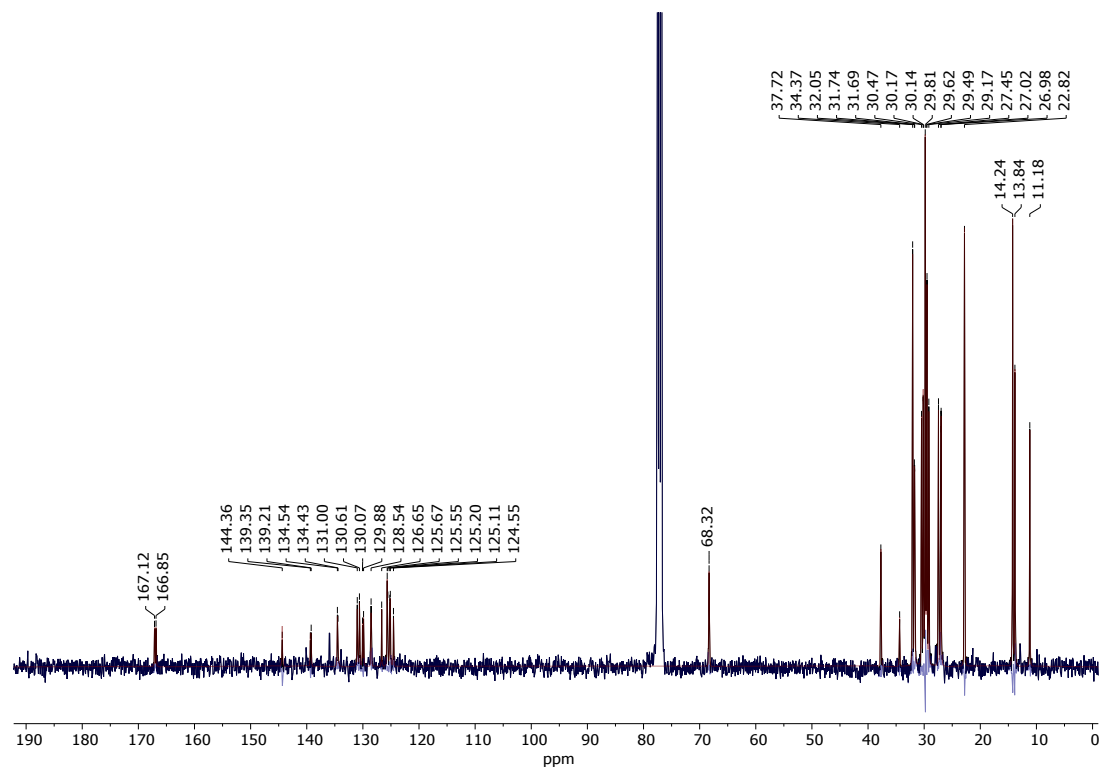
Compound 9

^{1}H NMR (400 MHz, CDCl3)
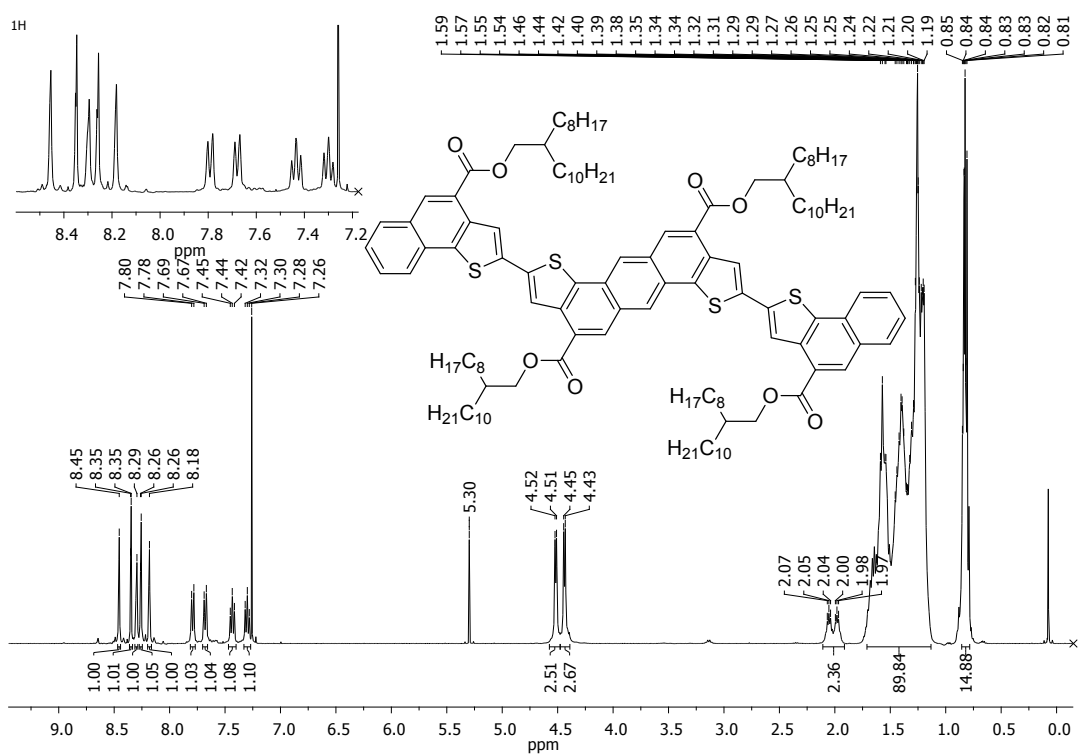
^{13}C NMR (400 MHz, CDCl3)

13C
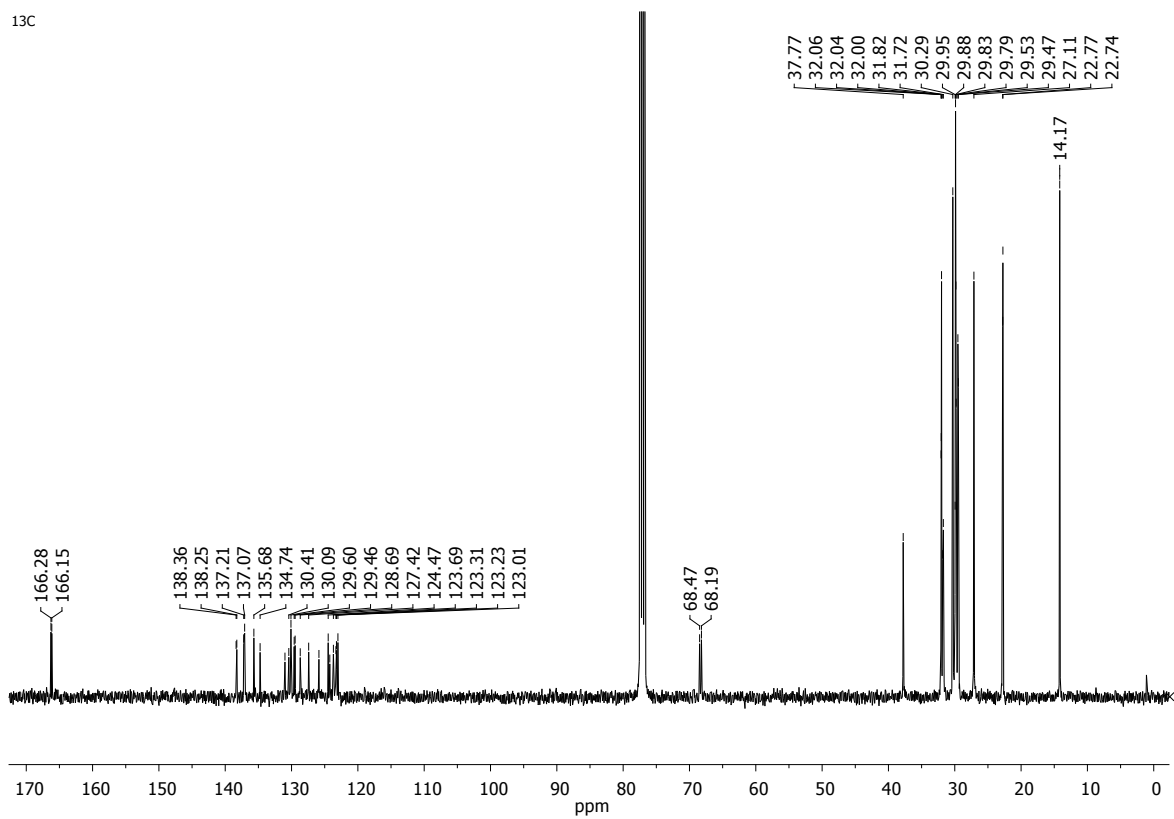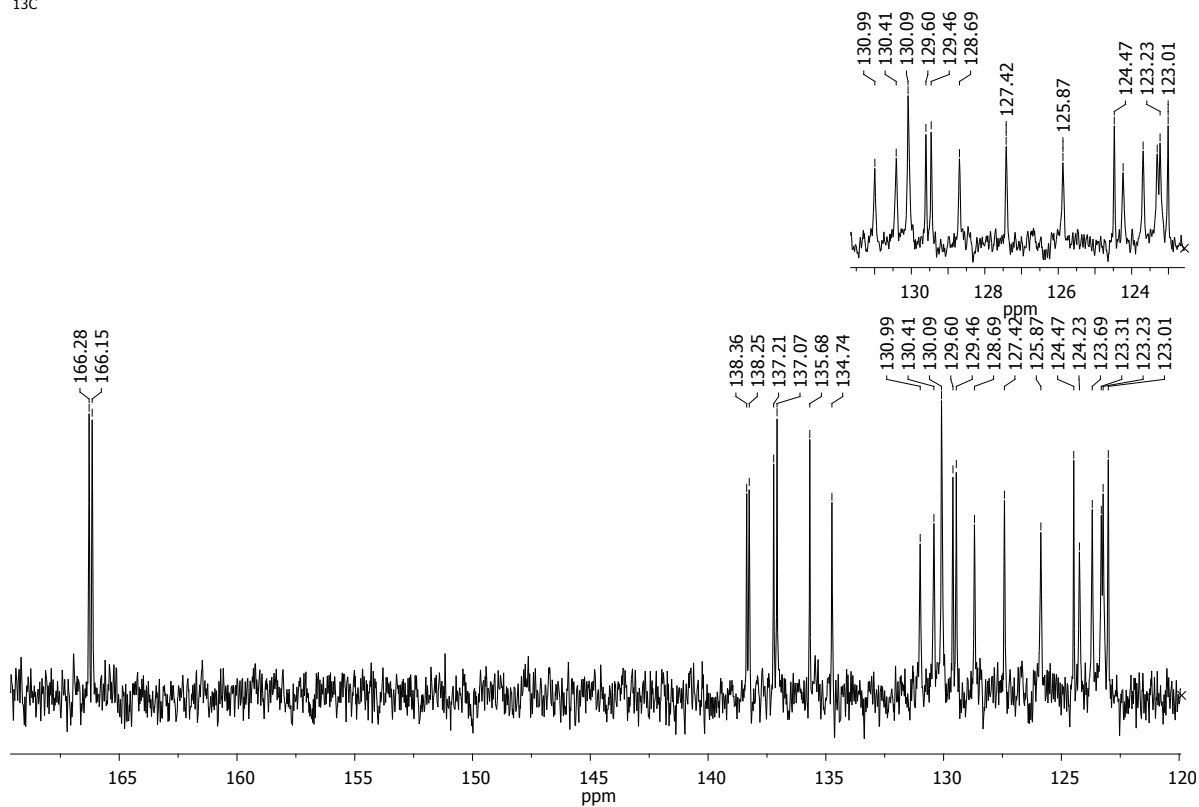
DEPT135deg

DEPT135deg

S35
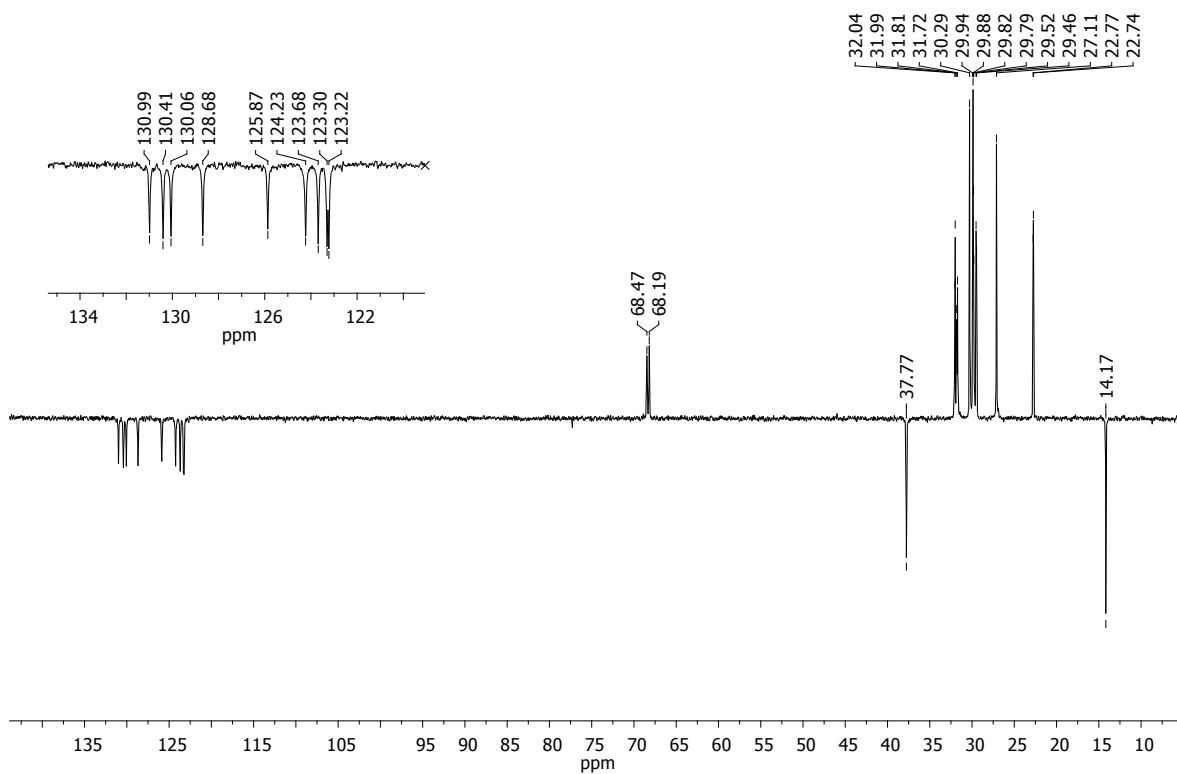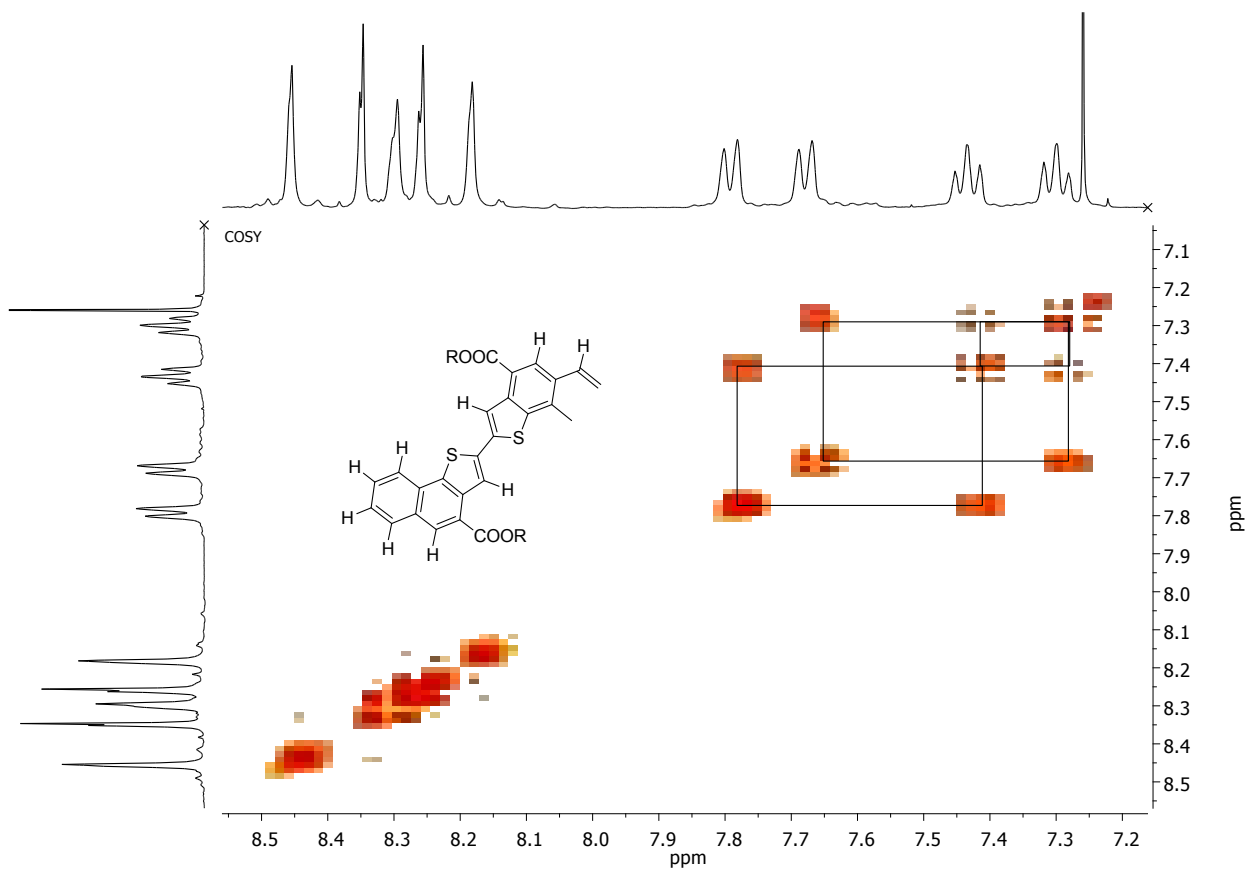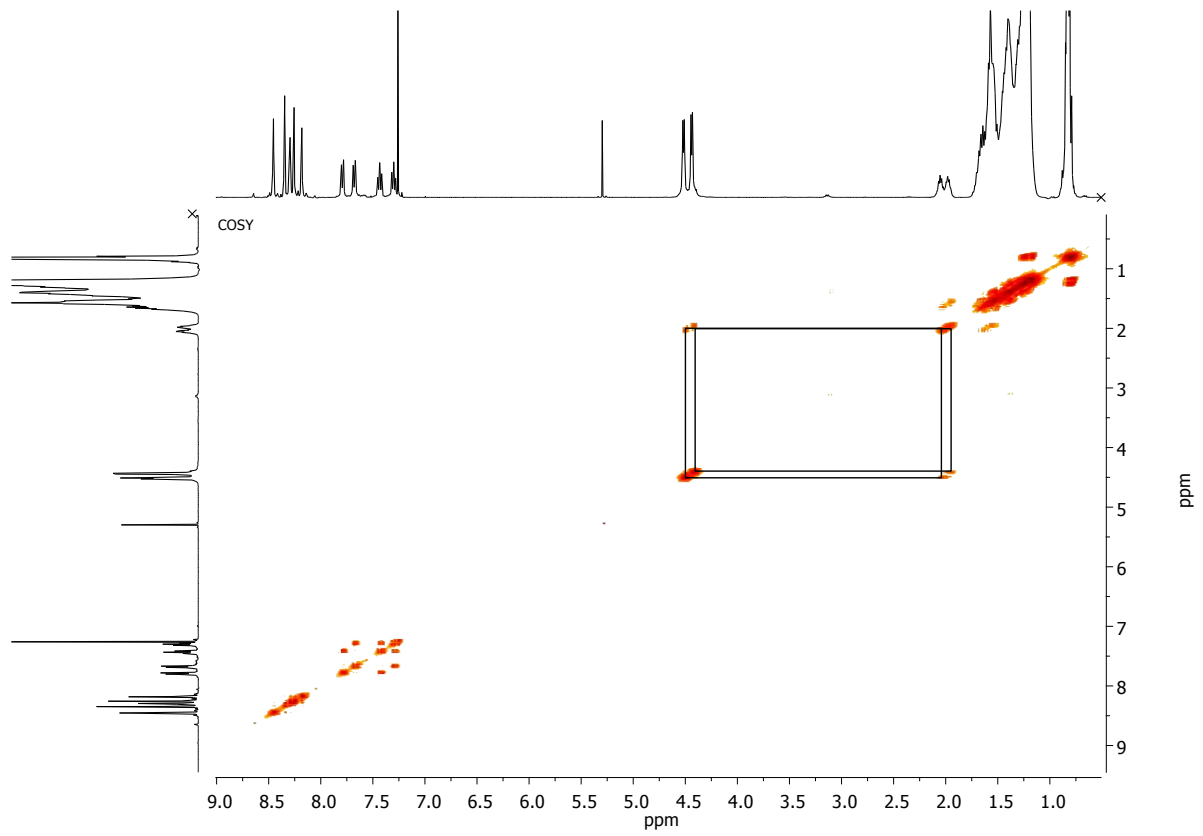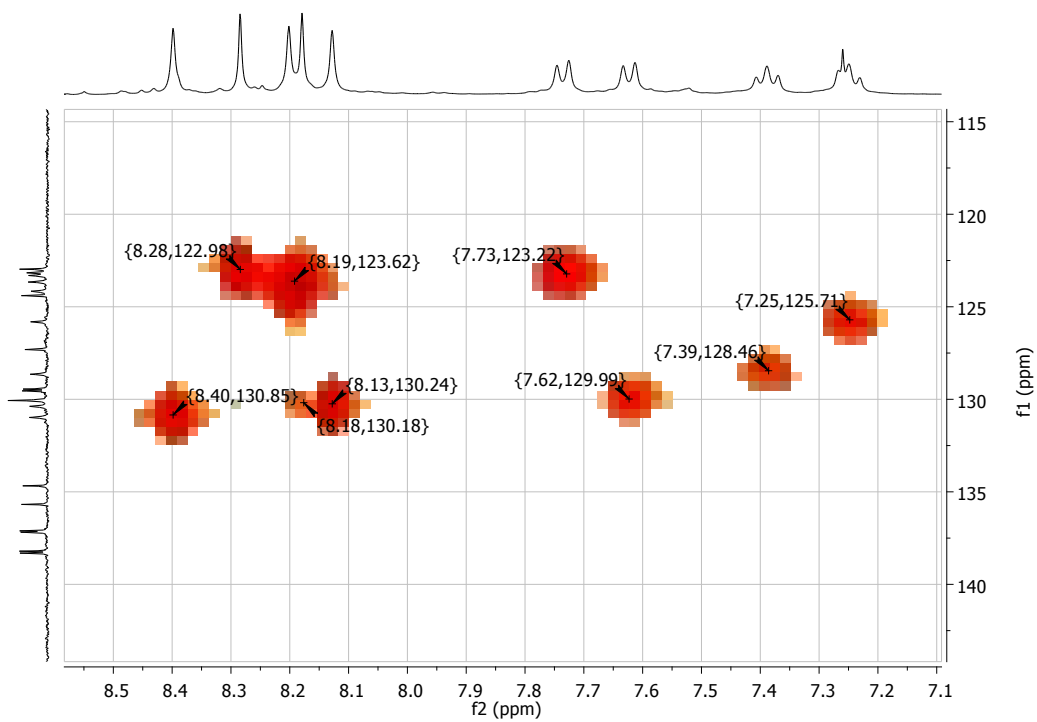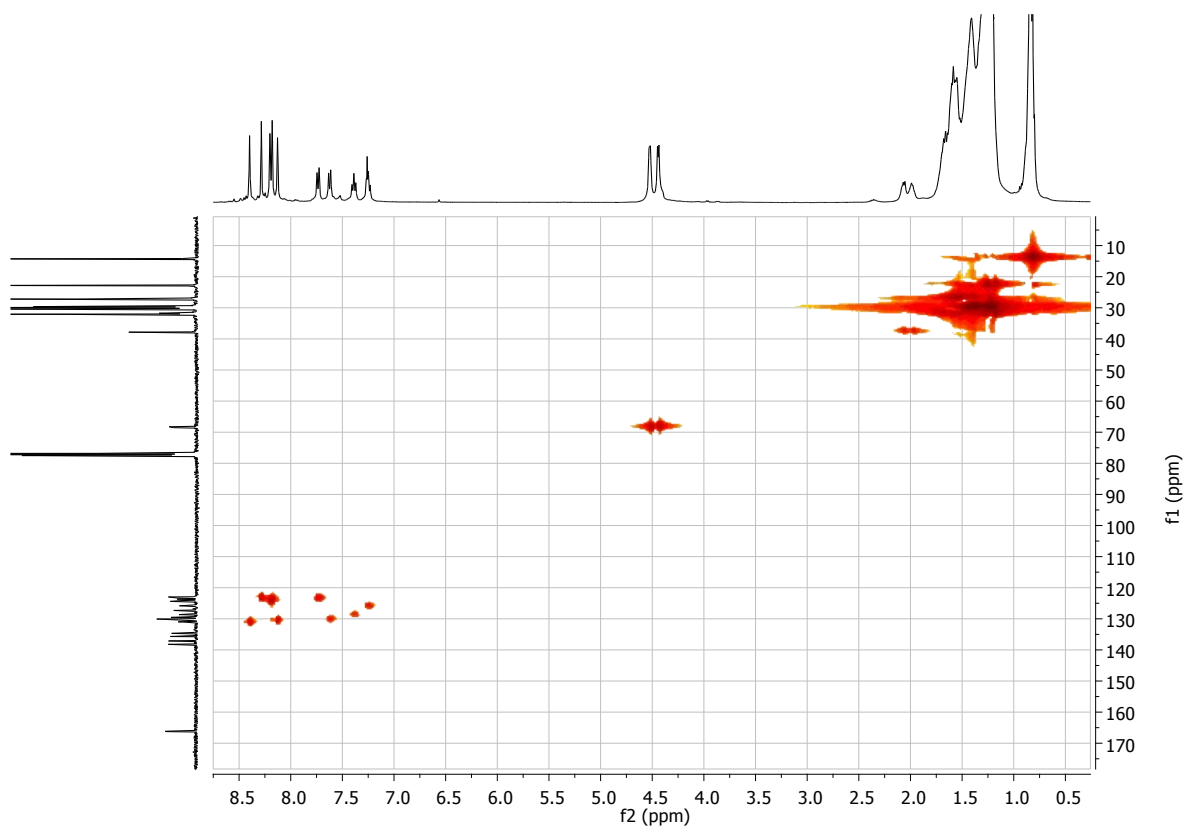
COSY

HMQC
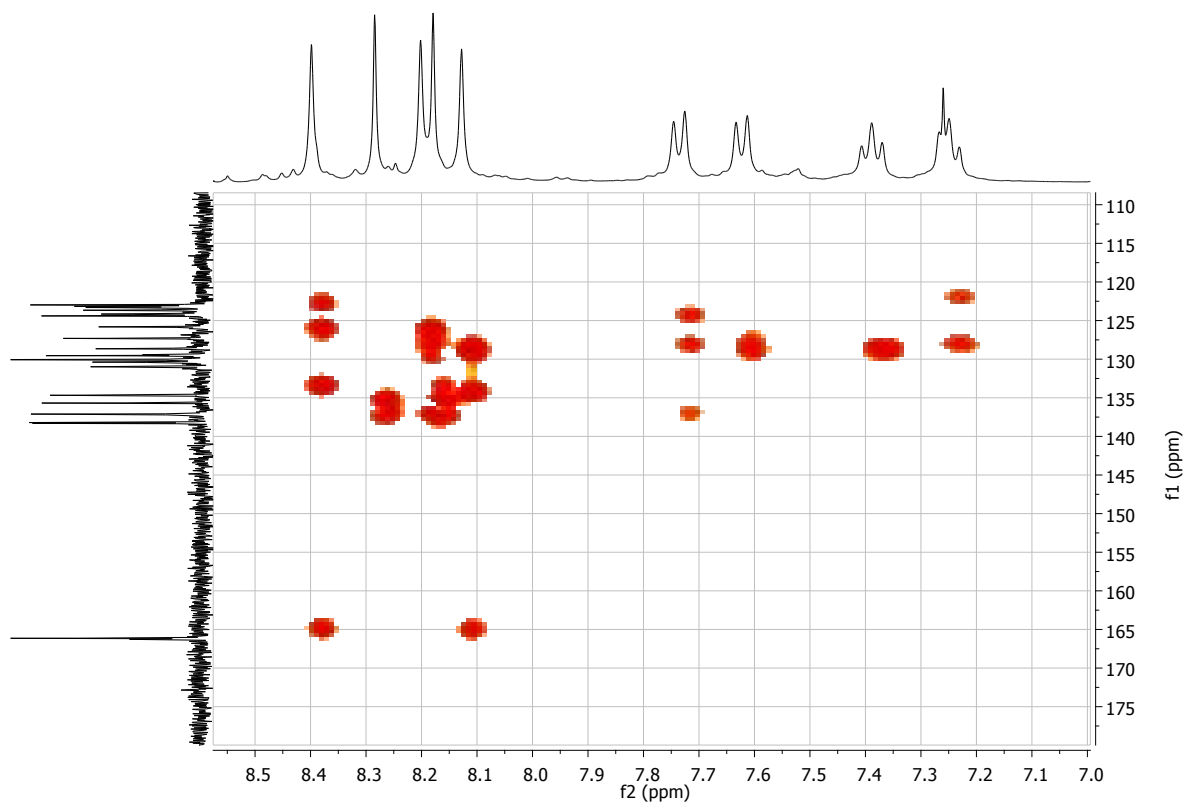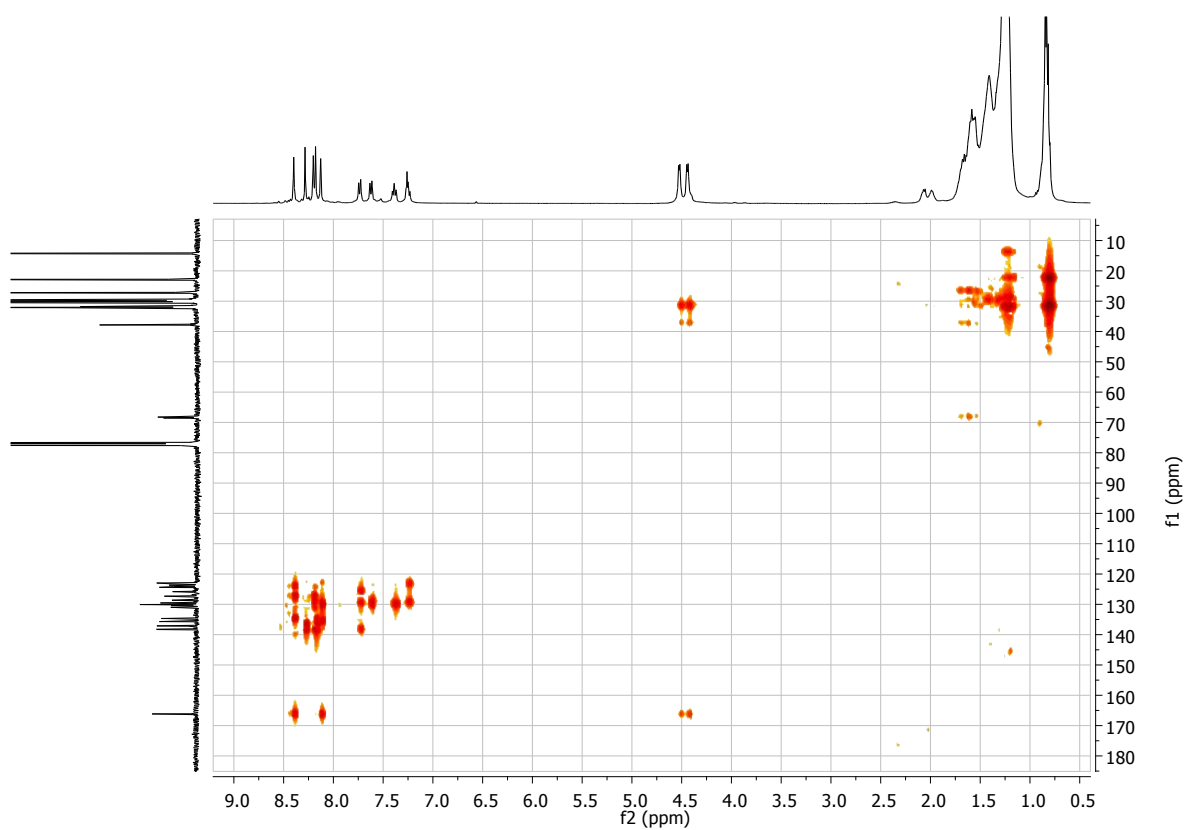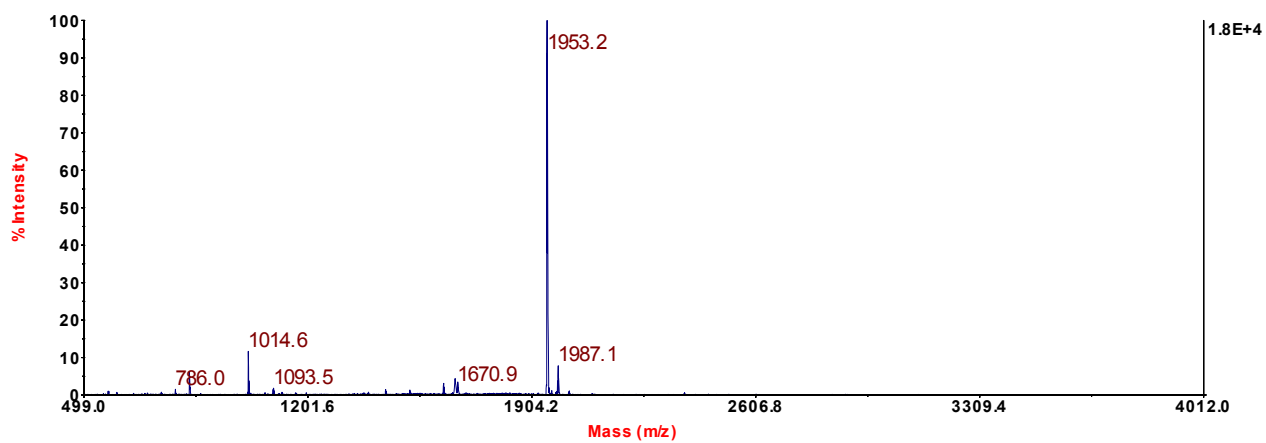
MALDI-TOF

Compound 10

¹H NMR (400 MHz, CDCl₃)

13C NMR (101 MHz, CDCl₃)

13C

165.73

138.39
133.98
133.26
130.74
130.50
129.05
126.48
126.39
124.35
124.07

68.58

37.79
37.58
32.14
31.67
31.50
30.46
30.27
30.02
29.90
29.67
29.56
29.54
29.47
27.11
26.92
22.85
14.25

220 200 180 160 140 120 100 80 60 40 20 0 -20
ppm

DEPT 135 deg

160 140 120 100 80 60 40 20 0
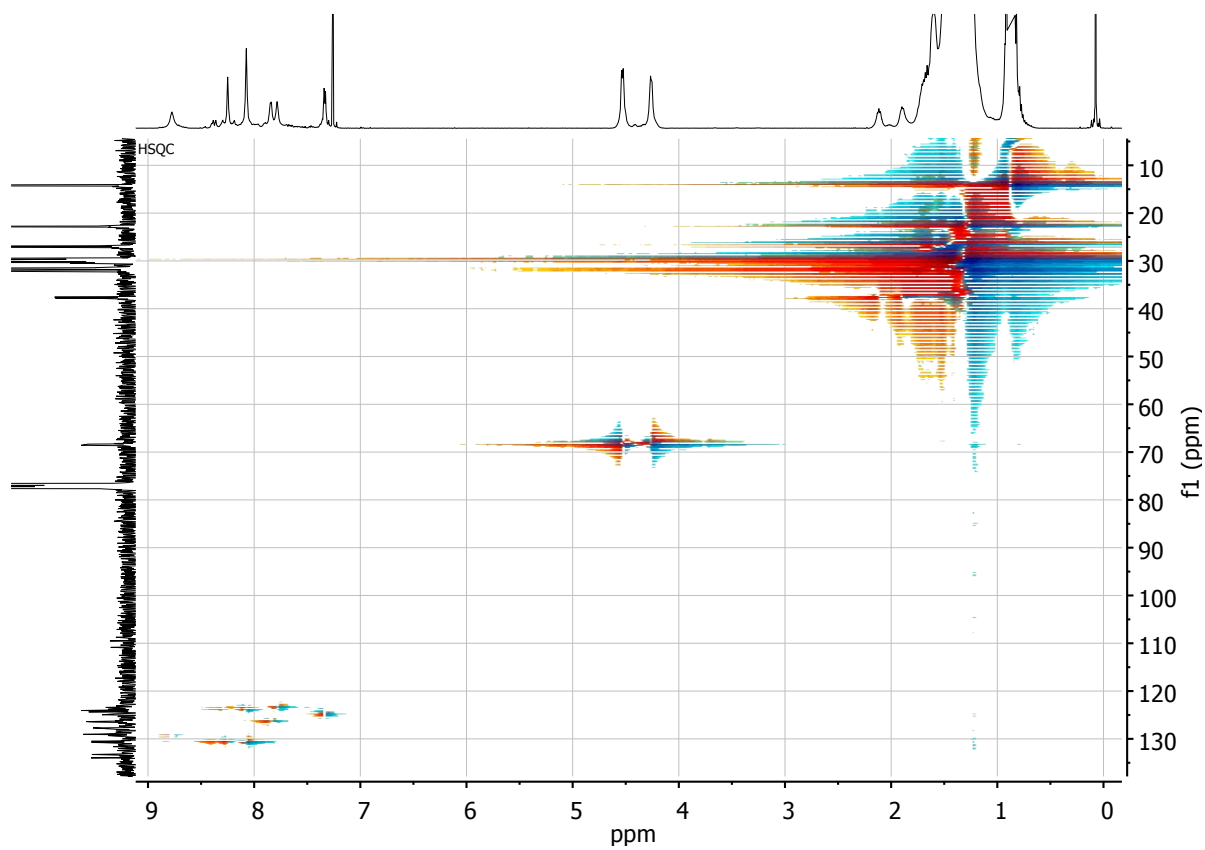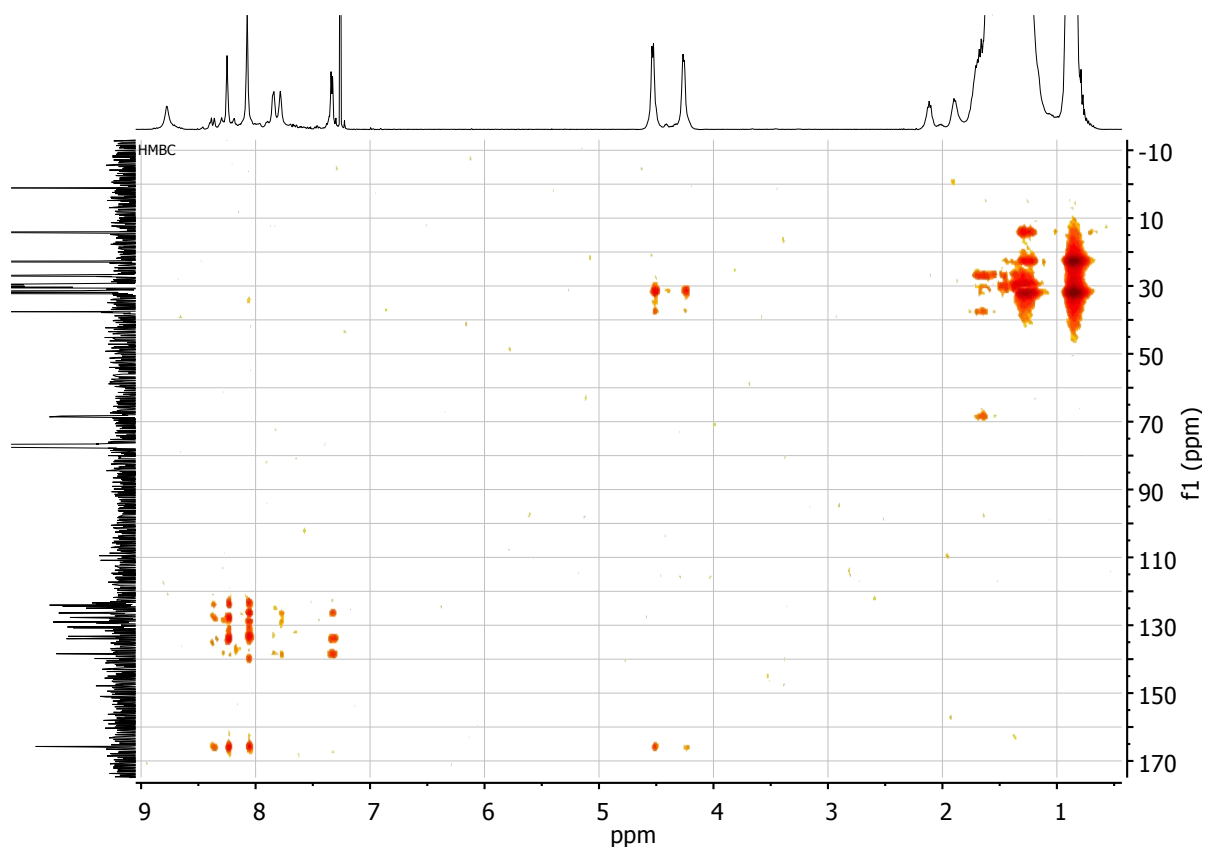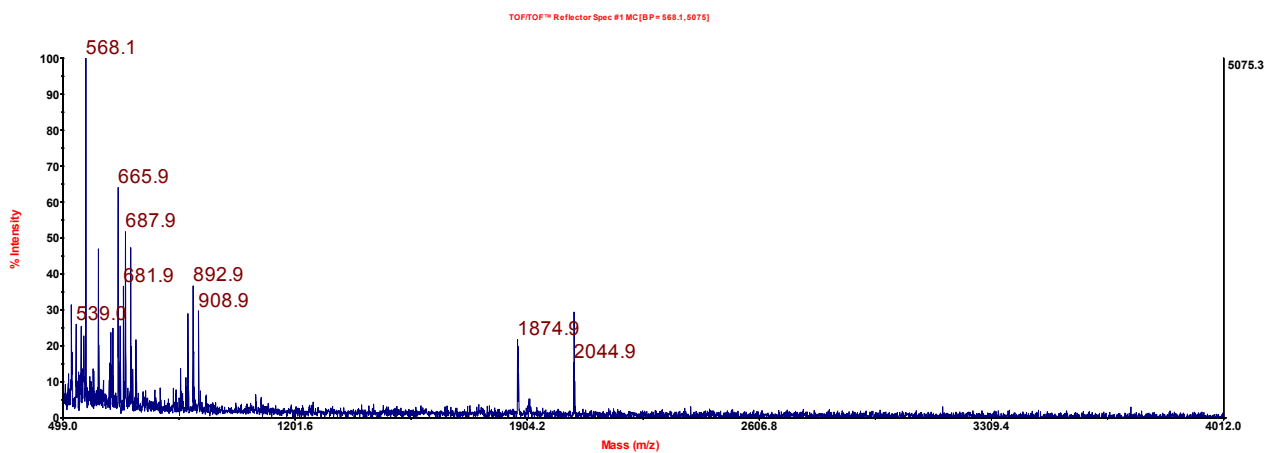ppm

COSY

HSQC

S42
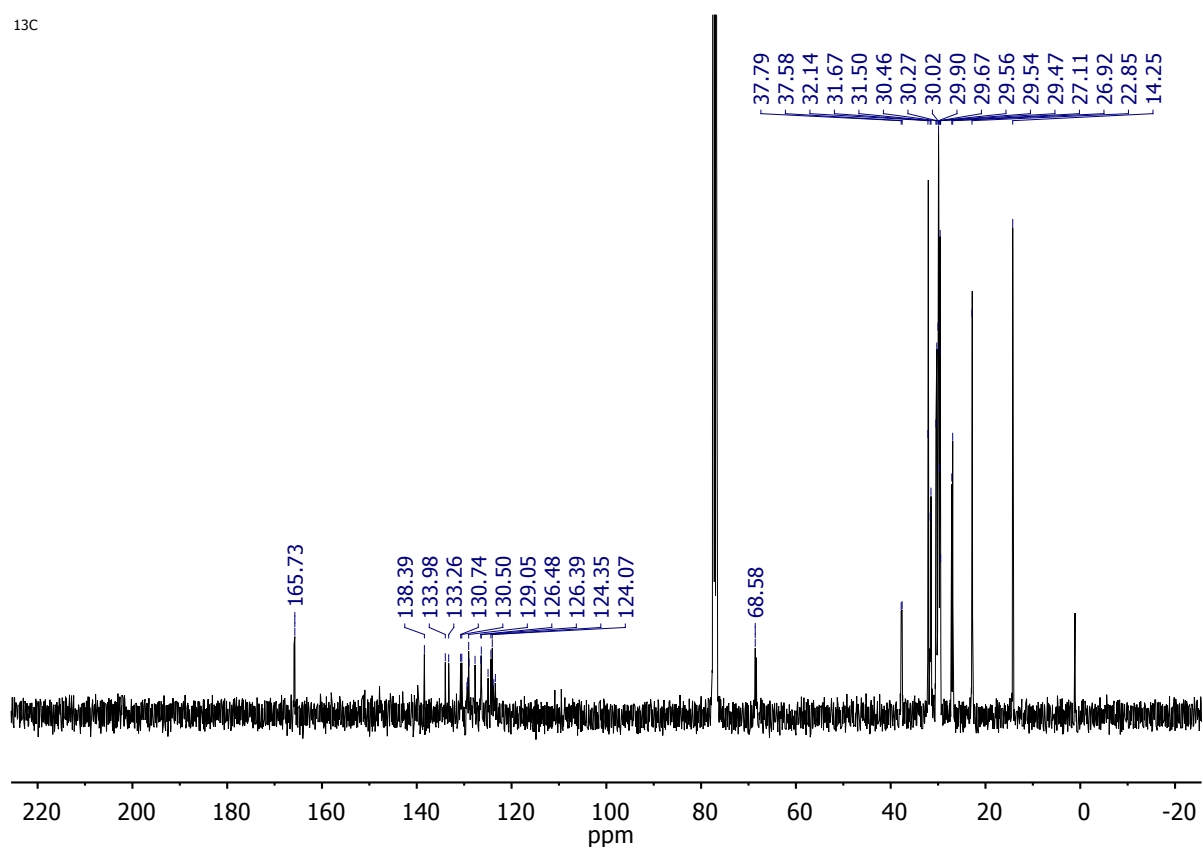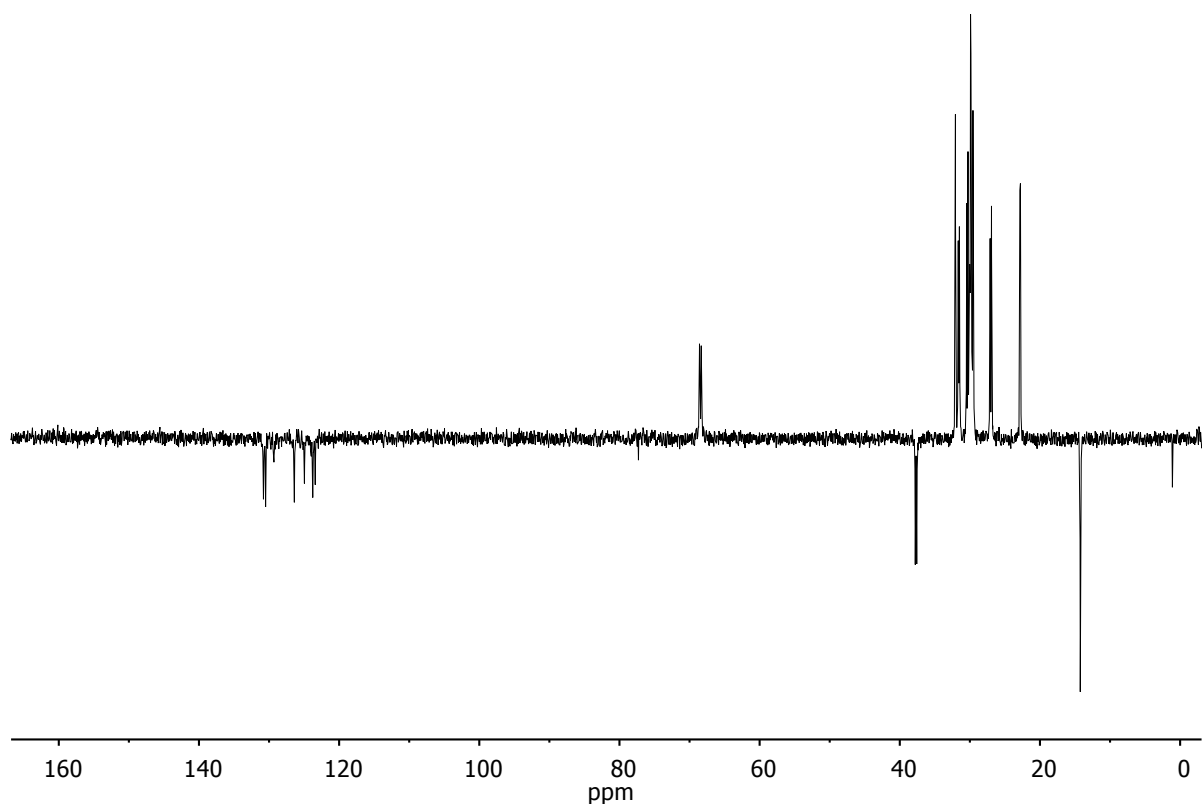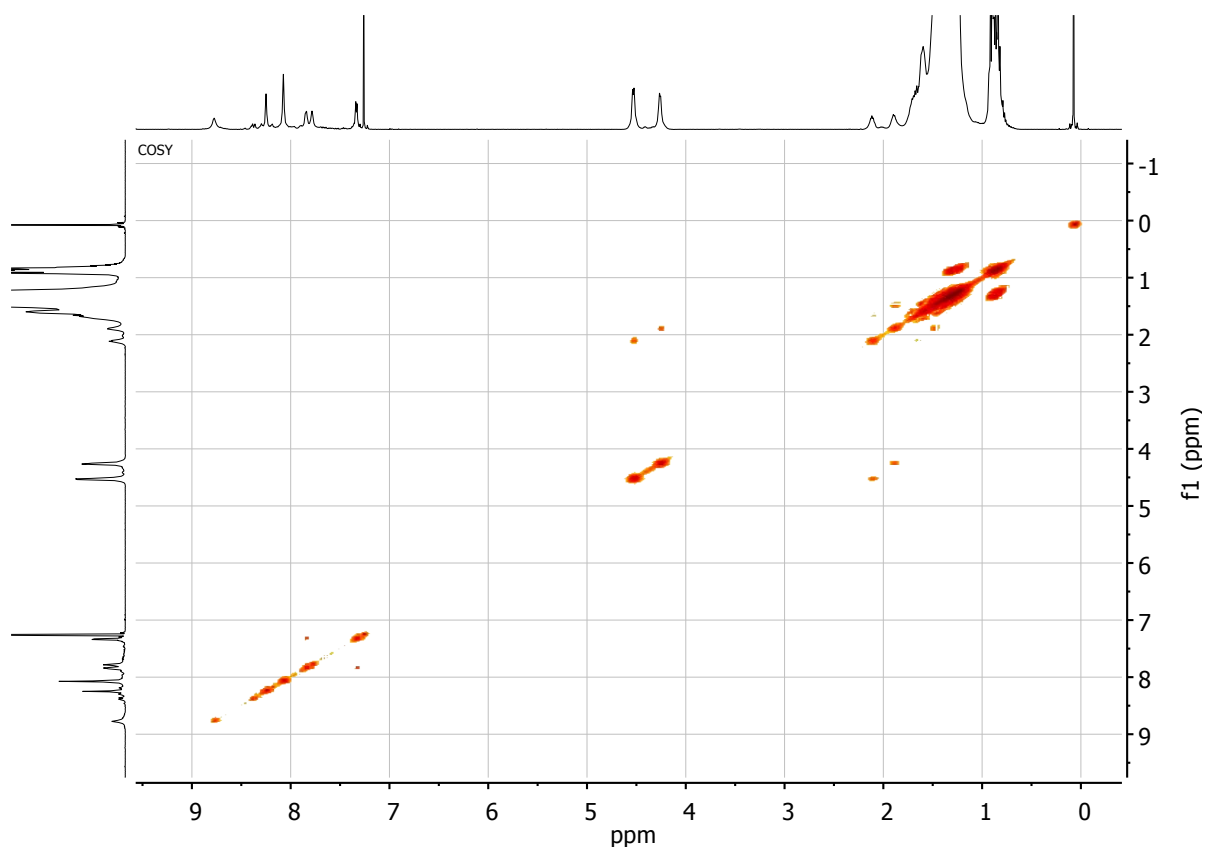
HMBC

MALDI-TOF

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