New Journal of Chemistry

Supporting Information

$FeCl_3$-Mediated Cyclization of Dithienyl Ethenes: Non-Photochemical Route to Simple Benzo[1,2-*b*:4,3-*b'*]dithiophenes

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1. General Methods

All reactions were run under inert atmosphere by means of standard Schlenk and vacuum-line techniques in flame-dried glassware. Commercial reagents were used as supplied. 1-(Thiophen-2-yl)butan-1-one was purchased from Aldrich. Anhydrous $FeCl_3$ (reagent grade, 97%) was purchased from Aldrich. Dry THF, DCM and DMF (Aldrich) were purchased. DCE was dried on $CaCl_2$. Solutions of *n*BuLi (1.6 M in hexane) were purchased and titrated prior to use. Thin layer chromatography (TLC) was performed on Merck precoated plates (silica gel 60 F254). The products were purified by flash chromatography on silica gel (Merck, Silica gel 60N, 230-400 mesh). Melting points were determined by a Büchi 510 apparatus and are uncorrected. ^{1}H NMR, ^{13}C NMR, HSQC NMR and HMBC NMR spectra were recorded at 25 °C in $CDCl_3$ (CD_2Cl_2 was used only for ^{1}H NMR of compound **2d**) by using a Bruker AMX 300. All ^{1}H NMR and ^{13}C NMR spectra are reported in parts per million (ppm), and referenced to the solvent peak at 7.26 ppm for proton and at 77.16 ppm for carbon in $CDCl_3$, or 5.32 ppm for proton in CD_2Cl_2. Infrared spectra (4000-400 cm^{-1}) were recorded with a Perkin–Elmer FT-IR 1725X spectrophotometer. High Resolution mass spectra were recorded on a Vg Analytical 7070 EQ spectrometer.

2. Experimental Procedures and Spectroscopic Data

(*Z*)-2,2'-(Oct-4-ene-4,5-diyl)dithiophene (1a).

To a solution of 1-(thiophen-2-yl)butan-1-one (24 mmol, 3.701 g) in dry THF (110 mL) at – 20 °C, $TiCl_4$ (5.4 mL, 28.7 mmol, 1.2 equiv) was added dropwise in 10 min. After 30 min at – 20 °C, Zn powder (3.90 g, 60 mmol, 2.5 equiv) was added in 3 portions in 10 min, and then the mixture was refluxed for 3 h. After this time, the mixture was cooled to room temperature, and ice-water (40 mL) along with an aqueous solution of HCl (1N, 40 mL) was added under vigorously stirring. THF was removed under reduced pressure, and the crude material was taken up with CH_2Cl_2 (50 mL). The aqueous phase was extracted into CH_2Cl_2 (4 × 20 mL), and the combined organic layers were dried on Na_2SO_4, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane) to give **1a** (2.45 g, 8.87 mmol, 74%) as yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.18 (m, 2 H), 6.90 (m, 2 H), 6.78 (m, 2 H), 2.60 (m, 4 H), 1.53 (m, 4 H), 1.02 (m, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 145.1, 133.0, 126.6, 126.4, 125.0, 37.7, 21.9, 14.2 ppm.

MS-EI: *m/z* (%) 276 (65, $[M]^+$), 247 (60), 97 (100).

HRMS-EI: *m/z* calcd for $C_{16}H_{20}S_2$ 276.0939, found 276.0948.

(*Z*)-5,5'-(Oct-4-ene-4,5-diyl)bis(2-bromothiophene) (1b).

To a solution of **1a** (0.200 g, 0.723 mmol) in dry DMF (2 mL) was added *N*-bromosuccinimide (0.270 g, 1.52 mmol, 2.1 equiv) at 0 °C. The mixture was stirred in the dark at 0 °C and the progress of the reaction was monitored by TLC (hexane). After 2 h, the mixture was quenched with water (10 mL), and the aqueous phase was extracted into CH_2Cl_2 (3 × 10 mL). The organic phase was washed with water, and dried with Na_2SO_4. The solvent was removed at reduced pressure, and the residue was purified by chromatography on silica gel (hexane) to give **1b** (0.201 g; 0.463 mmol, 64%) as pale yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 6.82 (d, J = 3.7 Hz, 2 H), 6.50 (d, J = 3.7 Hz, 2 H), 2.44 (m, 4 H), 1.44 (m, 4 H), 0.93 (t, J = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 145.9, 133.0, 129.4, 127.1, 111.8, 37.2, 21.7, 14.0 ppm.

MS-EI: *m/z* (%) 434 (100, $[M]^+$), 326 (52), 297 (18), 216 (20).

HRMS-EI: *m/z* calcd for $C_{16}H_{18}Br_2S_2$ 431.9217, found 431.9224.

(*Z*)-5,5'-(Oct-4-ene-4,5-diyl)bis(2-iodothiophene) (1c).
To a solution of **1a** (0.200 g, 0.723 mmol) in dry THF (5 mL) at − 78 °C was added dropwise a solution of *n*BuLi (1.6 M in hexane, 1.81 mL, 2.89 mmol, 4 equiv). The solution was stirred for 10 min at − 78 °C and 30 min at room temperature. The resulting yellow suspension was cooled to − 78 °C and a solution of I_2 (0.734 g, 2.89 mmol, 4 equiv) in dry THF (8 mL) was added dropwise. The mixture was stirred for 30 min at − 78 °C, and then warmed to room temperature. A saturated aqueous solution of $Na_2S_2O_3$ (20 mL) was added to quench the reaction, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (hexane) to give **1c** (0.332 g, 0.628 mmol, 87%) as a yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.00 (d, J = 3.7 Hz, 2 H), 6.40 (d, J = 3.7 Hz, 2 H), 2.44 (m, 4 H), 1.43 (m, 4 H), 0.93 (t, J = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 150.8, 136.6, 133.2, 128.5, 73.1, 37.5, 21.8, 14.1 ppm.

MS-EI: *m/z* (%) 528 (100, $[M]^+$), 402 (68), 372 (75), 246 (48), 203 (45), 171 (58).

HRMS-EI: *m/z* calcd for $C_{16}H_{18}I_2S_2$ 527.8939, found 527.8927.

(*Z*)-5,5'-(Oct-4-ene-4,5-diyl)bis(2-heptylthiophene) (1d).
To a solution of **1a** (0.200 g, 0.723 mmol) in dry THF (5 mL) at −78 °C was added dropwise a solution of *n*BuLi (1.6 M in hexane, 1.81 mL, 2.89 mmol, 4 equiv). The solution was stirred for 10 min at − 78 °C and 30 min at room temperature. The resulting yellow suspension was cooled to − 78 °C and treated with 1-bromoheptane (0.454 mL, 2.89 mmol, 4 equiv). The mixture was stirred for 30 min at − 78 °C, and then warmed to room temperature. After 4 h, the reaction was quenched with water (20 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to afford **1d** (0.175 g, 0.370 mmol, 51%) as yellow oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 6.51 (m, 4 H), 2.69 (m, 4 H), 2.46 (m, 4 H), 1.43 (m, 24 H), 0.91 (m, 12 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 145.5, 142.7, 132.6, 126.2, 123.4, 37.5, 32.1, 32.0, 31.8, 30.2, 29.9, 29.8, 29.5, 29.2, 29.1, 22.9, 22.1, 14.2 ppm.

MS-EI: *m/z* (%) 472 (100, $[M]^+$), 443 (15).

HRMS-EI: *m/z* calcd for $C_{30}H_{48}S_2$ 472.3197, found 472.3160.

(*Z*)-Diethyl 5,5'-(oct-4-ene-4,5-diyl)bis(thiophene-2-carboxylate) (1e).

To a solution of **1a** (0.200 g, 0.723 mmol) in dry THF (5 mL) at – 78 °C was added dropwise a solution of *n*BuLi (1.6 M in hexane, 1.81 mL, 2.89 mmol, 4 equiv). The solution was stirred for 10 min at – 78 °C and 30 min at room temperature. The resulting yellow suspension was cooled to – 78 °C, and treated with ethyl chloroformate (0.276 mL, 2.89 mmol, 4 equiv). The mixture was stirred for 30 min at – 78 °C and then warmed to room temperature. After 5 h, the reaction was quenched with water (20 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:AcOEt, gradient 100:0 to 90:10) to afford **1e** (0.230 g, 0.547 mmol, 76%) as a pale orange oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.50 (d, *J* = 3.7 Hz, 2 H), 6.62 (d, *J* = 3.7 Hz, 2 H), 4.30 (q, *J* = 7.1 Hz, 4 H), 2.50 (m, 4 H), 1.43 (m, 4 H), 1.34 (t, *J* = 7.1 Hz, 6 H), 0.94 (t, *J* = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 162.2, 151.8, 134.3 (2 C), 133.0, 127.7, 61.0, 37.6, 21.6, 14.3, 13.9 ppm.

IR (*neat*): 1707 (stretching C=O) cm^{-1}.

MS-EI: *m/z* (%) 420 (100, $[M]^+$), 391 (21), 375 (10), 318 (18).

HRMS-EI: *m/z* calcd for $C_{22}H_{28}O_4S_2$ 420.1429, found 420.1427.

(*Z*)-5,5'-(Oct-4-ene-4,5-diyl)bis(thiophene-2-carbaldehyde) (1f).

To a solution of **1a** (0.200 g, 0.723 mmol) in dry THF (5 mL) at – 78 °C was added dropwise a solution of *n*BuLi (1.6 M in hexane, 1.81 mL, 2.89 mmol, 4 equiv). The solution was stirred for 10 min at – 78 °C and 30 min at room temperature. The resulting yellow suspension was cooled to – 78 °C, and treated with DMF (0.223 mL, 2.89 mmol, 4 equiv). The mixture was stirred for 30 min at – 78 °C, and then warmed to room temperature. After 5 h, the reaction was quenched with water (20 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with water, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane:AcOEt, gradient 100:0 to 80:20) to afford **1f** (0.220 g, 0.662 mmol, 84%) as an orange oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 9.78 (s, 2 H), 7.49 (d, *J* = 3.0 Hz, 2 H), 6.76 (d, *J* = 3.0 Hz, 2 H), 2.55 (m, 4 H), 1.44 (m, 4 H), 0.95 (t, *J* = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 182.8, 154.8, 143.2, 136.3, 135.1, 128.5, 37.7, 21.7, 14.0 ppm.

IR (*neat*): 1665 (stretching C=O) cm^{-1}.

MS-EI: *m/z* (%) 332 (85, $[M]^+$), 303 (20), 275 (33), 134 (100).

HRMS-EI: *m/z* calcd for $C_{18}H_{20}O_2S_2$ 332.0905, found 332.0921.

General Procedure for the $FeCl_3$-mediated Cyclization of Alkenes 1b-f (Table 2).
To a solution of the alkene **1b-f** (0.25 mmol) in dry CH_2Cl_2 (20 mL), constantly sparged with nitrogen at the proper temperature (0, 25, 40 or 80 °C), $FeCl_3$ (1 mmol, 4 eq) was added. The resulting mixture was stirred under a nitrogen purge for 30 min, and then treated with methanol (ca. 50 mL) for 1h. The solvents were removed under reduced pressure, and the residue was purified by flash chromatography on silica gel.

2,7-Dibromo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2b).
Following the general procedure of the Table 2, **1b** (0.108 g, 0.250 mmol) was reacted with $FeCl_3$ (0.162 g, 1 mmol, 4 eq) at 0 °C for 30 min. After the treatment with MeOH, the solvents were removed under vacuum, and the residue was purified by column chromatography on silica gel (hexane) to afford **2b** (85 mg, 0.197 mmol, 79%) as a colourless solid.

Mp 94-95 °C (hexane).

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.54 (s, 2 H), 2.85 (t, J = 8.0 Hz, 4 H), 1.74 (m, 4 H), 1.07 (t, J = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 140.2, 131.8, 130.0, 125.2, 114.3, 34.4, 23.1, 14.7 ppm.

MS-EI: *m/z* (%) 432 (100, $[M]^+$), 403 (65), 375 (25), 322 (42).

HRMS-EI: *m/z* calcd for $C_{16}H_{16}Br_2S_2$ 429.9060, found 429.9072.

2,7-Diiodo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2c).
To a suspension of $FeCl_3$ (0.162 g, 1 mmol, 4 eq) in CH_2Cl_2 (20 mL) at 40 °C, a solution of the alkene **1c** (0.132 g, 0.250 mmol) in CH_2Cl_2 (5 mL) was added dropwise under a nitrogen purge. The resulting mixture was stirred for 30 min, and then treated with methanol (ca. 50 mL) for 1h. The solvents were removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (hexane) to afford **2c** (97 mg, 0.185 mmol, 74%) as a colourless solid.

Mp 117-118 °C (hexane).

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.77 (s, 2 H), 2.87 (m, 4 H), 1.72 (m, 4 H), 1.06 (t, J = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 143.8, 132.6, 132.3, 129.8, 76.6, 34.4, 23.1, 14.7 ppm.

MS-EI: *m/z* (%) 526 (100, $[M]^+$), 497 (60), 469 (21), 370 (50), 227 (37).

HRMS-EI: *m/z* calcd for $C_{16}H_{16}I_2S_2$ 525.8783, found 525.8773.

2,7-Diheptyl-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2d).
Following the general procedure of the Table 2, **1d** (0.118 g, 0.250 mmol) was reacted with $FeCl_3$ (0.162 g, 1 mmol, 4 eq) at 0 °C for 30 min. After the treatment with MeOH, the solvents were removed under vacuum, and the residue was purified by column chromatography on silica gel (hexane) to afford **2d** (77 mg, 0.165 mmol, 66%) as a pale yellow oil.

^{1}H NMR (CD_2Cl_2, 300 MHz): δ_H 7.28 (s, 2 H), 2.92 (m, 8 H), 1.75 (m, 8 H), 1.35 (m, 16 H), 1.06 (t, *J* = 7.3 Hz, 6 H), 0.92 (m, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 145.4, 137.7, 132.7, 129.2, 119.2, 34.5, 32.1, 31.9, 31.6, 31.1, 29.9, 29.8, 29.5, 29.3, 29.2, 23.3, 22.85, 22.81, 14.8, 14.3, 14.2 ppm.

MS-EI: *m/z* (%) 470 (100, $[M]^+$), 441 (12), 385 (20).

HRMS-EI: *m/z* calcd for $C_{30}H_{46}S_2$ 470.3041, found 470.3027.

Diethyl 4,5-dipropylbenzo[1,2-*b*:4,3-*b'*]dithiophene-2,7-dicarboxylate (2e).
Following the general procedure of the Table 2, **1e** (0.105 g, 0.250 mmol) was reacted with $FeCl_3$ (0.162 g, 1 mmol, 4 eq) at 80 °C for 30 min. After the treatment with MeOH, the solvents were removed under vacuum, and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 9:1) to afford **2e** (94 mg, 0.225 mmol, 89%) as a pale yellow solid.

Mp 179-180 °C (hexane/CH_2Cl_2).

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.39 (s, 2 H), 4.44 (q, *J* = 7.1 Hz, 4 H), 2.98 (m, 4 H), 1.79 (m, 4 H), 1.45 (t, *J* = 7.1 Hz, 6 H), 1.11 (t, *J* = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 162.9, 142.6, 133.3, 133.2, 133.1, 128.5, 61.8, 34.4, 23.1, 14.8, 14.5 ppm.

IR (*neat*): 1719 (stretching C=O) cm^{-1}.

MS-EI: *m/z* (%) 418 (100, $[M]^+$), 389 (22), 361 (15).

HRMS-EI: *m/z* calcd for $C_{22}H_{26}O_4S_2$ 418.1272, found 418.1280.

4,5-Dipropylbenzo[1,2-*b*:4,3-*b'*]dithiophene-2,7-dicarbaldehyde (2f). Following the general procedure of the Table 2, **1f** (0.105 g, 0.250 mmol) was reacted with $FeCl_3$ (0.162 g, 1 mmol, 4 eq) at 80 °C for 30 min. After the treatment with MeOH, the solvents were removed under vacuum, and the residue was purified by column chromatography on silica gel (hexane/AcOEt, 8:2) to afford **2f** (94 mg, 0.225 mmol, 40%) as a yellow solid.

Mp 145-147 °C (hexane/CH_2Cl_2).

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 10.2 (s, 2 H), 8.37 (s, 2 H), 3.00 (m, 4 H), 1.79 (m, 4 H), 1.11 (t, *J* = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 184.2, 143.9, 143.0, 135.1, 133.4, 131.5, 34.5, 23.1, 14.7 ppm.

IR (*neat*): 1672 (stretching C=O) cm^{-1}.

MS-EI: *m/z* (%) 330 (100, $[M]^+$), 301 (83), 273 (36).

HRMS-EI: *m/z* calcd for $C_{18}H_{18}O_2S_2$ 330.0714, found 330.0724.

1,2,7-Tribromo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (3).
To a solution of **2a** (50 mg, 0.115 mmol) in dry DCE (20 mL) at 80 °C, $FeCl_3$ (0.46 mmol, 4 eq) was added. The resulting mixture was stirred under nitrogen purge for 30', and then treated with methanol (ca. 50 mL). The solvents were removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (hexane) to afford **3** (23 mg, 0.046 mmol, 40%) as a colourless solid.

Mp 128-129 °C (MeCN/DCM).

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.60 (s, 1 H), 2.87 (m, 4 H), 1.72 (m, 4 H), 1.07 (m, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 142.0, 138.6, 131.5, 131.0, 129.9, 128.8, 124.9, 114.0, 113.6, 110.5, 34.3, 33.7, 23.1, 23.0, 14.7 (2 CH_3) ppm.

MS -EI: *m/z* (%) 511 (100, $[M]^+$), 480 (55), 454 (35), 402 (65).

HRMS-EI: *m/z* calcd for $C_{16}H_{15}Br_3S_2$ 507.8165, found 507.8164.

4,5-Dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2a).
A solution of *n*BuLi (1.6 M in hexane, 0.181 mL, 0.290 mmol, 2 eq) was added dropwise to a stirring solution of **2a** (40 mg, 0.145 mmol) in dry THF (5 mL) at 0 °C under a nitrogen atmosphere. The resulting mixture was stirred for 10 min at 0 °C and then warmed to room temperature. After 2 h at room temperature, the solution was cooled at 0 °C and treated with MeOH (0.5 mL). After 10 min at 0 °C, the mixture was warmed at room temperature, and slowly added to a saturated aqueous solution of NH_4Cl (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the organic phases were dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (hexane) to give **2a** (35.3 mg, 0.129 mmol, 89%) as a colorless solid.

Mp 65-66 °C (pentane).

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 7.68 (d, J = 5.4 Hz, 2 H), 7.48 (d, J = 5.4 Hz, 2 H), 3.01 (m, 4 H), 1.80 (m, 4 H), 1.11 (t, J = 7.3 Hz, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 138.9, 132.9, 130.3, 125.0, 122.5, 34.5, 23.3, 14.8 ppm.

MS-EI: *m/z* (%) 274 (90, $[M]^+$), 245 (100), 229 (17).

HRMS-EI: *m/z* calcd for $C_{16}H_{18}S_2$ 274.0850, found 274.0832.

1-Bromo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (4).
A solution of *n*BuLi (1.5 M in hexane, 0.430 mL, 0.646 mmol, 2.2 eq) was added dropwise to a stirring solution of **3** (150 mg, 0.294 mmol) in dry THF (10 mL) at – 78 °C under a nitrogen atmosphere. The resulting mixture was stirred for 10 min at – 78 °C, and then warmed to room temperature. After 40 min at room temperature, the solution was cooled at – 78 °C, and treated with MeOH (1.5 mL). After 30 min at – 78 °C, the mixture was warmed at room temperature, and slowly added to a saturated aqueous solution of NH_4Cl (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the organic phases were

dried with Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (hexane) to give **4** (71 mg, 0.213 mmol, 70%) as a colourless solid.

Mp 72-73 °C (hexane).

^{1}H NMR ($CDCl_3$, 300 MHz): δ_H 8.67 (d, J = 5.6 Hz, 1 H), 7.53 (d, J = 5.6 Hz, 1 H), 7.46 (s, 1 H), 2.99 (m, 4 H), 1.78 (m, 4 H), 1.10 (m, 6 H) ppm.

^{13}C NMR ($CDCl_3$, 75 MHz): δ_C 140.7, 138.5, 132.2, 131.6, 130.2, 129.7, 124.8, 122.8, 122.3, 106.6, 34.6, 33.6, 23.3, 23.2, 14.79, 14.77 ppm.

MS-EI: *m/z* (%) 352 (100, $[M]^+$), 323 (53), 295 (20), 244 (75), 227 (24).

HRMS-EI: *m/z* calcd for $C_{16}H_{17}S_2Br$ 351.9955, found 352.0005.

3. X-Ray Data of Compound 3

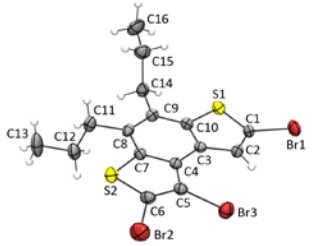
The intensity data of compound **3** were collected at room temperature on a Bruker AXS Smart 1000 single crystal diffractometer, equipped with area detector and using a graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic and experimental details of the structure are summarized in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares procedures (based on F_o^2) first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as xxxyyy CCDC. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.Uk).

Table 1. Selected data for X ray collection of **3**.

Formula	C_{16} H_{15} Br_3 S_2
Molecular weight	511.13
Crystal system	Triclinic
Space group	*P*-1
a/Å	7.932(6)
b/Å	10.674(8)
c/Å	10.901(9)
α/deg	91.188(12)
β/deg	106.211(11)
γ/deg	90.163(12)
Volume, Å^3	886.0(12)
Z	2
d_{calc} g cm^{-3}	1.916
F(000)	496
μ(Mo-Kα)/mm^{-1}	7.056
Rflns collected	14050
Rflns unique	5475 [R_{int}= 0.0585]
Rflns observed [I>2σ(I)]	2755
R [I>2σ(I)]	R1= 0.0463 wR2= 0.0885
R [all data]	R1= 0.1213 wR2= 0.1103

$$R1 = \Sigma|F_O-F_C|/|\Sigma (F_O); \; wR2 = [\Sigma [w (F_O^2-F_C^2)^2]/\Sigma [w (F_O^2)^2]]^{1/2}$$

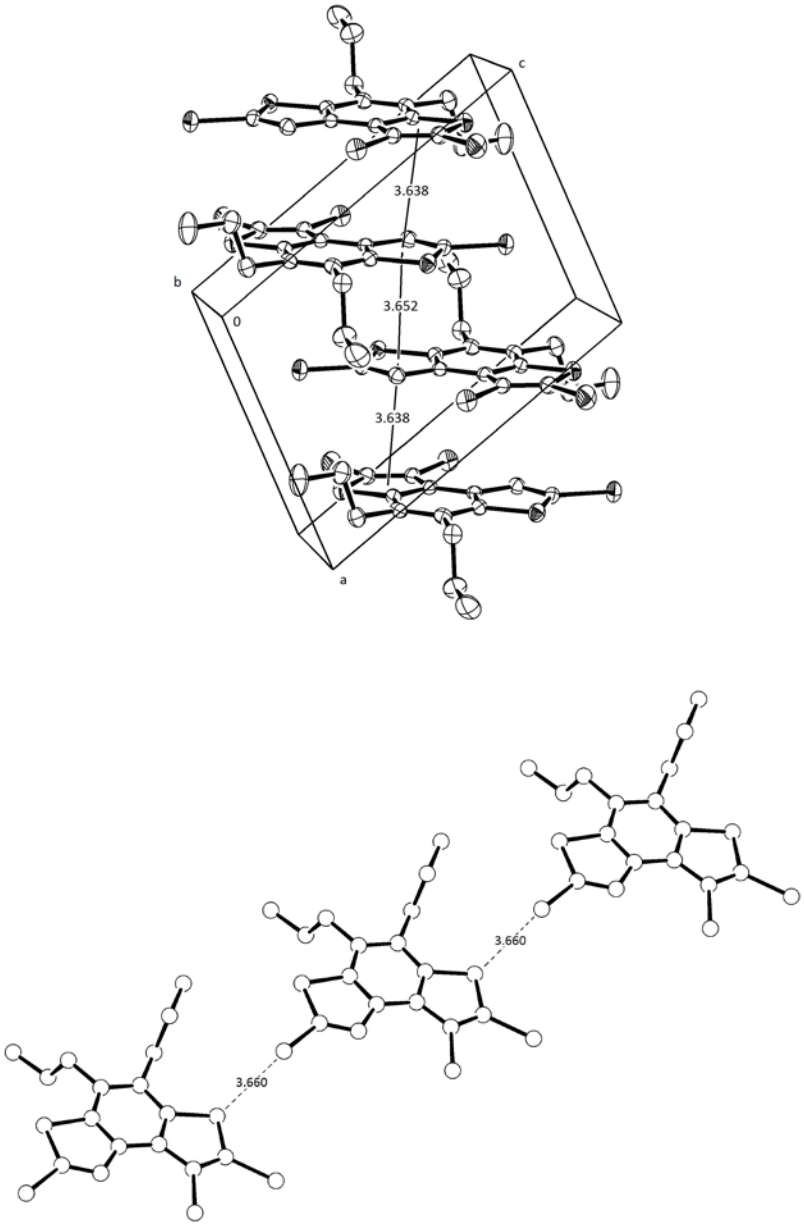
Figure S1. ORTEP view of the crystal structure of **3** (ellipsoids are drawn at their 30% probability level). Selected bond distances (Å) and angles (°): C1-C2 1.335(5), C1-Br1 1.884(4), C2-C3 1.423(5), C3-C4 1.423(5), C4-C5 1.436(5), C5-C6 1.350(5), C5-Br3 1.869(4), C6-Br2 1.865(4), C3-C10 1.398(5), C4-C7 1.401(5); C10-C3-C4 116.7(4), C10-C3-C2 112.3(3), C4-C3-C2 131.0(4), C7-C4-C3 117.0(3), C7-C4-C5 111.6(3), C3-C4-C5 131.3(4).



The ORTEP view of **3** is shown in Figure S1; the most important bond distances and angles are reported in the caption. The molecule is essentially planar neglecting the two *n*-propyl chains, which develop on two opposite sites of the mean plane of the benzodithiophene unit. An adventitious intramolecular contact is observed between C2 and Br3 atoms (C2···Br3 3.411(2) Å, C2-H2···Br3 124°). Considering the crystal packing of the compound the mean planes of the benzodithiophene moieties are parallel at a distance of ca 3.60 Å. The centroids of the tiophene rings of stacked molecules are at a distance of 3.638(3) and 3.652(3) Å. Moreover Br···S contacts exist between Br1 and S2 atoms of adjacent molecules, (Br1 (at x, y, z)···S2(at 1+x, y, 1+z) of 3.660(3)Å) as observed in other bromo-substituted π-conjugted organic molecules. [A.A.

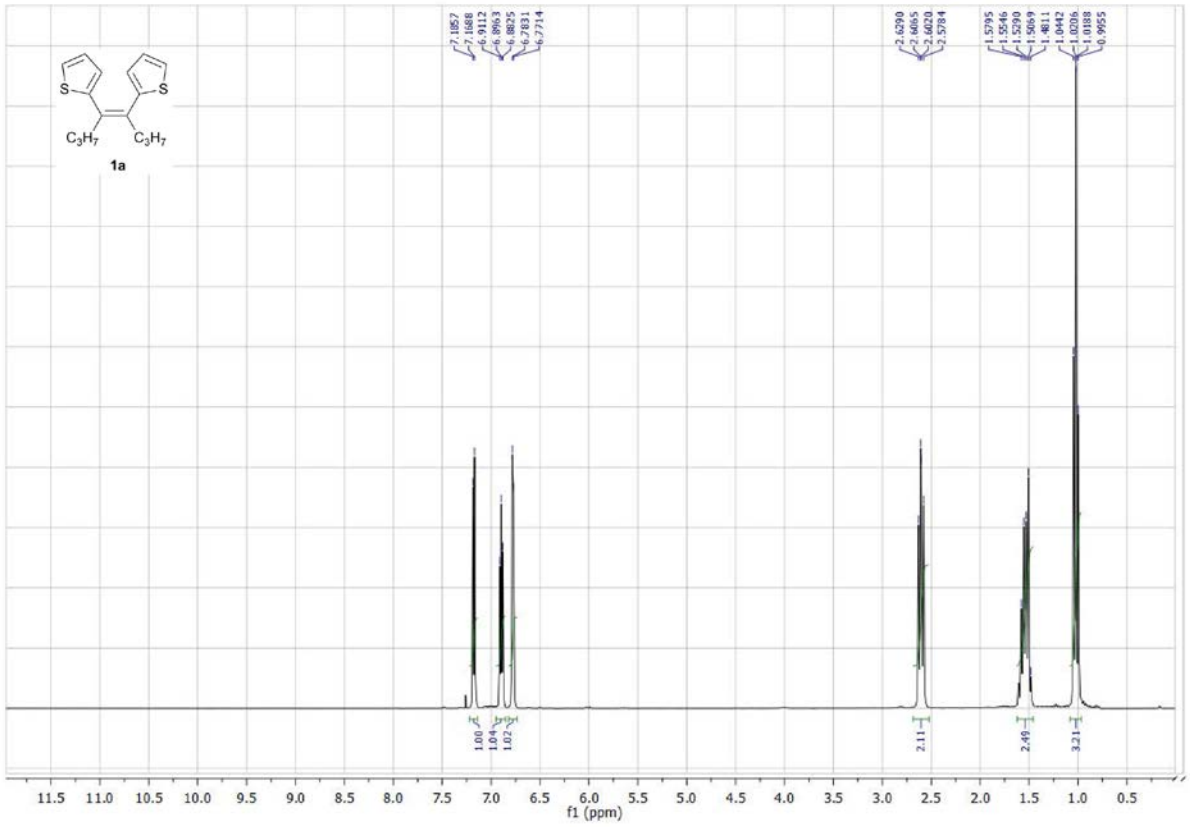
Leitch, A. Monsour, K. A. Stobo, I. Korobkov, J. L. Brusso, *Cryst. Growth Des*. **2012**, *12*, 1416 and ref therein].

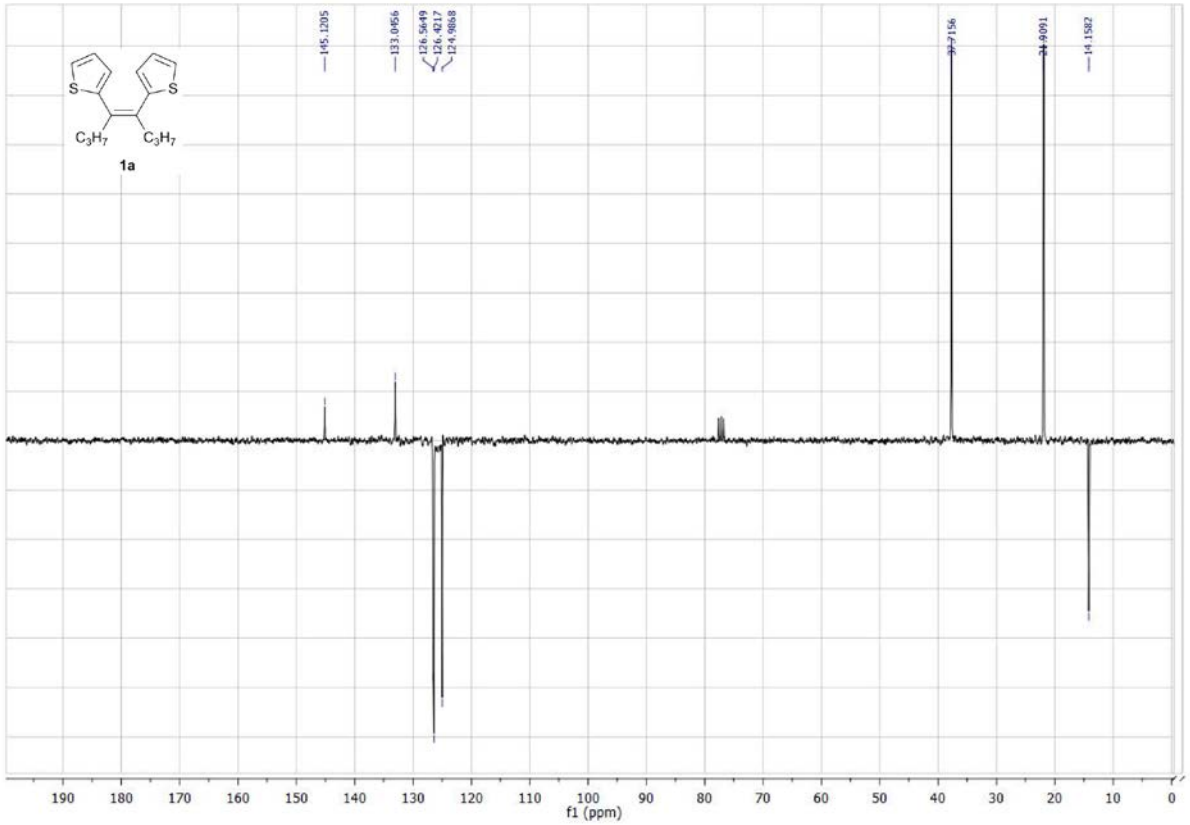
Figure S2. View of the crystal packing of compound **3**, showing the π stacked structure (top) and Br···S interactions (bottom).



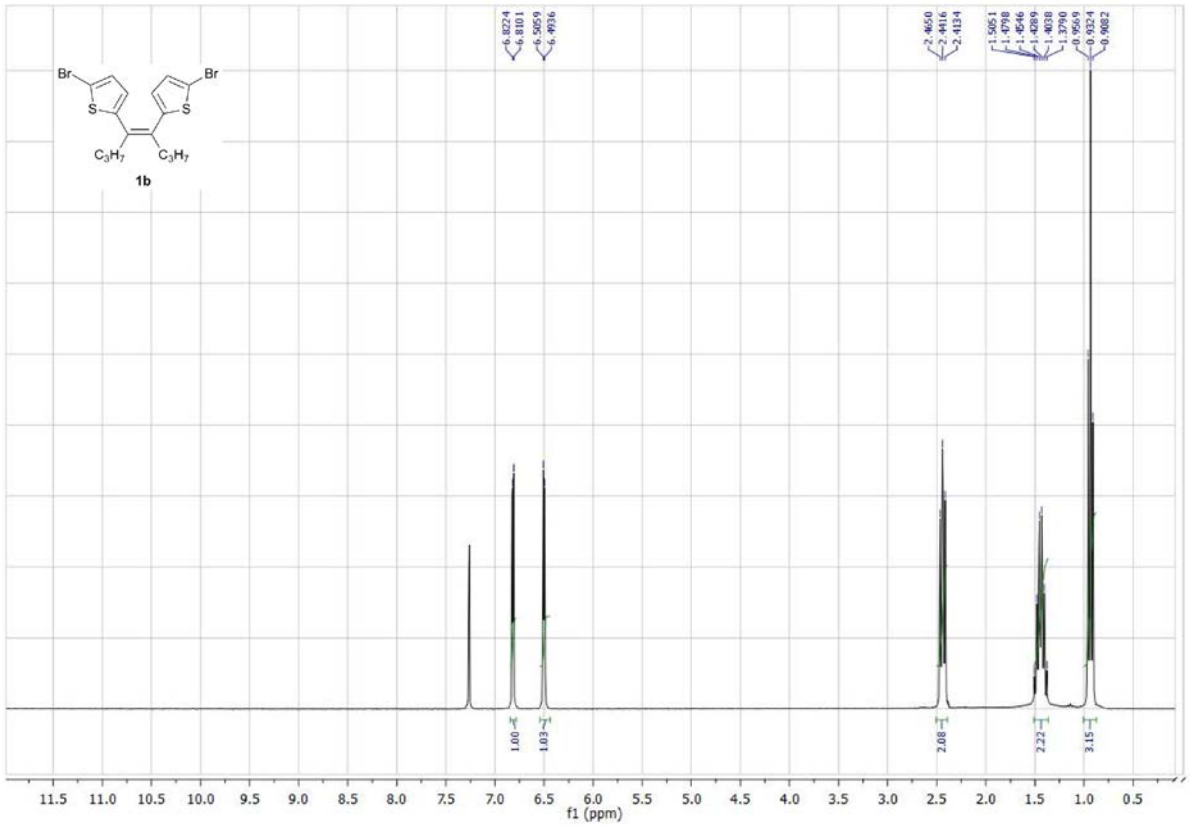
4. ^{1}H and ^{13}C NMR Spectra

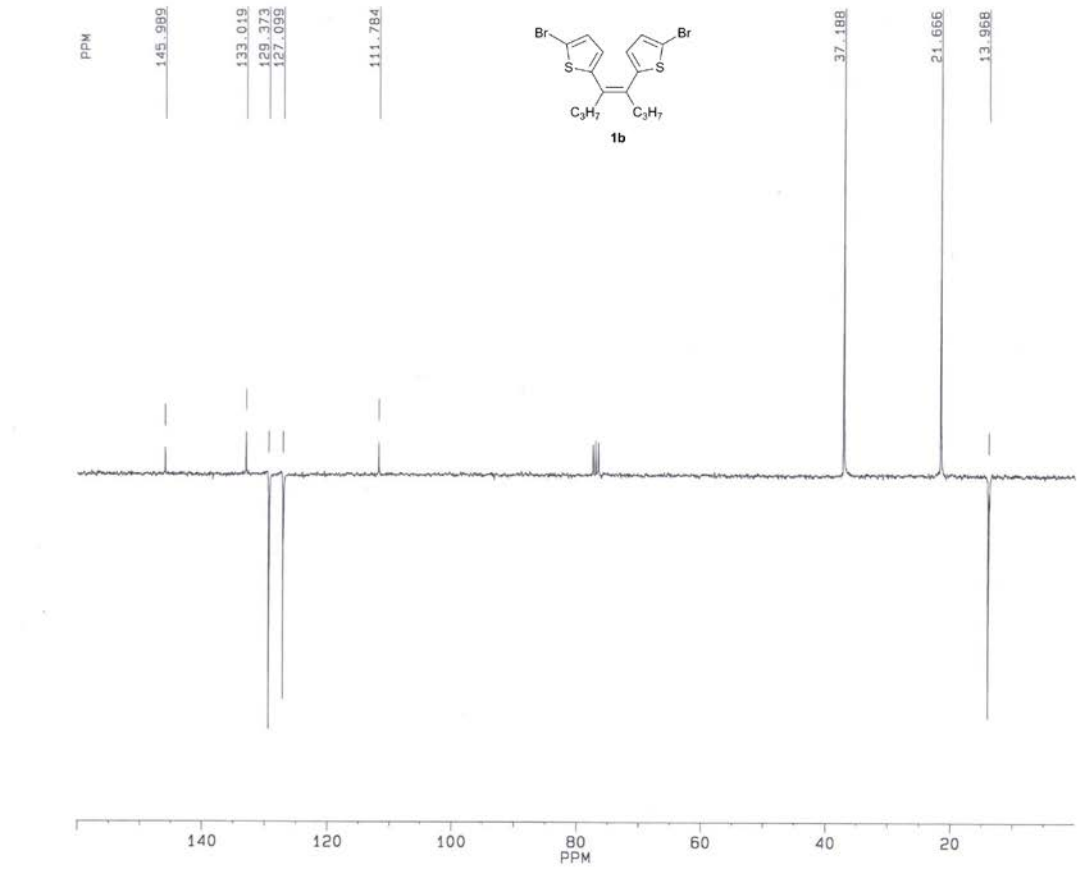
(*Z*)-2,2'-(Oct-4-ene-4,5-diyl)dithiophene (1a)



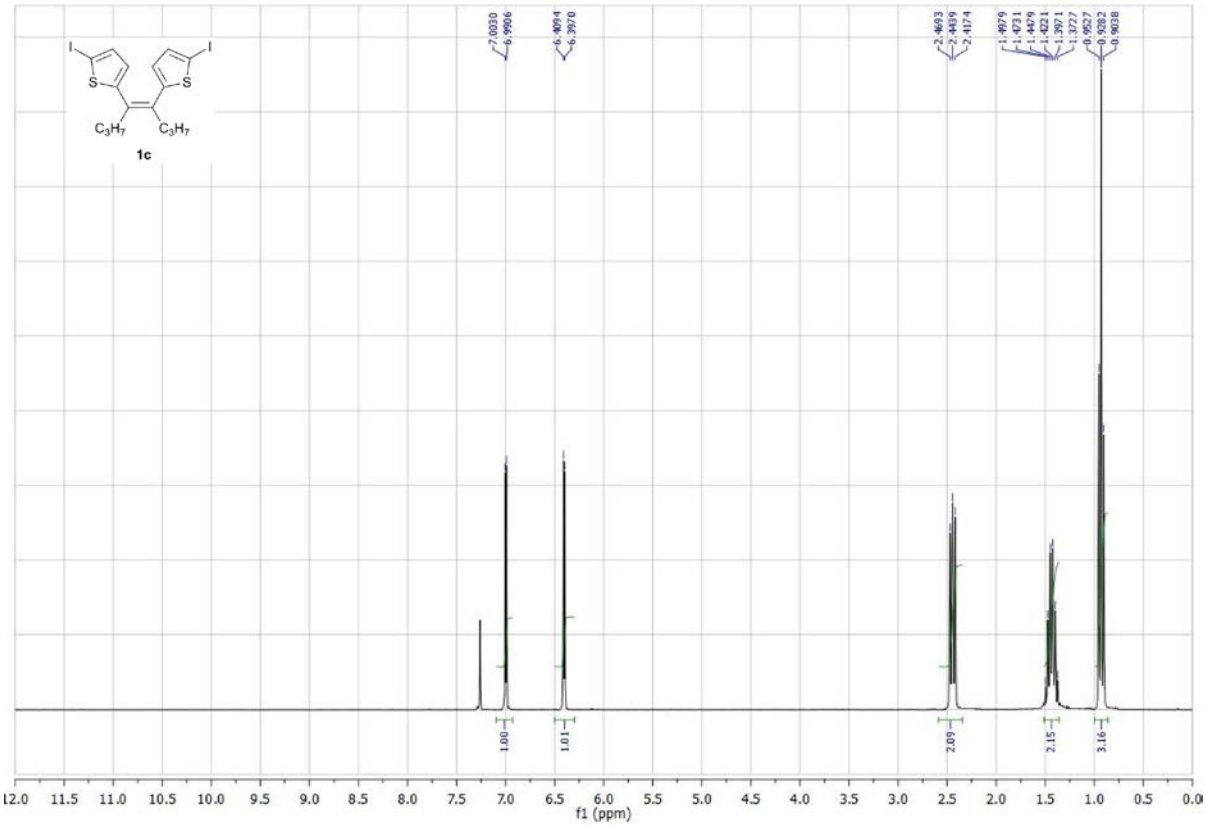


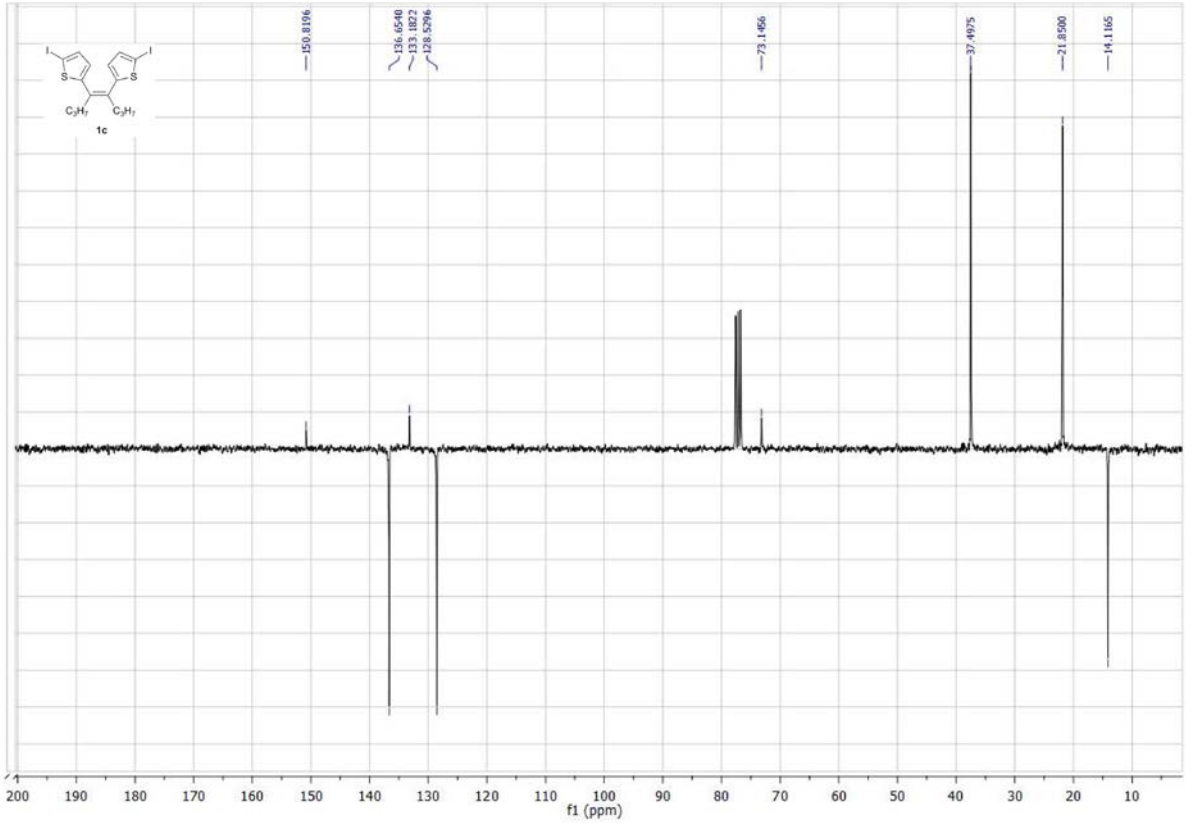
(*Z*)-5,5’-(Oct-4-ene-4,5-diyl)bis(2-bromothiophene) (1b)



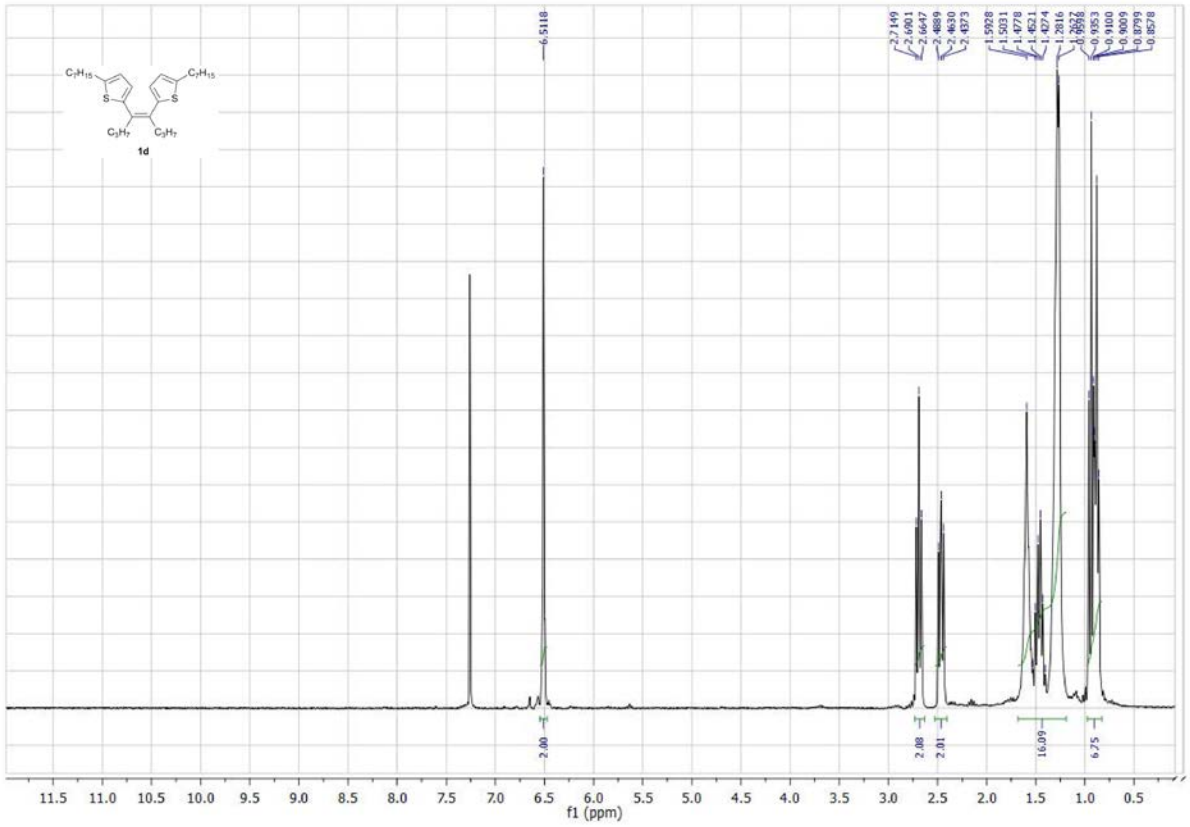


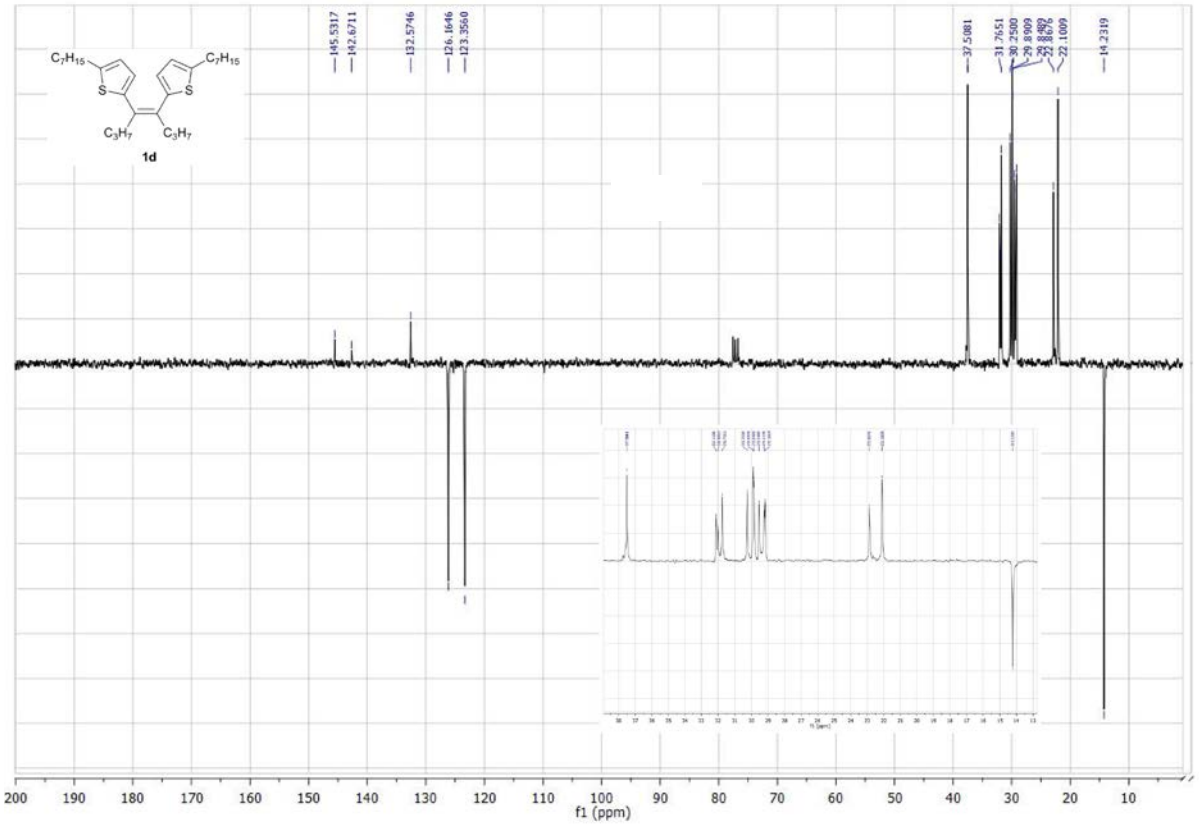
(*Z*)-5,5’-(Oct-4-ene-4,5-diyl)bis(2-iodothiophene) (1c)



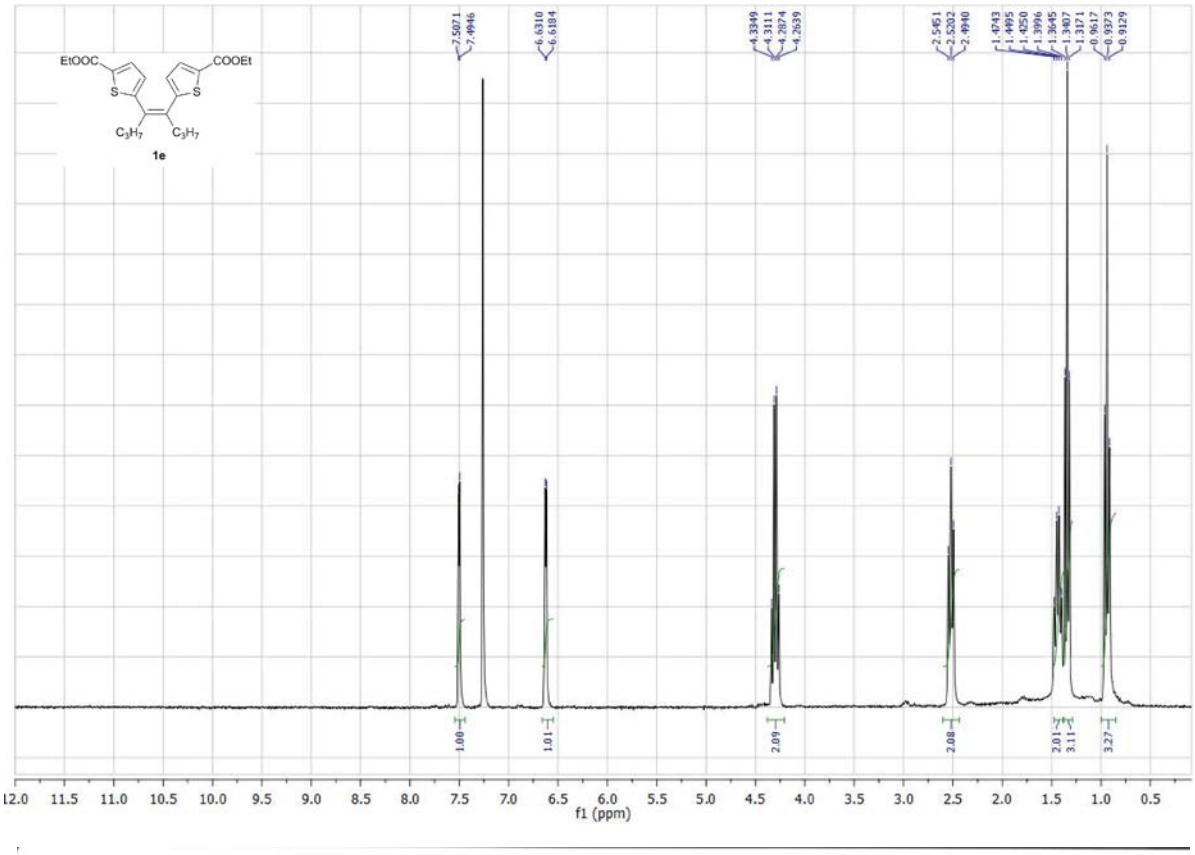


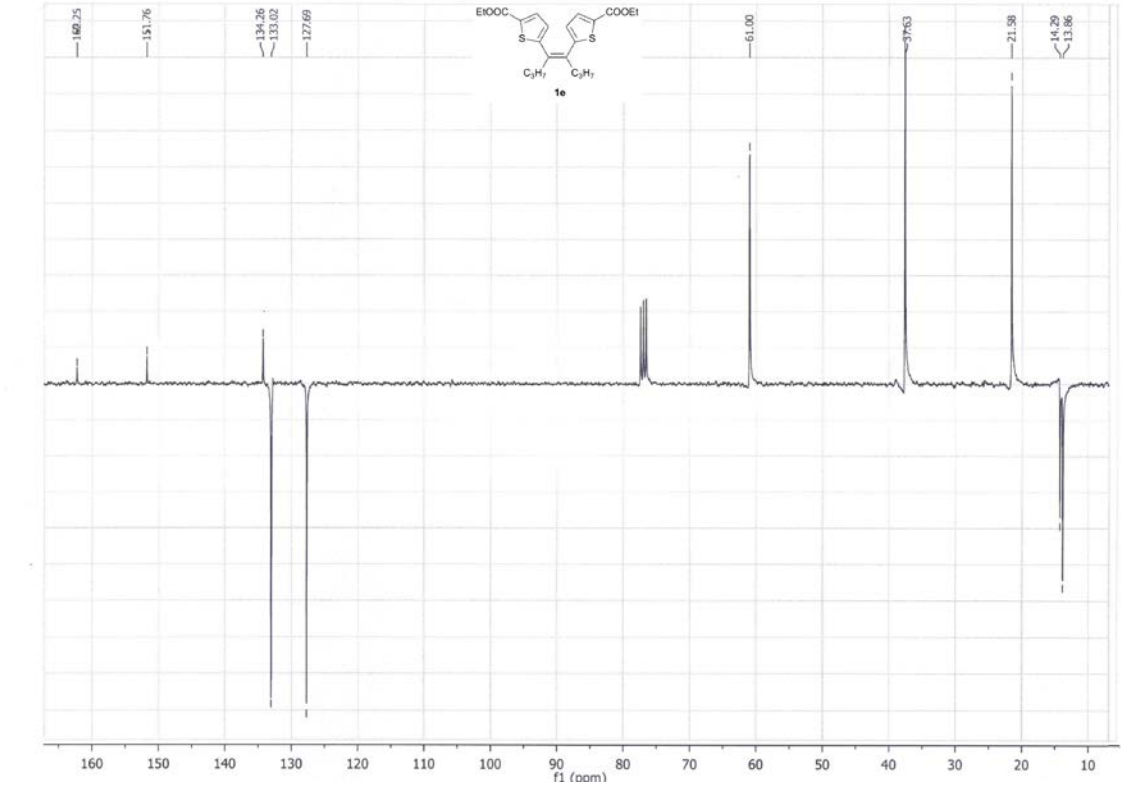
(*Z*)-5,5’-(Oct-4-ene-4,5-diyl)bis(2-heptylthiophene) (1d)



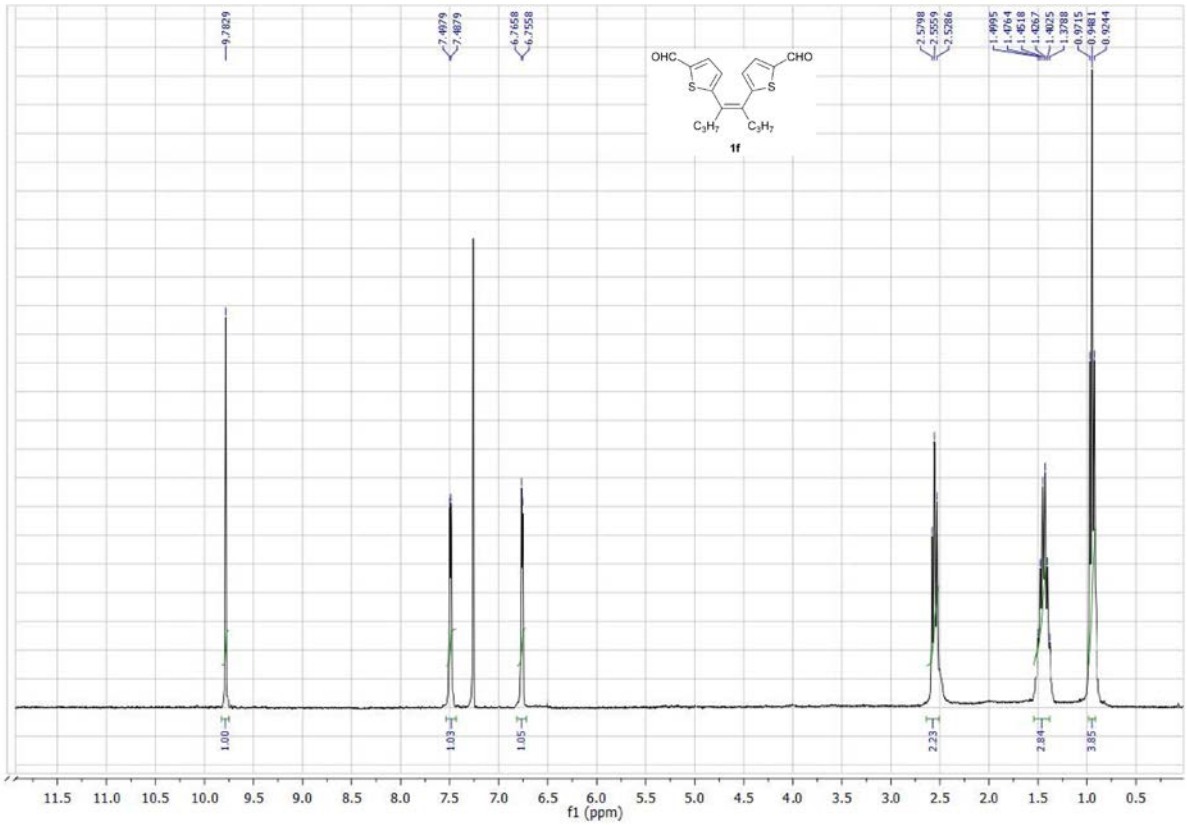


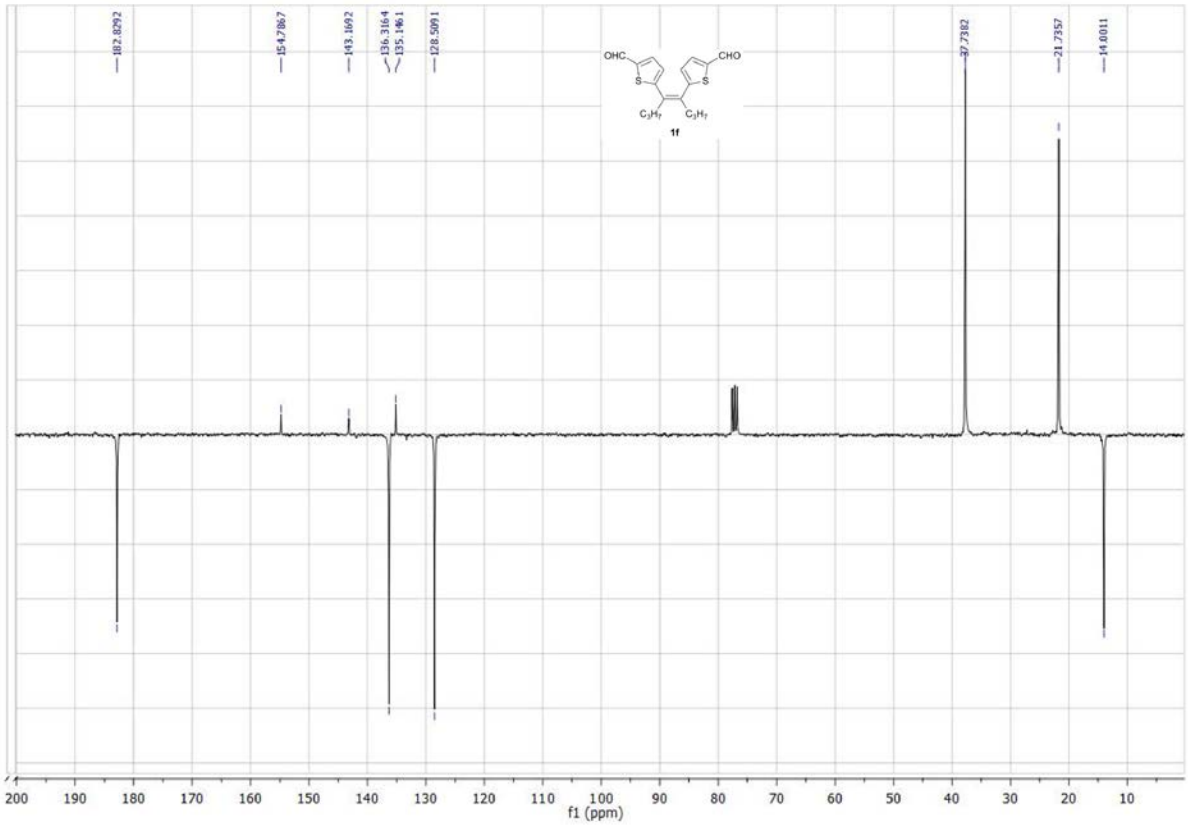
(*Z*)-Diethyl 5,5'-(oct-4-ene-4,5-diyl)bis(thiophene-2-carboxylate) (1e)



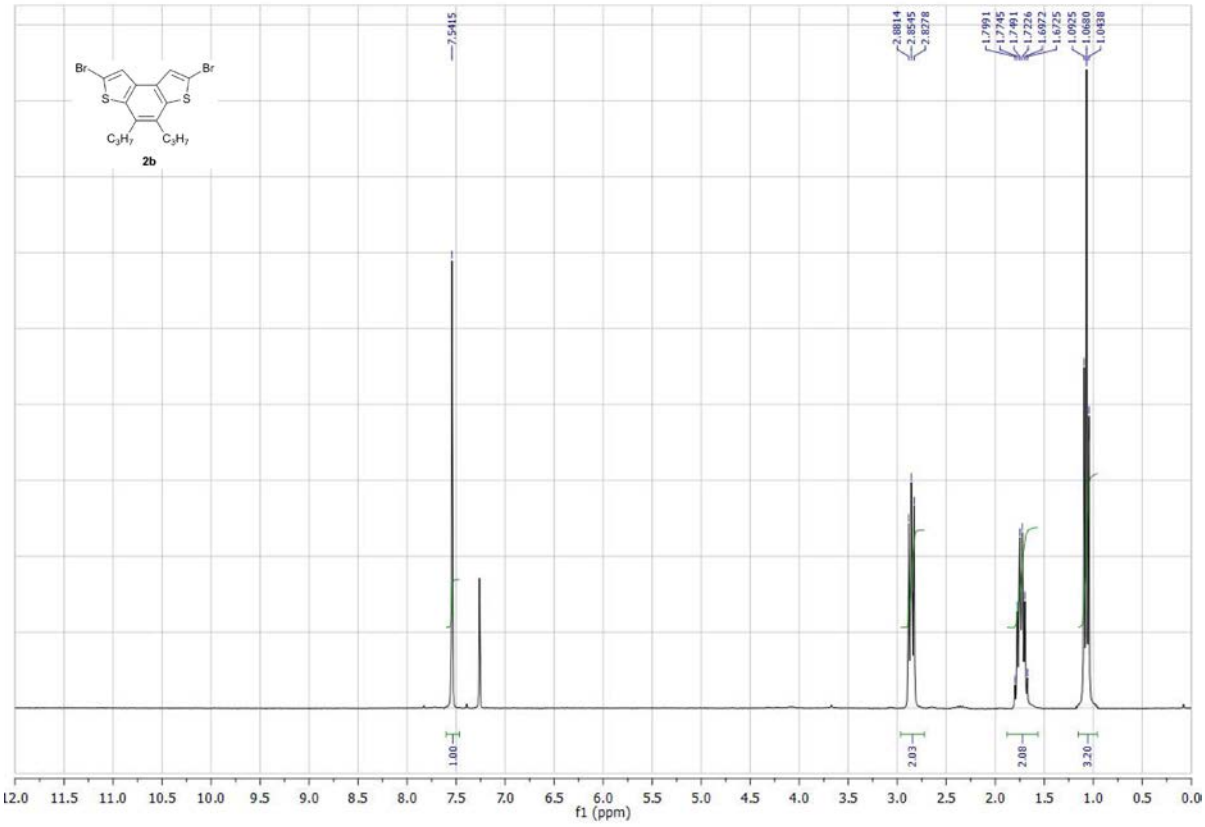


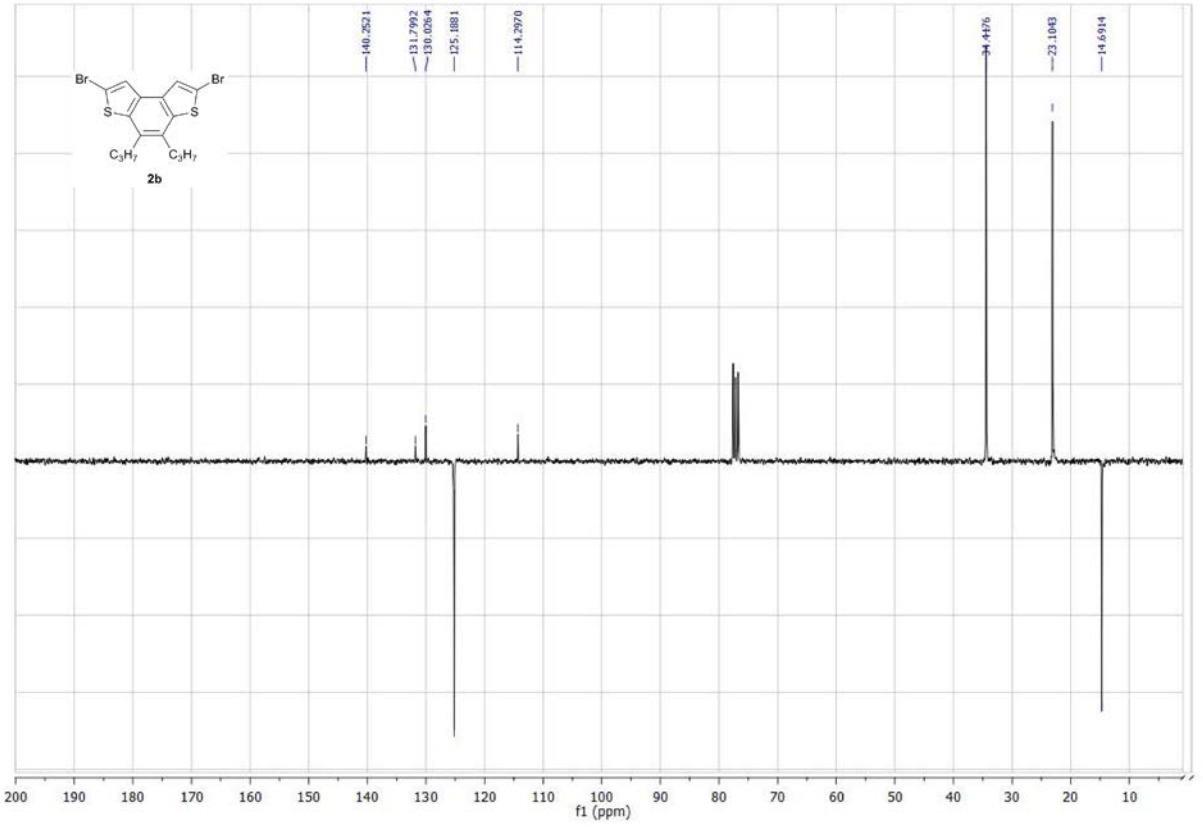
5-((Z)-5-(5-Formylthiophen-2-yl)oct-4-en-4-yl)thiophene-2-carbaldehyde (1f)



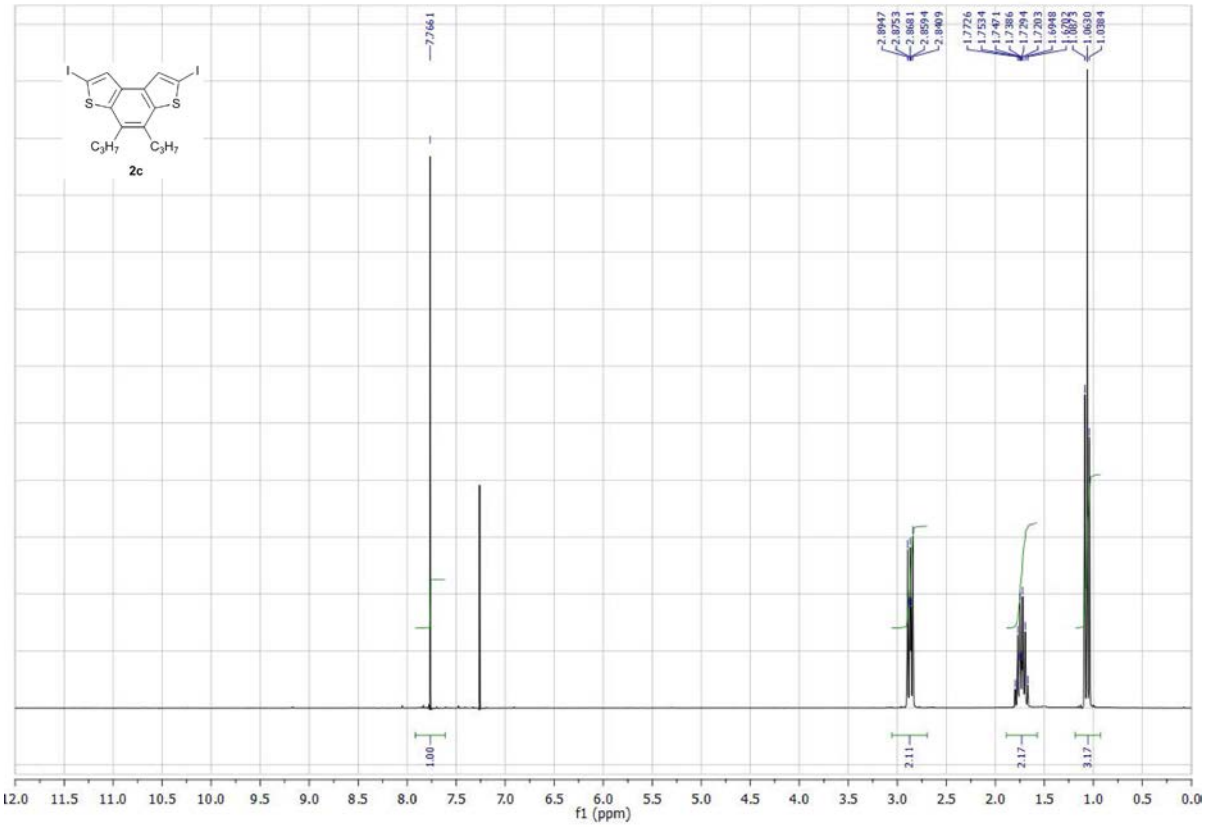


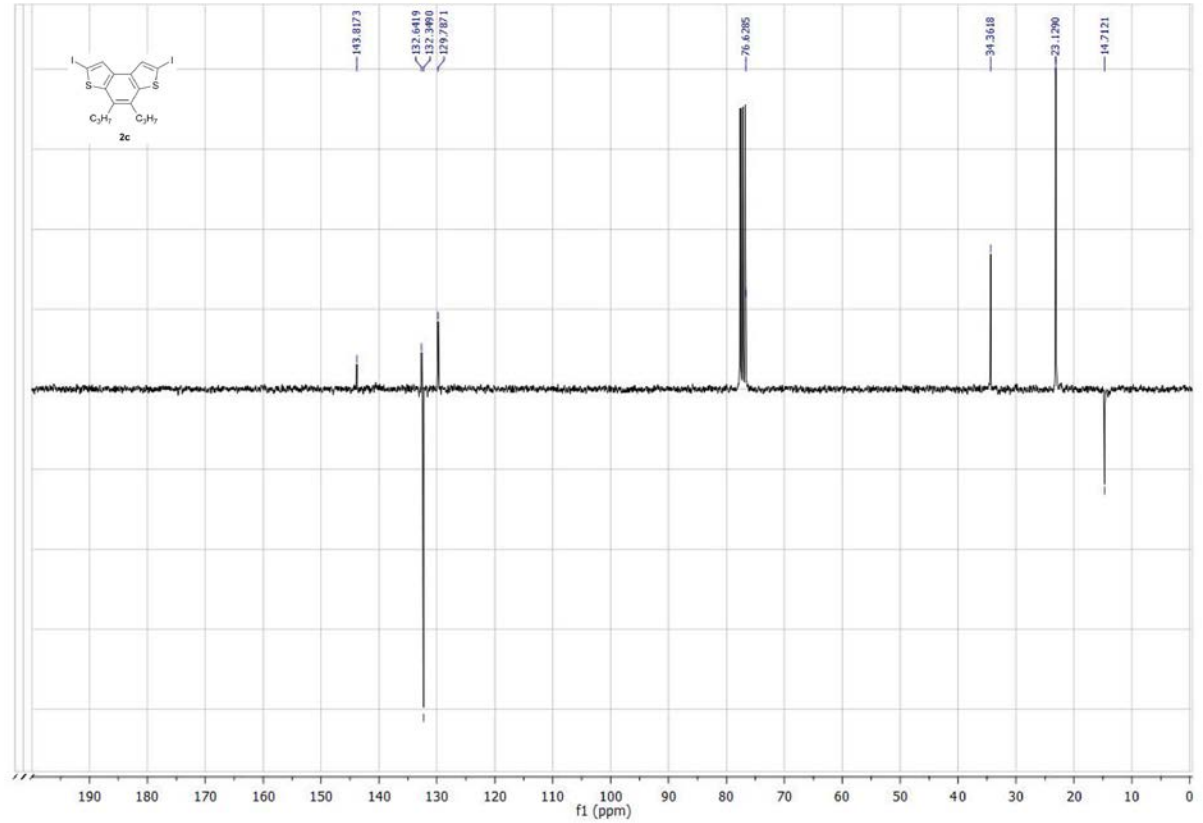
2,7-Dibromo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2b)



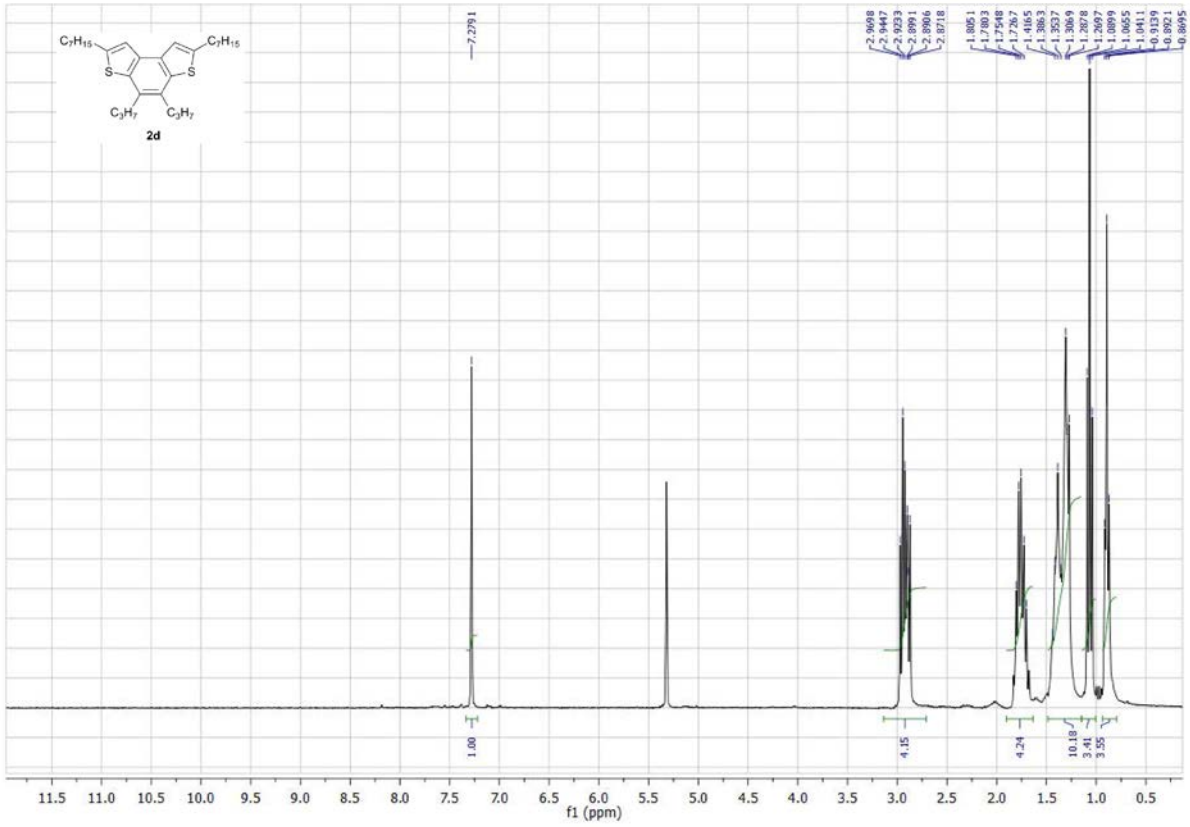


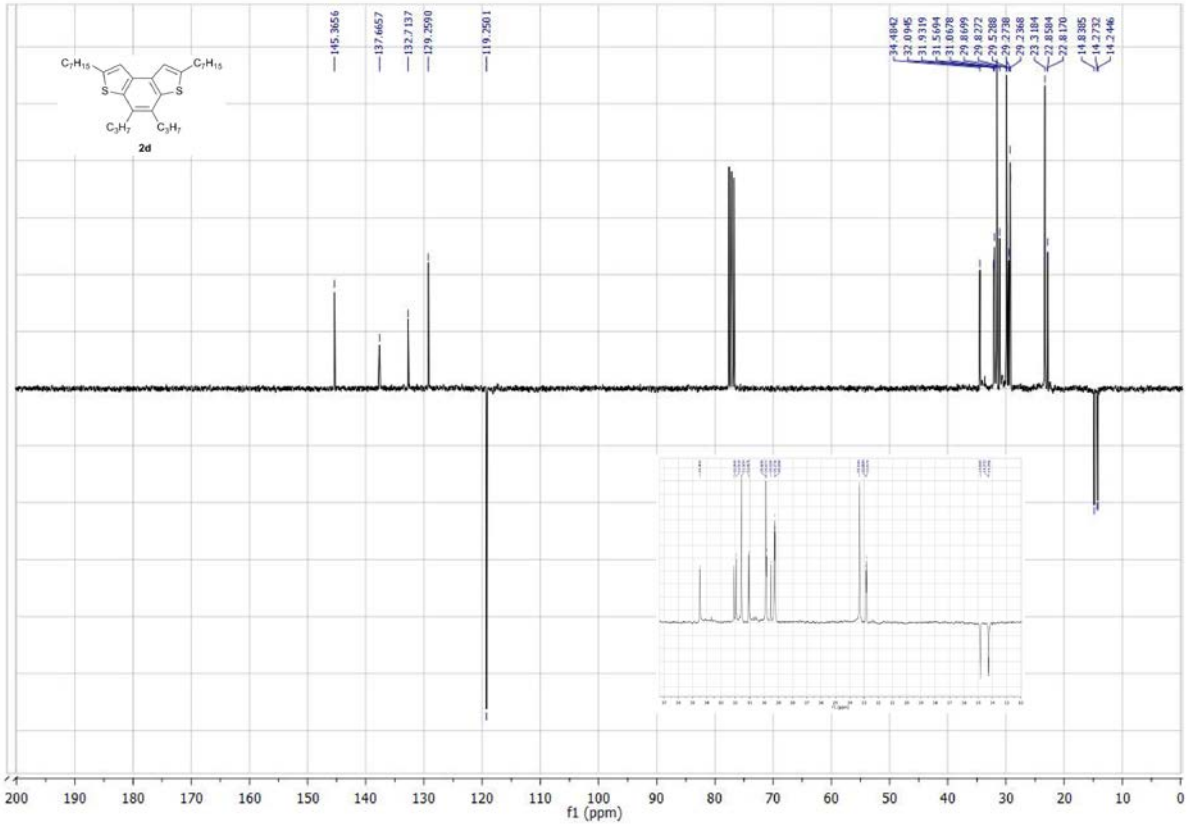
2,7-Diiodo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2c)



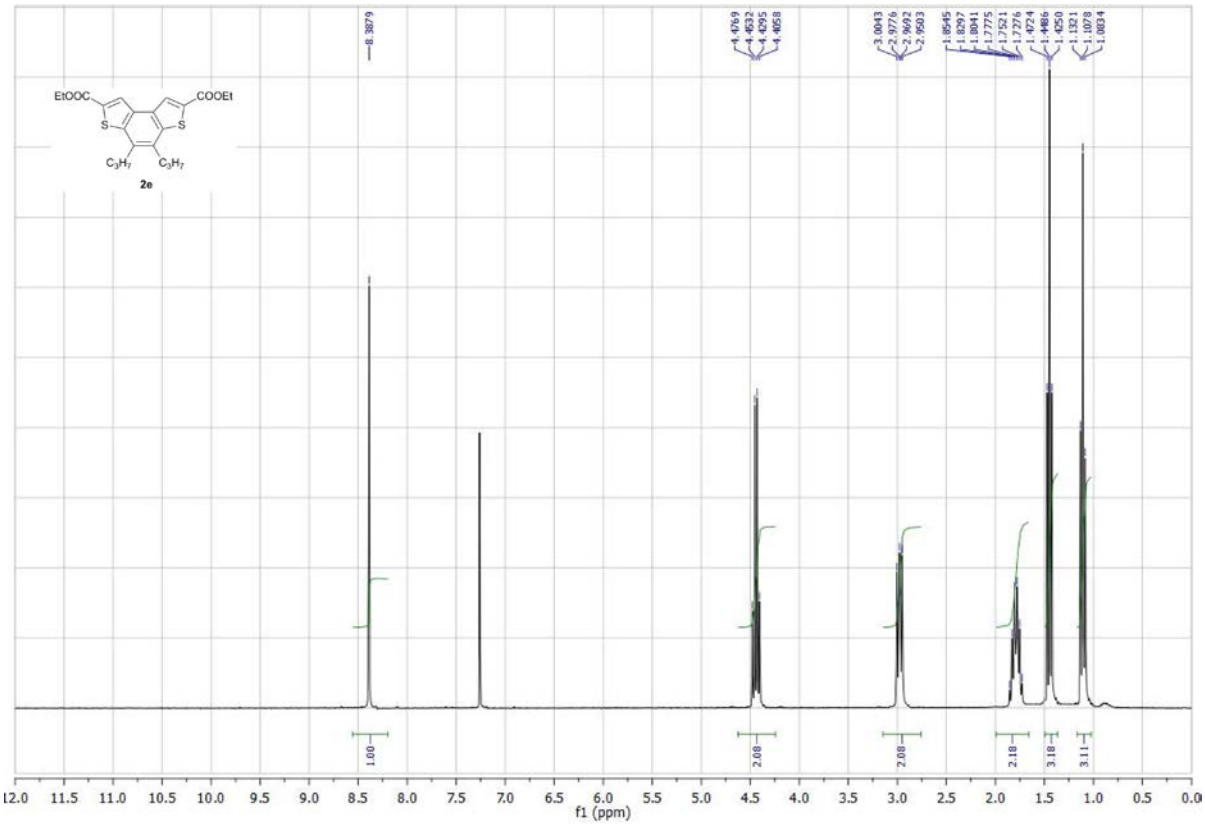


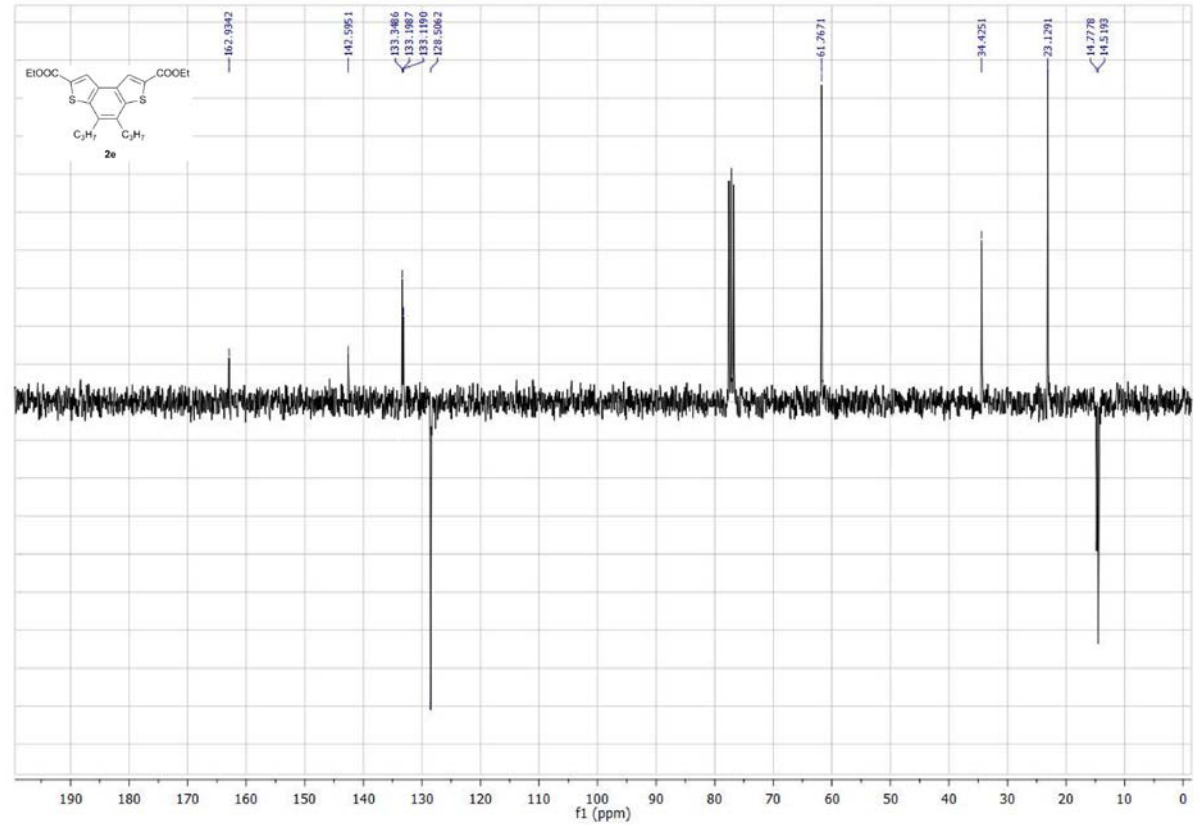
2,7-Diheptyl-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2d)



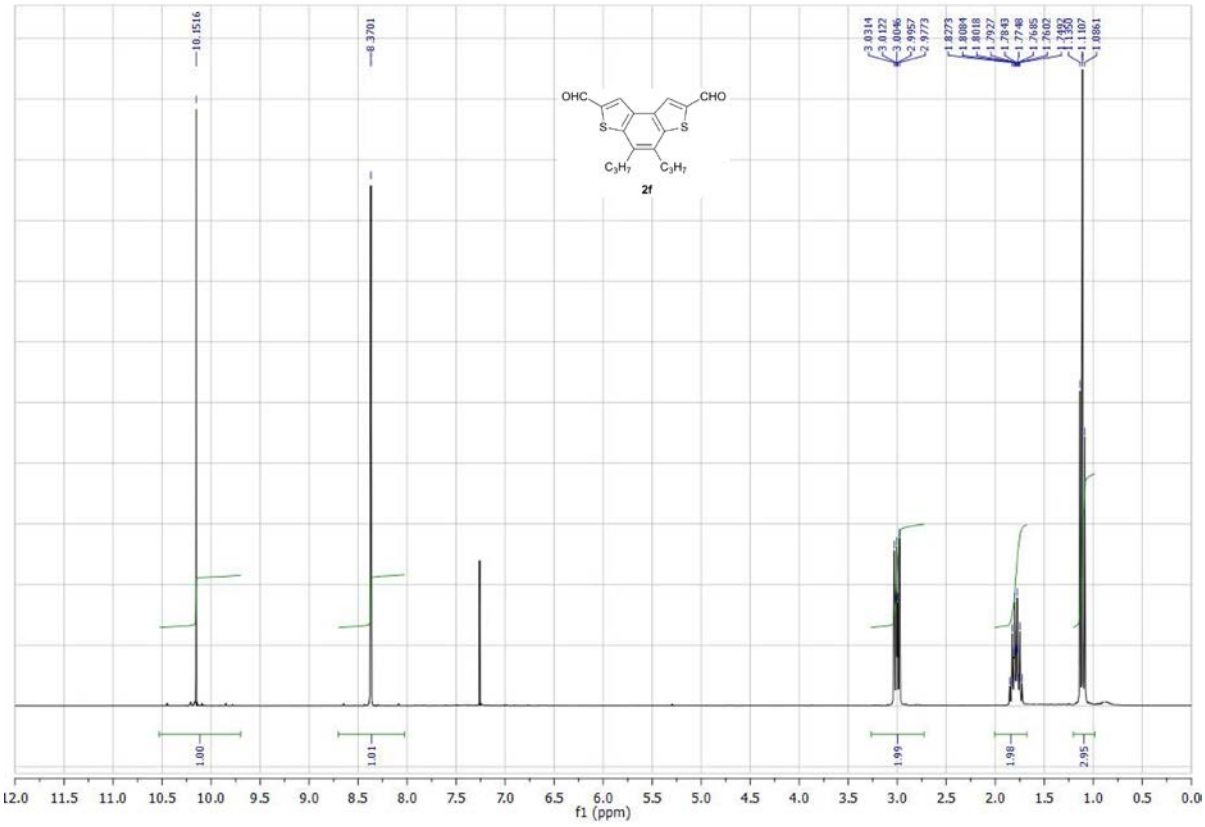


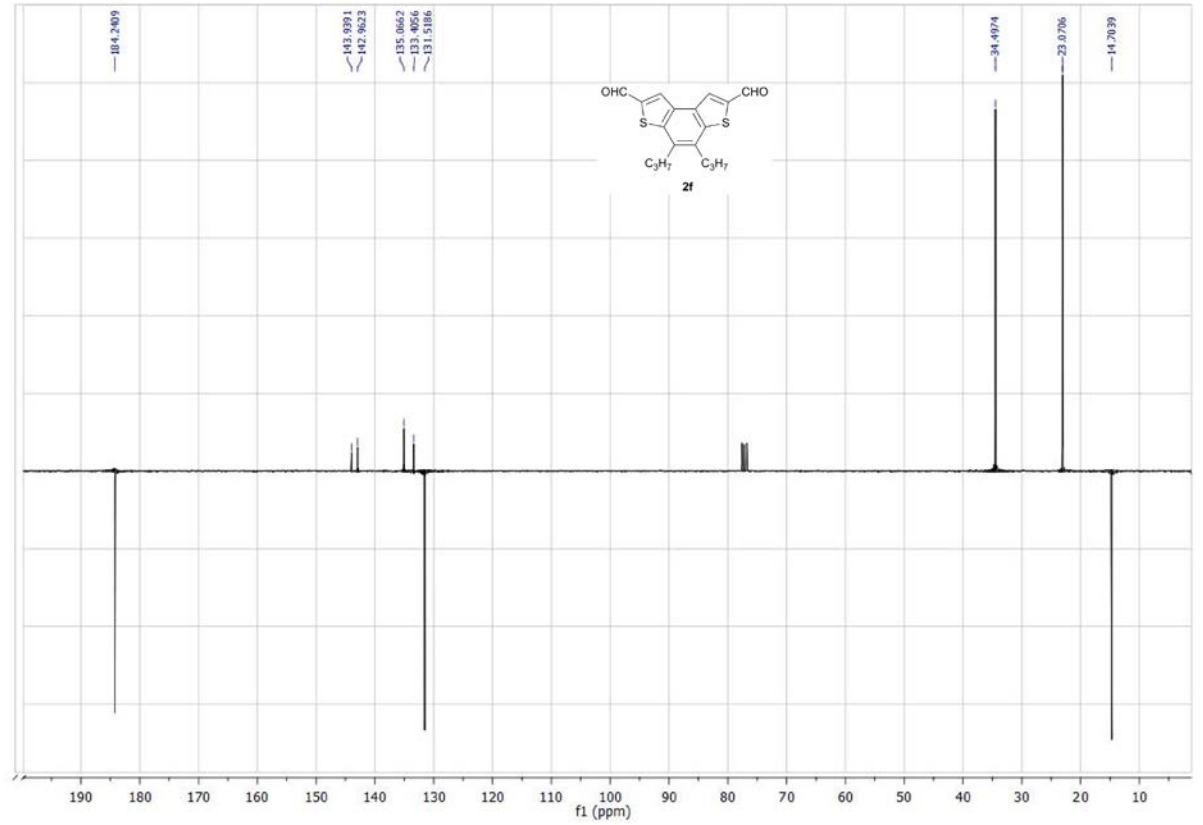
Diethyl 4,5-dipropylbenzo[1,2-*b*:4,3-*b*']dithiophene-2,7-dicarboxylate (2e)



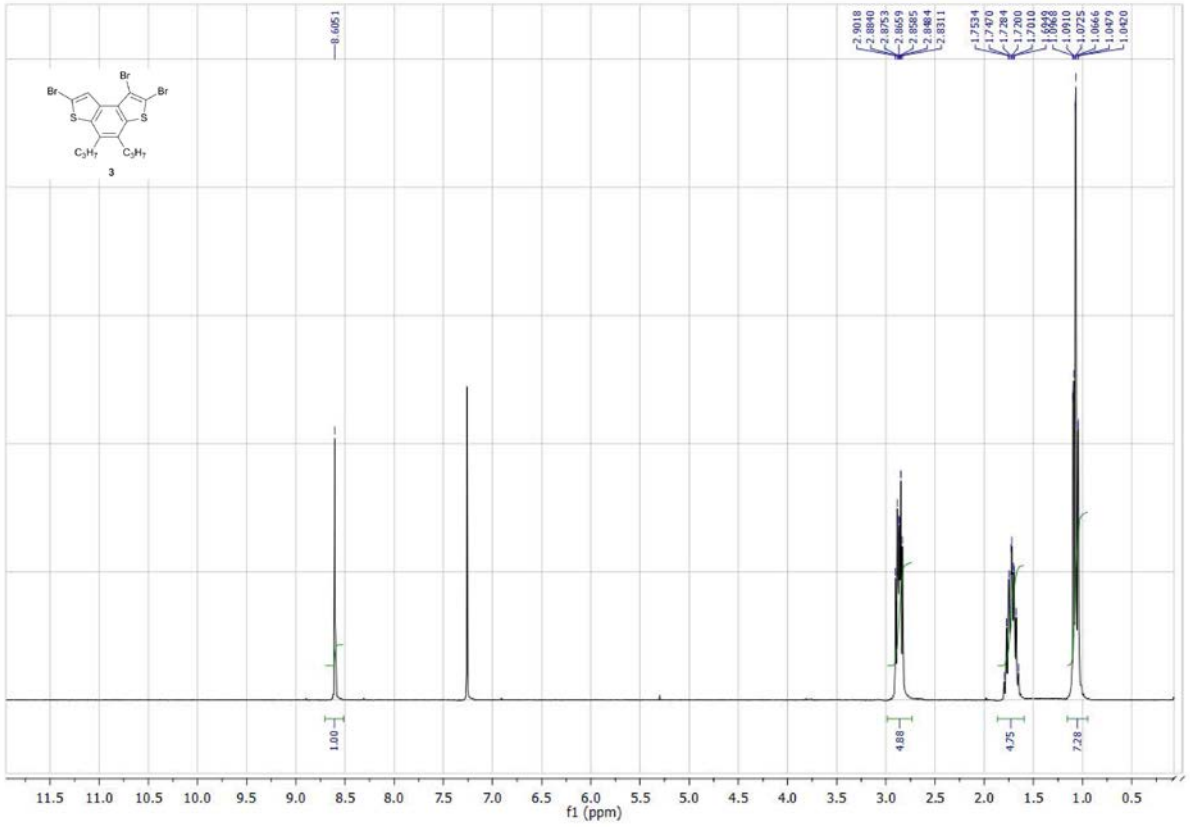


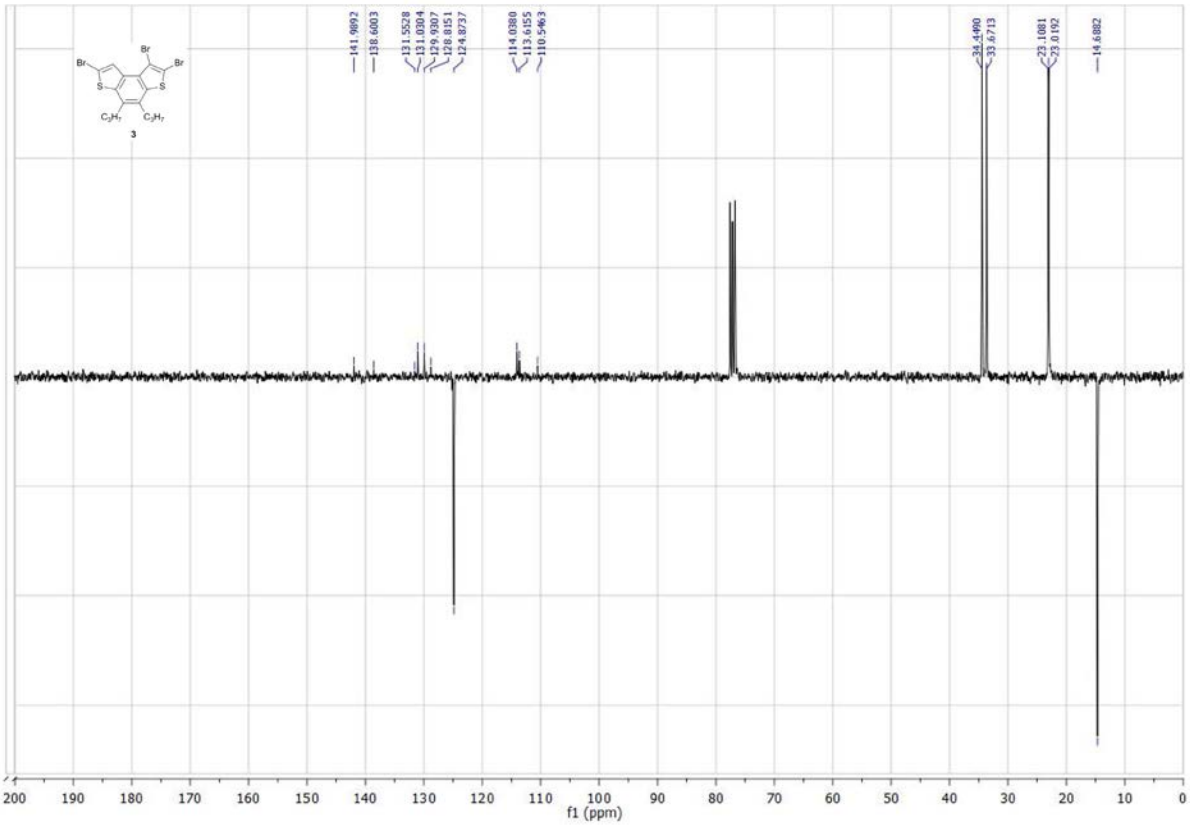
4,5-Dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene-2,7-dicarbaldehyde (2f)



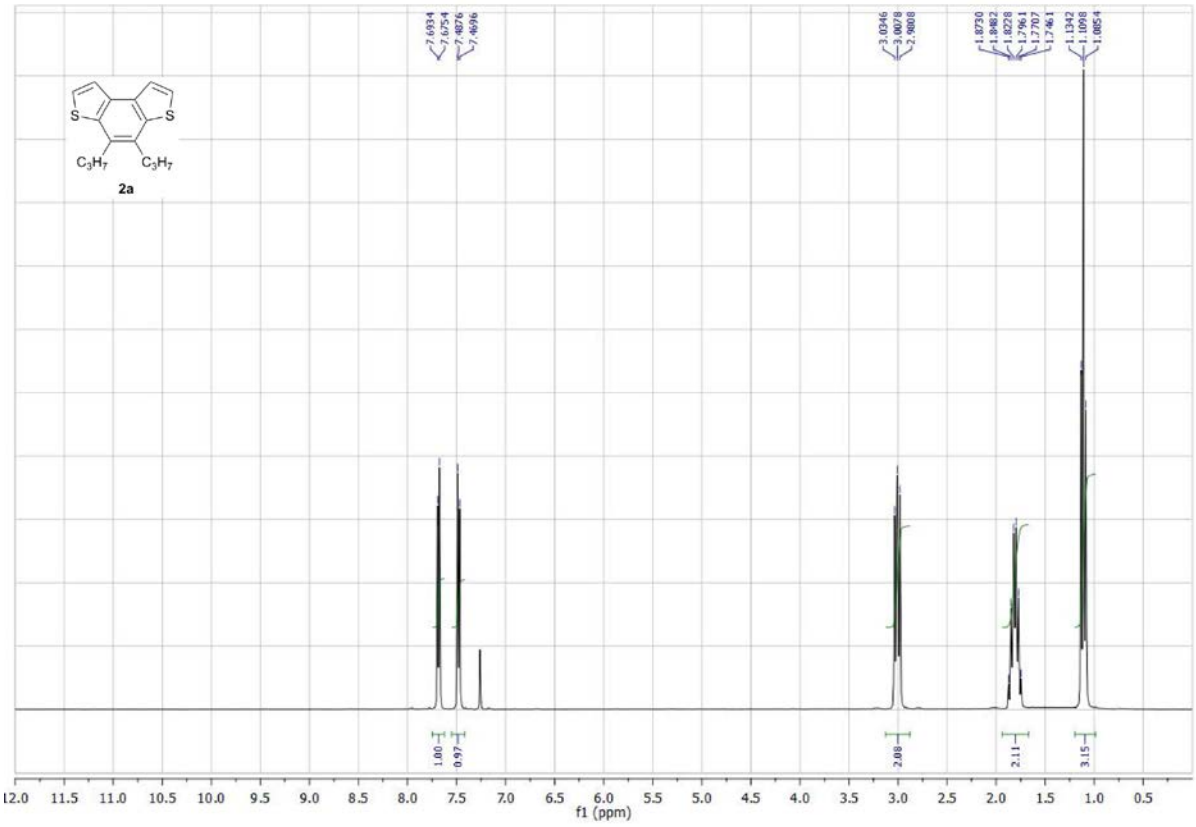


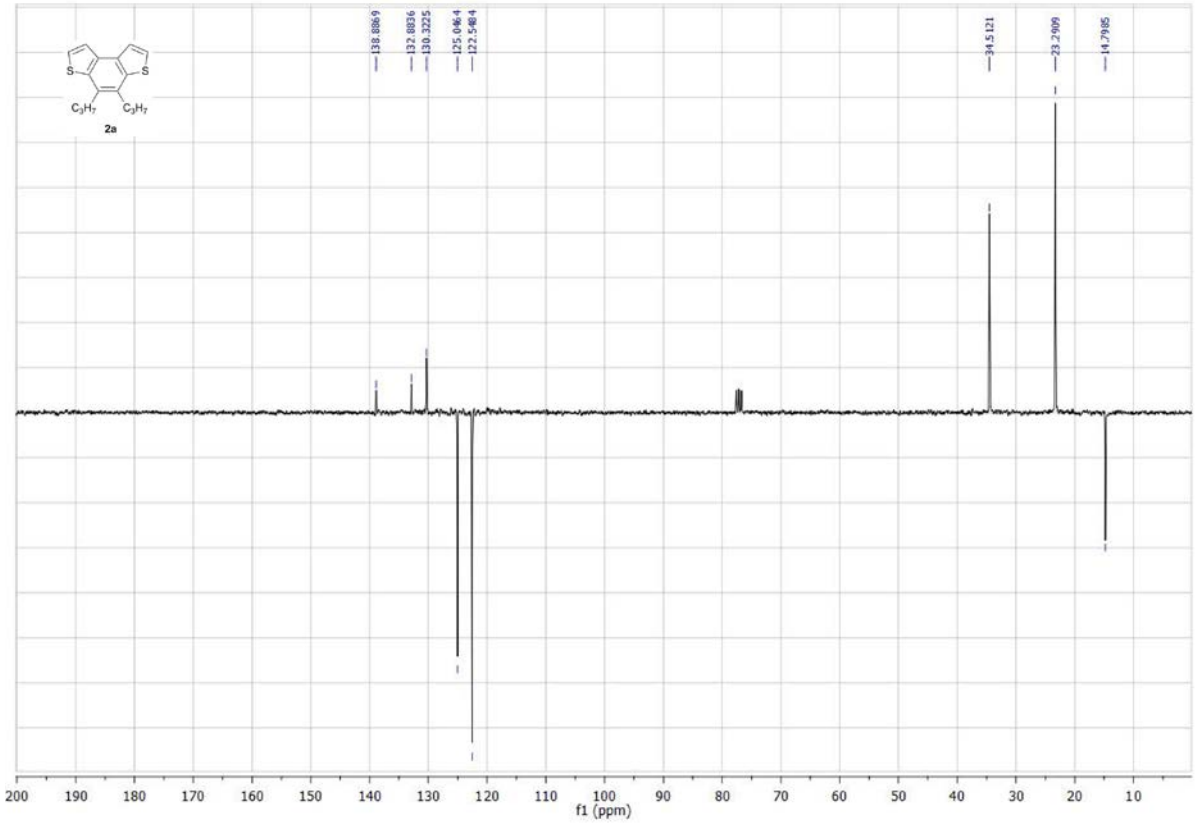
1,2,7-Tribromo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (3)



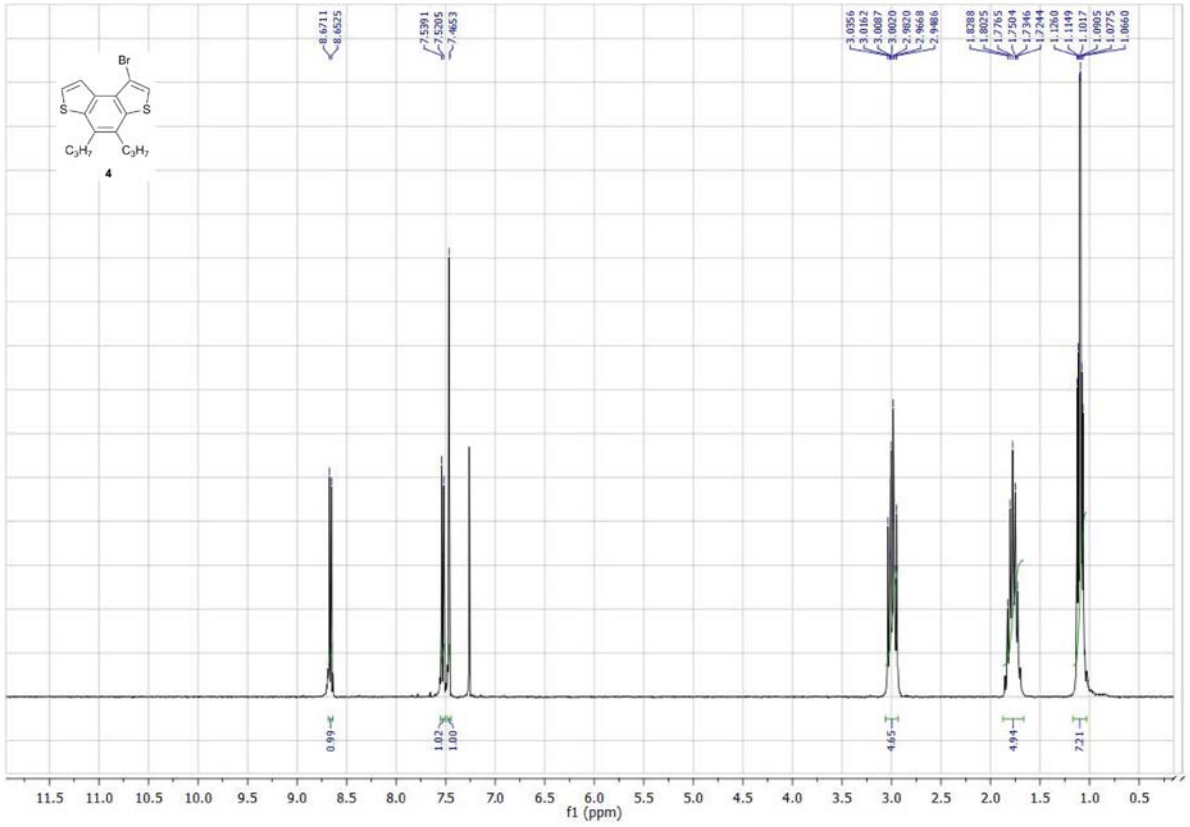


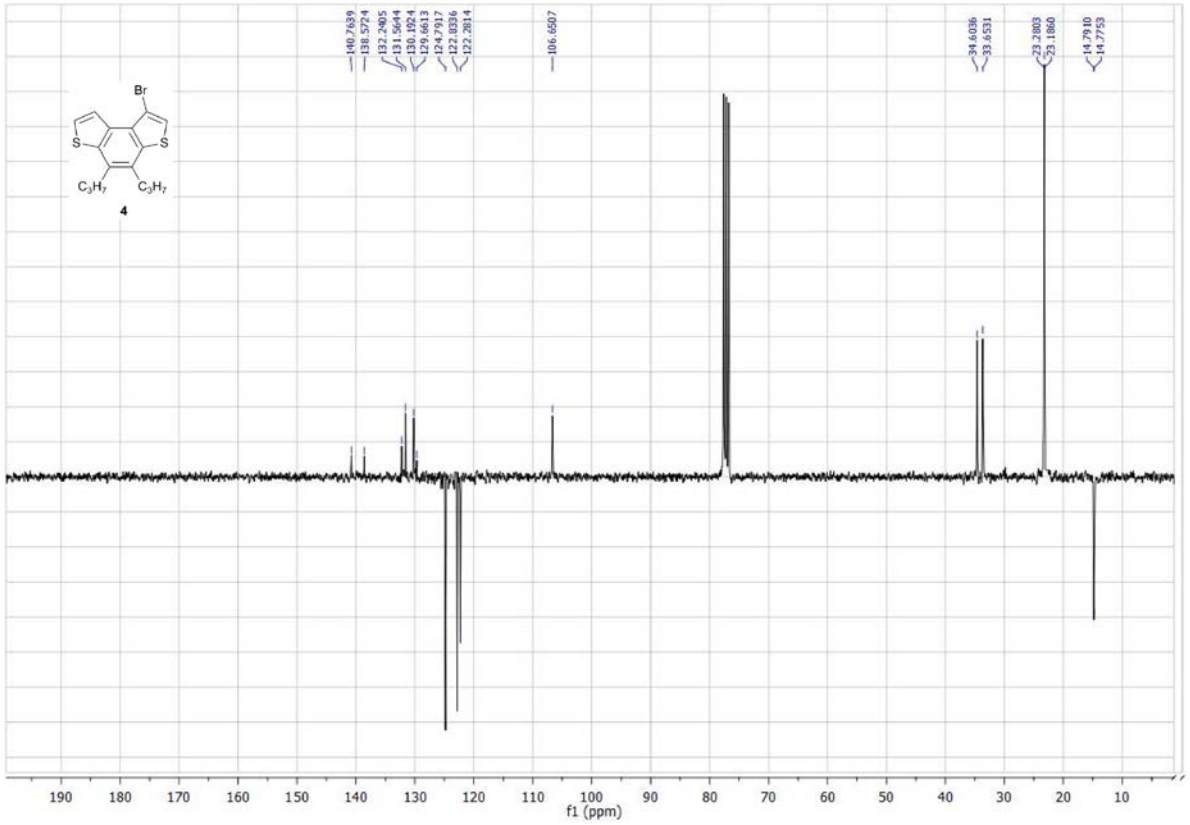
4,5-Dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (2a)



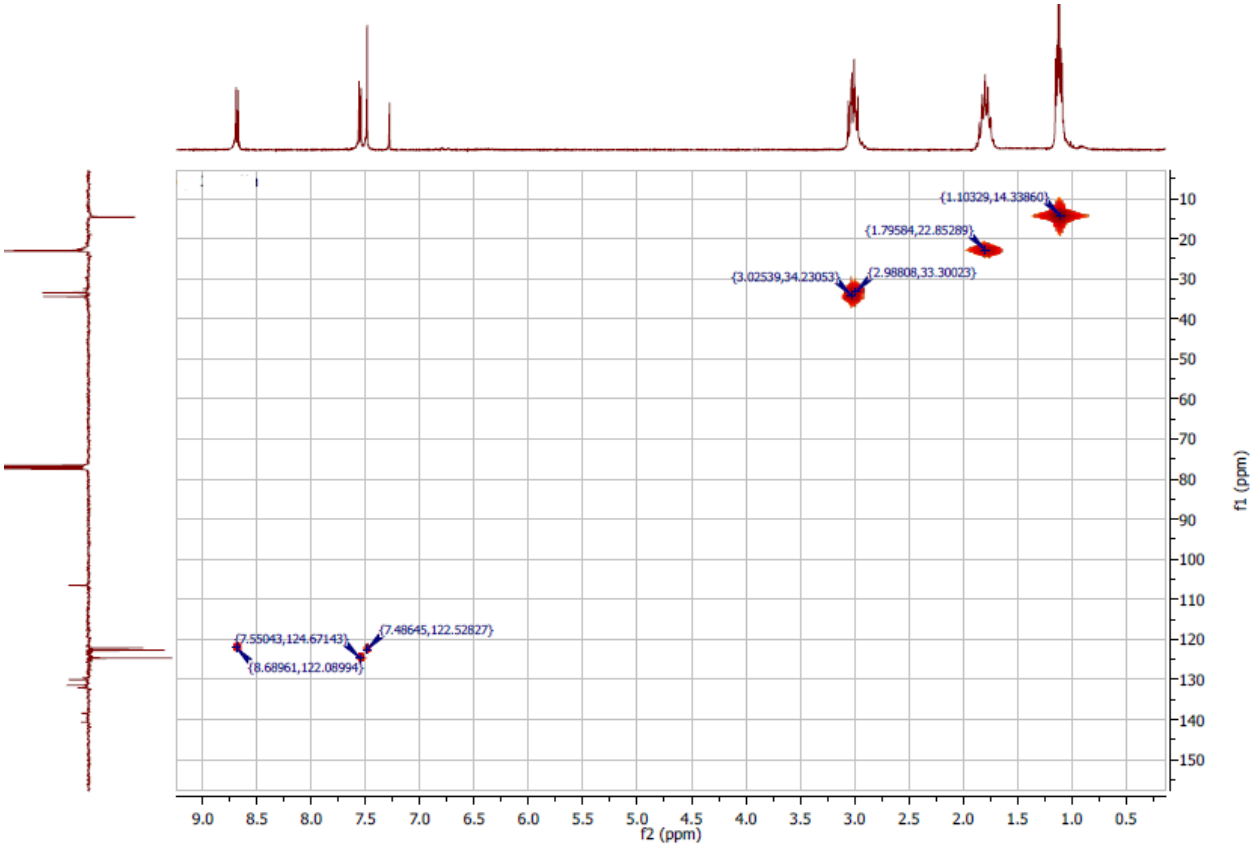


1-Bromo-4,5-dipropylbenzo[1,2-*b*:4,3-*b*′]dithiophene (4)





HSQC NMR of **4**



HMBC NMR of **4**