SUPPORTING INFORMATION

Efficient Conversion of Arylene Precursors into Photoluminescent Phosphonates for Surface Modification of Metal Oxides

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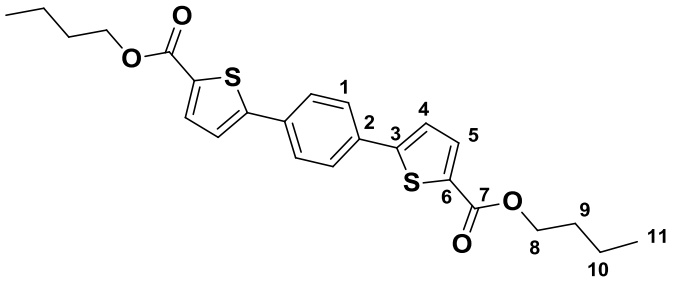
Experimental Procedures

Dibutyl-5,5'-(1,4-phenylene)bis(thiophene-2-carboxylate) (1b)



1,4-Bis(5-iodothiophen-2-yl)benzene (**1a**) (1.00 g, 2.02 mmol) was suspended in anhydrous DMF (10.00 mL) under a nitrogen atmosphere. PPh_3 (0.05 g, 0.17 mmol), anhydrous *n*-butanol (10.0 mL) and Et_3N (1.50 mL) were added to the mixture. After adding $Pd(OAc)_2$ (0.01 g, 0.06 mmol) the autoclave was closed and pressurized with 15 bar of CO. The reaction was stirred at 100 °C for 30 h. After releasing the CO pressure, the reaction mixture was filtered over celite®. Deionized water was added to the filtrate to precipitate the product. The resulting crystals were collected by filtration (yield 0.72 g, 81 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J*= 4.0 Hz, 2H, H5), 7.65 (s, 4H, H1), 7.31 (d, *J*= 4.0 Hz, 2H, H4), 4.31 (t, *J*= 6.8 Hz, 4H, H8), 1.78 – 1.71 (m, 4H, H9), 1.52 – 1.43 (m, 4H, H10), 0.98 (t, *J*= 7.2 Hz, 6H, H11) ppm.

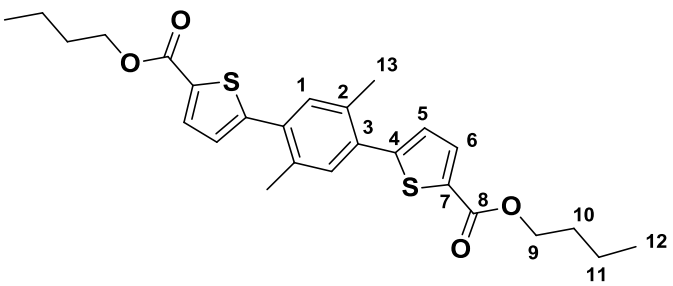
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.3 (C7), 150.0 (C3), 134.3 (C5), 133.8 (C6), 133.1 (C2), 126.8 (C1), 124.0 (C4), 65.2 (C8), 31.0 (C9), 19.3 (C10), 13.4 (C11) ppm.

IR (ATR, cm^{-1}): ν 2960, 2934, 2875, 1689, 1478, 1441.

Elemental analysis: $C_{24}H_{26}O_4S_2$ (442.59 g/mol)

Calculated	**:**	**C:** 65.13 %	**H:** 5.92 %	**S:** 14.49 %
Found	**:**	**C:** 64.87 %	**H:** 5.67 %	**S:** 14.79 %

Dibutyl-5,5`-(2,5-dimethyl-1,4-phenylene)bis(thiophene-2-carboxylate) (2b)



5,5`-(2,5-Dimethyl-1,4-phenylene)bis(2-iodothiophene) (**2a**) (3.00 g, 5.74 mmol) was suspended in anhydrous DMF (30.00 mL) under a nitrogen atmosphere. PPh_3 (0.10 g, 0.40 mmol), anhydrous *n*-butanol (30 mL) and Et_3N (3.00 mL) were added to the mixture. After adding $Pd(OAc)_2$ (0.03 g, 0.13 mmol) the autoclave was closed and pressurized with 15 bar of CO. The reaction was stirred at 100 °C for 30 h. The reaction mixture was filtered over celite®. Deionized water was added to the filtrate to precipitate the product. The resulting crystals were collected by filtration (yield: 2.20 g, 81 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J*= 3.7 Hz, 2H, H6), 7.34 (s, 2H, H1), 7.09 (d, *J*= 3.7 Hz, 2H, H5), 4.32 (t, *J*= 6.6 Hz, 4H, H9), 2.43 (s, 6H, H13), 1.78 – 1.71 (m, 4H, H10), 1.52 – 1.43 (m, 4H, H11), 0.98 (t, *J*= 7.4 Hz, 6H, H12) ppm.

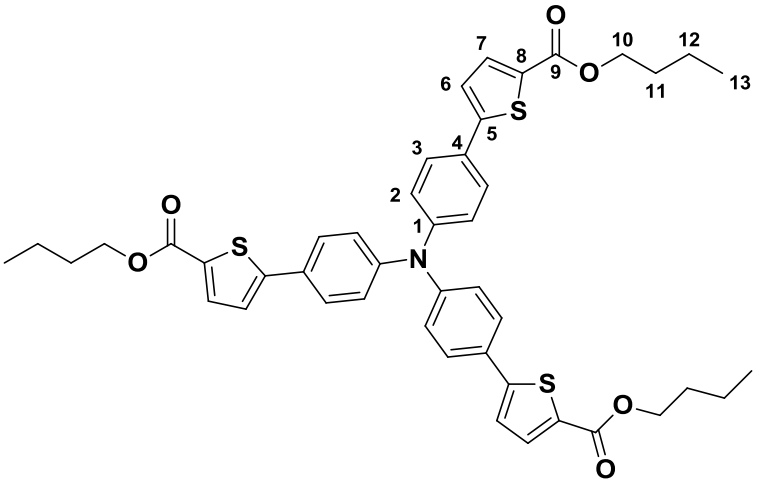
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5 (C8), 149.5 (C4), 133.8, 133.6, 133.6 (C7, C3, C2), 133.5 (C6), 132.9 (C1), 127.4 (C5) 65.2 (C9), 30.9 (C10), 20.7 (C13), 19.3 (C11), 13.9 (C12) ppm.

IR (ATR, cm^{-1}): ν 2959, 2935, 2873, 1697, 1541, 1506, 1450, 1327, 1318, 1254, 1231, 1092.

Elemental analysis: $C_{26}H_{30}O_4S_2$ (470.64 g/mol)

Calculated	**:**	**C:** 66.35 %	**H:** 6.42 %	**S:** 13.63 %
Found	**:**	**C:** 66.28 %	**H:** 6.45 %	**S:** 13.89 %

Tributyl 5,5`,5``-(nitriliotris(benzene-4,1-diyl))tris(thiophene-2-carboxylate) (3b)



Tris (4-(5-iodothiophen-2-yl)phenyl)amine (**3a**) (2.00 g, 2.30 mmol) was suspended in anhydrous DMF (30.00 mL) under a nitrogen atmosphere. PPh_3 (0.10 g, 0.35 mmol), anhydrous *n*-butanol (30 mL) and Et_3N (3.00 mL) were added to the mixture. After adding $Pd(OAc)_2$ (0.02 g, 0.12 mmol) the autoclave was closed and pressurized with 15 bar of CO. The reaction was stirred at 100 °C for 30 h. The reaction mixture was filtered over celite®. Deionized water was added to the filtrate to precipitate the product. The resulting crystals were collected by filtration (yield: 1.50 g, 82 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J*= 3.9 Hz, 3H, H7), 7.56 (d, *J*= 8.6 Hz, 6H, H2), 7.23 (d, *J*= 3.9 Hz, 3H, H6), 7.16 (d, *J*= 8.6 Hz, 6H, H3), 4.31 (t, *J*= 6.6 Hz, 6H, H10), 1.78 – 1.71 (m, 6H, H11), 1.52 – 1.43 (m, 6H, H12), 0.98 (t, *J*= 7.4 Hz, 9H, H13) ppm.

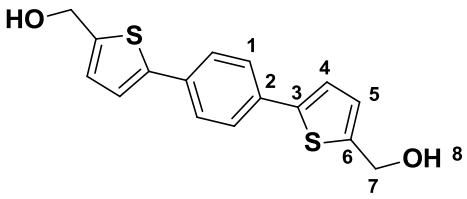
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5 (C9), 150.7 (C5), 147.3 (C1), 134.4 (C7), 132.1 (C8), 128.8 (C4), 127.4 (C3), 124.7 (C2), 123.2 (C6), 65.2 (C10), 30.9 (C11), 19.4 (C12), 13.9 (C13) ppm.

IR (ATR, cm^{-1}): ν 2959, 2934, 2873, 1698, 1443, 1261, 1090, 745, 660.

Elemental analysis: $C_{45}H_{45}NO_6S_3$ (792.04 g/mol)

Calculated	**:**	**C:** 68.24 %	**H:** 5.73 %	**N:** 1.77 %	**S:** 12.15 %
Found	**:**	**C:** 68.14 %	**H:** 5.67 %	**N:** 1.74 %	**S:** 12.34 %

5,5`-(1,4-Phenylene)bis(thiophene-5,2-diyl))dimethanol (1c)



$LiAlH_4$ (10.20 mmol, 0.38 g) was suspended in anhydrous THF (15 mL) under a nitrogen atmosphere. In another flask, 2.40 g (5.10 mmol) of **1b** were dissolved in anhydrous THF (50 mL) and the solution was added to the $LiAlH_4$ suspension. The reaction mixture was refluxed overnight. After cooling to room temperature, deionized water (20 mL) was added and the mixture was poured into a 10 % HCl solution (65 mL) and which then was stirred for 5 h. The resulting yellow precipitate was filtered off, washed with $CHCl_3$ and dried under ambient conditions (yield: 1.43 g, 93 %).

^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 7.64 (s, 4H, H1), 7.37 (d, *J*= 6.0 Hz, 2H, H4), 6.95 (d, *J*= 6.0 Hz, 2H, H5), 4.64 (s, 4H, H7) ppm.

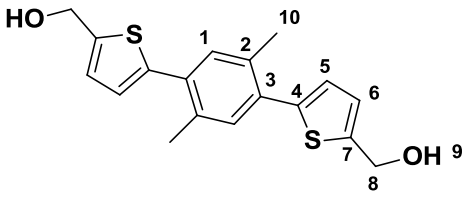
^{13}C NMR (151 MHz, $(CD_3)_2SO$): δ 146.3 (C6), 141.6 (C3), 132.9 (C2), 125.6 (C1), 125.4 (C5), 123.2 (C4), 58.5 (C7) ppm.

IR (ATR, cm^{-1}): ν 3280, 2952, 2870, 1717, 1286, 1109, 768.

Elemental analysis: $C_{16}H_{14}O_2S_2$ (302.41 g/mol)

Calculated	**:**	**C:** 63.55 %	**H:** 4.67 %	**S:** 21.21 %
Found	**:**	**C:** 63.31 %	**H:** 4.62 %	**S:** 21.01 %

5,5`-(2,5-Dimethyl-1,4-phenylene)bis(thiophene-5,2-diyl))dimethanol (2c)



$LiAlH_4$ (11.06 mmol, 0.41 g) was suspended in anhydrous THF (15 mL) under a nitrogen atmosphere. In another flask, 2.60 g (5.53 mmol) of **2b** were dissolved in anhydrous THF (50 mL) and the solution was added to the $LiAlH_4$ suspension. The reaction mixture was refluxed overnight. After cooling to room temperature, deionized water (20 mL) was added and the mixture was poured into a 10.00 % HCl solution (65 mL) and stirred for 5h. Aqueous mixture was extracted with dichloromethane. After stripping off the dichloromethane, obtained oily substance washed with pentane, leading to a yellow precipitate which was filtered off and dried under ambient conditions (yield: 1.63 g, 89 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 2H, H1), 7.00 (d, *J*= 4.0 Hz, 2H, H5), 6.95 (d, *J*= 4.0 Hz, 2H, H6), 4.84 (s, 4H, H8), 2.41 (s, 6H, H10), 2.25 (s, *2*H, H9) ppm.

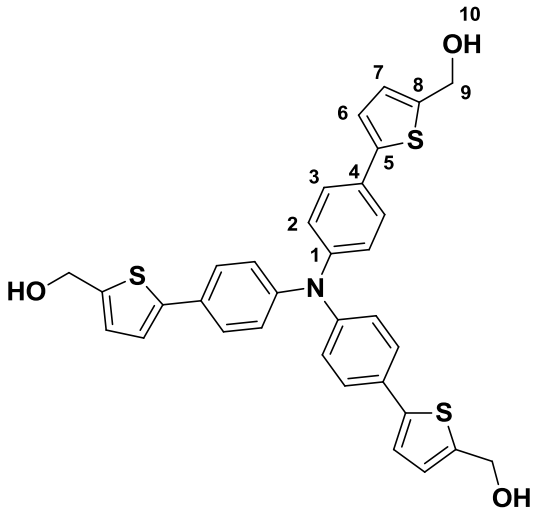
^{13}C NMR (101 MHz, $CDCl_3$): δ 143.8 (C7), 143.1 (C4), 133.6 (C2), 133.4 (C3), 132.7 (C1), 126.4 (C6), 125.8 (C5), 60.2 (C8), 20.7 (C10) ppm.

IR (ATR, cm^{-1}): ν 3264, 2922, 2861, 1002, 811, 734.

Elemental analysis: $C_{18}H_{18}O_2S_2$ (330.46 g/mol)

Calculated	**:**	**C:** 65.42 %	**H:** 5.49 %	**S:** 19.41 %
Found	**:**	**C:** 65.61 %	**H:** 5.64 %	**S:** 18.75 %

5,5`,5``-(Nitrilotris(benzene-4,1-diyl))tris(thiophene-5,2-diyl))trimethanol (3c)



$LiAlH_4$ (5.49 mmol, 0.21 g) was suspended in anhydrous THF (15 mL) under a nitrogen atmosphere. In another flask, 1.45 (1.83 mmol) of **3b** were dissolved in anhydrous THF (50 mL) and the solution was added to the $LiAlH_4$ suspension. The reaction mixture was refluxed overnight. After cooling to room temperature, deionized water (20 mL) was added and the mixture was poured into a 10.00 % HCl solution (60 mL) and stirred for 5 h. The resulting red precipitate was filtered off, washed with $CHCl_3$ and dried under ambient conditions (yield: 0.75 g, 70 %).

^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 7.57 (d, *J*= 8.0 Hz, 6H, H2), 7.26 (d, *J*= 3.0 Hz, 3H, H6), 7.07 (d, *J*= 8.0 Hz, 6H, H3), 6.93 (d, *J*= 3.0 Hz, 3H, H7), 4.62 (s, 6H, H9) ppm.

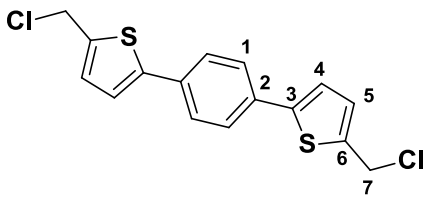
^{13}C NMR (151 MHz, $(CD_3)_2SO$): δ 145.8 (C1), 145.5 (C8), 141.8 (C5), 129.0 (C7), 126.4 (C4), 125.3 (C3), 124.2 (C2), 122.4 (C6), 58.4 (C9) ppm.

IR (ATR, cm^{-1}): ν 3027, 2924, 1506, 1264, 795, 687.

Elemental analysis: $C_{33}H_{27}NO_3S_3$ (581.77 g/mol)

Calculated	**:**	**C:** 68.13 %	**H:** 4.68 %	**N:** 2.41 %	**S:** 16.53 %
Found	**:**	**C:** 68.49 %	**H:** 4.67 %	**N:** 2.37 %	**S:** 16.26 %

1,4-Bis(5-chloromethyl)thiophen-2-yl)benzene (1d)



Oxalyl chloride (13.0 mmol, 1.68 g) was added to anhydrous THF (35 mL), the reaction medium was cooled down to 0 °C and DMF (13.0 mmol, 0.95 g) was dropwise added to the solution. The reaction mixture was warmed up slowly and stirred at room temperature for additional 15 min. The reaction mixture was again cooled down to 0°C, **1c** (1.65 mmol, 0.50 g) was added and the solution was stirred overnight. After stripping off the volatiles, H_2O was added. The resulting yellow precipitate was filtered off and washed with H_2O (yield: 0.50 g, 89 %).

^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 7.69 (s, 4H, H1), 7.44 (d, *J*= 3.5 Hz, 2H, H4), 7.22 (d, *J*= 3.5 Hz, 2H, H5), 5.07 (s, 4H, H7) ppm.

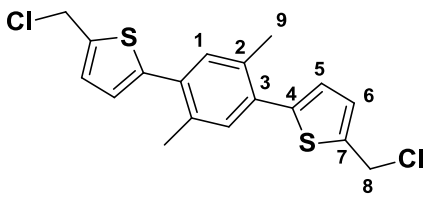
^{13}C NMR (151 MHz, $(CD_3)_2SO$): δ 144.2 (C3), 139.9 (C6), 132.8 (C2), 129.9 (C5), 126.0 (C1), 123.7 (C4), 40.9 (C7) ppm.

IR (ATR, cm^{-1}): ν 2974, 2954, 2865, 697, 660.

Elemental analysis: $C_{16}H_{12}Cl_2S_2$ (339.30 g/mol)

Calculated	**:**	**C:** 56.64 %	**H:** 3.56 %	**S:** 18.90 %
Found	**:**	**C:** 57.56 %	**H:** 3.91 %	**S:** 18.23 %

5,5`-(2,5-Dimethyl-1,4-phenylene)bis(2-(chloromethyl)thiophene) (2d)



Oxalyl chloride (35.00 mmol, 4.52 g) was added to anhydrous THF (75 mL), the reaction medium was cooled down to 0 °C and DMF (35.00 mmol, 2.56 g) was added dropwise to the solution. The reaction mixture was warmed up slowly and stirred at room temperature for additional 15 min. The reaction mixture was again cooled down to 0 °C. **2c** (4.45 mmol, 1.47 g) was added and the solution was stirred overnight. After stripping off the volatiles, deionized water was added. The resulting yellow precipitate was filtered and washed with deionized water (yield: 1.38 g, 84 %).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 (s, 2H, H1), 7.23 (d, *J*= 3.8 Hz, 2H, H5), 7.10 (d, *J*= 3.8 Hz, 2H, H6), 5.07 (s, 4H, H8), 2.38 (s, 6H, H9) ppm.

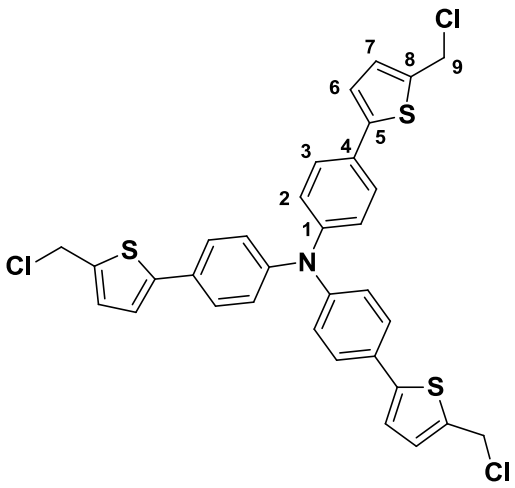
^{13}C NMR (151 MHz, $CDCl_3$): δ 143.2 (C7), 140.2 (C4), 132.9 (C2), 132.7 (C3), 132.2 (C1), 128.9 (C6), 126.7 (C5), 40.8 (C8), 20.3 (C9) ppm.

IR (ATR, cm^{-1}): ν 2954, 2922, 2853, 1664, 1450, 1227, 802, 669.

Elemental analysis: $C_{18}H_{16}Cl_2S_2$ (367.36 g/mol)

Calculated	**:**	**C:** 58.85 %	**H:** 4.39 %	**S:** 17.46 %
Found	**:**	**C:** 59.57 %	**H:** 4.70 %	**S:** 16.04 %

Tris(4-(5-(chloromethyl)thiophen-2-yl)phenyl)amine (3d)



Oxalyl chloride (10.31 mmol, 1.31 g) was added to anhydrous THF (30 mL), the solution was cooled down to 0 °C and DMF (10.31 mmol, 0.75 g) was added dropwise to the solution. The reaction mixture was warmed up slowly and stirred at room temperature for additional 15 min. The reaction mixture was again cooled down to 0 °C. **3c** (0.50 g, 0.86 mmol) was added and the mixture was stirred overnight. After stripping off the volatiles, deionized water was added. The resulting dark red precipitate was filtered and washed with deionized water (yield: 0.45 g, 81 %).

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 7.57 (d, *J*= 7.6 Hz, 6H, H2), 7.28 (s, 3H, H6), 7.17 (s, 3H, H7), 7.06 (d, *J*= 7.6 Hz, 6H, H3), 5.03 (s, 6H, H9) ppm.

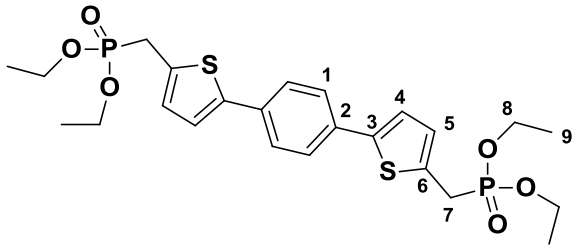
^{13}C NMR (101 MHz, $(CD_3)_2SO$): δ 146.1 (C1), 144.6 (C8), 139.0 (C5), 129.8 (C7), 128.4 (C4), 126.7 (C3), 124.2 (C2), 122.7 (C6), 41.1 (C9) ppm.

IR (ATR, cm^{-1}): ν 3027, 2924, 1507, 1255, 796, 657.

Elemental analysis: $C_{33}H_{24}Cl_3NS_3$ (637.10 g/mol)

Calculated	**:**	**C:** 62.21 %	**H:** 3.80 %	**N:** 2.20 %	**S:** 15.10 %
Found	**:**	**C:** 61.78 %	**H:** 4.24 %	**N:** 2.01 %	**S:** 15.21 %

Tetraethyl-((5,5`-(1,4-phenylene)bis(thiophene-5,2-diyl)) bis(methylene))bis(phosphonate) (1e)



0.50 g (1.47 mmol) of **1d** was placed in a Schlenk tube, 7.58 g (44.10 mmol) of triethyl phosphite were added and the reaction medium was heated to 120 °C for 72 h with continuous stirring. All volatiles were removed *in vacuo*. The remaining yellow solid was washed several times with *n*-pentane and dried at ambient conditions (yield: 0.43 g, 54 %).

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 7.63 (s, 4H, H1), 7.40 (d, *J*= 3.6 Hz, 2H, H4), 6.97 (t, *J*= 3.6 Hz, 2H, H5), 4.02 (dq, $^{3}J_{PH}$= 14.0 Hz, $^{3}J_{HH}$= 7.0 Hz, 8H, H8), 3.52 (d, $^{2}J_{PH}$= 20.8 Hz, 4H, H7), 1.22 (t, *J*= 7.0 Hz, 12H, H9) ppm.

^{13}C NMR (101 MHz, $(CD_3)_2SO$): δ 141.7 (d, $^{5}J_{PC}$= 4.2 Hz, C3), 133.3 (d, $^{2}J_{PC}$= 10.8 Hz, C6), 132.7 (s, C2), 128.8 (d, $^{3}J_{PC}$= 9.1 Hz, C5), 125.6 (s, C1), 123.5 (d, $^{4}J_{PC}$= 3.4 Hz, C4), 61.7 (d, $^{2}J_{PC}$= 6.5 Hz, C8), 27.1 (d, $^{1}J_{PC}$= 139.9 Hz, C7), 16.2 (d, $^{3}J_{PC}$= 5.6 Hz, C9) ppm.

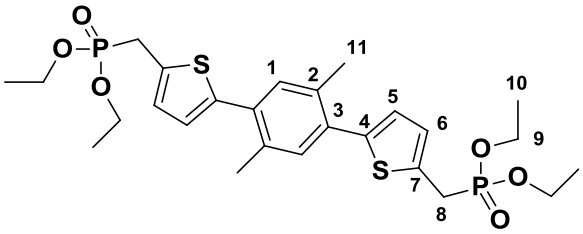
^{31}P NMR (162 MHz, $(CD_3)_2SO$): δ 24.35 ppm.

IR (ATR, cm^{-1}): ν 3069, 2931, 1443, 1163, 1021, 952, 712.

Elemental analysis: $C_{24}H_{32}O_6P_2S_2$ (542.58 g/mol)

Calculated	**:**	**C:** 53.13 %	**H:** 5.94 %	**S:** 11.82 %
Found	**:**	**C:** 54.53 %	**H:** 5.47 %	**S:** 12.97 %

Tetraethyl-((5,5`-(2,5-dimethyl-1,4-phenylene)bis(thiophene-5,2-diyl))bis(methylene))bis(phosphonate) (2e)



0.50 g (1.36 mmol) **2d** was placed in a Schlenk tube, 6.81 g (41.00 mmol) of triethyl phosphite were added and the reaction mixture was heated to 120 °C for 72 h under continuous stirring. All volatiles were removed *in vacuo*. The remaining yellow solid was washed several times with pentane and dried at ambient conditions (yield: 0.40 g. 51 %).

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 7.31 (s, 2H, H1), 7.09 (d, *J*= 3.6 Hz, 2H, H5), 6.99 (t, *J*= 3.6 Hz, 2H, H6), 4.02 (dq, $^{3}J_{PH}$= 14.1, $^{2}J_{HH}$= 7.1 Hz, 8H, H9), 3.52 (d, $^{2}J_{PH}$= 20.8 Hz, 4H, H8), 2.38 (s, 6H, H11), 1.22 (t, *J*= 7.0 Hz, 12H, H10) ppm.

^{13}C NMR (151 MHz, $(CD_3)_2SO$): δ 140.7 (d, $^{5}J_{PC}$= 3.5 Hz, C4), 133.5 (d, $^{2}J_{PC}$= 10.2 Hz, C7), 132.7 (s, C2), 132.7 (s, C3), 132.0 (s, C1), 127.8 (d, $^{3}J_{PC}$= 9.0 Hz, C6), 126.6 (d, $^{4}J_{PC}$= 2.3 Hz, C5), 61.7 (d, $^{2}J_{PC}$= 6.2 Hz, C9), 26.8 (d, $^{1}J_{PC}$= 135.9 Hz, C8), 20.4 (s, C11), 16.2 (d, $^{3}J_{PC}$= 5.7 Hz, C10) ppm.

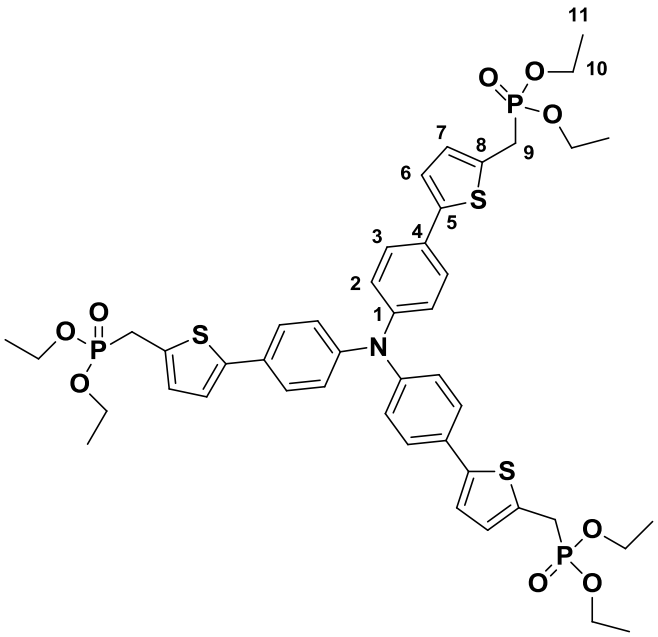
^{31}P NMR (162 MHz, $(CD_3)_2SO$): δ 24.48 ppm.

IR (ATR, cm^{-1}): ν 3062, 2905, 1436, 1246, 1182, 1151, 1019, 959, 699.

Elemental analysis: $C_{26}H_{36}O_6P_2S_2$ (570.64 g/mol)

Calculated	**:**	**C:** 54.72 %	**H:** 6.36 %	**S:** 11.24 %
Found	**:**	**C:** 54.62 %	**H:** 6.25 %	**S:** 11.23 %

Hexaethyl((5,5`,5``-(nitrilotris(benzene-4,1-diyl))tris(thiophene-5,2-diyl))tris(methylene)tris(phosphonate) (3e)



0.20 g (0.31 mmol) of **3d** was placed in a Schlenk tube, 3.39 g (13.95 mmol) of triethyl phosphite were added and the reaction medium was heated to 120 °C for 72 h under continuous stirring. All volatiles were removed *in vacuo*. The remaining yellow solid was washed several times with pentane and dried under vacuum (yield: 0.16 g, 55 %).

^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 7.55 (d, *J*= 8.5 Hz, 6H, H2), 7.27 (d, *J*= 3.4 Hz, 3H, H6), 7.07 (d, *J*= 8.5 Hz, 6H, H3), 6.95 – 6.93 (m, 3H, H7), 4.04 – 3.96 (m, 12H, H10), 3.50 (d, $^{2}J_{PH}$= 20.8 Hz, 6H, H9), 1.21 (t, *J*= 7.1 Hz, 18H, H11) ppm.

^{13}C NMR (101 MHz, $(CD_3)_2SO$): δ 145.8 (C1), 142.0 (C8), 136.8 (C5), 132.6 (C5), 128.7 (C4), 126.3 (C3), 124.2 (C2), 122.7 (C6), 61.7 (d, $^{2}J_{PC}$= 6.4 Hz, C10), 27.0 (d, $^{1}J_{PC}$= 139.6 Hz, C9), 16.3 (d, $^{3}J_{PC}$= 5.6 Hz, C11) ppm.

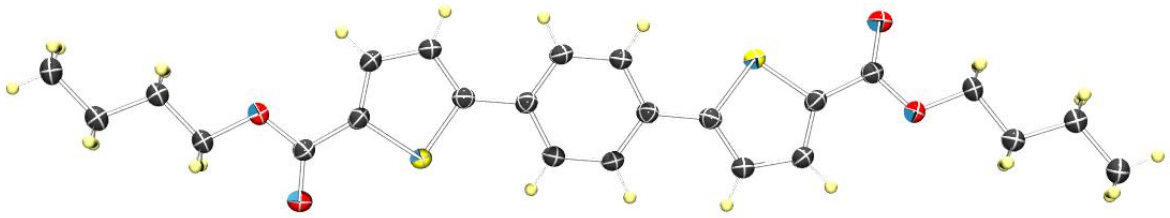
IR (ATR, cm^{-1}): ν 2958, 2541, 1658, 1533, 1441, 1263, 734.

Elemental analysis: $C_{45}H_{54}NO_9P_3S_3$ (942.03 g/mol)

Calculated	**:**	**C:** 57.37 %	**H:** 5.78 %	**N:** 1.49 %	**S:** 10.21 %
Found	**:**	**C:** 58.96 %	**H:** 4.91 %	**N:** 1.80 %	**S:** 12.09 %

Crystallographic data

Dibutyl-5,5'-(1,4-phenylene)bis(thiophene-2-carboxylate) (1b)



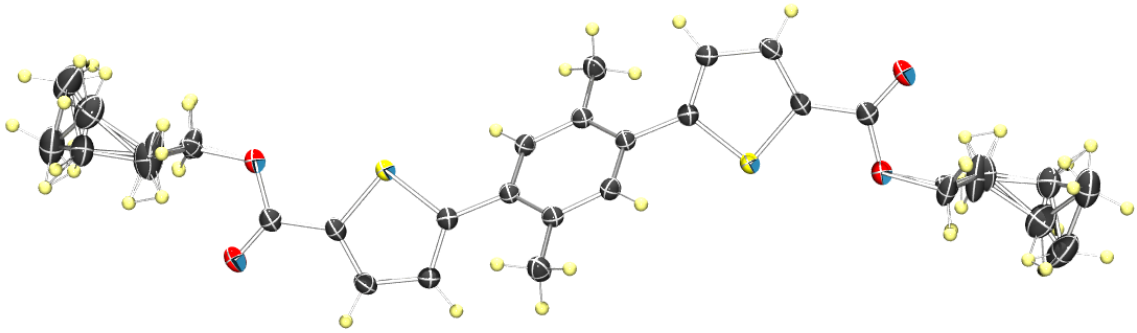
	1b
Empirical formula	$C_{24}H_{26}O_4S_2$
Formula weight [g × mol^{-1}]	442.57
Crystal size	0.31 × 0.12 × 0.06 mm^3
T [K]	150(2)
λ [Å]	1.54184
Crystal system	triclinic
Space group	P-1
a [Å]	8.5601(5)
b[Å]	11.8606(9)
c[Å]	12.1527(6)
α [°]	110.052(6)
β [°]	90.591(5)
γ [°]	108.776(6)
V [Å^3]	1087.22(14)
Z	2
$\rho_{calc.}$ [g × cm^{-1}]	1.352
μ [mm^{-1}]	2.452
θ-range [°]	3.91 to 62.65
Reflections collected	6517
Independent reflections	3424 [R(int) = 0.0226]
Data/restraints/parameters	3424 / 0 / 273
Final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0362, ωR2 = 0.1044
R indices (all data)	R1 = 0.0416, ωR2 = 0.1073
GooF[b]	1.069
$\Delta\rho_{max./min.}$ [e Å^{-3}]	0.350 and -0.178

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $\omega R_2 = [\Sigma\omega(F_o^2-F_c^2)^2/\Sigma\omega(F_o)^2]^{1/2}$. [b] GooF = $[\Sigma\omega(F_o^2-F_c^2)^2/(n-p)]^{1/2}$.

Bond lengths [Å] and angles [°] for **1b**.

C(1)-C(2)	1.525(3)	C(23)-H(23A)	0.9900	C(14)-C(13)-C(12)	117.90(16)
C(1)-H(1A)	0.9800	C(23)-H(23B)	0.9900	C(14)-C(13)-C(16)	120.42(15)
C(1)-H(1B)	0.9800	C(24)-H(24A)	0.9800	C(12)-C(13)-C(16)	121.67(15)
C(1)-H(1C)	0.9800	C(24)-H(24B)	0.9800	C(15)-C(14)-C(13)	121.26(16)
C(2)-C(3)	1.515(3)	C(24)-H(24C)	0.9800	C(15)-C(14)-H(14)	119.4
C(2)-H(2A)	0.9900	C(2)-C(1)-H(1A)	109.5	C(13)-C(14)-H(14)	119.4
C(2)-H(2B)	0.9900	C(2)-C(1)-H(1B)	109.5	C(14)-C(15)-C(10)	120.95(17)
C(3)-C(4)	1.509(2)	H(1A)-C(1)-H(1B)	109.5	C(14)-C(15)-H(15)	119.5
C(3)-H(3A)	0.9900	C(2)-C(1)-H(1C)	109.5	C(10)-C(15)-H(15)	119.5
C(3)-H(3B)	0.9900	H(1A)-C(1)-H(1C)	109.5	C(17)-C(16)-C(13)	128.33(16)
C(4)-O(1)	1.451(2)	H(1B)-C(1)-H(1C)	109.5	C(17)-C(16)-S(2)	110.41(13)
C(4)-H(4A)	0.9900	C(3)-C(2)-C(1)	112.10(15)	C(13)-C(16)-S(2)	121.26(13)
C(4)-H(4B)	0.9900	C(3)-C(2)-H(2A)	109.2	C(16)-C(17)-C(18)	113.21(16)
C(5)-O(2)	1.204(2)	C(1)-C(2)-H(2A)	109.2	C(16)-C(17)-H(17)	123.4
C(5)-O(1)	1.347(2)	C(3)-C(2)-H(2B)	109.2	C(18)-C(17)-H(17)	123.4
C(5)-C(6)	1.470(2)	C(1)-C(2)-H(2B)	109.2	C(19)-C(18)-C(17)	112.93(16)
C(6)-C(7)	1.363(2)	H(2A)-C(2)-H(2B)	107.9	C(19)-C(18)-H(18)	123.5
C(6)-S(1)	1.7203(17)	C(4)-C(3)-C(2)	112.32(15)	C(17)-C(18)-H(18)	123.5
C(7)-C(8)	1.401(3)	C(4)-C(3)-H(3A)	109.1	C(18)-C(19)-C(20)	129.63(16)
C(7)-H(7)	0.9500	C(2)-C(3)-H(3A)	109.1	C(18)-C(19)-S(2)	111.60(14)
C(8)-C(9)	1.382(2)	C(4)-C(3)-H(3B)	109.1	C(20)-C(19)-S(2)	118.76(13)
C(8)-H(8)	0.9500	C(2)-C(3)-H(3B)	109.1	O(4)-C(20)-O(3)	124.19(16)
C(9)-C(10)	1.464(3)	H(3A)-C(3)-H(3B)	107.9	O(4)-C(20)-C(19)	124.95(16)
C(9)-S(1)	1.7259(18)	O(1)-C(4)-C(3)	107.52(14)	O(3)-C(20)-C(19)	110.86(14)
C(10)-C(11)	1.398(2)	O(1)-C(4)-H(4A)	110.2	O(3)-C(21)-C(22)	106.72(14)
C(10)-C(15)	1.403(2)	C(3)-C(4)-H(4A)	110.2	O(3)-C(21)-H(21A)	110.4
C(11)-C(12)	1.379(2)	O(1)-C(4)-H(4B)	110.2	C(22)-C(21)-H(21A)	110.4
C(11)-H(11)	0.9500	C(3)-C(4)-H(4B)	110.2	O(3)-C(21)-H(21B)	110.4
C(12)-C(13)	1.404(2)	H(4A)-C(4)-H(4B)	108.5	C(22)-C(21)-H(21B)	110.4
C(12)-H(12)	0.9500	O(2)-C(5)-O(1)	123.90(16)	H(21A)-C(21)-H(21B)	108.6
C(13)-C(14)	1.395(2)	O(2)-C(5)-C(6)	124.29(16)	C(21)-C(22)-C(23)	110.93(15)
C(13)-C(16)	1.467(2)	O(1)-C(5)-C(6)	111.81(14)	C(21)-C(22)-H(22A)	109.5
C(14)-C(15)	1.375(3)	C(7)-C(6)-C(5)	131.35(16)	C(23)-C(22)-H(22A)	109.5
C(14)-H(14)	0.9500	C(7)-C(6)-S(1)	111.35(13)	C(21)-C(22)-H(22B)	109.5
C(15)-H(15)	0.9500	C(5)-C(6)-S(1)	117.30(13)	C(23)-C(22)-H(22B)	109.5
C(16)-C(17)	1.377(2)	C(6)-C(7)-C(8)	113.15(15)	H(22A)-C(22)-H(22B)	108.0
C(16)-S(2)	1.7292(17)	C(6)-C(7)-H(7)	123.4	C(22)-C(23)-C(24)	112.64(16)
C(17)-C(18)	1.406(3)	C(8)-C(7)-H(7)	123.4	C(22)-C(23)-H(23A)	109.1
C(17)-H(17)	0.9500	C(9)-C(8)-C(7)	113.11(16)	C(24)-C(23)-H(23A)	109.1
C(18)-C(19)	1.359(2)	C(9)-C(8)-H(8)	123.4	C(22)-C(23)-H(23B)	109.1
C(18)-H(18)	0.9500	C(7)-C(8)-H(8)	123.4	C(24)-C(23)-H(23B)	109.1
C(19)-C(20)	1.473(2)	C(8)-C(9)-C(10)	129.05(16)	H(23A)-C(23)-H(23B)	107.8
C(19)-S(2)	1.7205(17)	C(8)-C(9)-S(1)	110.37(14)	C(23)-C(24)-H(24A)	109.5
C(20)-O(4)	1.205(2)	C(10)-C(9)-S(1)	120.58(13)	C(23)-C(24)-H(24B)	109.5
C(20)-O(3)	1.347(2)	C(11)-C(10)-C(15)	117.94(16)	H(24A)-C(24)-H(24B)	109.5
C(21)-O(3)	1.448(2)	C(11)-C(10)-C(9)	120.91(15)	C(23)-C(24)-H(24C)	109.5
C(21)-C(22)	1.513(2)	C(15)-C(10)-C(9)	121.13(16)	H(24A)-C(24)-H(24C)	109.5
C(21)-H(21A)	0.9900	C(12)-C(11)-C(10)	121.01(16)	H(24B)-C(24)-H(24C)	109.5
C(21)-H(21B)	0.9900	C(12)-C(11)-H(11)	119.5	C(5)-O(1)-C(4)	115.21(13)
C(22)-C(23)	1.516(3)	C(10)-C(11)-H(11)	119.5	C(20)-O(3)-C(21)	115.70(13)
C(22)-H(22A)	0.9900	C(11)-C(12)-C(13)	120.94(16)	C(6)-S(1)-C(9)	92.02(8)
C(22)-H(22B)	0.9900	C(11)-C(12)-H(12)	119.5	C(19)-S(2)-C(16)	91.85(8)
C(23)-C(24)	1.520(3)	C(13)-C(12)-H(12)	119.5		

Dibutyl-5,5`-(2,5-dimethyl-1,4-phenylene)bis(thiophene-2-carboxylate) (2b)



	2b
Empirical formula	$C_{26}H_{30}O_4S_2$
Formula weight [g × mol^{-1}]	470.62
Crystal size	0.14 × 0.08 × 0.07 mm^3
T [K]	150(2)
λ [Å]	1.54184
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	12.8645(3)
b[Å]	6.0509(1)
c[Å]	15.8520(4)
α [°]	90
β [°]	96.708(2)
γ [°]	90
V [Å^3]	1225.50(5)
Z	2
$\rho_{calc.}$ [g × cm^{-1}]	1.275
μ [mm^{-1}]	2.205
θ-range [°]	4.19 to 62.62
Reflections collected	7561
Independent reflections	1949 [R(int) = 0.0221]
Data/restraints/parameters	1949 / 120 / 186
Final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0263, ωR2 = 0.0732
R indices (all data)	R1 = 0.0309, ωR2 = 0.0745
GooF[b]	1.059
$\Delta\rho_{max./min.}$ [e Å^{-3}]	0.264 and -0.192

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $\omega R_2 = [\Sigma\omega(F_o^2-F_c^2)^2/\Sigma\omega(F_o)^2]^{1/2}$. [b] GooF = $[\Sigma\omega(F_o^2-F_c^2)^2/(n-p)]^{1/2}$.

Bond lengths [Å] and angles [°] for **2b**.

C(1)-C(2)	1.502(8)	C(4)-C(3)-H(3A)	110.8	C(6)-S(1)-C(9)	92.05(7)
C(1)-H(1A)	0.9800	C(2)-C(3)-H(3A)	110.8	C(12)-C(10)-C(11)	119.54(12)
C(1)-H(1B)	0.9800	C(4)-C(3)-H(3B)	110.8	C(12)-C(10)-C(9)	118.34(12)
C(1)-H(1C)	0.9800	C(2)-C(3)-H(3B)	110.8	C(11)-C(10)-C(9)	122.12(12)
C(2)-C(3)	1.624(12)	H(3A)-C(3)-H(3B)	108.9	C(12)#1-C(11)-C(10)	117.29(12)
C(2)-H(2A)	0.9900	O(1)-C(4)-C(3)	120.2(12)	C(12)#1-C(11)-C(13)	119.50(12)
C(2)-H(2B)	0.9900	O(1)-C(4)-H(4A)	107.3	C(10)-C(11)-C(13)	123.20(12)
C(3)-C(4)	1.518(12)	C(3)-C(4)-H(4A)	107.3	C(11)#1-C(12)-C(10)	123.18(12)
C(3)-H(3A)	0.9900	O(1)-C(4)-H(4B)	107.3	C(11)#1-C(12)-H(12)	118.4
C(3)-H(3B)	0.9900	C(3)-C(4)-H(4B)	107.3	C(10)-C(12)-H(12)	118.4
C(4)-O(1)	1.443(11)	H(4A)-C(4)-H(4B)	106.9	C(11)-C(13)-H(13A)	109.5
C(4)-H(4A)	0.9900	C(2A)-C(1A)-H(1D)	109.5	C(11)-C(13)-H(13B)	109.5
C(4)-H(4B)	0.9900	C(2A)-C(1A)-H(1E)	109.5	H(13A)-C(13)-H(13B)	109.5
C(1A)-C(2A)	1.526(5)	H(1D)-C(1A)-H(1E)	109.5	C(11)-C(13)-H(13C)	109.5
C(1A)-H(1D)	0.9800	C(2A)-C(1A)-H(1F)	109.5	H(13A)-C(13)-H(13C)	109.5
C(1A)-H(1E)	0.9800	H(1D)-C(1A)-H(1F)	109.5	H(13B)-C(13)-H(13C)	109.5
C(1A)-H(1F)	0.9800	H(1E)-C(1A)-H(1F)	109.5		
C(2A)-C(3A)	1.591(8)	C(1A)-C(2A)-C(3A)	105.5(5)		
C(2A)-H(2C)	0.9900	C(1A)-C(2A)-H(2C)	110.7		
C(2A)-H(2D)	0.9900	C(3A)-C(2A)-H(2C)	110.7		
C(3A)-C(4A)	1.518(9)	C(1A)-C(2A)-H(2D)	110.7		
C(3A)-H(3C)	0.9900	C(3A)-C(2A)-H(2D)	110.7		
C(3A)-H(3D)	0.9900	H(2C)-C(2A)-H(2D)	108.8		
C(4A)-O(1)	1.475(7)	C(4A)-C(3A)-C(2A)	111.1(7)		
C(4A)-H(4C)	0.9900	C(4A)-C(3A)-H(3C)	109.4		
C(4A)-H(4D)	0.9900	C(2A)-C(3A)-H(3C)	109.4		
O(1)-C(5)	1.3445(18)	C(4A)-C(3A)-H(3D)	109.4		
C(5)-O(2)	1.2071(17)	C(2A)-C(3A)-H(3D)	109.4		
C(5)-C(6)	1.4662(19)	H(3C)-C(3A)-H(3D)	108.0		
C(6)-C(7)	1.367(2)	O(1)-C(4A)-C(3A)	105.5(8)		
C(6)-S(1)	1.7207(13)	O(1)-C(4A)-H(4C)	110.6		
C(7)-C(8)	1.410(2)	C(3A)-C(4A)-H(4C)	110.6		
C(7)-H(7)	0.9500	O(1)-C(4A)-H(4D)	110.6		
C(8)-C(9)	1.3686(19)	C(3A)-C(4A)-H(4D)	110.6		
C(8)-H(8)	0.9500	H(4C)-C(4A)-H(4D)	108.8		
C(9)-C(10)	1.4794(18)	C(5)-O(1)-C(4)	115.2(7)		
C(9)-S(1)	1.7220(13)	C(5)-O(1)-C(4A)	117.6(6)		
C(10)-C(12)	1.3964(19)	C(4)-O(1)-C(4A)	7.1(13)		
C(10)-C(11)	1.4037(19)	O(2)-C(5)-O(1)	124.21(13)		
C(11)-C(12)#1	1.3899(19)	O(2)-C(5)-C(6)	124.04(13)		
C(11)-C(13)	1.5090(19)	O(1)-C(5)-C(6)	111.73(11)		
C(12)-C(11)#1	1.3899(19)	C(7)-C(6)-C(5)	126.37(12)		
C(12)-H(12)	0.9500	C(7)-C(6)-S(1)	111.28(10)		
C(13)-H(13A)	0.9800	C(5)-C(6)-S(1)	122.33(10)		
C(13)-H(13B)	0.9800	C(6)-C(7)-C(8)	112.59(12)		
C(13)-H(13C)	0.9800	C(6)-C(7)-H(7)	123.7		
C(1)-C(2)-C(3)	102.2(9)	C(8)-C(7)-H(7)	123.7		
C(1)-C(2)-H(2A)	111.3	C(9)-C(8)-C(7)	113.37(13)		
C(3)-C(2)-H(2A)	111.3	C(9)-C(8)-H(8)	123.3		
C(1)-C(2)-H(2B)	111.3	C(7)-C(8)-H(8)	123.3		
C(3)-C(2)-H(2B)	111.3	C(8)-C(9)-C(10)	129.79(12)		
H(2A)-C(2)-H(2B)	109.2	C(8)-C(9)-S(1)	110.71(10)		
C(4)-C(3)-C(2)	104.6(10)	C(10)-C(9)-S(1)	119.45(10)		

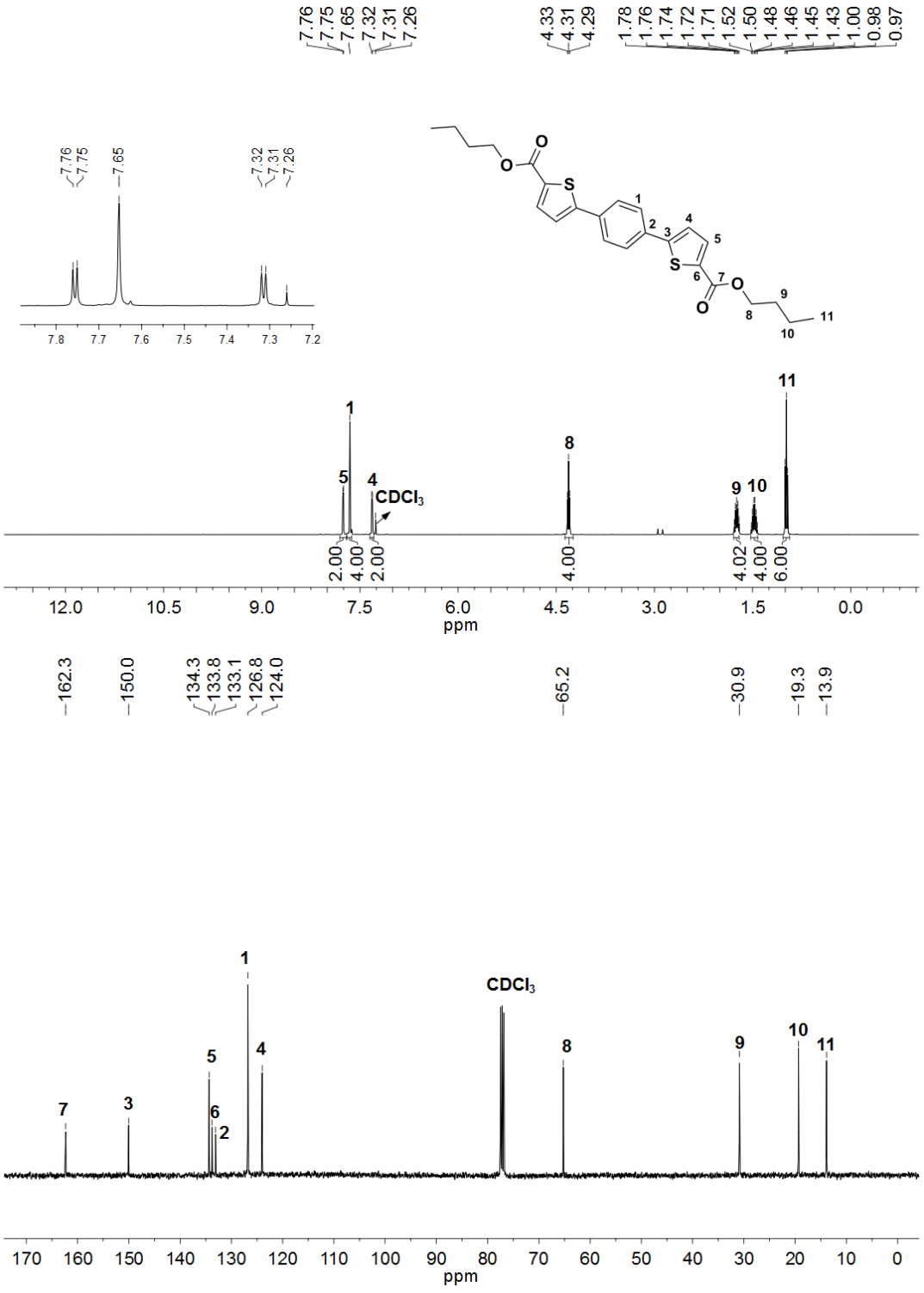
Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

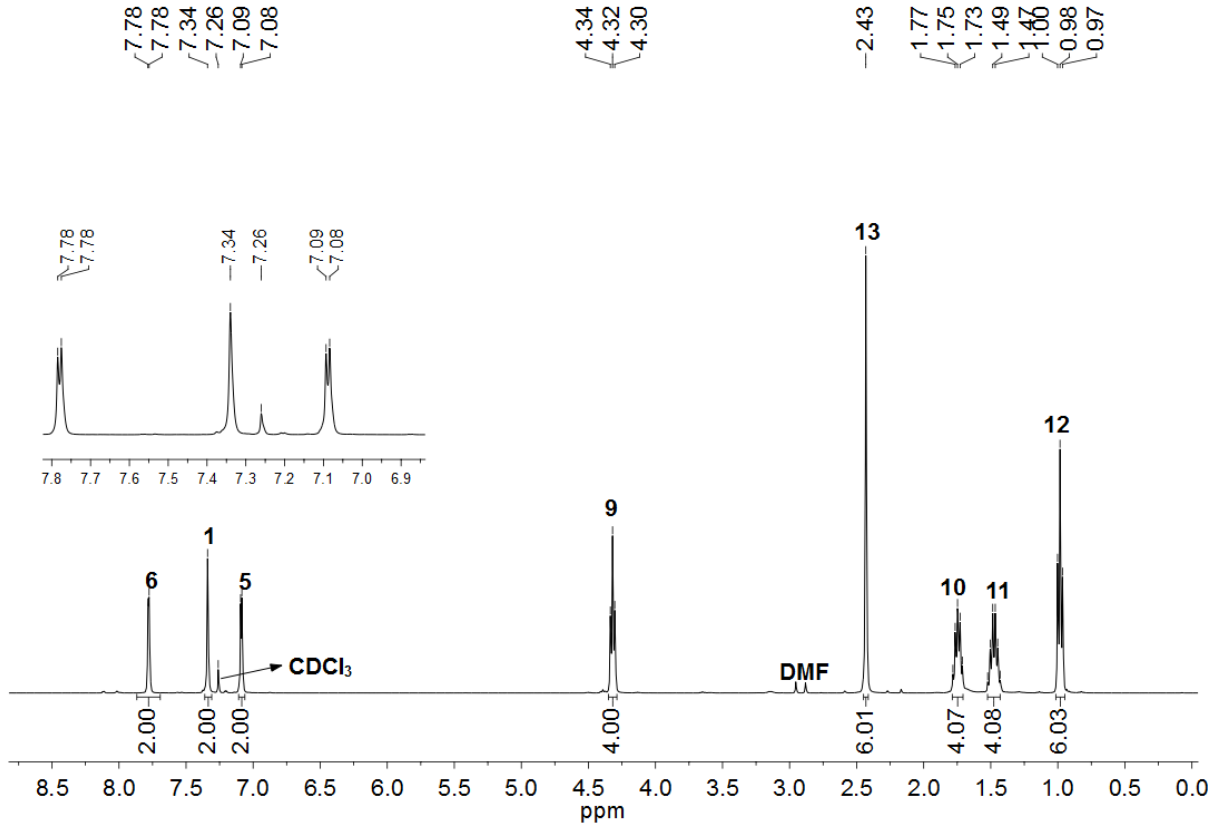
NMR spectra

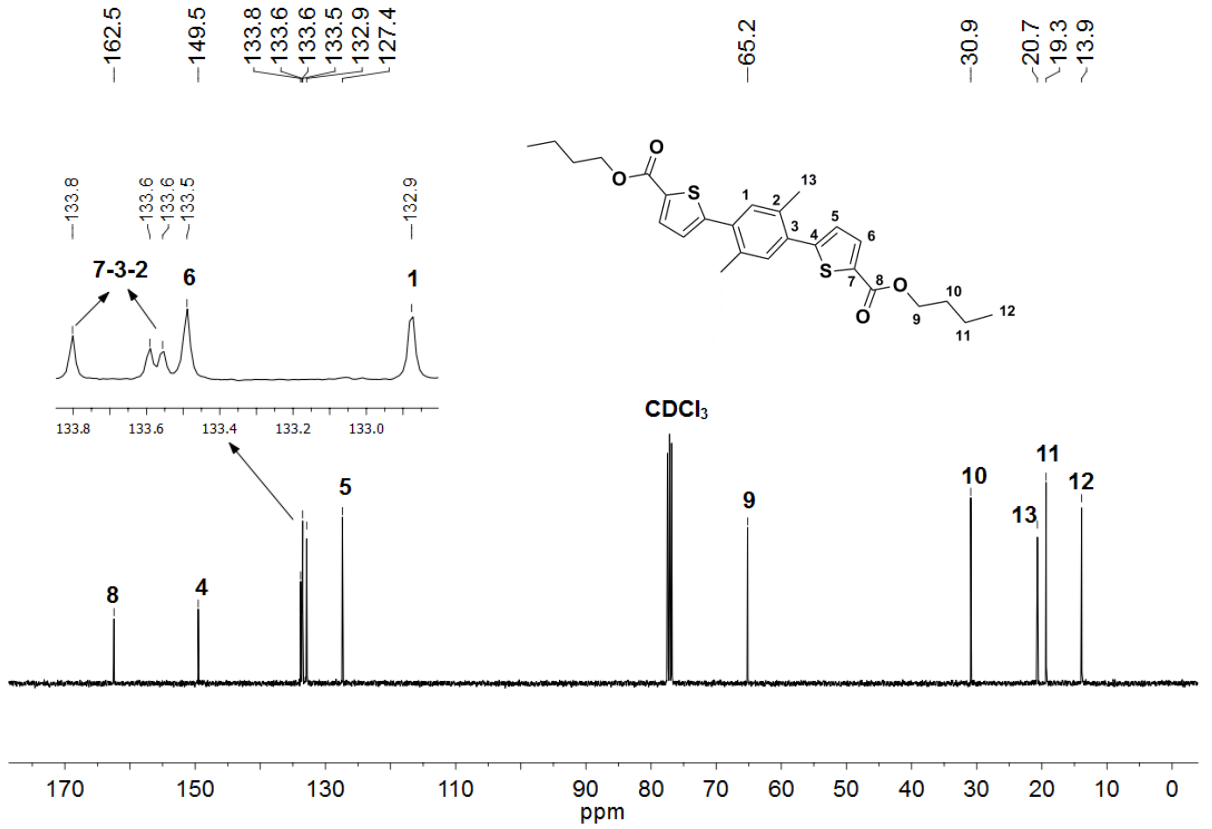
(The assignments of the carbon resonances were done by HMBC and HMQC techniques.)

Dibutyl-5,5'-(1,4-phenylene)bis(thiophene-2-carboxylate) (1b)

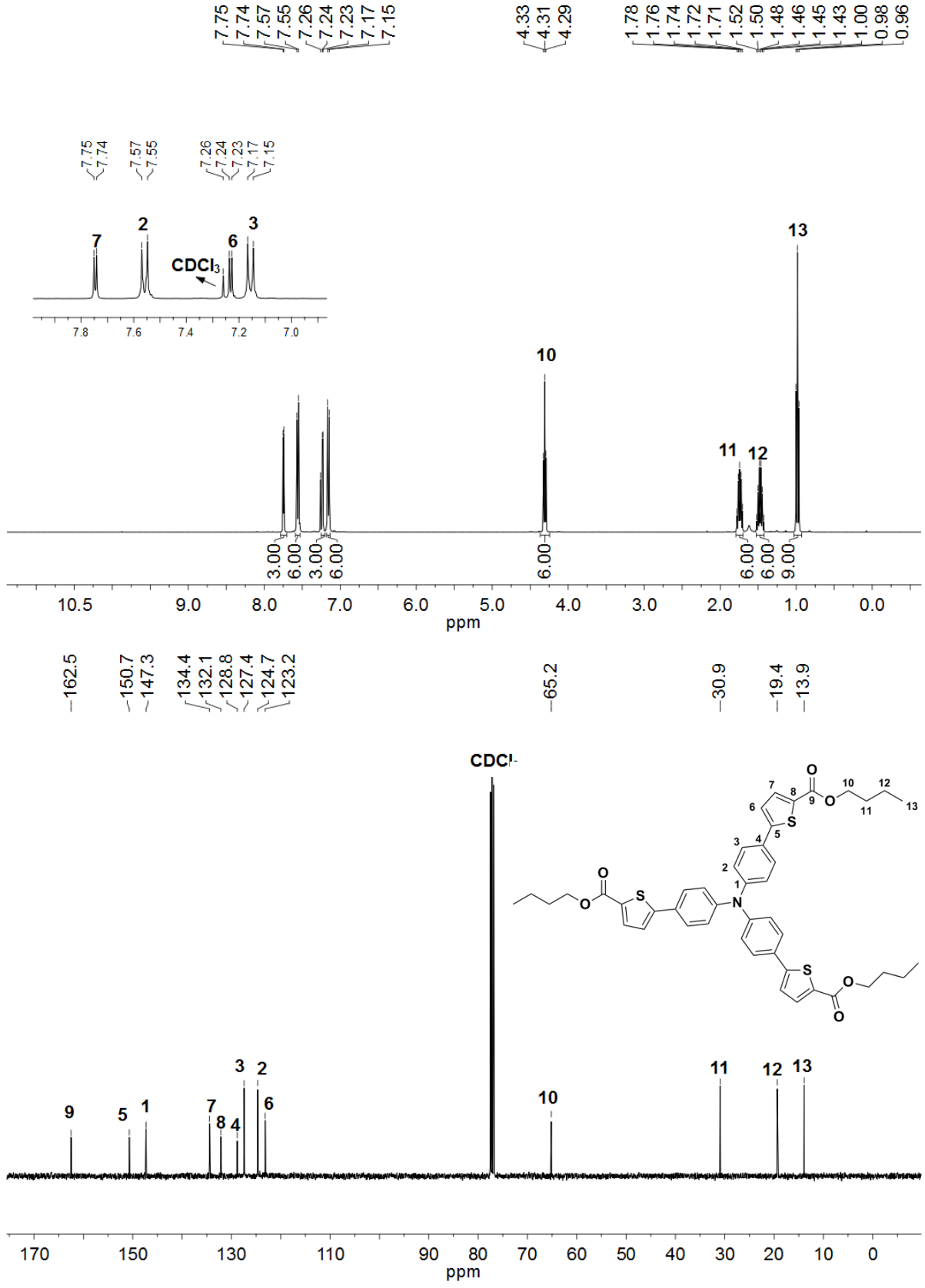


Dibutyl-5,5`-(2,5-dimethyl-1,4-phenylene)bis(thiophene-2-carboxylate) (2b)

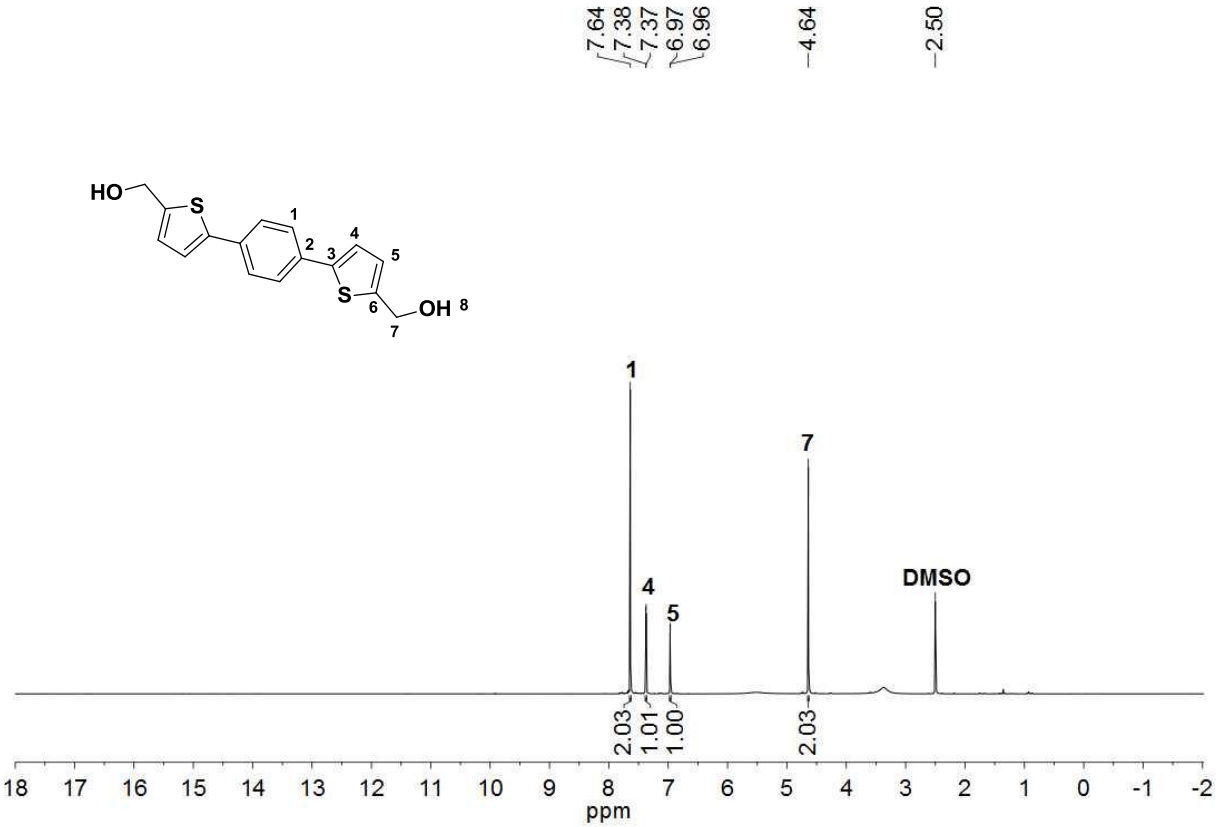


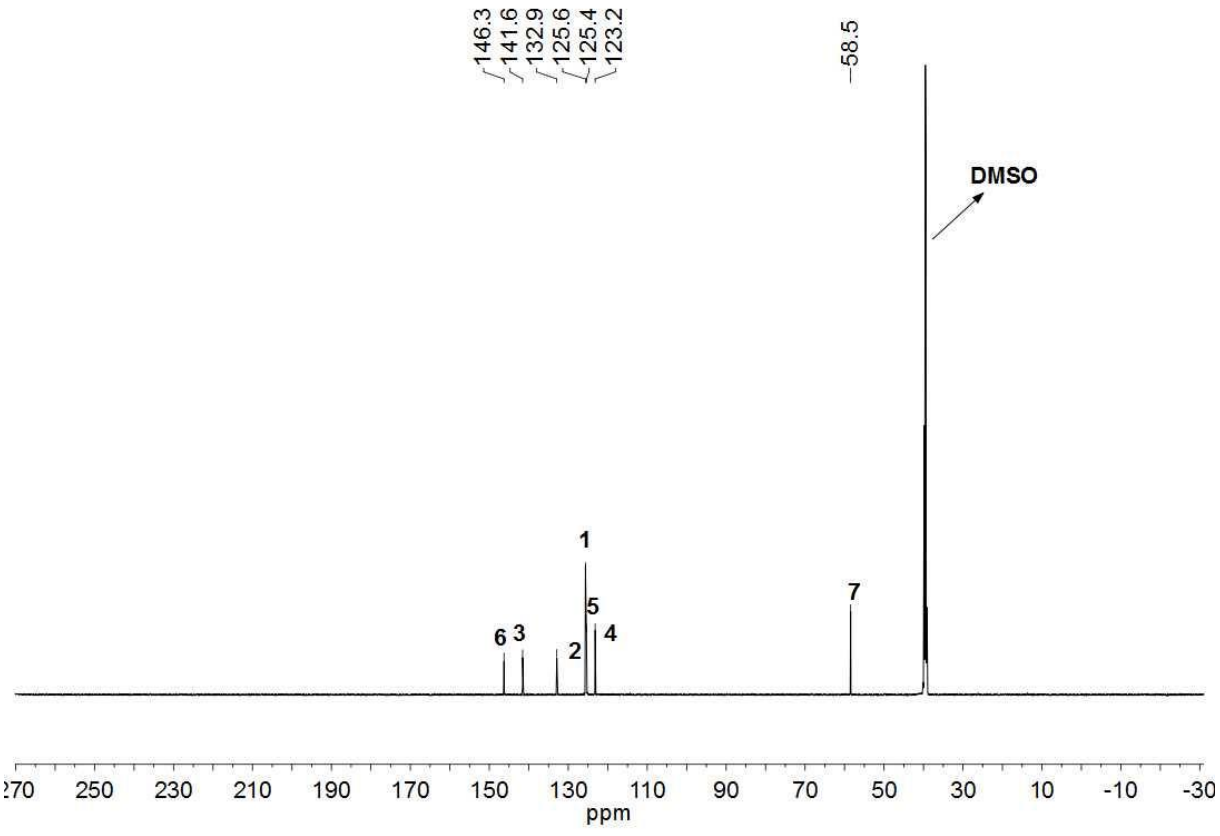


Tributyl 5,5`,5``-(nitriliotris(benzene-4,1-diyl))tris(thiophene-2-carboxylate) (3b)

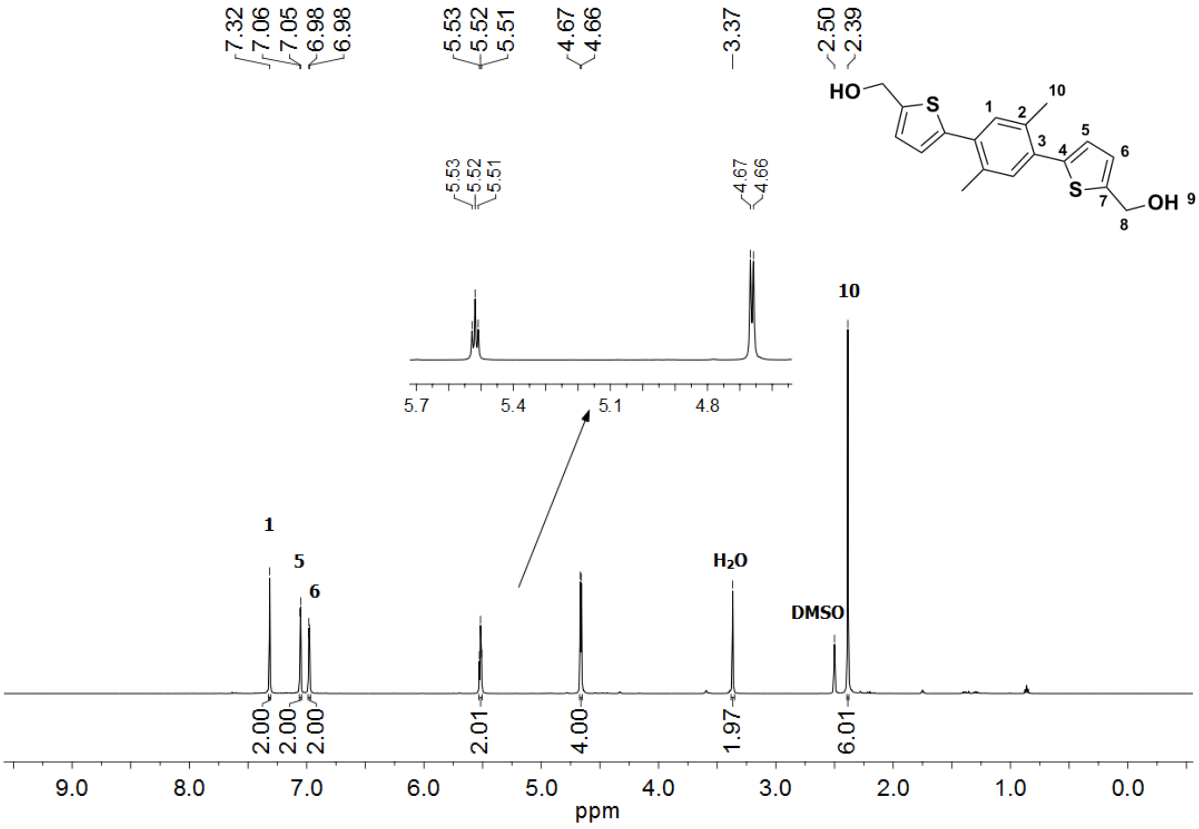


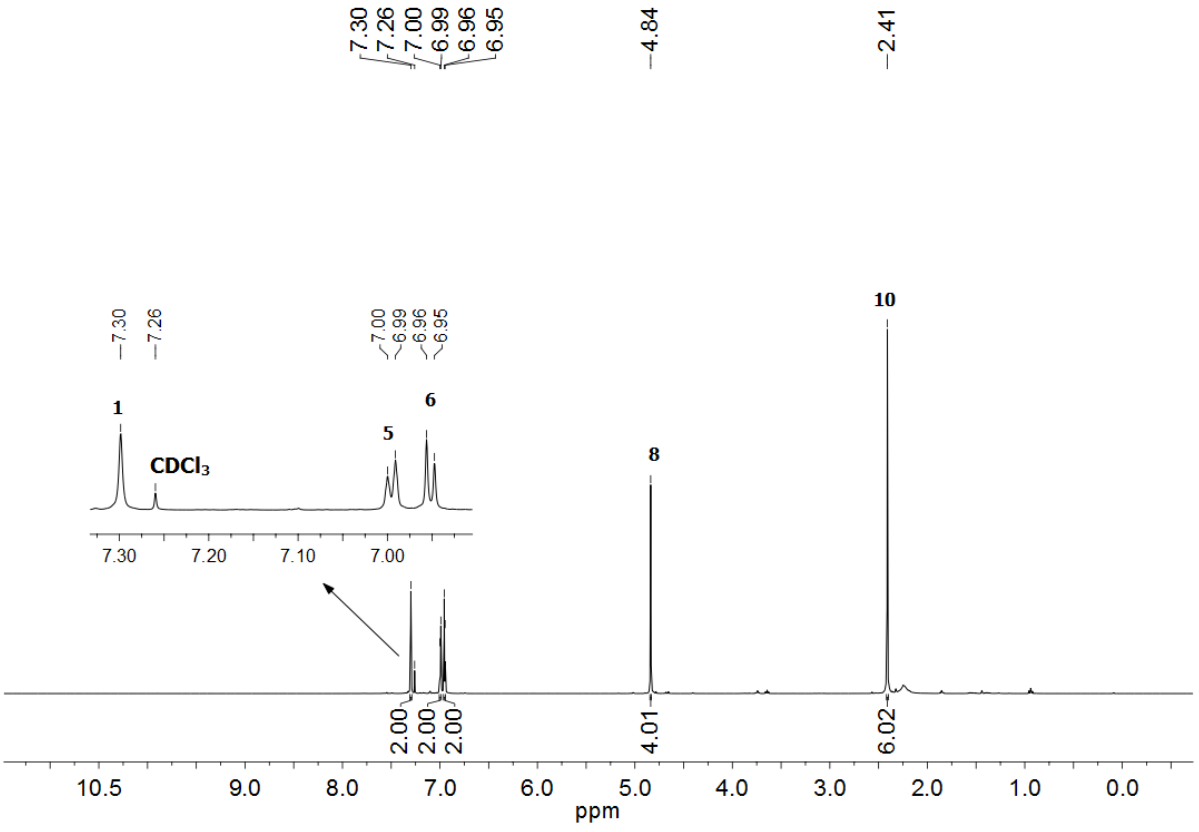
5,5`-(1,4-Phenylene)bis(thiophene-5,2-diyl))dimethanol (1c)



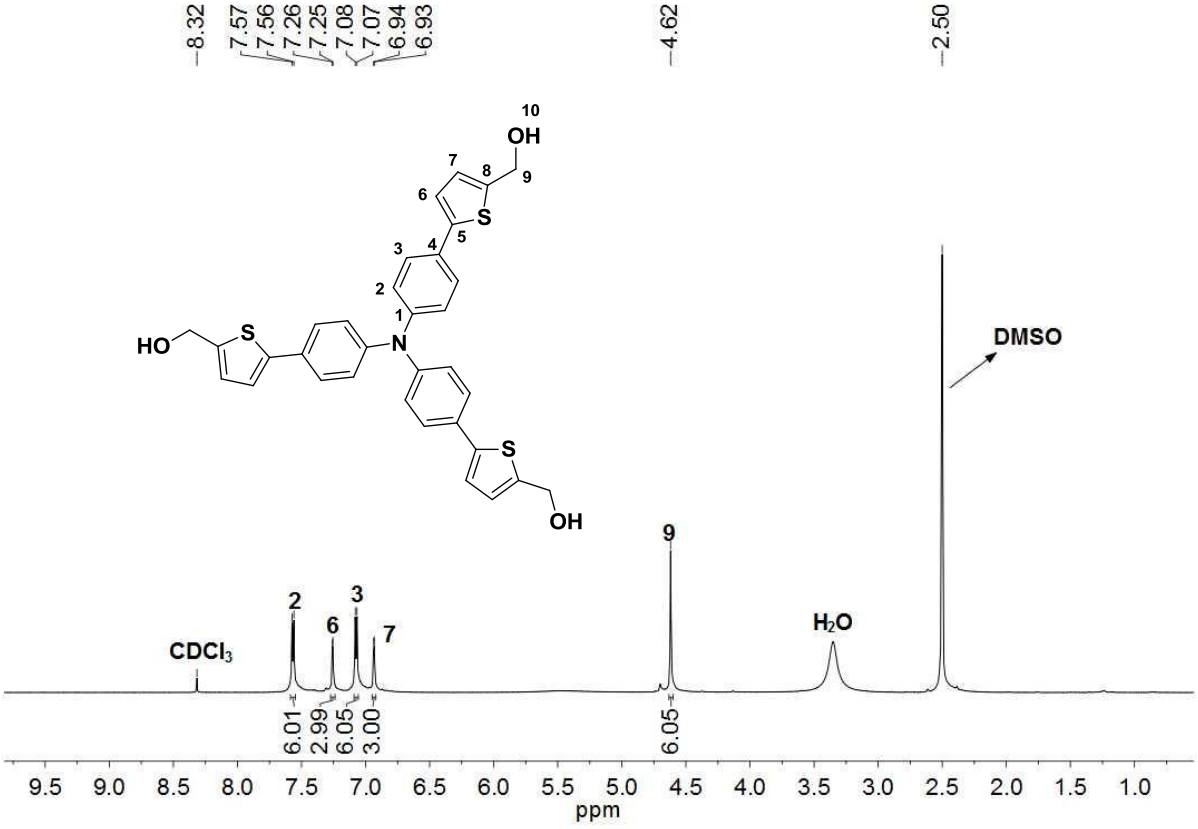


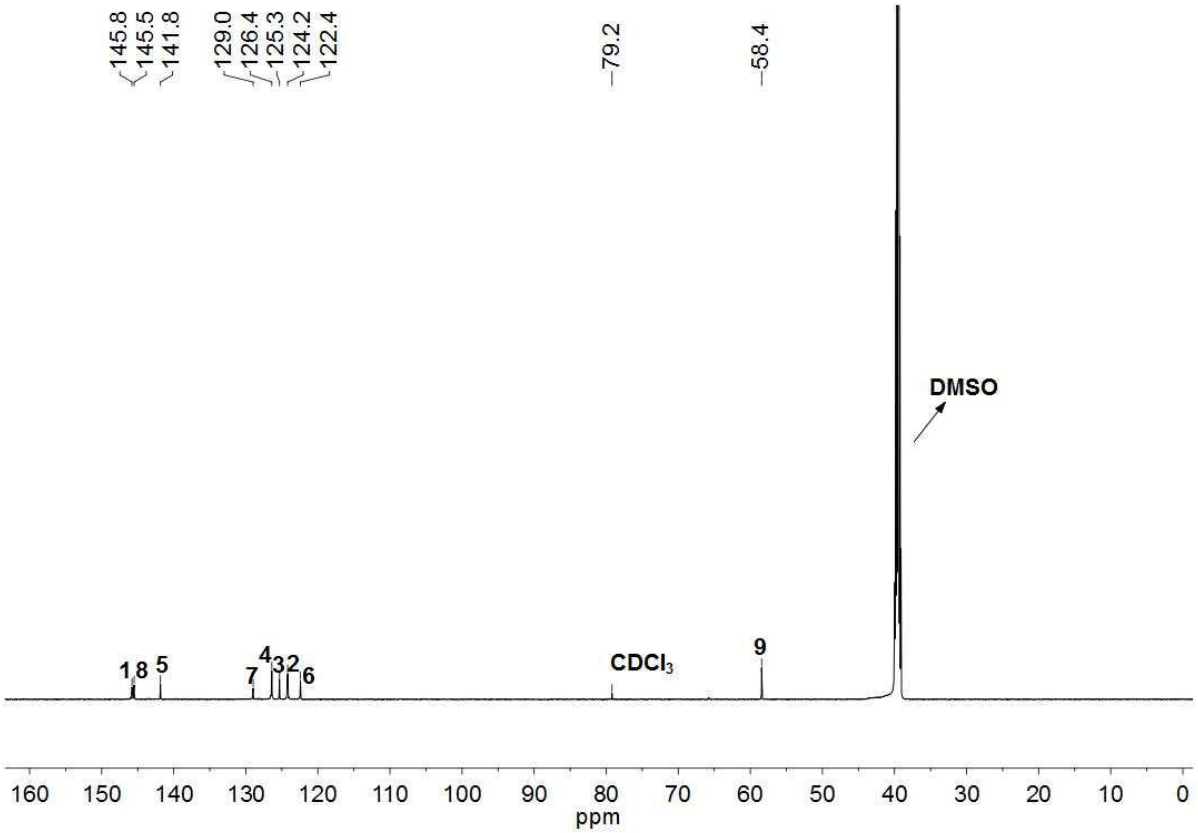
5,5`-(2,5-Dimethyl-1,4-phenylene)bis(thiophene-5,2-diyl))dimethanol (2c)



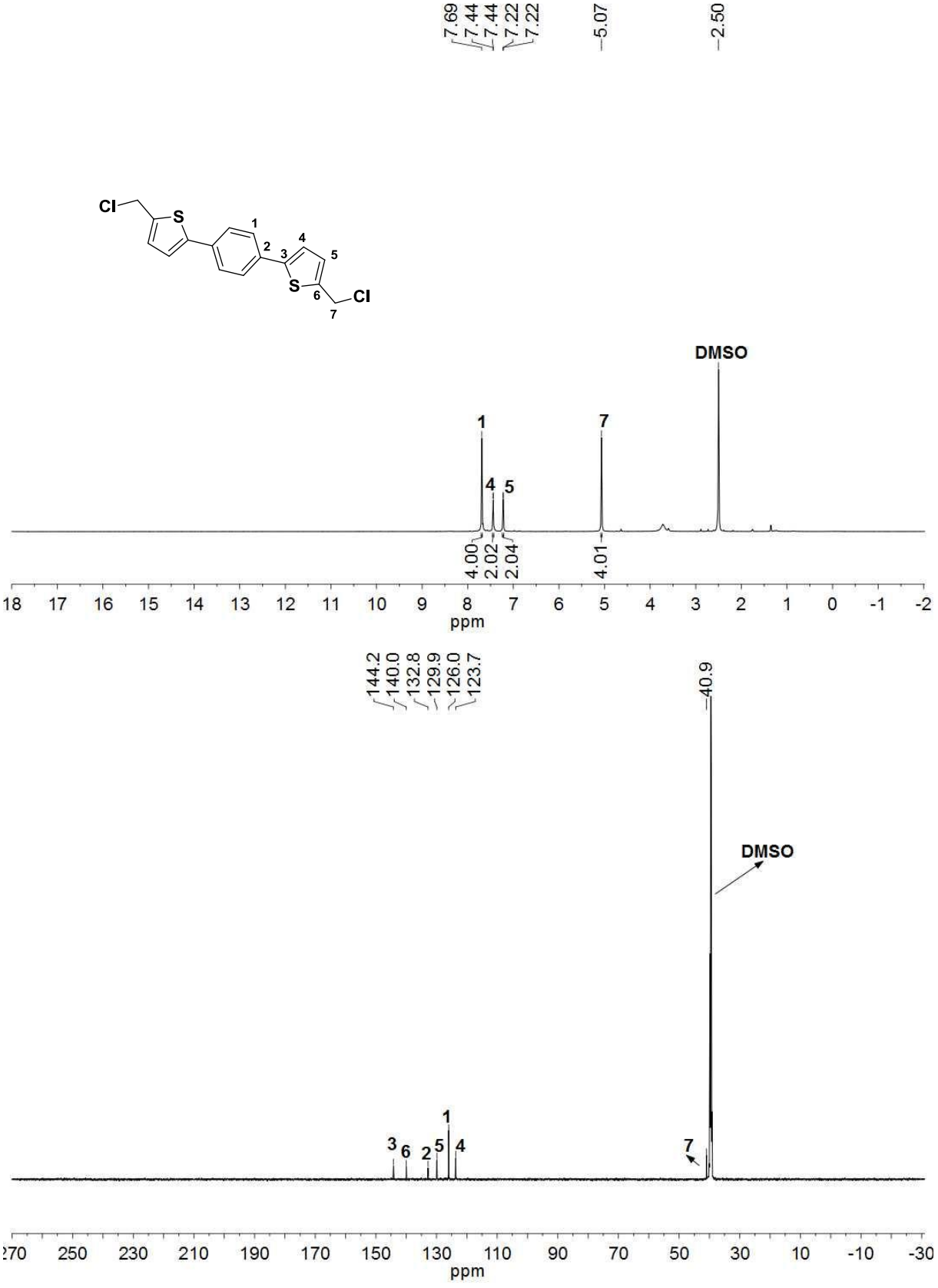


5,5`,5``-(Nitrilotris(benzene-4,1-diyl))tris(thiophene-5,2-diyl))trimethanol (3c)

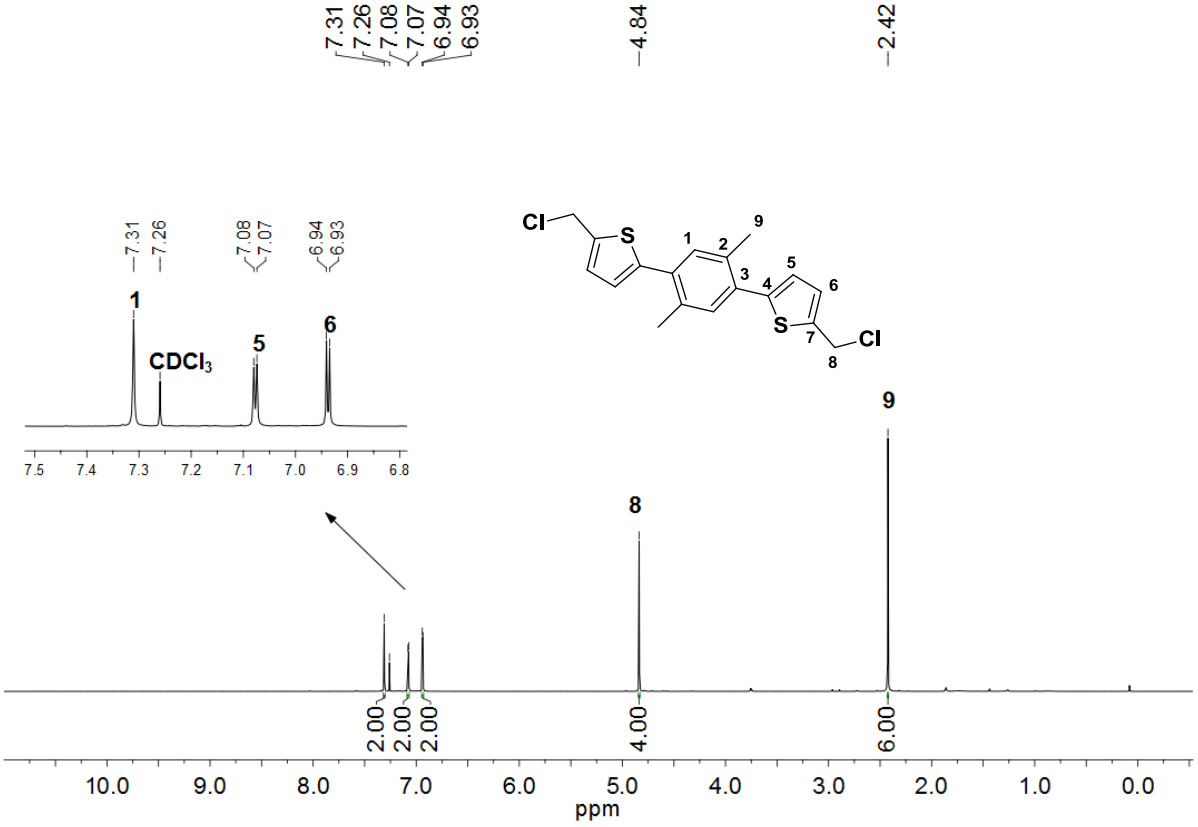


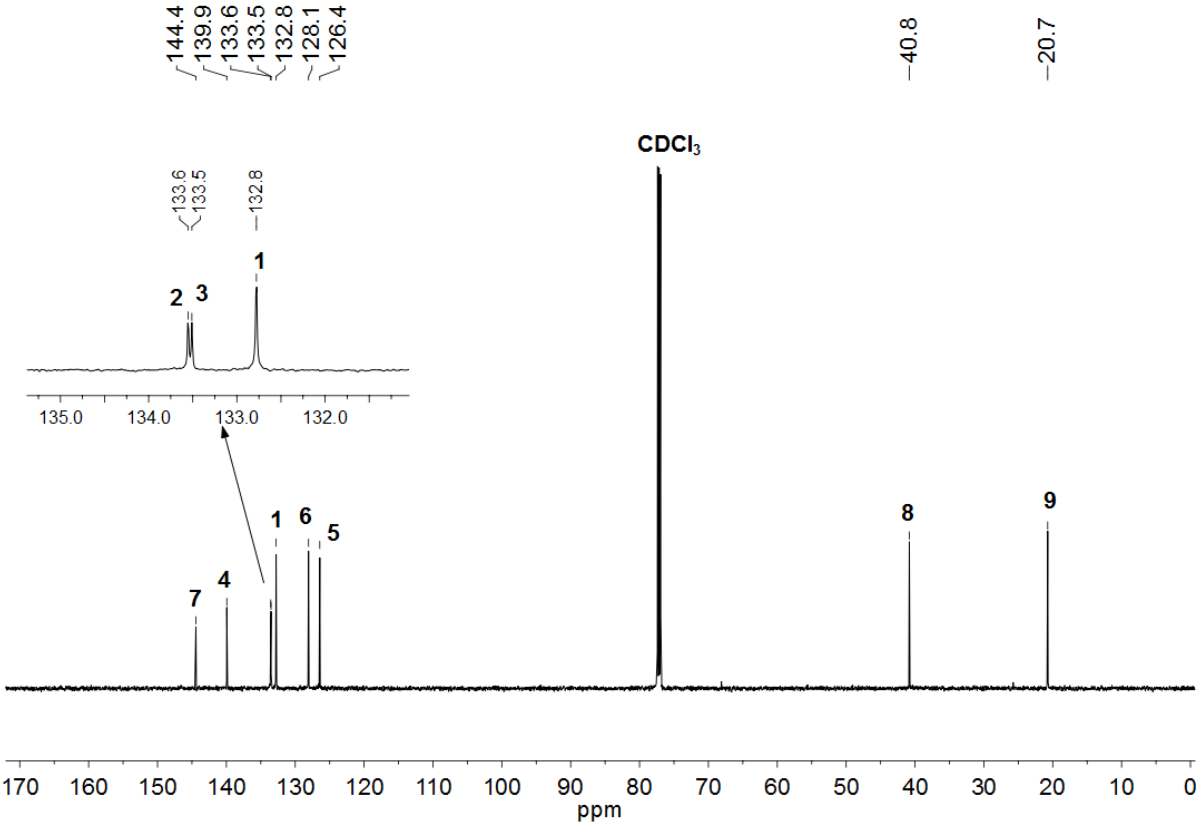


1,4-Bis(5-chloromethyl)thiophen-2-yl)benzene (1d)

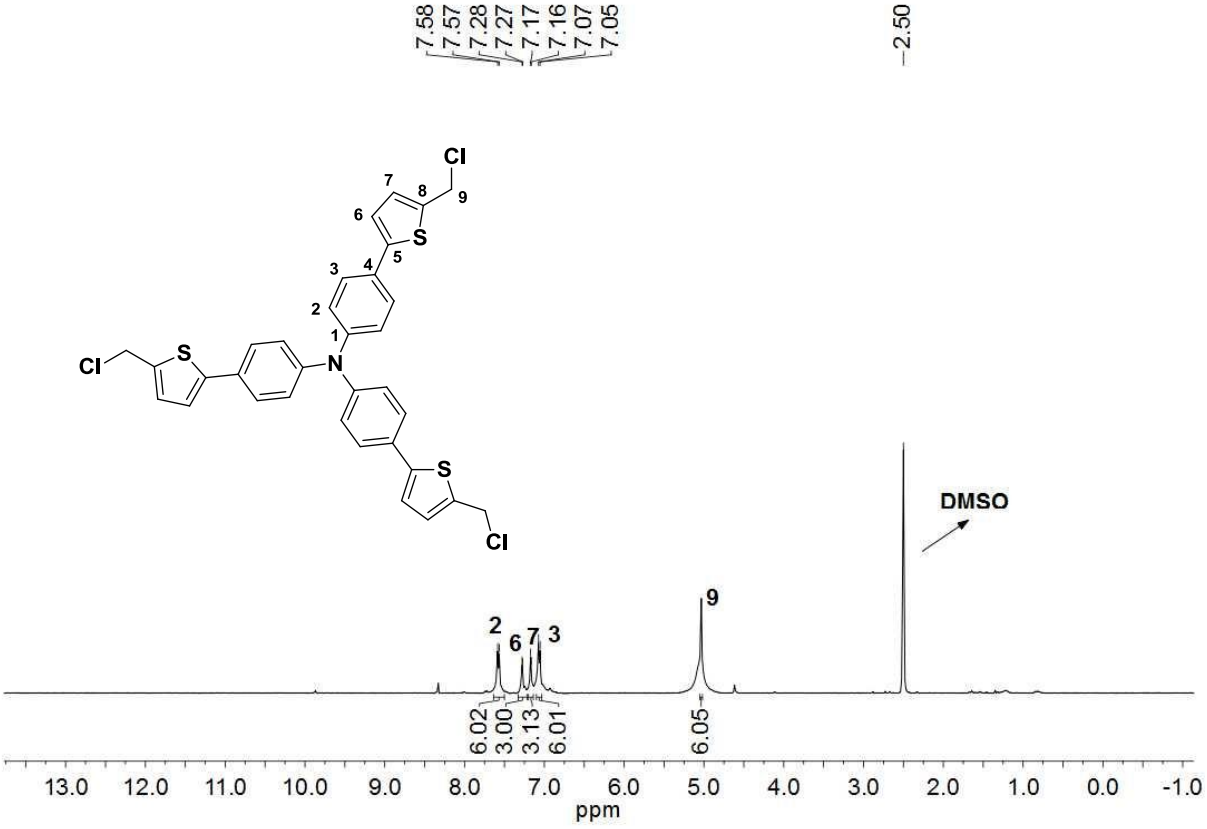


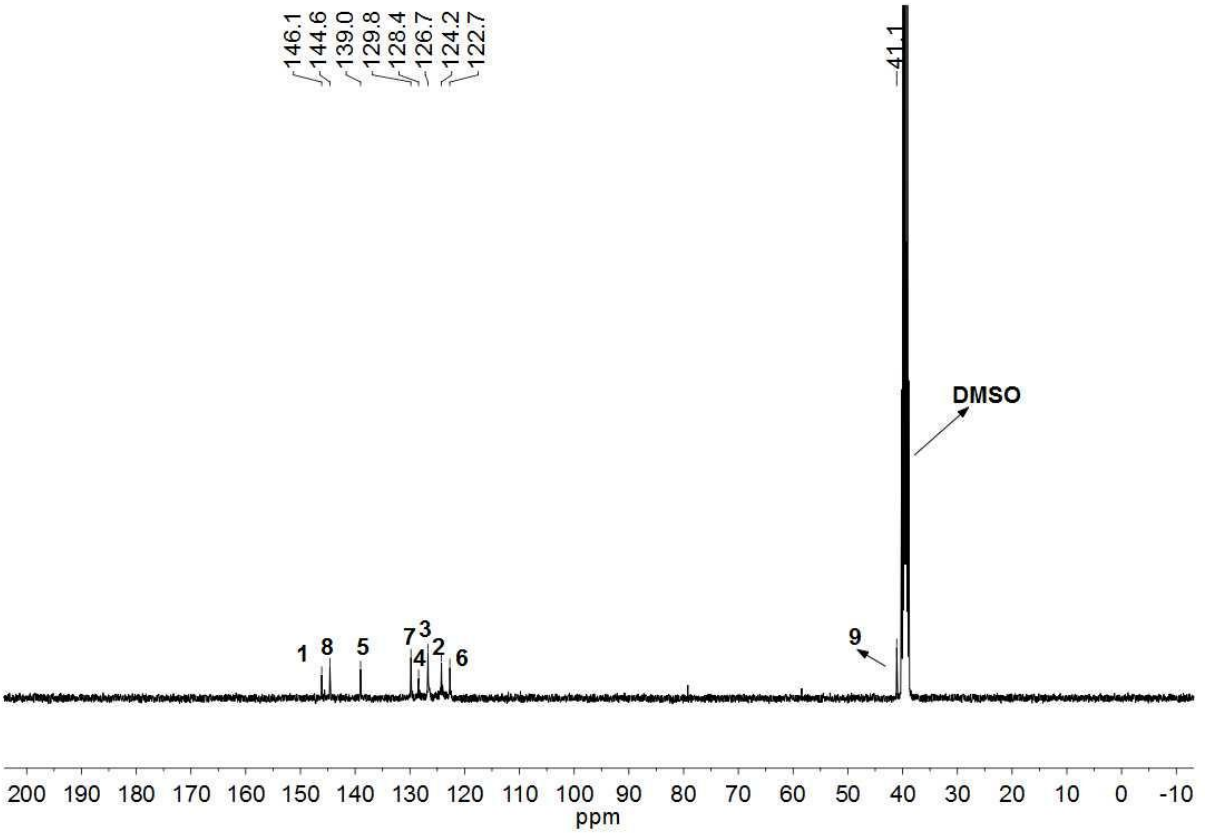
5,5`-(2,5-Dimethyl-1,4-phenylene)bis(2-(chloromethyl)thiophene) (2d)



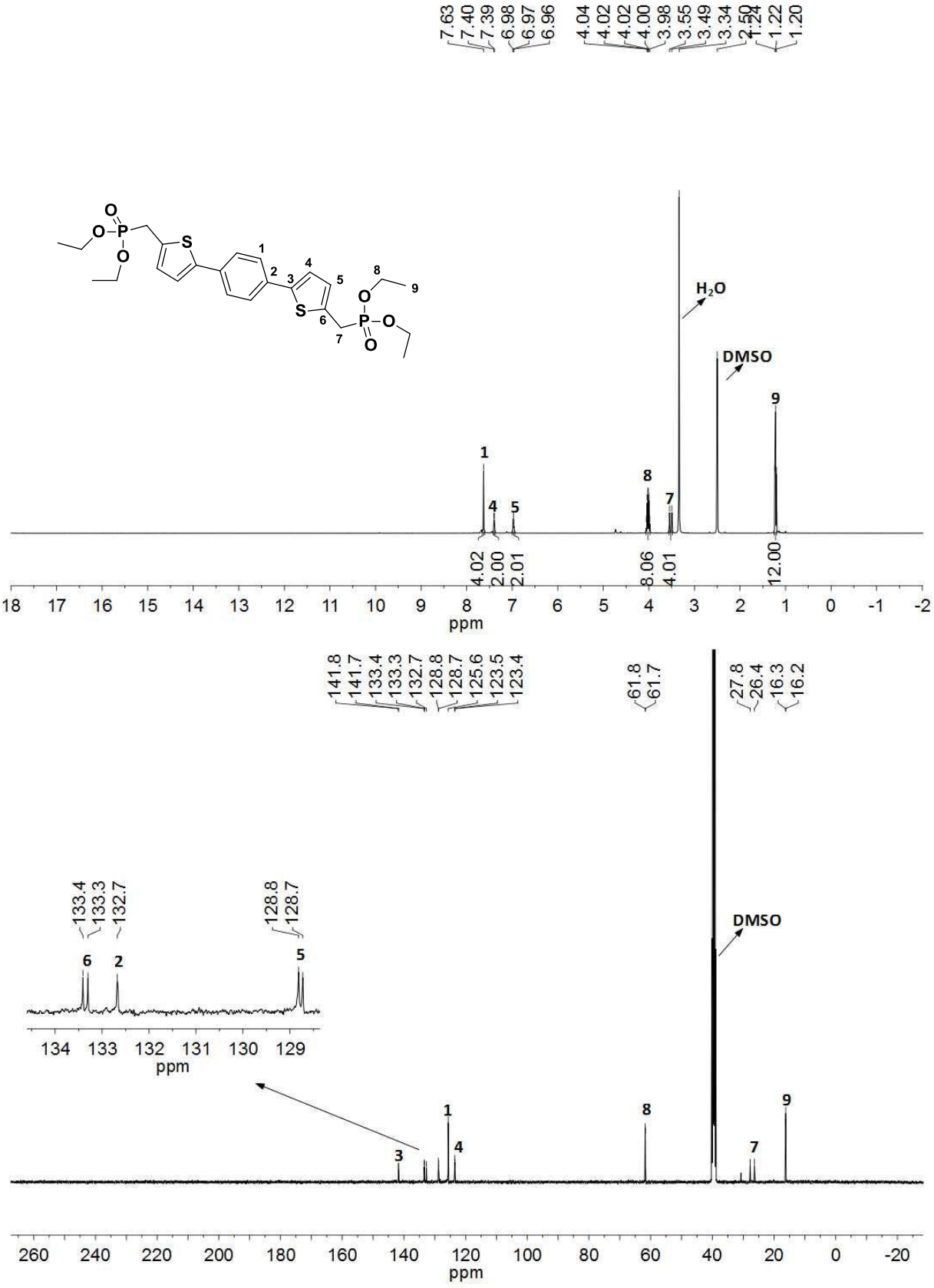


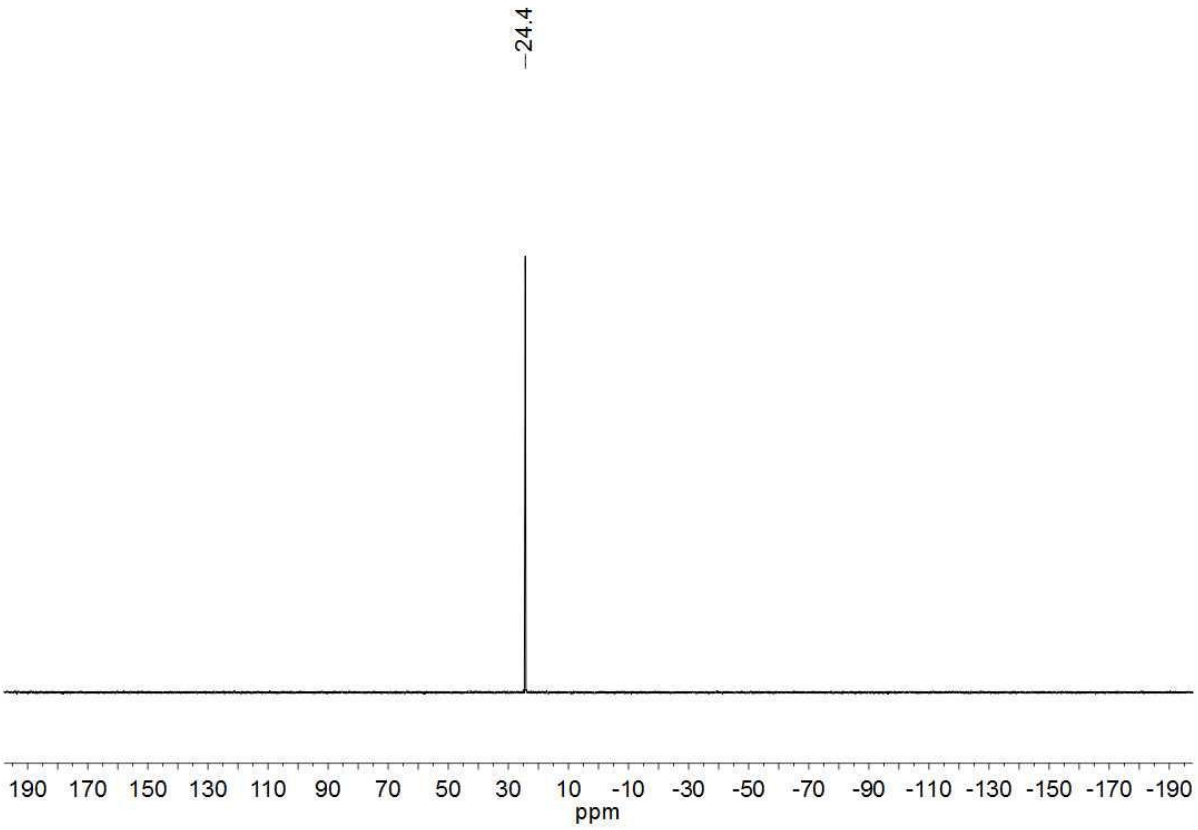
Tris(4-(5-(chloromethyl)thiophen-2-yl)phenyl)amine (3d)



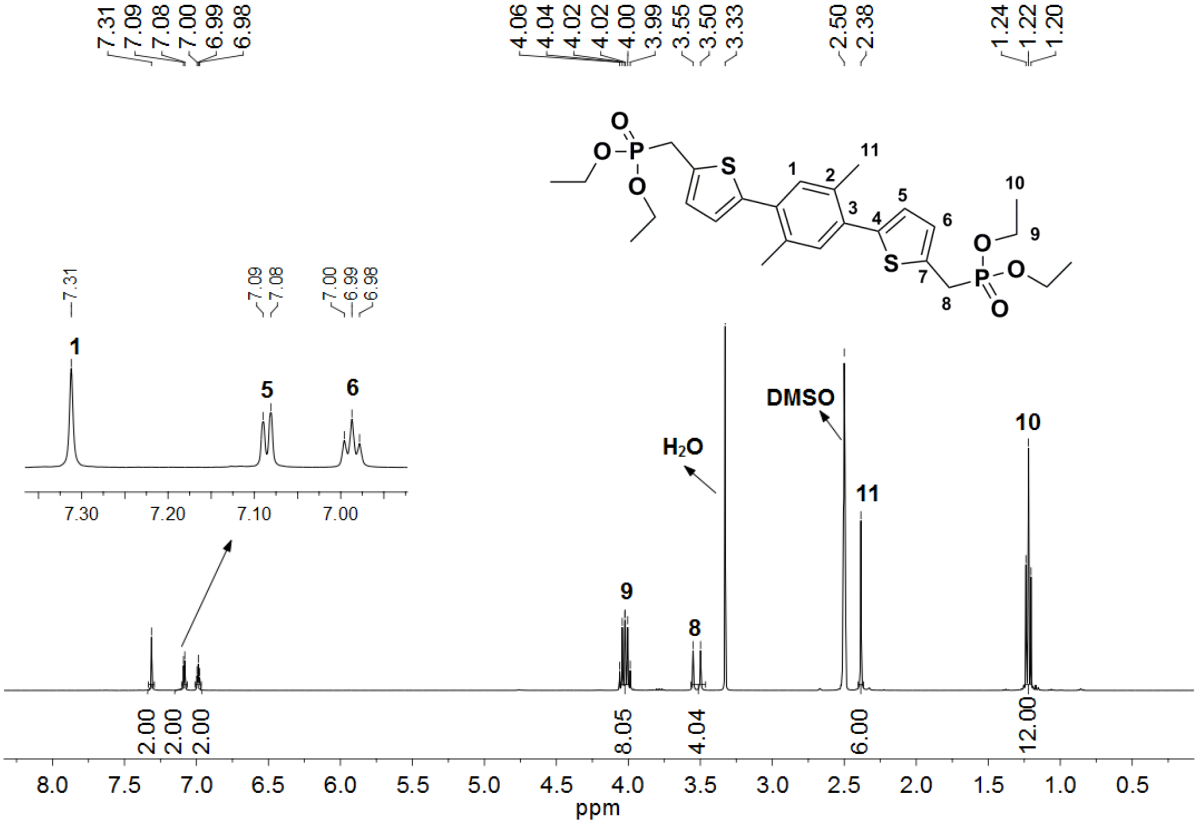


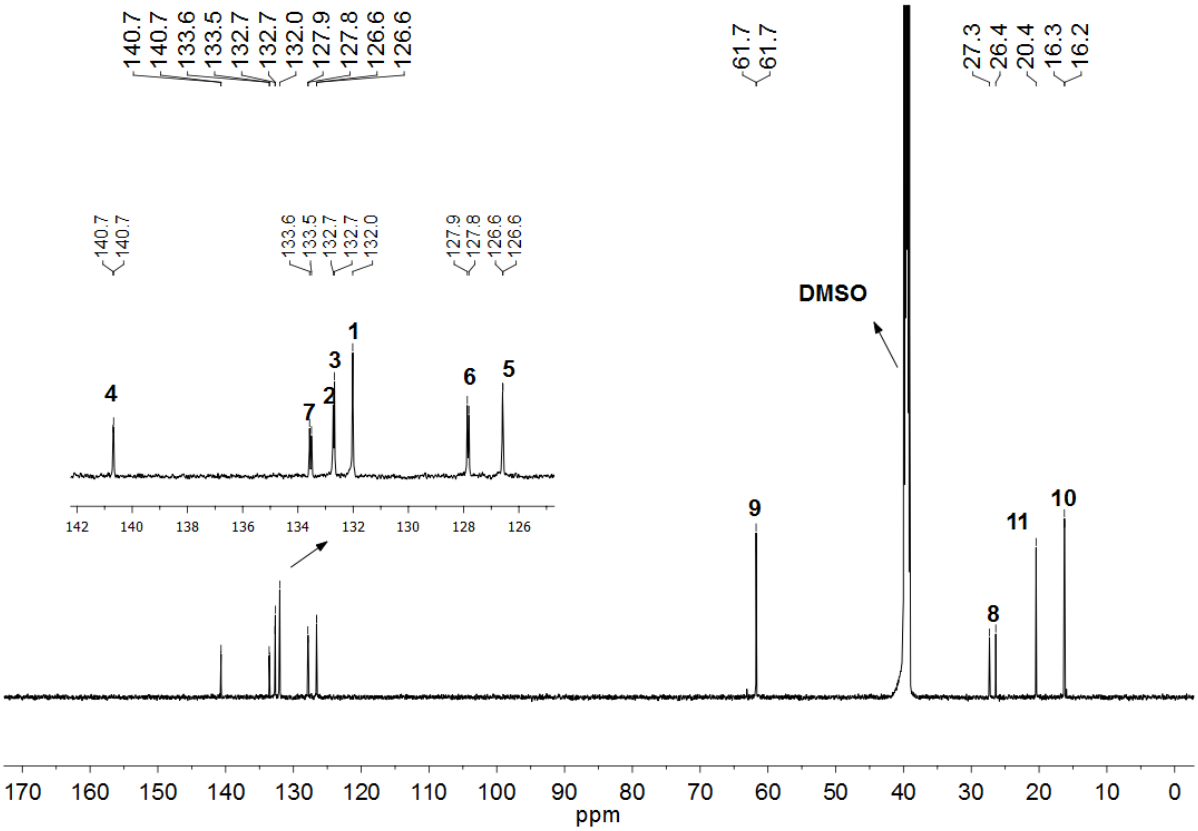
Tetraethyl-((5,5`-(1,4-phenylene)bis(thiophene-5,2-diyl)) bis(methylene))bis(phosphonate) (1e)

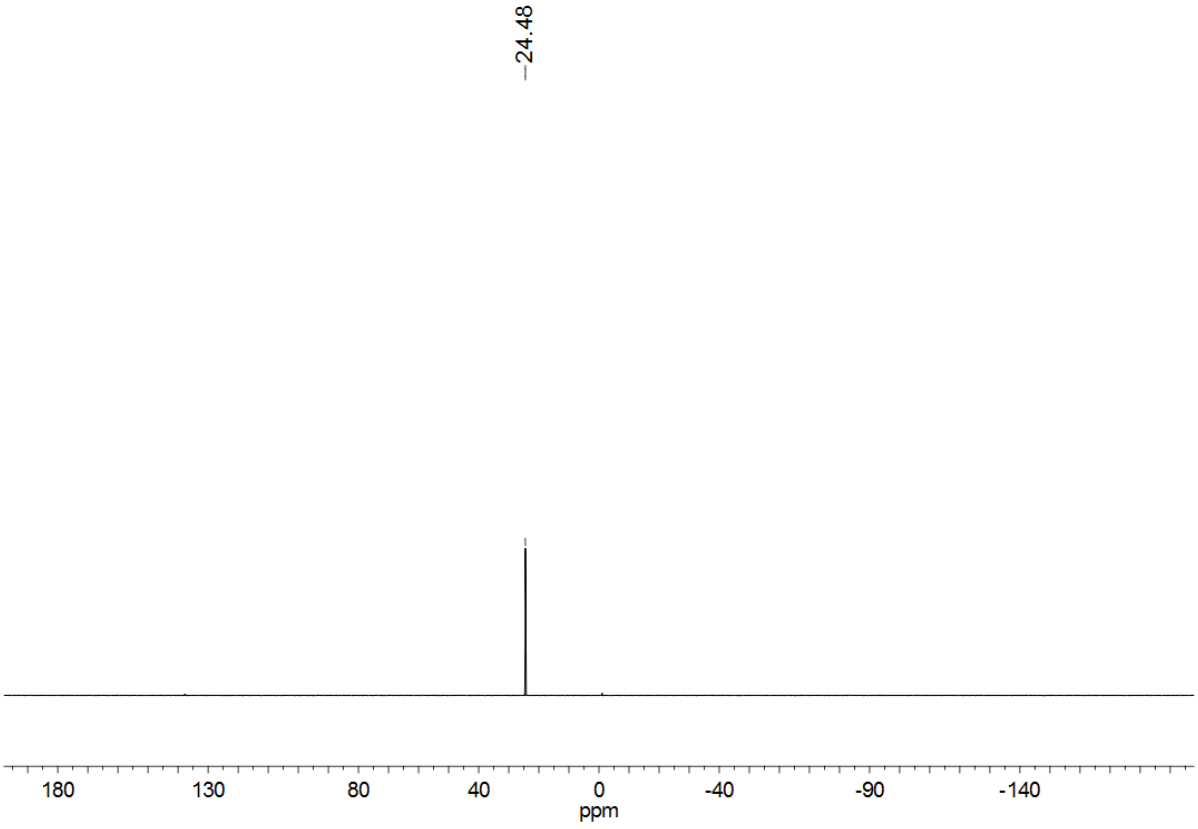




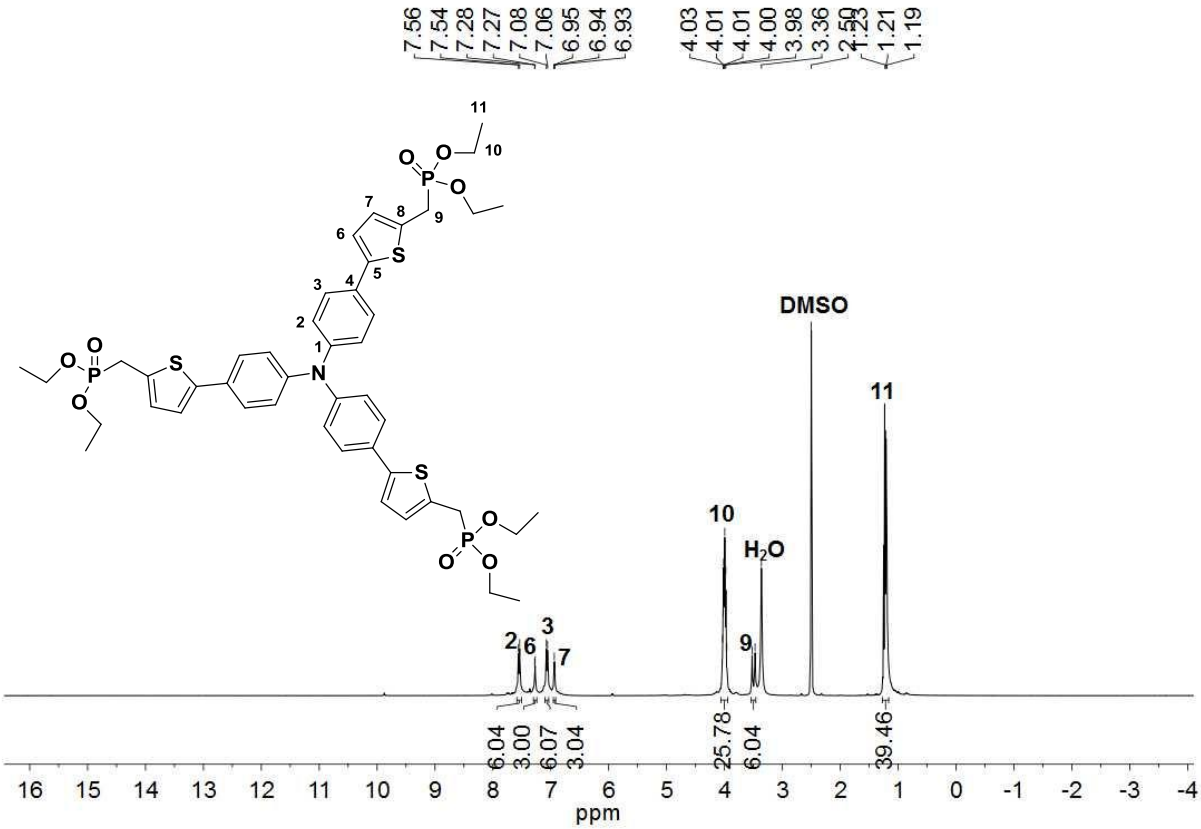
Tetraethyl-((5,5`-(2,5-dimethyl-1,4-phenylene)bis(thiophene-5,2-diyl))bis(methylene))bis(phosphonate) (2e)

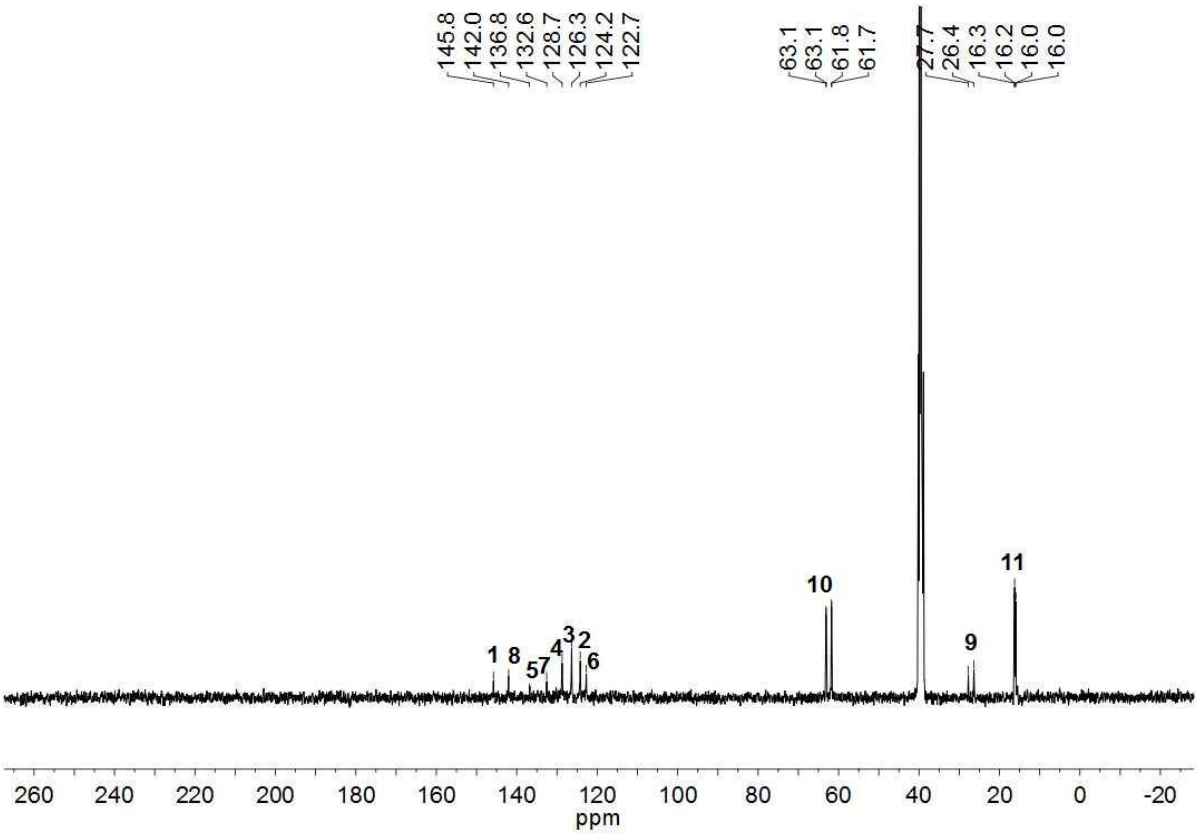


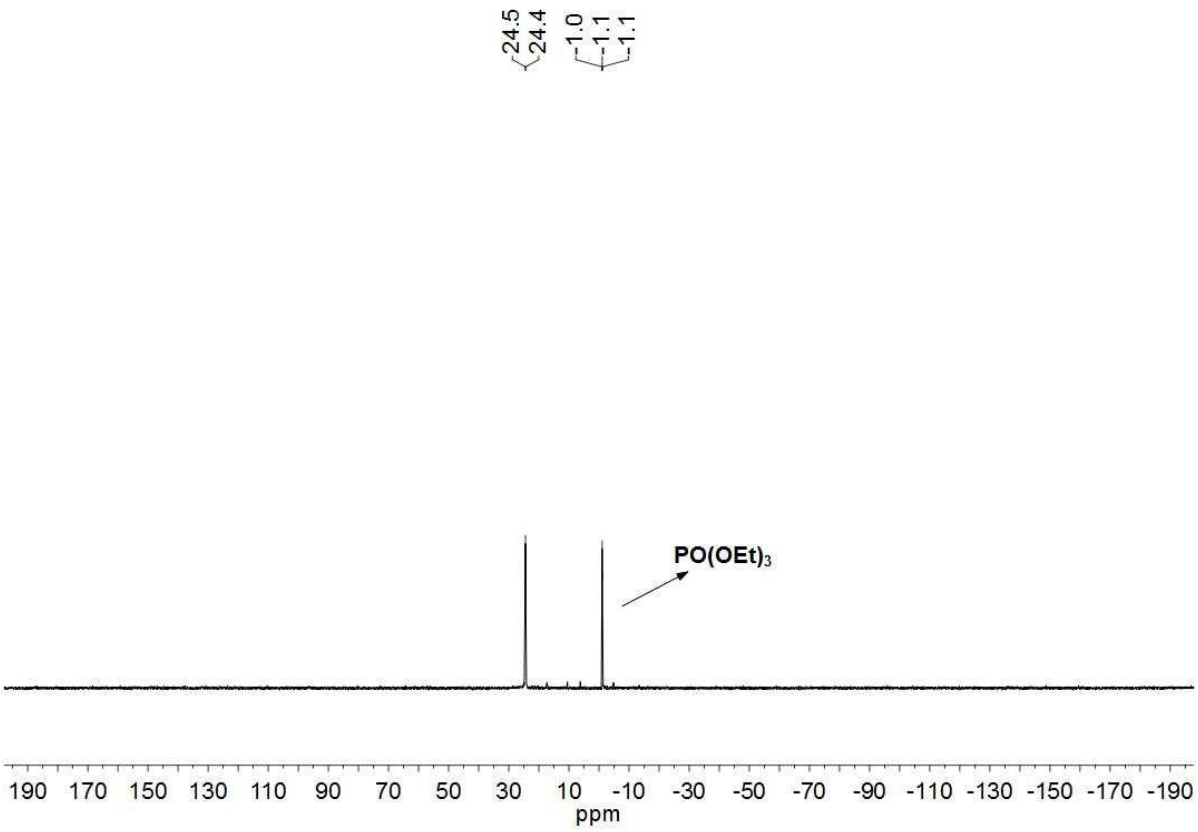

140.7
140.7
133.6
133.5
132.7
132.7
132.0
127.9
127.8
126.6
126.6
61.7
61.7
27.3
26.4
20.4
16.3
16.2
DMSO
1
2
3
4
5
6
7
8
9
10
11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


24.48
180 130 80 40 0 -40 -90 -140
ppm

Hexaethyl((5,5`,5``-(nitrilotris(benzene-4,1-diyl))tris(thiophene-5,2-diyl))tris(methylene)tris(phosphonate) (3e)

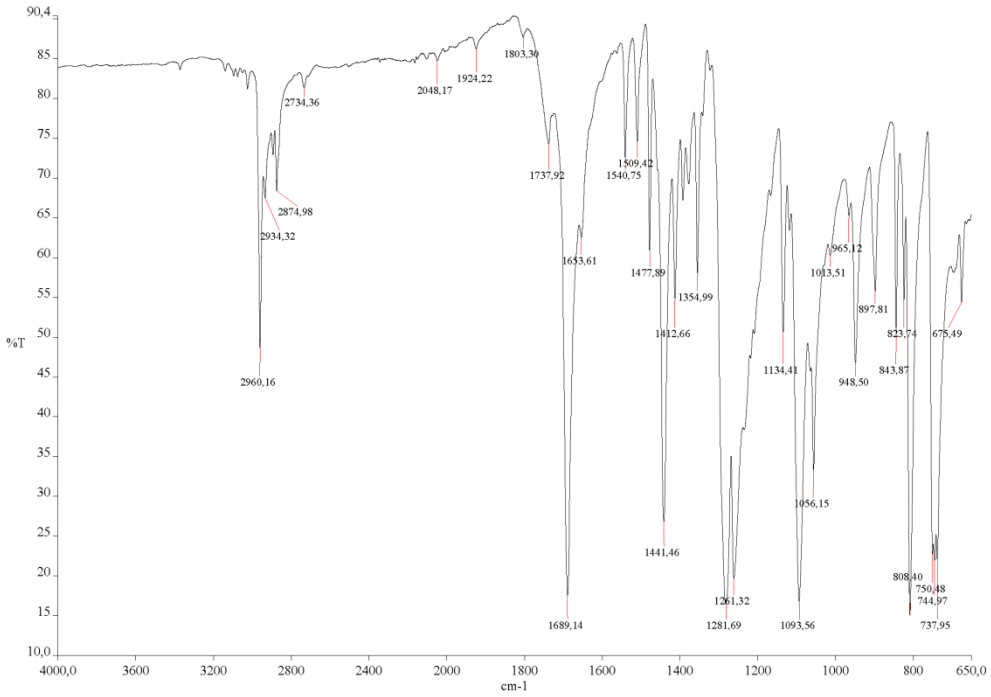




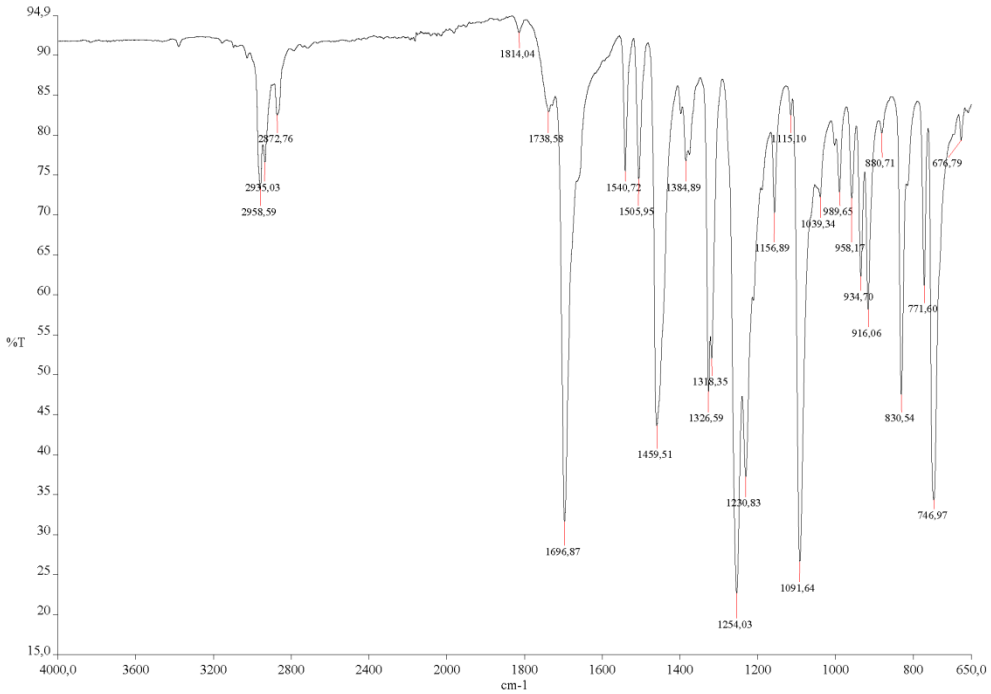

24.5
24.4
1.0
1.1
1.1
PO(OEt)3
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
ppm

IR spectra

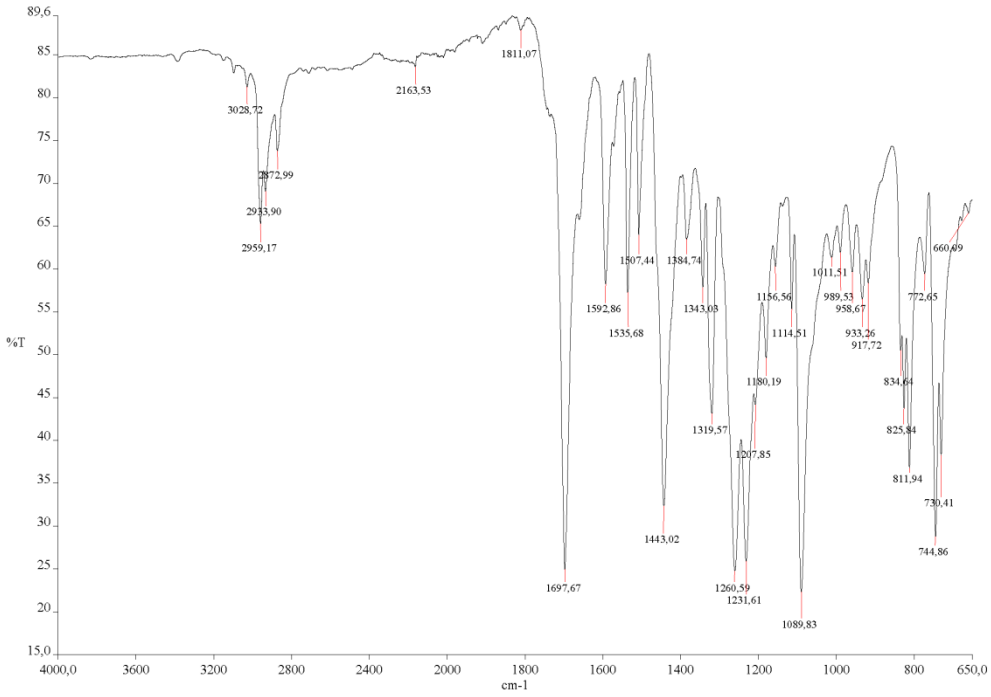
Dibutyl-5,5'-(1,4-phenylene)bis(thiophene-2-carboxylate) (1b)



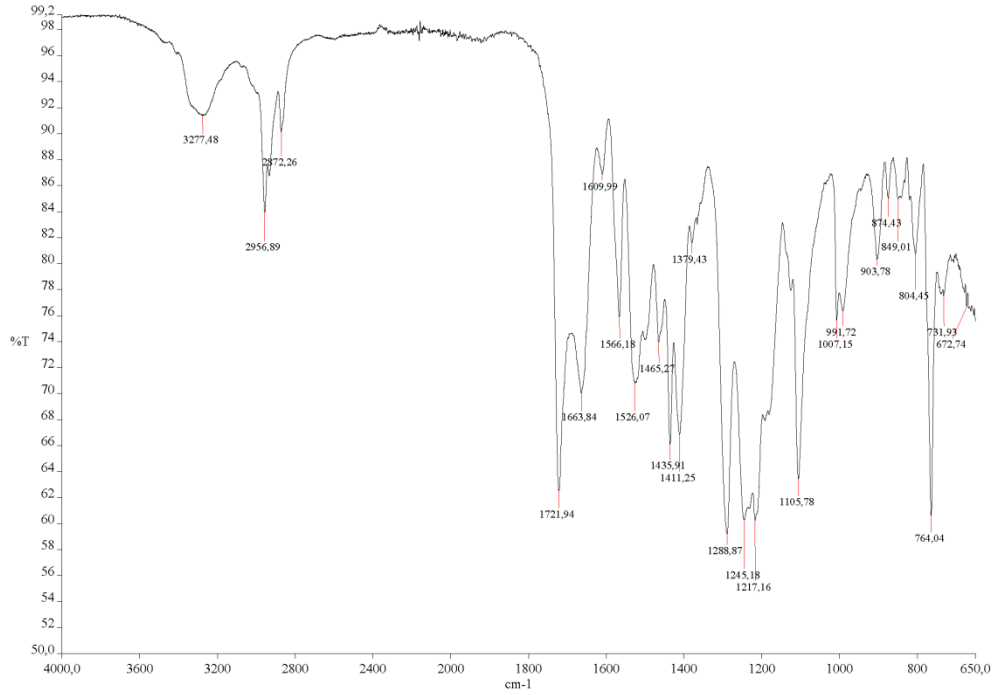
Dibutyl-5,5`-(2,5-dimethyl-1,4-phenylene)bis(thiophene-2-carboxylate) (2b)



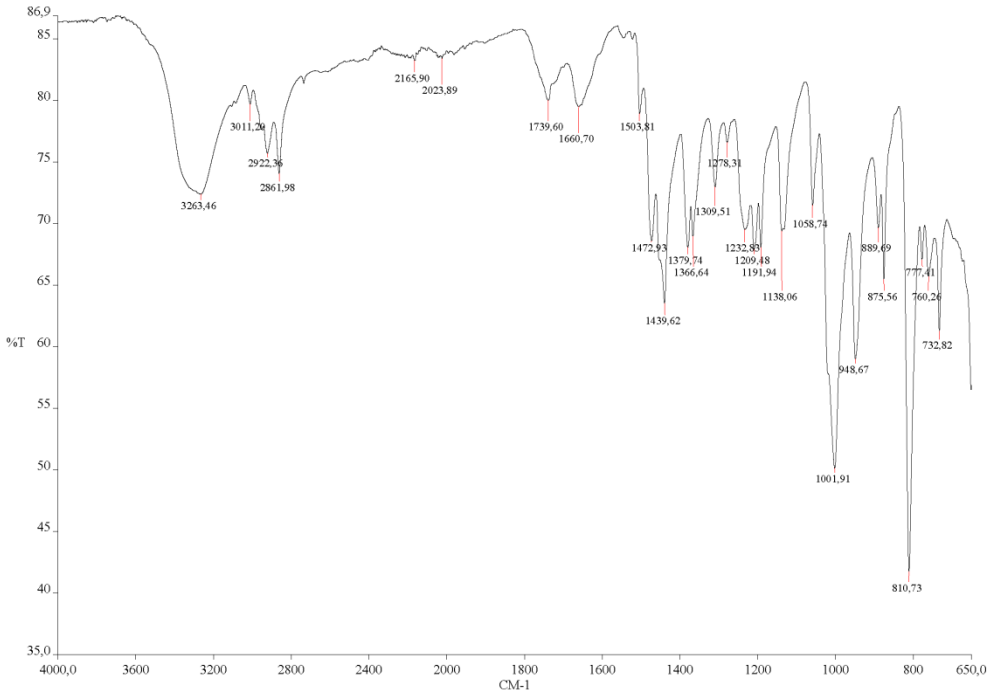
Tributyl 5,5`,5``-(nitriliotris(benzene-4,1-diyl))tris(thiophene-2-carboxylate) (3b)



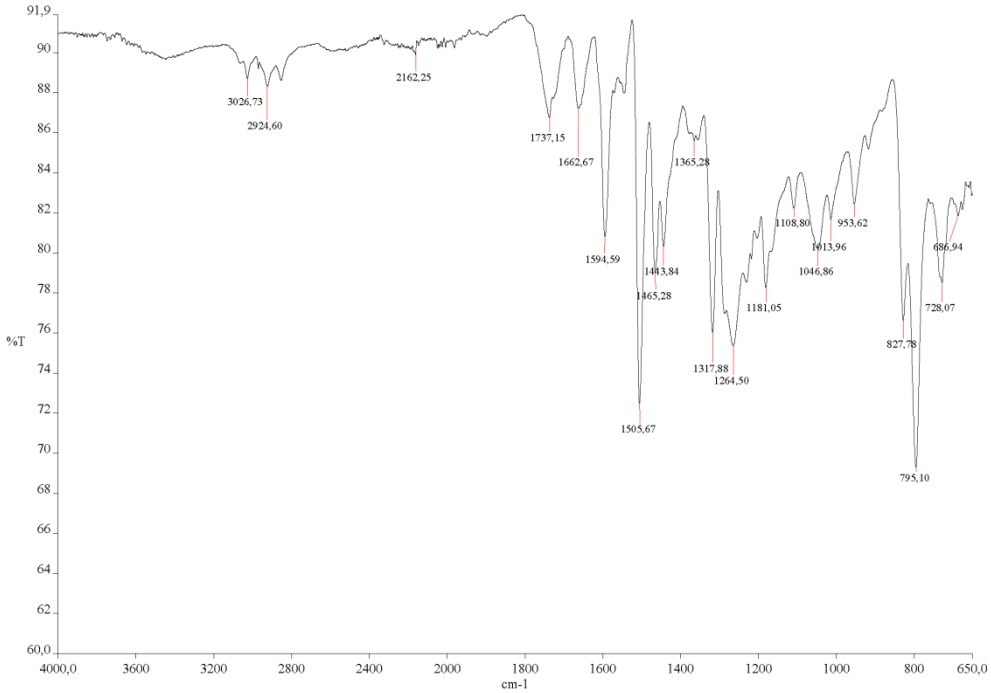
5,5`-(1,4-Phenylene)bis(thiophene-5,2-diyl))dimethanol (1c)



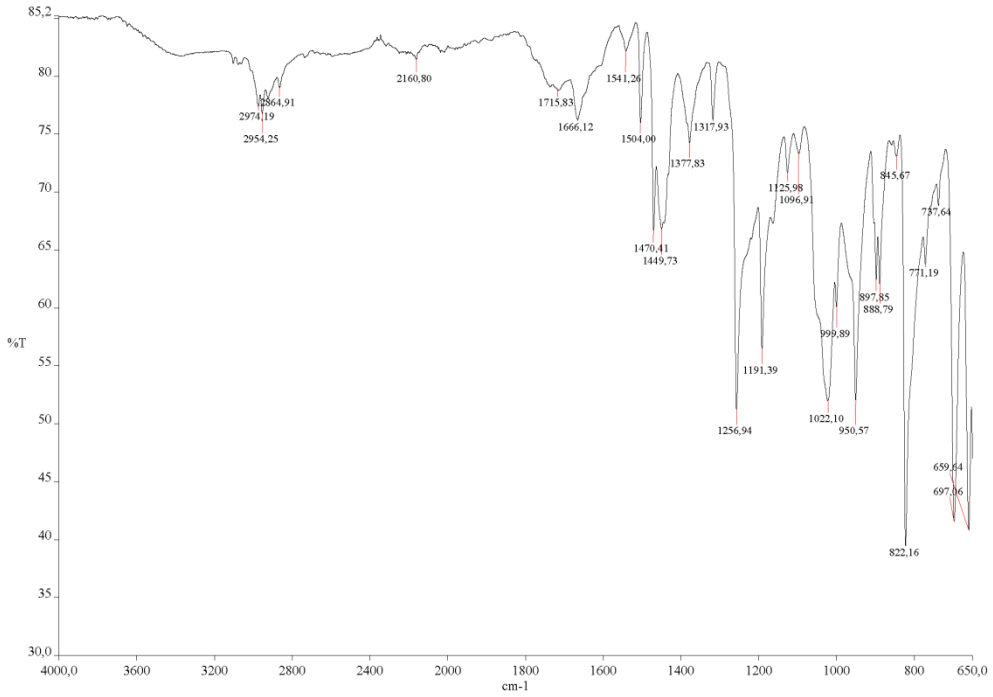
5,5`-(2,5-Dimethyl-1,4-phenylene)bis(thiophene-5,2-diyl))dimethanol (2c)



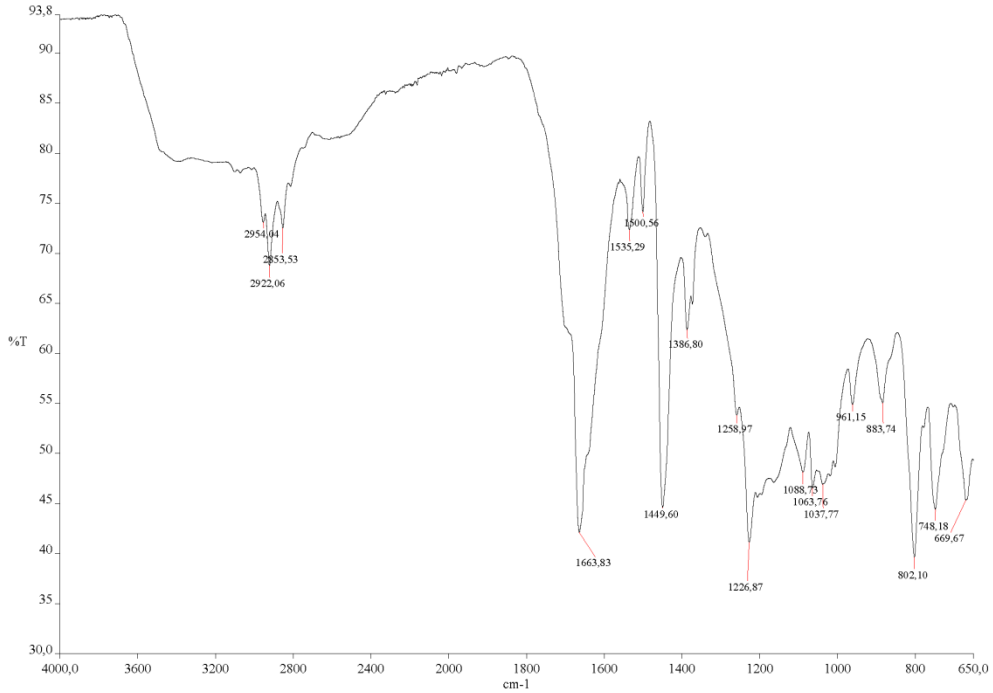
5,5`,5``-(Nitrilotris(benzene-4,1-diyl))tris(thiophene-5,2-diyl)) trimethanol (3c)



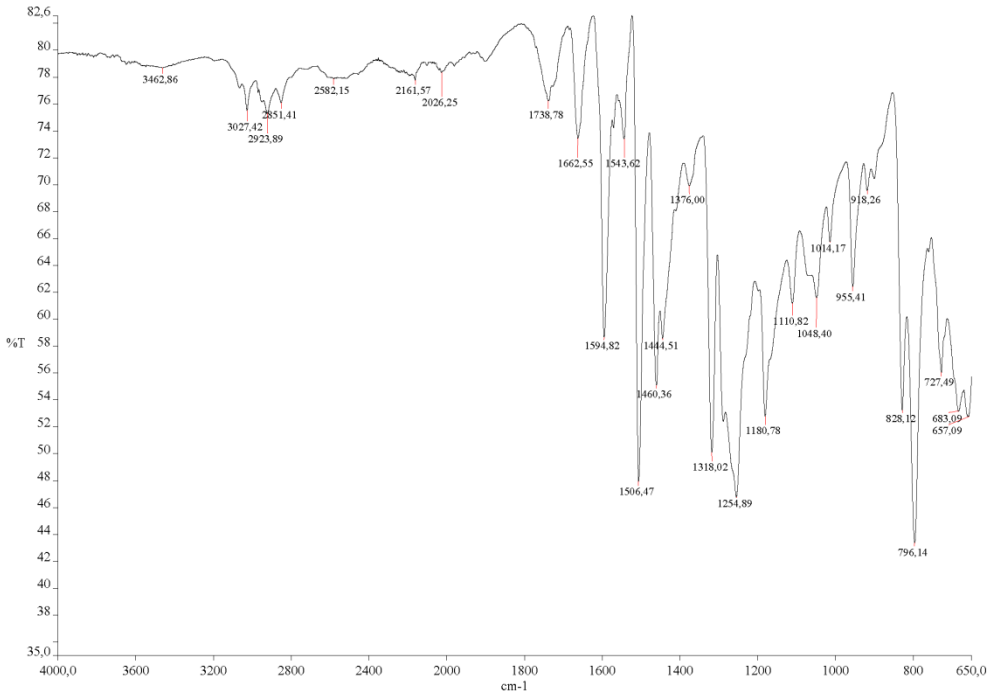
1,4-Bis(5-chloromethyl)thiophen-2-yl)benzene (1d)



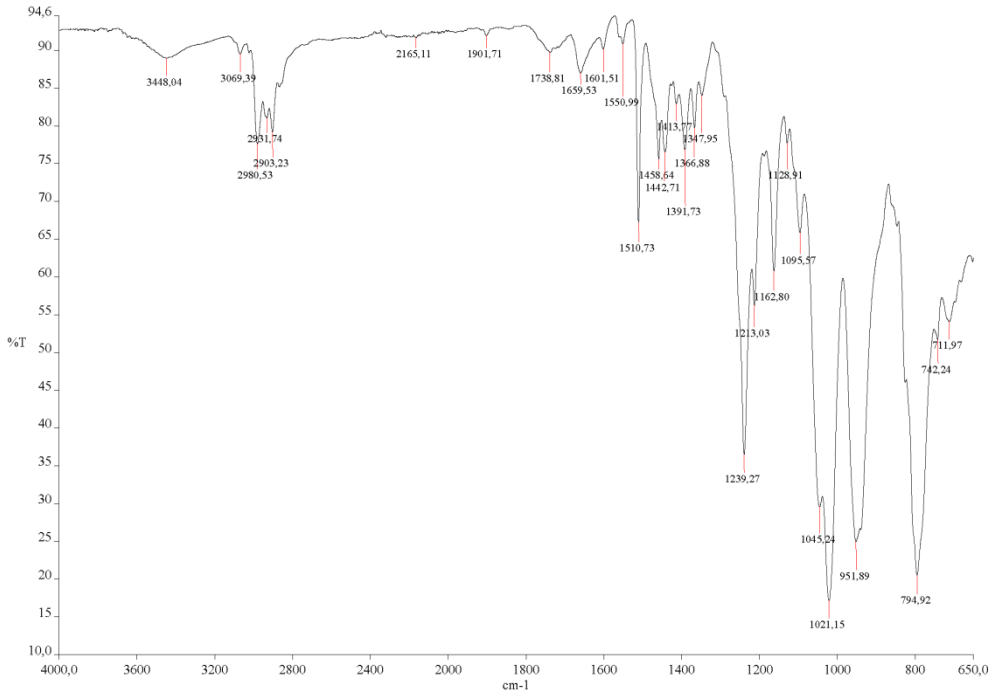
5,5`-(2,5-Dimethyl-1,4-phenylene)bis(2-(chloromethyl)thiophene) (2d)



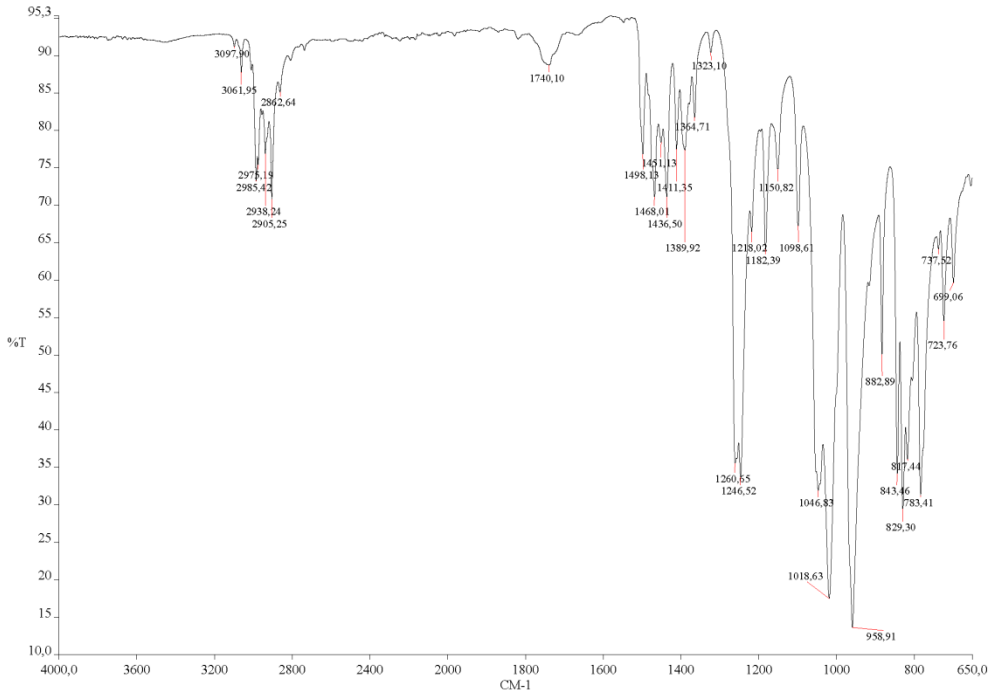
Tris(4-(5-(chloromethyl)thiophen-2-yl)phenyl)amine (3d)



Tetraethyl-((5,5`-(1,4-phenylene)bis(thiophene-5,2-diyl)) bis(methylene))bis(phosphonate) (1e)



Tetraethyl-((5,5`-(2,5-dimethyl-1,4-phenylene)bis(thiophene-5,2-diyl))bis(methylene))bis(phosphonate) (2e)



Hexaethyl((5,5`,5``-(nitrilotris(benzene-4,1-diyl))tris(thiophene-5,2-diyl))tris(methylene)tris(phosphonate) (3e)