Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Diversity-Oriented Approach to Functional Thiophene Dyes by Suzuki Coupling-Lithiation One-Pot Sequences

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1 General Considerations

All reactions were carried out in flame-dried Schlenk tubes by using syringes under nitrogen atmosphere. Dry solvents for reactions and analytics were directly used from a MB-SPS 800 solvent drying system (MBraun). 4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**2a**), [1] tris(4-bromophenyl)amine (**9b**), [2] 4-bromo-*N,N*-diphenylaniline (**3d**), [3] 2-(4-(hexyl-oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2c**), [4] 9,9-dihexyl-*N,N*-diphenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-2-amine (**2d**), [5] 10-(4-iodo-phenyl)-10*H*-phenothiazine (**10**) and [6] 2-(2,2-dibromovinyl)thiophene (**5b**) [7] were synthesized according to literature procedures as indicated. Commercial grade reagents were purchased from Sigma Aldrich, Alfa Aesar, ABCR, Fluorochem and ACROS and used as supplied without further purification. Crude mixtures were adsorbed on Celite® 545 (0.02-0.20 mm) from Carl Roth GmbH Co.KG. The purification of products was performed on silica gel 60 M (0.04–0.063 mm) from Macherey–Nagel by using the flash technique under a pressure of 2 bar. For TLC silica gel coated aluminium plates (60, F_{254}) from Merck were employed and analyzed with UV light at 254 or 365 nm.

^{1}H, ^{13}C, and 135-DEPT NMR spectra were recorded at 293 K or 353 K on 300 MHz (Bruker AVIII 300), 500 MHz (Bruker Avance DRX 500) or 600 MHz (Bruker Avance III 600) and the resonances of the residues of non-deuterated $CDCl_3$ (^{1}H δ= 7.26 ppm, ^{13}C δ= 77.00 ppm), acetone-d_6 (^{1}H δ= 2.05 ppm, ^{13}C δ= 29.84 ppm), DMSO-d_6 (^{1}H δ= 2.50 ppm, ^{13}C δ= 39.52 ppm) or THF-d_8 (^{1}H δ= 3.58 ppm, ^{13}C δ= 67.57 ppm) were locked as internal standards. The multiplicities of signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets and m = multiplet. The assignments of C_{quat}, CH, CH_2 and CH_3 nuclei are based on DEPT spectra.

IR spectra were recorded on a Shimadzu IR Affinity-1 with ATR technique. The intensities of IR signals are abbreviated as s (strong), m (medium) and w (weak).

EI mass spectra were recorded on Triple-Quadrupole mass spectrometer TSQ 7000 (Finnigan MAT). ESI mass spectra were recorded on the Ion-Trap-API-mass spectrometer Finnigan LCQ Deca (Thermo Quest) and high-resolution ESI mass spectra were recorded on a UHR-QTOF maXis 4G apparatus (Bruker Daltonics). MALDI-TOF mass spectra were measured on an UltrafleXtreme apparatus (Bruker Daltonics).

The elemental analyses were carried out on a Perkin Elmer Series II Analyser 2400 at the Institute for Pharmaceutical and Medicinal Chemistry at Heinrich-Heine-University Düsseldorf.

Melting points (uncorrected) were measured with a Büchi B545 apparatus.

Absorption spectra were recorded in dichloromethane high performance liquid chromatography (HPLC) grade at 293 K on Perkin Elmer UV/vis/NIR Lambda 19 spectrometer. For the determination of the extinction coefficients ε absorption measurements at five different concentrations were carried out. Emission spectra were recorded in dichloromethane HPLC grade at 293 K on a Perkin Elmer LS55 spectrometer.

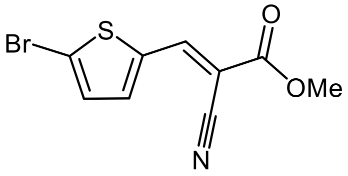
Quantum chemical calculations were carried out utilizing the HPC-Cluster Ivybridge of the Zentrum for Informations- und Medientechnologie (ZIM) at the Heinrich-Heine-University Düsseldorf.

Cyclic voltammetry experiments (EG&G Princeton Applied Research Model 263A potentiostat) were performed under argon atmosphere in dry and degassed dichloromethane at 293 K using n-Bu_4NPF_6 (0.1 M) as electrolyte and at scan rates v of 100, 250, 500 and 1000 mVs^{-1}. The three-electrode array consists of a working electrode with a 2 mm platinum disk, a platinum wire counter electrode, and a Ag/AgCl (3.0 M NaCl) reference electrode. The potentials were corrected by adding the internal standard decamethylferrocene to each measurement. Decamethylferrocene was referenced to the internal redox standard ferrocene ($E_0^{0/+1}$(deca-methylferrocene) = -95 mV vs. $E_0^{0/+1}$(ferrocene) = 450 mV).[8] Therefore the outlined potentials are indirectly referenced to ferrocene.

The preparation of the DSSC devices as well as the measurements of the DSSCs were carried out following a procedure published previously.[9]

2 Syntheses

2.1 Methyl-3-(5-bromothiophen-2-yl)-2-cyanoacrylate (3k)



In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere 2,5-dibromothiophene (**3l**) (1.20 g, 5.00 mmol) was dissolved in dry THF (6 mL) and cooled down to -78 °C (isopropanol/dry ice). Then, n-butyllithium (3.13 mL, 5.00 mmol, 1.6 M in hexane) was added dropwise via syringe over a period of 10 min to the vigorously stirred solution. Stirring was continued for 30 min at -78°C. Then dry DMF (0.58 mL, 7.50 mmol) was added, stirring was continued for another 90 min at -78 °C and then for 30 min at ambient temperature. To the reaction mixture acetic acid (0.570 mL, 10.0 mmol) was added. After stirring for 15 min at ambient temperature, methyl 2-cyanoacetate (0.88 mL, 10.00 mmol) was added and the stirring was continued for 16 h at ambient temperature. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography (*n*-hexane/ethyl acetate), which led to 1.23 g (4.50 mmol, 90%) of the product **3k** in form of a light-yellow solid, Mp.: 145 °C. R_f (*n*-hexane/ethyl acetate 1:1) = 0.75. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (s, 3H), 7.19 (d, $^3J_{HH}$ = 4.08 Hz, 1H), 7.51 (dd, $^3J_{HH}$ = 4.08 Hz, $^4J_{HH}$ = 0.63 Hz, 1H), 8.22 (d, $^4J_{HH}$ = 0.62 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.5 (CH_3), 99.2 (C_{quat}), 115.7 (C_{quat}),124.6 (C_{quat}), 131.6 (CH), 137.6 (C_{quat}), 138.1 (CH), 146.1 (CH), 163.1 (C_{quat}). MS(EI) *m/z*: 273 ([^{79}Br – M]$^+$, 25), 271 ([^{81}Br – M]$^+$, 24), 194 (6), 193 (11), 192 ([M – Br]$^+$, 100), 177 (15), 161 ([M – $C_5H_4NO_2$]$^+$, 15), 134 (5), 133 (25), 82 (6). IR: $\tilde{\nu}$ [cm^{-1}] = 3113 (w), 3082 (w), 3024 (w), 2961(w), 2216 (w), 1717 (s), 1589 (s), 1555 (w), 1524 (w), 1503 (w), 1452 (w), 1429 (m), 1412 (s), 1360 (w), 1312 (m), 1246 (s), 1202 (s), 1184 (m), 1113 (w), 1090 (m), 1063 (s), 1011 (w), 980 (m), 961 (w), 934 (w), 901 (w), 866 (s), 806 (s), 758 (s), 664 (w), 629 (w). Anal. calcd. for $C_9H_6BrNO_2S$ (272.1): C 39.73., H 2.22, N 5.15, S 11.78; Found: C 39.96, H 2.04, N 5.11, S 11.64.

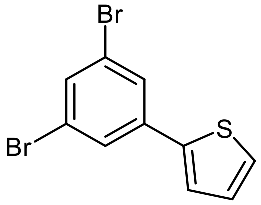
2.2 General procedure 1 (GP1) for the synthesis of thienyl dibromides 5

In a Schlenk vessel with magnetic stir bar under nitrogen atmosphere were added 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**2a**) (1.00 eq.) and 1,3,5-tribromobenzene (**9a**) (1.60 eq.) or tris(4-bromophenyl)amine (**9b**) (1.10 eq.) and were dissolved in toluene (3.5 mL/mmol). Then potassium carbonate (3.00 eq., 2 M in H_2O) was added and the biphasic, vigorously stirred solution was degassed with nitrogen for 5 min. Then tetrakis(triphenylphosphine)palladium(0) (1 mol%) was added and the reaction mixture was stirred at 80 °C overnight. The reaction was quenched by the addition of 50 mL H_2O, the organic layer was separated and the aqueous phase was extracted with dichloromethane three times. The combined organic phases were dried with anhydrous magnesium sulfate. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography. For Experimental details see table 1.

Table 1: Experimental details **GP1**.

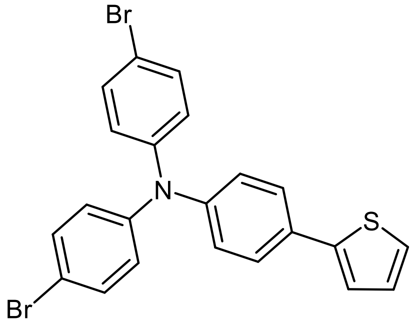
9 [g] (mmol)	**2a** [g] (mmol)	Product **5** yield [g] (%)
1,3,5-tribromobenzene **9a**		**5a**
5.318 (16.89)	2.218 (10.56)	1.944 (61)
tris(4-bromophenyl)amine **9b**		**5d**
7.000 (14.52)	2.773 (13.20)	3.017 (48)

2.2.1 2-(3,5-Dibromophenyl)thiophene (5a)



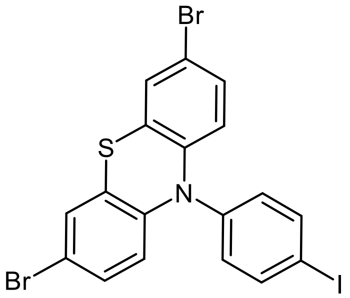
The crude product was synthesized following **GP1** and purified by flash column chromatography (*n*-hexane), which led to 1.944 g (6.110 mmol, 61%) of the product **5a** in form of a colorless solid, Mp.: 60 °C. R_f (*n*-hexane) = 0.74. ^{1}H-NMR (300 MHz, Acetone-d_6): δ 7.16 (dd, $^3J_{HH}$ = 5.11 Hz, $^3J_{HH}$ = 3.68 Hz, 1H), 7.57 (dd, $^3J_{HH}$ = 5.10 Hz, $^4J_{HH}$ = 1.15 Hz, 1H), 7.62 (dd, $^3J_{HH}$ = 3.69 Hz, $^4J_{HH}$ = 1.16 Hz, 1H), 7.65 (t, $^4J_{HH}$ = 1.71 Hz, 1H), 7.82 (d, $^4J_{HH}$ = 1.72 Hz, 2H). ^{13}C-NMR (75 MHz, acetone-d_6): 124.1 ($C_{quat.}$), 126.4 (CH), 127.9 (CH), 128.0 (CH), 129.4 (CH), 133.1 (CH), 139.0 ($C_{quat.}$), 141.1 ($C_{quat.}$). MS(EI) *m/z*: 320 ([2^{81}Br – M]$^+$, 50), 318 ([^{79}Br ^{81}Br – M]$^+$, 100), 316 ([2^{79}Br – M]$^+$, 50), 159 ([M – 2Br]$^+$, 16), 158 ([M – 2Br]$^+$, 98), 114 (18), 113 (14), 79 (16). IR: $\tilde{\nu}$ [cm^{-1}] = 3067 (w), 1784 (w), 1582 (m), 1549 (m), 1526 (m), 1443 (m), 1418 (m), 1346 (w), 1331 (w), 1288 (w), 1215 (w), 1105 (w), 1092 (w), 1057 (w), 999 (w), 982 (w), 895 (w), 858 (m), 833 (m), 820 (s), 754 (m), 743 (m), 729 (m), 692 (s), 664 (m). Anal. calcd. for $C_{10}H_6Br_2S$ (318.0): C 37.77, H 1.90, S 10.08; Found: C 38.01, H 1.92, S 10.07.

2.2.2 2-(3,5-Dibromophenyl)thiophene (5d)



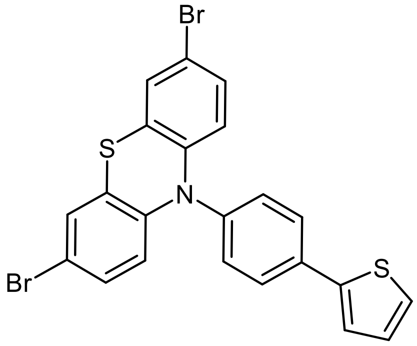
The crude product was synthesized following **GP1** and purified by flash column chromatography (*n*-hexane/CH_2Cl_2 20:1), which led to 3.017 g (6.220 mmol, 48%) of the product **5d** in form of a colorless solid, Mp.: 54 °C. R_f (*n*-hexane) = 0.39. ^{1}H NMR (300 MHz, Acetone-d_6): δ 7.00 - 7.07 (m, 4H), 7.07 - 7.17 (m, 3H), 7.38 - 7.43 (m, 2H), 7.43 - 7.50 (m, 4H), 7.58 - 7.65 (m, 2H).^{13}C NMR (75 MHz, acetone-d_6): δ 116.2 (C_{quat}), 123.8 (CH), 125.52 (CH), 125.54 (CH), 126.7 (CH), 127,7 (CH), 129.1 (CH), 130.7 (C_{quat}), 133.3 (CH), 144.4 (C_{quat}), 147.1 (C_{quat}), 147.4 (C_{quat}). MS(EI) *m/z*: 478 ([2^{81}Br – M]$^+$, 50), 485 ([^{79}Br ^{81}Br – M]$^+$, 100), 483 ([2^{79}Br – M]$^{+}$, 50), 405 ([^{81}Br-M – Br]$^{+}$, 8), 403 ([^{79}Br-M – Br]$^{+}$, 7), 325 ([M – 2Br]$^{+}$, 20), 249 ([M – Br – C_6H_4Br]$^{+}$, 19), 223 (13), 204 (18), 163 (36), 140 (16), 115 (27), 76 (25), 63 (14), 50 (11). IR: $\tilde{\nu}$ [cm^{-1}] = 3065 (w), 3028 (w), 1605 (w), 1578 (w), 1533 (w), 1499 (m), 1481 (s), 1450 (w), 1431 (w), 196 (w), 1310 (s), 1269 (s), 1209 (w), 1192 (w), 1175 (w), 1103 (w), 1071 (m), 1051 (w), 1007 (m), 959 (w), 916 (w), 893 (w), 849 (w), 814 (s), 768 (w), 727 (w), 692 (s), 667 (w), 621 (w). Anal. calcd. for $C_{22}H_{15}Br_2NS$ (485.2): C 54.56, H 3.12, N 2.89, S 6.61; Found: C 54.53, H 3.18, N 2.81, S 6.75.

2.3 3,7-Dibromo-10-(4-iodophenyl)-10*H*-phenothiazine (11)



In a Schlenk vessel with magnetic stir bar under nitrogen atmosphere 10-(4-Iodphenyl)-10*H*-phenothiazin (**10**) (2.719 g, 5.430 mmol) was dissolved in dry THF (20 mL). Then *N*-bromo-succinimide (1.933 g, 10.86 mmol) was added in one portion and the reaction mixture was stirred at ambient temperature for 17 h. The reaction was quenched by the addition of 50 mL of a saturated sodium thiosulfate solution, the organic layer was separated and the aqueous phase was extracted with dichloromethane three times. The combined organic phases were dried with anhydrous magnesium sulfate. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography using gradient elution (*n*-hexane/dichloromethane 20:1 → 10:1), which led to 3.023 g (5.410 mmol, 99%) of the product **11** in form of a light-yellow powder. Mp.: 235 °C. R_f (*n*-hexane) = 0.52. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 6.06 (d, $^{3}J_{HH}$ = 8.80 Hz, 2H), 7.11 (dd, $^{3}J_{HH}$ = 8.81 Hz, $^{4}J_{HH}$ = 2.34 Hz, 2H), 7.20 - 7.27 (m, 2H), 7.31 (d, $^{4}J_{HH}$ = 2.31 Hz 2H), 7.97 - 8.05 (m, 2H). ^{13}C NMR (150 MHz, DMSO-d$_6$): δ 99.6 (C_{quat}), 114.5 (C_{quat}), 117.9 (CH), 121.4 (C_{quat}), 128.6 (CH), 130.2 (CH), 132.5 (CH), 139.5 (C_{quat}), 140.3 (CH), 142.3 (C_{quat}). MS(EI) *m*/*z*: 561 ([2^{79}Br-M]$^{+}$, 10), 559 ([^{79}Br^{81}Br-M]$^{+}$, 21), 557 ([2^{81}Br-M]$^{+}$, 9), 513 (14), 511 (13), 487 (13), 485 (26), 483 (18), 482 (21), 481 (100), 480 (26), 479 ([M – Br]$^{+}$, 97), 430 ([2^{79}Br – M – I]$^{+}$, 6), 432 ([^{79}Br^{81}Br-M – I]$^{+}$, 13), 434 ([2^{81}Br-M]$^{+}$, 8), 401 ([M – 2Br]$^{+}$, 25), 400 ([M – 2Br]$^{+}$, 90), 356 (11), 354 ([M – Br – I]$^{+}$, 18), 353 ([M – Br – I]$^{+}$, 12), 351 ([M – Br – I]$^{+}$, 10), 278 ([^{81}Br-M – C_6H_3BrI]$^{+}$, 24), 276 ([^{79}Br-M – C_6H_3BrI]$^{+}$, 23), 275 (10), 274 ([M – 2Br – I]$^{+}$, 18), 273 ([M – 2Br – I]$^{+}$, 74), 272 ([M – 2Br – I]$^{+}$, 43), 271 (30), 242 (10), 241 (43), 239 (17), 228 (13), 197 (42), 176 (12), 163 (11), 153 (16), 137 (44), 136 (21), 76 (21), 58 (10). IR: $\tilde{\nu}$ [cm^{-1}] = 3076 (w), 3053 (w), 1877 (w), 1477 (m), 1452 (s), 1416 (w), 1406 (w), 1379 (w), 1364 (w), 1304 (s), 1269 (m), 1258 (m), 1242 (m), 1188 (w), 1148 (w), 1117 (w), 1094 (m), 1084 (w), 1053 (w), 1011 (m), 941 (w), 922 (w), 866 (m), 826 (s), 810 (s), 781 (w), 764 (w), 710 (m), 698 (w). Anal. calcd. for $C_{18}H_{10}Br_2INS$ (559.1): C 38.67, H 1.80, N 2.51, S 5.73; Found: C 38.67, H 1.69, N 2.49, S 5.86.

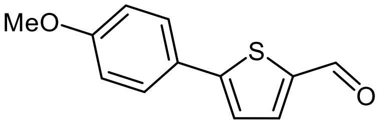
2.4 3,7-Dibromo-10-(4-(thiophen-2-yl)phenyl)-10*H*-phenothiazine (5c)



In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere thiophene (178 mg, 2.12 mmol) was dissolved in dry THF (20 mL) and cooled down to -78 °C (isopropanol/dry ice). Then, *n*-butyllithium (1.33 mL, 2.12 mmol, 1.6 M in hexane) was added via syringe. The reaction solution was stirred for 2 h at -78°C, whereas zinc dibromide (1.13 g, 5.00 mmol) were vacuum dried at 120 °C for 1.5 h. After the dried zinc dibromide had been cooled to ambient temperature, dry THF (5 mL) was added. Then the resulting zinc dibromide solution (2.54 mL, 2.54 mmol) was dropped into the reaction mixture at -78 °C, which was stirred at ambient temperature for 30 min then. Tetrakis(triphenylphosphine)palladium(0) (74.0 mg, 64.0 µmol) and 3,7-Dibromo-10-(4-iodophenyl)-10*H*-phenothiazine (**11**) (1.19 g, 2.12 mmol) were added and the reaction solution was stirred at ambient temperature for 20 h. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography using gradient elution (*n*-hexane/dichloromethane 30:1 → 10:1), which led to 795 mg (1.54 mmol, 73%) of the product **5c** in form of a light-yellow solid. Mp.: 205 °C. R_f (*n*-hexane/ethyl acetate 30:1) = 0.43. ^{1}H NMR (300 MHz, THF-d_8): δ 6.15 (d, $^3J_{HH}$ = 8.80 Hz, 2H), 6.98 (dd, $^3J_{HH}$ = 8.79 Hz, $^4J_{HH}$ = 2.31 Hz, 2H), 7.13 (dd, $^3J_{HH}$ = 5.11 Hz, $^4J_{HH}$ = 3.62 Hz, 1H), 7.18 (d, $^4J_{HH}$ = 2.31 Hz, 2H), 7.38 - 7.44 (m, 2H), 7.46 (dd, $^3J_{HH}$ = 5.11 Hz, $^4J_{HH}$ = 1.13 Hz, 1H), 7.52 (dd, $^3J_{HH}$ = 3.64 Hz, $^4J_{HH}$ = 1.16 Hz, 1H), 7.90 - 7.97 (m, 2H). ^{13}C-NMR (75 MHz, THF-d_8): δ 115.5 (C_{quat}), 118.3 (CH), 122.6 (C_{quat}), 125.1 (CH), 126.7 (CH), 129.09 (CH), 129.13 (CH), 129.6 (CH), 130.7 (CH), 132.1 (CH), 136.1 (C_{quat}), 140.2 (C_{quat}), 143.8 (C_{quat}), 144.1 (C_{quat}). MS(ESI) *m*/*z*: 513.3

([2^{79}Br-M]$^+$), 515.3 ([^{79}Br^{81}Br-M]$^+$), 517.3 ([2^{81}Br-M]$^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 1533 (w), 1497 (w), 1477 (w), 1456 (s), 1431 (w), 1404 (w), 1391 (w), 1379 (w), 1298 (m), 1269 (w), 1258 (m), 1240 (m), 1213 (w), 1192 (w), 1148 (w), 1128 (w), 1099 (w), 1082 (w), 1047 (w), 1020 (w), 959 (w), 878 (w), 853 (w), 839 (m), 827 (w), 804 (s), 766 (w), 746 (w), 723 (m), 694 (s), 669 (w). Anal. calcd. for $C_{22}H_{13}Br_2NS_2$ (515.3): C 51.28, H 2.54, N 2.72, S 12.44; Found: C 51.30, H 2.43, N 2.79, S 12.70.

2.5 5-(4-Methoxyphenyl)thiophene-2-carbaldehyde (12)



Compound **12** is known in the literature [10], but was synthesized following another procedure:

In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere were filled 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**2a**) (210 mg, 1.00 mmol), 4-iodoanisole (**3a**) (246 mg, 1.05 mmol), cesium fluoride (456 mg, 3.00 mmol), bis(dibenzylideneacetone)palladium(0) (29.0 mg, 50.0 µmol) and tri-*tert*-butyl phosphonium tetrafluoroborate (29.0 mg, 0.100 mmol) and dissolved in dry THF (10 mL). The reaction mixture was stirred at 70 °C for 30 min. Then the reaction mixture was cooled slowly to ambient temperature and then to -78 °C (isopropanol/dry ice). To the cooled, viscous reaction mixture was dropped *n*-butyllithium (1.25 mL, 2.00 mmol, 1.6 M in hexane). Vigorous stirring was continued at -78 °C for 2 h. Then dry DMF (150 µL, 2.00 mmol) was added and the stirring was continued for another 90 min at -78 °C. Then the reaction mixture was stirred for 30 min at ambient temperature, before the reaction was quenched by adding water (10 mL). The organic layer was separated and the aqueous phase was extracted with dichloromethane three times. The combined organic phases were dried with anhydrous magnesium sulfate. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography (*n*-hexane/ethyl acetate 5:1), which led to 98.0 mg (0.450 mmol, 45%) of the product **12** in form of a beige solid. Mp.: 184 °C. R_f (*n*-hexane/ethyl acetate 5:1) = 0.36. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.93-6.98 (m, 2H), 7.30 (d, $^3J_{HH}$ = 3.94 Hz, 1H), 7.59-7.64 (m, 2H), 7.71 (d, $^3J_{HH}$ = 3.96 Hz, 1H), 9.86 (s,1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6 (CH_3), 114.8 (CH), 123.2 (CH), 126.1 (C_{quat}), 128.0 (CH), 137.6 (CH), 141.9 (C_{quat}), 154.7 (C_{quat}), 161.0 (C_{quat}), 182.6 (CH). MS(EI) *m*/*z*: 219 ([M + H]$^+$, 15), 218 ([M]$^+$, 100), 217 ([M – H]$^+$, 31), 203 ([M – CH_3]$^+$, 45), 175 ([$C_{10}H_7OS$]$^+$, 27), 147 (40), 145 (28), 115 (10), 102 (17), 77 (11). IR: $\tilde{\nu}$ [cm^{-1}] = 2980 (w), 2891 (w), 1647 (s), 1601 (m), 1506 (w), 1449 (m), 1439 (m), 1418 (m), 1385 (w), 1288 (m), 1256 (m), 1223 (m), 1182 (m), 1113 (w), 1057 (m), 1024 (m), 957 (w), 833 (m), 802 (s), 756 (m), 689 (m), 667 (m).

2.6 General procedure 2 (GP2) for the synthesis of thiophens 1 via Suzuki-Lithiation-Formylation-Knoevenagel sequence (SLiForK)

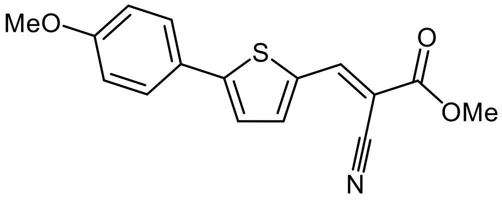
In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere were filled 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**2a**) (1.00 eq.), an aryl halide **3** (1.05 eq), cesium fluoride (3.00 eq.), bis(dibenzylideneacetone)palladium(0) (5 mol%) and tri-*tert*-butyl phosphonium tetrafluoroborate (10 mol%) and dissolved in dry THF (8 mL/mmol). The reaction mixture was stirred at 70 °C until full conversion of the starting materials could be observed via TLC. Then, the reaction mixture was cooled slowly to ambient temperature and then to -78 °C (isopropanol/dry ice). To the cooled, viscous reaction mixture was dropped *n*-butyllithium (2.00 eq., 1.6 M in hexane). Vigorous stirring was continued at -78 °C for 2 h. After that dry DMF (2.00 eq.) was added and the stirring was continued at -78 °C for another 90 min. Then the reaction mixture was stirred at ambient temperature for 30 min. Acetic acid (10.00 eq.) was added and stirring was continued at ambient temperature for another 15 min. Then a CH-acidic compound **4** (2.00 eq.) was added. The reaction mixture was stirred overnight at ambient temperature. The next day volatiles were removed by evaporation and the mostly intense coloured crude product was purified by flash column chromatography and additional recrystallisation if necessary. For Experimental details see table 2.

Table 2: Experimental details **GP2**.

2a [mg] (mmol)	Aryl halide **3** [mg] (mmol)	*CH*-comp. **4** [mg] (mmol)	t_{Suzuki} [h]	$t_{Knoevenagel}$ [h]	Yield **1** [mg] (%)
	4-iodoanisole **3a**	[b] **4a**			**1a**
105 (0.50)	124 (0.530)	99.0 (1.00)	1	15	131 (88)
	3a	[c] **4b**			**1b**
210 (1.00)	246 (1.05)	132 (2.00)	1.5	16.5	118 (44)
	3a	[d] **4c**			**1c**
210 (1.00)	246 (1.05)	324 (2.00)	1.5	16.5	68.0 (19)
	3a	[e] **4d**			**1d**
210 (1.00)	246 (1.05)	294 (2.00)	1.5	16.5	175 (50)
	[a] **3b**	[b] **4a**			**1e**
486 (2.31)	788 (2.43)	482 (4.86)	24	24	612 (61)

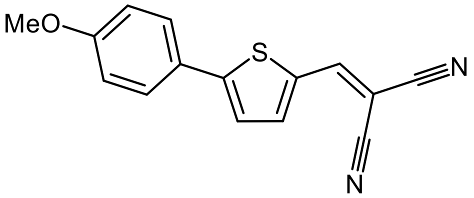
a: 4-bromo-*N,N*-diphenylaniline ; b: methyl 2-cyanoacetate; c: malononitrile;
d: 2-(4-nitrophenyl)acetoneitrile; e: 3-methyl-2-thioxothiazolidin-4-one.

2.6.1 2-Cyano-3-(5-(4-methoxyphenyl)thiophen-2-yl)acrylate (1a)



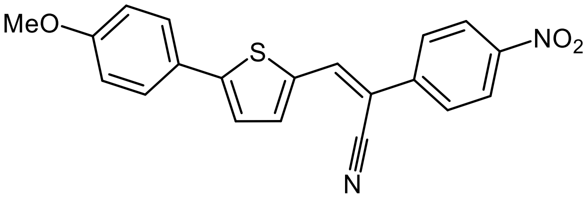
The crude product was synthesized following **GP2** and purified by flash column chromatography (*n*-hexane/ethyl acetate 5:1), which led to 131 mg (0.470 mmol, 88%) of the product **1a** in form of an orange solid. Mp.: 145 - 150 °C. R_f (*n*-hexane/ethyl acetate 3:1) = 0.30. ^{1}H NMR (300 MHz, acetone-d$_6$): δ 3.78 (s, 3H), 3.88 (s, 3H), 7.03 - 7.10 (m, 2H), 7.59 (d, $^{3}J_{HH}$ = 4.06 Hz, 1H), 7.73 - 7.80 (m, 2H), 7.69 (dd, $^{3}J_{HH}$ = 4.08 Hz, $^{4}J_{HH}$ = 0.59 Hz, 1H), 8.43 (d, $^{4}J_{HH}$ = 0.52 Hz, 1H). ^{13}C NMR (150 MHz, acetone-d$_6$): δ 53.3 (CH$_3$), 55.9 (CH$_3$), 97.7 (C$_{quat}$), 115.7 (CH), 116.7 (C$_{quat}$), 124.6 (CH), 126.3 (C$_{quat}$), 128.8 (CH), 134.8 (C$_{quat}$), 142.0 (CH), 147.6 (CH), 155.4 (C$_{quat}$), 162.1 (C$_{quat}$), 163.9 (C$_{quat}$). MS(EI) *m/z*: 300 ([M + H]$^+$, 18), 299 ([M]$^+$, 100), 284 ([M – CH$_3$]$^+$, 32), 278 (12), 277 (29), 268 ([M – CH$_3$O]$^+$, 10), 262 (18), 240 ([M – C$_2$H$_3$O$_2$]$^+$, 9), 196 (16), 192 ([M – C$_7$H$_7$O]$^+$, 9), 183 (18), 149 (14). IR: $\tilde{\nu}$ [cm^{-1}] = 3038 (w), 3007 (w), 2953 (w), 2837 (w), 2216 (w), 1709 (s), 1607(w), 1578 (s), 1557 (w), 1526 (w), 1495 (m), 1427 (s), 1393 (w), 1368 (w), 1337 (w), 1280 (m), 1252 (s), 1211 (s), 1204 (s), 1180 (s), 1117 (m), 1080 (m), 1063 (s), 1024 (s), 1009 (m), 955 (m), 930 (w), 799 (s), 758 (s), 719 (w), 692 (m), 662 (m), 629 (m). Anal. calcd. for $C_{16}H_{13}NO_3S$ (299.3): C 64.20, H 4.38, N 4.68, S 10.71; Found: C 64.23, H 4.51, N 4.68, S 10.41.

2.6.2 2-((5-(4-Methoxyphenyl)thiophen-2-yl)methylene)malononitrile (1b) [11]



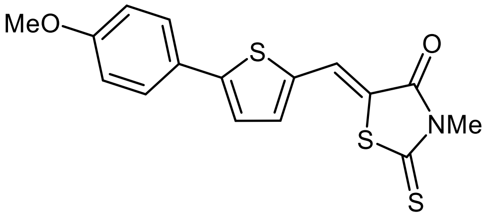
The crude product was synthesized following **GP2** and purified by flash column chromatography (*n*-hexane/ethyl acetate 1:1) and recrystallization from ethanol, which led to 118 mg (0.440 mmol, 44%) of the product **1b** in form of an orange solid. Mp.: 191 °C. R_f (*n*-hexane/ethyl acetate 3:1) = 0.35. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 3.83 (s, 3H), 7.02 - 7.10 (m, 2H), 7.72 (d, $^3J_{HH}$ = 4.11 Hz, 1H), 7.73 - 7.80 (m, 2H), 7.91 (dd, $^3J_{HH}$ = 4.14 Hz, $^4J_{HH}$ = 0.59 Hz, 1H), 8.60 (d, $^4J_{HH}$ = 0.56 Hz, 1H). ^{13}C NMR (150 MHz, THF-d$_8$): δ 55.5 (CH$_3$), 73.7 (C$_{quat}$), 114.0 (C$_{quat}$), 114.7 (C$_{quat}$), 115.0 (CH), 124.5 (CH), 128.1 (CH), 133.1 (C$_{quat}$), 142.7 (CH), 152.6 (CH), 155.5 (C$_{quat}$), 161.0 (C$_{quat}$). MS(EI) *m*/*z*: 267 ([M + H]$^+$, 18), 266 ([M]$^+$, 100), 252 ([M – CH$_3$]$^+$, 11), 251 ([M – CH$_3$]$^+$, 65), 223 (46), 196 (11). IR: $\tilde{\nu}$ [cm^{-1}] = 3098 (w), 3026 (w), 2980 (w), 2959 (w), 2938 (w), 2839 (w), 2218 (m), 1607 (w), 1568 (s), 1558 (m), 1493 (w), 1435 (m), 1417 (m), 1360 (w), 1331 (m), 1292 (w), 1250 (m), 1209 (m), 1177 (s), 1144 (m), 1125 (w), 1113 (w), 1080 (s), 1034 (m), 939 (m), 903 (w), 826 (s), 804 (s), 783 (s), 748 (w), 683 (m), 669 (m), 631 (w), 606 (s).

2.6.3 3-(5-(4-Methoxyphenyl)thiophen-2-yl)-2-(4-nitrophenyl)acrylonitrile (1c)



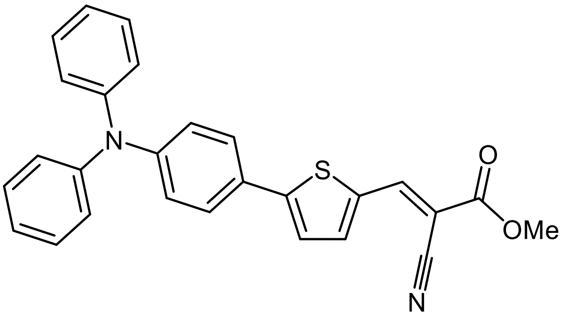
The crude product was synthesized following **GP2** and purified by flash column chromatography (*n*-hexane/ethyl acetate 1:1) and suspension in boiling ethanol, which led to 68 mg (0.19 mmol, 19%) of the product **1c** in form of a red powder. Mp.: 210 °C. R_f (*n*-hexane/ethyl acetate 3:1) = 0.35. ^{1}H NMR (300 MHz, DMSO-d$_6$): δ 3.82 (s, 3H), 7.01 - 7.09 (m, 2H), 7.61 (d, $^3J_{HH}$ = 3.96 Hz, 1H), 7.68 - 7.75 (m, 2H), 7.82 (d, $^3J_{HH}$ = 4.02 Hz, 1H), 7.93 - 8.01 (m, 2H), 8.27 - 8.37 (m, 2H), 8.52 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d$_6$, 80 °C): δ 55.1 (CH$_3$), 102.8 (C$_{quat}$), 114.6 (CH), 117.2 (C$_{quat}$), 123.3 (CH), 123.9 (CH), 125.0 (C$_{quat}$), 126.0 (CH), 127.2 (CH), 135.0 (C$_{quat}$), 137.4 (CH), 138.3 (CH), 139.8 (C$_{quat}$), 146.7 (C$_{quat}$), 150.0 (C$_{quat}$), 160.0 (C$_{quat}$). MS(EI) *m*/*z*: 363 ([M + H]$^+$, 22), 362 ([M]$^+$, 100), 347 ([M – CH$_3$]$^+$, 22), 273 (12), 272 (13), 240 ([M – $C_6H_4NO_2$]$^+$, 13). IR: $\tilde{\nu}$ [cm^{-1}] = 2978 (w), 1599 (w), 1570 (m), 1512 (s), 1501 (m), 1491 (m), 1439 (m), 1431 (s), 1416 (m), 1369 (w), 1337 (s), 1296 (m), 1258 (s), 1219 (m), 1175 (s), 1148 (w), 1111 (m), 1067 (m), 1026 (s), 1009 (m), 989 (m), 959 (w), 934 (m), 893 (w), 835 (s), 806 (s), 797 (m), 748 (s), 686 (s), 679 (w), 652 (m). Anal. calcd. for $C_{20}H_{14}N_2O_3S$ (362.4): C 66.13, H 3.89, N 7.73, S 8.85; Found: C 66.29, H 3.94, N 7.72, S 8.65.

2.6.4 5-((5-(4-Methoxyphenyl)thiophen-2-yl)methylene)-3-methyl-2-thioxothiazo-lidin -4-one (1d)



The crude product was synthesized following **GP2** and purified by flash column chromatography (*n*-hexane/ethyl acetate 1:1) and suspension in boiling ethanol, which led to 175 mg (0.500 mmol, 50%) of the product **1d** in form of an orange solid. Mp.: 195 - 197 °C. R_f (*n*-hexane/ethyl acetate 3:1) = 0.50. ^{1}H NMR (600 MHz, DMSO-d$_6$, 80 °C): δ 3.42 (s, 3H), 3.83 (s, 3H), 7.00 - 7.07 (m, 2H), 7.56 (d, $^3J_{HH}$ = 3.97 Hz, 1H), 7.69 (d, $^3J_{HH}$ = 4.05 Hz, 1H), 7.70 - 7.72 (m, 2H), 8.00 (s, 1H). ^{13}C NMR (150 MHz, DMSO-d$_6$, 80 °C): δ 30.8 (CH_3), 55.1 (CH_3), 114.6 (CH), 118.8 (C_{quat}), 124.2 (CH), 124.9 (C_{quat}), 125.4 (CH), 127.0 (CH), 135.2 (C_{quat}), 136.8 (CH), 151.6 (C_{quat}), 160.0 (C_{quat}), 166.2 (C_{quat}), 191.9 (C_{quat}). MS(EI) *m/z*: 348 ([M + H]$^+$, 10), 347 ([M]$^+$, 51), 247 (16), 246 ([M – C_3H_3NOS]$^+$, 100), 231 ([M – C_3H_3NOS – CH_3]$^+$, 57), 203 (21), 123 (18). IR: $\tilde{\nu}$ [cm^{-1}] = 2945 (w), 1697 (s), 1605 (w), 1582 (s), 1526 (w), 1433 (m), 1420 (s), 1348 (m), 1285 (s), 1248 (s), 1204 (m), 1182 (m), 1173 (m), 1113 (s), 1067 (s), 1055 (m), 1028 (s), 1007 (m), 988 (m), 957 (m), 939 (m), 923 (m), 907 (m), 878 (w), 826 (s), 812 (m), 789 (s), 731 (s), 700 (m), 652 (m), 640 (m), 627 (m). Anal. calcd. for $C_{16}H_{13}NO_2S_3$ (347.5): C 55.31, H 3.77, N 4.03, S 27.68; Found: C 55.33, H 3.80, N 4.03, S 27.38.

2.6.5 Methyl 2-cyano-3-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)acrylate (1e)



The crude product was synthesized following **GP2** and purified by flash column chromatography (*n*-hexane/ethyl acetate 5:1), which led to 612 mg (1.41 mmol, 61%) of the product **1e** in form of a dark red solid. Mp.: 171 °C. R_f (*n*-hexane/ethyl acetate 5:1) = 0.29. ^{1}H NMR (300 MHz, acetone-d$_6$): δ 3.87 (s, 3H), 7.01 - 7.08 (m, 2H), 7.11 - 7.19 (m, 6H), 7.32 - 7.40 (m, 4H), 7.60 (d, $^3J_{HH}$ = 4.08 Hz, 1H), 7.67 - 7.74 (m, 2H), 7.97 (dd, $^3J_{HH}$ = 4.08 Hz, $^4J_{HH}$ = 0.59 Hz, 1H), 8.42 (d, $^4J_{HH}$ = 0.58 Hz, 1H). ^{13}C NMR (150 MHz, THF-d$_8$): δ 53.3 (CH$_3$), 97.6 (C$_{quat}$), 116.7 (C$_{quat}$), 122.9 (CH), 124.5 (CH), 125.0 (CH), 126.2 (CH), 126.7 (C$_{quat}$), 128.3 (CH), 130.5 (CH), 134.9 (C$_{quat}$), 141.9 (CH), 147.4 (CH), 147.9 (C$_{quat}$), 150.3 (C$_{quat}$), 155.4 (C$_{quat}$), 164.0 (C$_{quat}$). MS(MALDI) *m*/*z*: 436.167 ([M]$^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 3090 (w), 2957 (w), 1722 (m), 1695 (w), 1574 (s), 1558 (m), 1458 (s), 1427 (s), 1315 (m), 1292 (s), 1279 (s), 1254 (s), 1213 (s), 1188 (s), 1179 (s), 1155 (m), 1125 (w), 1092 (w), 1067 (s), 1028 (m), 1003 (m), 968 (m), 955 (m), 939 (m), 918 (w), 895 (w), 843 (m), 814 (s), 804 (m), 752 (s), 723 (m), 696 (s), 664 (m), 638 (m). Anal. calcd. for $C_{27}H_{20}N_2O_2S$ (436.5): C 74.29, H 4.62, N 6.42, S 7.34; Found: C 74.01, H 4.77, N 6.25, S 7.14.

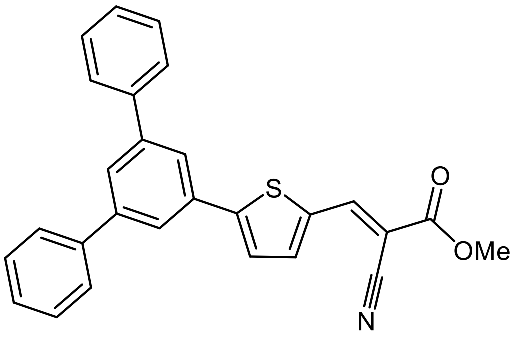
2.7 General procedure 3 (GP3) for the synthesis of thiophens 6 via twofold Suzuki-Lithiation-Formylation-Knoevenagel sequence (S²LiForK)

In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere were filled 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (**2b**) (2.10 eq.), thienyl bromide **5a** or **5b** (1.00 eq.), cesium fluoride (6.00 eq.), bis(dibenzylideneacetone)palladium(0) (5 mol%) and tri-*tert*-butylphosphonium tetrafluoroborate (10 mol%) and dissolved in dry THF (8 mL/mmol). The reaction mixture was stirred at 70 °C until full conversion of the starting materials could be observed via TLC. Then, the reaction mixture was slowly cooled to ambient temperature and then to -78 °C (isopropanol/dry ice). To the cooled, viscous reaction mixture was dropped *n*-butyllithium (2.00 eq., 1.6 M in hexane). Vigorous stirring was continued at -78 °C for 2 h. Then dry DMF (2.00 eq.) was added and the stirring was continued at -78 °C for another 90 min. Then the reaction mixture was stirred at ambient temperature for 30 min, Acetic acid (15.00 eq.) was added and stirring was continued at ambient temperature for another 15 min. Then methyl 2-cyanoacetate (**4a**) (2.00 eq.) was added. The reaction mixture was stirred at ambient temperature overnight. The next day volatiles were removed by evaporation and the intense coloured crude products were purified by flash column chromatography. For Experimental details see table 3.

Table 3: Experimental details **GP3**.

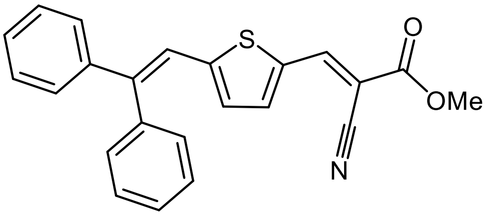
2b	**Thienyl bromide 5**	t_{Suzuki}	$t_{Knoevenagel}$	**Yield 6**
[mg] (mmol)	[mg] (mmol)	[h]	[h]	[mg] (%)
	5a			**6a**
223 (1.09)	165 (0.520)	2	15	168 (77)
	5b			**6b**
429 (2.10)	268 (1.00)	3.5	16	186 (50)

2.7.1 Methyl 3-(5-([1,1':3',1''-terphenyl]-5'-yl)thiophen-2-yl)-2-cyanoacrylate (6a)



The crude product was synthesized following **GP3** and purified by flash column chromatography (*n*-hexane/ethyl acetate 5:1), which led to 168 mg (0.400 mmol, 77%) of the product **6a** in form of an orange solid. Mp.: 192 - 202 °C. R_f (*n*-hexane/ethyl acetate 5:1) = 0.32. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (s, 3H), 6.95 - 7.03 (m, 2H), 7.04 - 7.12 (m, 4H), 7.37 - 7.44 (m, 4H), 7.52 (t, $^4J_{HH}$ = 1.65 Hz, 1H), 7.57 (d, $^4J_{HH}$ = 1.65 Hz, 2H), 7.59 (d, $^3J_{HH}$ = 4.05 Hz, 1H), 7.69 (dd, $^3J_{HH}$ = 4.05 Hz, $^4J_{HH}$ = 0.60 Hz, 1H), 8.19 (d, $^4J_{HH}$ = 0.60 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 53.1 (CH_3), 97.0 ($C_{quat.}$), 115.9 ($C_{quat.}$), 123.6 (CH), 126.3 (CH), 126.6 (CH), 127.2 (CH), 128.1 (CH), 129.0 (CH), 133.7 ($C_{quat.}$), 134.9 ($C_{quat.}$), 139.4 ($C_{quat.}$), 142.0 (CH), 142.3 ($C_{quat.}$), 147.4 (CH), 153.2 ($C_{quat.}$), 162.8 ($C_{quat.}$). MS(EI) *m/z*: 422 ($[M + H]^+$, 30), 421 ($[M]^+$, 100), 363 ($[M – C_2H_3O_2]^+$, 12), 362 ($[M – C_2H_3O_2]^+$, 12), 340 (11), 211 (14), 195 (20), 181 (29). IR: $\tilde{\nu}$ [cm^{-1}] = 3061(w), 3022 (w), 2953 (w), 2930 (w), 2870 (w), 1715 (s), 1578 (s), 1497 (w), 1433 (s), 1406 (m), 1368 (m), 1323 (w), 1267 (s), 1206 (m), 1142 (m), 1126 (w), 1096 (m), 1076 (m), 1059 (m), 1034 (w), 914 (w), 864 (m), 816 (s), 748 (s), 743 (s), 692 (s), 650 (m), 611 (m). Anal. calcd. for $C_{27}H_{19}NO_2S$ (421.5): C 76.94, H 4.54, N 3.32, S 7.61; Found: C 77.08, H 4.62, N 3.27, S 7.38.

2.7.2 Methyl 2-cyano-3-(5-(2,2-diphenylvinyl)thiophen-2-yl)acrylate (6b)



The crude product was synthesized following **GP3** and purified by flash column chromatography (*n*-hexane/ethyl acetate 5:1), which led to 186 mg (0.500 mmol, 50%) of the product **6b** in form of a red solid. Mp.: 165 °C. R_f (*n*-hexane/ethyl acetate 3:1) = 0.33. ^{1}H NMR (300 MHz, acetone-d_6): δ 3.82 (s, 3H), 7.15 (dd, $^3J_{HH}$ = 4.05 Hz, $^4J_{HH}$ = 0.65 Hz, 1H), 7.26 - 7.32 (m, 2H), 7.32 - 7.41 (m, 3H), 7.41 - 7.46 (m, 2H), 7.50 - 7.60 (m, 4H), 7.79 (dd, $^3J_{HH}$ = 4.08 Hz, $^4J_{HH}$ = 0.64 Hz, 1H), 8.19 (d, $^4J_{HH}$ = 0.64 Hz, 1H). ^{13}C NMR (75 MHz, acetone-d_6): δ 53.3 (CH_3), 98.1 (C_{quat}), 116.3 (C_{quat}), 121.0 (CH), 128.0 (CH), 129.3 (CH), 129.4 (CH), 129.9 (CH), 130.5 (CH), 130.7 (CH), 131.4 (CH), 136.6 (C_{quat}), 138.7 (CH), 139.3 (C_{quat}), 141.7 (C_{quat}), 146.1 (C_{quat}), 146.9 (CH), 152.2 (C_{quat}), 163.8 (C_{quat}). MS(EI) *m/z*: 372 ($[M + H]^+$, 27), 371 ($[M]^+$, 100), 340 ($[M – CH_3O]^+$, 3), 338 (15), 312 ($[M – C_2H_3O_2]^+$, 8), 310 (13), 293 (13), 278 (11), 277 (10), 271 (12), 58 (10). IR: $\tilde{\nu}$ [cm^{-1}] = 2949 (w), 2868 (w), 1719 (w), 1622 (w), 1599 (w), 1557 (m), 1497 (w), 1472 (w), 1460 (w), 1447 (w), 1427 (m), 1391 (w), 1369 (w), 1317 (m), 1287 (w), 1254 (m), 1211 (w), 1182 (m), 1109 (w), 1090 (w), 1078 (w), 1053 (w), 1020 (w), 991 (w), 962 (w), 933 (w), 903 (w), 828 (s), 804 (m), 772 (m), 758 (m), 741 (w), 702 (m), 664 (w). Anal. calcd. for $C_{23}H_{17}NO_2S$ (371.5): C 74.37, H 4.61, N 3.77, S 8.63; Found: C 74.18, H 4.65, N 3.77, S 8.43.

2.8 General procedure 4 (GP4) for the preparation of DSSC-dyes 7 via twofold Suzuki-Lithiation-Formylation-Knoevenagel sequence (S²LiForK) and saponification

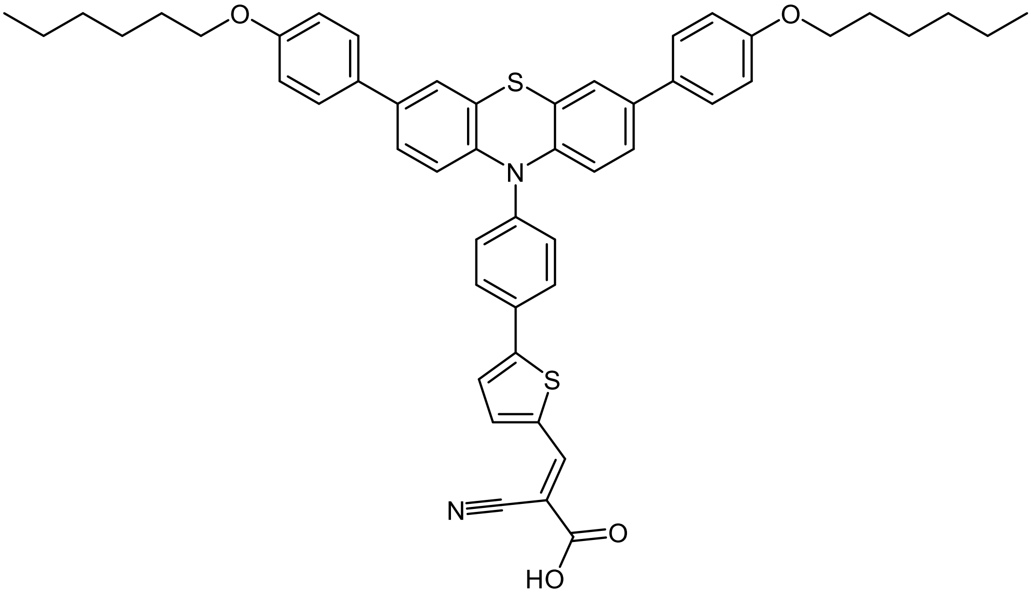
In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere were filled pinacol ester **2c** or **2d** (2.10 eq.), thiophene derivative **5c** or **5d** (1.00 eq.), cesium fluoride (6.00 eq.), bis(dibenzlidene-acetone)palladium(0) (5 mol%) and tri-*tert*-butylphosphonium tetrafluoroborate (10 mol%) or *S*-Phos (10 mol%) as ligand instead and dissolved in dry THF (8 mL/mmol). The reaction mixture was stirred at 70 °C until full conversion of the starting materials could be observed via TLC. Then the reaction mixture was cooled slowly to ambient temperature and then to -78 °C (isopropanol/dry ice). To the cooled, viscous reaction mixture was dropped *n*-butyllithium (2.00 eq., 1.6 M in hexane). Vigorous stirring was continued at -78 °C for 2 h. Then dry DMF (2.00 eq.) was added and the stirring was continued at -78 °C for another 90 min. Then, the reaction mixture was stirred at ambient temperature for 30 min. Acetic acid (15.00 eq.) was added and stirring at ambient temperature for another 15 min followed. Then methyl 2-cyanoacetate (**4a**) (2.00 eq.) was added. The reaction mixture was stirred at ambient temperature overnight. The next day volatiles were removed by evaporation and the intense coloured crude products were purified by flash column chromatography. The isolated methyl esters were saponificated directly. In a Schlenk vessel with magnetic stir bar under nitrogen atmosphere were dissolved the ester and lithium hydroxide (10.00 eq.) in a 5:1 THF/H_2O mixture. The reaction mixture was stirred at ambient temperature until full conversion of the ester could be observed via TLC. Then the mixture was acidified (pH ≈ 2) using hydrochloric acid (1 M). The organic layer was separated and the aqueous phase was extracted with dichloromethane three times. The combined organic phases were dried with anhydrous magnesium sulfate. The volatiles were removed by evaporation and the crude product was purified by flash column chromatography. For Experimental details see table 4.

Table 4: Experimental details **GP4**.

5 [mg] (mmol)	**2** [mg] (mmol)	Ligand	t_{Suzuki} [h]	$t_{Knoev.}$ [h]	$t_{sapon.}$ [h]	Yield **7** [mg] (%)
5c 557 (1.08)	**2c** [a] 688 (2.26)	$HP^tBu_3BF_4$	5.5	13	2	**7a** 374 (43)
5d 200 (0.410)	**2c** [a] 271 (0.890)	*S*-Phos	16	19	24	**7b** 127 (40)
5d 243 (0.500)	**2d** [b] 659 (1.05)	*S*-Phos	17	16	4	**7c** 156 (22)

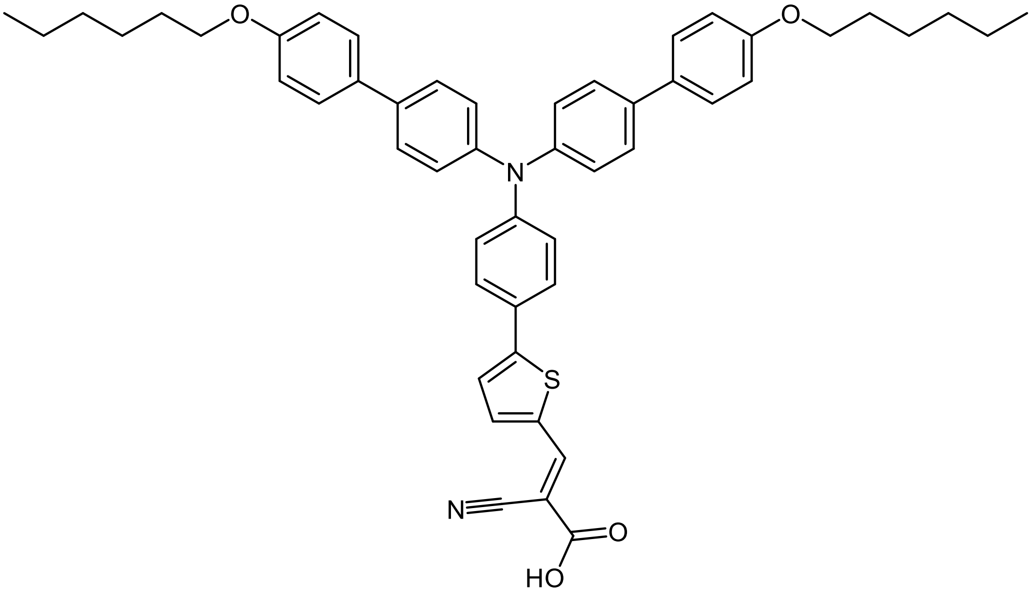
a: 4,4,5,5-tetramethyl-2-(4-(hexyloxy)phenyl)-1,3-dioxolane; b: 9,9-dihexyl-*N,N*-diphenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluoren-2-amine.

2.8.1 3-(5-(4-(3,7-Bis(4-(hexyloxy)phenyl)-10*H*-phenothiazin-10-yl)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (7a)



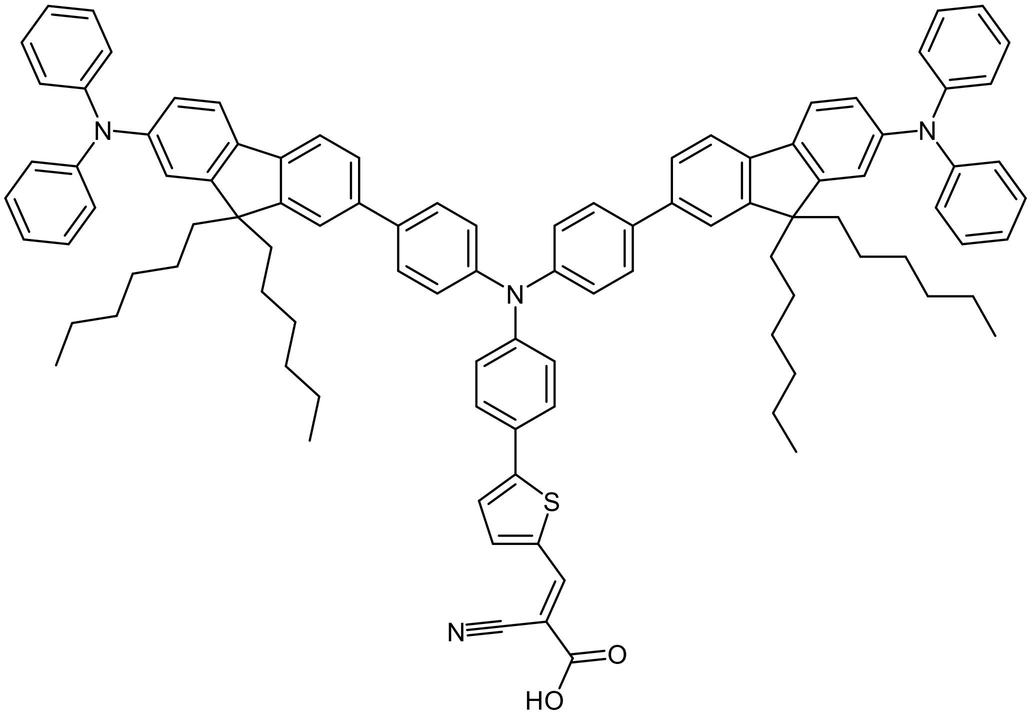
The crude product was synthesized following **GP4**. The ester intermediate was purified by flash column chromatography (*n*-hexane/ethyl acetate 6:1). The acid was purified by flash column chromatography using gradient elution (dichloromethane → dichloromethane/methanol 20:1), which led to 374 mg (0.460 mmol, 43%) of the product **7a** in form of a dark red solid. Mp.: 125 °C. R_f (dichloromethane /methanol 10:1) = 0.28. ^{1}H NMR (600 MHz, THF-d_8): δ 0.89 - 0.95 (m, 6H), 1.33 - 1.40 (m, 8H), 1.44 - 1.53 (m, 4H), 1.74 - 1.80 (m, 4H), 3.97 (t, $^3J_{HH}$ = 6.48 Hz, 4H), 6.49 (d, $^3J_{HH}$ = 8.56 Hz, 2H), 6.88 - 6.94 (m, 4H), 7.16 (dd, $^3J_{HH}$ = 8.61 Hz, $^4J_{HH}$ = 2.20 Hz, 2H), 7.35 (d, $^4J_{HH}$ = 2.16 Hz, 2H), 7.42 - 7.47 (m, 4H), 7.48 - 7.52 (m, 2H), 7.66 (d, $^3J_{HH}$ = 4.00 Hz, 1H), 7.91 (d, $^3J_{HH}$ = 4.01 Hz, 1H), 8.00 - 8.04 (m, 2H), 8.39 (s, 1H). ^{13}C NMR (150 MHz, Acetone-d_6): δ 14.4 (CH_3), 23.6 (CH_2), 26.8 (CH_2), 30.3 (CH_2), 32.6 (CH_2), 68.6 (CH_2), 101.0 (C_{quat}), 115.5 (CH), 116.7 (C_{quat}), 118.8 (CH), 123.6 (C_{quat}), 125.5 (CH), 125.7 (CH), 125.8 (CH), 127.1 (C_{quat}), 128.1 (CH), 129.5 (CH), 130.3 (CH), 132.8 (C_{quat}), 132.9 (C_{quat}), 136.8 (C_{quat}), 137.0 (C_{quat}), 140.0 (C_{quat}), 143.0 (C_{quat}), 143.9 (C_{quat}), 146.6 (CH), 153.2 (C_{quat}), 159.9 (C_{quat}). MS(ESI-HRMS) *m*/*z*: Calcd. for $C_{50}H_{48}N_2O_4S_2$: 804.3050, Found: 804.3045 ($[M]^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 3032 (w), 3024 (w), 2951 (w), 2926 (w), 2857 (w), 2222 (w), 1719 (w), 1686 (w), 1607 (m), 1570 (s), 1516 (w), 1491 (m), 1464 (s), 1439 (m), 1412 (s), 1385 (m), 1356 (w), 1307 (m), 1283 (m), 1256 (s), 1236 (s), 1221 (s), 1198 (s), 1175 (s), 1111 (w), 1061 (m), 1047 (w), 1017 (m), 936 (w), 922 (w), 882 (w), 802 (s), 762 (m), 745 (w), 729 (m), 718 (w), 698 (w), 677 (w), 640 (m), 631 (m).

2.8.2 3-(5-(4-(Bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (7b)



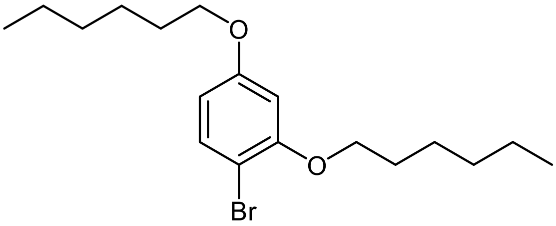
The crude product was synthesized following **GP4**. The ester intermediate was purified by flash column chromatography (*n*-hexane/ethyl acetate 5:1). The acid was purified by flash column chromatography using gradient elution (dichloromethane → dichloromethane/methanol 10:1), which led to 127 mg (0.160 mmol, 40%) of the product **7b** in form of a dark red solid. Mp.: 95 °C. R_f (dichloromethane /methanol 10:1) = 0.13. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 - 0.95 (m, 6H), 1.30 - 1.42 (m, 8H), 1.42 - 1.54 (m, 4H), 1.75 - 1.88 (m, 4H), 4.00 (t, $^3J_{HH}$ = 6.57 Hz, 4H), 6.92 - 7.01 (m, 4H), 7.09 - 7.17 (m, 2H), 7.17 - 7.24 (m, 4H), 7.34 (d, $^3J_{HH}$ = 3.88 Hz, 1H), 7.46 - 7.55 (m, 8H), 7.55 - 7.62 (m, 2H), 7.77 (d, $^3J_{HH}$ = 3.90 Hz, 1H), 8.32 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 (CH_3), 22.8 (CH_2), 25.9 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 68.3 (CH_2), 93.2 ($C_{quat.}$), 106.0 ($C_{quat.}$), 115.0 (CH), 122.3 (CH), 123.51 (CH), 123.53 (CH), 125.6 (CH), 125.7 ($C_{quat.}$), 127.6 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH), 132.8 ($C_{quat.}$), 133.8 ($C_{quat.}$), 136.8 ($C_{quat.}$), 140.5 ($C_{quat.}$), 145.4 ($C_{quat.}$), 149.5 ($C_{quat.}$), 156.5 ($C_{quat.}$), 158.8 ($C_{quat.}$). MS(ESI-HRMS) *m*/*z*: Calcd. for $C_{51}H_{52}N_2O_4S$: 774.3491, Found: 774.3486 ($[M]^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 3032 (w), 2949 (w), 2926 (w), 2857 (w), 2216 (w), 1684 (w), 1595 (m), 1574 (s), 1559 (s), 1516 (w), 1493 (s), 1472 (m), 1427 (m), 1410 (m), 1354 (w), 1323 (m), 1283 (s), 1244 (s), 1221 (s), 1175 (s), 1110 (m), 1096 (m), 1063 (m), 1036 (m), 1015 (m), 999 (m), 959 (w), 936 (m), 847 (w), 818 (s), 806 (s), 762 (m), 725 (m), 718 (m), 691 (m), 679 (m), 635 (m).

2.8.3 3-(5-(4-(Bis(4-(7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)amino) phenyl)thiophen-2-yl)-2-cyanoacrylic acid (7c)



The crude product was synthesized following **GP4**. The ester intermediate was purified by flash column chromatography (*n*-hexane/ethyl acetate 6:1). The acid was purified by flash column chromatography using gradient elution (dichloromethane → dichloromethane/methanol 10:1), which led to 156 mg (0.110 mmol, 22%) of the product **7c** in form of a dark red solid. Mp.: 140 °C. R_f (dichloromethane /methanol 10:1) = 0.29. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.63 - 0.76 (m, 8H), 0.80 (t, $^3J_{HH}$ = 6.93 Hz, 12H), 1.01 - 1.11 (m, 16H), 1.11 - 1.22 (m, 8H), 1.81 - 2.03 (m, 8H), 6.97 - 7.07 (m, 6H), 7.10 - 7.17 (m, 10H), 7.18 - 7.26 (m, 7H), 7.26 - 7.32 (m, 7H), 7.38 (d, $^3J_{HH}$ = 4.04 Hz, 1H), 7.51 - 7.70 (m, 14H), 7.97 (d, $^3J_{HH}$ = 4.03 Hz, 1H), 8.34 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.2 (CH_3), 22.7 (CH_2), 23.9 (CH_2), 29.8 (CH_2), 31.7 (CH_2), 40.5 (CH_2), 55.3 ($C_{quat.}$), 95.8 ($C_{quat.}$), 116.1 ($C_{quat.}$), 119.6 (CH), 120.5 (CH), 121.0 (CH), 122.58 (CH), 122.62 (CH), 123.6 (CH), 123.8 (CH), 123.92 (CH), 123.94 (CH), 125.6 (CH), 125.8 (CH), 126.0 ($C_{quat.}$), 127.7 (CH), 128.2 (CH), 129.3 (CH), 133.9 ($C_{quat.}$), 136.1 ($C_{quat.}$), 137.5 ($C_{quat.}$), 137.7 ($C_{quat.}$), 138.5 ($C_{quat.}$), 140.3 ($C_{quat.}$), 140.5 (CH), 145.8 ($C_{quat.}$), 147.2 ($C_{quat.}$), 147.9 (CH), 148.1 ($C_{quat.}$), 151.6 ($C_{quat.}$), 152.5 ($C_{quat.}$), 156.4 ($C_{quat.}$). MS(ESI-HRMS) *m*/*z*: Calcd. for $C_{100}H_{100}N_4O_2S$: 1420.7562, Found: 1420.7555 ([M]$^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 2926 (w), 2849 (w), 1715 (w), 1695 (w), 1568 (m), 1516 (w), 1489 (m), 1464 (m), 1456 (m), 1418 (m), 1319 (m), 1269 (m), 1219 (m), 1180 (m), 1063 (w), 1028 (w), 1011 (w), 876 (w), 814 (m), 748 (m), 725 (m), 694 (s), 665 (m), 605 (m).

2.9 1-Bromo-2,4-bis(hexyloxy)benzene (3e)



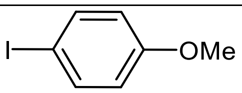
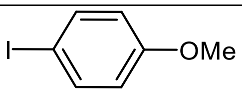
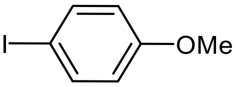
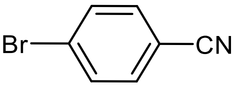
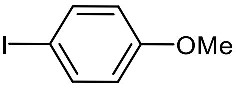
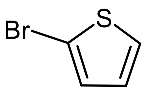
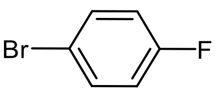
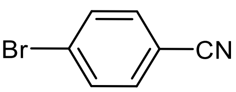
Compound **3e** is known in the literature [12], but was synthesized following another procedure:

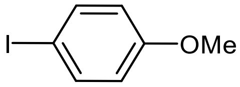
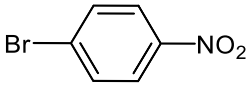
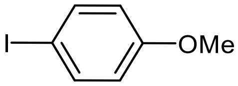
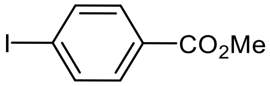
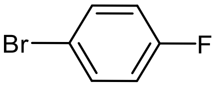
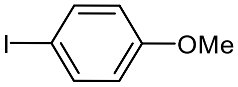
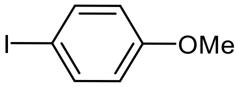
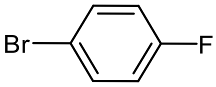
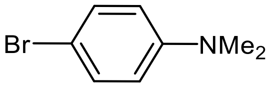
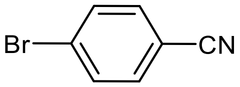
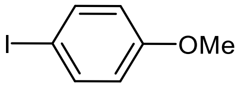
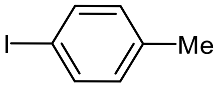
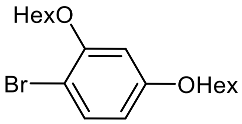
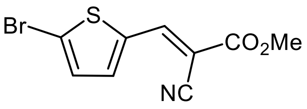
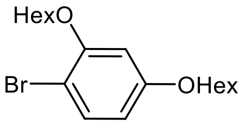
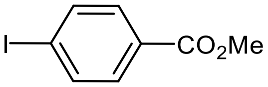
In a Schlenk vessel with magnetic stir bar under nitrogen atmosphere resorcinol (**13**) (1.10 g, 10.0 mmol) was dissolved in DMF (50 mL) and cooled down to 0 °C (ice bath). Then *N*-bromosuccinimide (1.78 g, 10.0 mmol) was added portion wise and the reaction mixture was stirred at 0 °C for 2 h. Then the reaction mixture was stirred at ambient temperature for 23 h. The reaction was quenched by the addition of a saturated sodium thiosulfate solution (30 mL). The organic layer was separated and the aqueous phase was extracted with dichloromethane three times. The combined organic phases were dried with anhydrous magnesium sulfate. The volatiles were removed by evaporation, which led to crude 4-bromobenzene-1,3-diol (1.89 g, 10.0 mmol) in form of a yellowish oil. In a Schlenk vessel with magnetic stir bar under nitrogen atmosphere 4-bromobenzene-1,3-diol (1.89 g, 10.0 mmol), 1-bromohexane (3.38 mL, 24.0 mmol) and potassium carbonate (5.53 g, 40.0 mmol) were filled. The reagents were diluted with acetone (30 mL) and the resulting suspension was stirred at 50 °C for 18 h. Then the volatiles were removed by evaporation and the crude product was purified by flash column chromatography (*n*-hexane), which led to 1.60 g (4.49 mmol, 45%) of the product **3e** in form of a colorless oil. R_f (*n*-hexane): 0.28. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.86-0.96 (m, 6H), 1.29-1.40 (m, 8H), 1.41 - 1.53 (m, 4H), 1.69-1.88 (m, 4H), 3.92 (t, $^3J_{HH}$= 6.56 Hz, $^3J_{HH}$= 6.56 Hz, 2H), 3.98 (t, $^3J_{HH}$= 6.53 Hz, $^3J_{HH}$= 6.53 Hz, 2H), 6.37 (dd, $^4J_{HH}$= 2.70 Hz, $^3J_{HH}$= 8.69 Hz, 1H), 6.47 (d, $^4J_{HH}$= 2.69 Hz, 1H), 7.37 (d, $^3J_{HH}$= 8.68 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 25.8 (CH_2) 25.9 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 31.7 (CH_2), 31.8 (CH_2), 68.6 (CH_2), 69.4 (CH_2), 101.8 (CH), 103.1 (C_{quat}), 106.9 (CH), 133.2 (CH), 156.4 (C_{quat}), 159.9 (C_{quat}). MS(EI) m/z (%): 358 ([^{81}Br-M]$^+$, 19), 356 ([^{79}Br-M]$^+$, 18), 274 ([^{81}Br-M – C_6H_{13}]$^+$, 16), 272 ([^{79}Br-M – C_6H_{13}]$^+$, 17), 190 ([^{81}Br-M – $C_{12}H_{26}$]$^+$, 99), 188 ([^{79}Br-M – $C_{12}H_{26}$]$^+$, 100), 55 (17). IR: $\tilde{\nu}$ [cm^{-1}] = 2953 (w), 2928 (m), 2870 (w), 2859 (w), 1578 (m), 1487 (m), 1468 (m), 1427 (w), 1416 (w), 1379 (w), 1304 (m), 1281 (m), 1254 (w), 1182 (s), 1138 (m), 1121 (w), 1055 (m), 1018 (m), 934 (w), 907 (w), 833 (w), 820 (w), 783 (w), 760 (w), 725 (w), 687 (w), 644 (w), 624 (w).

2.10 General procedure 5 (GP5) for the synthesis of thiophens 8 via Suzuki-Lithiation-Borylation-Suzuki sequence (SLiBS)

In a flame-dried Schlenk vessel with magnetic stir bar under nitrogen atmosphere were filled 4,4,5,5-Tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (**2a**) (1.00 eq.), aryl halide **3** (1.05 eq.), cesium fluoride (3.00 eq.), bis(dibenzylideneacetone)palladium(0) (5 mol%) and tri-*tert*-butyl-phosphonium tetrafluoroborate (10 mol%) and dissolved in dry THF (8 mL/mmol). The reaction mixture was stirred at 70 °C until full conversion of the starting materials could be observed via TLC. Then, the reaction mixture was cooled slowly to ambient temperature and then to -78 °C (isopropanol/dry ice). To the cooled, viscous reaction mixture was dropped *n*-butyllithium (2.00 eq., 1.6 M in hexane). Vigorous stirring was continued at -78 °C for 2 h. Then, trimethyl borate (2.00 eq.) was added and the stirring was continued at ambient temperature for 30 min. Then, another aryl halide **3** (1.20 eq.) and a second portion of cesium fluoride (3.00 eq.) were added. The reaction mixture was stirred at 70 °C overnight. The next day volatiles were removed by evaporation and the crude product was purified by flash column chromatography. For Experimental details see table 5.

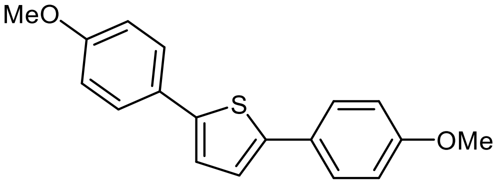
Table 5: Experimental details **GP5**.

2a [mg] (mmol)	1st Aryl halide **3** [mg] (mmol)	2nd Aryl halide **3** [mg] (mmol)	$t_{Suzuki\ 1}$ [h]	$t_{Suzuki\ 2}$ [h]	Yield **8** [mg] (%)
105 (0.500)	 **3a** 123 (0.530)	 **3a** 140 (0.600)	2	18	**8a** 104 (70)
105 (0.500)	 **3a** 123 (0.530)	 **3f** 109 (0.600)	2	23.5	**8b** 125 (86) [a]
105 (0.500)	 **3a** 123 (0.530)	 **3g** 101 (0.620)	1.5	18	**8c** 108 (79)
110 (0.520)	 **3c** 96.0 (0.550)	 **3f** 113 (0.620)	1.5	16	**8d** 84 (60)

2a [mg] (mmol)	1st Aryl halide **3** [mg] (mmol)	2nd Aryl halide **3** [mg] (mmol)	$t_{Suzuki\ 1}$ [h]	$t_{Suzuki\ 2}$ [h]	Yield **8** [mg] (%)
105 (0.500)	 **3a** 123 (0.530)	 **3h** 121 (0.600)	1.5	18	**8e** 127 (82)
105 (0.500)	 **3a** 123 (0.530)	 **3i** 157 (0.600)	1.5	16	**8f** 35 (22)
105 (0.500)	 **3c** 92.0 (0.530)	 **3a** 140 (0.600)	1.5	17.5	**8g** 137 (96)
105 (0.500)	 **3a** 123 (0.530)	 **3c** 104 (0.600)	1	18.5	**8g** 134 (94)
105 (0.500)	 **3d** 105 (0.520)	 **3f** 109 (0.600)	1.5	18	**8h** 48 (36)
105 (0.500)	 **3a** 123 (0.530)	 **3j** 131 (0.600)	2	18	**8i** 123 (87)
94.0 (0.450)	 **3e** 167 (0.470)	 **3k** 147 (0.540)	17	20.5	**8j** 123 (36)
94.0 (0.450)	 **3e** 169 (0.470)	 **3i** 142 (0.540)	2	18	**8k** 176 (79)

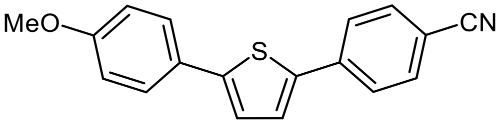
a: Tetrakis(triphenylphosphine)palladium(0) was used as catalyst.

2.10.1 2,5-Bis(4-methoxyphenyl)thiophene (8a) [13]



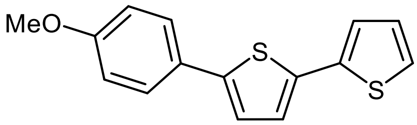
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 10:1, which led to 104 mg (0.351 mmol, 70%) of the product **8a** in form of a yellow solid. Mp.: 218 °C. R_f (*n*-hexane/ethyl acetate 20:1): 0.43. ^{1}H NMR (600 MHz, DMSO-d_6, 373 K): δ 3.81 (s, 6H), 6.99 (d, $^3J_{HH}$ = 8.64 Hz, 4H), 7.28 (s, 2H), 7.57 (d, $^3J_{HH}$ = 8.65 Hz, 4H). ^{13}C NMR (150 MHz, DMSO-d_6, 373 K): δ 54.9 (CH_3), 114.3 (CH), 122.9 (CH), 126.1 (CH), 126.2 (C_{quat}), 141.4 (C_{quat}), 158.7 (C_{quat}). MS(EI) m/z (%): 297 ($[M + H]^+$, 20), 296 ($[M]^+$, 100), 282 ($[M - CH_3 + H]^+$, 14), 281 ($[M - CH_3]^+$, 73), 266 ($[M - OCH_3]^+$, 10), 238 (13), 210 (25), 148 (11). IR: $\tilde{\nu}$ [cm^{-1}] = 3013 (w), 2957 (w), 2914 (w), 2839 (w), 1605 (w), 1493 (m), 1456 (w), 1439 w), 1412 (w), 1296 (w), 1281 (w), 1248 (m), 1180 (m), 1153 (w), 1113 (w), 1028 (m), 968 (w), 831 (s), 793 (s), 637 (m), 617 (m).

2.10.2 4-(5-(4-Methoxyphenyl)thiophen-2-yl)benzonitrile (8b) [14]



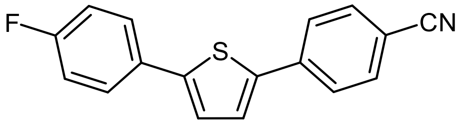
The crude product was synthesized following **GP5** with the exception that tetrakis(triphenylphosphine)palladium(0) was used as catalyst and purified by flash column chromatography (*n*-hexane/ethyl acetate 10:1), which led to 125 mg (0.430 mmol, 86%) of the product **8b** in form of a light yellow solid. Mp.: 160 °C. R_f (*n*-hexane/ethyl acetate 10:1): 0.23. ^{1}H NMR (600 MHz, acetone-d_6): δ 3.85 (s, 3H), 7.00-7.04 (m, 2H), 7.41 (d, $^3J_{HH}$= 3.84 Hz, 1H), 7.65 (d, $^3J_{HH}$= 3.90 Hz, 1H), 7.65-7.68 (m, 2H), 7.79-7.82 (m, 2H), 7.87-7.90(m, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 55.8 (CH_3), 111.1 (C_{quat}), 115.4 (CH), 119.3 (C_{quat}), 124.6 (CH), 126.5 (CH), 127.2 (C_{quat}), 127.7 (CH), 127.8 (CH), 133.7 (CH), 139.4 (C_{quat}), 140.6 (C_{quat}), 146.7 (C_{quat}), 160.9 (C_{quat}). MS(EI) m/z (%): 291 ($[M]^+$, 10), 150 (10), 127 (16), 85 (11), 57 (12), 71 (15). IR: $\tilde{\nu}$ [cm^{-1}] = 3053 (w), 3026 (w), 2965 (w), 2839 (w), 2230 (w), 1599 (w), 1537 (w), 1495 (w), 1452 (w), 1435 (w), 1398 (w), 1294 (w), 1277 (w), 1252 (w), 1177 (m), 1142 (w), 1126 (w), 1113 (w), 1070 (w), 1024 (m), 939 (w), 849 (w), 829 (m), 820 (w), 799 (s), 743 (w), 719 (w), 704 (w), 679 (w).

2.10.3 5-(4-Methoxyphenyl)-2,2'-bithiophene (8c) [15]



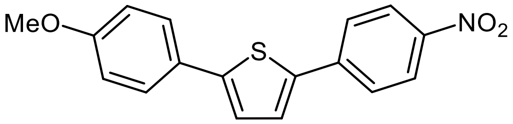
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 20:1), which led to 108 mg (0.397 mmol, 79%) of the product **8c** in form of a beige solid. Mp.: 153-155 °C. R$_f$ (*n*-hexane/ethyl acetate 20:1): 0.37. ^{1}H NMR (600 MHz, CDCl$_3$): δ 3.84 (s, 3H), 6.90-6.94 (m, 2H), 7.03 (dd, $^3J_{HH}$= 3.55 Hz, $^3J_{HH}$= 5.09 Hz, 1H), 7.10-7.13 (m, 2H), 7.18 (dd, $^4J_{HH}$= 1.18 Hz, $^3J_{HH}$= 3.59 Hz, 1H), 7.21 (dd, $^4J_{HH}$= 1.16 Hz, $^3J_{HH}$= 5.10 Hz, 1H), 7.51-7.55 (m, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 55.5 (CH$_3$), 114.5 (CH), 122.8 (CH), 123.5 (CH), 124.3 (CH), 124.7 (CH), 127.0 (CH), 127.1 (C$_{quat}$), 127.9 (CH) 135.8 (C$_{quat}$), 137.7 (C$_{quat}$), 143.3 (C$_{quat}$), 159.4 (C$_{quat}$). MS(EI) m/z (%): 273 ([M + H]$^+$, 18), 272 ([M]$^+$, 100), 259 (10), 258 (16), 257 ([M – CH$_3$]$^+$, 98), 229 (41), 136 (10). IR: $\tilde{\nu}$ [cm^{-1}] = 3098 (w), 3082 (w), 3067 (w), 2835 (w), 1601 (w), 1572 (w), 1522 (w), 1495 (w), 1460 (w), 1429 (w), 1417 (w), 1364 (w), 1312 (w), 1287 (w), 1265 (w), 1244 (m), 1223 (w), 1180 (m), 1113 (w), 1067 (w), 1049 (w), 1030 (m), 957 (w), 885 (w), 831 (m), 826 (s), 797 (s), 691 (m), 640 (w).

2.10.4 4-(5-(4-Fluorophenyl)thiophen-2-yl)benzonitrile (8d) [14]



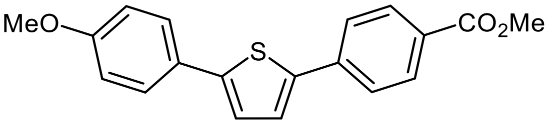
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 10:1), which led to 84 mg (0.30 mmol, 60%) of the product **8d** in form of a yellow solid. Mp.: 162 °C. R$_f$ (*n*-hexane/ethyl acetate 10:1): 0.42. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.07-7.15 (m, 2H), 7.25 (d, $^3J_{HH}$= 3.97 Hz, 1H), 7.39 (d, $^3J_{HH}$= 3.87, 1H), 7.56-7.63 (m, 2H), 7.63-7.72 (m, 4). ^{13}C NMR (75 MHz, CDCl$_3$): δ 110.6 (C$_{quat}$), 116.2 (d, $^2J_{CF}$= 22.02 Hz, CH), 118.9 (C$_{quat}$), 124.5 (d, $^5J_{CF}$= 1.24 Hz, CH), 125.8 (CH), 126.2 (CH), 127.6 (d, $^3J_{CF}$= 8.10 Hz, CH), 130.1 (d, $^4J_{CF}$= 3.40 Hz, C$_{quat}$), 132.9 (CH), 138.5 (C$_{quat}$), 141.1 (d, $^6J_{CF}$= 2.29 Hz, C$_{quat}$), 145.0 (C$_{quat}$), 162.8 (d, $^1J_{CF}$= 248.51 Hz, C$_{quat}$) MS(EI) m/z (%): 280 ([M + H]$^+$, 19), 279 ([M]$^+$, 100), 207 (13), 146 (14), 139 (14), 131 (12), 129 (19), 128 (11), 117 (46), 115 (11), 105 (10), 103 (18), 91 (40), 85 (13), 77 (12), 57 (10). IR: $\tilde{\nu}$ [cm^{-1}] = 2218 (w), 1061 (m), 1543 (w), 1495 (m), 1450 (m), 1412 (w), 1339 (w), 1300 (w), 1275 (w), 1227 (m), 1177 (w), 1161 (m), 1123 (w), 1099 (w), 1069 (w), 1013 (w), 945 (w), 829 (m), 793 (s).

2.10.5 2-(4-Methoxyphenyl)-5-(4-nitrophenyl)thiophene (8e) [16]



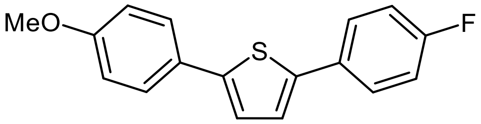
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 5:1), which led to 127 mg (0.408 mmol, 82%) of the product **8e** in form of an orange solid. Mp.: 151 °C. R_f (*n*-hexane/ethyl acetate 5:1): 0.53. ^{1}H NMR (300 MHz, acetone-d_6): δ 3.85 (s, 3H), 6.98-7.06 (m, 2H), 7.44 (d, $^3J_{HH}$= 3,90 Hz, 1H), 7.63-7.73 (m, 3H), 7.91-7.97 (m, 2H), 8.24-8.31 (m, 2H). ^{13}C NMR (75 MHz, acetone-d_6): δ 55.7 (CH_3), 115.4 (C_{quat}), 124.8 (C_{quat}), 125.3 (C_{quat}), 126.4 (C_{quat}), 127.1 (CH), 127.9 (C_{quat}), 128.5 (C_{quat}), 140.1 (CH), 141.4 (CH), 147.4 (CH), 147.5 (CH), 160.9 (CH). MS(EI) m/z (%): 311 ($[M]^+$, 5), 296 ($[M - CH_3]^+$, 1), 250 ($[M - CH_3NO_2]^+$, 1). IR: $\tilde{\nu}$ [cm^{-1}] = 3098 (w), 3021 (w), 2959 (w), 2920 (w), 2837 (w), 2436 (w), 2359 (w), 1589 (m), 1501 (m), 1487 (m), 1439 (m), 1329 (s), 1317 (s), 1275 (m), 1246 (m), 1184 (m), 1150 (w), 1105 (s), 1069 (m), 1022 (m), 1009 (m), 963 (w), 851 (s), 829 (s), 799 (s), 748 (s), 689 (m), 673 (w).

2.10.6 Methyl 4-(5-(4-methoxyphenyl)thiophen-2-yl)benzoate (8f) [17]



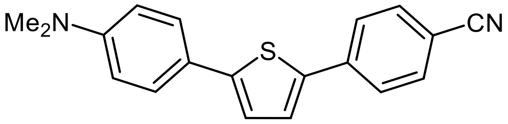
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 10:1), which led to 35 mg (0.11 mmol, 22%) of the product **8f** in form of a beige solid. Mp.: 220 °C. R_f (*n*-hexane/ethyl acetate 10:1): 0.25. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.85 (s, 3H), 3.93 (s, 3H), 6.91-6.96 (m, 2H), 7.21 (d, $^3J_{HH}$= 3.79 Hz, 1H), 7.38 (d, $^3J_{HH}$= 3.77, 1H), 7.55-7.58 (m, 2H), 7.66-7.69 (m, 2H), 8.02-8.05 (m, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 52.2 (CH_3), 55.6 (CH_3), 114.5 (CH), 123.4 (CH), 125.2 (CH), 125.6 (CH), 127.1 (C_{quat}), 127.3 (CH), 128.8 (C_{quat}), 130.5 (CH), 138.9 (C_{quat}), 141.3 (C_{quat}), 145.5 (C_{quat}), 159.8 (C_{quat}), 166,9 (C_{quat}). MS(MALDI-TOF) m/z (%): 324 ($[M]^+$). IR: $\tilde{\nu}$ [cm^{-1}] = 2999 (w), 2951 (w), 2841 (w), 1705 (s), 1599 (m), 1499 (m), 1452 (m), 1427 (m), 1410 (w), 1287 (m), 1273 (s), 1249 (s), 1178 (s), 1111 (s), 1026 (m), 1014 (m), 962 (m), 939 (w), 852 (m), 831 (s), 799 (s), 768 (s), 696 (m).

2.10.7 2-(4-Fluorophenyl)-5-(4-methoxyphenyl)thiophene (8g) [18]



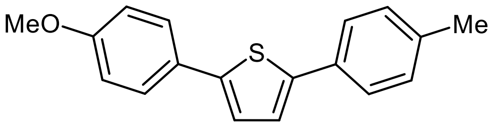
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 10:1), which led to 137 mg (0.482 mmol, 96%) of the product **8g** in form of a beige solid, if 1-bromo-4-fluorobenzene (**3c**) was coupled first. If 4-iodoanisole (**3a**) was coupled first, the yield was 94% (see table 5). Mp.: 171 °C. R_f (*n*-hexane/ethyl acetate 10:1): 0.57. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H), 6.90-6.96 (m, 2H), 7.03-7.11 (m, 2H), 7.14-7.20 (m, 2H), 7.52-7.60 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5 (CH_3), 114.6 (CH), 116.0 (d, $^2J_{CF}$= 21.86 Hz, CH), 123.1 (CH), 124.1 (d, $^5J_{CF}$= 0.93 Hz, CH), 127.1 (CH), 127.4 (d, $^3J_{CF}$= 8.15 Hz, CH), 130.9 (d, $^4J_{CF}$=3.36 Hz, C_{quat}), 141.7 (C_{quat}), 143.9 (C_{quat}), 159.6 (C_{quat}), 162.4 (d, $^1J_{CF}$= 247.27 Hz, C_{quat}). MS(EI) m/z (%): 285 ($[M + H]^+$, 19), 284 ($[M]^+$, 100), 270 (14), 269 ($[M - CH_3]^+$, 86), 240 (45), 239 (13). IR: $\tilde{\nu}$ [cm^{-1}] = 3011 (w), 2957 (w), 2918 (w), 2839 (w), 1601 (w), 1491 (m), 1456 (m), 1439 (w), 1406 (w), 1292 (m), 1275 (w), 1242 (m), 1180 (m), 1159 (m), 1115 (m), 1099 (m), 1072 (m), 1032 (m), 1011 (m), 970 (w), 955 (w), 939 (w), 833 (s), 810 (m), 795 (s), 762 (w), 743 (w), 700 (w), 633 (m), 617 (m).

2.10.8 4-(5-(4-(Dimethylamino)phenyl)thiophen-2-yl)benzonitrile (8h) [17]



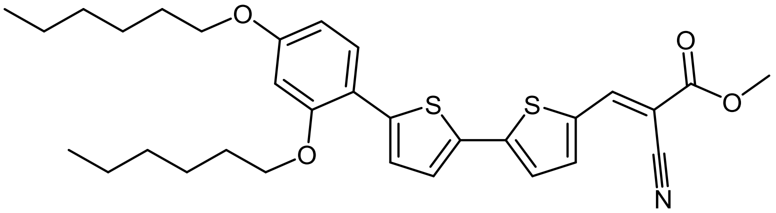
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 10:1) and recrystallization from acetone, which led to 48 mg (0.16 mmol, 36%) of the product **8h** in form of a yellow solid. Mp.: 272 °C. R_f (*n*-hexane): 0.38. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.02 (s, 6H), 7.17 (d, $^3J_{HH}$=3.84 Hz, 1H), 7,37 (d, $^3J_{HH}$=3.86 Hz, 1H), 7.51-7.55 (m, 2H), 7.62-7.69 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 40.9 (CH_3), 43.7 (CH_3), 100.2 (C_{quat}), 110.1 (C_{quat}), 113.3 (C_{quat}), 119.1 (C_{quat}), 122.5 (CH, 125.6 (CH), 125.9 (CH), 126.3 (CH), 127.1 (CH), 132.8 (CH), 132.9 (C_{quat}), 139.1 (C_{quat}), 147.3 (C_{quat}). MS(EI) m/z (%): 305 ($[M + H]^+$, 22), 304 ($[M]^+$, 100), 303 ($[M]^+$, 33), 289 (13), 288 (17), 261 (6), 151 (19), 143 (18). IR: $\tilde{\nu}$ [cm^{-1}] = 2990 (w), 2893 (w), 2806 (w), 2357 (w), 2220 (w), 1597 (m), 1491 (m), 1356 (w), 1325 (w), 1287 (w), 1256 (w), 1223 (m), 1198 (w), 1177 (w), 1123 (w), 1111 (w), 1065 (m), 937 (w), 835 (m), 810 (m), 795 (s), 756 (w), 719 (w).

2.10.9 2-(4-Methoxyphenyl)-5-(*p*-tolyl)thiophene (8i)[19]



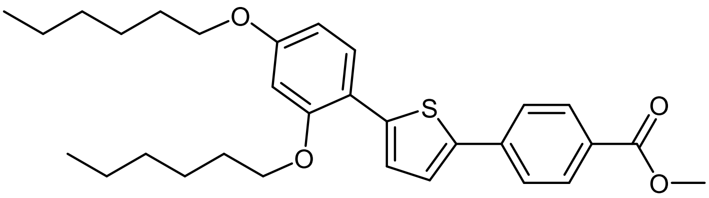
The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 20:1), which led to 123 mg (0.439 mmol, 87%) of the product **8i** in form of a colourless solid. Mp.: 172 °C. R$_f$ (*n*-hexane/ethyl acetate 20:1): 0.43. ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.37 (s, 3H), 3.84 (s, 3H), 6.90-6.96 (m, 2H), 7.15-7.24 (m, 4H), 7.45-7.62 (m, 4H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 21.3 (CH$_3$), 55.5 (CH$_3$), 114.4 (CH), 123.0 (CH), 123.6 (CH), 125.6 (CH), 127.0 (CH), 127.4 (C$_{quat}$), 129.7 (CH), 131.8 (C$_{quat}$), 137.3 (C$_{quat}$), 142.9 (C$_{quat}$), 143.2 (C$_{quat}$), 159.3 (C$_{quat}$). MS(EI) m/z (%): 281 ([M + H]$^+$, 6), 280 ([M]$^+$, 30), 265 ([M – CH$_3$]$^+$, 27), 237 (10), 131 (10), 127 (18), 85 (11), 71 (16), 57 (13). IR: $\tilde{\nu}$ [cm^{-1}] = 3075 (w), 2957 (w), 2911 (w), 2855 (w), 2839 (w), 2721 (w), 1607 (w), 1543 (w), 1495 (m), 1468 (w), 1456 (m), 1441 (w), 1414 (w), 1377 (w), 1290 (w), 1273 (w), 1248 (m), 1180 (m), 1125 (w), 1113 (w), 1070 (w), 1030 (m), 970 (w), 939 (w), 829 (s), 795 (s), 681 (w), 633 (w), 617 (m).

2.10.10 Methyl 3-(5'-(2,4-bis(hexyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-2-cyano-acrylate (8j)



The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 8:1) and recrystallization from *n*-hexane, which led to 91 mg (0.16 mmol, 36%) of the product **8j** in form of red crystals. Mp.: 109 °C. R$_f$ (*n*-hexane/ethyl acetate 8:1): 0.32. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.87-0.98 (m, 6H), 1.33-1.55 (m, 10H), 1.43-1.51 (m, 2H), 1.77-1.83 (m, 2H), 1.93 (dq, $^4J_{HH}$= 6.52 Hz, $^4J_{HH}$= 6.52 Hz, $^4J_{HH}$= 6.42 Hz, $^3J_{HH}$= 8.28 Hz, 2H), 3.91 (s, 3H), 3.99 (t, $^3J_{HH}$= 6.54 Hz, 2H), 4.09 (t, $^3J_{HH}$= 6.45 Hz, 2H), 6.50-6.56 (m, 2H), 7.22 (d, $^3J_{HH}$= 4.08 Hz, 1H), 7.36 (d, $^3J_{HH}$= 3.79 Hz, 2H), 7.57 (d, $^3J_{HH}$= 9.19 Hz, 1H), 7.67 (d, $^3J_{HH}$= 4.08 Hz, 1H), 8.25 (s, 1H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 14.1 (CH$_3$), 14.2 (CH$_3$), 22.7 (CH$_2$), 22.8 (CH$_2$), 25.9 (CH$_2$), 26.1 (CH$_2$), 29.3 (CH$_2$), 29.4 (CH$_2$), 31.6 (CH$_2$), 31.7 (CH$_2$), 53.2 (CH$_3$), 68.5 (CH$_2$). 69.2 (CH$_2$), 96.5 (C$_{quat}$), 100.2 (CH), 106.3 (CH), 115.6 (C$_{quat}$), 116.4 (C$_{quat}$), 123.8 (CH), 125.0 (CH), 126.7 (CH), 128.9 (CH), 133.7 (C$_{\mathrm{quat}}$), 133.9 (C$_{\mathrm{quat}}$), 139.4 (CH), 143. (C$_{\mathrm{quat}}$), 146.5 (CH), 149.1 (C$_{\mathrm{quat}}$), 156.6 (C$_{\mathrm{quat}}$), 160.7 (C$_{\mathrm{quat}}$), 163.9 (C$_{\mathrm{quat}}$). MS(EI) m/z (%): 552 ([M + H]$^+$, 32), 551 ([M]$^+$, 100), 467 ([M – C_6H_{12}]$^+$, 32), 466 ([M – C_6H_{13}]$^+$, 10), 384 ([M – $C_{12}H_{25}$]$^+$, 17), 383 ([M – $C_{12}H_{26}$]$^+$, 71), 382 ([M – $C_{12}H_{27}$]$^+$, 18). IR: $\tilde{\nu}$ [cm$_{-1}$] = 3649 (m), 3628 (m), 2924 (w), 2858 (w), 2210 (w), 1716 (w), 1604 (w), 1516 (m), 1554 (s), 1533 (w), 1506 (w), 1423 (m), 1373 (w), 1284 (w), 1251 (m), 1209 (m), 1178 (m), 1126 (w), 1055 (m), 1035 (w), 831 (w), 806 (m), 786 (s), 690 (w), 667 (w), 611 (s). Anal. calcd. for $C_{31}H_{37}NO_4S_2$ (551.8): C 72.84, H 7.74, S 6.48; Found: 72.98, H 7.47, S 6.77.

2.10.11 Methyl 4-(5-(2,4-bis(hexyloxy)phenyl)thiophen-2-yl)benzoate (8k)



The crude product was synthesized following **GP5** and purified by flash column chromatography (*n*-hexane/ethyl acetate 20:1, which led to 176 mg (0.356 mmol, 79%) of the product **8k** in form of a light yellow solid. Mp.: 104 °C. R$_f$ (*n*-hexane/ethyl acetate 20:1): 0.28. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.85-0.97 (m, 6H), 1.33-1.54 (m, 10H), 1.44-1.52 (m, 2H), 1.77-1.83 (m, 2H), 1.87-1.93 (m, 2H), 3.93 (s, 3H), 3.99 (t, $^3J_{HH}$= 6.56 Hz, $^3J_{HH}$= 6.56 Hz, 2H), 4.08 (t, $^3J_{HH}$= 6.43 Hz, $^3J_{HH}$= 6.43 Hz, 2H), 6.50-6.57 (m, 2H), 7.39 (q, $^3J_{HH}$= 3.95 Hz, 2H), 7.55-7.60 (m, 1H), 7.65-7.71 (m, 2H), 8.00-8.06 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 13.9 (CH$_3$), 14.0 (CH$_3$), 22.4 (CH$_2$), 22.5 (CH$_2$), 25.6 (CH$_2$), 25.9 (CH$_2$), 29.1 (CH$_2$), 29.2 (CH$_2$), 31.4 (CH$_2$), 31.5 (CH$_2$), 51.9 (CH$_3$), 68.2 (CH$_2$), 68.9 (CH$_2$), 100.1 (CH), 105.8 (CH), 115.9 (C$_{\mathrm{quat}}$), 124.2 (CH), 124.9 (CH), 125.0 (CH), 128.1 (C$_{\mathrm{quat}}$), 128.7 (CH), 130.1 (CH), 139.2 (C$_{\mathrm{quat}}$), 140.8 (C$_{\mathrm{quat}}$), 141.2 (C$_{\mathrm{quat}}$), 156.3 (C$_{\mathrm{quat}}$), 159.9 (C$_{\mathrm{quat}}$), 166.7 (C$_{\mathrm{quat}}$). MS(EI) m/z (%): 495 ([M + H]$^+$, 30), 494 ([M]$^+$, 100), 410 ([M – C_6H_{12}]$^+$, 16), 409 ([M – C_6H_{13}]$^+$, 6), 327 ([M – $C_{12}H_{26}$]$^+$, 12), 326 ([M – $C_{12}H_{24}$]$^+$, 58), 325 ([M – $C_{12}H_{25}$]$^+$, 11), 55 (10). IR: $\tilde{\nu}$ [cm^{-1}] = 2949 (w), 2926 (w), 2870 (w), 1712 (s), 1600 (m), 1573 (w), 1558 (w), 1537 (w), 1492 (w), 1467 (w), 1435 (m), 1303 (w), 1276 (s), 1255 (m), 1222 (w), 1182 (s), 1130 (m), 1107 (s), 1024 (m), 997 (w), 964 (w), 894 (w), 848 (w), 835 (m), 823 (w), 798 (m), 767 (s), 727. Anal. calcd. for $C_{30}H_{38}O_4S$ (494.7): C 72.84, H 7.74, S 6.48; Found: C 72.98, H 7.47, S 6.77.

3 ^{1}H- and ^{13}C-NMR spectra

3.1 Methyl-3-(5-bromothiophen-2-yl)-2-cyanoacrylate (3k)

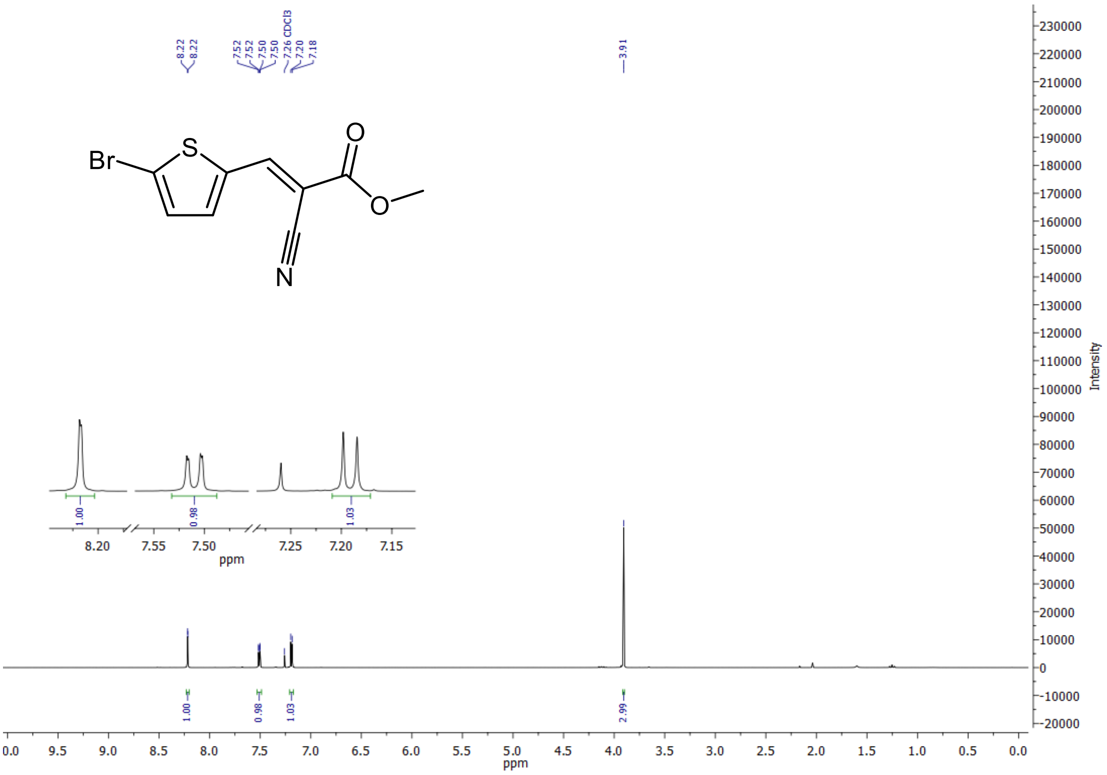


Figure 1: ^{1}H-NMR spectrum of **3k** ($CDCl_3$, 293K, 300MHz).

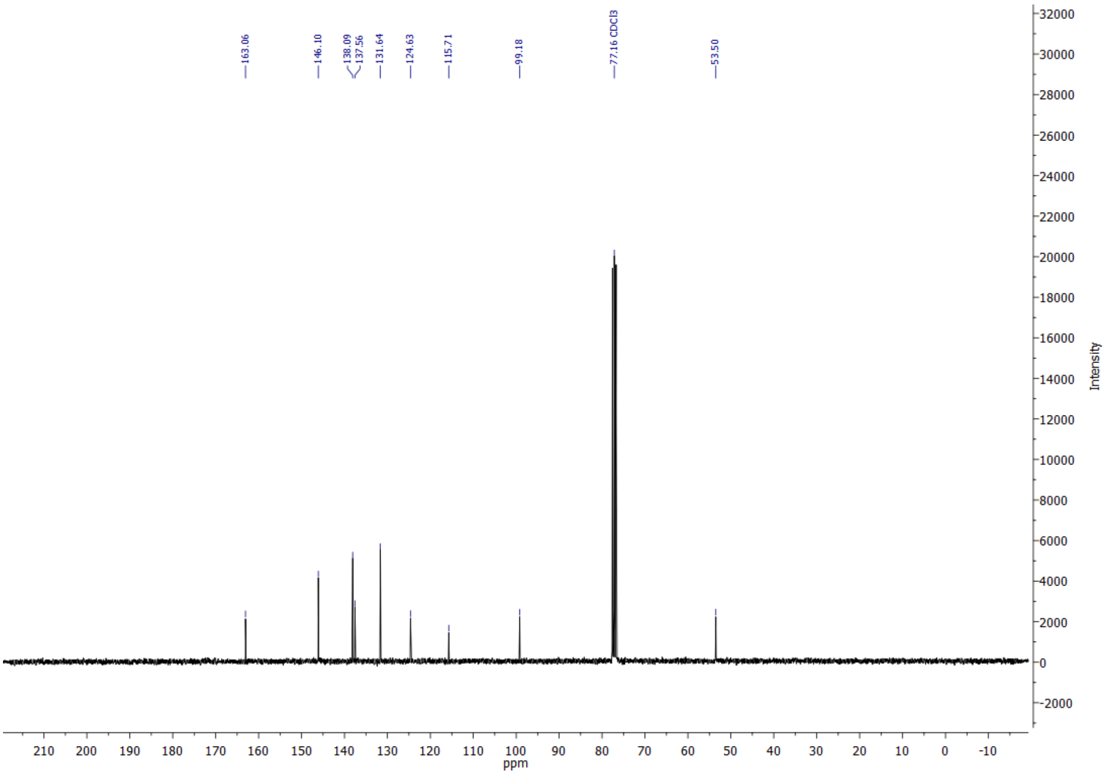


Figure 2: ^{13}C-NMR spectrum of **3k** ($CDCl_3$, 293K, 75MHz).

3.2 2-(3,5-Dibromophenyl)thiophene (5a)

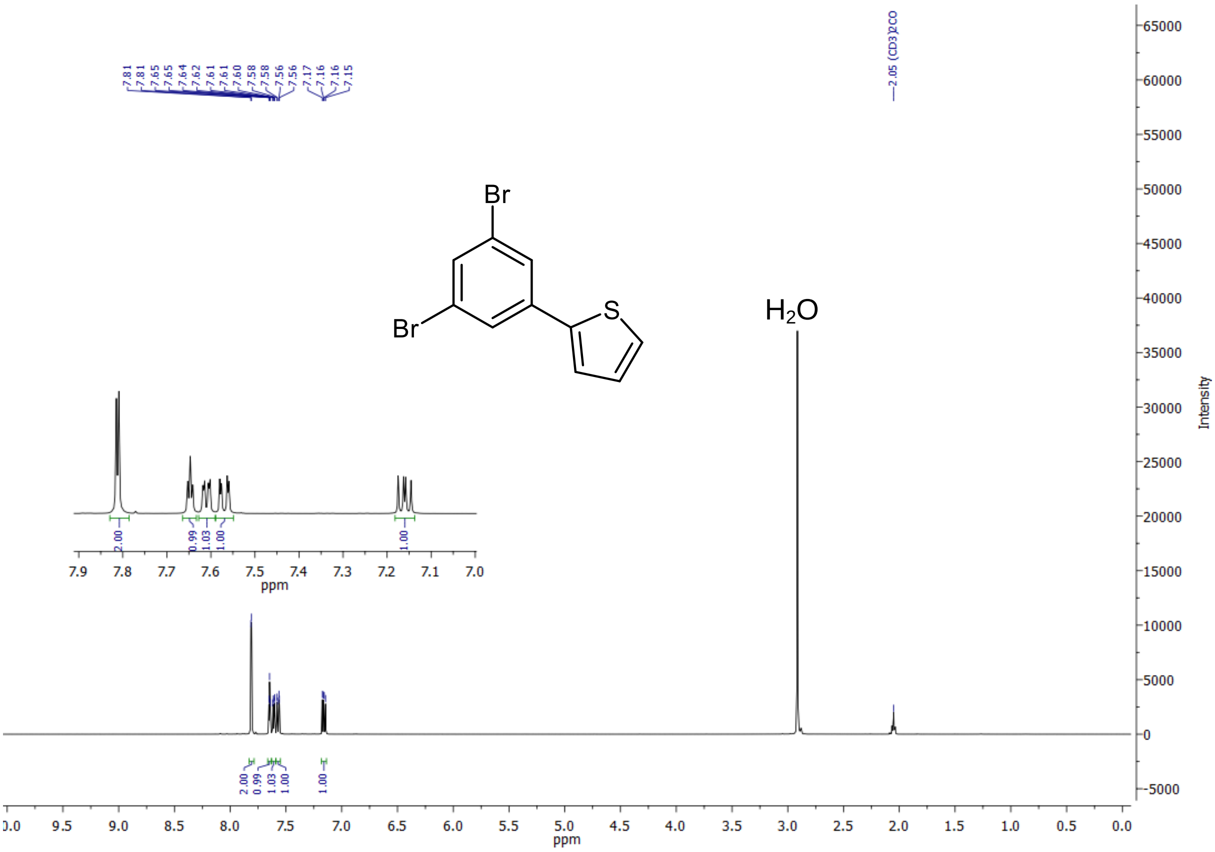


Figure 3: ^{1}H-NMR spectrum of **5a** (acetone-d_6, 293K, 300MHz).

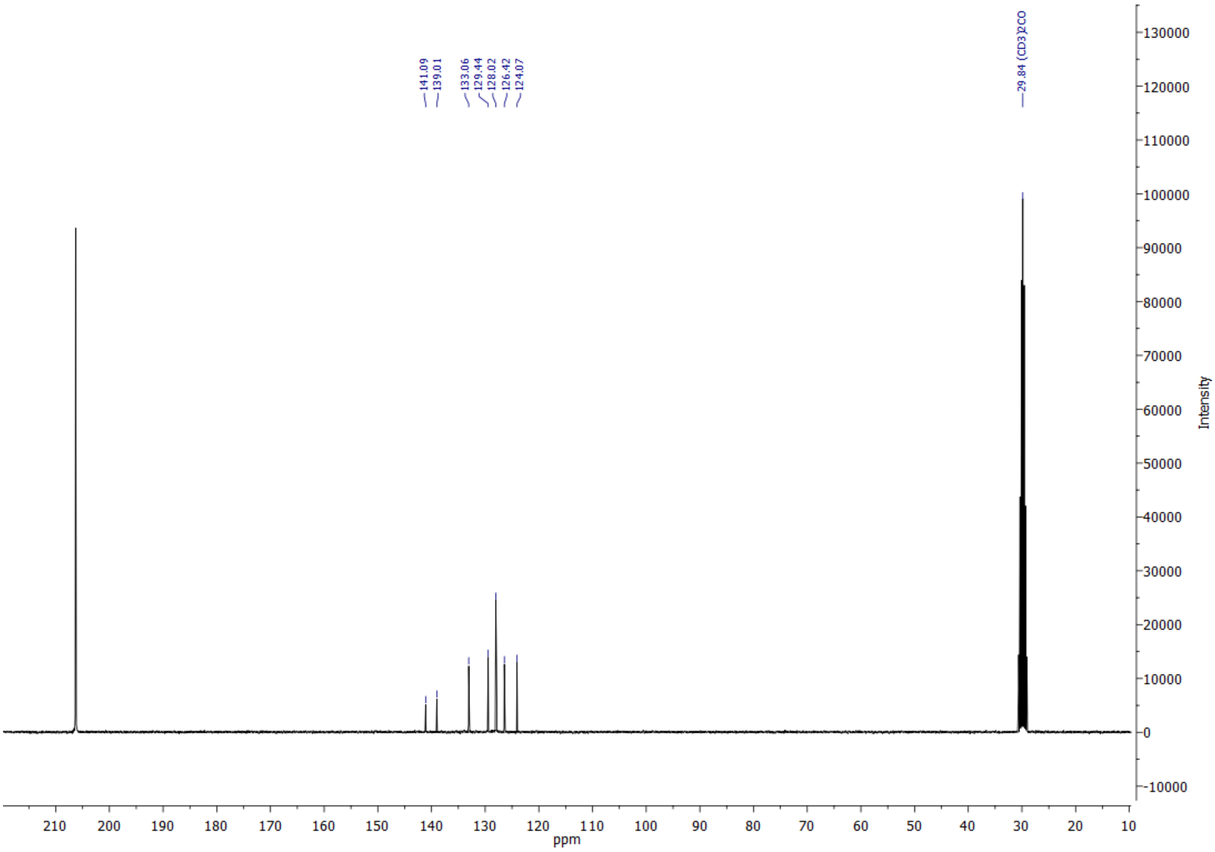


Figure 4: ^{13}C-NMR spectrum of **5a** (acetone-d_6, 293K, 75MHz).

3.3 2-(3,5-Dibromophenyl)thiophene (5d)

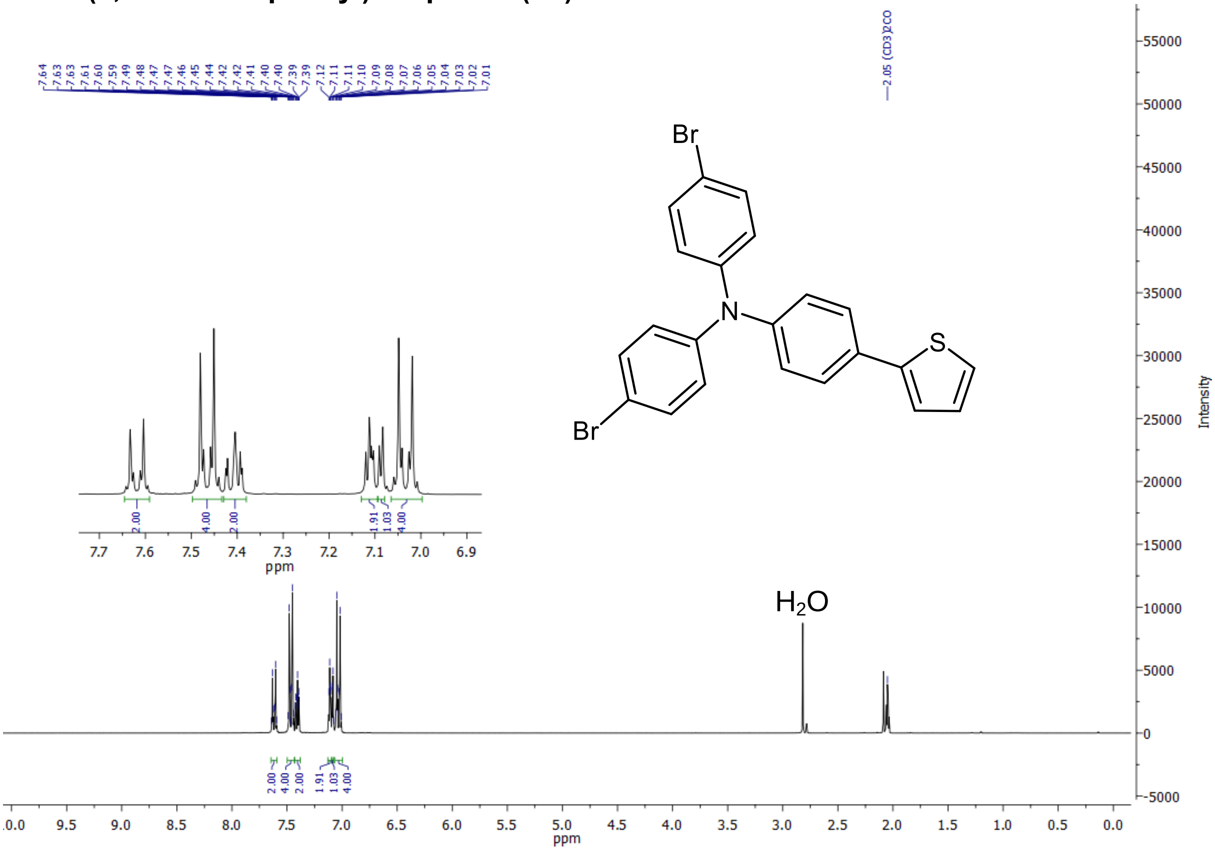


Figure 5: ^{1}H-NMR spectrum of **5d** (acetone-d$_6$, 293K, 300MHz).

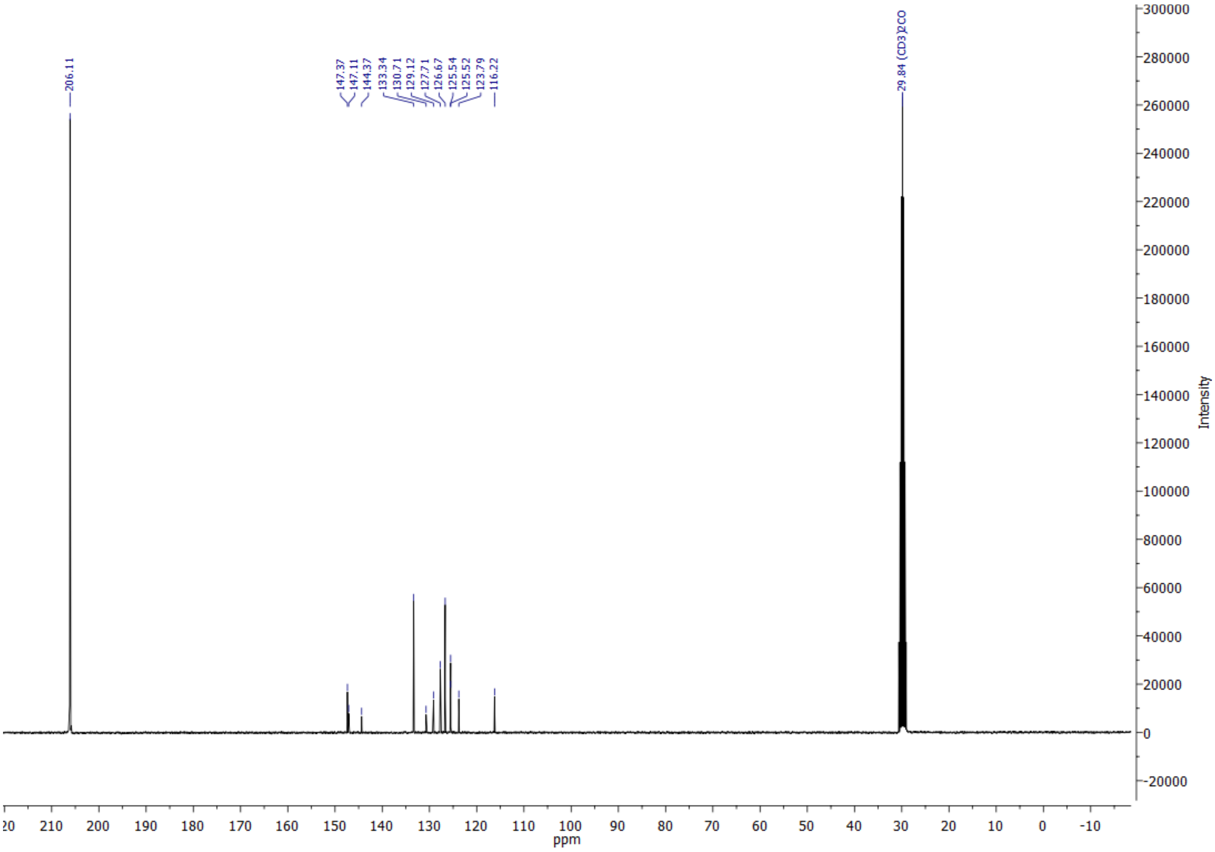


Figure 6: ^{13}C-NMR spectrum of **5d** (acetone-d$_6$, 293K, 75MHz).

3.4 3,7-Dibromo-10-(4-iodophenyl)-10*H*-phenothiazine (11)

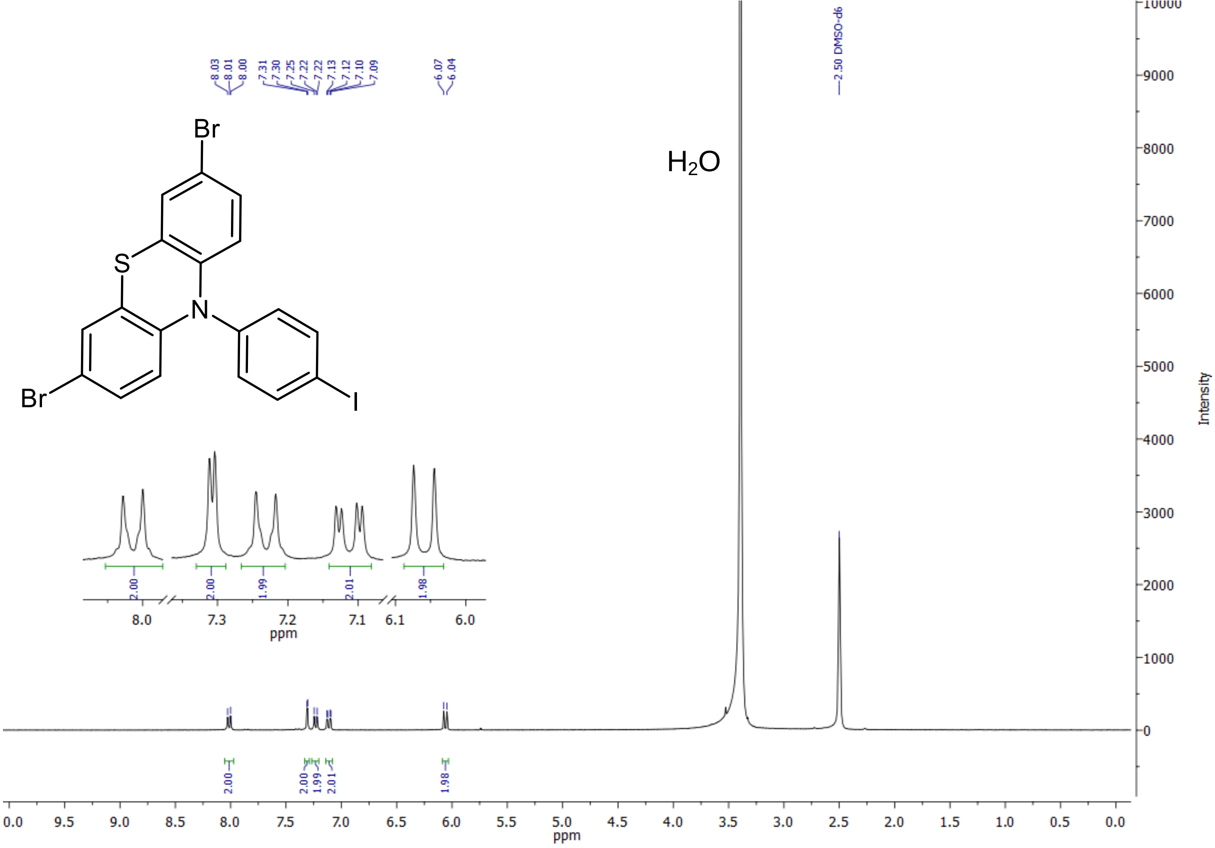


Figure 7: ^{1}H-NMR spectrum of **11** (DMSO-d_6, 293K, 300MHz).

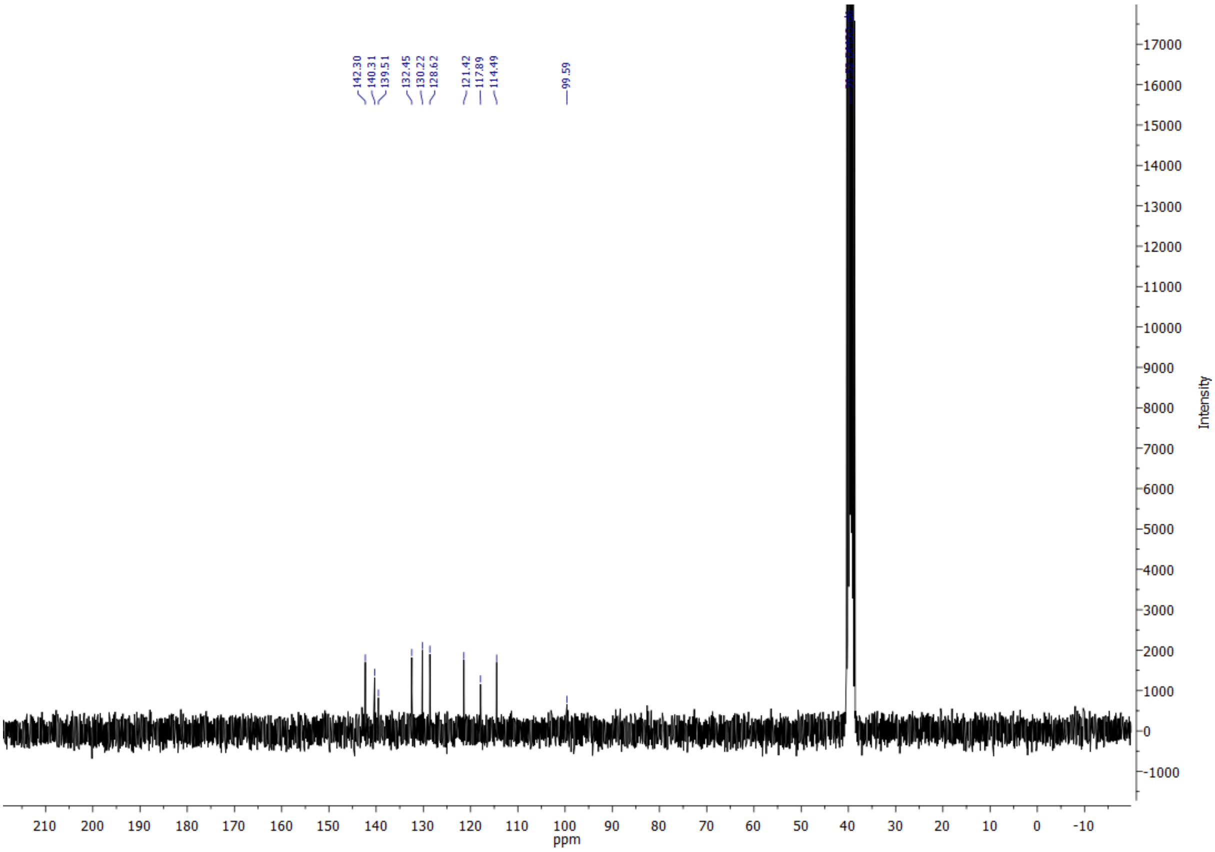


Figure 8: ^{13}C-NMR spectrum of **11** (DMSO-d_6, 293K, 75MHz).

3.5 3,7-Dibromo-10-(4-(thiophen-2-yl)phenyl)-10*H*-phenothiazine (5c)

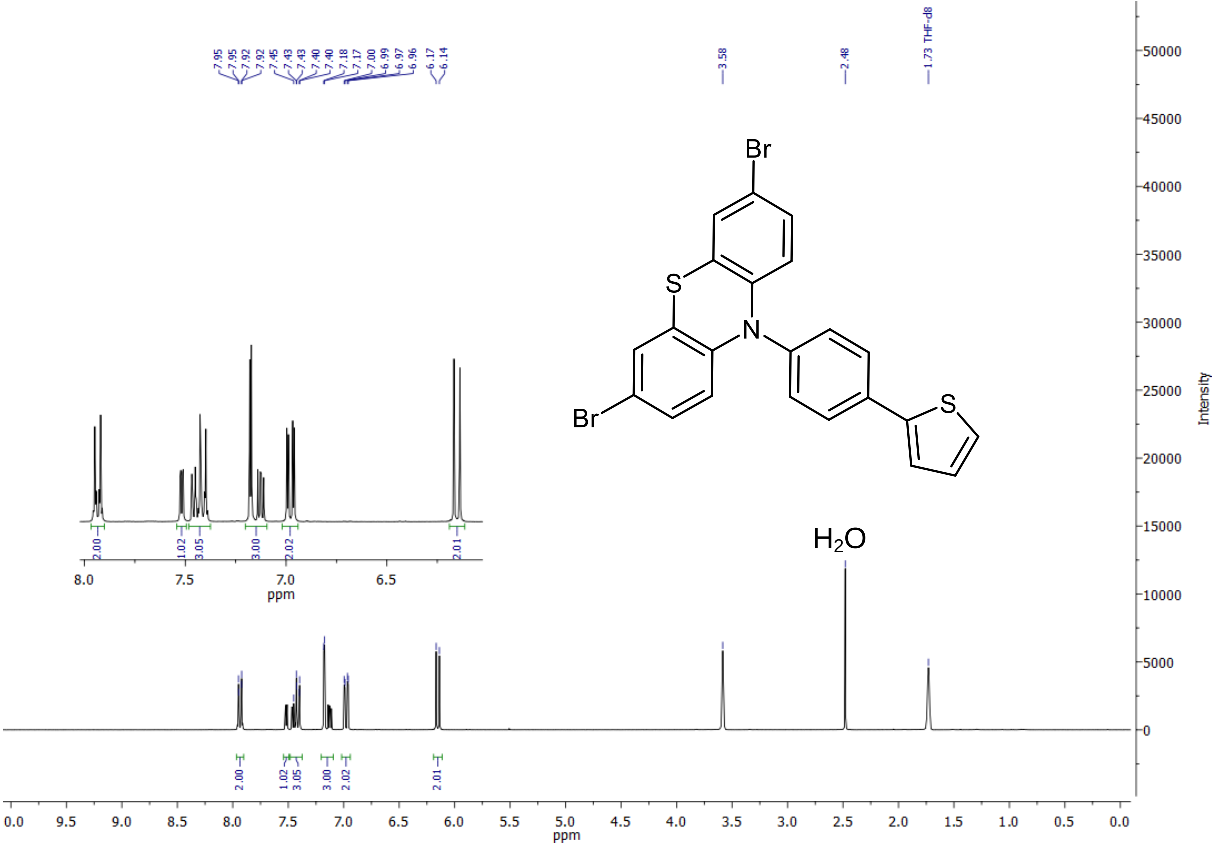


Figure 9: ^{1}H-NMR spectrum of **5c** (THF-d_8, 293K, 300MHz).

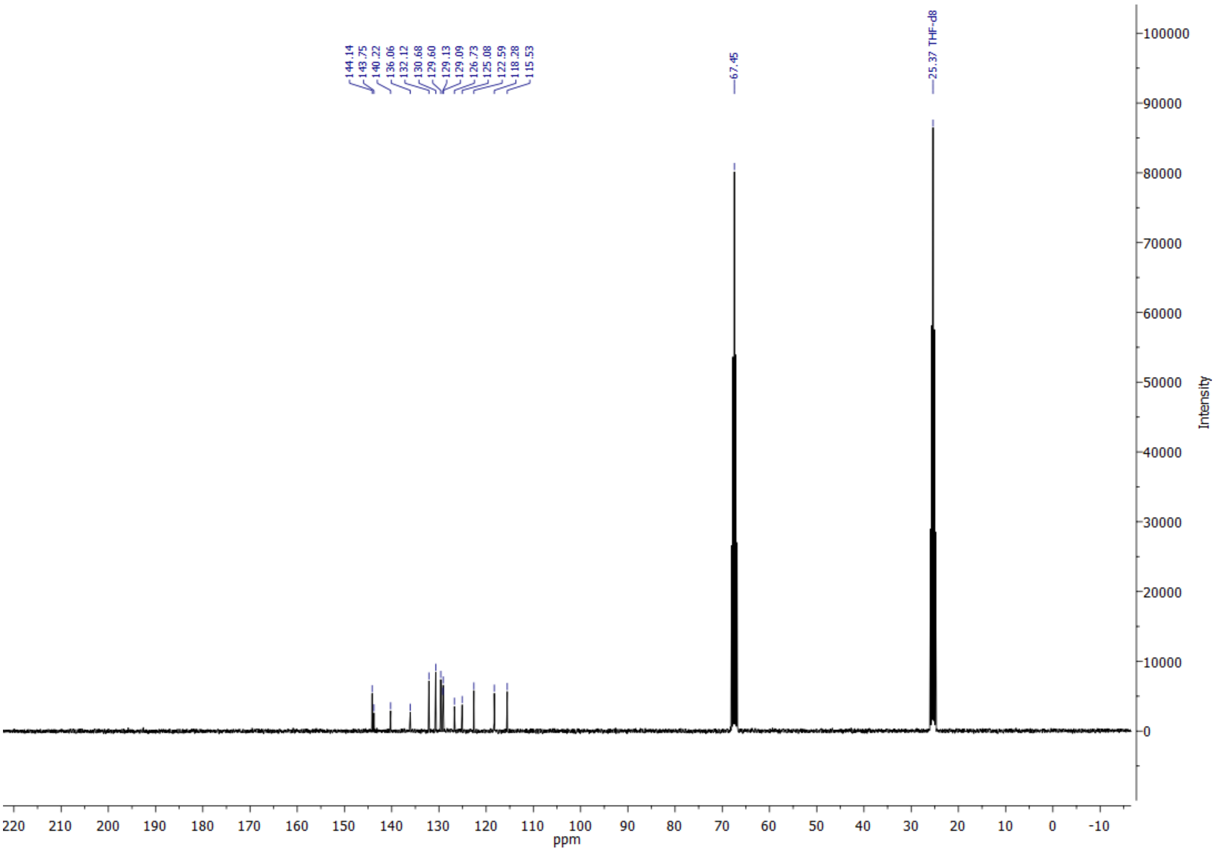


Figure 10: ^{13}C-NMR spectrum of **5c** (THF-d_8, 293K, 75MHz).

3.6 5-(4-Methoxyphenyl)thiophene-2-carbaldehyde (12)

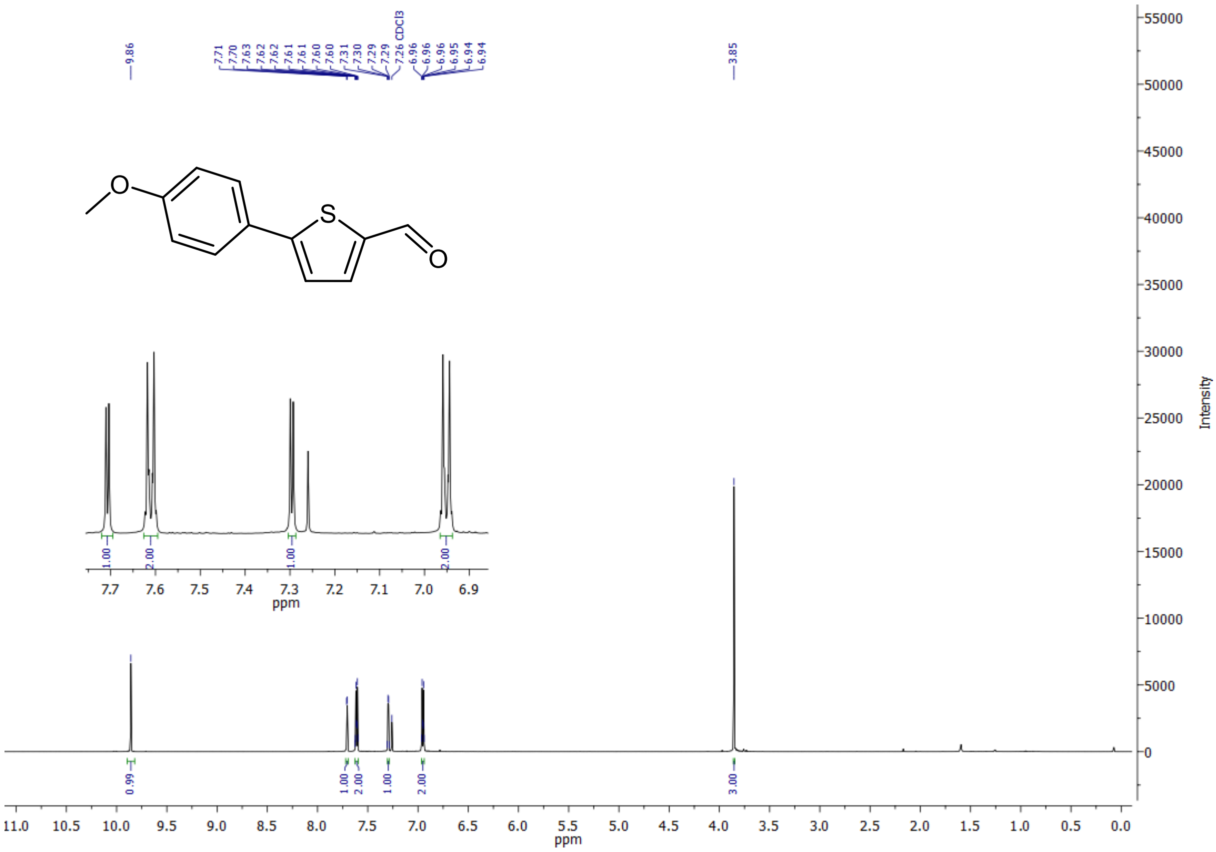


Figure 11: ^{1}H-NMR spectrum of **12** ($CDCl_3$, 293K, 300MHz).

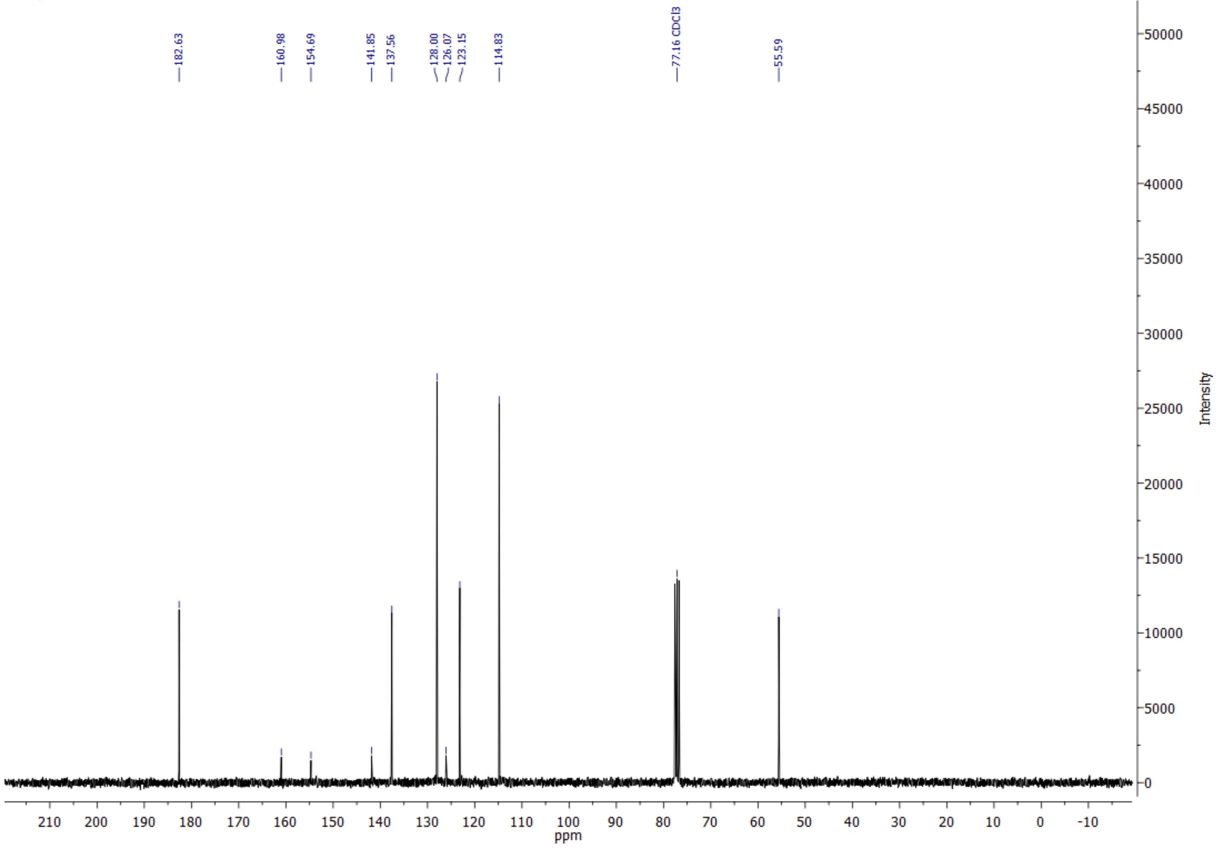


Figure 12: ^{13}C-NMR spectrum of **12** ($CDCl_3$, 293K, 75MHz).

3.7 2-Cyano-3-(5-(4-methoxyphenyl)thiophen-2-yl)acrylate (1a)

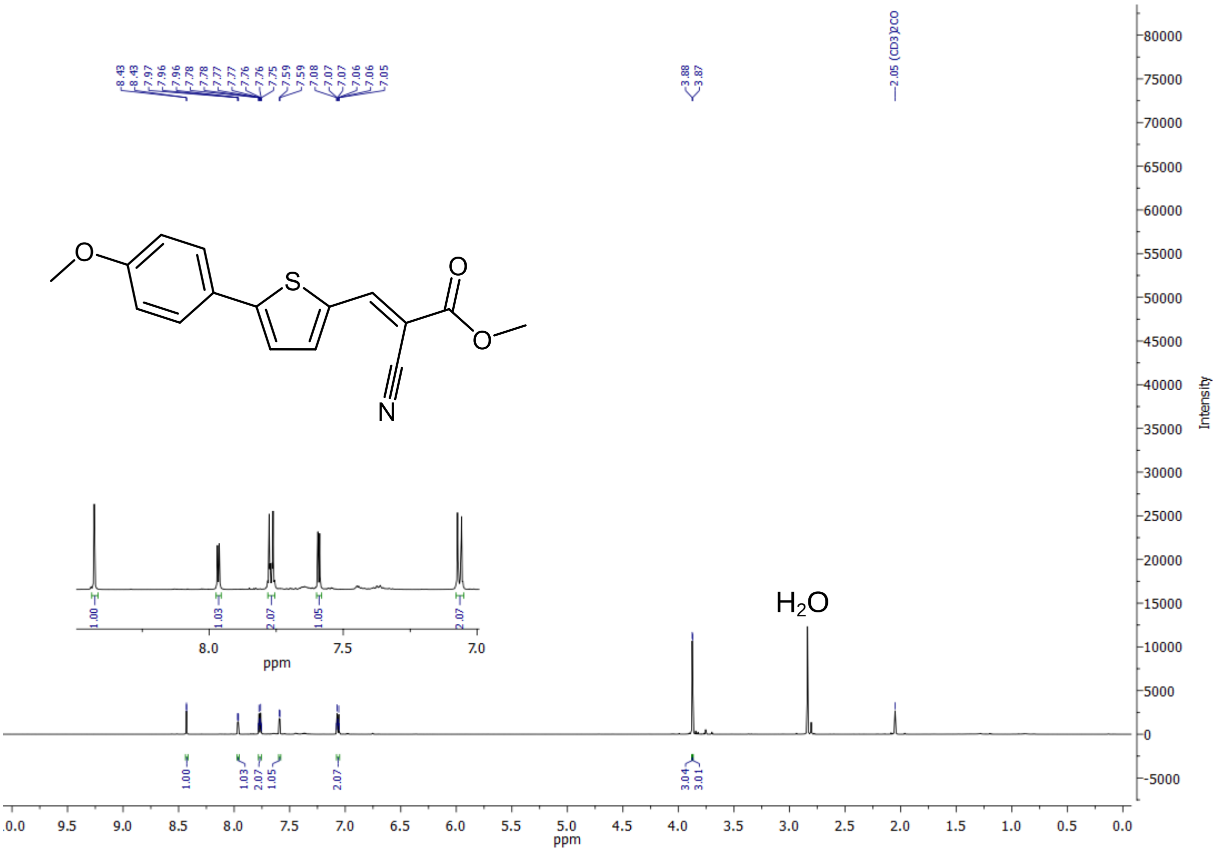


Figure 13: ^{1}H-NMR spectrum of **1a** (acetone-d_6, 293K, 600MHz).

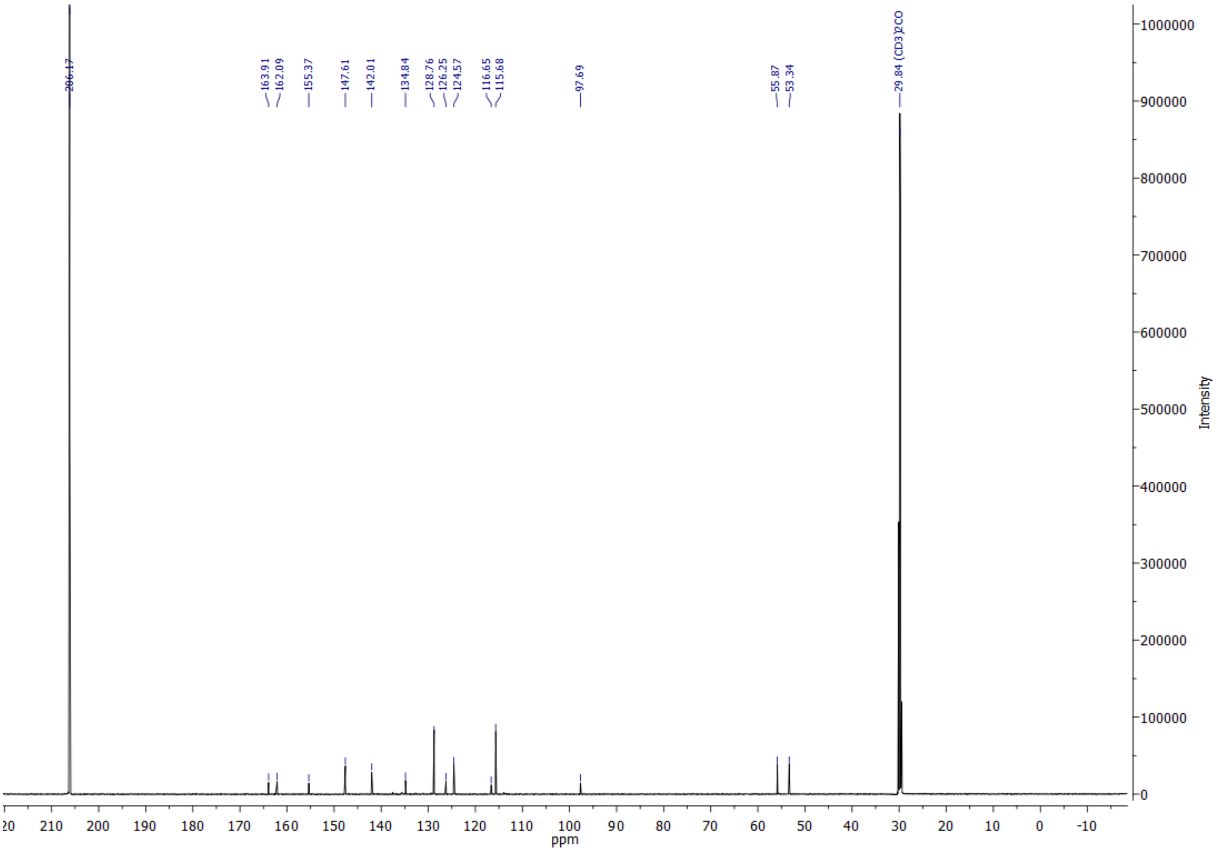


Figure 14: ^{13}C-NMR spectrum of **1a** (acetone-d_6, 293K, 150MHz).

3.8 2-((5-(4-Methoxyphenyl)thiophen-2-yl)methylene)malononitrile (1b)

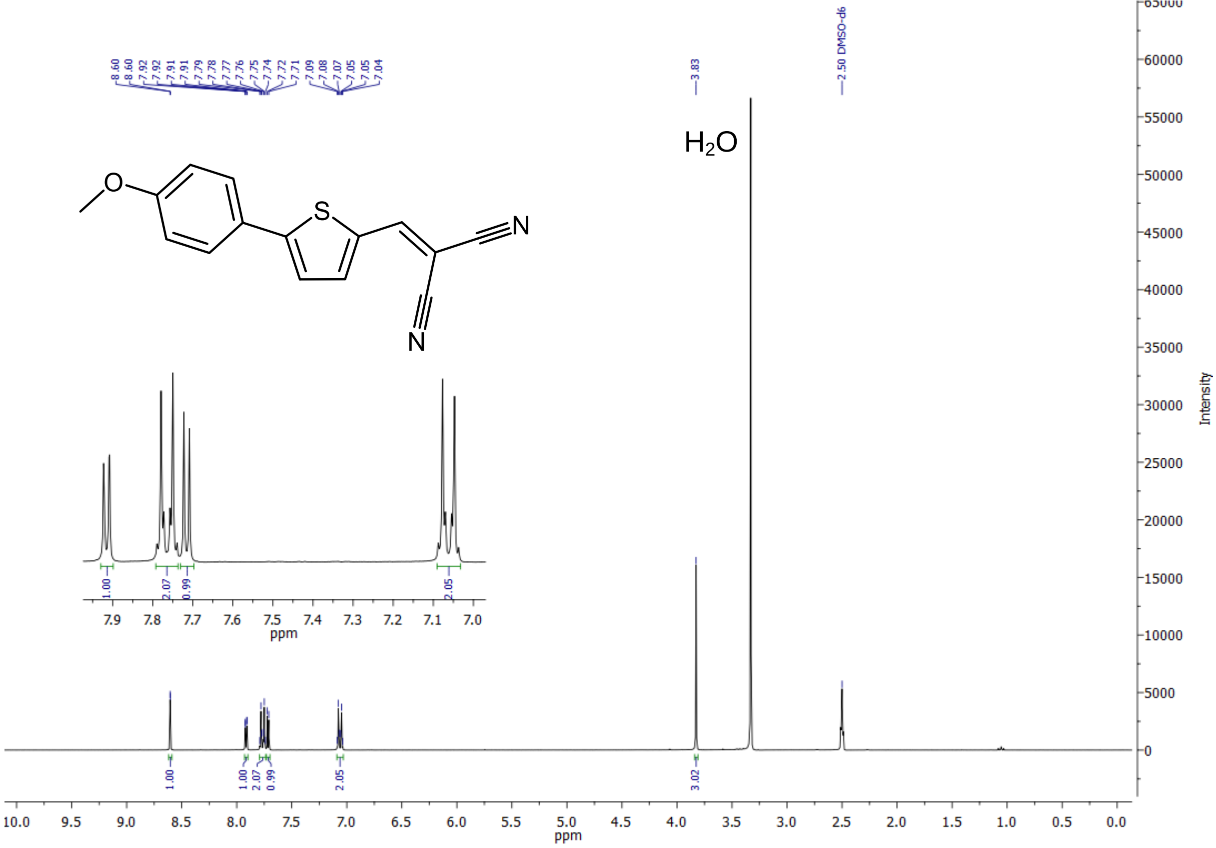


Figure 15: ^{1}H-NMR spectrum of **1b** (DMSO-d_6, 293K, 300MHz).

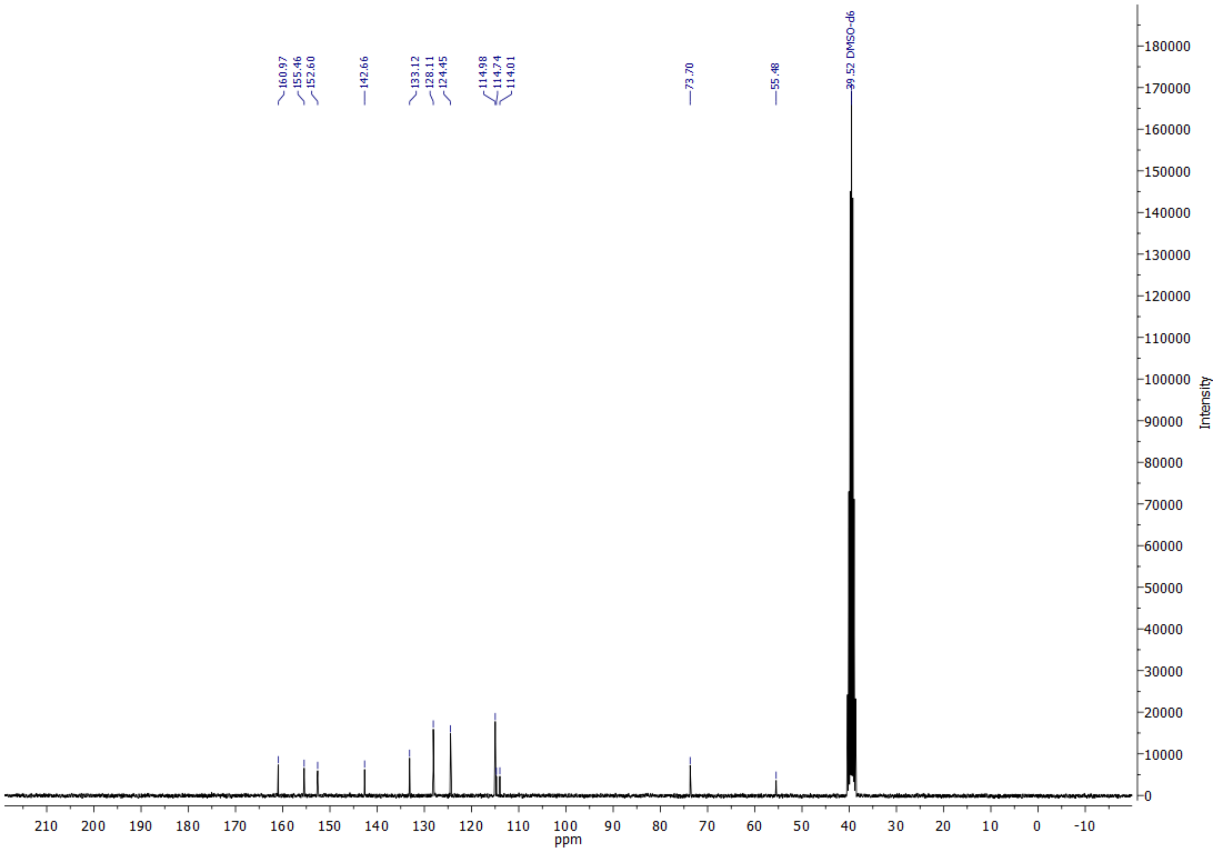


Figure 16: ^{13}C-NMR spectrum of **1b** (DMSO-d_6, 293K, 75MHz).

3.9 3-(5-(4-Methoxyphenyl)thiophen-2-yl)-2-(4-nitrophenyl)acrylonitrile (1c)

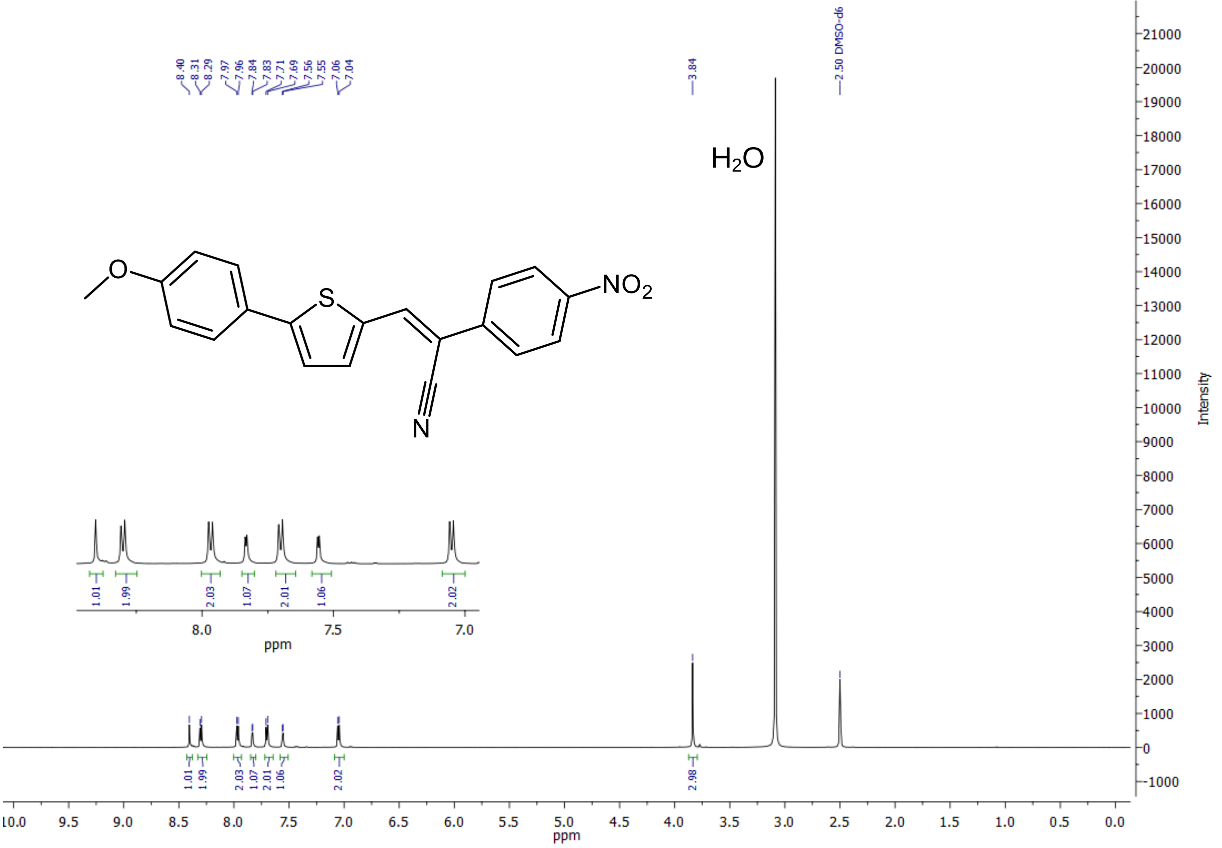


Figure 17: ^{1}H-NMR spectrum of **1c** (DMSO-d$_6$, 353K, 600MHz).

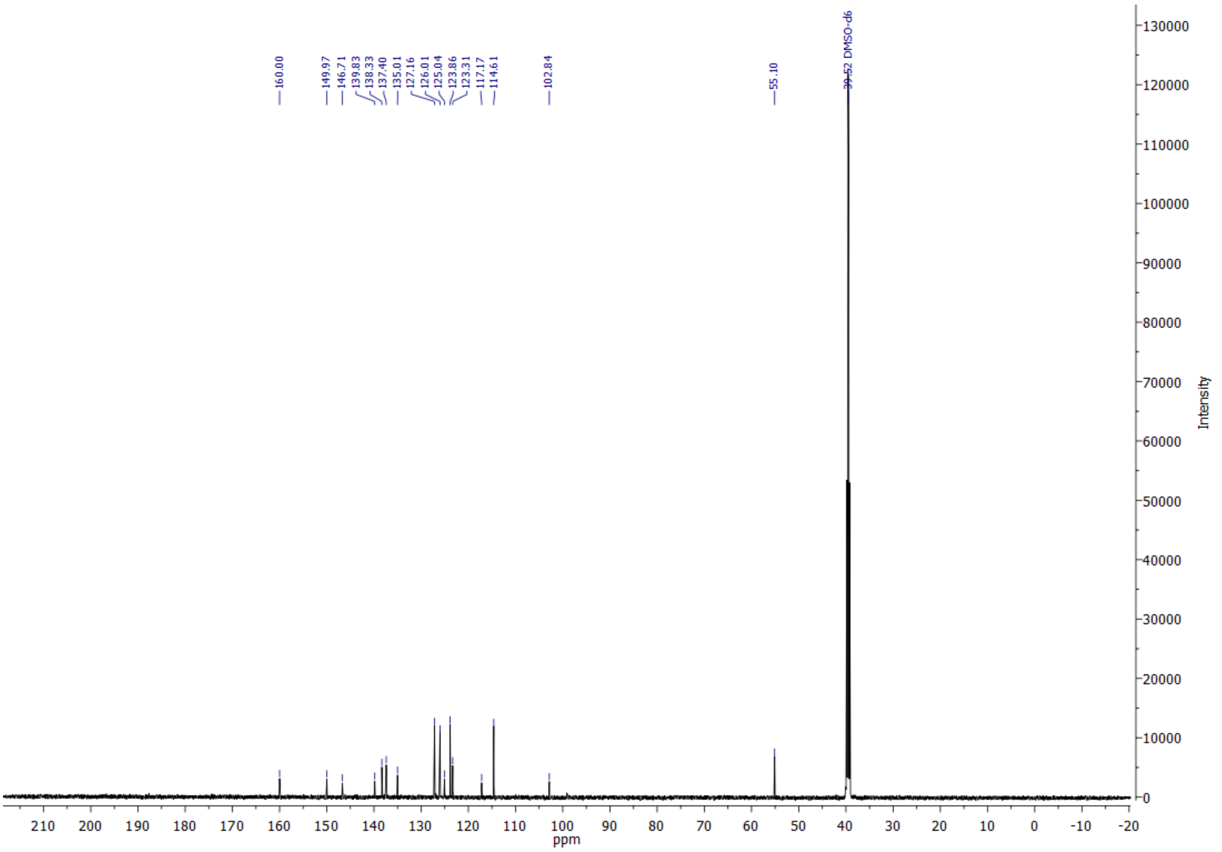


Figure 18: ^{13}C-NMR spectrum of **1c** (DMSO-d$_6$, 353K, 150 MHz).

3.10 5-((5-(4-Methoxyphenyl)thiophen-2-yl)methylene)-3-methyl-2-thioxothiazo-lidin- 4-one (1d)

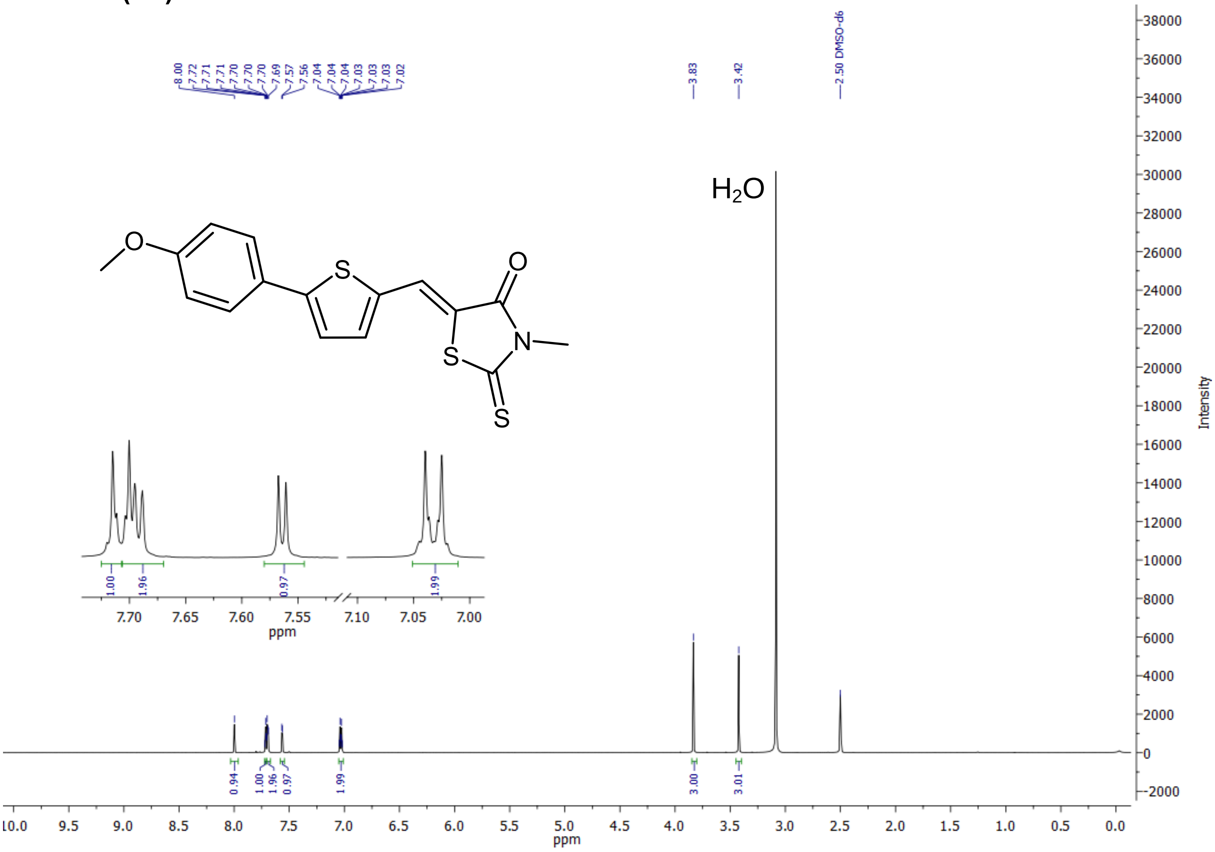


Figure 19: ^{1}H-NMR spectrum of **1d** (DMSO-d_6, 353K, 600MHz).

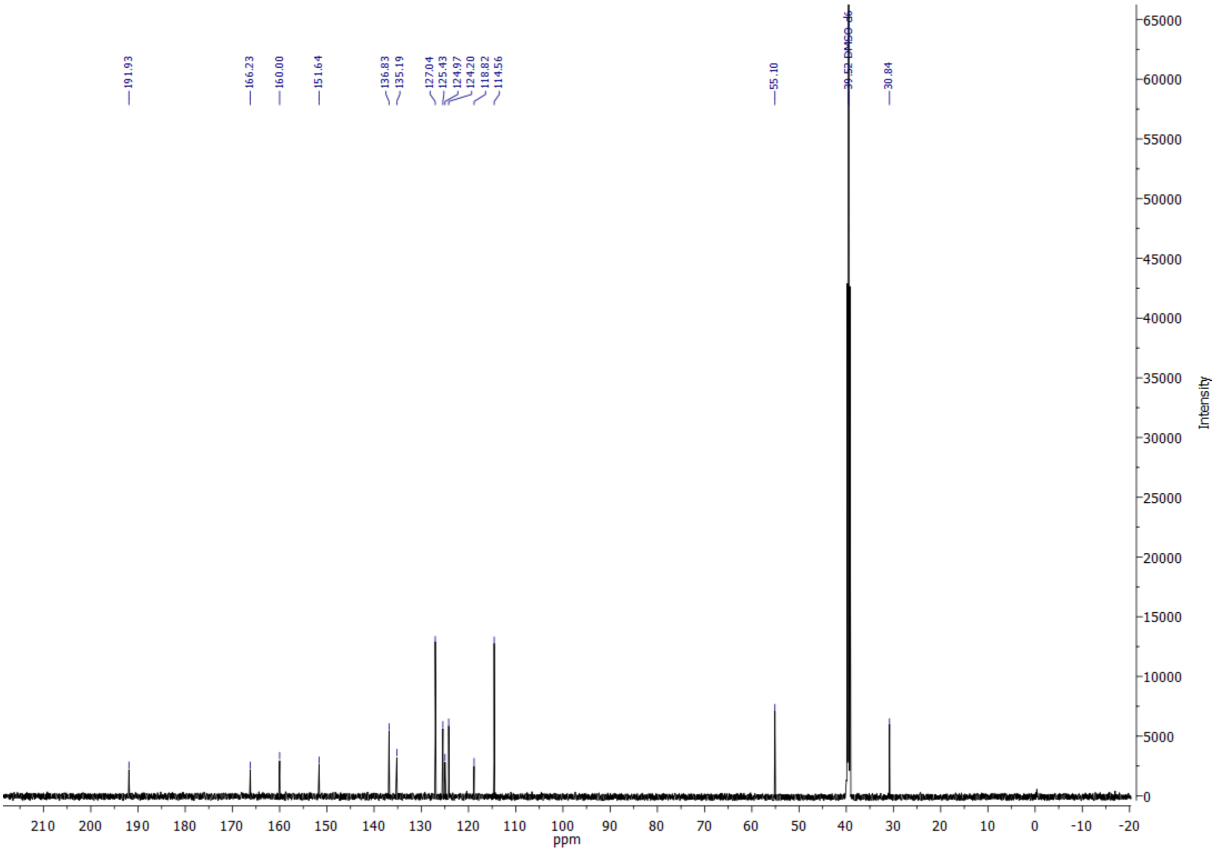


Figure 20: ^{13}C-NMR spectrum of **1d** (DMSO-d_6, 353K, 150MHz).

3.11 Methyl 2-cyano-3-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)acrylate (1e)

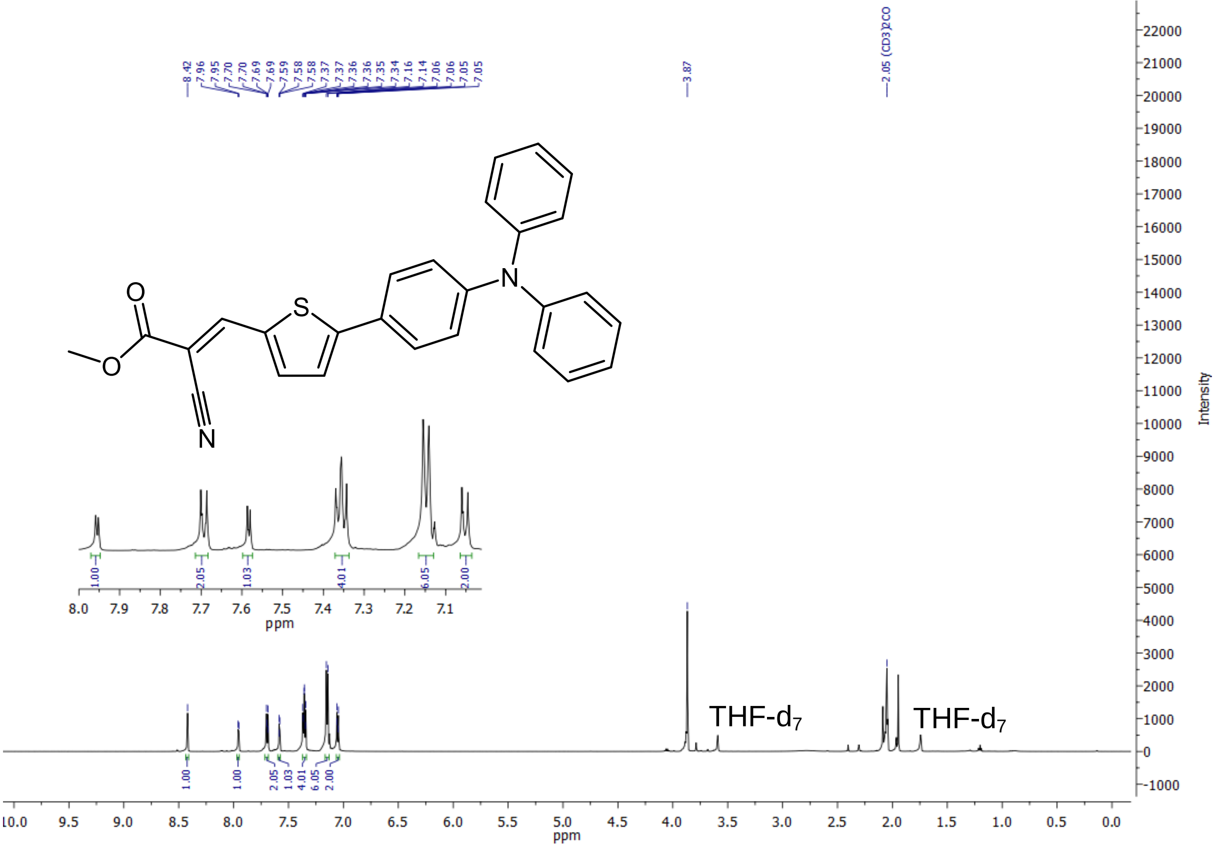


Figure 21: ^{1}H-NMR spectrum of **1e** (acetone-d_6 + 20% THF-d_8, 293K, 600MHz).

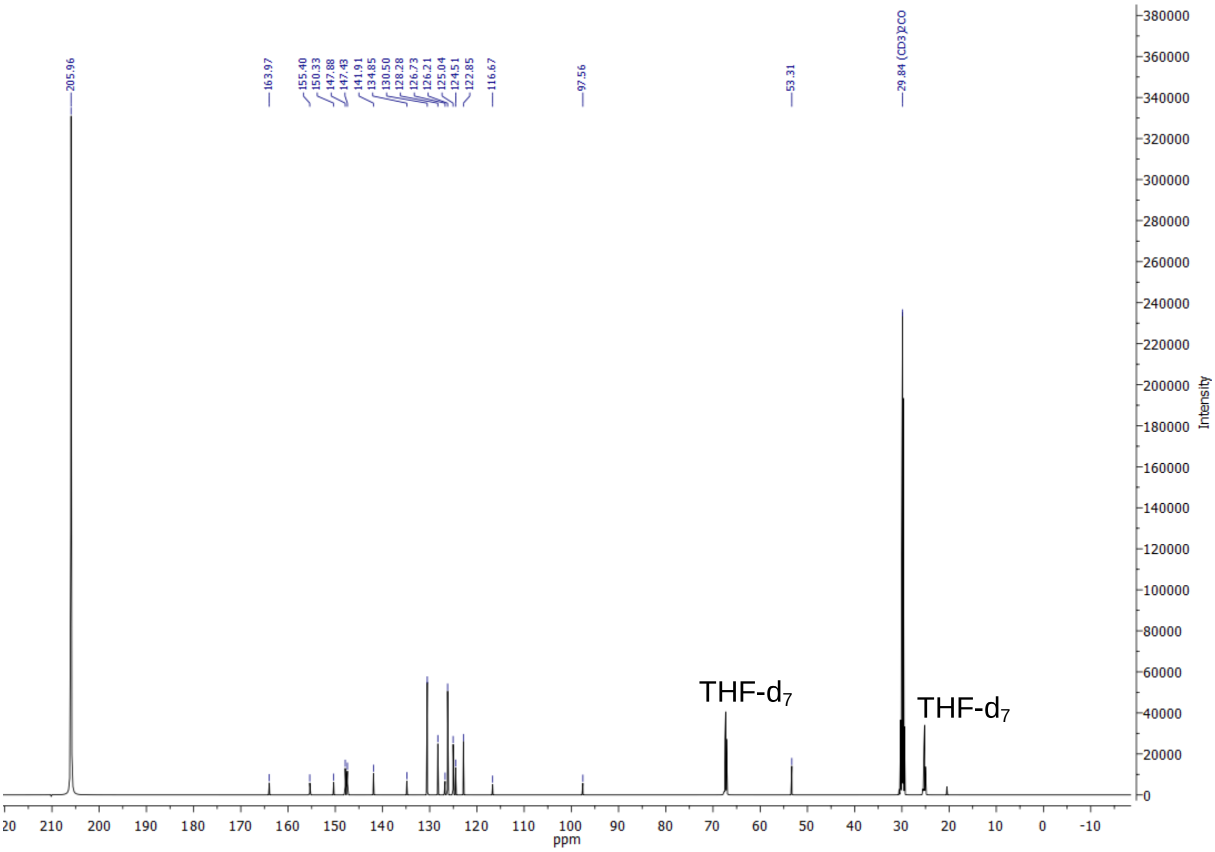


Figure 22: ^{13}C-NMR spectrum of **1e** (DMSO-d_6 + 20% THF-d_8, 293K, 150MHz).

3.12 Methyl 3-(5-([1,1':3',1''-terphenyl]-5'-yl)thiophen-2-yl)-2-cyanoacrylate (6a)

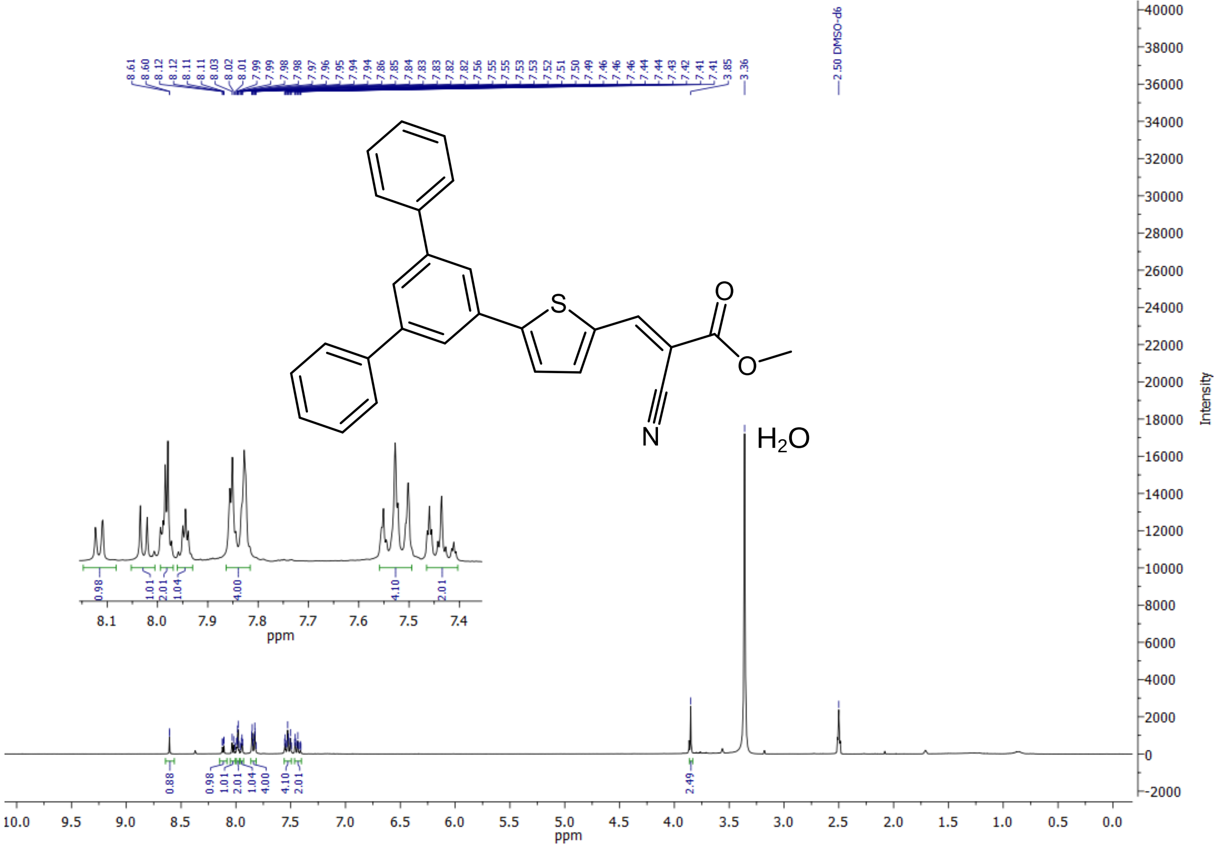


Figure 23: ^{1}H-NMR spectrum of **6a** (DMSO-d_6, 293K, 300MHz).

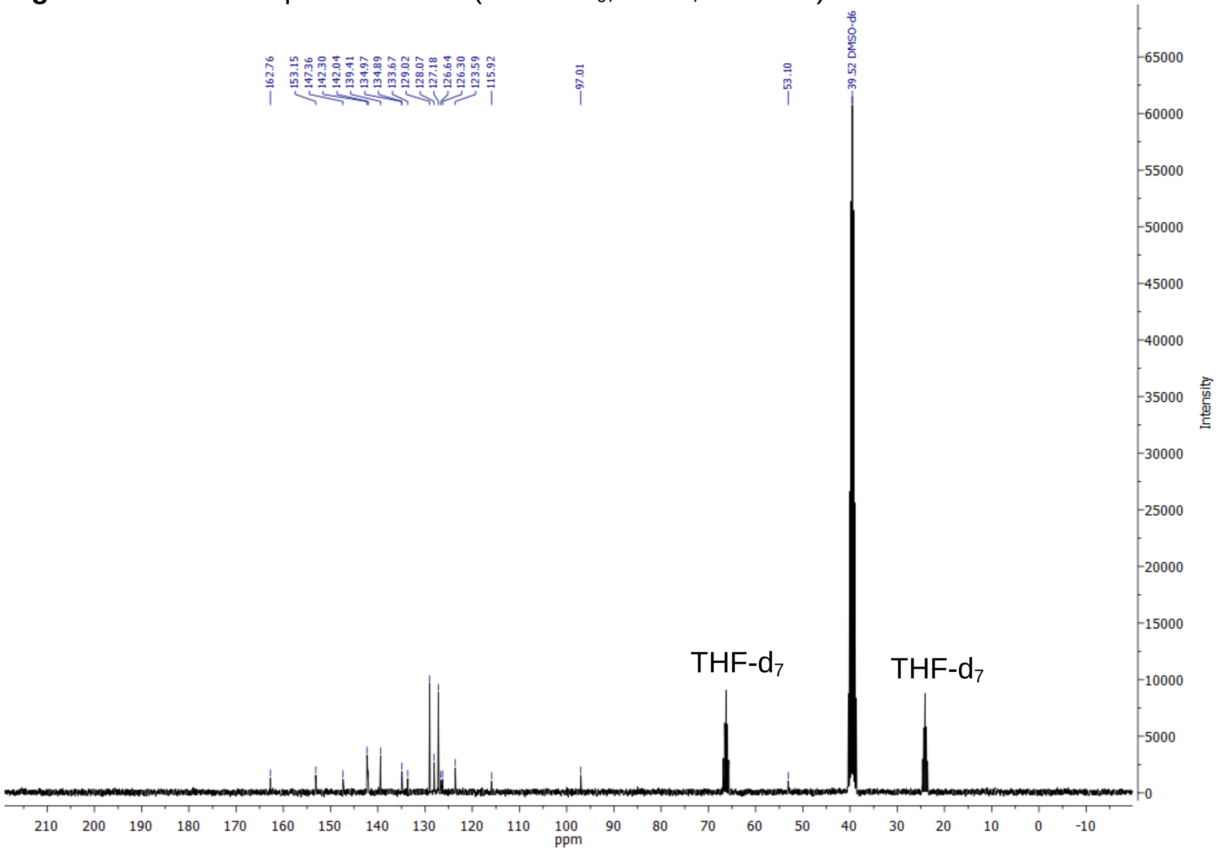


Figure 24: ^{13}C-NMR spectrum of **6a** (DMSO-d_6 + 30% THF-d_8, 293K, 75MHz).

3.13 Methyl 2-cyano-3-(5-(2,2-diphenylvinyl)thiophen-2-yl)acrylate (6b)

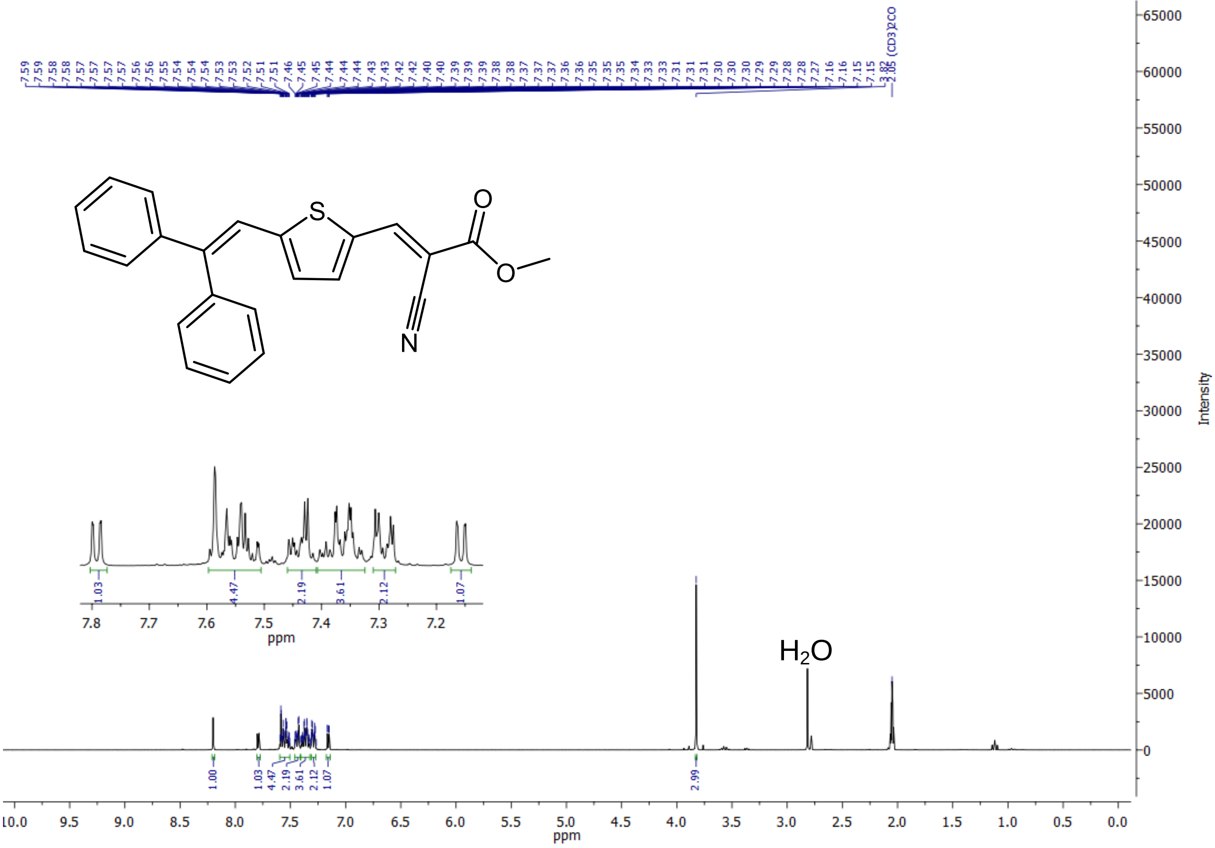


Figure 25: ^{1}H-NMR spectrum of **6b** (acetone-d$_6$, 293K, 300MHz).

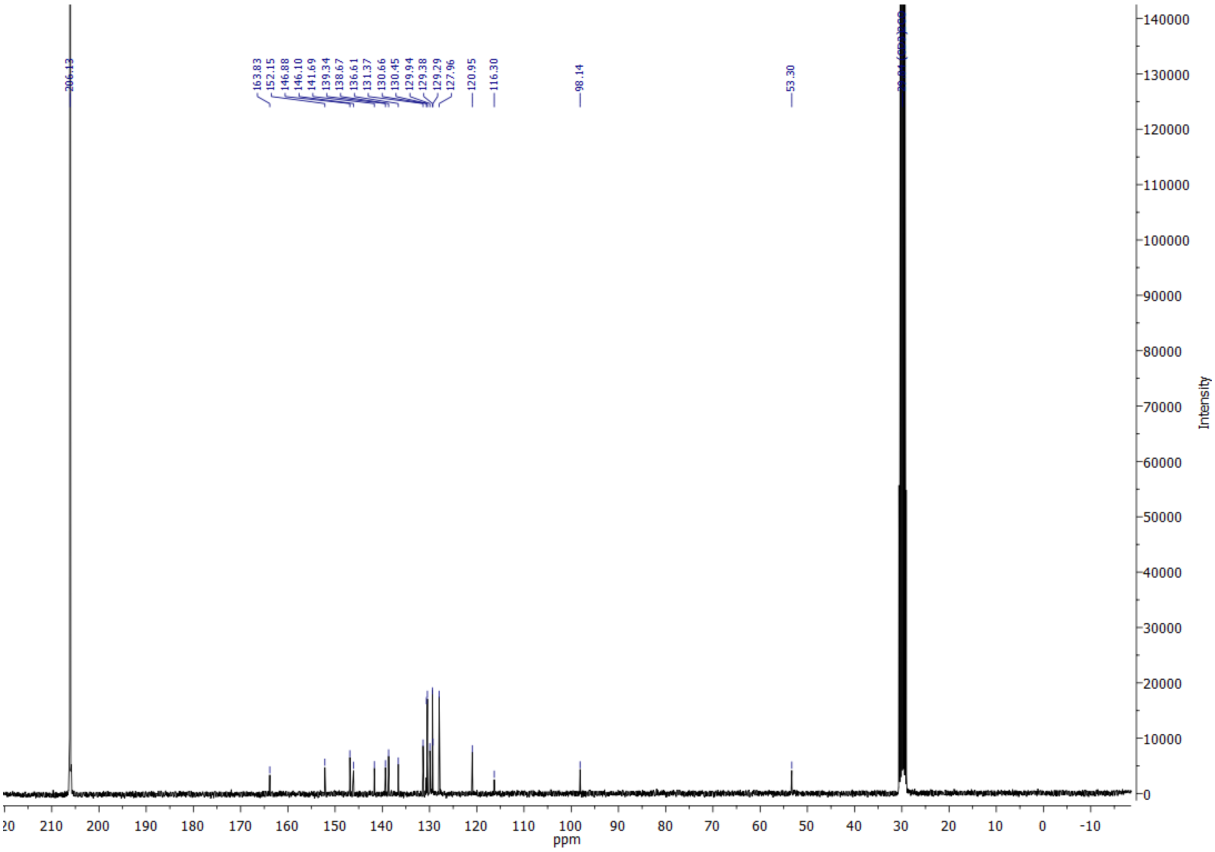


Figure 26: ^{13}C-NMR spectrum of **6b** (acetone-d$_6$, 293K, 75MHz).

3.14 3-(5-(4-(3,7-Bis(4-(hexyloxy)phenyl)-10*H*-phenothiazin-10-yl)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (7a)

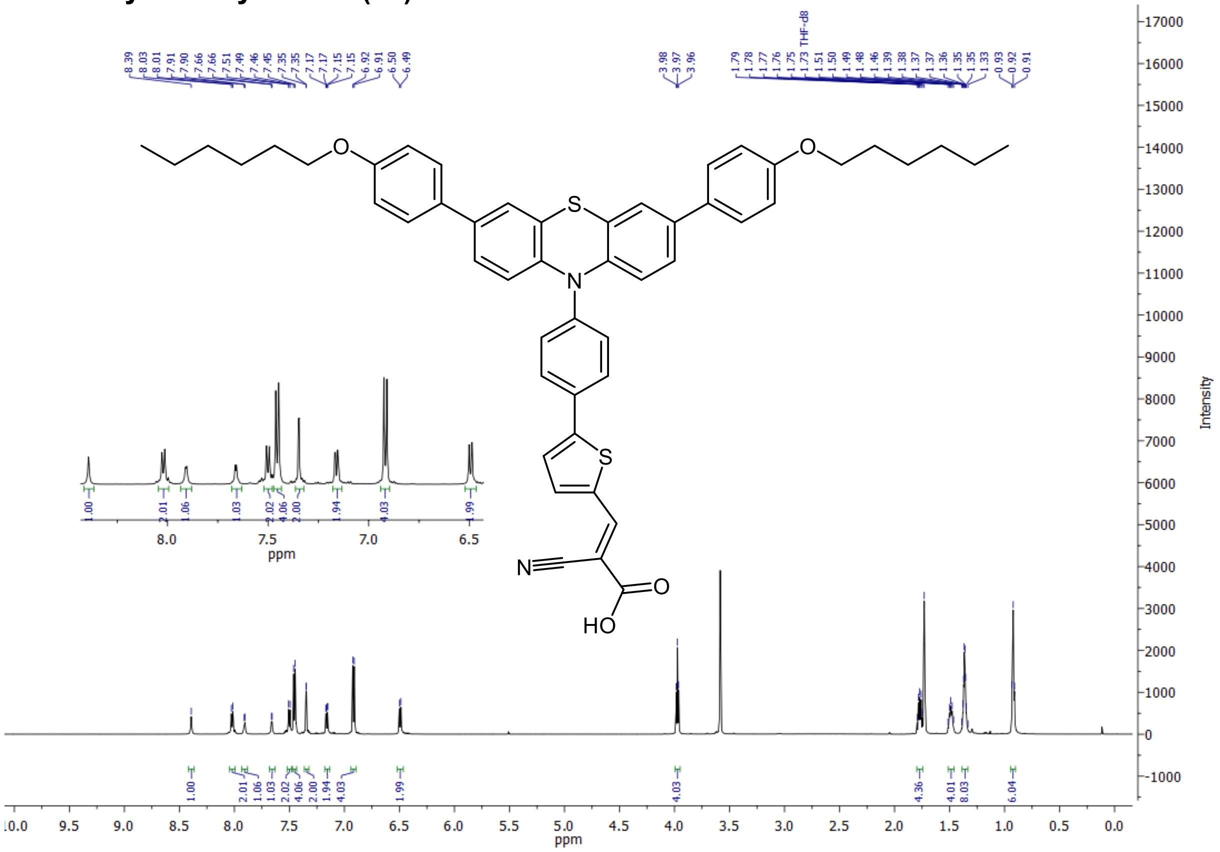


Figure 27: ^{1}H-NMR spectrum of **7a** (THF-d_8, 293K, 300MHz).

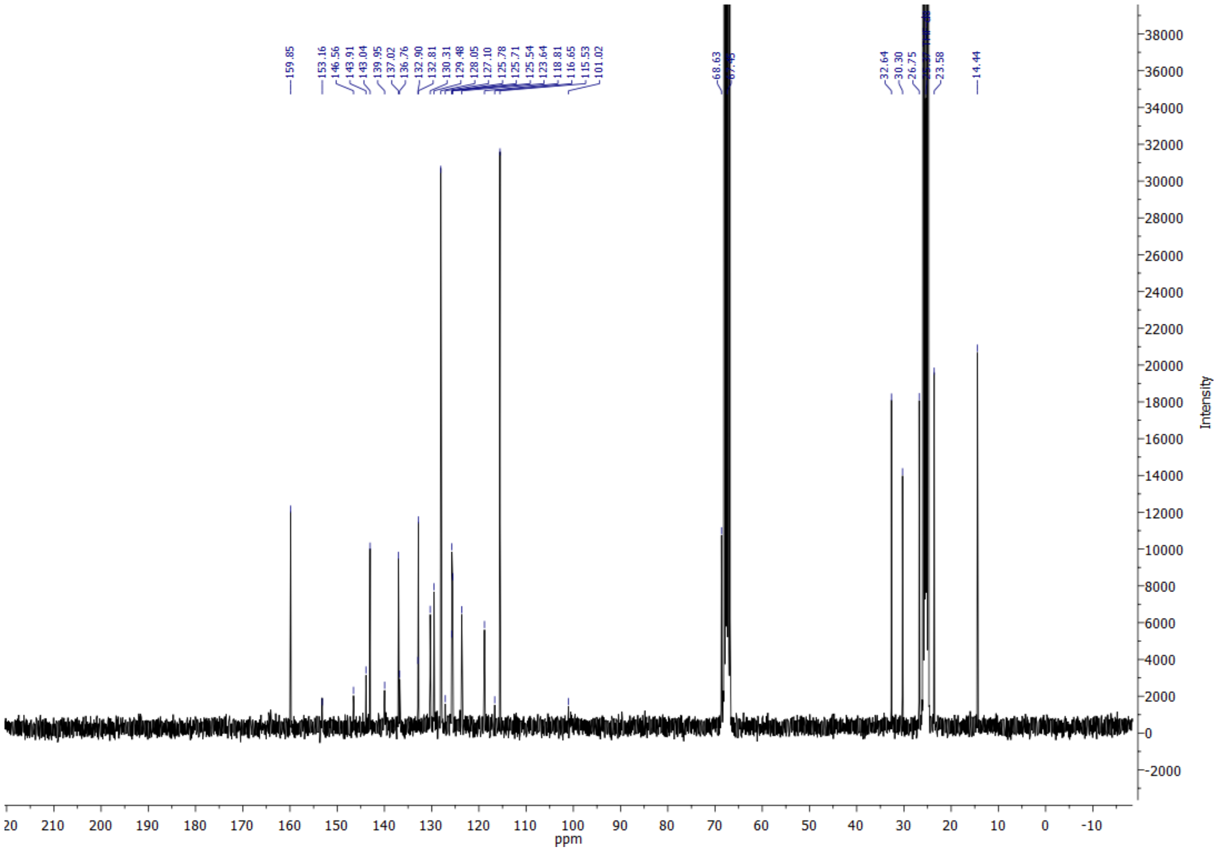


Figure 28: ^{13}C-NMR spectrum of **7a** (THF-d_8, 293K, 75MHz).

3.15 3-(5-(4-(Bis(4'-(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (7b)

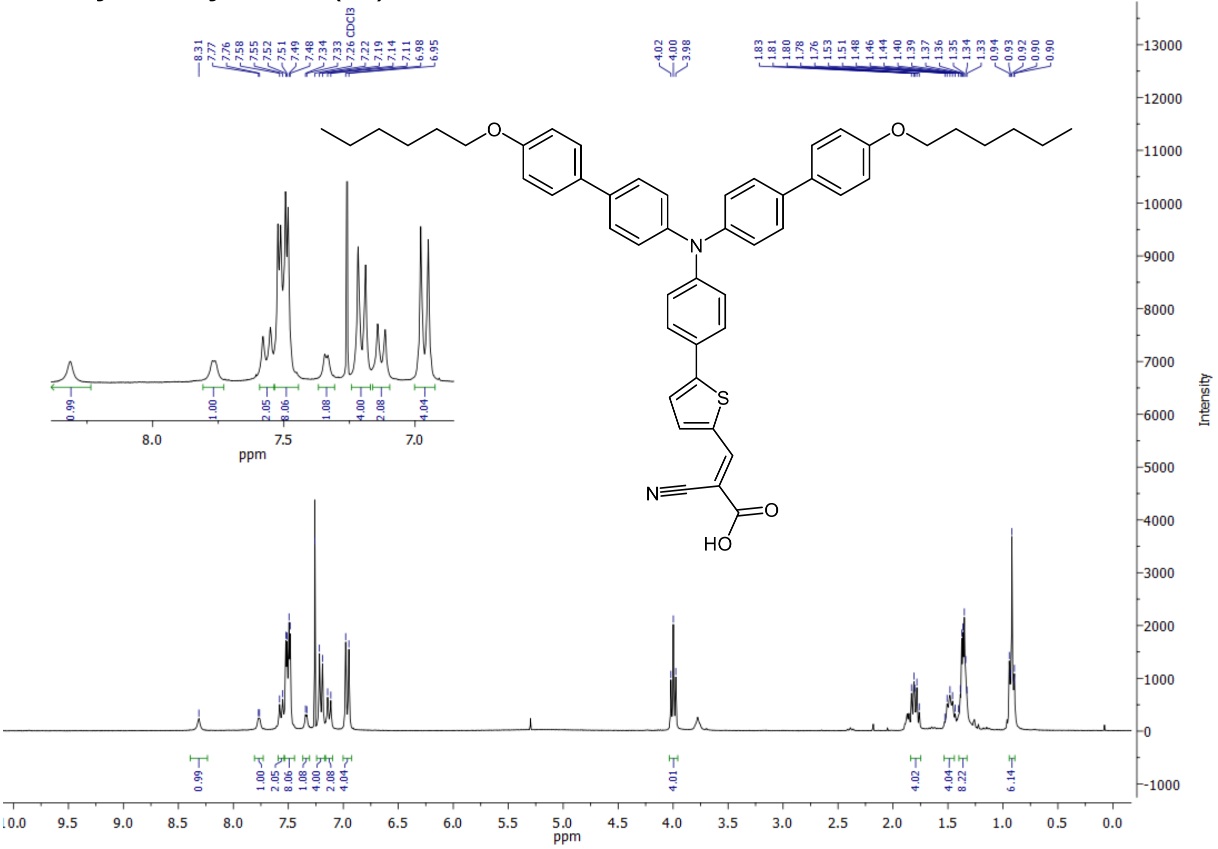


Figure 29: ^{1}H-NMR spectrum of **7b** ($CDCl_3$, 293K, 300MHz).

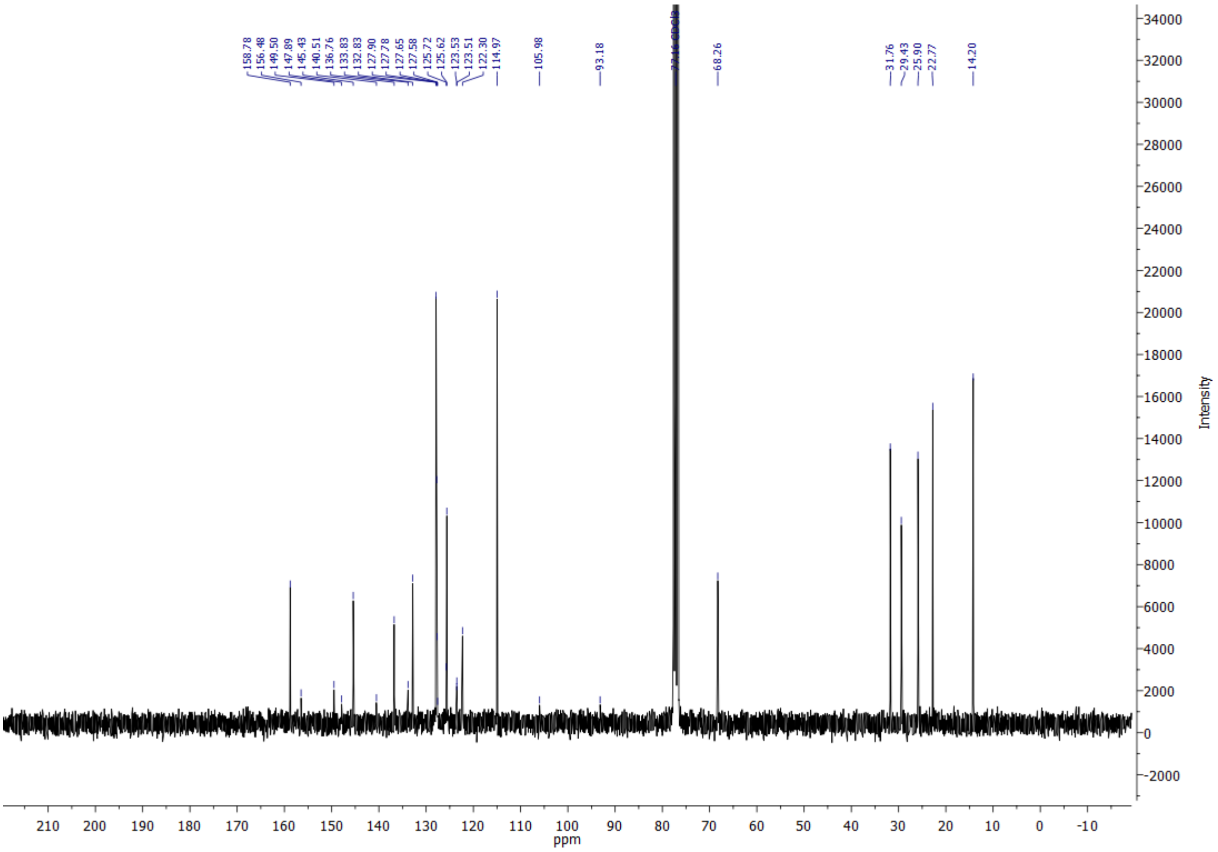


Figure 30: ^{13}C-NMR spectrum of **7b** ($CDCl_3$, 293K, 75MHz).

3.16 3-(5-(4-(Bis(4-(7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)phenyl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (7c)

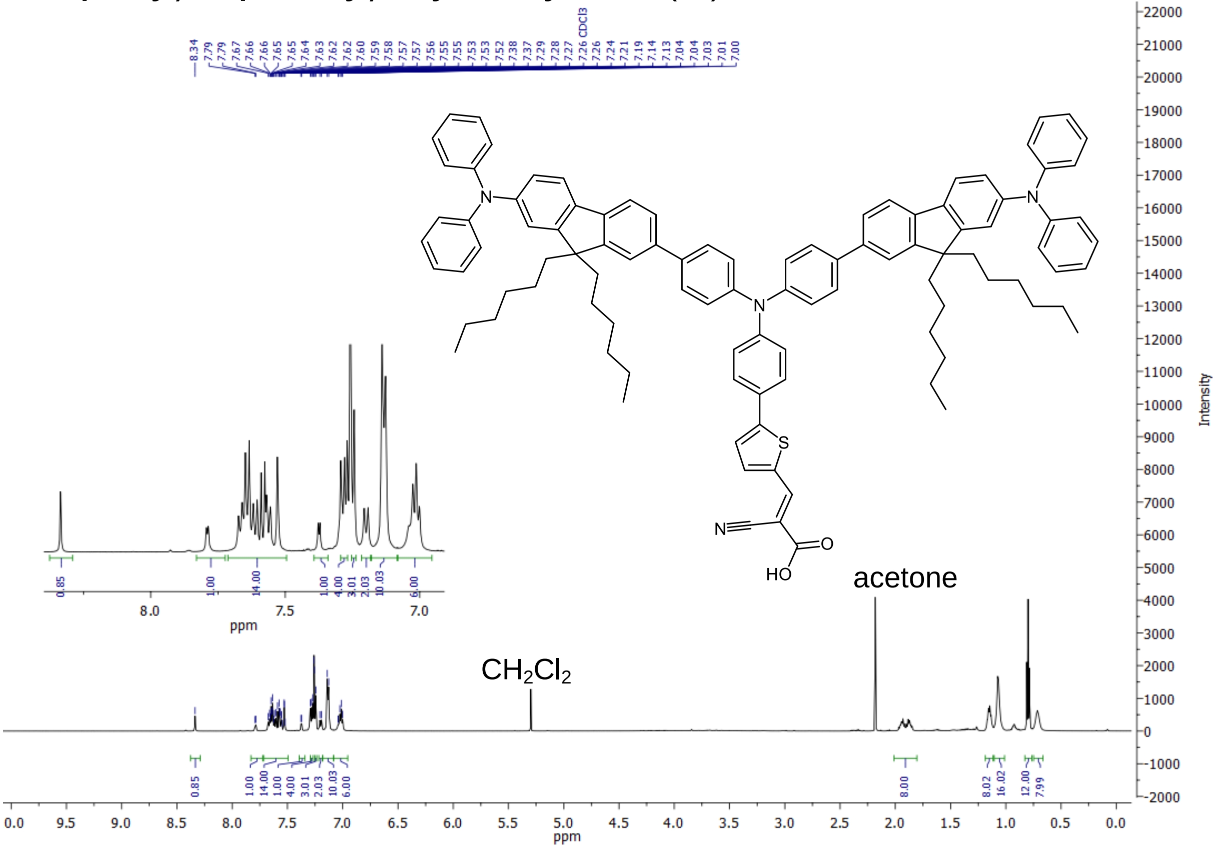


Figure 31: ^{1}H-NMR spectrum of **7c** ($CDCl_3$, 293K, 600MHz).

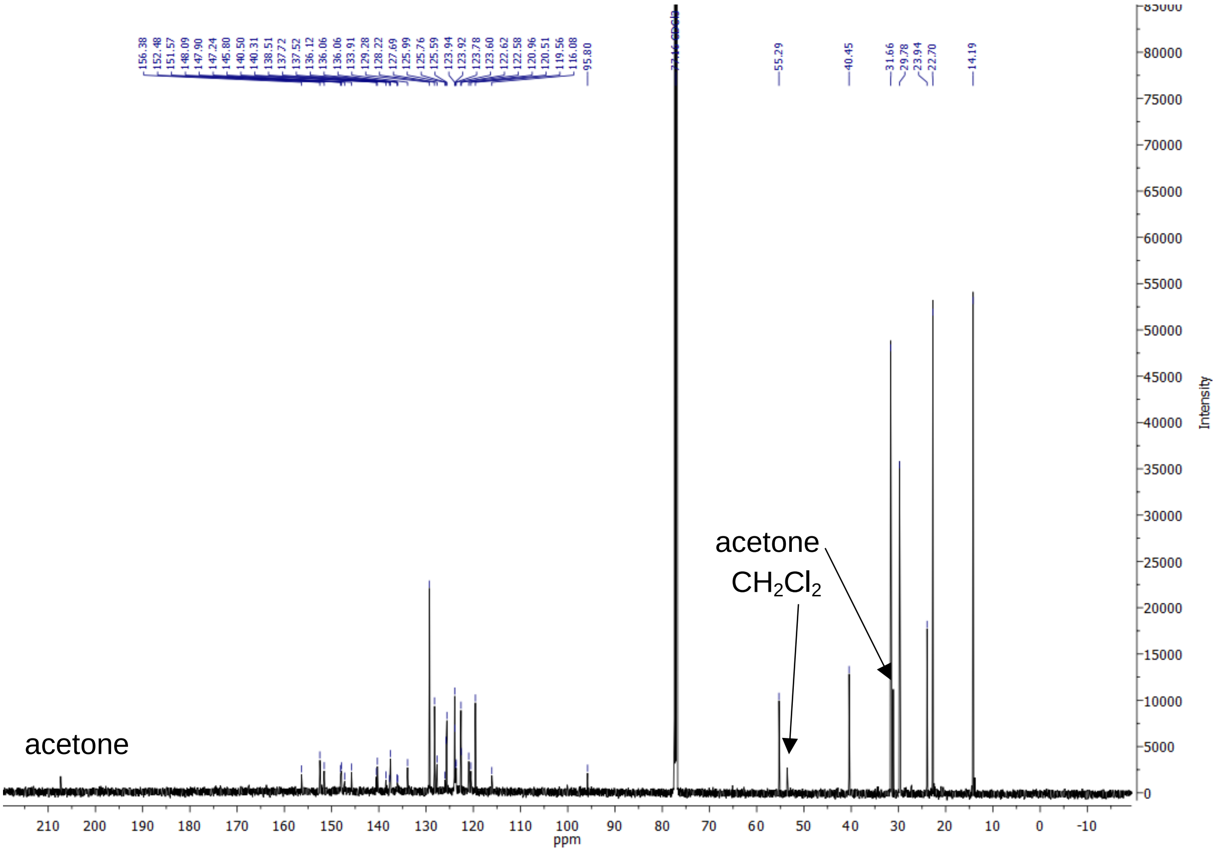


Figure 32: ^{13}C-NMR spectrum of **7c** ($CDCl_3$, 293K, 150MHz).

3.17 1-Bromo-2,4-bis(hexyloxy)benzene (3e)

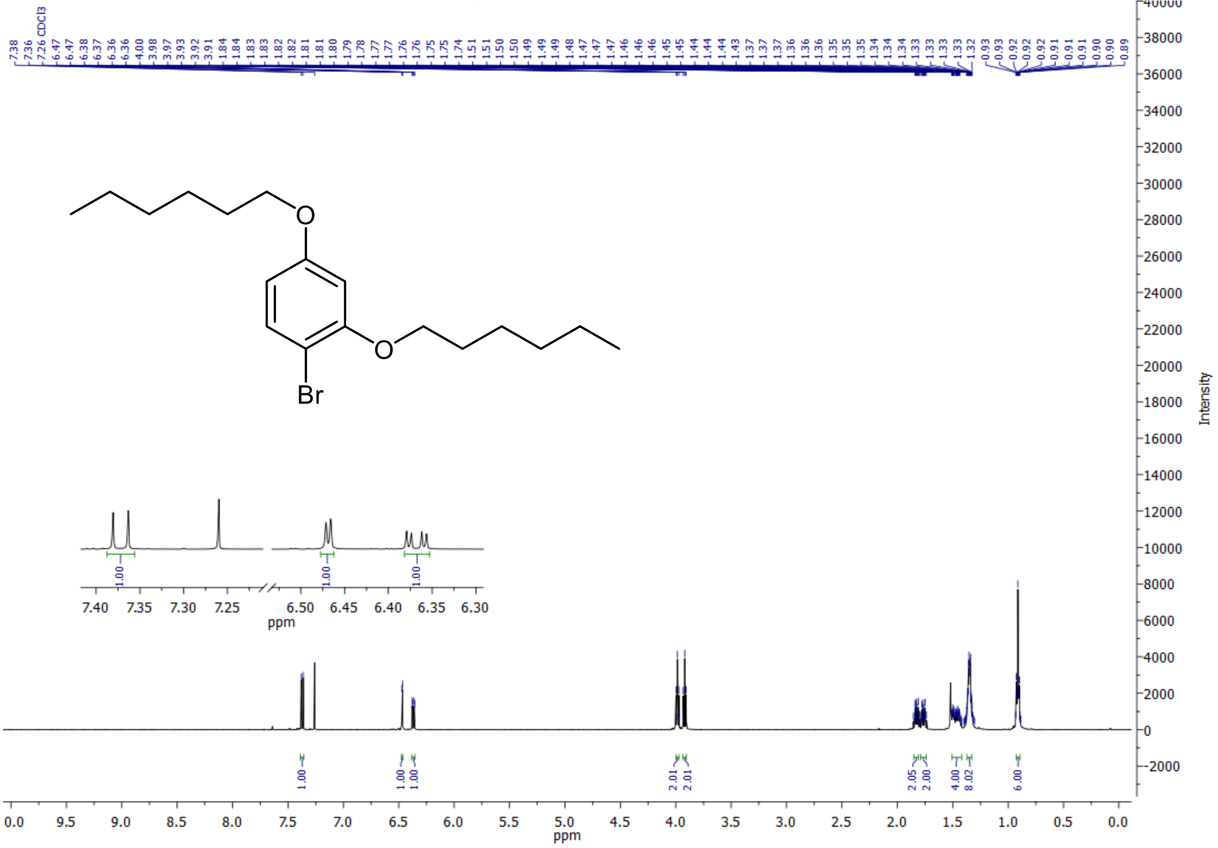


Figure 33: ^{1}H-NMR spectrum of **3e** (CDCl$_3$, 293K, 300MHz).

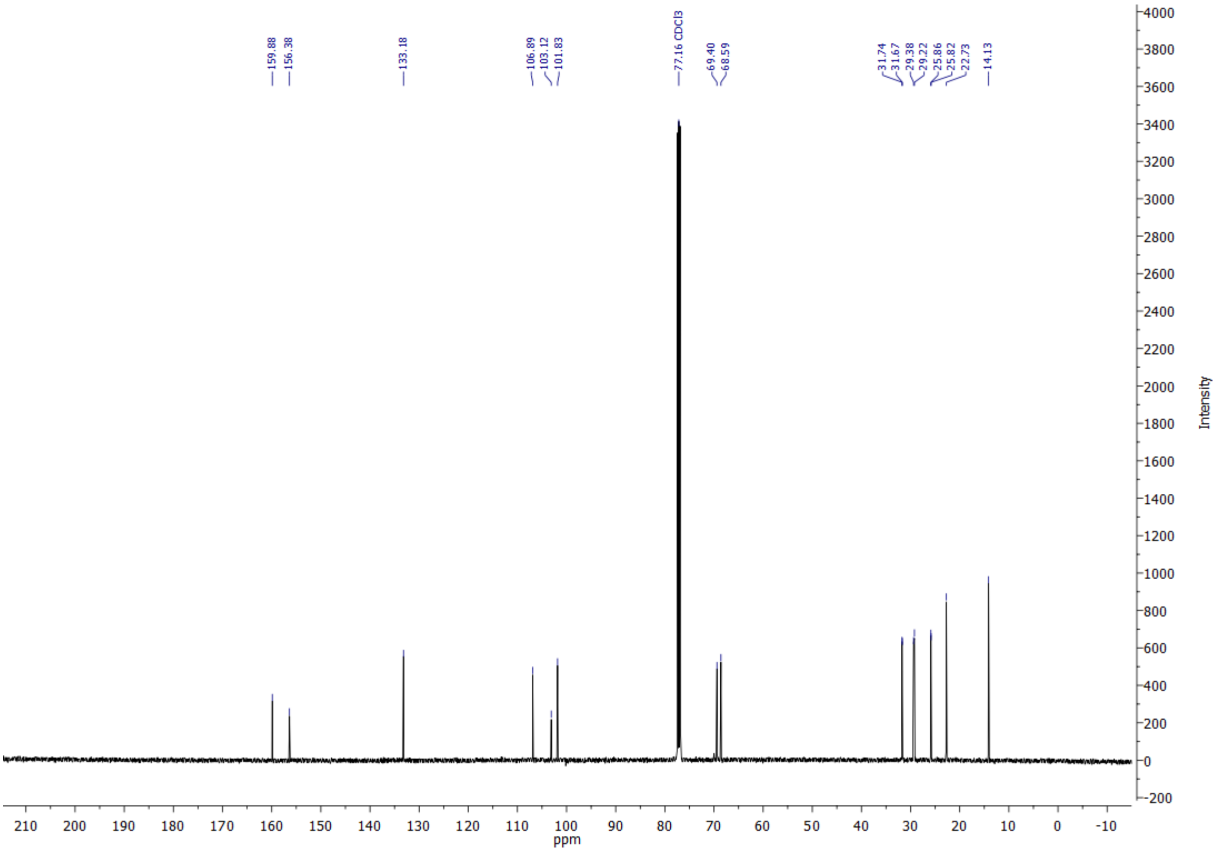


Figure 34: ^{13}C-NMR spectrum of **3e** (CDCl$_3$, 293K, 75MHz).

3.18 2,5-Bis(4-methoxyphenyl)thiophene (8a) [22]

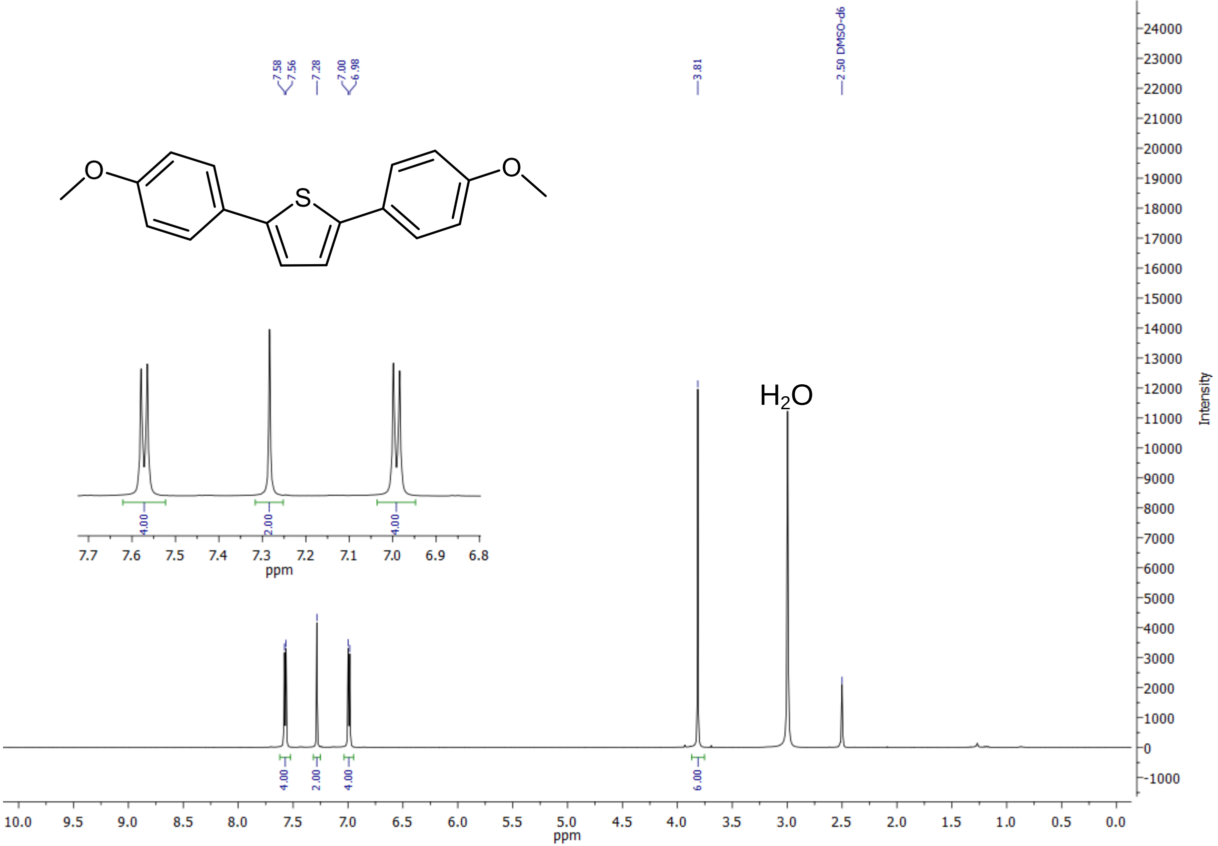


Figure 35: ^{1}H-NMR spectrum of **8a** (DMSO-d_6, 373K, 600MHz).

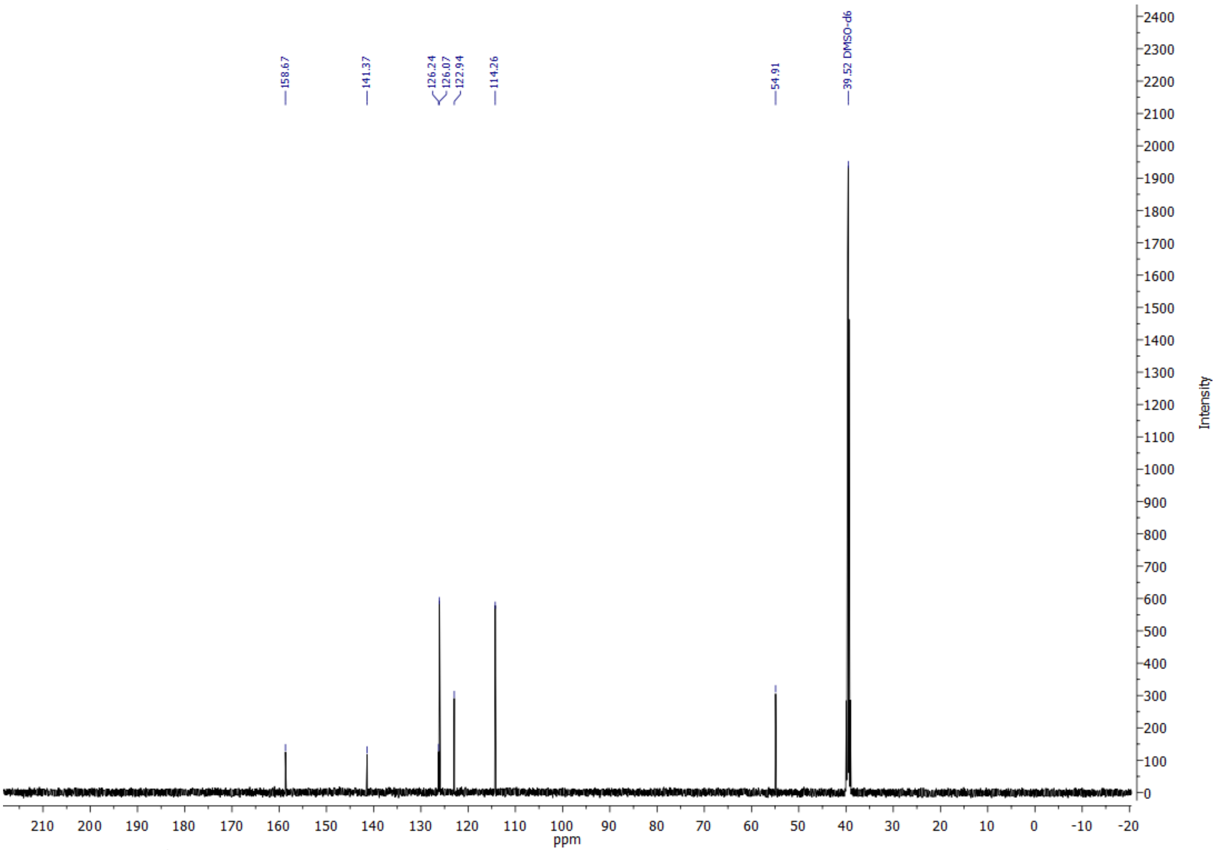


Figure 36: ^{13}C-NMR spectrum of **8a** (DMSO-d_6, 373K, 150MHz).

3.19 4-(5-(4-Methoxyphenyl)thiophen-2-yl)benzonitrile (8b)

Figure 37: ^{1}H-NMR spectrum of **8b** (actone-d$_6$, 293K, 600MHz).

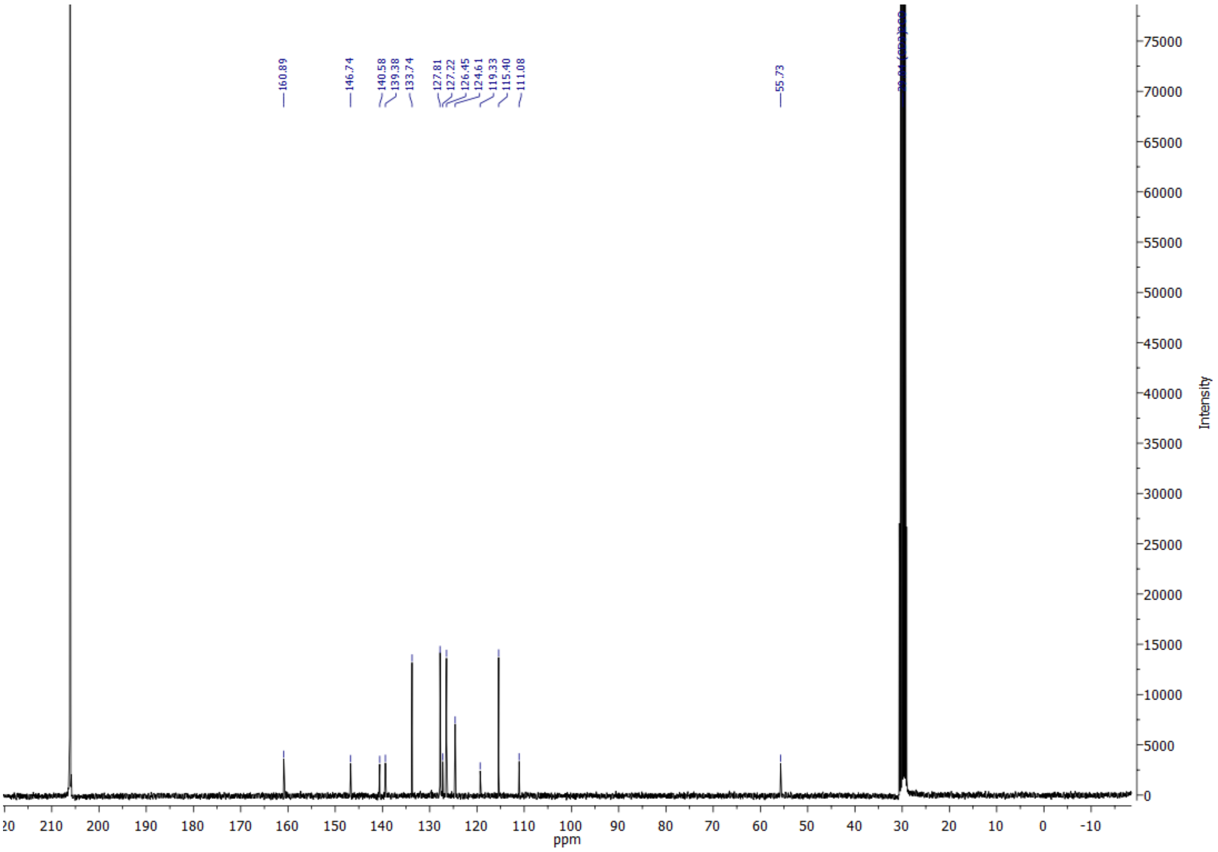


Figure 38: ^{13}C-NMR spectrum of **8b** (actone-d$_6$, 293K, 75MHz).

3.20 5-(4-Methoxyphenyl)-2,2'-bithiophene (8c)

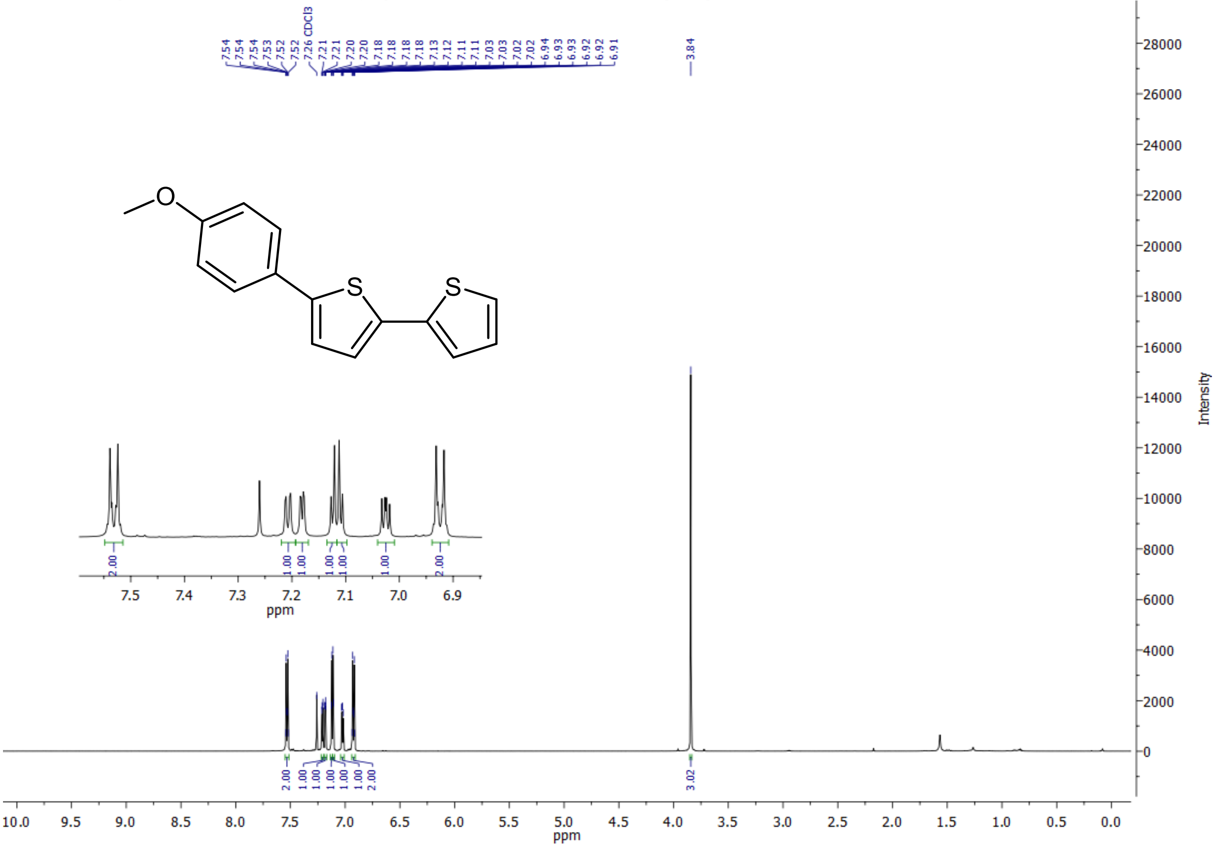


Figure 39: ^{1}H-NMR spectrum of **8c** ($CDCl_3$, 293K, 600MHz).

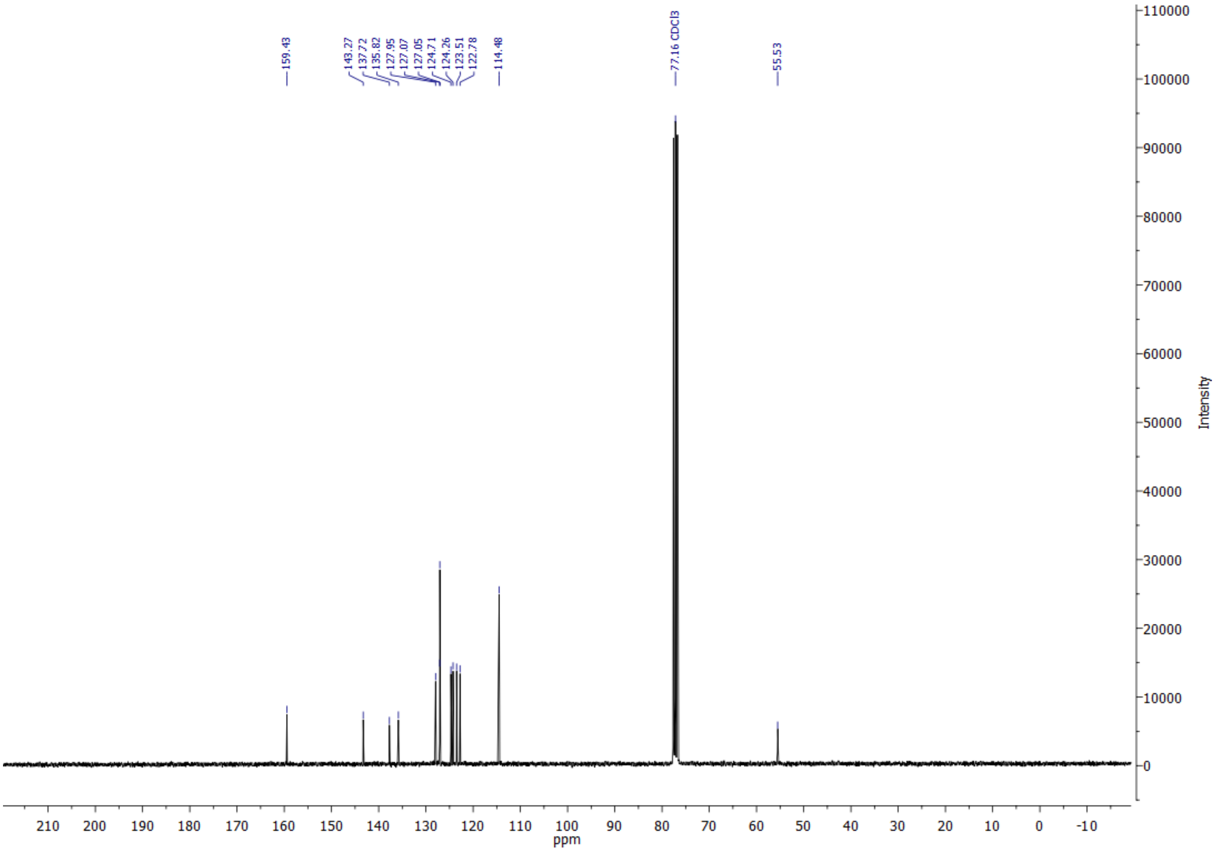


Figure 40: ^{13}C-NMR spectrum of **8c** ($CDCl_3$, 293K, 75MHz).

3.21 4-(5-(4-Fluorophenyl)thiophen-2-yl)benzonitrile (8d)

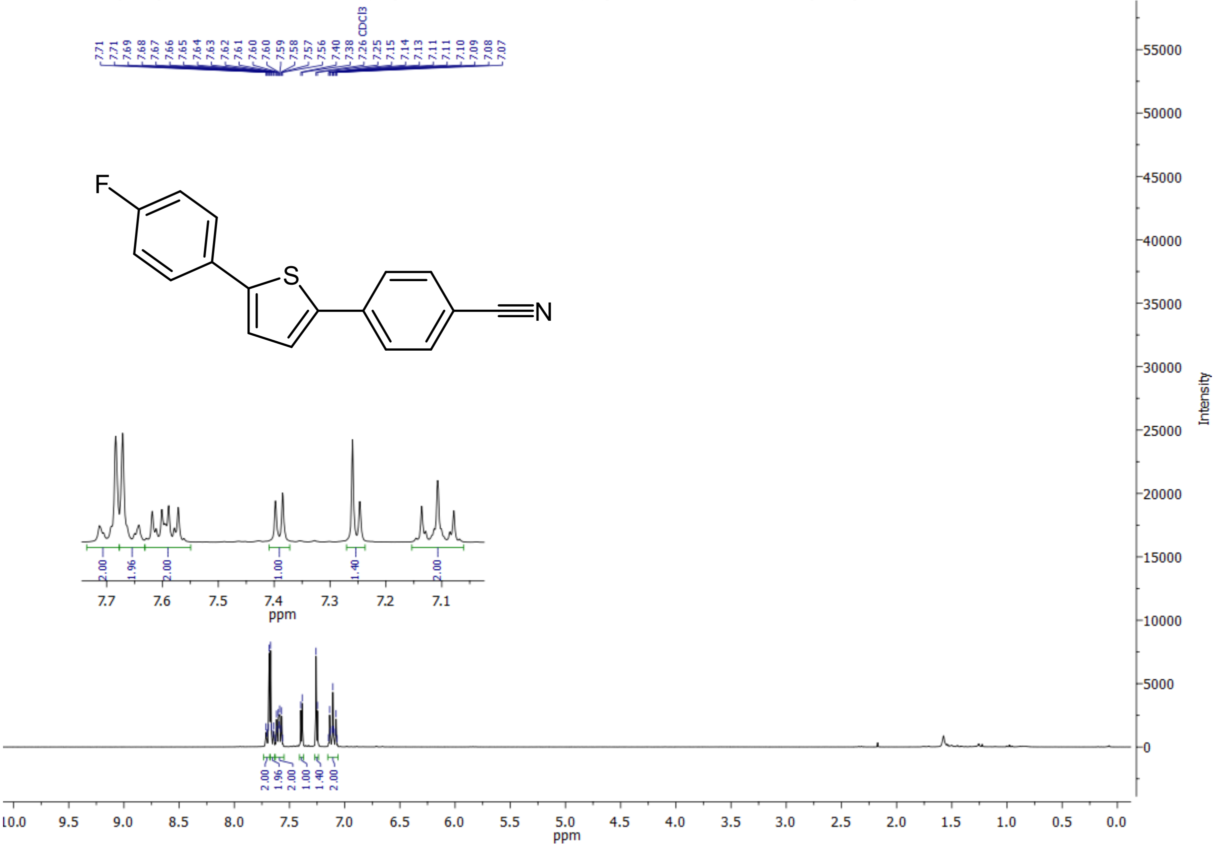


Figure 41: ^{1}H-NMR spectrum of **8d** ($CDCl_3$, 293K, 300MHz).

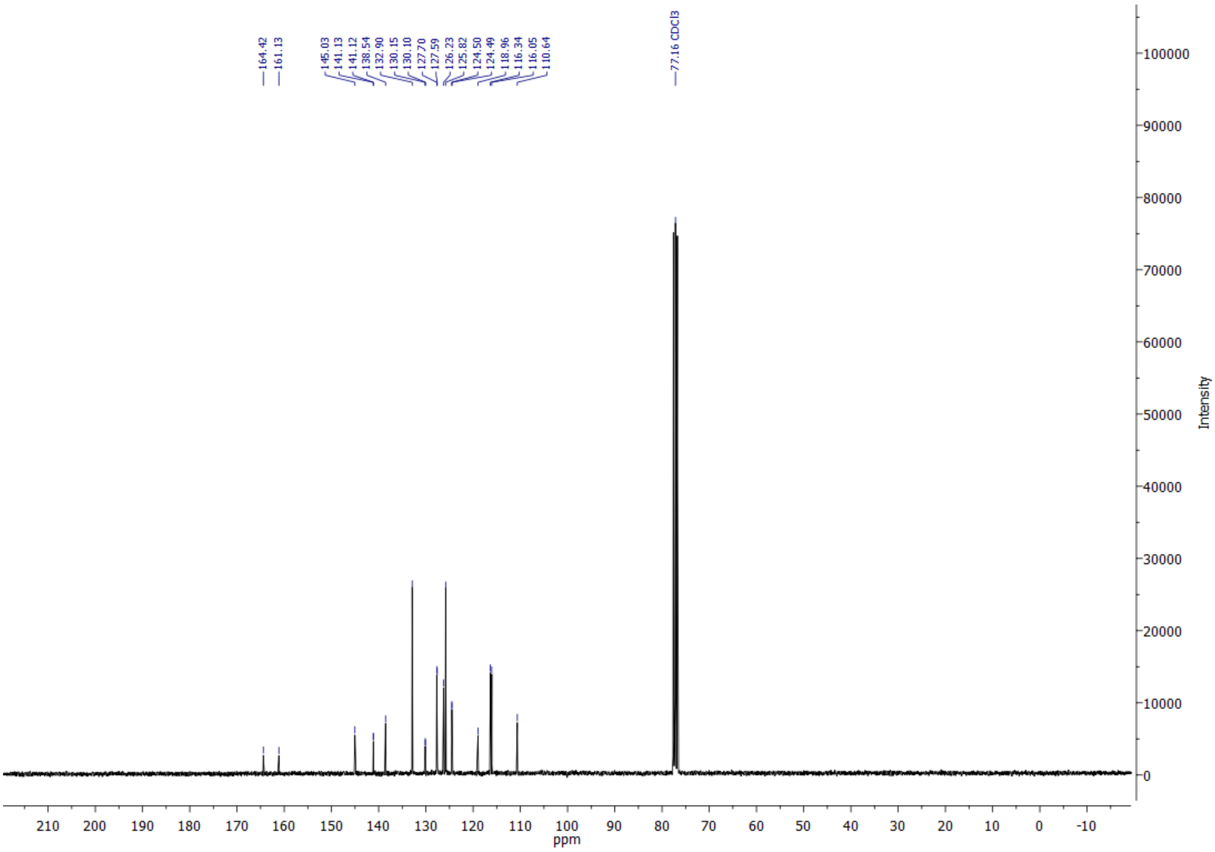


Figure 42: ^{13}C-NMR spectrum of **8d** ($CDCl_3$, 293K, 75MHz).

3.22 2-(4-Methoxyphenyl)-5-(4-nitrophenyl)thiophene (8e)

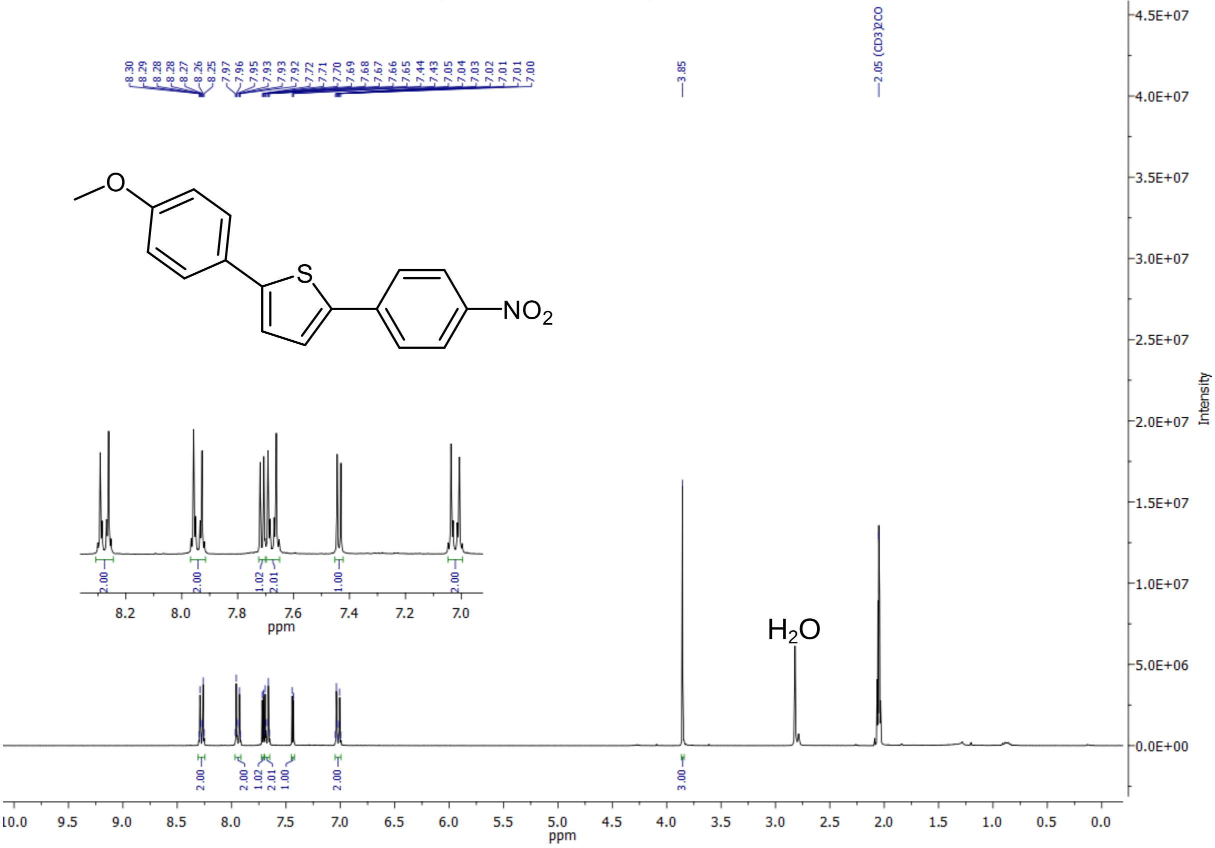


Figure 43: ^{1}H-NMR spectrum of **8e** (acetone-d$_6$, 293K, 300MHz).

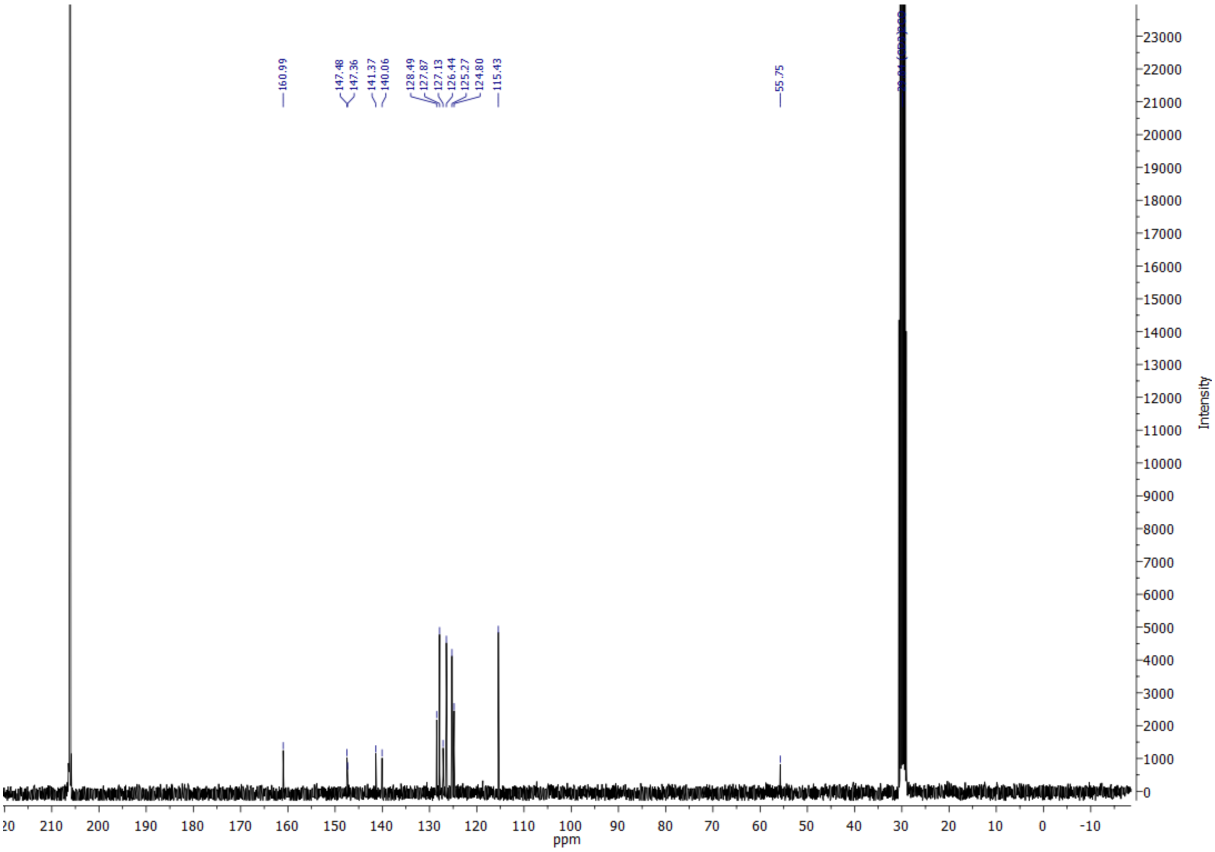


Figure 44: ^{13}C-NMR spectrum of **8e** (acetone-d$_6$, 293K, 75MHz).

3.23 Methyl 4-(5-(4-methoxyphenyl)thiophen-2-yl)benzoate (8f)

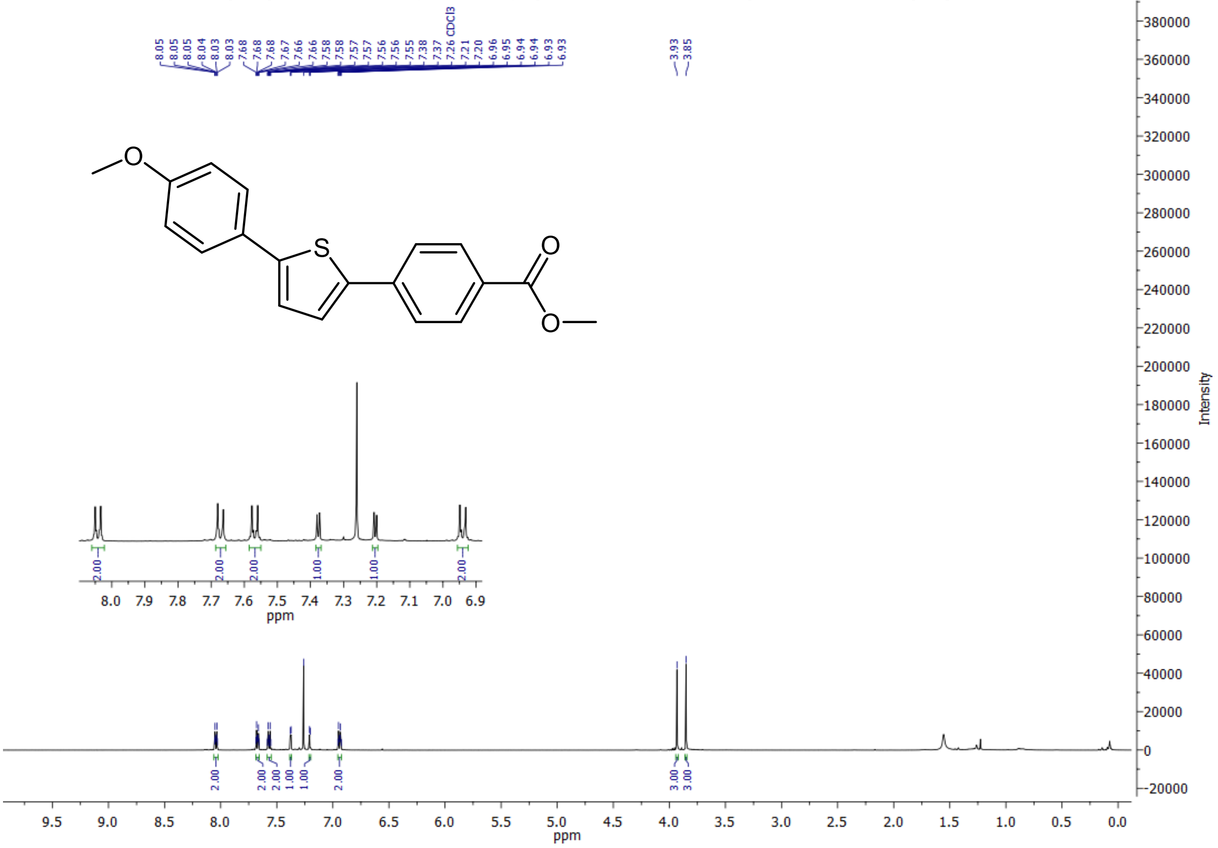


Figure 45: ^{1}H-NMR spectrum of **8f** (CDCl$_3$, 293K, 500MHz).

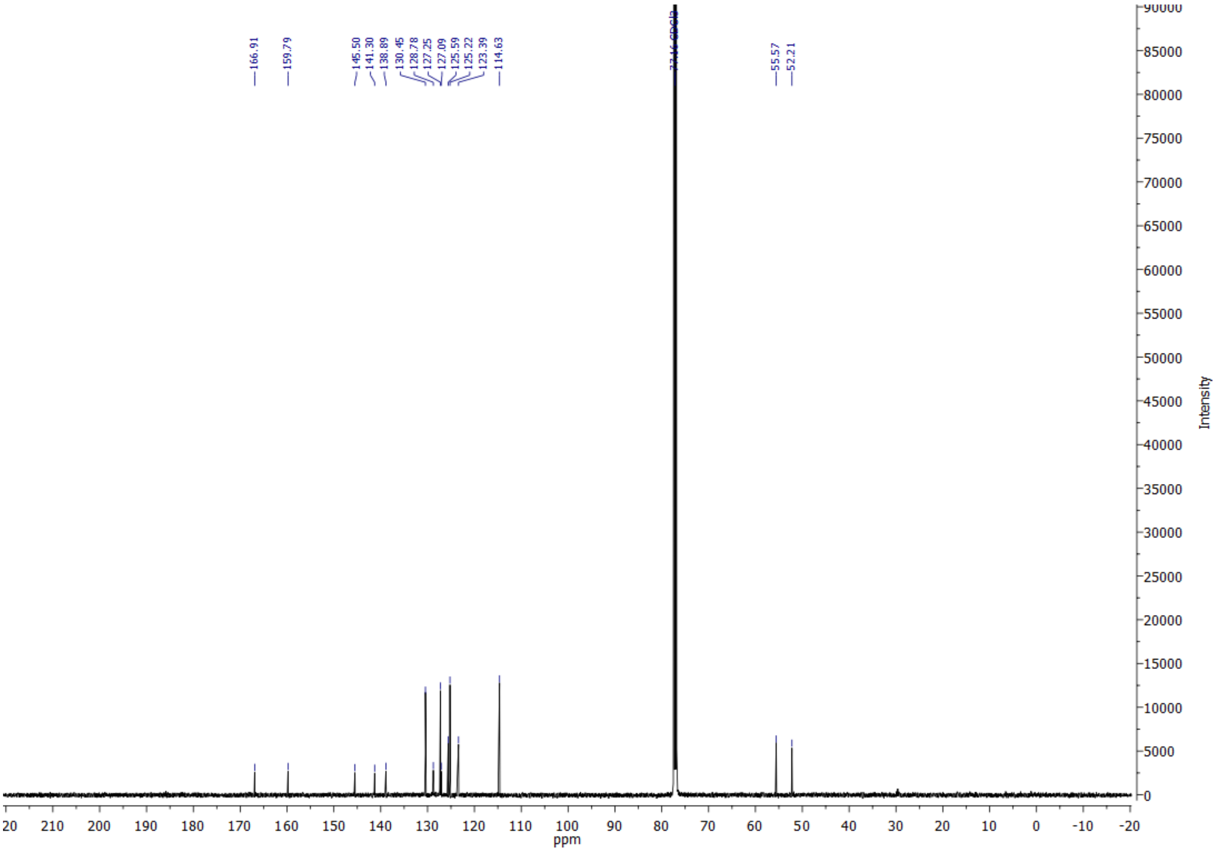


Figure 46: ^{13}C-NMR spectrum of **8f** (CDCl$_3$, 293K, 125MHz).

3.24 2-(4-Fluorophenyl)-5-(4-methoxyphenyl)thiophene (8g)

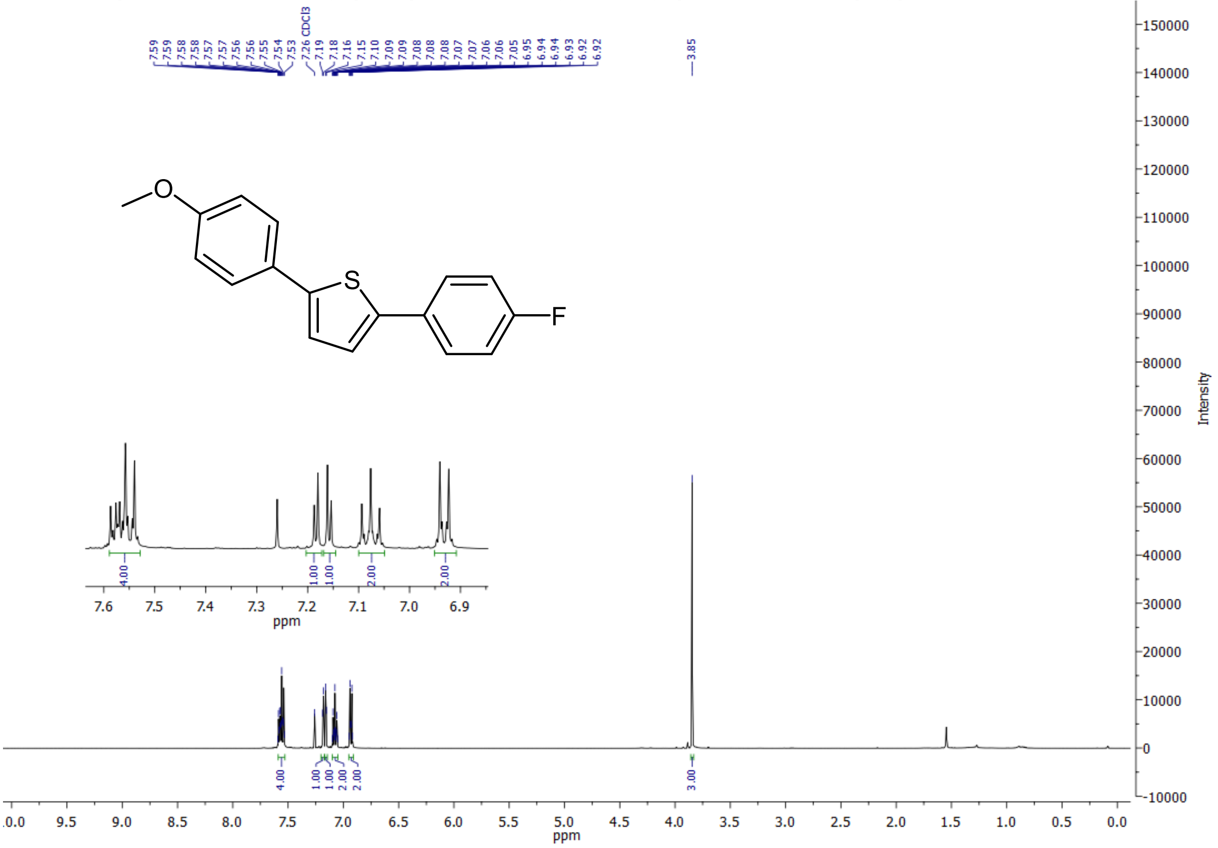


Figure 47: ^{1}H-NMR spectrum of **8g** (CDCl$_3$, 293K, 500MHz).

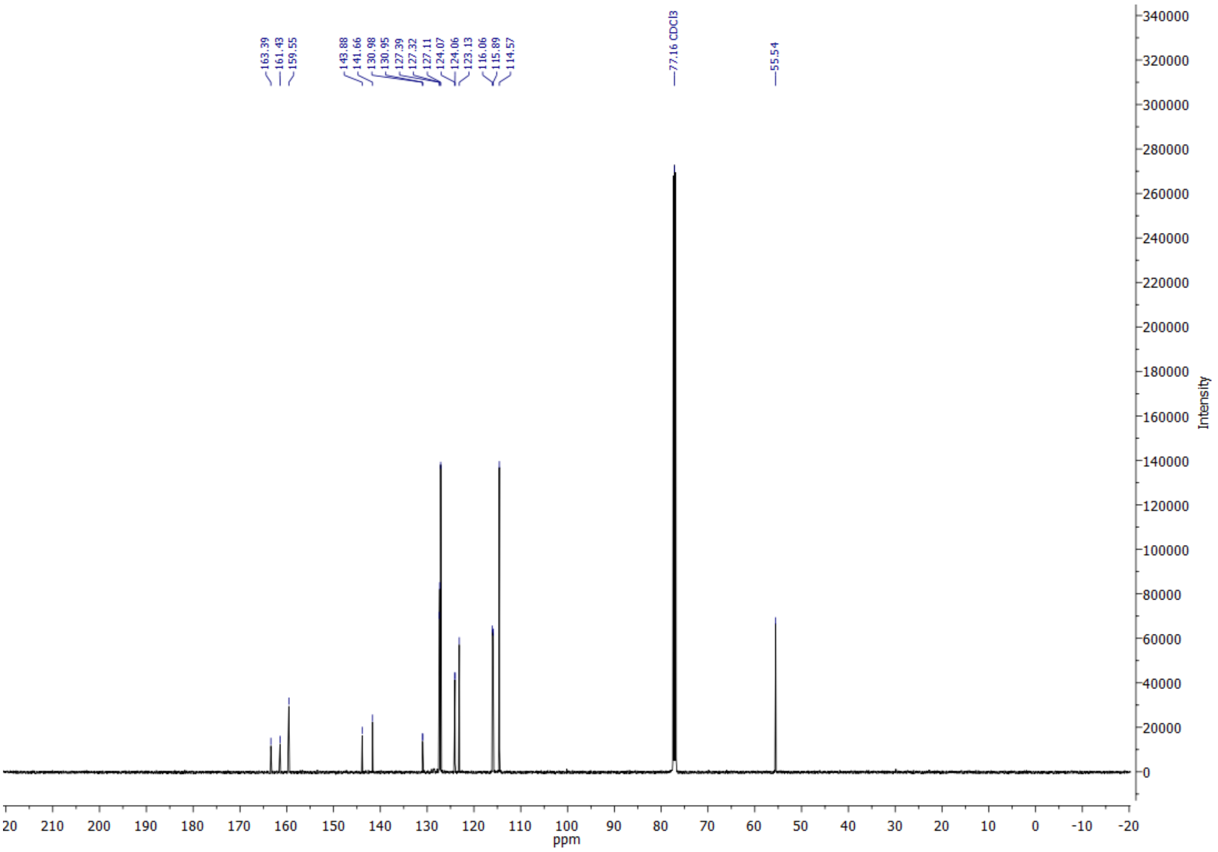


Figure 48: ^{13}C-NMR spectrum of **8g** (CDCl$_3$, 293K, 125MHz).

3.25 4-(5-(4-(Dimethylamino)phenyl)thiophen-2-yl)benzonitrile (8h)

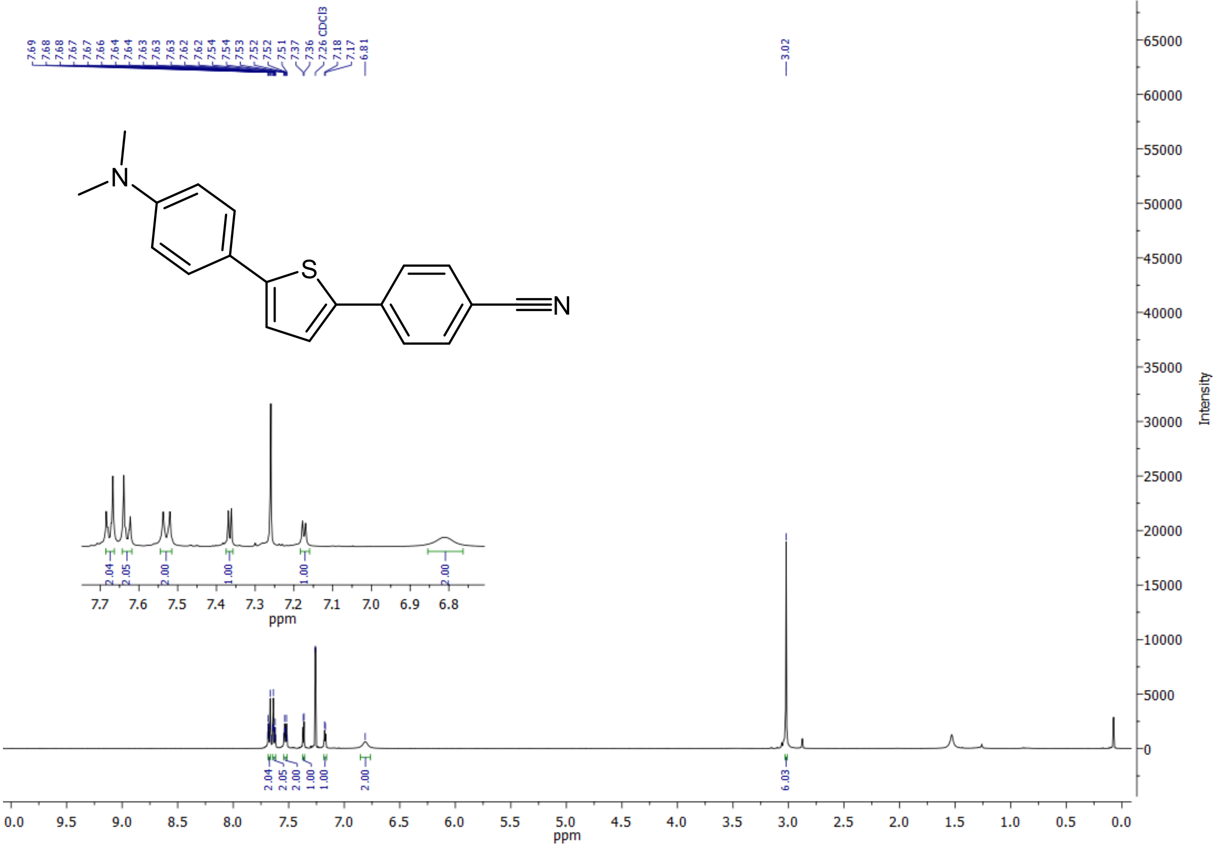


Figure 49: ^{1}H-NMR spectrum of **8h** ($CDCl_3$, 293K, 500MHz).

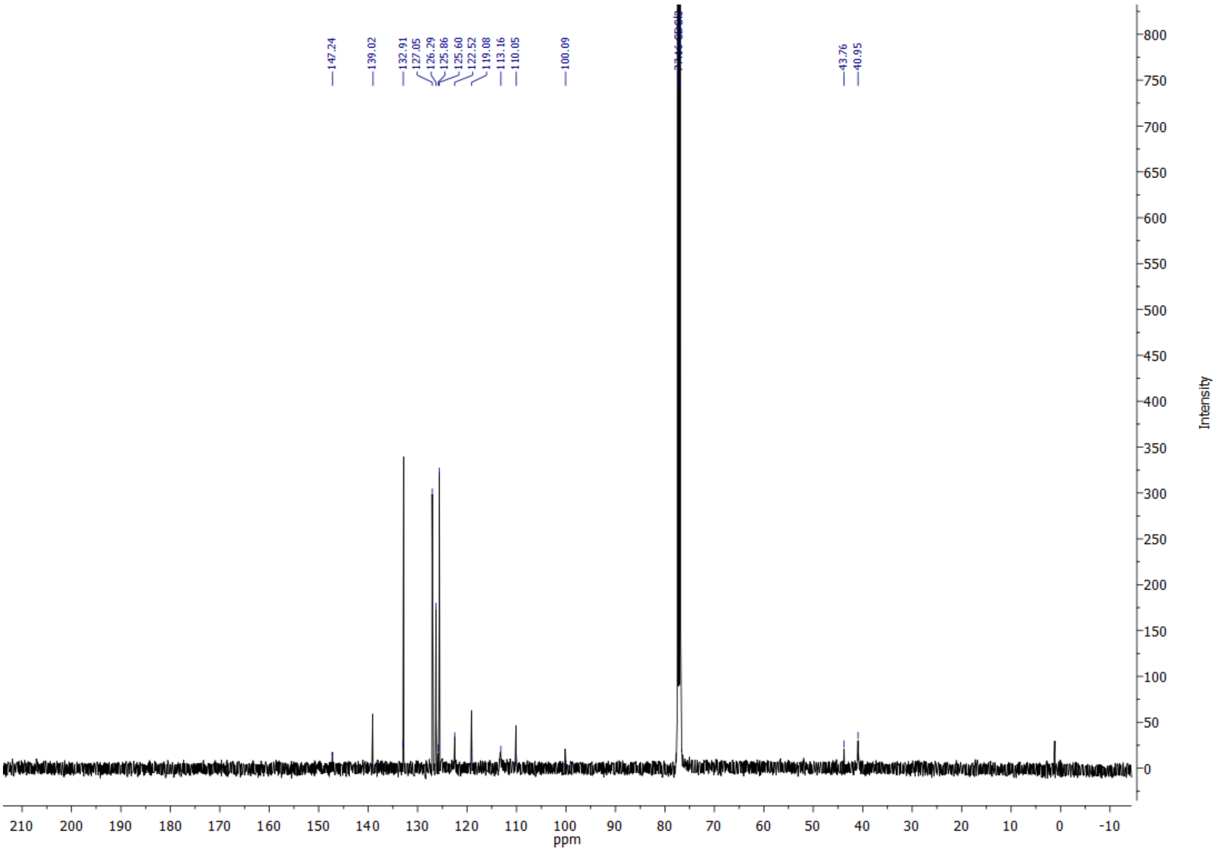


Figure 50: ^{13}C-NMR spectrum of **8h** ($CDCl_3$, 293K, 125MHz).

3.26 2-(4-Methoxyphenyl)-5-(*p*-tolyl)thiophene (8i)

Figure 51: ^{1}H-NMR spectrum of **8i** (CDCl$_3$, 293K, 300MHz).

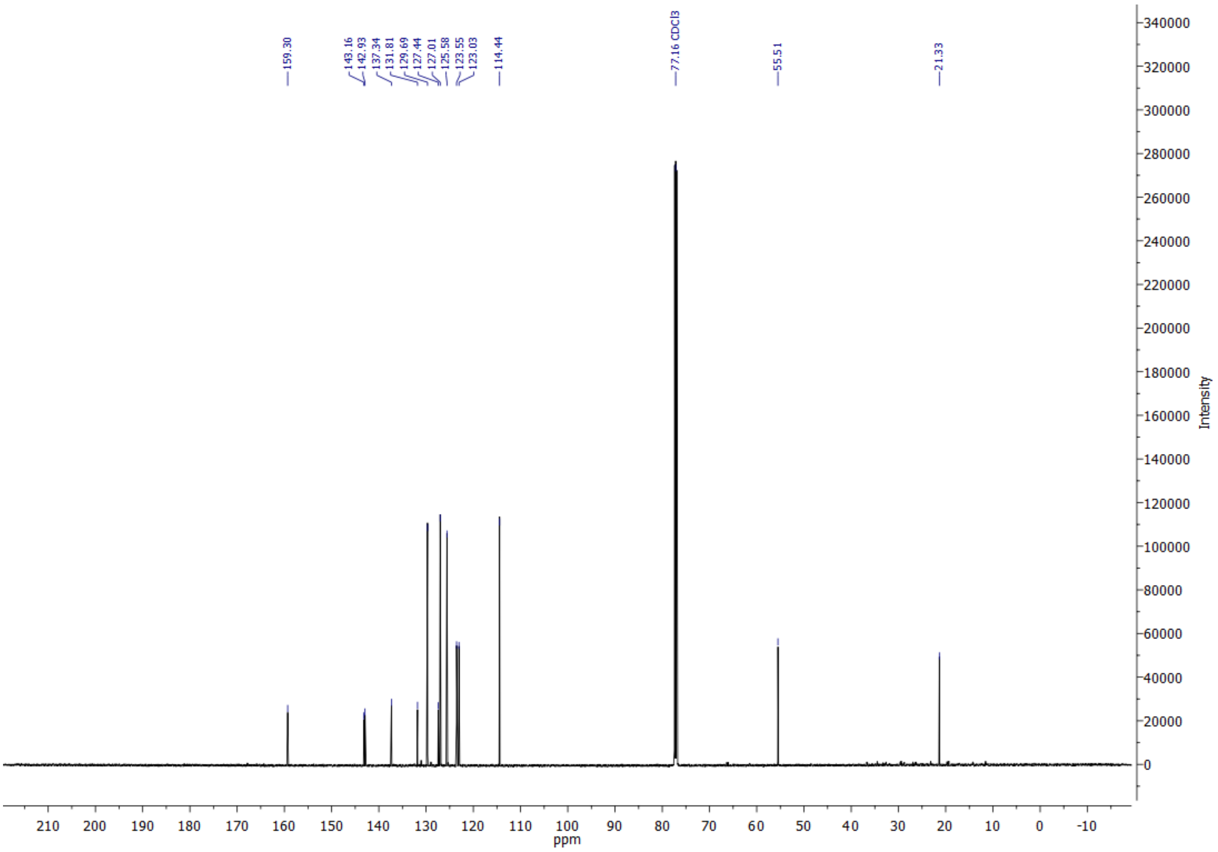


Figure 52: ^{13}C-NMR spectrum of **8i** (CDCl$_3$, 293K, 150MHz).

3.27 Methyl 3-(5'-(2,4-bis(hexyloxy)phenyl)-[2,2'-bithiophen]-5-yl)-2-cyano-acrylate (8j)

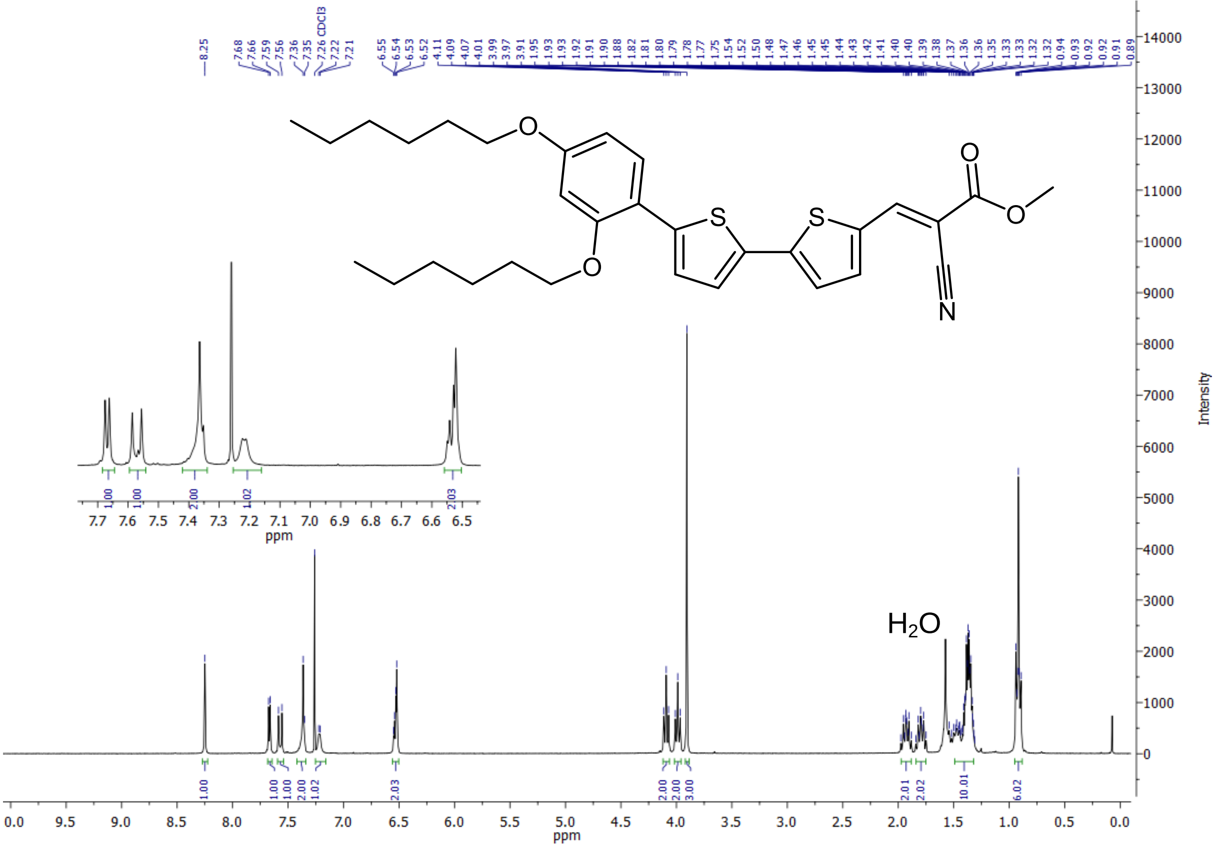


Figure 53: ^{1}H-NMR spectrum of **8j** ($CDCl_3$, 293K, 300MHz).

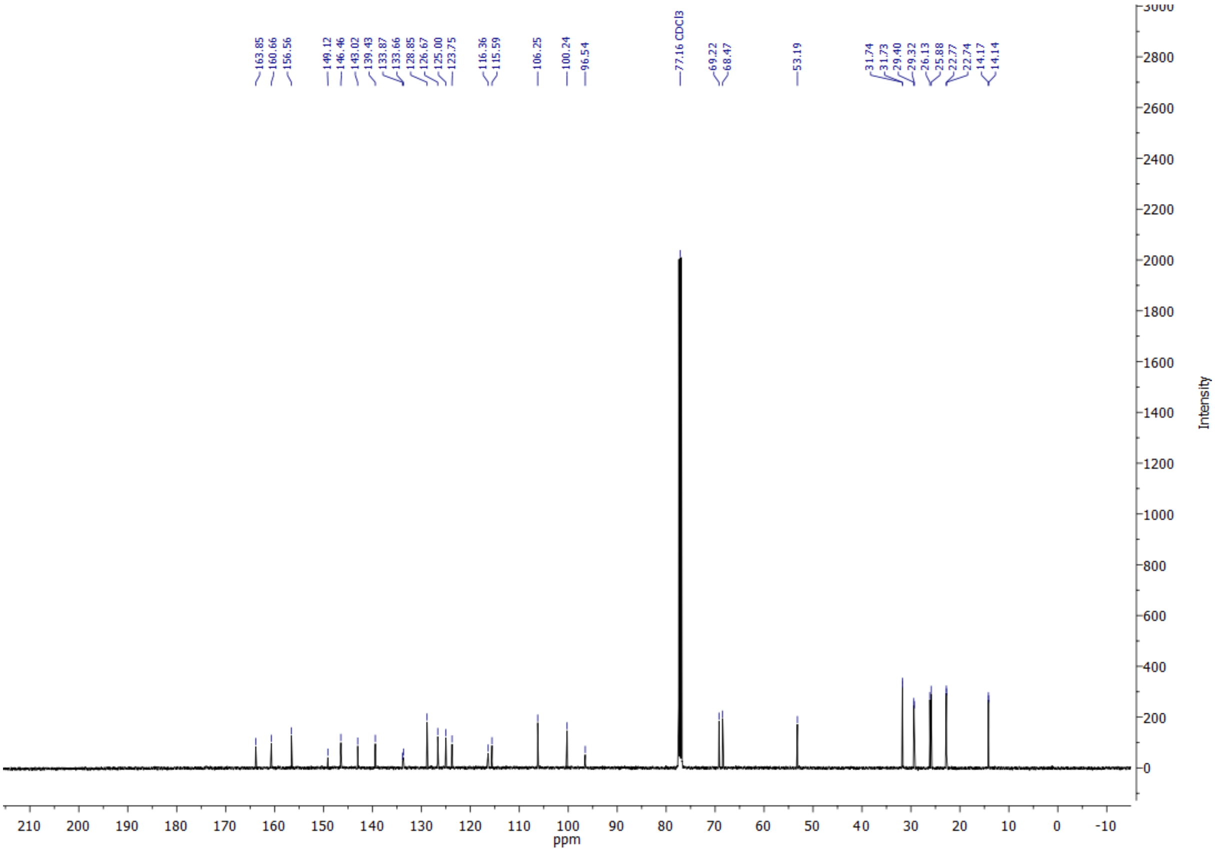


Figure 54: ^{13}C-NMR spectrum of **8j** ($CDCl_3$, 293K, 125MHz).

3.28 Methyl 4-(5-(2,4-bis(hexyloxy)phenyl)thiophen-2-yl)benzoate (8k)

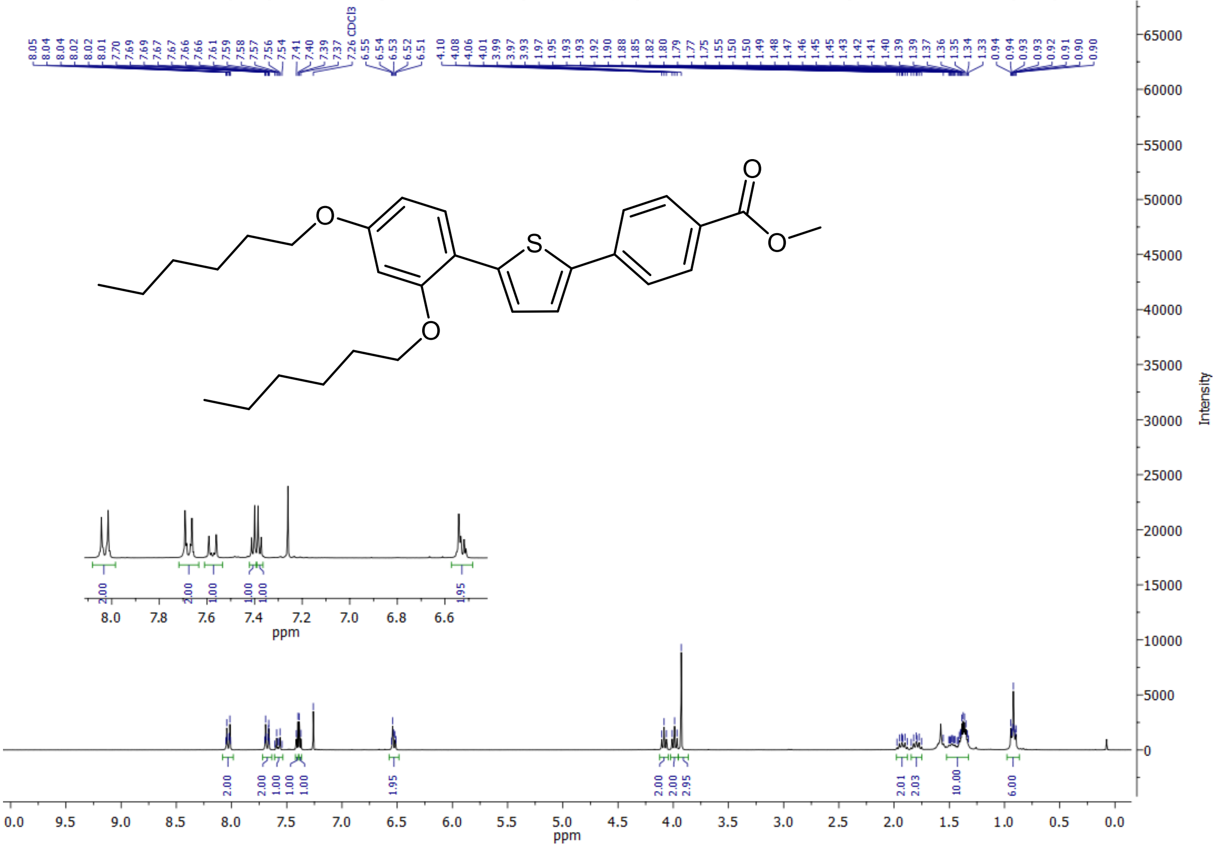


Figure 55: ^{1}H-NMR spectrum of **8k** ($CDCl_3$, 293K, 300MHz).

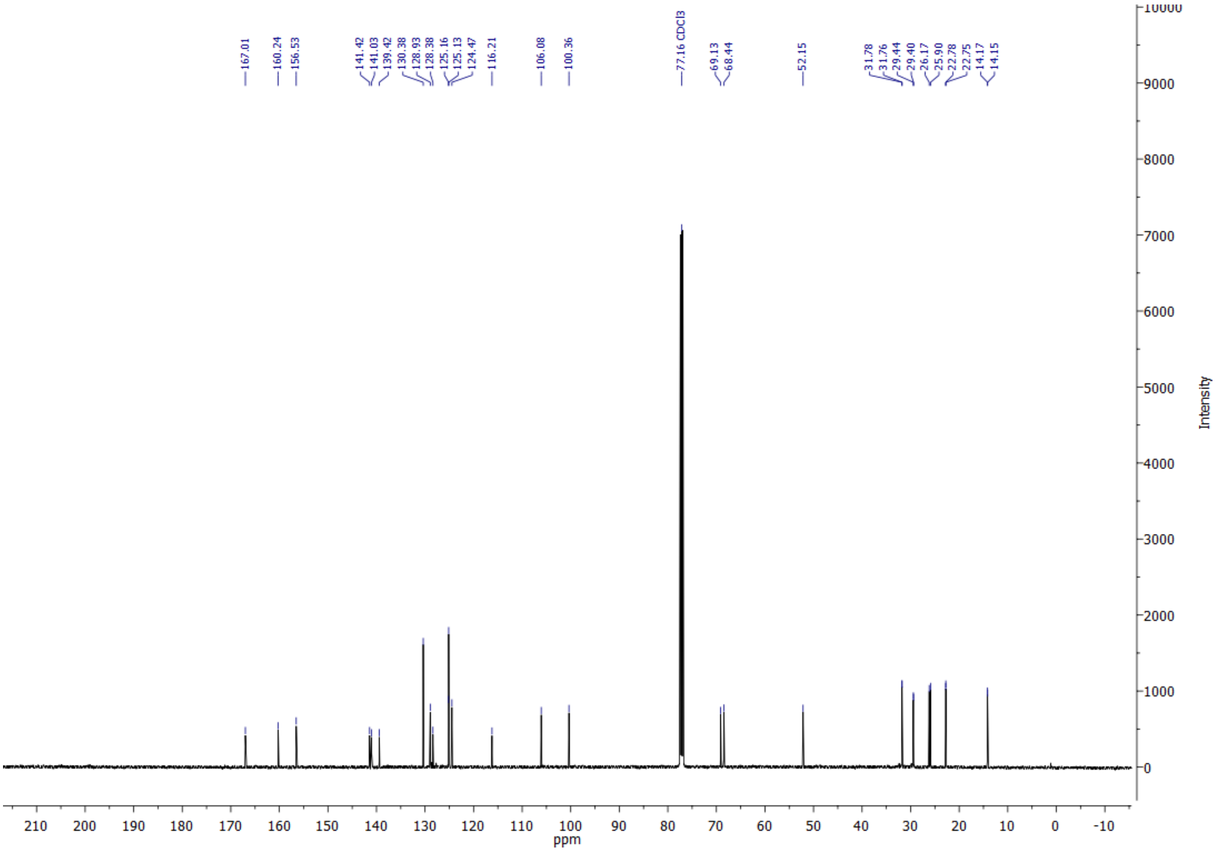


Figure 56: ^{13}C-NMR spectrum of **8k** ($CDCl_3$, 293K, 125MHz).

4 Cyclovoltammetric data

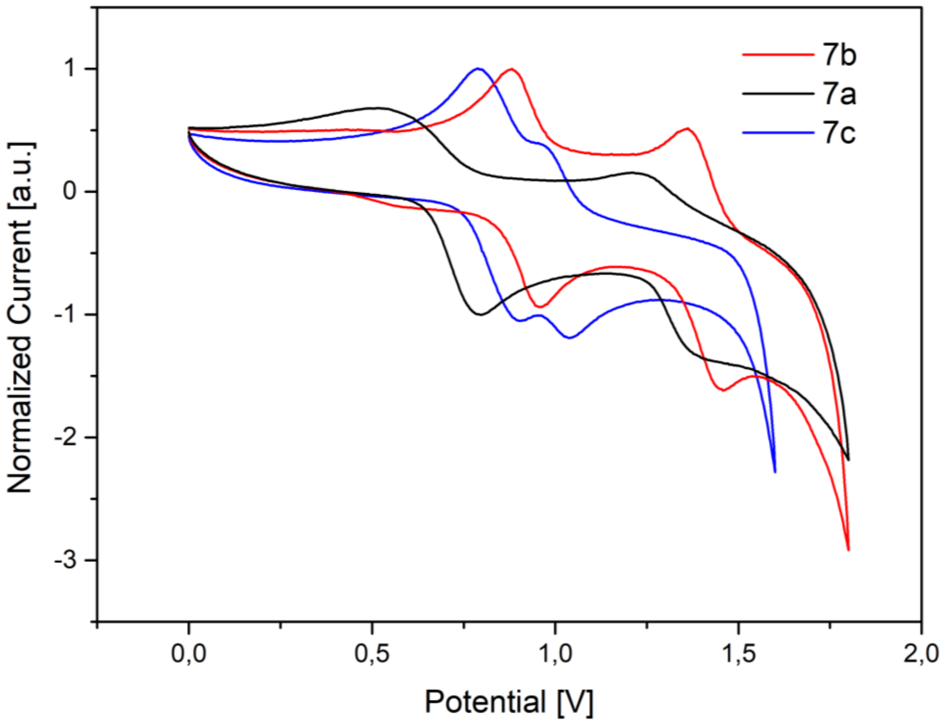


Figure 57: Cyclic voltammograms of the dyes **7a-c** (0.1 m $[Bu_4N][PF_6]$, *v* = 100 mV/s, Pt-working, Ag/AgCl-reference and Pt-counter electrode, $[Me_{10}Fc]/[Me_{10}Fc]^+$ as an internal standard; $Me_{10}Fc$ = decamethylferrocene).

Table 6: Cyclovoltammetric data of the dyes **7a-c**.

	$E_0^{0/+1}$ [a] [mV]	$E_0^{+1/+2}$ [a] [mV]
7a	664	1264
7b	860	1348
7c	793	942

a: 0.1 M $[Bu_4N][PF_6]$, *v* = 100 mV/s, Pt-working-, Ag/AgCl-reference- and Pt-counter electrode, $[Me_{10}Fc]/[Me_{10}Fc]^+$ as internal standard ($Me_{10}Fc$ = decamethylferrocene).

5 Data of Quantum chemical calculations

The ground state geometries of the dyes **7a-c** were optimized using the Gaussian09 program package,[20] the PBEh1PBE [21] and the 6-31G** basis set [22]. The optimized geometries were confirmed as minima by analytical frequency analyses. Excitation energies were calculated with TDDFT [23] methods implemented in the Gaussian09 program package using the same functional and basis set. The polarizable continuum model (PCM) with dichloromethane as a solvent was applied for the calculations each. [24]
Hexyl groups were trunctated to methyl groups in order to save computation time as alkyl side chains to not change the electronic structure of the π-system very much.

We performed several benchmark calculations on the excitation energies of compound **7b** (Table 7). The results should not only match the experimental data well, but also be as cheap as possible in terms of computational time due to the large atom number of **7c**, which we wanted to compare with the same functional and basis set. The PBEh1PBE functional gave the most balanced results and therefore was employed (Table 8). With cam-B3LYP we could obtain closer energies, but we needed larger basis sets for the calculations, so that the calculations on the UV/vis spectra of **7c** failed due to too high computational cost.

Table 7 Comparison of the TDDFT calculated excitation energy corresponding to the longest wavelength absorption bands of **7b** varying functional and basis set.

Functional	Basis set	Excitation energy [eV]	$\Delta E_{\text{DFT-exp.}}$ [eV]
B3LYP	6-31G(d,p)	2.084	-0.401
B3LYP	6-311G(d,p)	2.106	-0.379
B3LYP	6-311+G(d,p)	2.055	-0.430
cam-B3LYP	6-311G(d,p)	2.776	0.291
cam-B3LYP	6-311+G(d,p)	2.716	0.231
cam-B3LYP	6-311++G(d,p)	2.716	0.231
PBE1PBE	6-311G(d,p)	2.246	-0.239
PBE1PBE	6-311+G(d,p)	2.198	-0.287
PBEh1PBE	6-31G(d,p)	2.222	-0.263

[a]Recorded in CH_2Cl_2, $c = 10^{-5}$ M, T = 293 K; [b]6-311G(d,p) was used instead.

Table 8 Comparison of the TDDFT calculated excitation energy corresponding to the longest wavelength absorption bands of the dyes **7a-7c** using B3LYP and PBEh1PBE.

dye	λ_{abs} (ε)[a] [nm] ([$Lmol^{-1}cm^{-1}$])	$\lambda_{\text{abs,calcd}}$ (oscillatory strength)[b] [nm]			
		PBEh1PBE/ 6-31G(d,p)	$\Delta E_{\text{DFT-exp.}}$ [eV]	B3LYP/ 6-31G(d,p)	$\Delta E_{\text{DFT-exp.}}$ [eV]
7a	465 (11400)	494 (1.1231)	0.157	614 (1.1672)[c]	0.647

7b	499 (30400)	558 (0.9228)	-0.263	595 (0.8610)	0.401
7c	500 (29100)	577 (0.7094)	0.331	633 (0.4896)	0.521

[a] Recorded in CH_2Cl_2, *c* = 10^{-5} M, *T* = 293 K; [b] pcm (CH_2Cl_2) was applied each; [c] 6-311G(d,p) was used instead.

5.1.1 Computed xyz-Coordinates of Compound 7a (PBEh1PBE/6-31G** PCM CH_2Cl_2)

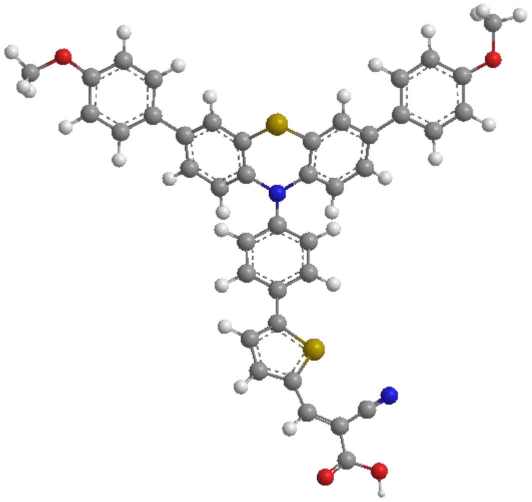


Figure 58: Optimized ground state geometry of **7a** (PBEh1PBE/6-31G** PCM CH_2Cl_2).

C	-2.88709	-0.90575	0.58170
C	-1.90454	-1.07447	-0.39998
N	-0.81569	-0.16266	-0.44449
C	-1.18468	1.20880	-0.40573
C	-2.08570	1.63807	0.57489
S	-2.72747	0.44505	1.72104
C	-3.96751	-1.77918	0.65857
C	-4.09354	-2.84397	-0.24127
C	-3.12495	-2.97712	-1.24728
C	-2.05652	-2.09622	-1.33764
C	-0.72311	2.12946	-1.34674
C	-1.09409	3.46400	-1.26207
C	-1.96508	3.91408	-0.25876
C	-2.47038	2.97314	0.64628
C	-5.23012	-3.78291	-0.14938
C	0.50519	-0.57796	-0.27254
C	-2.36178	5.33446	-0.17448

C	-6.50612	-3.34928	0.24492
C	-7.56963	-4.23013	0.33132
C	-7.39111	-5.58455	0.02440
C	-6.13008	-6.03756	-0.36984
C	-5.07099	-5.13829	-0.45202
C	1.55515	0.35409	-0.16443
C	2.86105	-0.06431	0.00607
C	3.19918	-1.42431	0.08565
C	2.14474	-2.34810	0.00244
C	0.83455	-1.94330	-0.16758
C	-1.45695	6.35853	-0.49787
C	-1.82089	7.69117	-0.41903
C	-3.11208	8.04712	-0.01120
C	-4.02876	7.04456	0.31372
C	-3.64674	5.70899	0.22862
O	-8.48937	-6.36772	0.13721
C	-8.35546	-7.74189	-0.17320
O	-3.37483	9.37415	0.03569
C	-4.66495	9.77771	0.45479
C	4.56961	-1.87139	0.25694
C	5.01669	-3.11775	0.67619
C	6.40879	-3.21139	0.73626
C	7.06853	-2.04385	0.36503
S	5.90537	-0.81758	-0.07641
C	8.47502	-1.90523	0.35340
C	9.27589	-0.84469	0.02377
C	10.73725	-1.03313	0.11859
C	8.77536	0.41297	-0.40195
O	11.41581	0.06742	-0.23096
O	11.27504	-2.06341	0.47138
N	8.36164	1.44331	-0.75197
H	-4.70757	-1.63721	1.44042
H	-3.23015	-3.75843	-1.99339
H	-1.33026	-2.19566	-2.13820
H	-0.06972	1.79164	-2.14492
H	-0.73163	4.16142	-2.01057
H	-3.15655	3.28471	1.42801
H	-6.67480	-2.29840	0.46187
H	-8.55704	-3.88888	0.62527

H	-5.95889	-7.08189	-0.60347
H	-4.09147	-5.51282	-0.73539
H	1.34720	1.41617	-0.19256
H	3.63389	0.69343	0.10478
H	2.35097	-3.41229	0.05676
H	0.05836	-2.69653	-0.21378
H	-0.44197	6.10674	-0.79161
H	-1.11475	8.47956	-0.65904
H	-5.03885	7.28876	0.62128
H	-4.38229	4.94337	0.45838
H	-9.34187	-8.18231	-0.02841
H	-8.04292	-7.88981	-1.21342
H	-7.63850	-8.23604	0.49268
H	-4.66374	10.86735	0.43070
H	-5.44248	9.40275	-0.22087
H	-4.87968	9.43915	1.47501
H	4.34834	-3.92290	0.95495
H	6.94730	-4.09820	1.05226
H	9.02418	-2.79525	0.65724
H	12.35867	-0.13853	-0.14290

```
SCF Done:  E(RPBEh1PBE) =  -2745.65550123     A.U. after    1 cycles
Sum of electronic and zero-point Energies= -2745.070724
Sum of electronic and thermal Energies= -2745.029869
Sum of electronic and thermal Enthalpies= -2745.028924
Sum of electronic and thermal Free Energies= -2745.150387
```

5.1.2 Computed Excitations of Compound 7a (PBEh1PBE/6-31G** PCM CH_2Cl_2)

```
Excited State   1:      Singlet-A      2.5083 eV  494.30 nm  f=1.1231  <S**2>=0.000
    173 ->174         0.70148
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2745.56332297
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.1818 eV  389.66 nm  f=0.0229  <S**2>=0.000
    172 ->174         0.70415
```

```
Excited State   3:      Singlet-A      3.2721 eV  378.91 nm  f=0.2233  <S**2>=0.000
    170 ->174       -0.18019
    171 ->174        0.67454

Excited State   4:      Singlet-A      3.4455 eV  359.85 nm  f=0.0160  <S**2>=0.000
    170 ->174        0.68100
    171 ->174        0.18157

Excited State   5:      Singlet-A      3.8298 eV  323.73 nm  f=0.1925  <S**2>=0.000
    169 ->174        0.22426
    173 ->175        0.65005

Excited State   6:      Singlet-A      3.9089 eV  317.19 nm  f=0.1862  <S**2>=0.000
    173 ->176        0.68018

Excited State   7:      Singlet-A      3.9152 eV  316.67 nm  f=0.0595  <S**2>=0.000
    163 ->174       -0.10789
    169 ->174        0.63746
    173 ->175       -0.21635

Excited State   8:      Singlet-A      4.1268 eV  300.44 nm  f=0.0066  <S**2>=0.000
    164 ->174       -0.13410
    166 ->174        0.50786
    173 ->177       -0.15860
    173 ->178        0.39692
    173 ->180        0.11191

Excited State   9:      Singlet-A      4.2234 eV  293.56 nm  f=0.0402  <S**2>=0.000
    163 ->174        0.21431
    164 ->174        0.11461
    170 ->175       -0.15644
    173 ->177        0.46214
    173 ->178        0.33766
    173 ->179       -0.20413

Excited State  10:      Singlet-A      4.2421 eV  292.27 nm  f=0.0764  <S**2>=0.000
    163 ->174        0.19292
    164 ->174        0.17156
    166 ->174       -0.31616
```

```
     173 ->177        -0.31279
     173 ->178         0.34777
     173 ->179         0.23366

 Excited State  11:      Singlet-A      4.3272 eV  286.52 nm  f=0.0071  <S**2>=0.000
     163 ->174         0.54159
     164 ->174         0.13938
     166 ->174         0.17812
     173 ->178        -0.23541
     173 ->179         0.10611
     173 ->180         0.18246

 Excited State  12:      Singlet-A      4.4448 eV  278.94 nm  f=0.9111  <S**2>=0.000
     161 ->174        -0.18025
     168 ->174        -0.12962
     171 ->176        -0.18800
     172 ->175         0.60414

 Excited State  13:      Singlet-A      4.4492 eV  278.67 nm  f=0.0649  <S**2>=0.000
     161 ->174         0.66337
     172 ->175         0.16340

 Excited State  14:      Singlet-A      4.4696 eV  277.40 nm  f=0.0345  <S**2>=0.000
     168 ->174         0.68522
     172 ->175         0.11687

 Excited State  15:      Singlet-A      4.4988 eV  275.59 nm  f=0.0123  <S**2>=0.000
     167 ->174         0.67116
     173 ->179         0.15351
```

5.1.3 Computed xyz-Coordinates of intra conformation of Compound 7a (PBEh1PBE/ 6-31G** PCM CH_2Cl_2)

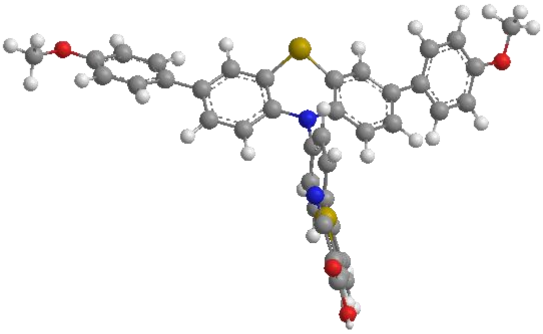


Figure 59: Optimized ground state geometry of intra-**7b** (PBEh1PBE/6-31G** PCM CH_2Cl_2).

C	2.63821	1.64459	0.62665
C	1.38061	1.30434	0.10201
N	0.91404	-0.02427	0.16282
C	1.80537	-1.11579	0.10846
C	3.09922	-1.00812	0.64336
S	3.56692	0.44474	1.53623
C	3.12181	2.94390	0.53961
C	2.35888	3.97297	-0.02612
C	1.09342	3.63482	-0.51553
C	0.61724	2.33097	-0.46467
C	1.44022	-2.34187	-0.45832
C	2.32878	-3.40875	-0.49439
C	3.63148	-3.29530	0.00116
C	3.99778	-2.06471	0.56009
C	2.87706	5.35354	-0.10072
C	4.58308	-4.42293	-0.05713
C	-0.46329	-0.26711	-0.13340
C	4.24195	5.60686	-0.31389
C	4.73238	6.89885	-0.38859
C	3.86702	7.99085	-0.25444
C	2.50562	7.76330	-0.04231
C	2.02938	6.45713	0.03367
C	4.56816	-5.32911	-1.13016
C	5.45596	-6.38897	-1.19179
C	6.40007	-6.57875	-0.17587
C	6.43464	-5.68964	0.90030
C	5.53160	-4.63103	0.94864
C	-1.36372	-0.41237	0.91927

C	-2.70538	-0.65692	0.66054
C	-3.17486	-0.75524	-0.65707
C	-2.25960	-0.59880	-1.71004
C	-0.91784	-0.36113	-1.45116
O	4.43894	9.21597	-0.34436
C	3.59739	10.34668	-0.22451
O	7.22801	-7.64107	-0.32455
C	8.20738	-7.85742	0.67316
C	-4.58287	-1.01870	-0.94613
C	-5.12112	-1.58172	-2.08951
C	-6.51575	-1.69913	-2.03650
C	-7.07002	-1.22756	-0.85374
S	-5.81876	-0.62185	0.19768
C	-8.46419	-1.24947	-0.57756
C	-9.16061	-0.83935	0.52318
C	-8.54122	-0.27264	1.67148
C	-10.63116	-0.95647	0.60770
O	-11.28005	-0.60572	1.57076
O	-11.17612	-1.49229	-0.49266
N	-8.02753	0.19030	2.60644
H	4.09694	3.16413	0.96469
H	0.47502	4.39572	-0.98206
H	-0.36119	2.11048	-0.87484
H	0.44167	-2.47358	-0.85786
H	1.98992	-4.35338	-0.90876
H	5.00470	-1.92079	0.94113
H	4.92792	4.77530	-0.44854
H	5.78669	7.08855	-0.56322
H	1.81290	8.58851	0.07623
H	0.97187	6.29988	0.22638
H	3.86301	-5.18621	-1.94401
H	5.44575	-7.08014	-2.02861
H	7.14672	-5.81593	1.70762
H	5.55654	-3.96724	1.80830
H	-1.00171	-0.34257	1.93970
H	-3.38907	-0.79433	1.49317
H	-2.60368	-0.64231	-2.73805
H	-0.21615	-0.23767	-2.27039
H	4.24317	11.21805	-0.33337

H	2.83278	10.36370	-1.01001
H	3.10734	10.38146	0.75556
H	8.76569	-8.74083	0.36325
H	8.89380	-7.00639	0.75356
H	7.75038	-8.04493	1.65191
H	-4.51906	-1.92326	-2.92245
H	-7.12201	-2.12592	-2.82777
H	-9.06763	-1.66367	-1.38146
H	-12.13298	-1.52884	-0.34543

SCF Done: E(RPBEh1PBE) = -2745.65255068   A.U. after   1 cycles
Sum of electronic and zero-point Energies= -2745.067799
Sum of electronic and thermal Energies= -2745.026814
Sum of electronic and thermal Enthalpies= -2745.025869
Sum of electronic and thermal Free Energies= -2745.148348

5.2.1 Computed xyz-Coordinates of Compound 7b (PBEh1PBE/6-31G** PCM CH_2Cl_2)

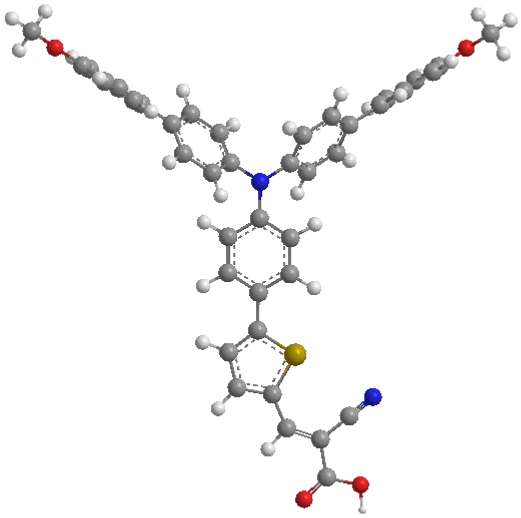


Figure 60: Optimized ground state geometry of **9b** (PBEh1PBE/6-31G** PCM CH_2Cl_2).

C	1.33763	0.14188	0.48268
C	2.62838	-0.34881	0.43189
C	2.91950	-1.59204	-0.15497
C	1.84513	-2.32070	-0.69522
C	0.55185	-1.83650	-0.65309
C	0.26907	-0.59302	-0.06035
N	-1.03552	-0.09894	-0.01391

C	-1.27966	1.29776	-0.03819
C	-2.14494	-0.97906	0.03425
C	-2.20201	1.86768	0.84444
C	-2.46347	3.22964	0.80162
C	-1.80342	4.07273	-0.10378
C	-0.87439	3.48745	-0.97593
C	-0.62245	2.12321	-0.95585
C	-3.26540	-0.74659	-0.76939
C	-4.36069	-1.59591	-0.70845
C	-4.37317	-2.71443	0.13685
C	-3.24083	-2.93670	0.93354
C	-2.14931	-2.08106	0.89578
C	-2.07961	5.52324	-0.14239
C	-5.53447	-3.62568	0.18669
C	4.27156	-2.11797	-0.21151
C	4.66882	-3.42830	-0.44376
C	6.05554	-3.59342	-0.42997
C	6.75992	-2.41840	-0.18683
S	5.64742	-1.08687	0.01281
C	-2.04975	6.23658	-1.35202
C	-2.30905	7.59516	-1.39472
C	-2.61096	8.29318	-0.21941
C	-2.64638	7.60513	0.99530
C	-2.38167	6.23855	1.02041
C	-5.92068	-4.24888	1.38474
C	-7.00589	-5.10621	1.43420
C	-7.74931	-5.37129	0.27797
C	-7.38435	-4.76267	-0.92478
C	-6.28927	-3.90370	-0.95695
O	-2.85165	9.61859	-0.36175
C	-3.17280	10.35953	0.79998
O	-8.79313	-6.22197	0.42545
C	-9.57605	-6.50993	-0.71722
C	8.17039	-2.34807	-0.12051
C	9.01306	-1.29569	0.11665
C	10.46480	-1.56686	0.11671
C	8.56472	0.02824	0.36104
O	11.18780	-0.46588	0.35849
O	10.95847	-2.65909	-0.07884

N	8.19375	1.11338	0.56110
H	1.14415	1.09580	0.96064
H	3.42335	0.23431	0.88916
H	2.02943	-3.26850	-1.19081
H	-0.25137	-2.41356	-1.09785
H	-2.72339	1.23412	1.55514
H	-3.20567	3.64432	1.47729
H	-0.33199	4.11153	-1.67990
H	0.09362	1.69183	-1.64833
H	-3.27799	0.11086	-1.43478
H	-5.22916	-1.37867	-1.32333
H	-3.20829	-3.80057	1.59098
H	-1.28847	-2.27022	1.52941
H	3.96904	-4.24158	-0.59045
H	6.55816	-4.54285	-0.57898
H	-1.84361	5.71185	-2.28050
H	-2.29491	8.13898	-2.33392
H	-2.86661	8.12010	1.92318
H	-2.38850	5.72612	1.97829
H	-5.37432	-4.03897	2.29984
H	-7.30585	-5.57700	2.36502
H	-7.93393	-4.95659	-1.83862
H	-6.00508	-3.46039	-1.90715
H	-3.33458	11.38559	0.46962
H	-4.08688	9.98497	1.27539
H	-2.35387	10.34045	1.52856
H	-10.35301	-7.19908	-0.38632
H	-10.04461	-5.60517	-1.12196
H	-8.97992	-6.98894	-1.50274
H	8.68299	-3.29432	-0.28735
H	12.12084	-0.72732	0.34182

SCF Done: E(RPBEh1PBE) = -2348.79463362   A.U. after   1 cycles

Sum of electronic and zero-point Energies= -2348.189982

Sum of electronic and thermal Energies= -2348.149358

Sum of electronic and thermal Enthalpies= -2348.148414

Sum of electronic and thermal Free Energies= -2348.271111

5.2.2 Computed Excitations of Compound 7b (PBEh1PBE/6-31G** PCM CH_2Cl_2)

```
Excited State   1:      Singlet-A      2.2224 eV  557.89 nm  f=0.9228  <S**2>=0.000
     166 ->167         0.70266
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -2348.71296247
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:      Singlet-A      3.1486 eV  393.78 nm  f=0.0896  <S**2>=0.000
     164 ->167         0.16121
     165 ->167         0.68585

 Excited State   3:      Singlet-A      3.1774 eV  390.20 nm  f=0.4298  <S**2>=0.000
     164 ->167         0.66905
     165 ->167        -0.16542
     166 ->169        -0.10891

 Excited State   4:      Singlet-A      3.6241 eV  342.11 nm  f=0.7619  <S**2>=0.000
     166 ->168         0.69510

 Excited State   5:      Singlet-A      3.7091 eV  334.27 nm  f=0.2810  <S**2>=0.000
     163 ->167         0.49491
     164 ->167         0.14186
     166 ->169         0.47247

 Excited State   6:      Singlet-A      3.8057 eV  325.79 nm  f=0.0586  <S**2>=0.000
     163 ->167        -0.47254
     166 ->169         0.47255
     166 ->170        -0.16297

 Excited State   7:      Singlet-A      3.8560 eV  321.54 nm  f=0.0965  <S**2>=0.000
     159 ->167         0.12893
     166 ->169         0.14612
     166 ->170         0.65001

 Excited State   8:      Singlet-A      4.1391 eV  299.55 nm  f=0.0117  <S**2>=0.000
     158 ->167        -0.40675
     159 ->167         0.50992
     166 ->170        -0.14881
     166 ->174         0.10085
```

```
Excited State   9:      Singlet-A      4.2229 eV  293.60 nm  f=0.0016  <S**2>=0.000
    157 ->167         0.12195
    159 ->167         0.10641
    160 ->167        -0.22919
    162 ->167         0.61234

Excited State  10:      Singlet-A      4.2836 eV  289.44 nm  f=0.0158  <S**2>=0.000
    155 ->167        -0.12995
    156 ->167         0.19980
    157 ->167         0.51033
    158 ->167         0.24082
    159 ->167         0.17375
    162 ->167        -0.15090
    166 ->172        -0.10316
    166 ->173         0.10783
    166 ->174         0.11395

Excited State  11:      Singlet-A      4.3656 eV  284.00 nm  f=0.0320  <S**2>=0.000
    158 ->167         0.24230
    159 ->167         0.34682
    161 ->167        -0.21282
    166 ->172         0.33606
    166 ->173        -0.21398
    166 ->174        -0.29068

Excited State  12:      Singlet-A      4.3844 eV  282.78 nm  f=0.0009  <S**2>=0.000
    159 ->167         0.10573
    160 ->167        -0.24767
    161 ->167         0.59532
    162 ->167        -0.19613
    166 ->174        -0.11327

Excited State  13:      Singlet-A      4.4088 eV  281.22 nm  f=0.0002  <S**2>=0.000
    160 ->167         0.61111
    161 ->167         0.28642
    162 ->167         0.17358

Excited State  14:      Singlet-A      4.4253 eV  280.17 nm  f=0.0133  <S**2>=0.000
    162 ->167         0.13998
```

```
     165 ->170         0.10240
     166 ->171        -0.17568
     166 ->172         0.27685
     166 ->173         0.43418
     166 ->175        -0.35819

 Excited State  15:      Singlet-A      4.4339 eV  279.63 nm  f=0.0002  <S**2>=0.000
     154 ->167         0.68548
     154 ->169         0.10755
```

5.3.1 Computed xyz-Coordinates of Compound 7c (PBEh1PBE/6-31G** PCM CH_2Cl_2)

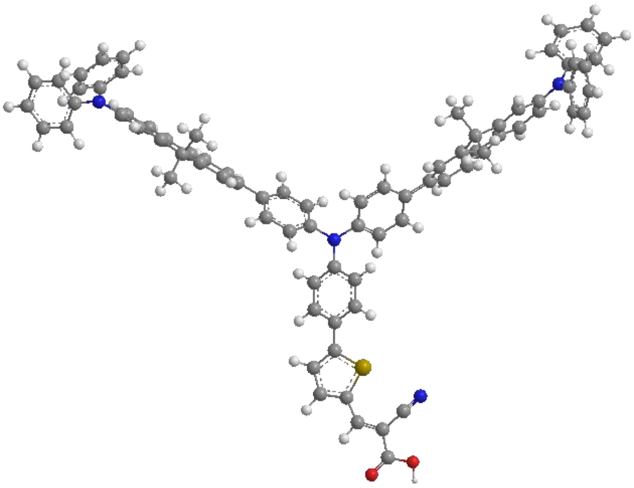


Figure 61: Optimized ground state geometry of **7c** (PBEh1PBE/6-31G** PCM CH_2Cl_2).

C	-3.51517	0.46822	-1.06499
C	-4.74480	-0.34589	-1.15461
C	-5.19932	-1.08266	-0.04671
C	-6.34705	-1.84847	-0.14911
C	-7.06959	-1.89787	-1.35398
C	-6.63338	-1.17126	-2.46013
C	-5.47831	-0.40520	-2.35113
C	-7.00800	-2.70815	0.91695
C	-8.19676	-3.26604	0.15018
C	-8.21707	-2.78113	-1.16866
C	-9.16394	-4.14801	0.59820
C	-10.18889	-4.54662	-0.27511
C	-10.21315	-4.04871	-1.58804

C	-9.22988	-3.17823	-2.04027
N	-11.18808	-5.44279	0.16052
C	-11.64983	-6.46127	-0.70421
C	-11.71172	-5.34035	1.46903
C	-11.98794	-4.08597	2.02773
C	-12.49537	-3.99031	3.31836
C	-12.75278	-5.13754	4.06600
C	-12.48752	-6.38646	3.50848
C	-11.96313	-6.49185	2.22539
C	-13.01221	-6.78051	-0.76100
C	-13.46036	-7.78955	-1.60574
C	-12.56635	-8.48291	-2.41879
C	-11.21174	-8.16070	-2.37018
C	-10.75154	-7.16586	-1.51525
C	-6.07130	-3.82702	1.39350
C	-7.46867	-1.86212	2.11256
C	-2.42487	0.05196	-0.28770
C	-1.26833	0.81253	-0.19745
C	-1.15689	2.01569	-0.90126
C	-2.23221	2.43946	-1.68917
C	-3.39209	1.68144	-1.75738
N	0.03524	2.77785	-0.82939
C	-0.01270	4.16413	-0.66280
C	1.27824	2.10376	-0.91880
C	2.32060	2.40239	-0.03526
C	3.53041	1.72963	-0.12621
C	3.73889	0.72452	-1.08163
C	2.68126	0.42991	-1.95390
C	1.47445	1.11032	-1.88340
C	0.99186	4.98915	-1.19803
C	0.94424	6.35967	-1.02871
C	-0.10497	6.97497	-0.32349
C	-1.10693	6.14304	0.20393
C	-1.06549	4.77094	0.04330
C	5.02311	-0.00166	-1.16002
C	5.53397	-0.42428	-2.39834
C	6.73810	-1.11331	-2.49255
C	7.45284	-1.38872	-1.32835
C	6.95632	-0.96944	-0.08162

C	5.75701	-0.28513	0.00518
C	8.71698	-2.08618	-1.11111
C	8.98817	-2.09540	0.26763
C	7.89059	-1.38535	1.04365
C	9.60659	-2.69037	-1.99807
C	10.74924	-3.30542	-1.50237
C	11.02849	-3.30891	-0.12586
C	10.13535	-2.68870	0.76294
N	12.19501	-3.93492	0.36161
C	13.41007	-3.83162	-0.35272
C	12.15157	-4.66795	1.56978
C	8.43606	-0.16484	1.79833
C	7.19711	-2.34359	2.02260
C	13.19606	-4.56953	2.49731
C	13.15384	-5.29946	3.67964
C	12.06704	-6.12265	3.96634
C	11.02275	-6.21532	3.04865
C	11.06452	-5.50341	1.85545
C	14.25731	-4.94018	-0.47299
C	15.45887	-4.83202	-1.16356
C	15.82765	-3.62842	-1.76057
C	14.98121	-2.52723	-1.65091
C	13.78622	-2.62033	-0.94668
C	-0.13651	8.41722	-0.15627
C	0.90952	9.31726	-0.31050
C	0.53586	10.64143	-0.06951
C	-0.80312	10.79406	0.27614
S	-1.59858	9.23934	0.28167
C	-1.40215	12.04086	0.56994
C	-2.68122	12.36453	0.93407
C	-2.98743	13.79003	1.17014
C	-3.71608	11.40706	1.09569
O	-4.26528	13.98395	1.52012
O	-2.18122	14.69177	1.06218
N	-4.56188	10.61818	1.22768
H	-4.65758	-1.02805	0.89449
H	-7.17470	-1.20649	-3.40142
H	-5.11940	0.13888	-3.21995
H	-9.14203	-4.53939	1.61129

H	-11.01484	-4.35402	-2.25256
H	-9.26809	-2.80656	-3.06044
H	-11.80221	-3.18981	1.44416
H	-12.70440	-3.00959	3.73571
H	-13.15571	-5.05917	5.07085
H	-12.67638	-7.28986	4.08113
H	-11.74587	-7.46687	1.80098
H	-13.71453	-6.23376	-0.13976
H	-14.52038	-8.02419	-1.63757
H	-12.92114	-9.26517	-3.08243
H	-10.50133	-8.69741	-2.99222
H	-9.69347	-6.92801	-1.47063
H	-5.18910	-3.40532	1.88599
H	-6.58191	-4.47395	2.11398
H	-5.73539	-4.44338	0.55491
H	-6.60836	-1.41513	2.62101
H	-8.13515	-1.05683	1.79128
H	-8.00401	-2.48350	2.83770
H	-2.47621	-0.89199	0.24669
H	-0.43766	0.47028	0.41157
H	-2.15836	3.37023	-2.24275
H	-4.22232	2.04452	-2.35577
H	2.18100	3.16948	0.71999
H	4.33216	1.99679	0.55584
H	2.79889	-0.35647	-2.69355
H	0.67029	0.86500	-2.56989
H	1.80377	4.54621	-1.76441
H	1.71909	6.96772	-1.48453
H	-1.92013	6.57332	0.78238
H	-1.84369	4.15523	0.48067
H	4.98721	-0.18597	-3.30609
H	7.11253	-1.42111	-3.46488
H	5.36268	0.01123	0.97413
H	9.41046	-2.70197	-3.06658
H	11.43995	-3.79427	-2.18167
H	10.35516	-2.68408	1.82676
H	7.62356	0.37155	2.29900
H	9.15580	-0.47593	2.56237
H	8.93680	0.52812	1.11640

H	7.90357	-2.69224	2.78277
H	6.37166	-1.83927	2.53529
H	6.79569	-3.21674	1.50062
H	14.03863	-3.91914	2.28482
H	13.97237	-5.21135	4.38811
H	12.03439	-6.68558	4.89384
H	10.17235	-6.85902	3.25396
H	10.25512	-5.58960	1.13744
H	13.96804	-5.88361	-0.02101
H	16.10419	-5.70169	-1.24668
H	16.76341	-3.54952	-2.30493
H	15.25806	-1.57998	-2.10452
H	13.13768	-1.75527	-0.85112
H	1.91813	9.01438	-0.56269
H	1.21353	11.48620	-0.12739
H	-0.73461	12.89795	0.49421
H	-4.38338	14.93636	1.65489

Sum of electronic and zero-point Energies= -3847.514460
Sum of electronic and thermal Energies= -3847.441938
Sum of electronic and thermal Enthalpies= -3847.440993
Sum of electronic and thermal Free Energies= -3847.637534

5.3.2 Computed Excitations of Compound 7c (PBEh1PBE/6-31G** PCM CH_2Cl_2)

Excited State 1: Singlet-A 2.1500 eV 576.66 nm f=0.7094 <S**2>=0.000
298 -> 301 0.22892
300 -> 301 0.66567
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -3848.62081748
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 2.3603 eV 525.30 nm f=0.0319 <S**2>=0.000
299 -> 301 0.70511

Excited State 3: Singlet-A 2.4973 eV 496.48 nm f=0.3929 <S**2>=0.000
298 -> 301 0.66071
300 -> 301 -0.23410

```
Excited State   4:      Singlet-A      3.1563 eV  392.81 nm  f=1.9932  <S**2>=0.000
    299 -> 303        0.26270
    300 -> 302        0.62756

Excited State   5:      Singlet-A      3.2673 eV  379.47 nm  f=0.9619  <S**2>=0.000
    295 -> 301       -0.10794
    296 -> 301        0.24791
    297 -> 301        0.42111
    299 -> 302        0.28781
    300 -> 303        0.37365

Excited State   6:      Singlet-A      3.3421 eV  370.98 nm  f=0.1607  <S**2>=0.000
    296 -> 301        0.21745
    297 -> 301        0.40635
    298 -> 303        0.10088
    299 -> 302       -0.39611
    300 -> 303       -0.30899

Excited State   7:      Singlet-A      3.4175 eV  362.79 nm  f=0.0104  <S**2>=0.000
    296 -> 301        0.60406
    297 -> 301       -0.34791

Excited State   8:      Singlet-A      3.5582 eV  348.45 nm  f=0.0250  <S**2>=0.000
    298 -> 302        0.50275
    299 -> 303       -0.41826
    300 -> 302        0.11222
    300 -> 303        0.10667

Excited State   9:      Singlet-A      3.5772 eV  346.60 nm  f=0.0148  <S**2>=0.000
    297 -> 301       -0.12154
    298 -> 302       -0.10365
    298 -> 303        0.27526
    299 -> 302       -0.41409
    299 -> 303        0.11065
    300 -> 303        0.43878

Excited State  10:      Singlet-A      3.7679 eV  329.05 nm  f=0.0868  <S**2>=0.000
    295 -> 301       -0.12192
    298 -> 302        0.43490
```

```
    299 -> 303        0.45056
    300 -> 302       -0.27228

 Excited State  11:      Singlet-A      3.7798 eV  328.02 nm  f=0.0624  <S**2>=0.000
    295 -> 301        0.62126
    297 -> 301        0.11269
    298 -> 303       -0.11461
    299 -> 303        0.11460
    300 -> 304        0.13709

 Excited State  12:      Singlet-A      3.8210 eV  324.48 nm  f=0.0107  <S**2>=0.000
    298 -> 303        0.12273
    298 -> 305        0.36448
    300 -> 305        0.53068

 Excited State  13:      Singlet-A      3.8456 eV  322.41 nm  f=0.0182  <S**2>=0.000
    295 -> 301        0.20657
    298 -> 303        0.47428
    299 -> 302        0.20714
    299 -> 306        0.22280
    300 -> 303       -0.13286
    300 -> 304       -0.18085
    300 -> 305       -0.13659
    300 -> 307        0.18711

 Excited State  14:      Singlet-A      3.8696 eV  320.40 nm  f=0.0220  <S**2>=0.000
    298 -> 306       -0.17369
    299 -> 307        0.44658
    300 -> 306        0.44818

 Excited State  15:      Singlet-A      3.8774 eV  319.76 nm  f=0.0212  <S**2>=0.000
    298 -> 303       -0.26740
    298 -> 305        0.11428
    298 -> 307       -0.15392
    299 -> 306        0.38279
    299 -> 309        0.11238
    300 -> 307        0.41542
```

6 References

[1] G. Trippé-Allard, J.-C. Lacroix, *Synthesis of nitro- and amino-functionalized π-conjugated oligomers incorporating 3,4-ethylenedioxythiophene (EDOT) units Tetrahedron* **2013**, *69*, 861-866; DOI: 10.1016/j.tet.2012.10.088.

[2] M. Paramasivam, A. Gupta, N. Jagadeesh Babu, K. Bhanuprakash, S. V. Bhosale, V. Jayathirtha Rao, *Funnel shaped molecules containing benzo/pyrido[1,2,5]thiadiazole functionalities as peripheral acceptors for organic photovoltaic applications RSC Adv.* **2016**, *6*, 66978-66989. DOI: 10.1039/C6RA06616J

[3] H.-Y. Wang, G. Chen, X.-P. Xu, H. Chen, S.-J. Ji, *The synthesis and photophysical properties of novel poly(diarylamino)styrenes Dyes and Pigments* **2011**, *88*, 358-365. DOI: 10.1016/j.dyepig.2010.08.003

[4] W. Huang, L. Su, Z. Bo, *Hyperbranched Polymers with a Degree of Branching of 100% Prepared by Catalyst Transfer Suzuki-Miyaura Polycondensation J. Am. Chem. Soc.* **2009**,*131*, 10348–10349. DOI: 10.1021/ja9033846

[5] (a) D. W. Price, J. M. Tour, *Tetrahedron Lett. Biphenyl- and fluorenyl-based potential molecularelectronic devices* **2003**, *59*, 3131 – 3156. DOI: 10.1016/S0040-4020(03)00334-X; (b) D. Sahu, H. Padhy, D. Patra, D. Kekuda, C.-W. Chu, I.-H. Chiang, H.-C. Lin, *Polymer Synthesis and application of H-Bonded cross-linking polymers containing a conjugated pyridyl H-Acceptor side-chain polymer and various carbazole-based H-Donor dyes bearing symmetrical cyanoacrylic acids for organic solar cells* **2010**, *51*, 6182 – 6192. DOI: 10.1016/j.polymer.2010.10.018; (c) P. Chen, H.-M. Wang, G.-J. Liu, S. X.-A. Sean, *Design, synthesis and properties of near-infrared molecular switches containing a fluorene ring Org. Biomol. Chem.* **2016***, 14,* 4456–4463. DOI: 10.1039/C6OB00379F; (d) H. Zhang, X. Liu, T.-T. Lu, P. Lv, W.-Y. Lai, *Monodisperse Six-Armed Starbursts based on Truxene-Cored Multibranched Oligofluorenes: Design, Synthesis, and Stabilized Lasing Characteristics Chem. Eur.J.* **2019***, 25,* 3909–3917. DOI: DOI:10.1002/chem.201805813

[6] D. Hanss, O. S. Wenger, *Conformational Effects on Long-Range Electron Transfer: Comparison of Oligo-p-phenylene and Oligo-p-xylene Bridges, Eur. J. Inorg. Chem.* ***2009****,* 3778–3790. DOI: 10.1002/ejic.200900396

[7] A. Rosiak, W. Frey, J. Christoffers, *Synthesis of Tetrahydropyran-4-ones and Thiopyran-4-ones from Donor-Substituted α-Bromostyrene Derivatives Eur. J. Org. Chem.* **2006**, 4044-4054. DOI: 10.1002/ejoc.200600372

[8] P. Zanello, in: *Ferrocenes* A. Togni (Ed.), T. Hayashi(Ed.), Wiley VHC, Weinheim **1995**, 317-430.

[9] T. Meyer, D. Ogermann, A. Pankrath, K. Kleinermanns, T. J. J. Müller, *Phenothiazinyl Rhodanylidene Merocyanines for Dye-Sensitized Solar Cells J. Org. Chem.* **2012**, *77*, 3704. DOI: 10.1021/jo202608w

[10] A. Mitsch, M. Altenkämper, I. Sattler, M. Schlitzer, *Non-Thiol Farnesyltransferase Inhibitors: Utilization of the Far Aryl Binding Site by Arylthienylacryloylaminobenzophenones Arch. Pharm. Chem. Life Sci.* **2005***, 338,* 9−17. DOI: DOI 10.1002/ardp.200400886

[11] D. Mignani, F. Leising, R. Meyrueix, H. Samson, *Synthesis of new thiophene compounds with large second order optical non-linearities Tetrahedron Lett.* **1990**, *33*, 4743-4746.

[12] M. J. Braun, I. Jung, *Dye-sensitized solar cells, metal complex dyes therefor, and methods for making such dyes, Solvay SA* EP2720238 (A1), 16.04.2014.

[13] X. W. a Wan-Li He, Z. Yang, D. Wang, H. Cao, Z.-G. Zheng, Z. Liu, X. Liu, *The effects of asymmetric bent-shaped compounds on the temperature range and electro-optical performances of liquid crystalline blue phases RSC Adv.* **2016**, *6*, 110750-110757, DOI: 10.1039/C6RA22704J.

[14] M. A. Ismail, M. M. Youssef, R. K. Arafa, S. S. Al-Shihry, W. M. El-Sayed, *Synthesis and antiproliferative activity of monocationic arylthiophene derivatives Eur. J. Med. Chem*. **2017**,*126*, 789-798, DOI: 10.1016/j.ejmech.2016.12.007.

[15] K. Kobayashi, M. S. M. Ahmed, A. Mori, *Introduction of ethynylene and thienylene spacers into 2,5-diarylthiazole and 2,5-diarylthiophene Tetrahedron* **2006**, *62*, 9548-9553, DOI: 10.1016/j.tet.2006.07.097.

[16] R. Chandra, M. Kunga, H. F. Kung*, Design, synthesis, and structure–activity relationship of novel thiophene derivatives for b-amyloid plaque imaging* Bioorganic & *Med. Chem. Lett.* **2006**, *16*, 1350–1352, DOI: 10.1016/j.bmcl.2005.11.055.

[17] G. Kirsch, D. Prim, F. Leising, G. Mignani, *New thiophene derivatives as potential materials for non linear optics Heterocy. Chem.* **1994**, *31*, 1005 – 1010, DOI: 10.1002/jhet.5570310451.

[18] T. Komiyama, Dr. Y. Minami, Y. Furuya, Prof. Dr. T. Hiyama, *Palladium/Copper Dual Catalysis for the Cross-Coupling of Aryl(trialkyl)silanes with Aryl Bromides Angew.*

Chem. **2018**, *130*, 2005-2008, DOI: 10.1002/ange.201712081, *Angew. Chem. Int. Ed.* **2018**, *57*, 1987-1990, DOI: 10.1002/anie.201712081.

[19] S. Tanaka, D. Tanaka, A. Sugie, A. Mori, *Generation of metalated thiophenes with Grignard reagent and catalytic secondary amine for the cross coupling reaction with aryl halides Tetrahedron Lett.* **2012**, *53*, 1173-1176, DOI: 10.1016/j.tetlet.2011.12.108.

[20] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[21] (a) C. Lee, W. Yang, R. G. Parr, *Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density Phys. Rev. B* **1988**, *37*, 785–789. DOI: 10.1103/PhysRevB.37.785; (b) A. D. Becke, *A new mixing of Hartree–Fock and local density‐functional theories J. Chem. Phys.* **1993**, *98*, 1372–1377. DOI: 10.1063/1.464304; (c) A. D. Becke, *Density‐functional thermochemistry. III. The role of exact exchange J. Chem. Phys.* **1993**, *98*, 5648– 5652. DOI: 10.1063/1.464913; (d) K. Kim, K. D. Jordan, *Comparison of Density Functional and MP2 Calculations on the Water Monomer and Dimer J. Phys. Chem.* **1994**, *98*, 10089–10094. DOI: 10.1021/j100091a024; (e) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields J. Phys. Chem.* **1994**, *98*, 11623–11627. DOI: 10.1021/j100096a001

[22] W. J. Hehre, R. Ditchfeld and J. A. Pople, *Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules J. Chem. Phys.* **1972**, *56*, 2257. DOI: 10.1063/1.1677527

[23] (a) Bauernschmitt R, Ahlrichs R., *Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory Chem Phys Lett* **1996**, *256*,

454-464. DOI: 10.1016/0009-2614(96)00440-X; (b) M. E. Casida, C. Jamorski, K. C. Casida, D. R. Salahub, *Molecular excitation energies to high-lying bound states from time-dependent density-functional response theory: Characterization and correction of the time-dependent local density approximation ionization threshold J Chem Phys* **1998**, *108*, 4439-4449. DOI: 10.1063/1.475855; (c) R. E. Stratmann, G. E. Scuseria, M. J. Frisch, *An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large molecules J Chem Phys* **1998**, *109*, 8218-8224. DOI: 10.1063/1.477483

[24] G. Scalmani, M. J. Frisch, *Continuous surface charge polarizable continuum models of solvation. I. General formalism J. Chem. Phys.* **2010**, *132*, 114110-114115. DOI 10.1063/1.3359469