Supporting Information

Cu-Catalyzed [2+2+1] Cascade Annulation of Vinyl Iodonium Salts with Element Sulfur/Selenium for the Modular Synthesis of Thiophenes and Selenophens

Yaxing Wu,[a] Chao Wu,[a] Fei Wang,[a] and Chao Chen[a,b,c*]

a. Key Laboratory of Bioorganic Phosphorus Chemistry & Chemical Biology (Ministry of Education), Department of Chemistry, Tsinghua University, Beijing 100084, China. Tel: +86-10-62773684. * E-mail: chenchao01@mails.tsinghua.edu.cn.

b. School of Biotechnology and Health Sciences, Wuyi University & International Healthcare Innovation Institute (Jiangmen), Jiangmen, 529020, China.

c. State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

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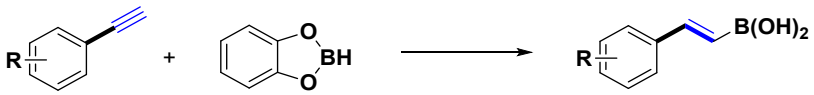
General Comments

All the reactions were carried out in pre-dried Schlenk tubes with a Teflon-lined septum under N_2 atmosphere. All of the solvents were fresh distilled. Column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). 1 H NMR and 13C NMR spectra were recorded on a JEOL AL-400MHz spectrometer at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) are reported in parts per million (ppm), referenced to the residual proton resonance of $CDCl_3$ (7.26 ppm), to the carbon resonance of $CDCl_3$ (77.16 ppm). Coupling constants (J) were given in Hertz (Hz). The term m, dq, q, t, d, s referred to multiplet, doublet quartet, quartet, triplet, doublet, singlet. Mass spectra were obtained using Bruker Esquire ion trap mass spectrometer in positive mode. The reaction progress was monitored by GC-MS and TLC. Unless otherwise noted, commercially available reagents were used as received.

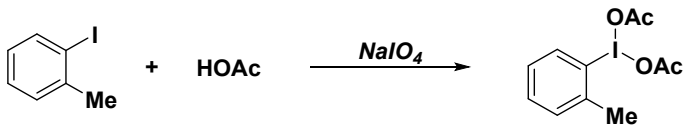
Preparation of Starting Materials[1-4]

Synthesis of (*E*)-2-(aryl)ethenylboronic acid



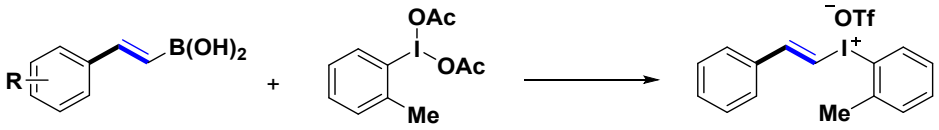
Terminal aromatic alkyne (3 mmol) was added to a solution of catechol borane (1 M in THF, 4.5 mL) and the mixture was stirred under nitrogen atmosphere at 75 °C for 16 h. The solution was cooled to room temperature and water (15 mL) was added. The precipitate was isolated by filtration and washed with water. The pure product was obtained by further purification through chromatography on silica.

Synthesis of 2-methyl-(diacetoxyiodo)benzene



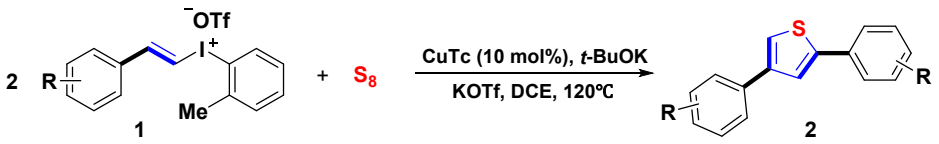
The $NaIO_4$ (30 mmol), 2-methyliodobenzene (10 mmol) and acetic acid (50 mL) were dissolved in a 250 mL round-bottom flask. Then Ac_2O (5 mL) was added. The mixture was stirred at 100 °C for 24 h. After completion, water (50 mL) was added. The solid was separated by filtration. The filtrate was extracted with DCM (3 x10 mL), dried over Na_2SO_4, then concentrated under reduced pressure. The combined crude products were purified by recrystallization from diethyl ether.

Synthesis of aryl-vinyl iodonium triflate salts

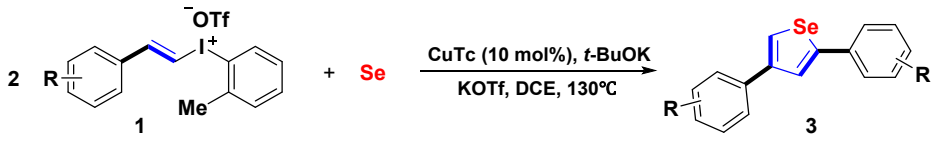


The boronic acid (2.0 mmol, 1 eq.) was suspended in dry CH_2Cl_2 (10 mL) under nitrogen gas. The reaction was cooled to 0 °C and $BF_3 \cdot Et_2O$ (1.2 eq.) was added dropwise and stirred at 0 °C for 15 minutes. Iodoarene diacetate (2.4 mmol, 1.2 eq.) was then added as a solution in CH_2Cl_2 (10 mL) under nitrogen gas. The reaction mixture was stirred for an hour. Then Sodium trifluomethanesulfonate (6.0 mmol, 3 eq.) added as a solution in water (10 mL). The reaction mixture was vigorously stirred for 15 minutes. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic phases dried (Na_2SO_4), filtered, then concentrated in vacuo. The crude residue was then recrystallized or stirred with Et_2O to obtain the desired compound as a white powder.

General Synthesis of Thiophenes and Selenophens



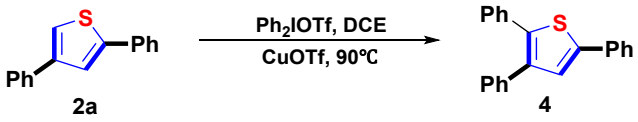
Under a N_2 atmosphere, aryl-vinyl iodonium triflate salt **1** (0.2 mmol), S_8 (0.08 mmol, 20.5 mg), *t*-BuOK (0.6 mmol, 67.4 mg), KOTf (0.4 mmol, 75.2 mg), CuTc (0.02 mmol, 3.8 mg) and dry DCE (2 mL) were added to a flame-dried Schlenk tube. The resulting mixture was stirred at 120℃ for 24 hours, and water (5 mL) was added. The solution was extracted with ethyl acetate and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products 2.



Under a N_2 atmosphere, aryl-vinyl iodonium triflate salt **1** (0.2 mmol), Se (0.6 mmol, 47.4 mg), *t*-BuOK (0.6 mmol, 67.4 mg), KOTf (0.4 mmol, 75.2 mg), CuTc (0.02 mmol, 3.8 mg) and dry DCE (2 mL) were added to a flame-dried Schlenk tube. The resulting mixture was stirred at 130℃ for 24 hours, and water (5 mL) was added. The solution was extracted with ethyl acetate and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products 3.

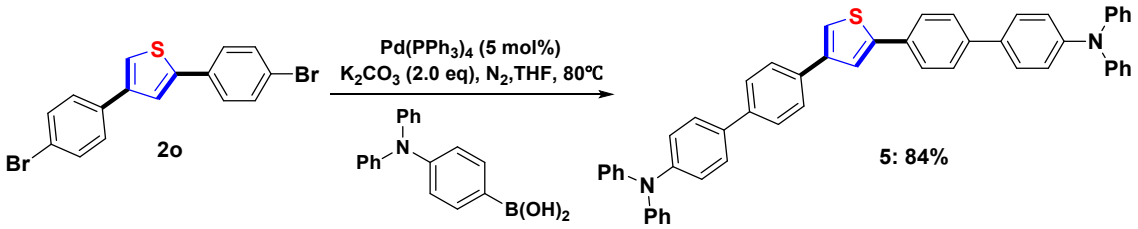
Procedure for the Preparation of Compound 4 and 5

Procedure 1 for preparation of 4 from 2a



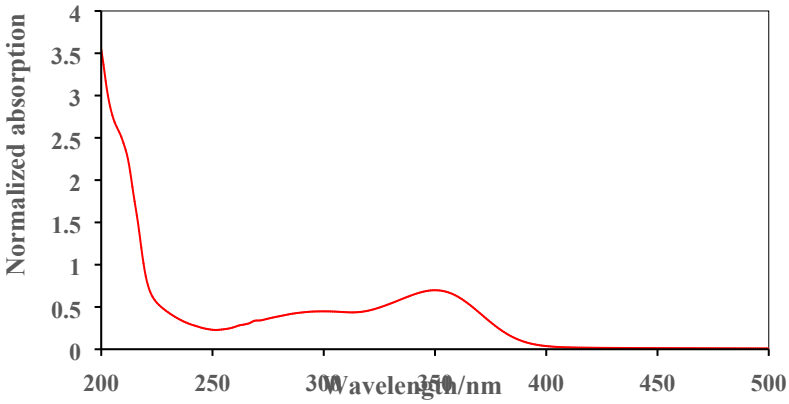
Under a N_2 atmosphere, 2,4-diphenyl thiophene **2a** (0.2 mmol), diphenyliodonium salt (0.24 mmol, 103.2 mg), CuOTf (0.02 mmol, 4.3 mg) and dry DCE (2 mL) were added to a flame-dried Schlenk tube. The resulting mixture was stirred at 90℃ for 8 hours, and water (5 mL) was added. The solution was extracted with ethyl acetate and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **4**.

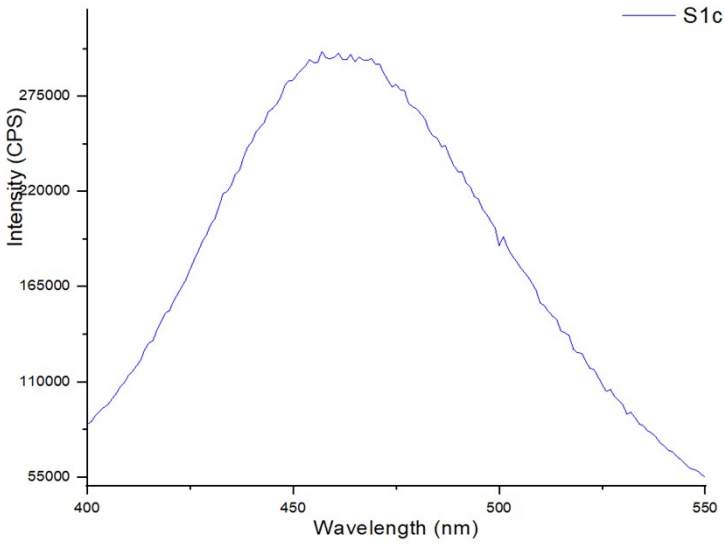
Procedure 2 for preparation of 5 from 2o



Under a N_2 atmosphere, 2,4-bis(4-bromophenyl)thiophene **2o** (0.2 mmol), [4-(diphenylamino)phenyl]boronic acid (0.5 mmol, 144.5 mg), K_2CO_3 (0.6 mmol, 82.9 mg), $Pd(PPh_3)_4$ (0.01 mmol, 11.6 mg) and dry THF (2 mL) were added to a flame-dried Schlenk tube. The resulting mixture was stirred at 80℃ for 4 hours, and water (10 mL) was added. The solution was extracted with ethyl acetate and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **5**.

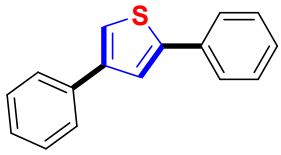
UV-vis absorption (Abs) and PL spectra of 5 in diluted solution (CH_3CN) at room temperature[5]





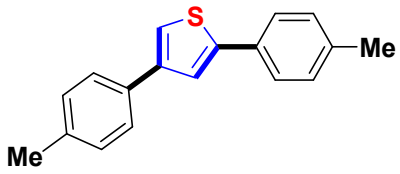
Characterization of Products

2,4-Diphenylthiophene (2a)



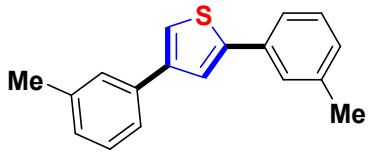
Prepared according to the general procedure as described above in 82% yield (38.7 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.68-7.56 (m, 5H), 7.44-7.37 (m, 5H), 7.33-7.28 (m, 2H). 13C NMR (101 MHz, Chloroform-d) δ 145.30, 143.37, 136.08, 134.54, 129.30, 129.20, 127.97, 127.50, 126.56, 126.12, 122.53, 119.92. GC-MS: 236.

2,4-Di-*p*-tolylthiophene (2b)



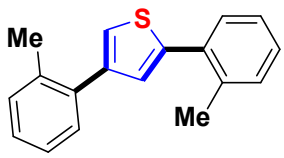
Prepared according to the general procedure as described above in 70% yield (37.0 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.52 (t, J = 8.5 Hz, 5H), 7.30 (s, 1H), 7.23-7.16 (m, 4H), 2.37 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 145.14, 143.12, 137.62, 137.06, 133.26, 131.73, 129.67, 129.58, 126.28, 125.85, 121.94, 118.70, 21.25. GC-MS: 264.

2,4-Di-*m*-tolylthiophene (2c)



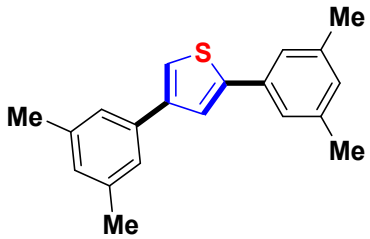
Prepared according to the general procedure as described above in 67% yield (35.4 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.58 (d, J = 1.5 Hz, 1H), 7.50-7.42 (m, 4H), 7.36 (d, J = 1.5 Hz, 1H), 7.34-7.26 (m, 2H), 7.13 (d, J = 7.5 Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 145.18, 143.28, 138.68, 138.51, 135.97, 134.40, 128.93, 128.83, 128.57, 128.12, 127.21, 126.67, 123.55, 123.11, 122.42, 119.57, 21.64, 21.57. GC-MS: 264.

2,4-Di-*o*-tolylthiophene (2d)



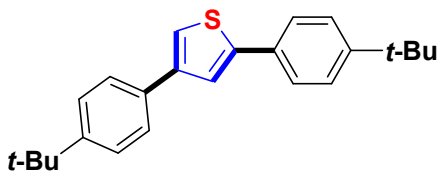
Prepared according to the general procedure as described above in 62% yield (32.7 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.45 (dd, J= 7.5 Hz, 1.5 Hz, 1H), 7.35 (dd, J= 7.5 Hz, 1.5 Hz, 1H), 7.32-7.23 (m, 6H), 7.20 (d, J = 1.5 Hz, 1H), 7.11 (d, J = 1.5 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 142.72, 142.38, 136.87, 136.18, 135.81, 134.16, 130.96, 130.29, 130.19, 129.82, 128.49, 127.86, 127.50, 126.13, 125.91, 122.86, 21.35, 20.97. GC-MS: 264.

2,4-Di-(3, 5-dimethylphenyl)-thiophene (2e)



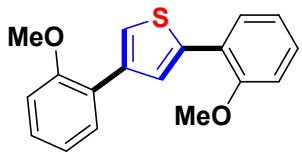
Prepared according to the general procedure as described above in 58% yield (33.9 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.56 (s, 1H), 7.34 (s, 1H), 7.29 (s, 2H), 7.26 (s, 2H), 6.96 (s, 2H), 2.38 (s, 12H). 13C NMR (101 MHz, Chloroform-d) δ 145.19, 143.31, 138.55, 138.38, 135.98, 134.36, 129.46, 128.98, 124.34, 123.84, 122.39, 119.32, 21.49. GC-MS: 292.

2,4-Di-(4-(tert-butylphenyl)-thiophene (2f)



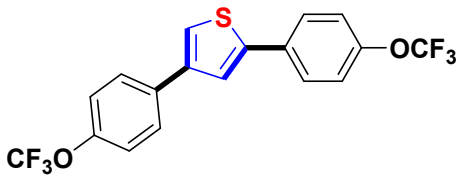
Prepared according to the general procedure as described above in 66% yield (45.9 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.62-7.53 (m, 5H), 7.47-7.39 (m, 4H), 7.32 (s, 1H), 1.36 (s, 18H). 13C NMR (101 MHz, Chloroform-d) δ 150.87, 150.32, 145.00, 143.06, 133.32, 131.76, 126.13, 125.93, 125.82, 125.71, 122.08, 118.95, 34.66, 31.38. GC-MS: 348.

2,4-Di-(2-methoxyphenyl)-thiophene (2g)



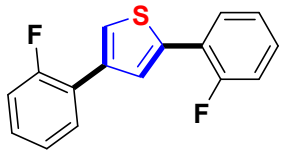
Prepared according to the general procedure as described above in 79% yield (46.8 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a yellow solid. 1H NMR (400 MHz, Chloroform-d) δ 7.83 (s, 1H), 7.70 (d, J = 7.5 Hz, 1H), 7.61 (s, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.32-7.23 (m, 2H), 7.06-6.99 (m, 4H), 3.95 (s, 3H), 3.89 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 156.68, 155.88, 138.50, 138.01, 129.84, 128.74, 128.47, 128.33, 127.16, 125.62, 125.58, 123.75, 121.06, 120.93, 111.78, 111.51, 55.81, 55.72. GC-MS: 296.

2,4-Di-(4-trifluoromethoxyphenyl)-thiophene (2h)



Prepared according to the general procedure as described above in 84% yield (46.8 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a yellow solid. 1H NMR (400 MHz, Chloroform-d) δ 7.62 (dd, J = 11.9, 8.7 Hz, 4H), 7.50 (s, 1H), 7.38 (s, 1H), 7.25 (m, 4H). 13C NMR (101 MHz, Chloroform-d) δ 148.84 (q, J = 8.8 Hz), 148.58 (q, J = 8.6 Hz), 143.93, 141.97, 134.50, 132.99, 127.71, 127.28, 122.78, 121.58, 121.46, 120.77, 120.57 (q, J = 257 Hz). 19F NMR (565 MHz, Chloroform-d) δ -50.97 (s, 3F), -60.20 (s, 3F). GC-MS: 404.

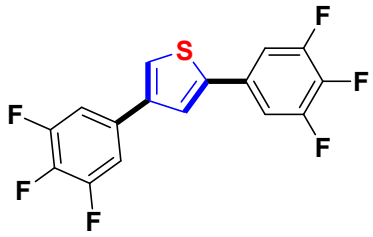
2,4-Di-(2-fluorophenyl)-thiophene (2i)



Prepared according to the general procedure as described above in 63% yield (34.3 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.80 (d, J = 1.4 Hz, 1H), 7.68 (td, J = 7.9, 1.9 Hz, 1H), 7.65-7.57 (m, 2H), 7.33-7.23 (m, 2H), 7.22-7.12 (m, 4H). 13C NMR (101 MHz, Chloroform-d) δ 159.93 (d, J = 247 Hz), 159.23 (d, J = 249 Hz), 136.28, 129.50 (d, J = 4.6 Hz), 129.00 (d, J = 8.0 Hz), 128.85-128.77 (m), 126.80 (q, J = 3.4 Hz), 124.54 (dd, J = 11.2 Hz, 3.4 Hz), 124.01 (m), 123.67 (d,

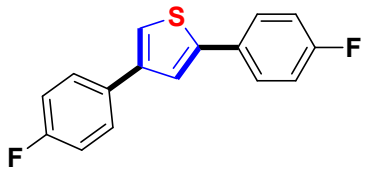
J = 13.2 Hz), 122.12 (J = 13.2 Hz), 116.49 (d, J = 23.5 Hz), 116.39 (d, J = 22.8 Hz). 19F NMR (565 MHz, Chloroform-d) δ -108.32 (s, 1F), -108.42 (s, 1F). GC-MS: 272.

2,4-Di-(3,4,5-trifluorophenyl)-thiophene (2j)



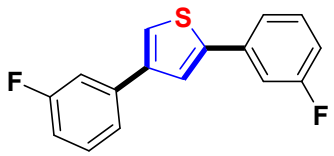
Prepared according to the general procedure as described above in 80% yield (55.0 mg). It was purified by flash chromatography (PE/EA 50:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.39 (s, 2H), 7.26-7.14 (m, 4H). 13C NMR (101 MHz, Chloroform-d) δ 153.09-152.51 (m), 150.50-150.25 (m), 142.71-142.52 (m), 140.57-140.37 (m), 131.49 (td, J = 6.8 Hz, 2.3 Hz), 130.06 (td, J = 6.8 Hz, 2.4 Hz), 123.02, 122.03, 110.56-110.00 (m). 19F NMR (565 MHz, Chloroform-d) δ -133.07 (dd, J = 20.5, 8.5 Hz, 2F), -133.56 (dd, J = 20.6, 8.5 Hz, 2F), -160.56 (dd, *J* = 33.7, 13.2 Hz, 1F), -161.53 (dd, *J* = 27.0, 14.1 Hz, 1F). GC-MS: 344. HRMS (ESI+) calcd for C16H6F6S $[M + H]^+$ 345.0128. Found 345.0110. Melt point: 94.6-96.3°C

2,4-Di-(4-fluorophenyl)-thiophene (2k)



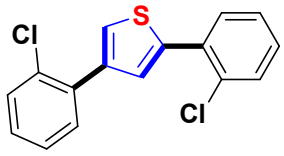
Prepared according to the general procedure as described above in 72% yield (39.2 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.63-7.52 (m, 4H), 7.44 (s, 1H), 7.30 (s, 1H), 7.09 (td, J = 8.8, 2.3 Hz, 4H). 13C NMR (101 MHz, Chloroform-d) δ 162.58 (d, J = 245.3 Hz), 162.54 (d, J = 245.1 Hz), 144.28, 142.26, 132.12 (d, J = 8.0 Hz), 130.65 (d, J = 7.8 Hz), 127.98 (d, J = 8.0 Hz), 127.65 (J = 8.0 Hz), 122.36, 119.49, 116.10 (d, J = 35.6 Hz), 115.82 (d, J = 35.2 Hz). 19F NMR (565 MHz, Chloroform-d) δ -114.03 (s, 1F), -114.93 (s, 1F). GC-MS: 272.

2,4-Di-(3-fluorophenyl)-thiophene (2l)



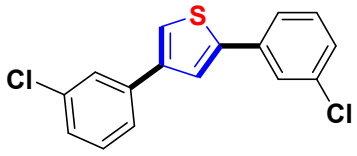
Prepared according to the general procedure as described above in 63% yield (34.3 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.55 (d, J = 1.5 Hz, 1H), 7.44-7.27 (m, 7H), 7.05-6.96 (m, 2H). 13C NMR (101 MHz, Chloroform-d) δ 164.50 (d, J = 6.4 Hz), 162.06 (d, J = 6.8 Hz), 144.05, 142.07, 137.83 (d, J = 8.0 Hz), 136.29 (d, J = 8.0 Hz), 130.61 (d, J = 8.2 Hz), 130.47 (d, J = 8.4 Hz), 122.87, 122.04 (d, J = 3.0 Hz), 121.63 (d, J = 3.0 Hz), 121.09, 114.71 (d, J = 21.5 Hz), 114.28 (d, J = 21.2 Hz), 113.30 (d, J = 23.0 Hz), 112.81 (d, J = 23.0 Hz). 19F NMR (565 MHz, Chloroform-d) δ -112.48 (s, 1F), -112.74 (s, 1F). GC-MS: 272.

2,4-Di-(2-chlorophenyl)-thiophene (2m)



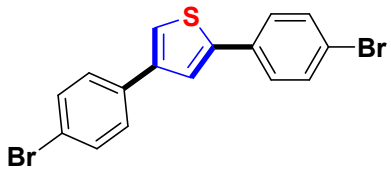
Prepared according to the general procedure as described above in 64% yield (38.9 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.62 (s, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.53-7.45 (m, 4H), 7.35-7.22 (m, 4H). 13C NMR (101 MHz, Chloroform-d) δ 139.68, 139.45, 135.27, 133.06, 132.53, 132.45, 131.46, 131.19, 130.71, 130.38, 129.56, 128.89, 128.65, 127.11, 127.04, 125.00. GC-MS: 304.

2,4-Di-(3-chlorophenyl)-thiophene (2n)



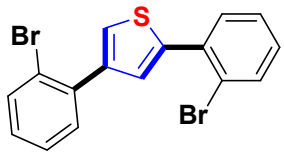
Prepared according to the general procedure as described above in 45% yield (27.4 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.60 (d, J = 13.6 Hz, 2H), 7.55-7.44 (m, 3H), 7.41 (s, 1H), 7.37-7.24 (m, 4H). 13C NMR (101 MHz, Chloroform-d) δ 143.84, 141.88, 137.40, 135.89, 135.01, 134.88, 130.29, 130.19, 127.86, 127.47, 126.51, 125.91, 124.50, 124.06, 122.86, 121.21. GC-MS: 304.

2,4-Di-(4-bromophenyl)-thiophene (2o)



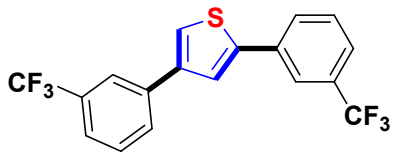
Prepared according to the general procedure as described above in 68% yield (53.6 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.55-7.44 (m, 9H), 7.38 (d, J = 1.5 Hz, 1H). 13C NMR (101 MHz, Chloroform-d) δ 144.21, 142.17, 134.64, 133.16, 132.16, 132.06, 127.94, 127.41, 122.46, 121.81, 121.41, 120.46. GC-MS: 394.

2,4-Di-(2-bromophenyl)-thiophene (2p)



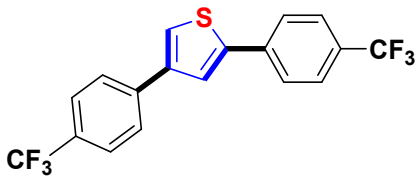
Prepared according to the general procedure as described above in 60% yield (47.3 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a yellow solid. 1H NMR (400 MHz, Chloroform-d) δ 7.68 (t, J = 8.0 Hz, 2H), 7.58-7.50 (m, 2H), 7.48-7.43 (m, 2H), 7.38-7.30 (m, 2H), 7.18 (t, J = 7.7 Hz, 2H). 13C NMR (101 MHz, Chloroform-d) δ 141.14, 141.01, 137.45, 135.15, 133.89, 133.53, 131.99, 131.38, 129.73, 129.23, 128.90, 127.59, 127.56, 124.69, 122.88, 122.61. GC-MS: 394.

2,4-Di-(3-trifluoromethylphenyl)-thiophene (2q)



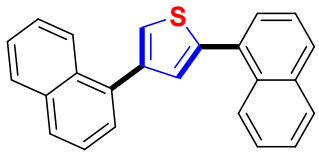
Prepared according to the general procedure as described above in 74% yield (55.1 mg). It was purified by flash chromatography (PE/EA 50:1) to afford a yellow solid. 1H NMR (400 MHz, Chloroform-d) δ 7.87 (d, J = 10.9 Hz, 2H), 7.81 (t, J = 7.3 Hz, 2H), 7.64 (s, 1H), 7.60-7.49 (m, 5H). 13C NMR (101 MHz, Chloroform-d) δ 144.00, 141.99, 136.33, 134.89, 129.63, 129.49, 129.15, 124.55-124.47 (m), 124.19-124.13 (m), 123.18-123.09 (m), 122.63, 122.57, 121.73, 121.66. 19F NMR (565 MHz, Chloroform-d) δ -62.57 (s, 3F), -62.67 (s, 3F). GC-MS: 372. HRMS (ESI+) calcd for C18H10F6S $[M + H]^+$ 373.0409. Found 373.0401. Melt point: 84.7-85.9°C

2,4-Di-(4-trifluoromethylphenyl)-thiophene (2r)



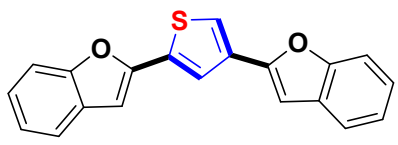
Prepared according to the general procedure as described above in 80% yield (59.5 mg). It was purified by flash chromatography (PE/EA 50:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.78-7.69 (m, 5H), 7.69-7.64 (m, 6H), 7.54 (s, 1H). 13C NMR (101 MHz, Chloroform-d). 13C NMR (101 MHz, Chloroform-d) δ 142.65, 142.20, 138.09, 137.49, 130.62 (d, J = 3.0 Hz), 130.29 (d, J = 3.0 Hz), 130.12, 127.52, 124.01-124.34 (m), 123.91, 121.59. 19F NMR (565 MHz, Chloroform-d) δ -62.38 (s, 3F), -62.47 (s, 3F). GC-MS: 372.

2,4-Di-(naphthalen-1-yl)-thiophene (2s)



Prepared according to the general procedure as described above in 44% yield (29.6 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a brown solid. 1H NMR (400 MHz, Chloroform-d) δ 8.38 (dt, J = 7.0, 3.4 Hz, 1H), 8.26-8.19 (m, 1H), 7.96-7.84 (m, 4H), 7.69 (dd, J = 7.1, 1.3 Hz, 1H), 7.61 (dd, J = 7.1, 1.3 Hz, 1H), 7.58-7.46 (m, 8H). 13C NMR (101 MHz, Chloroform-d) δ 141.84, 141.45, 135.11, 134.03, 133.99, 132.45, 131.85, 129.99, 128.67, 128.51, 128.49, 128.33, 127.98, 127.11, 126.68, 126.35, 126.19, 126.01, 125.97, 125.82, 125.56, 125.42, 123.94, 123.84. GC-MS: 336. HRMS (ESI+) calcd for C24H16S $[M + H]^+$ 337.0979. Found 337.0986. Melt point: 84.2-85.7°C.

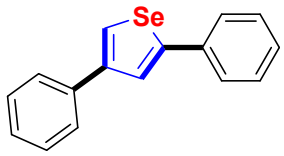
2,4-Di-(benzofuran-2-yl)-thiophene (2t)



Prepared according to the general procedure as described above in 50% yield (31.6 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.57-7.53 (m, 2H), 7.50-7.46 (m, 2H), 7.38-7.35 (m, 2H), 7.32-7.19 (m, 4H), 6.87 (s, 2H). 13C NMR (101 MHz, Chloroform-d) δ

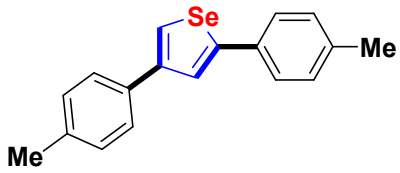
154.71, 153.83, 149.87, 148.85, 134.48, 129.08, 128.86, 126.88, 126.33, 125.33, 124.97, 123.44, 122.80, 122.30, 121.14, 111.28, 110.81, 110.17, 103.36, 102.10. GC-MS: 316. HRMS (ESI+) calcd for C20H12O2S $[M + H]^+$ 317.0592. Found 317.0578. Melt point: 94.6-95.7℃.

2,4-Diphenylselenophen (3a)



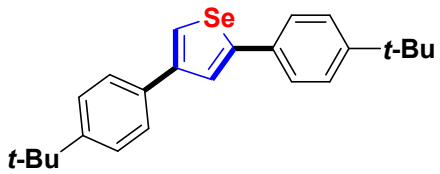
Prepared according to the general procedure as described above in 37% yield (21.0 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.71-7.59 (m, 5H), 7.45-7.36 (m, 5H), 7.34-7.29 (m, 2H). 13C NMR (101 MHz, Chloroform-d) δ 144.14, 143.22, 136.74, 133.98, 128.75, 128.65, 127.78, 127.50, 126.75, 125.86, 121.55, 120.28. GC-MS: 284. HRMS (ESI+) calcd for C16H12Se $[M + H]^+$ 285.1104. Found 285.1113. Melt point: 101.6-103.1℃.

2,4-Di-*p*-tolylselenophen (3b)



Prepared according to the general procedure as described above in 42% yield (26.2 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.49 (t, J = 8.5 Hz, 5H), 7.31 (s, 1H), 7.23-7.16 (m, 4H), 2.24 (s, 6H). 13C NMR (101 MHz, CDCl3) δ 144.79, 143.33, 137.22, 136.70, 133.11, 131.90, 129.03, 128.94, 126.10, 125.85, 121.94, 117.72, 18.90. GC-MS: 312. HRMS (ESI+) calcd for C18H16Se $[M + H]^+$ 313.1418. Found 313.1416. Melt point: 106.6-107.9℃.

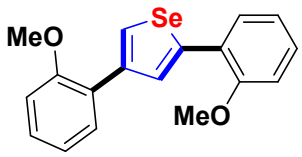
2,4-Di-(4-(tert-butylphenyl)-selenophen (3c)



Prepared according to the general procedure as described above in 31% yield (24.6 mg). It was purified by flash

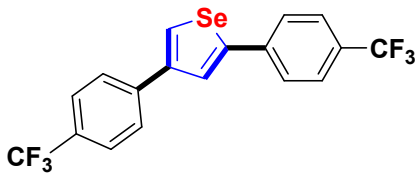
chromatography (PE/EA 100:1) to afford a yellow solid. 1H NMR (400 MHz, Chloroform-d) δ 7.65-7.55 (m, 5H), 7.45-7.37 (m, 4H), 7.32 (s, 1H), 1.33-1.28 (m, 18H). 13C NMR (101 MHz, Chloroform-d) δ 150.58, 150.42, 144.07, 142.97, 133.71, 129.98, 125.43, 125.23, 125.12, 125.00, 120.59, 119.27, 34.22, 30.00. GC-MS: 396. HRMS (ESI+) calcd for C24H28Se $[M + H]^+$ 397.1356. Found 397.1351. Melt point: 97.6-98.4℃

2,4-Di-(2-methoxyphenyl)-selenophen (3d)



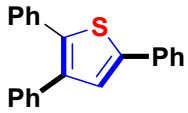
Prepared according to the general procedure as described above in 32% yield (22.0 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a brown solid. 1H NMR (400 MHz, Chloroform-d) δ 7.82 (dd, J= 7.5 Hz, 1.5 Hz, 1H), 7.45 (dd, J= 7.5 Hz, 1.5 Hz, 1H), 7.41-7.33 (m, 6H), 7.30 (d, J = 1.5 Hz, 1H), 7.21 (d, J = 1.5 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H). 13C NMR (101 MHz, Chloroform-d) δ 155.18, 154.38, 139.80, 139.31, 131.76, 128.44, 128.16, 128.03, 127.17, 125.62, 123.75, 123.67, 119.62, 119.50, 113.65, 113.37, 52.24, 52.15. GC-MS: 344. HRMS (ESI+) calcd for C18H16O2Se $[M + H]^+$ 345.0316. Found 345.0312. Melt point: 109.6-111.1℃.

2,4-Di-(4-trifluoromethylphenyl)-selenophen (3e)



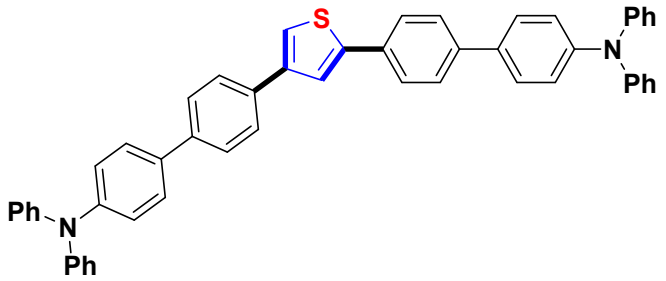
Prepared according to the general procedure as described above in 20% yield (16.8 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.83-7.67 (m, 11H), 7.36 (s, 1H). 13C NMR (101 MHz, CDCl3). 13C NMR (101 MHz, Chloroform-d) δ 142.16, 141.70, 137.65, 137.05, 131.27 (d, J = 3.0 Hz), 130.95 (d, J = 3.0 Hz), 130.12, 127.52, 124.90-124.52 (m), 123.91, 121.59. 19F NMR (565 MHz, Chloroform-d) δ -61.35 (s, 3F), -61.59 (s, 3F). GC-MS: 420. HRMS (ESI+) calcd for C18H10F6Se $[M + H]^+$ 420.9852. Found 420.9863. Melt point: 118.3-119.8℃.

2,3,5-triphenylthiophene (4)



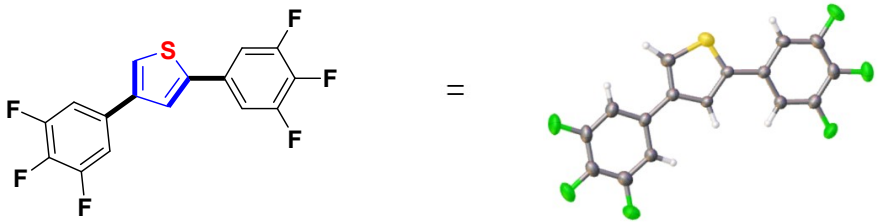
Prepared according to the general procedure as described above in 91% yield (56.8 mg). It was purified by flash chromatography (PE/EA 100:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.65 (dd, J = 8.2, 1.3 Hz, 2H), 7.45-7.22 (m, 14H).13C NMR (101 MHz, Chloroform-d) δ 142.67, 139.10, 138.10, 136.70, 134.32, 134.21, 129.25, 129.18, 129.05, 128.57, 128.51, 127.72, 127.54, 127.11, 126.61, 125.71. GC-MS: 312.

2,4-Di-(4-(4-diphenylaminophenyl)-phenyl)-thiophene (5)



Prepared according to the general procedure as described above in 84% yield (121.5 mg). It was purified by flash chromatography (PE/EA 70:1) to afford a white solid. 1H NMR (400 MHz, Chloroform-d) δ 7.70 (t, J = 8.4 Hz, 4H), 7.66-7.59 (m, 4H), 7.51 (dd, J = 8.7, 2.8 Hz, 4H), 7.46-7.40 (m, 2H), 7.31-7.27 (m, 6H), 7.17-7.12 (m, 13H), 7.06-7.00 (m, 5H). 13C NMR (101 MHz, Chloroform-d) δ 147.75, 147.72, 147.38, 142.89, 139.58, 134.56, 134.40, 132.89, 129.40, 129.34, 127.67, 127.63, 127.39, 127.11, 127.07, 126.75, 126.27, 124.61, 124.56, 124.39, 124.17, 123.97, 123.90, 123.13, 123.08, 122.91, 122.16, 119.56. HRMS (ESI+) calcd for C52H38N2S $[M + H]^+$ 723.2828. Found 723.2833. Melt point: 149.1-150.3℃

X-Ray Crystal Structures



The low temperature (173±2°K) single-crystal X-ray experiments were performed on a SuperNova diffractometer with Cu K_α radiation. Unit cell was obtained and refined by 5388 reflections with $4.5° < \theta < 74.7°$. No decay was observed in data collection. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with C-H bonds of 0.93 Å according to criteria described in the SHELXTL manual (Bruker, 1997). They were included in the refinement with $U_{iso}(H) = 1.2U_{eq}$ of their parent atoms. There are two molecules, $C_{16}H_6F_6S$, in an independent area. It was found that the thiophene groups were diorientational disordered which were represented by S(1), C(4), S(1′), C(4′) and S(2), C(20), S(2′), C(20′), respectively. Their occupancies were fixed in the final refinement to be 0.65 for S(1), C(4), 0.35 for S(1′), C(4′) and 0.75 for S(2), C(20), 0.25 for S(2′), C(20′), respectively, according to the result of refinement for their occupancies before. The final full-matric least-square refinement on F^2 converged with $R1 = 0.0912$ and $wR2 = 0.1818$ for 3927 observed reflections [$I \geq 2\sigma(I)$]. The final difference electron density map shows no features. Details of crystal parameters, data collection and structure refinement are given in Table 1.

Data collection was controlled by CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (Oxford, 2013). Computations were performed using the SHELXTL NT ver. 5.10 program package (Bruker, 1997) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1989). Crystal drawings were produced with XP (Bruker, 1997).

References

Bruker. (1997) SHELXTL. Structure Determination Programs, Version 5.10, Bruker AXS Inc.,6300 Enterprise Lane, Madison, WI 53719-1173, USA.

International Tables for X-ray Crystallography: (1989) Vol. C (Kluwer Academic Publishers, Dordrecht) Tables 4.2.6.8 and 6.1.1.4.

Oxford. (2013) CrysAlisPro, Agilent Technologies, Version 1.171.36.32, Oxford Diffraction Ltd., 68 Milton Park, Abingdon, Oxfordshire, OX14 4RX, UK.

Table 1. Details of Data Collection, Processing and Structure Refinement

Sample code	**2j**
Molecular formula	$C_{16}H_6F_6S$
Molecular weight	344.27
Color and habit	colorless needle
Crystal size	0.19 mm × 0.20 mm × 0.27 mm
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell parameters	a = 9.4232(4) Å α = 90.00° b = 19.3491(8) Å β = 103.331(5)° c = 14.9248(7) Å γ = 90.00° V = 2647.9(2) Å^3 Z = 8 F(000) = 1376
Density (calcd)	1.727 g/cm^3
Diffractometer	SuperNova, Dual, Cu at home/near, AtlaS2
Radiation	Cu K_α, λ = 1.54178 Å
Temperature	173±2K
Scan type	ω-scan
Data collection range	$-9 < h < 11$, $-20 < k < 24$, $-17 < l < 18$; θ_{max} = 75.4°
Reflections measured	Total: 17966 Unique (n): 5371 Observed [$I \geq 2\sigma(I)$]: 3927
Absorption coefficient	2.840 mm^{-1}
Minimum and maximum transmission	0.430, 1.000
No. of variables, p	429
Weighting scheme	$w = \frac{1}{\sigma^2(F_o^2) + (0.001P)^2 + 4.5P}$ $P = (F_o^2 + 2F_c^2)/3$
$R1 = \frac{\Sigma\|\|F_o\|-\|F_c\|\|}{\Sigma\|F_o\|}$ (for all reflections)	0.1229 0.0912 (for observed data)
$wR2 = \sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{\Sigma w(F_o^2)^2}}$ (for all reflections)	0.1897 0.1818 (for observed data)
Goof = S = $\sqrt{\frac{\Sigma[w(F_o^2 - F_c^2)^2]}{n - p}}$	1.507
Largest and mean Δ/σ	0.001, 0.000
Residual extrema in final difference map	-0.532 to 0.643 e Å^{-3}

Table 2. Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

Atoms	*x*	*y*	*z*	$U_{eq.}$	*Occupancy*
S(1)	0.7270(3)	0.64340(10)	0.73180(19)	0.0330(5)	0.65
C(4)	0.5743(15)	0.6639(7)	0.6494(11)	0.0291(10)	0.65
S(1')	0.5935(6)	0.6795(2)	0.6589(5)	0.0291(10)	0.35
C(4')	0.718(3)	0.6256(10)	0.7236(17)	0.0330(5)	0.35
S(2)	0.7596(2)	0.75397(9)	0.20980(18)	0.0350(5)	0.75
C(20)	0.6052(17)	0.7335(8)	0.1294(14)	0.0346(16)	0.75
S(2')	0.6254(13)	0.7192(5)	0.1400(10)	0.0346(16)	0.25
C(20')	0.745(3)	0.7708(15)	0.213(3)	0.0350(5)	0.25
F(1)	0.7831(5)	0.31715(18)	0.7942(3)	0.0646(11)	1.00
F(2)	1.0354(4)	0.3481(2)	0.9149(2)	0.0581(10)	1.00
F(3)	1.1185(4)	0.4821(2)	0.9408(3)	0.0617(11)	1.00
F(4)	0.0636(4)	0.50689(17)	0.4175(2)	0.0482(8)	1.00
F(5)	-0.0245(3)	0.62966(19)	0.3390(2)	0.0496(8)	1.00
F(6)	0.1411(4)	0.74394(19)	0.3903(3)	0.0577(10)	1.00
F(7)	1.1236(4)	0.9111(2)	0.4444(2)	0.0582(10)	1.00
F(8)	1.0443(4)	1.04533(19)	0.4186(2)	0.0529(9)	1.00
F(9)	0.7964(4)	1.07781(17)	0.2946(3)	0.0593(10)	1.00
F(10)	0.1119(4)	0.6502(2)	-0.0750(3)	0.0602(10)	1.00
F(11)	-0.0179(4)	0.7649(2)	-0.1592(2)	0.0583(10)	1.00
F(12)	0.1072(4)	0.88966(19)	-0.1128(3)	0.0553(9)	1.00
C(1)	0.6914(5)	0.5578(2)	0.7131(3)	0.0276(9)	1.00
C(2)	0.5662(5)	0.5483(2)	0.6451(3)	0.0265(9)	1.00
C(3)	0.4987(5)	0.6105(2)	0.6077(3)	0.0268(9)	1.00
C(5)	0.7812(5)	0.5032(3)	0.7672(3)	0.0276(9)	1.00
C(6)	0.7382(6)	0.4344(3)	0.7570(3)	0.0348(11)	1.00
C(7)	0.8252(7)	0.3834(3)	0.8068(4)	0.0427(13)	1.00
C(8)	0.9538(6)	0.3985(3)	0.8685(4)	0.0391(12)	1.00
C(9)	0.9939(6)	0.4673(3)	0.8800(4)	0.0414(13)	1.00
C(10)	0.9106(6)	0.5185(3)	0.8302(4)	0.0397(12)	1.00
C(11)	0.3629(5)	0.6154(2)	0.5365(3)	0.0258(9)	1.00
C(12)	0.2756(5)	0.5573(2)	0.5093(3)	0.0291(10)	1.00
C(13)	0.1479(5)	0.5629(3)	0.4438(3)	0.0334(11)	1.00
C(14)	0.1013(6)	0.6262(3)	0.4036(3)	0.0348(11)	1.00
C(15)	0.1859(6)	0.6827(3)	0.4298(4)	0.0380(12)	1.00
C(16)	0.3151(5)	0.6791(3)	0.4952(4)	0.0338(11)	1.00
C(17)	0.7018(5)	0.8380(2)	0.2117(3)	0.0290(10)	1.00
C(18)	0.5666(5)	0.8463(2)	0.1520(3)	0.0274(9)	1.00
C(19)	0.5111(5)	0.7848(2)	0.1056(3)	0.0313(10)	1.00
C(21)	0.7909(5)	0.8921(2)	0.2675(3)	0.0272(9)	1.00

(Table 2. continued)

Atoms	*x*	*y*	*z*	$U_{eq.}$	*Occupancy*
C(22)	0.9183(5)	0.8753(3)	0.3331(3)	0.0342(11)	1.00
C(23)	1.0012(6)	0.9273(3)	0.3824(3)	0.0391(12)	1.00
C(24)	0.9626(6)	0.9955(3)	0.3701(3)	0.0382(12)	1.00
C(25)	0.8363(6)	1.0115(3)	0.3062(4)	0.0405(12)	1.00
C(26)	0.7508(6)	0.9622(3)	0.2554(3)	0.0344(11)	1.00
C(27)	0.3717(5)	0.7792(3)	0.0364(3)	0.0308(10)	1.00
C(28)	0.3055(6)	0.7150(3)	0.0126(4)	0.0392(12)	1.00
C(29)	0.1754(6)	0.7113(3)	-0.0516(4)	0.0424(13)	1.00
C(30)	0.1086(6)	0.7692(3)	-0.0954(4)	0.0395(12)	1.00
C(31)	0.1730(6)	0.8329(3)	-0.0709(4)	0.0359(11)	1.00
C(32)	0.3024(5)	0.8380(3)	-0.0065(3)	0.0339(11)	1.00

*$U_{eq.}$ defined as one third of the trace of the orthogonalized **U** tensor.

Table 3. Bond lengths (Å) and bond angles (°)

Molecule **I**		Molecule **II**	
S(1)-C(1)	1.700(5)	S(2)-C(20)	1.705(10)
S(1)-C(4)	1.710(9)	S(2)-C(17)	1.718(4)
C(4)-C(3)	1.326(14)	C(20)-C(19)	1.323(16)
S(1')-C(3)	1.688(5)	S(2')-C(19)	1.666(7)
S(1')-C(4')	1.694(10)	S(2')-C(20')	1.699(10)
C(4')-C(1)	1.34(2)	C(20')-C(17)	1.36(3)
F(1)-C(7)	1.343(7)	F(7)-C(23)	1.338(6)
F(2)-C(8)	1.333(6)	F(8)-C(24)	1.338(6)
F(3)-C(9)	1.339(6)	F(9)-C(25)	1.337(6)
F(4)-C(13)	1.347(6)	F(10)-C(29)	1.336(6)
F(5)-C(14)	1.345(6)	F(11)-C(30)	1.345(6)
F(6)-C(15)	1.347(6)	F(12)-C(31)	1.342(6)
C(1)-C(2)	1.380(6)	C(17)-C(18)	1.385(6)
C(1)-C(5)	1.472(7)	C(17)-C(21)	1.473(7)
C(2)-C(3)	1.415(6)	C(18)-C(19)	1.416(7)
C(3)-C(11)	1.465(6)	C(19)-C(27)	1.476(7)
C(5)-C(10)	1.389(7)	C(21)-C(22)	1.401(6)
C(5)-C(6)	1.391(7)	C(21)-C(26)	1.410(7)
C(6)-C(7)	1.384(7)	C(22)-C(23)	1.377(8)
C(7)-C(8)	1.374(8)	C(23)-C(24)	1.370(8)
C(8)-C(9)	1.383(8)	C(24)-C(25)	1.377(8)
C(9)-C(10)	1.372(8)	C(25)-C(26)	1.361(7)
C(11)-C(12)	1.397(7)	C(27)-C(32)	1.392(7)
C(11)-C(16)	1.404(7)	C(27)-C(28)	1.398(7)
C(12)-C(13)	1.369(7)	C(28)-C(29)	1.372(7)
C(13)-C(14)	1.390(7)	C(29)-C(30)	1.374(9)
C(14)-C(15)	1.357(8)	C(30)-C(31)	1.386(8)
C(15)-C(16)	1.376(7)	C(31)-C(32)	1.371(7)
C(1)-S(1)-C(4)	90.4(5)	C(20)-S(2)-C(17)	90.5(6)
C(3)-C(4)-S(1)	115.5(9)	C(19)-C(20)-S(2)	115.2(10)
C(3)-S(1')-C(4')	89.8(9)	C(19)-S(2')-C(20')	92.1(13)
C(1)-C(4')-S(1')	116.8(14)	C(17)-C(20')-S(2')	113.6(19)
C(4')-C(1)-C(2)	108.8(8)	C(20')-C(17)-C(18)	110.3(9)
C(4')-C(1)-C(5)	124.8(8)	C(20')-C(17)-C(21)	122.7(9)
C(2)-C(1)-C(5)	126.4(4)	C(18)-C(17)-C(21)	127.0(4)
C(2)-C(1)-S(1)	110.7(3)	C(18)-C(17)-S(2)	110.3(3)
C(5)-C(1)-S(1)	122.8(4)	C(21)-C(17)-S(2)	122.6(4)
C(1)-C(2)-C(3)	114.0(4)	C(17)-C(18)-C(19)	113.5(4)
C(4)-C(3)-C(2)	109.4(6)	C(20)-C(19)-C(18)	110.5(6)
C(4)-C(3)-C(11)	125.1(6)	C(20)-C(19)-C(27)	124.5(7)

(Table 3. continued)

C(2)-C(3)-C(11)	125.5(4)	C(18)-C(19)-C(27)	124.9(4)
C(2)-C(3)-S(1')	110.5(4)	C(18)-C(19)-S(2')	110.5(5)
C(11)-C(3)-S(1')	124.0(4)	C(27)-C(19)-S(2')	124.6(5)
C(10)-C(5)-C(6)	117.7(5)	C(22)-C(21)-C(26)	118.3(4)
C(10)-C(5)-C(1)	121.5(5)	C(22)-C(21)-C(17)	121.1(4)
C(6)-C(5)-C(1)	120.8(4)	C(26)-C(21)-C(17)	120.6(4)
C(7)-C(6)-C(5)	120.2(5)	C(23)-C(22)-C(21)	119.6(5)
F(1)-C(7)-C(8)	118.9(5)	F(7)-C(23)-C(22)	119.4(5)
F(1)-C(7)-C(6)	119.0(5)	F(7)-C(23)-C(24)	118.5(5)
C(8)-C(7)-C(6)	122.1(5)	C(22)-C(23)-C(24)	122.1(5)
F(2)-C(8)-C(7)	120.5(5)	F(8)-C(24)-C(25)	120.6(5)
F(2)-C(8)-C(9)	122.1(5)	F(8)-C(24)-C(23)	121.3(5)
C(7)-C(8)-C(9)	117.4(5)	C(25)-C(24)-C(23)	118.0(5)
F(3)-C(9)-C(10)	121.0(6)	F(9)-C(25)-C(26)	119.1(5)
F(3)-C(9)-C(8)	117.5(5)	F(9)-C(25)-C(24)	118.5(5)
C(10)-C(9)-C(8)	121.5(5)	C(26)-C(25)-C(24)	122.3(5)
C(9)-C(10)-C(5)	121.1(5)	C(25)-C(26)-C(21)	119.7(5)
C(12)-C(11)-C(16)	118.1(4)	C(32)-C(27)-C(28)	118.3(5)
C(12)-C(11)-C(3)	121.0(4)	C(32)-C(27)-C(19)	120.6(4)
C(16)-C(11)-C(3)	120.9(4)	C(28)-C(27)-C(19)	121.1(5)
C(13)-C(12)-C(11)	120.4(4)	C(29)-C(28)-C(27)	119.9(5)
F(4)-C(13)-C(12)	120.5(5)	F(10)-C(29)-C(30)	117.9(5)
F(4)-C(13)-C(14)	118.5(4)	F(10)-C(29)-C(28)	120.2(6)
C(12)-C(13)-C(14)	121.0(5)	C(30)-C(29)-C(28)	121.8(5)
F(5)-C(14)-C(15)	121.9(5)	F(11)-C(30)-C(29)	121.3(5)
F(5)-C(14)-C(13)	119.4(5)	F(11)-C(30)-C(31)	120.3(5)
C(15)-C(14)-C(13)	118.7(5)	C(29)-C(30)-C(31)	118.3(5)
F(6)-C(15)-C(14)	118.6(5)	F(12)-C(31)-C(32)	120.6(5)
F(6)-C(15)-C(16)	119.5(5)	F(12)-C(31)-C(30)	118.5(5)
C(14)-C(15)-C(16)	121.9(5)	C(32)-C(31)-C(30)	120.9(5)
C(15)-C(16)-C(11)	119.8(5)	C(31)-C(32)-C(27)	120.7(5)

Table 4. Anisotropic thermal parameters* (Å^2)

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	0.0281(9)	0.0284(13)	0.0396(10)	-0.0055(10)	0.0019(7)	-0.0061(10)
C(4)	0.028(2)	0.016(3)	0.041(2)	-0.0034(19)	0.0035(13)	-0.0087(18)
S(1')	0.028(2)	0.016(3)	0.041(2)	-0.0034(19)	0.0035(13)	-0.0087(18)
C(4')	0.0281(9)	0.0284(13)	0.0396(10)	-0.0055(10)	0.0019(7)	-0.0061(10)
S(2)	0.0351(9)	0.0245(11)	0.0412(8)	0.0052(9)	0.0001(7)	0.0056(8)
C(20)	0.041(3)	0.014(4)	0.045(4)	0.007(3)	0.001(2)	0.009(3)
S(2')	0.041(3)	0.014(4)	0.045(4)	0.007(3)	0.001(2)	0.009(3)
C(20')	0.0351(9)	0.0245(11)	0.0412(8)	0.0052(9)	0.0001(7)	0.0056(8)
F(1)	0.079(3)	0.0329(19)	0.070(3)	0.0079(17)	-0.007(2)	0.0078(18)
F(2)	0.061(2)	0.055(2)	0.051(2)	0.0104(17)	-0.0024(17)	0.0234(18)
F(3)	0.0447(19)	0.073(3)	0.053(2)	0.0014(18)	-0.0185(17)	0.0045(18)
F(4)	0.0459(18)	0.0419(19)	0.0458(18)	-0.0084(14)	-0.0119(15)	-0.0117(15)
F(5)	0.0407(17)	0.064(2)	0.0379(17)	0.0038(15)	-0.0026(14)	0.0117(16)
F(6)	0.061(2)	0.043(2)	0.064(2)	0.0193(17)	0.0040(18)	0.0176(17)
F(7)	0.0408(18)	0.078(3)	0.0440(19)	-0.0050(18)	-0.0147(15)	0.0044(18)
F(8)	0.052(2)	0.059(2)	0.0448(19)	-0.0165(16)	0.0054(15)	-0.0139(17)
F(9)	0.071(2)	0.0310(18)	0.065(2)	-0.0070(16)	-0.0066(19)	-0.0006(17)
F(10)	0.059(2)	0.050(2)	0.070(2)	-0.0247(18)	0.0121(19)	-0.0220(18)
F(11)	0.0403(17)	0.080(3)	0.049(2)	-0.0195(18)	-0.0009(15)	-0.0104(18)
F(12)	0.0460(18)	0.050(2)	0.058(2)	0.0009(17)	-0.0124(16)	0.0099(16)
C(1)	0.029(2)	0.025(2)	0.029(2)	-0.0002(18)	0.0074(18)	0.0014(19)
C(2)	0.027(2)	0.022(2)	0.028(2)	-0.0013(17)	0.0023(18)	0.0016(18)
C(3)	0.026(2)	0.024(2)	0.032(2)	-0.0013(18)	0.0100(18)	-0.0001(18)
C(5)	0.023(2)	0.030(2)	0.028(2)	-0.0060(18)	0.0015(17)	-0.0013(18)
C(6)	0.035(3)	0.032(3)	0.034(3)	0.000(2)	-0.001(2)	0.006(2)
C(7)	0.054(3)	0.032(3)	0.041(3)	0.003(2)	0.010(3)	0.009(3)
C(8)	0.040(3)	0.040(3)	0.035(3)	0.006(2)	0.004(2)	0.015(2)
C(9)	0.031(3)	0.056(4)	0.032(3)	-0.002(2)	-0.005(2)	0.005(2)
C(10)	0.034(3)	0.043(3)	0.038(3)	-0.007(2)	0.001(2)	0.001(2)
C(11)	0.027(2)	0.024(2)	0.026(2)	-0.0012(17)	0.0061(17)	-0.0009(18)
C(12)	0.029(2)	0.026(2)	0.030(2)	0.0026(18)	0.0028(19)	0.0010(19)
C(13)	0.035(3)	0.031(3)	0.034(3)	-0.004(2)	0.007(2)	-0.004(2)
C(14)	0.035(2)	0.042(3)	0.026(2)	0.005(2)	0.0024(19)	0.008(2)
C(15)	0.043(3)	0.031(3)	0.039(3)	0.009(2)	0.008(2)	0.014(2)
C(16)	0.035(2)	0.026(2)	0.041(3)	-0.002(2)	0.008(2)	-0.001(2)
C(17)	0.033(2)	0.022(2)	0.034(2)	0.0035(18)	0.010(2)	0.0006(19)
C(18)	0.027(2)	0.023(2)	0.032(2)	0.0032(18)	0.0050(18)	0.0003(18)
C(19)	0.035(2)	0.029(3)	0.031(2)	-0.0009(19)	0.011(2)	-0.004(2)
C(21)	0.031(2)	0.025(2)	0.026(2)	-0.0005(18)	0.0062(18)	-0.0021(19)

(Table 4. continued)

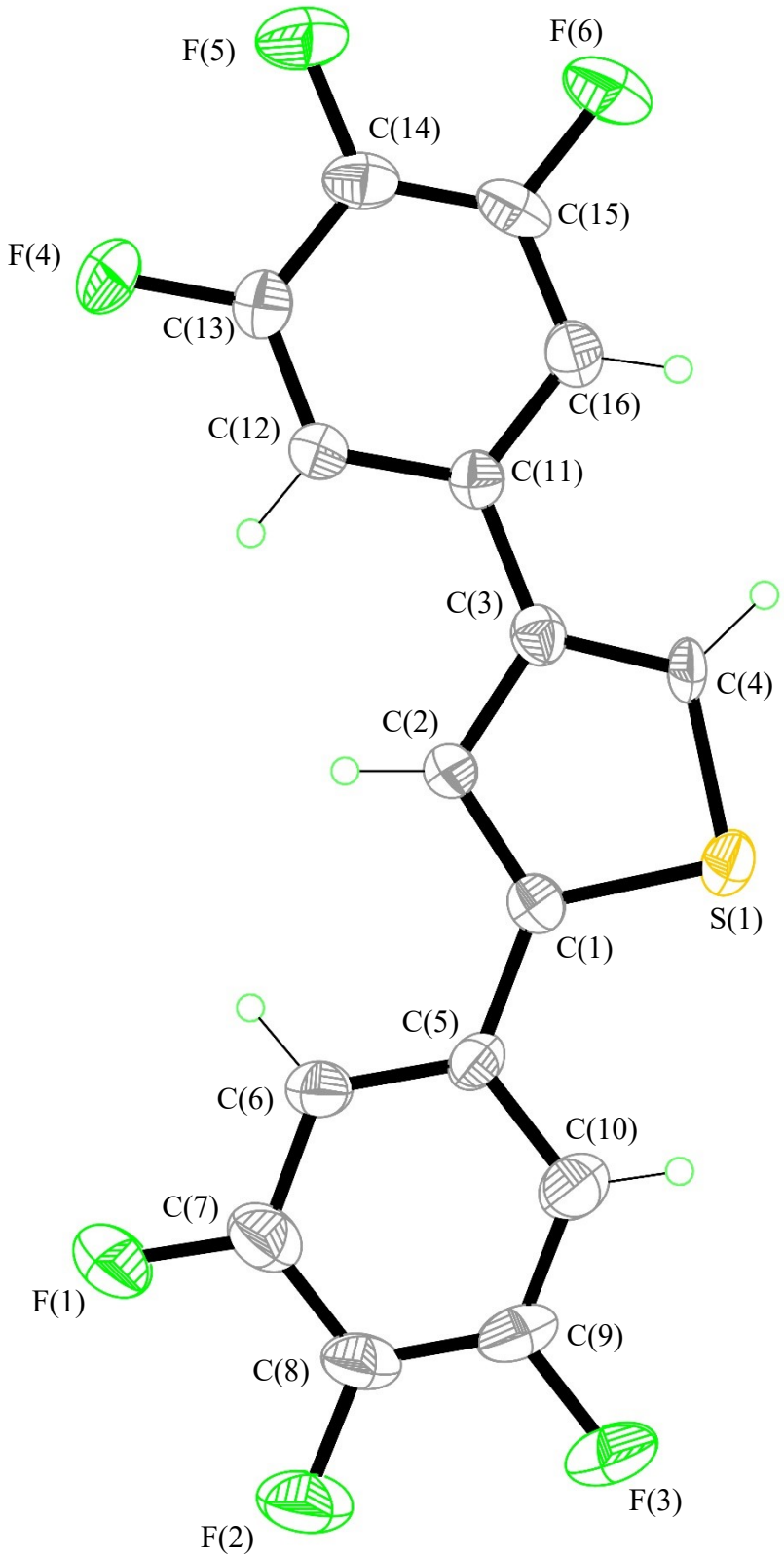
Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(22)	0.030(2)	0.043(3)	0.029(2)	0.003(2)	0.0039(19)	0.007(2)
C(23)	0.034(3)	0.055(4)	0.025(2)	-0.003(2)	0.001(2)	0.002(2)
C(24)	0.045(3)	0.039(3)	0.030(2)	-0.012(2)	0.008(2)	-0.014(2)
C(25)	0.053(3)	0.029(3)	0.040(3)	-0.003(2)	0.011(2)	-0.005(2)
C(26)	0.036(3)	0.032(3)	0.032(2)	-0.002(2)	0.001(2)	0.005(2)
C(27)	0.030(2)	0.031(3)	0.032(2)	-0.0035(19)	0.0103(19)	-0.004(2)
C(28)	0.039(3)	0.039(3)	0.039(3)	-0.006(2)	0.008(2)	0.002(2)
C(29)	0.038(3)	0.044(3)	0.045(3)	-0.019(2)	0.010(2)	-0.014(2)
C(30)	0.035(3)	0.048(3)	0.035(3)	-0.012(2)	0.007(2)	-0.007(2)
C(31)	0.034(2)	0.034(3)	0.038(3)	-0.001(2)	0.005(2)	0.003(2)
C(32)	0.032(2)	0.034(3)	0.035(2)	-0.004(2)	0.005(2)	-0.002(2)

*The exponent takes the form: $-2\pi^2\Sigma\Sigma U_{ij}h_ih_j\mathbf{a}_i^*\mathbf{a}_j^*$

Table 5. Coordinates and isotropic temperature factors* (Å^2) for H atoms

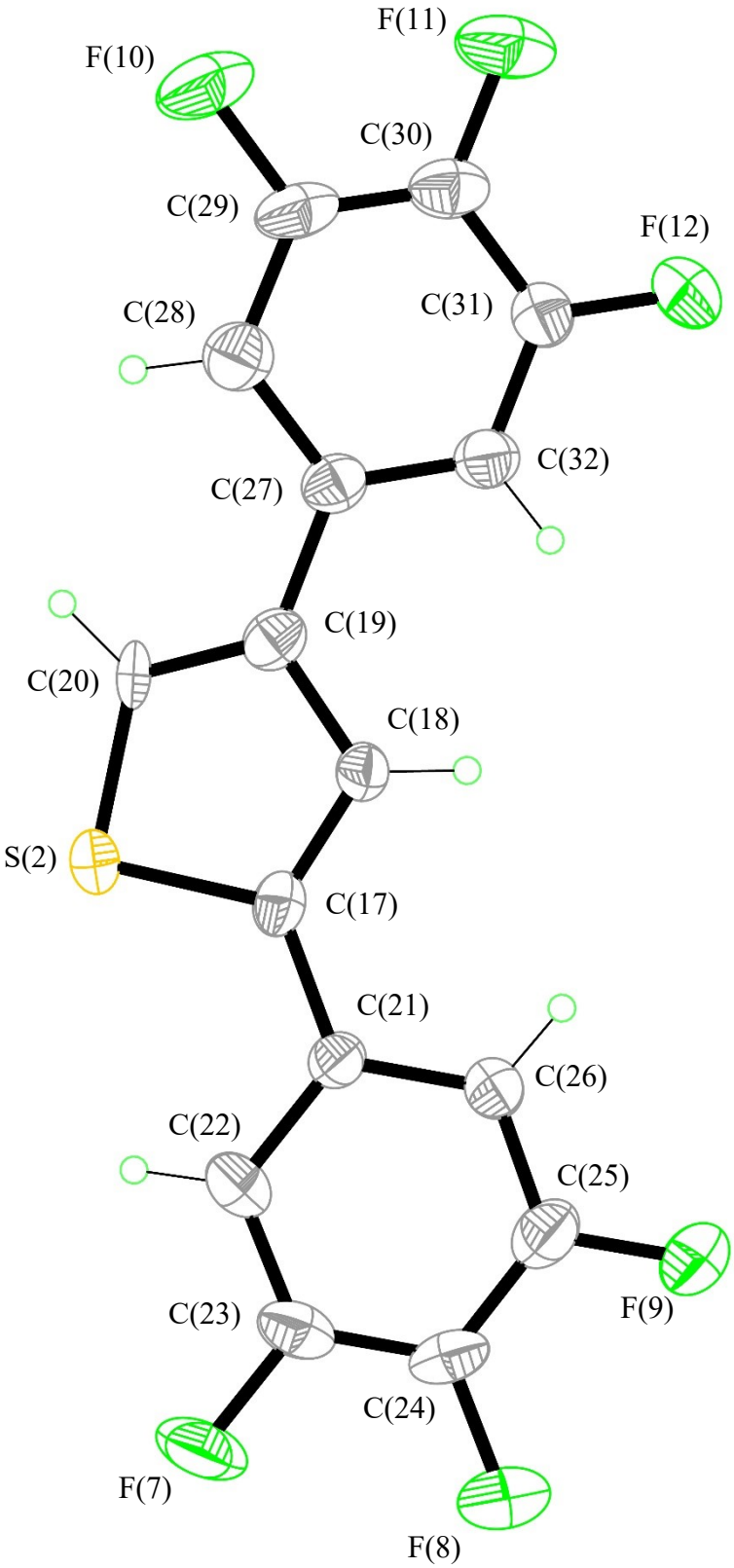
Atoms	*x*	*y*	*z*	$U_{eq.}$	*Occupancy*
H(4A)	0.5463	0.7093	0.6348	0.035	0.65
H(4B)	0.8004	0.6423	0.7645	0.040	0.35
H(20A)	0.5884	0.6896	0.1041	0.042	0.75
H(20B)	0.8316	0.7547	0.2503	0.042	0.25
H(2A)	0.5296	0.5048	0.6255	0.032	1.00
H(6A)	0.6508	0.4225	0.7167	0.042	1.00
H(10A)	0.9413	0.5642	0.8388	0.048	1.00
H(12A)	0.3044	0.5146	0.5360	0.035	1.00
H(16A)	0.3707	0.7188	0.5121	0.041	1.00
H(18A)	0.5171	0.8883	0.1432	0.033	1.00
H(22A)	0.9468	0.8294	0.3434	0.041	1.00
H(26A)	0.6662	0.9748	0.2128	0.041	1.00
H(28A)	0.3495	0.6749	0.0402	0.047	1.00
H(32A)	0.3444	0.8812	0.0087	0.041	1.00

*The exponent takes the form: $-8\pi^2 U \sin^2\theta/\lambda^2$



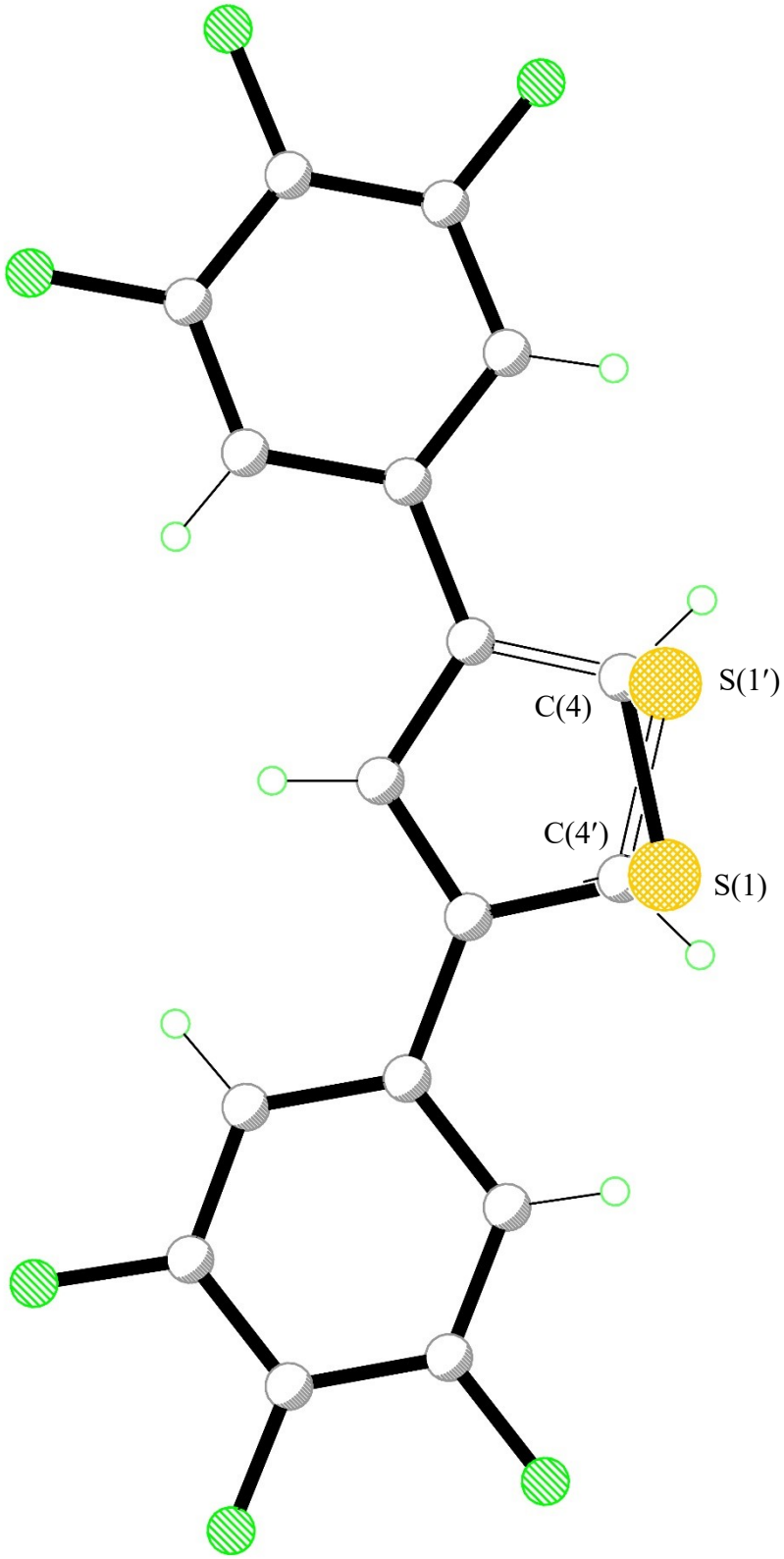
Molecule **I**

ORTEP drawing of $C_{16}H_6F_6S$ with 50% probability ellipsoids, showing the atomic numbering scheme.

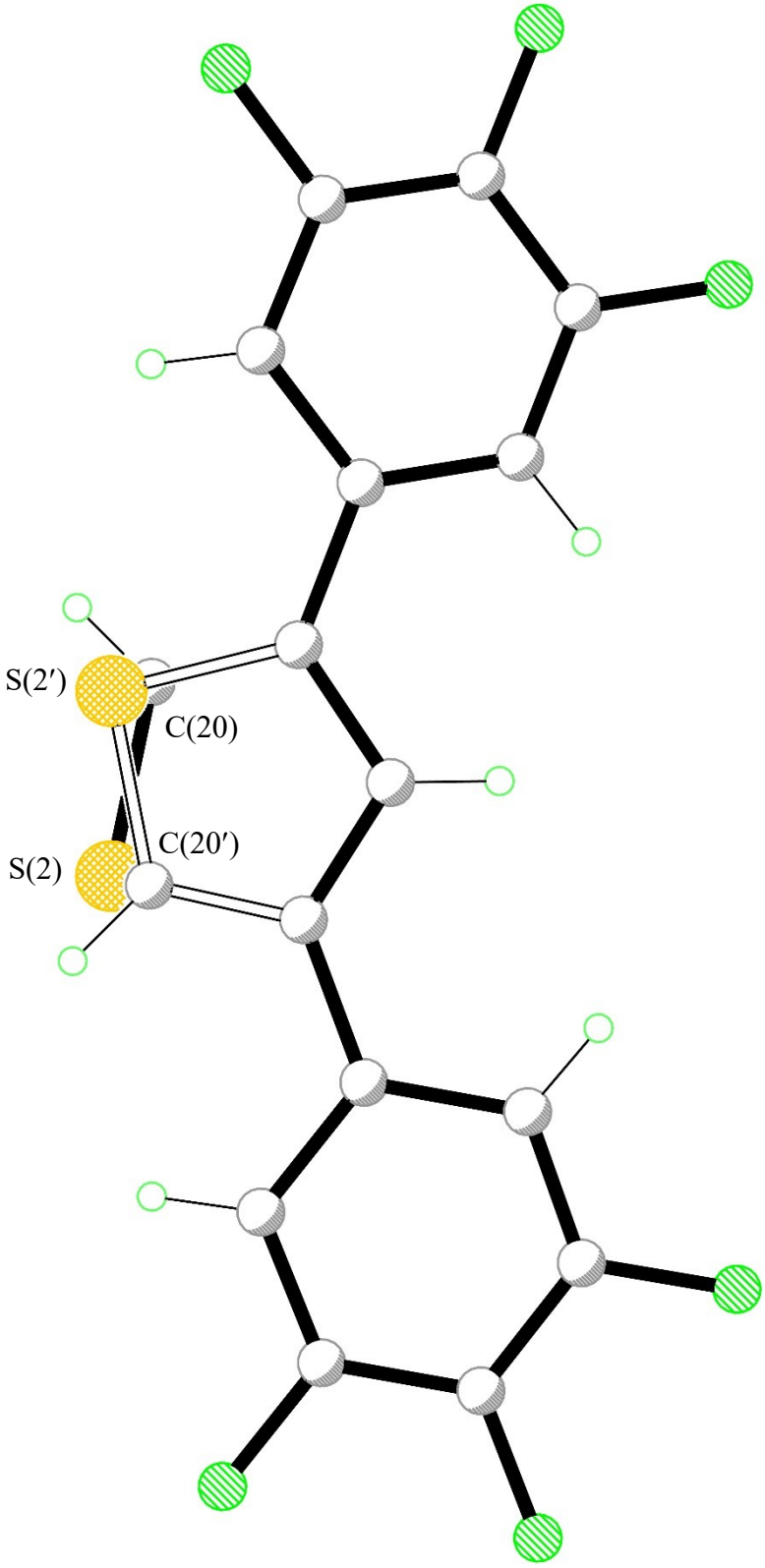


Molecule **II**

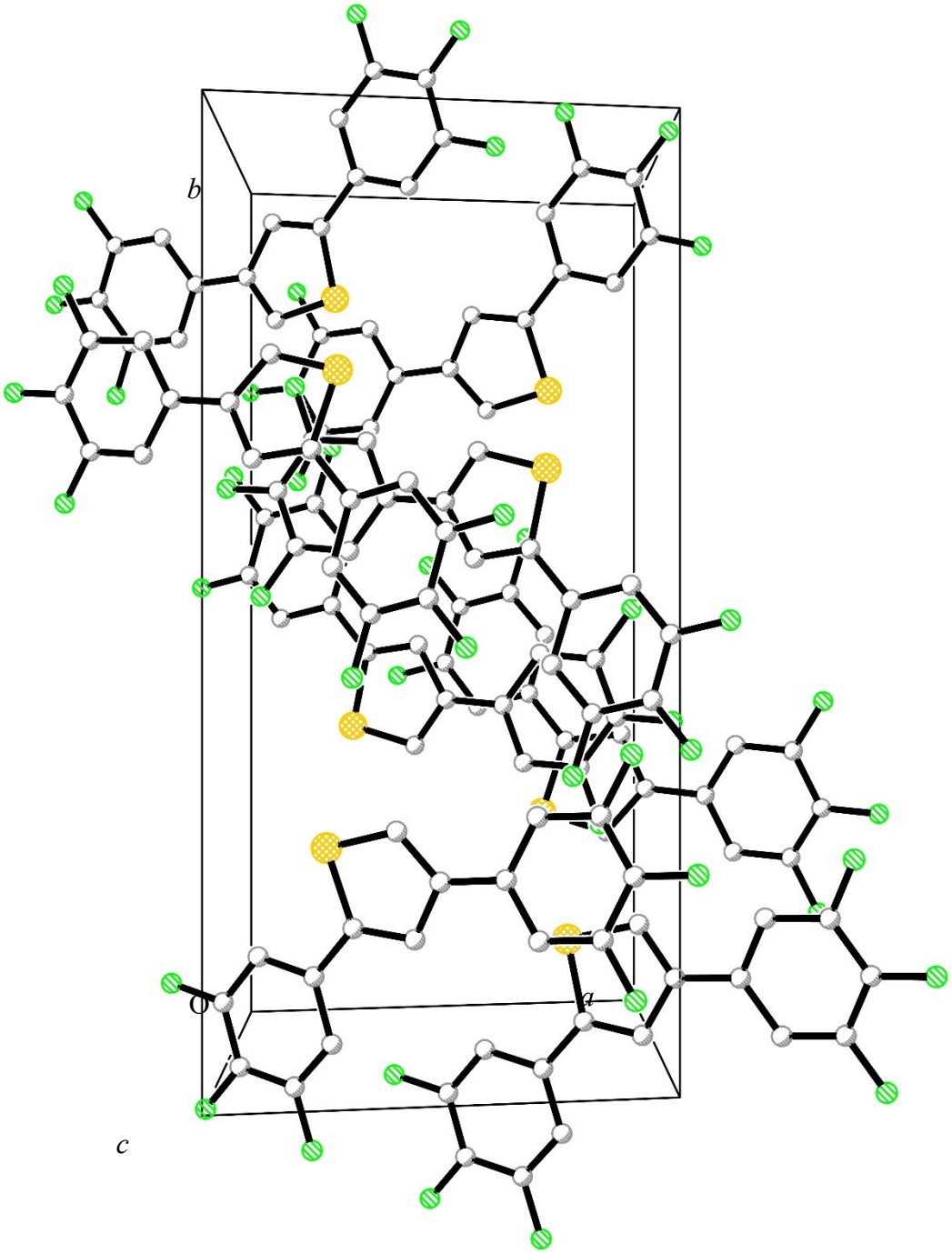
ORTEP drawing of $C_{16}H_6F_6S$ with 50% probability ellipsoids, showing the atomic numbering scheme.



A view to show the diorientational disorder of thiophene group in molecule **I**, solid bonds for an orientation and open bonds for another.



A view to show the diorientational disorder of thiophene group in molecule **II**, solid bonds for an orientation and open bonds for another.



A packing view along the *c* direction

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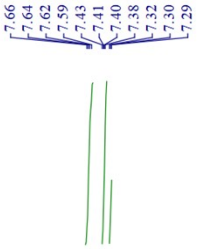
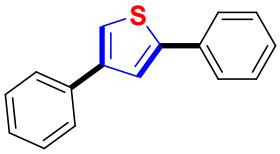
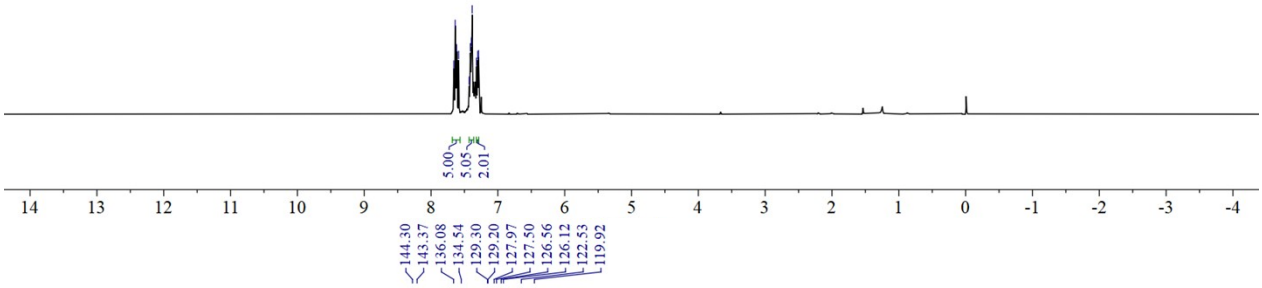
1H and 13C NMR Spectra

2,4-Diphenylthiophene (2a)

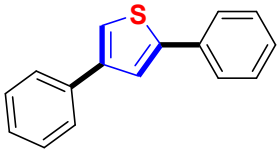


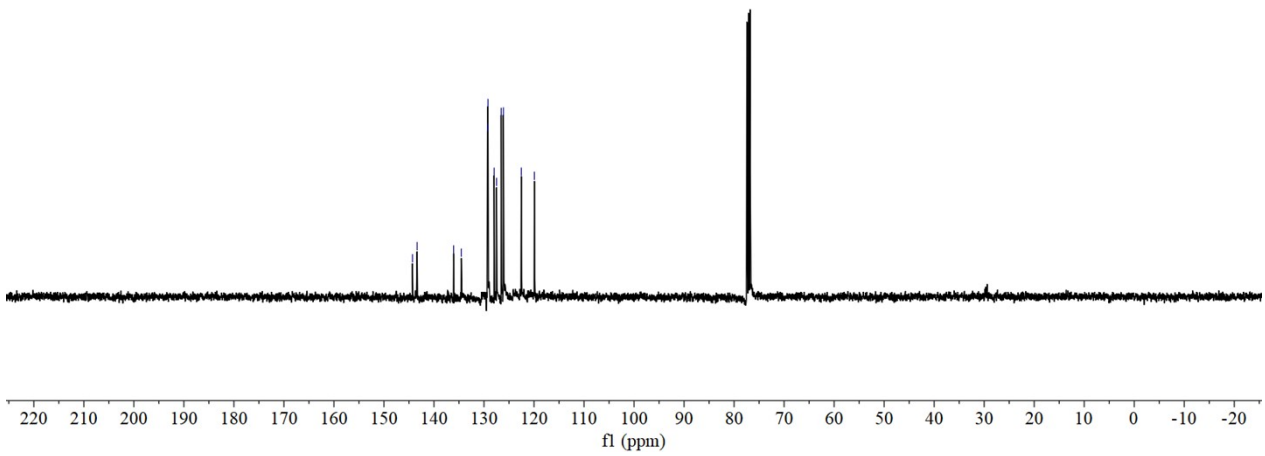
$CDCl_3$, ^{1}HNMR, 400 MHz





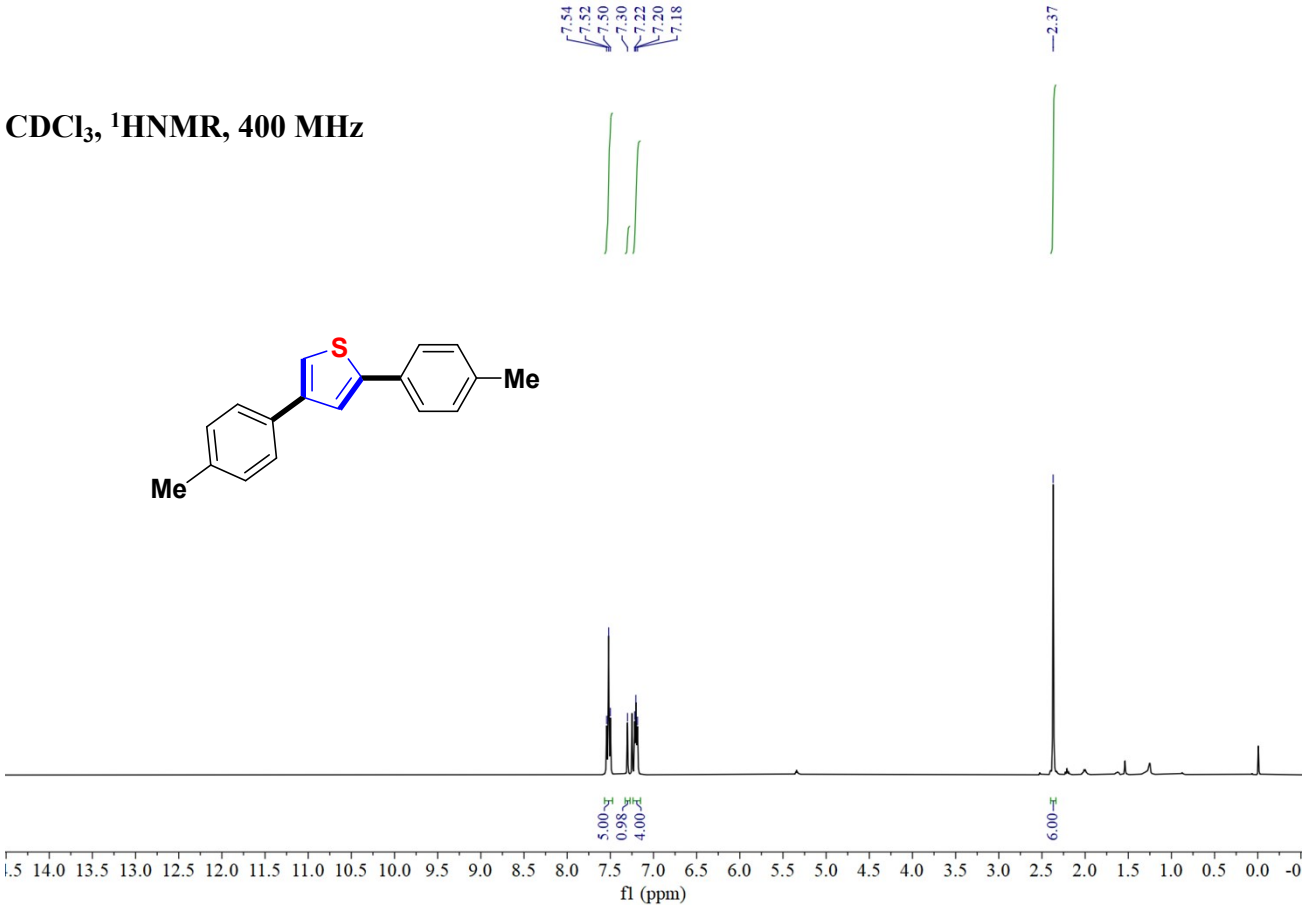
$CDCl_3$, ^{13}CNMR, 101 MHz



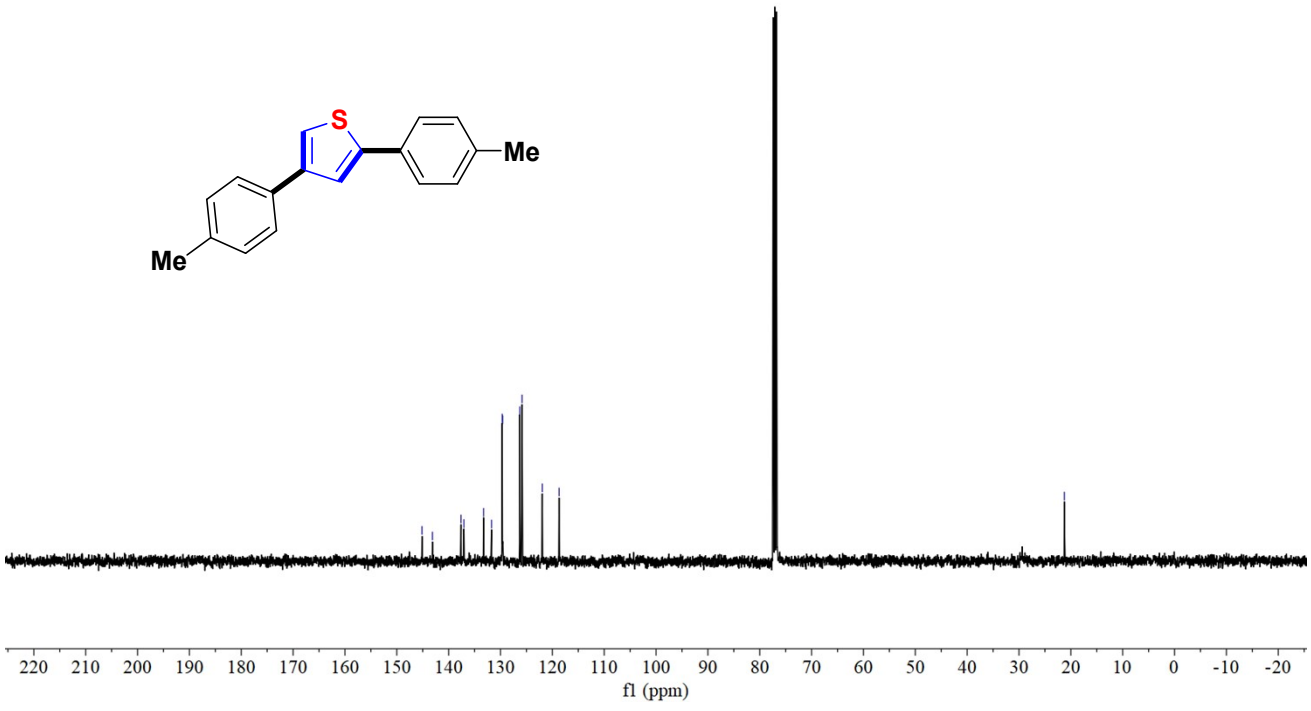


2,4-Di-*p*-tolylthiophene (2b)

$CDCl_3$, ^{1}HNMR, 400 MHz

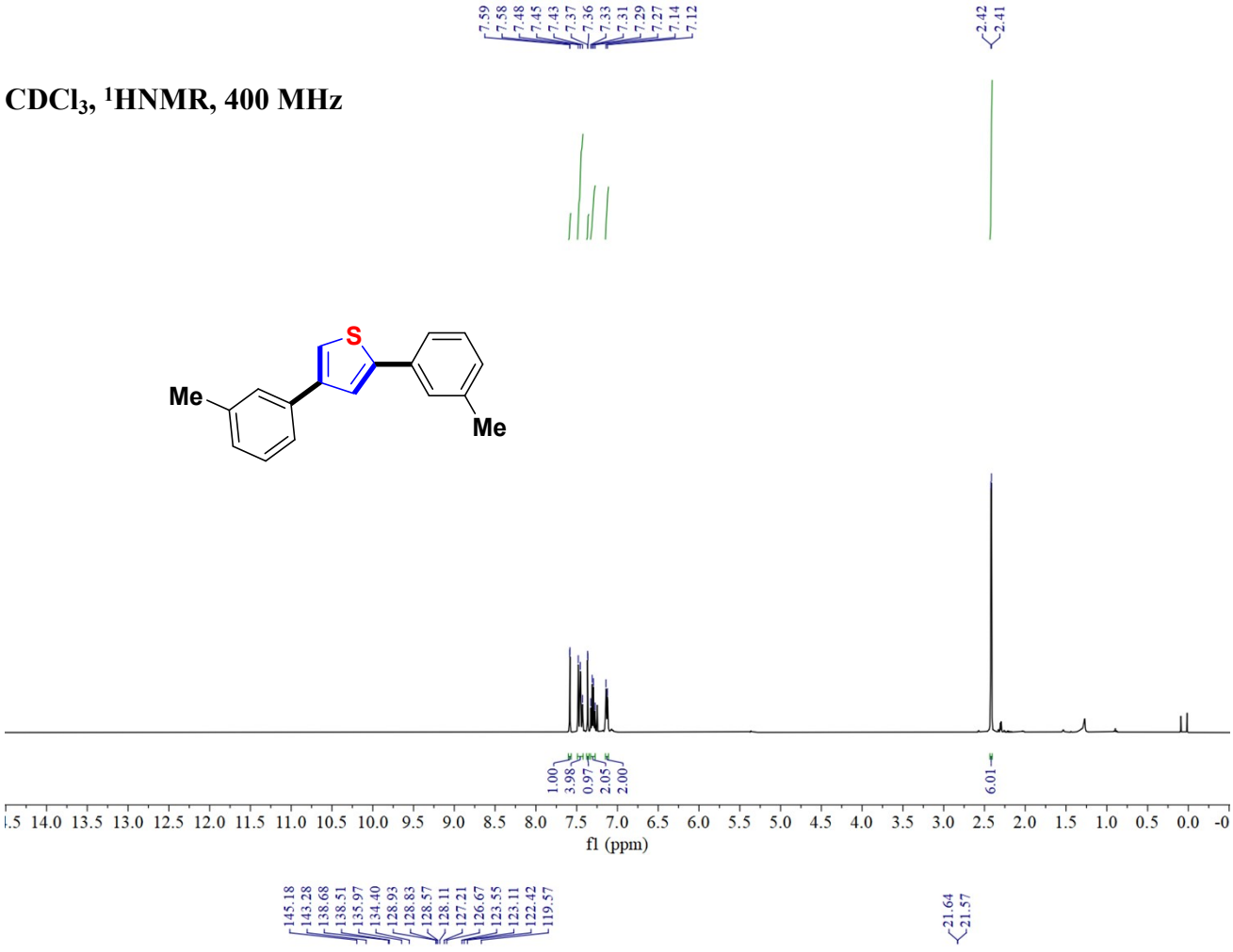


$CDCl_3$, ^{13}CNMR, 101 MHz

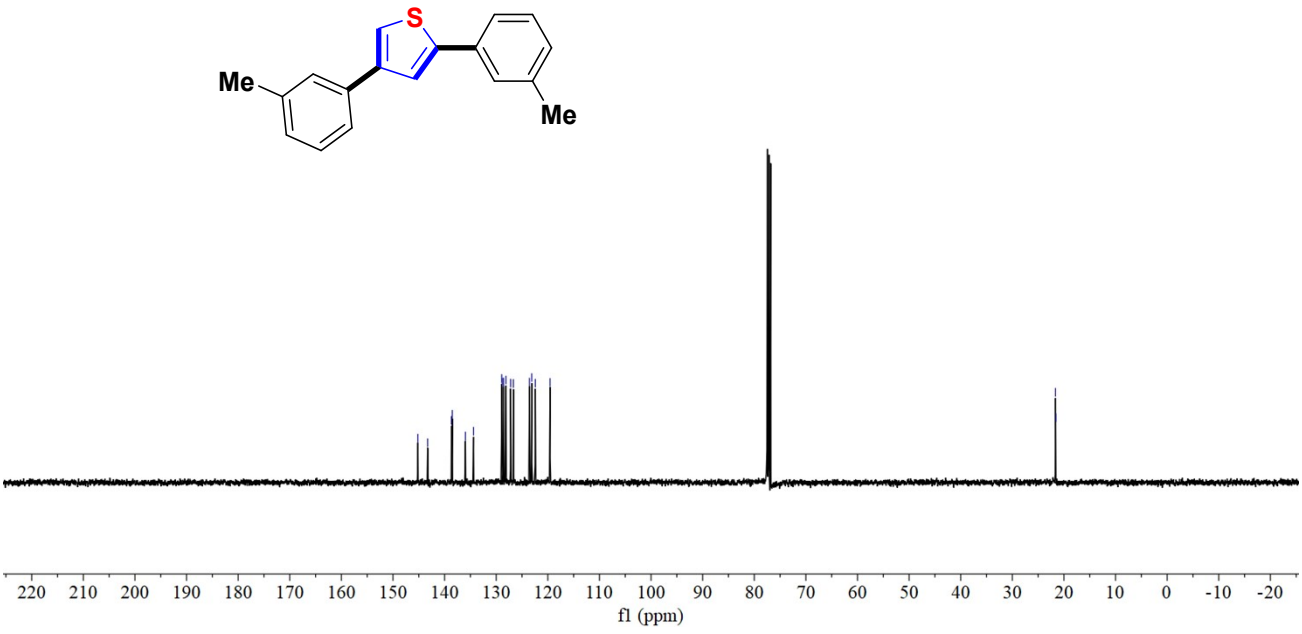


2,4-Di-*m*-tolylthiophene (2c)

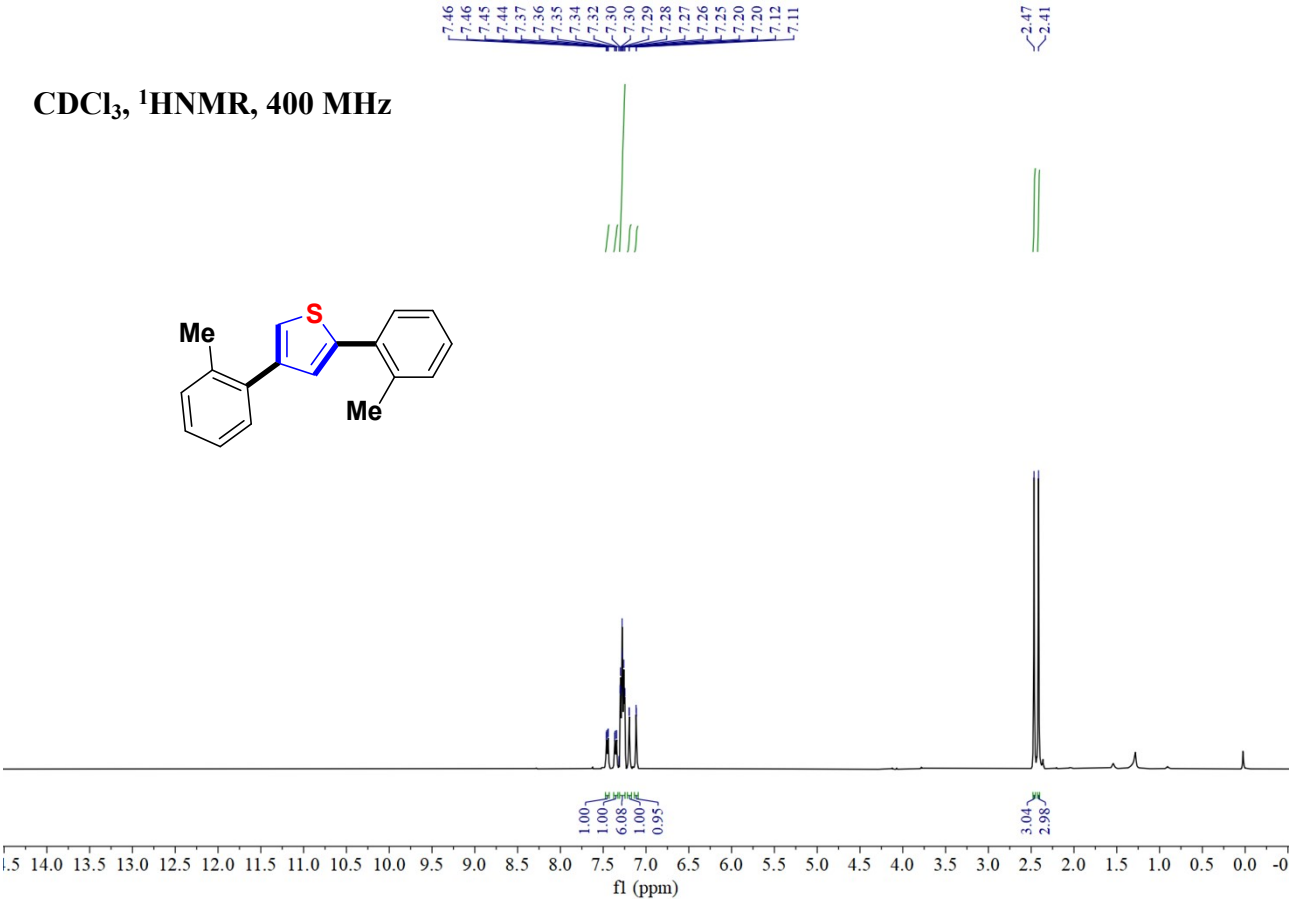
$CDCl_3$, ^{1}HNMR, 400 MHz



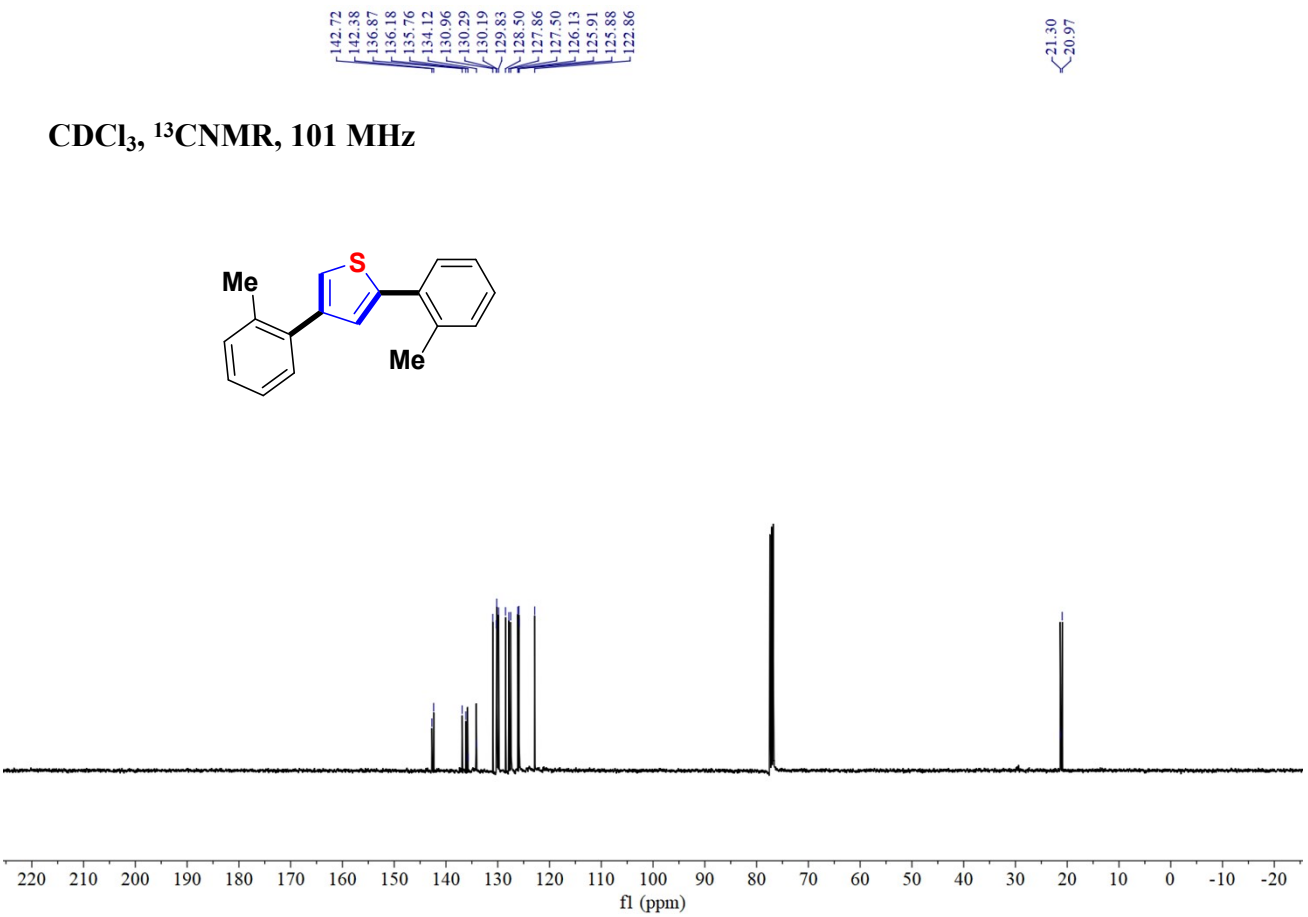
$CDCl_3$, ^{13}CNMR, 101 MHz



2,4-Di-*o*-tolylthiophene (2d)

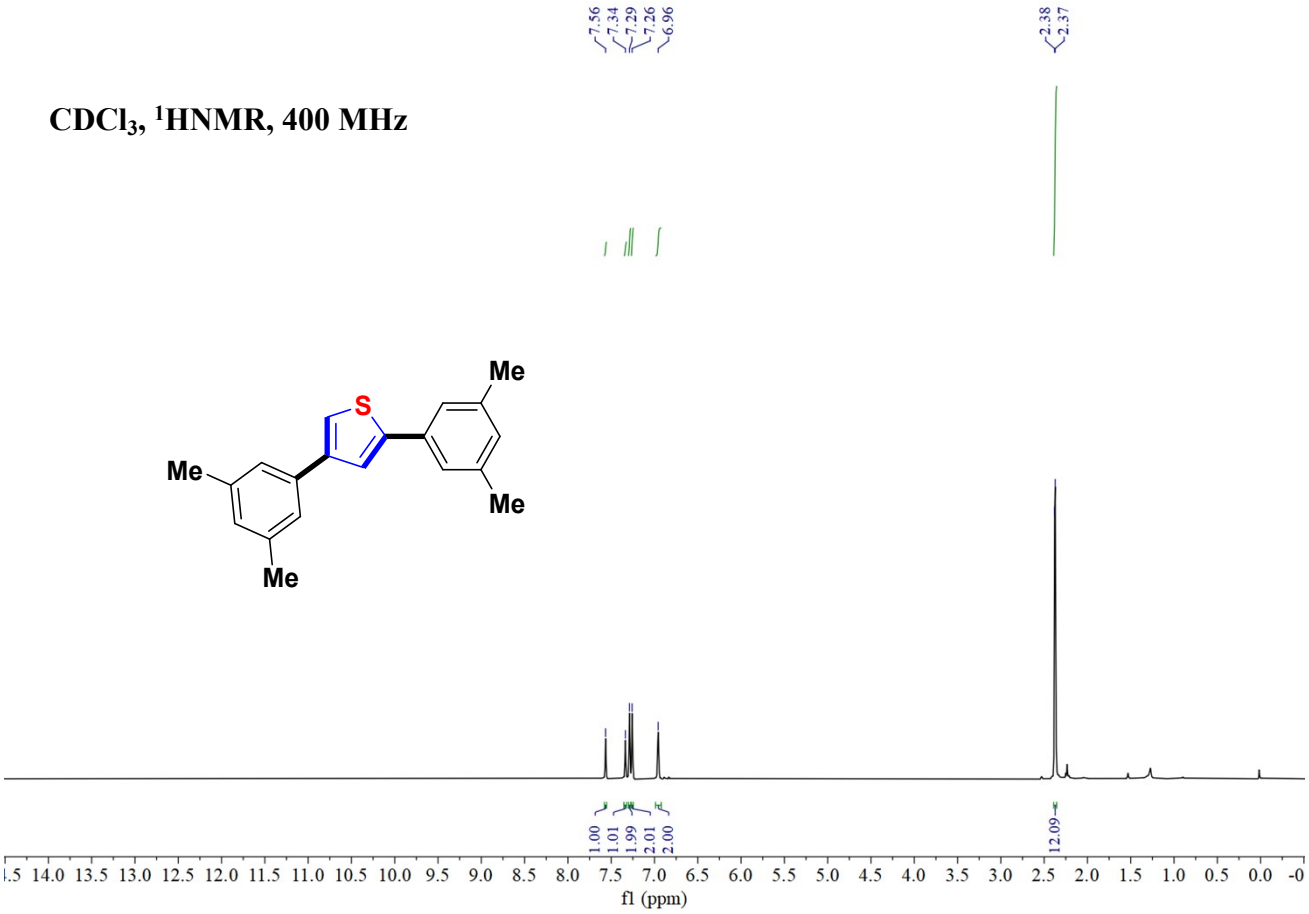


$CDCl_3$, ^{1}HNMR, 400 MHz

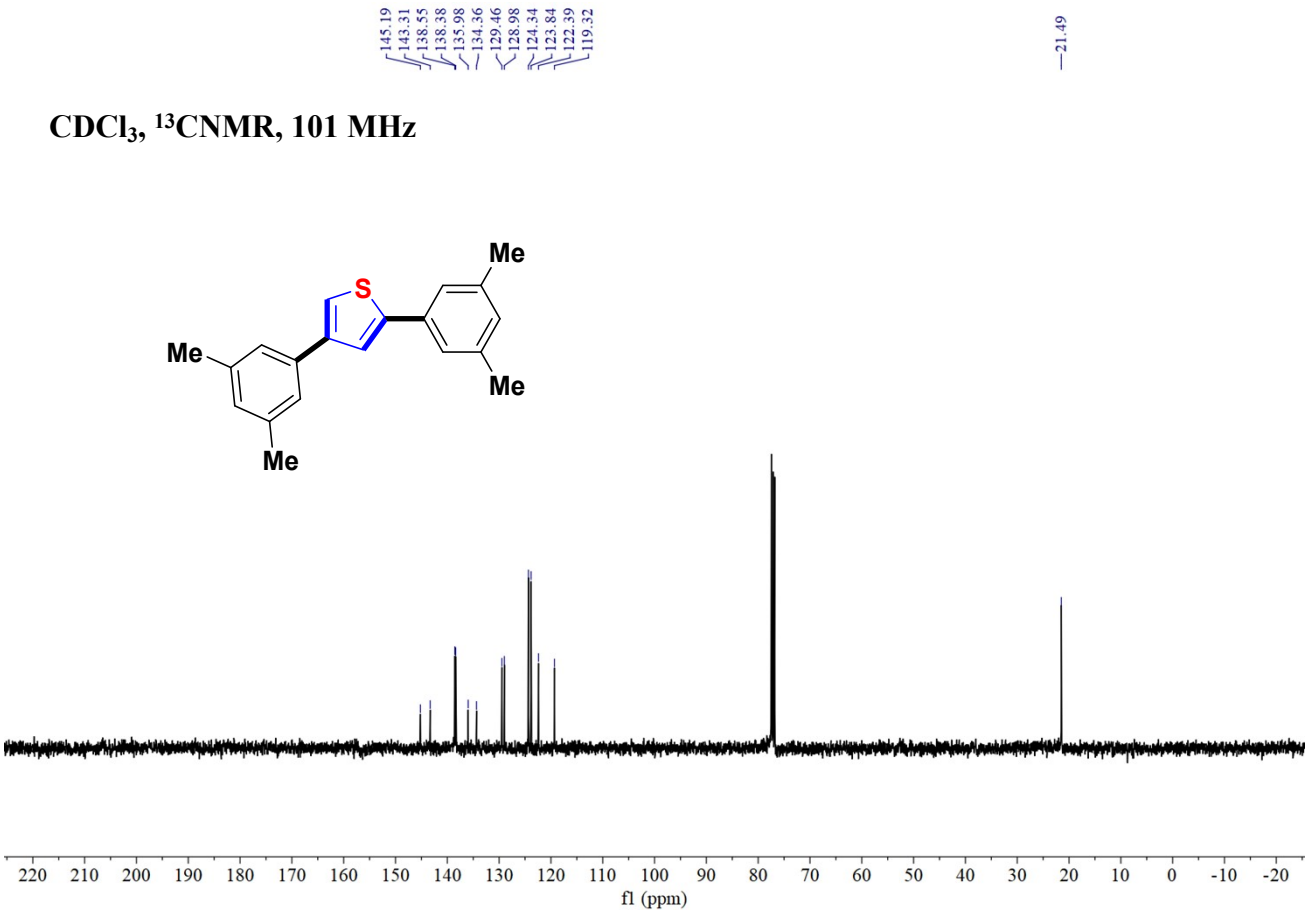


$CDCl_3$, ^{13}CNMR, 101 MHz

2,4-Di-(3, 5-dimethylphenyl)-thiophene (2e)

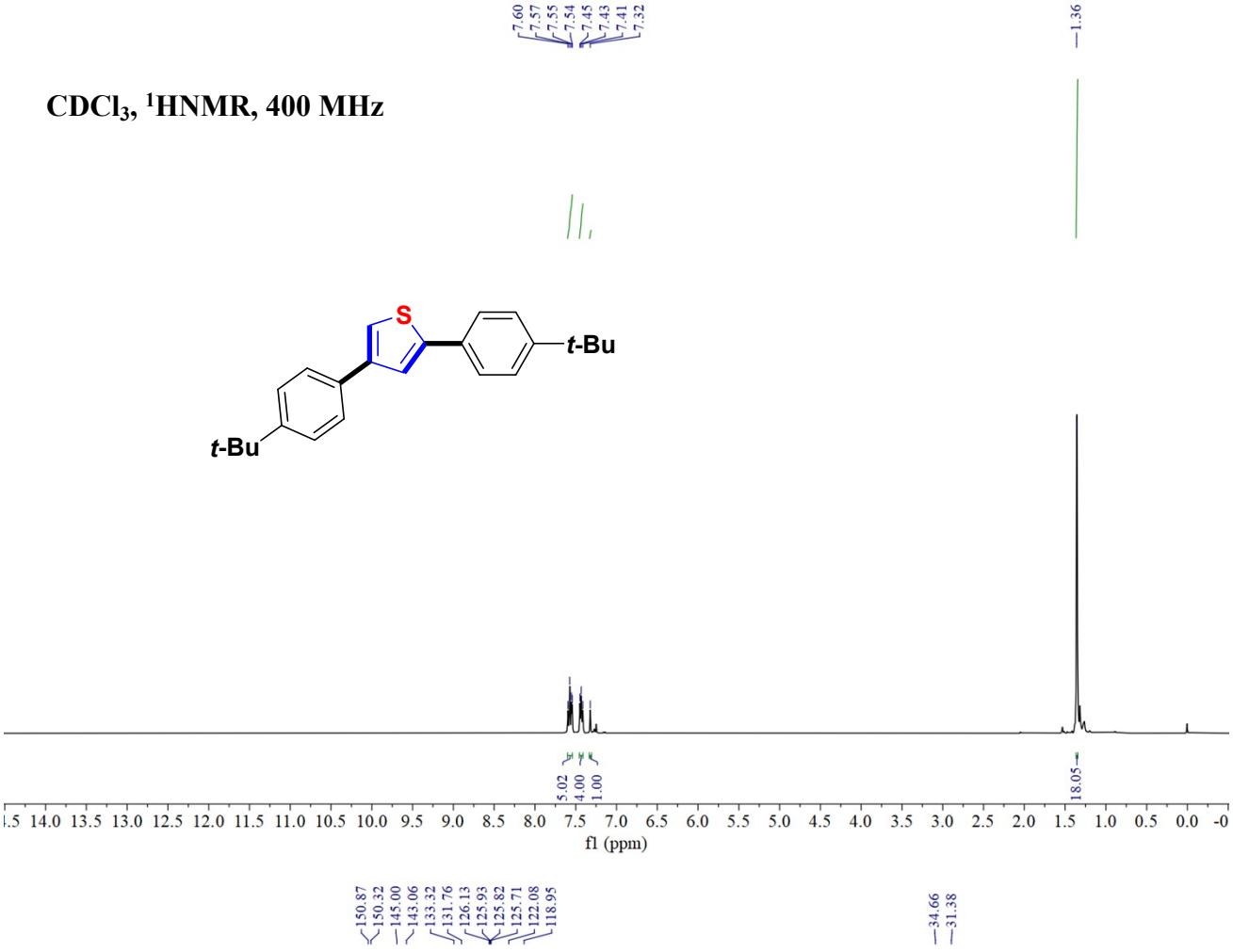


$CDCl_3$, ^{1}HNMR, 400 MHz

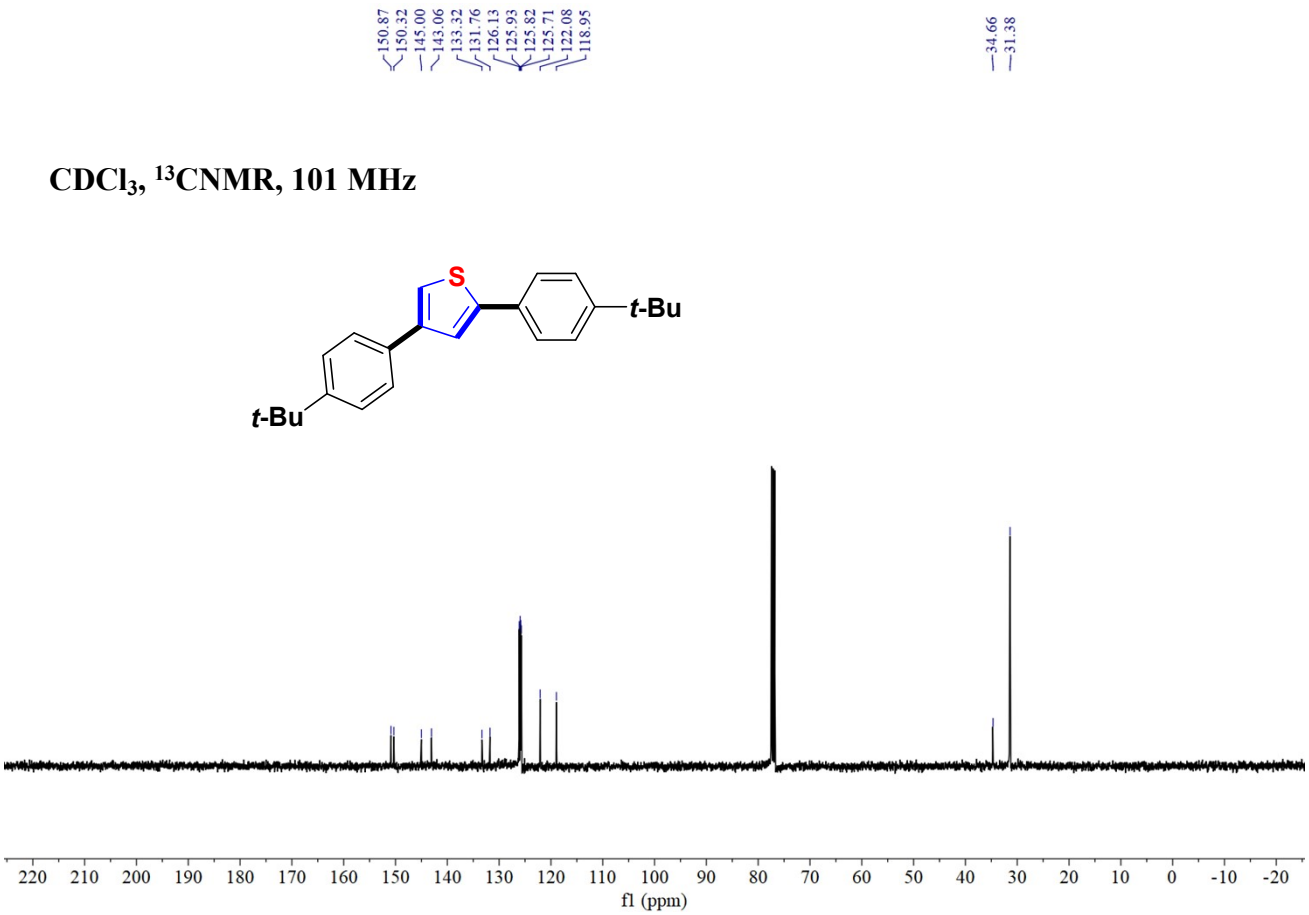


$CDCl_3$, ^{13}CNMR, 101 MHz

2,4-Di-(4-(tert-butylphenyl)-thiophene (2f)



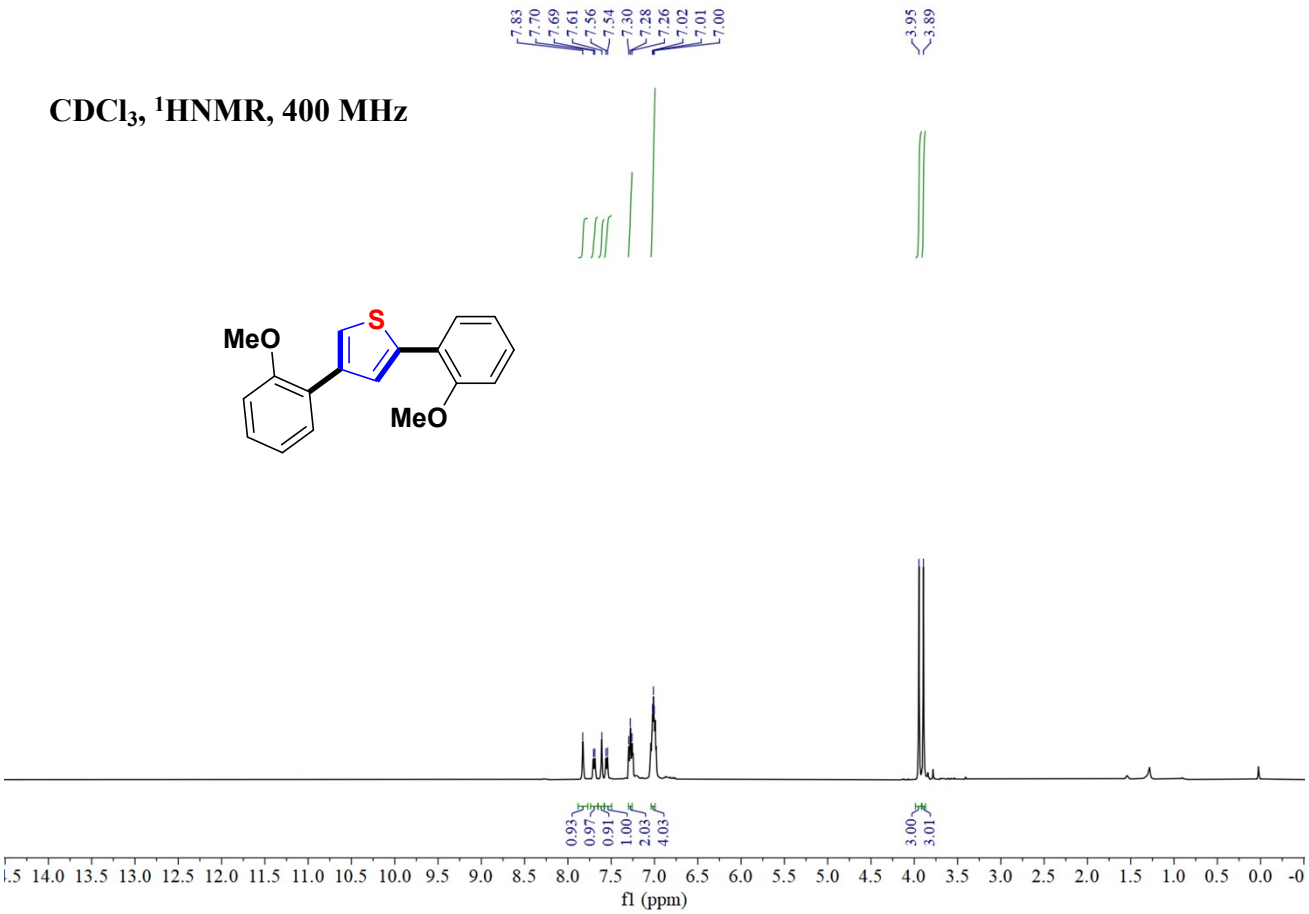
$CDCl_3$, ^{1}HNMR, 400 MHz



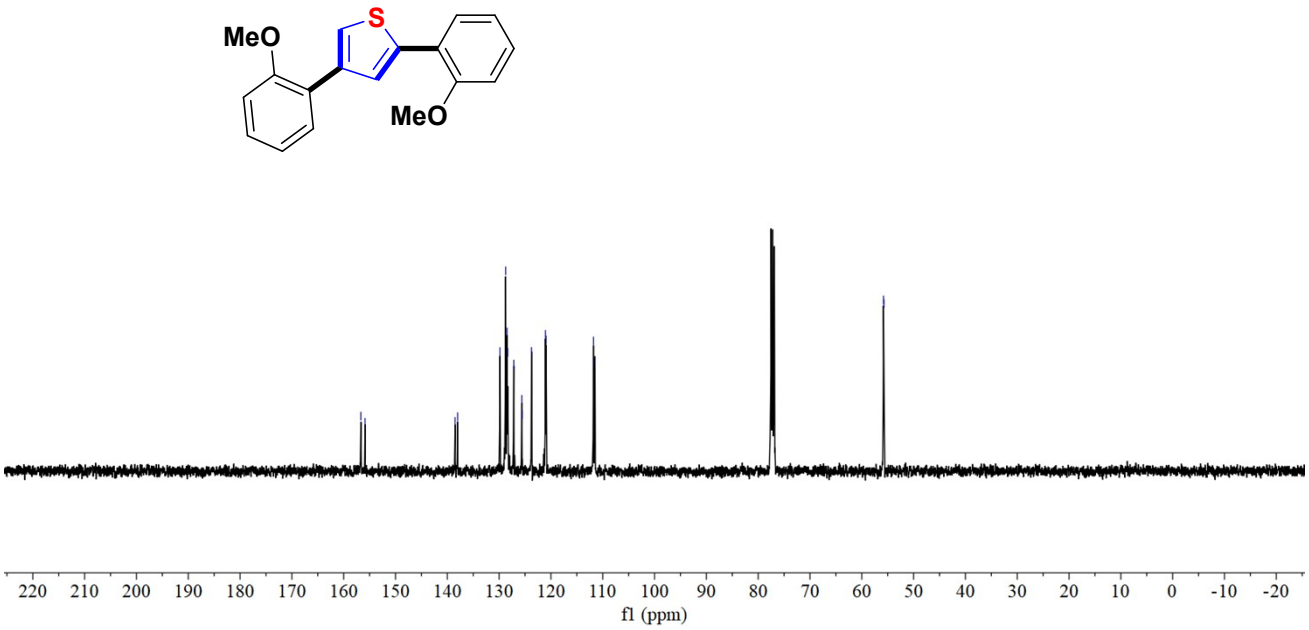
$CDCl_3$, ^{13}CNMR, 101 MHz

2,4-Di-(2-methoxyphenyl)-thiophene (2g)

$CDCl_3$, ^{1}HNMR, 400 MHz

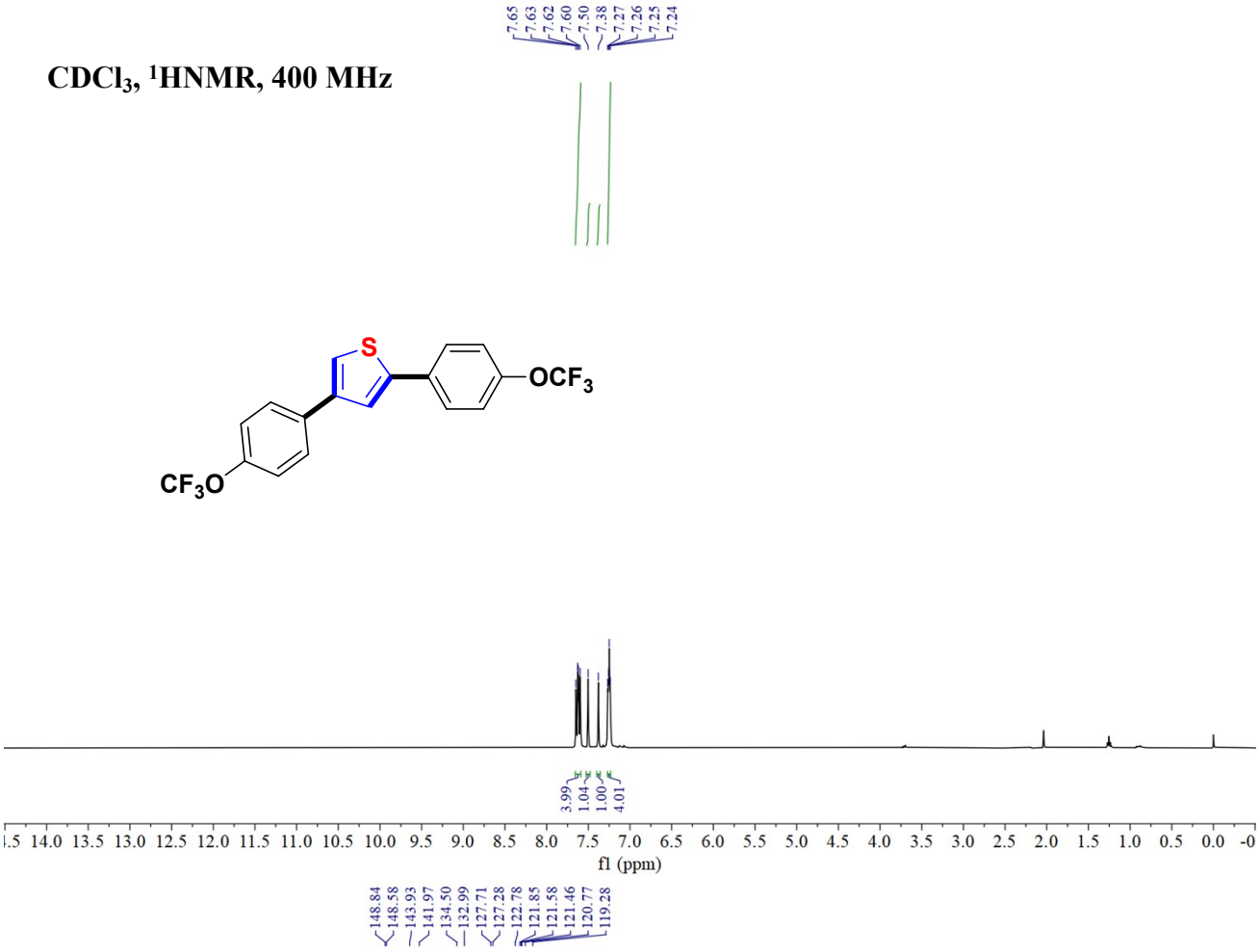


$CDCl_3$, ^{13}CNMR, 101 MHz

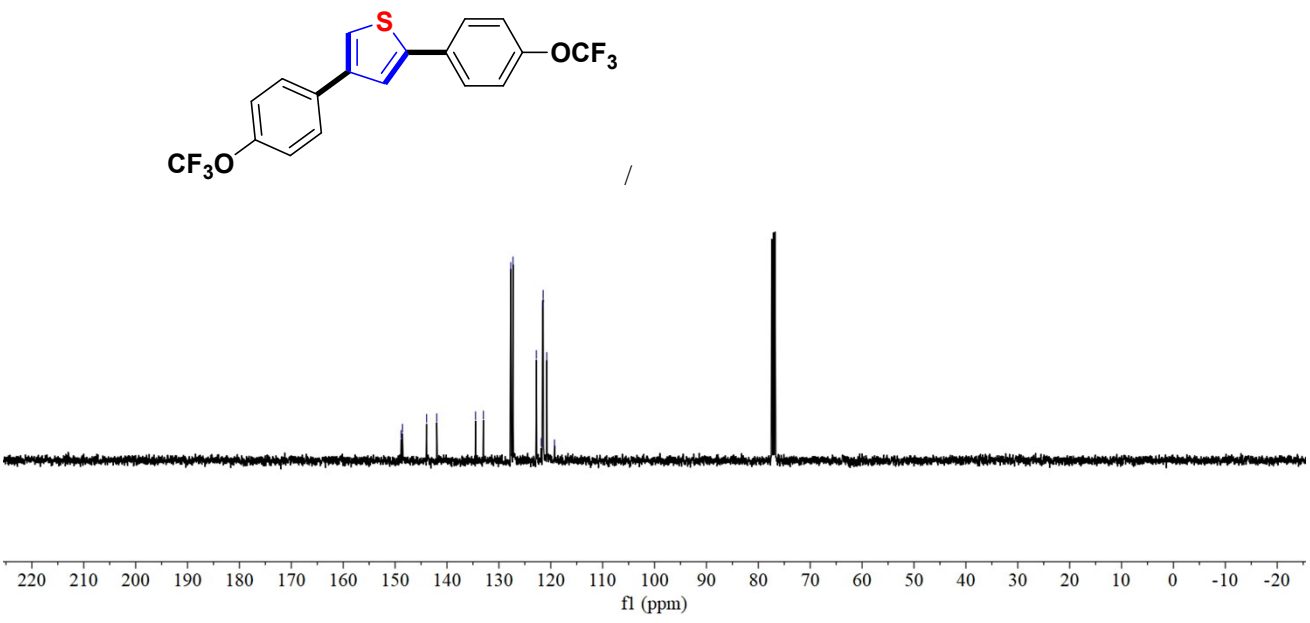


2,4-Di-(4-trifluoromethoxyphenyl)-thiophene (2h)

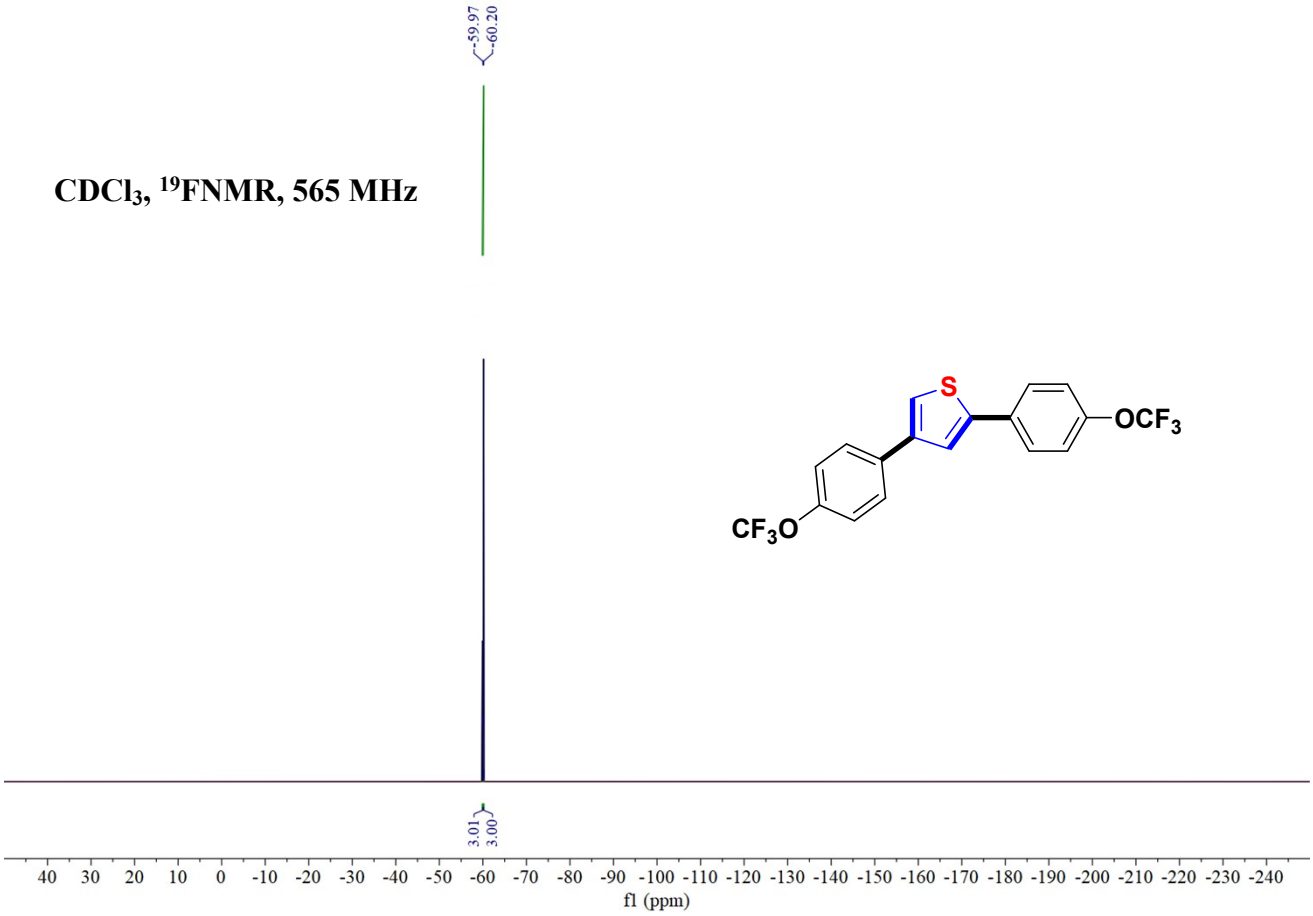
$CDCl_3$, ^{1}HNMR, 400 MHz



$CDCl_3$, ^{13}CNMR, 101 MHz

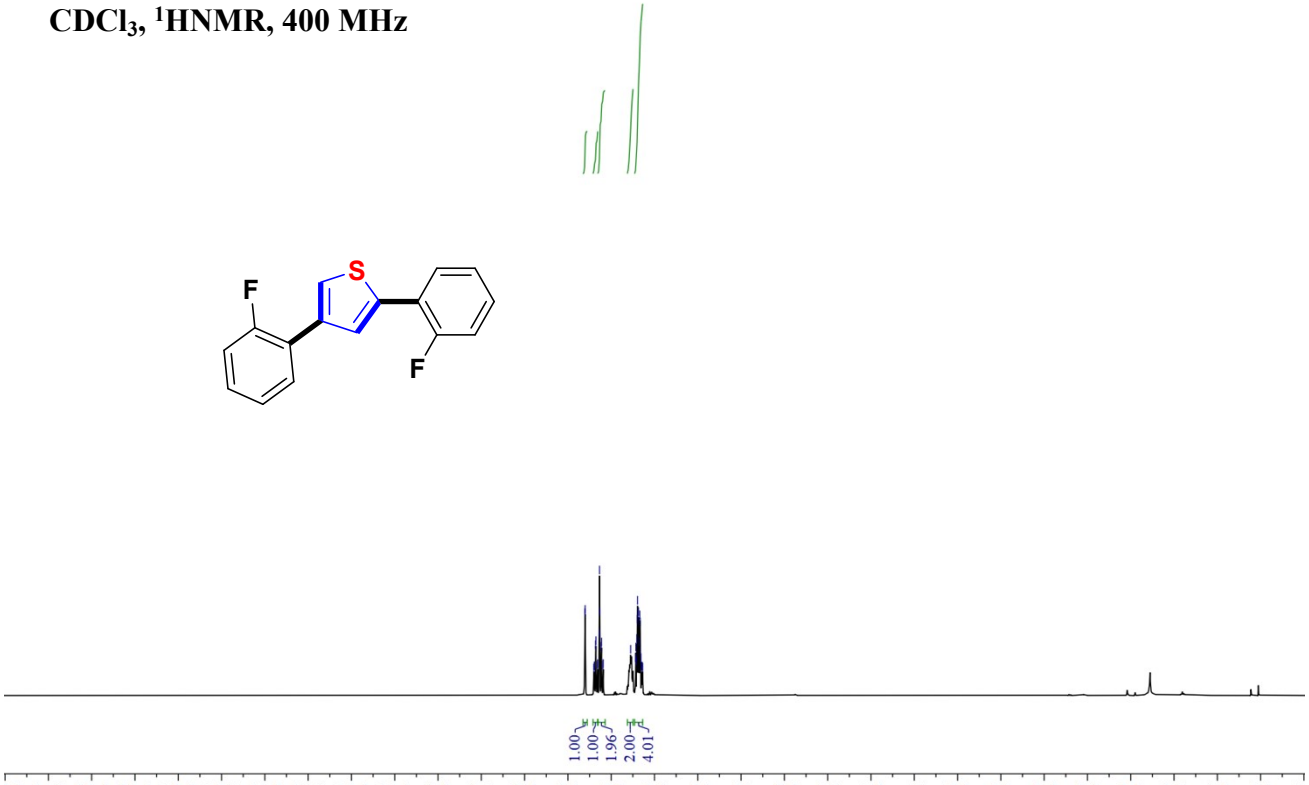


$CDCl_3$, ^{19}FNMR, 565 MHz

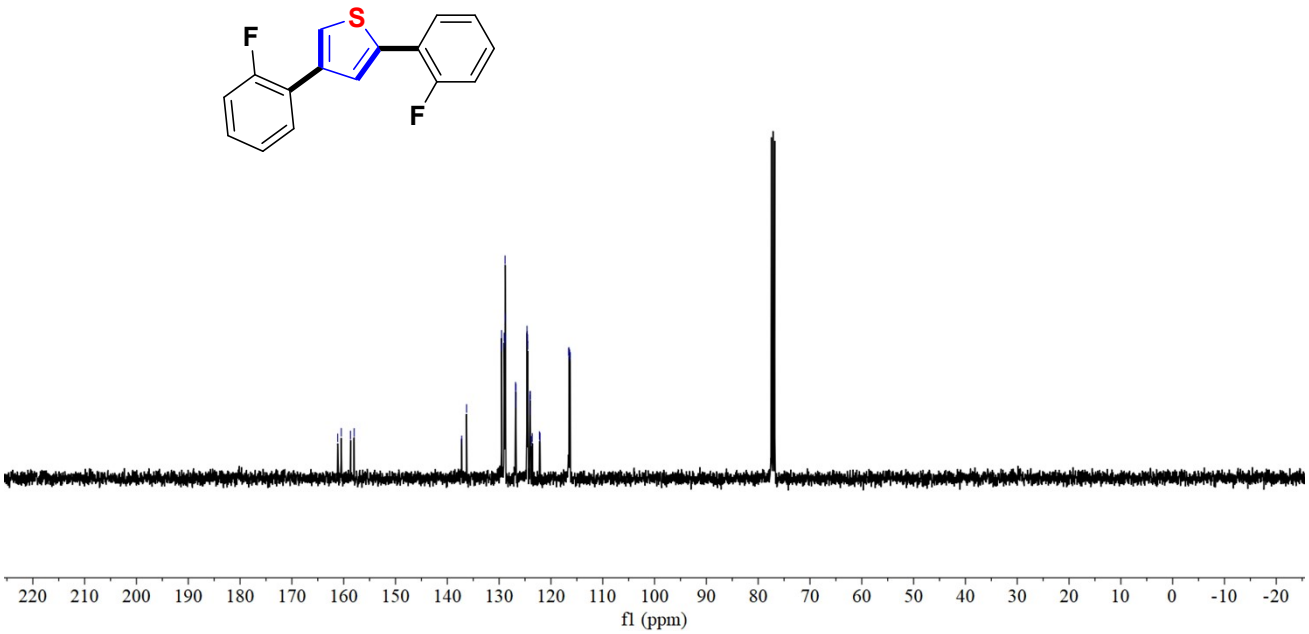


2,4-Di-(2-fluorophenyl)-thiophene (2i)

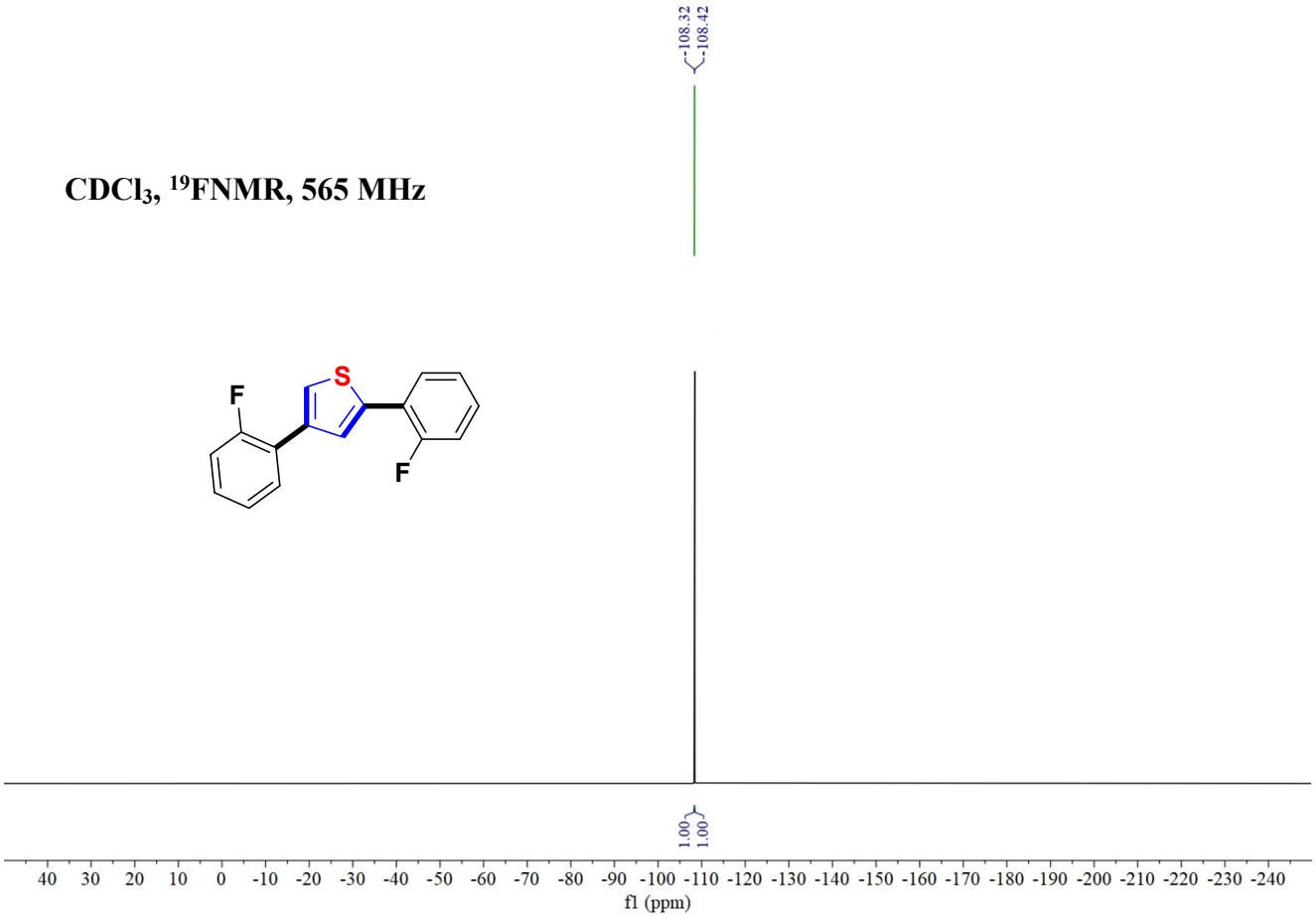
$CDCl_3$, ^{1}HNMR, 400 MHz



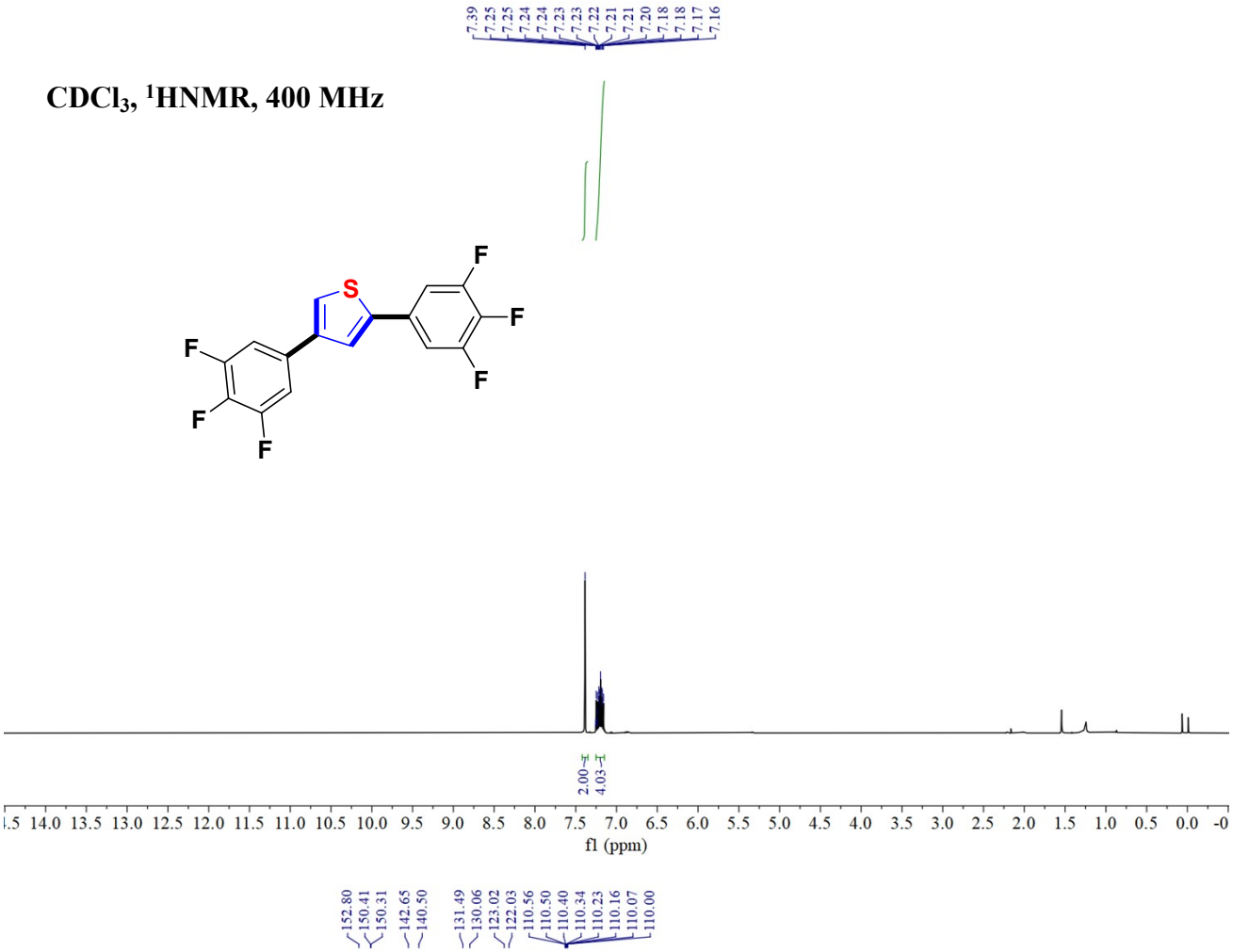
$CDCl_3$, ^{13}CNMR, 101 MHz



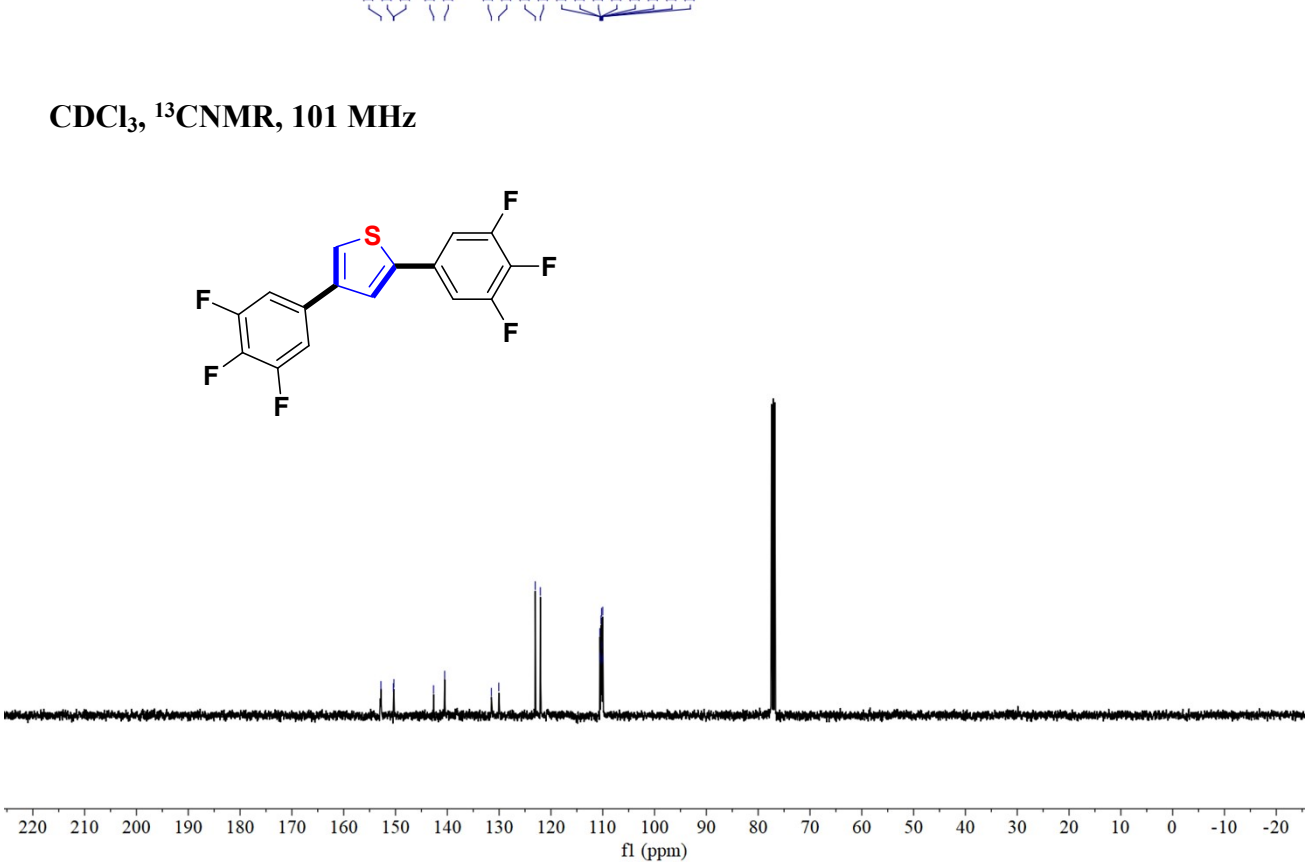
$CDCl_3$, ^{19}FNMR, 565 MHz



2,4-Di-(3,4,5-trifluorophenyl)-thiophene (2j)

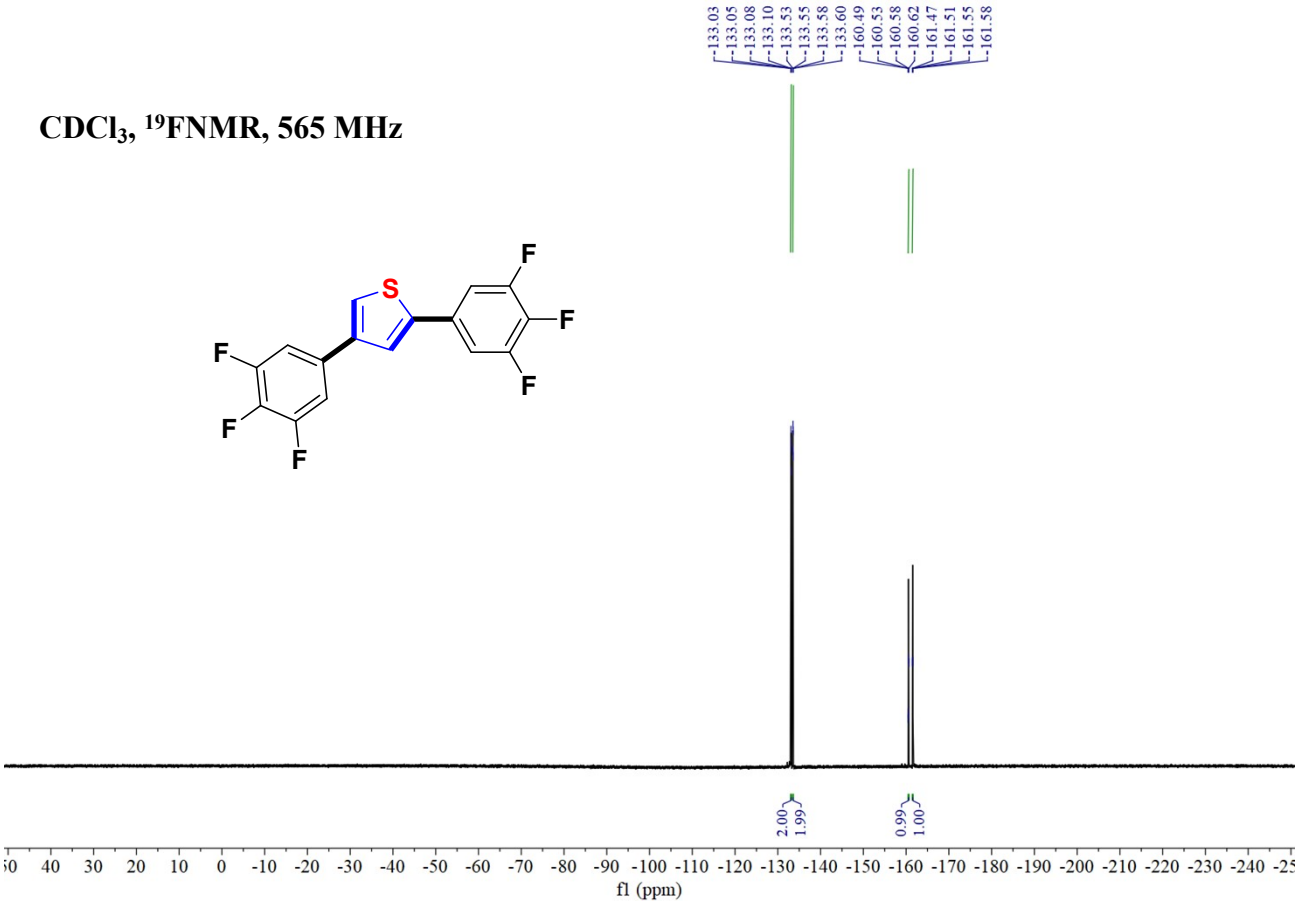


$CDCl_3$, ^{1}HNMR, 400 MHz



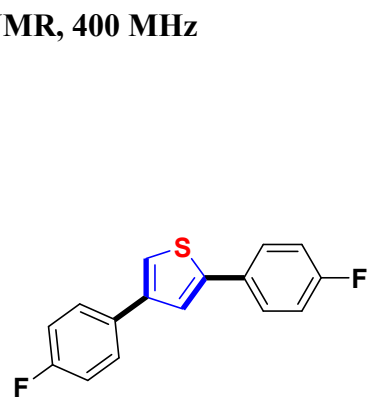
$CDCl_3$, ^{13}CNMR, 101 MHz

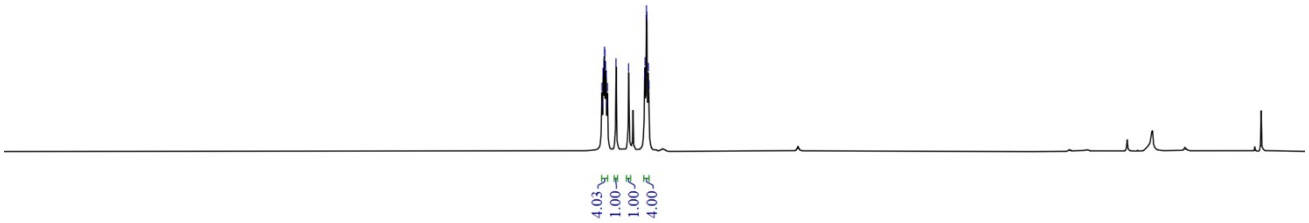
$CDCl_3$, ^{19}FNMR, 565 MHz

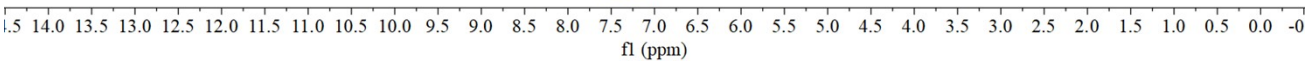


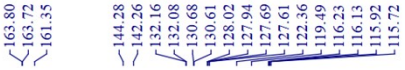
2,4-Di-(4-fluorophenyl)-thiophene (2k)

$CDCl_3$, ^{1}HNMR, 400 MHz

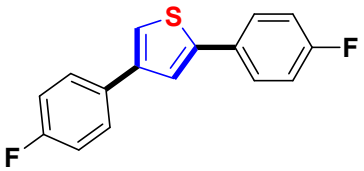


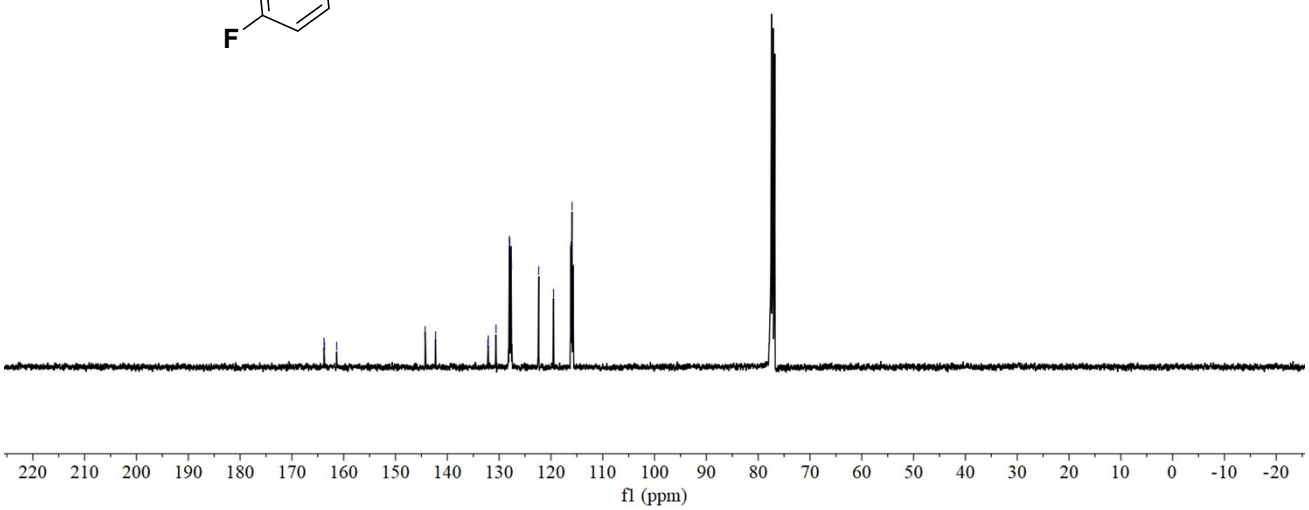




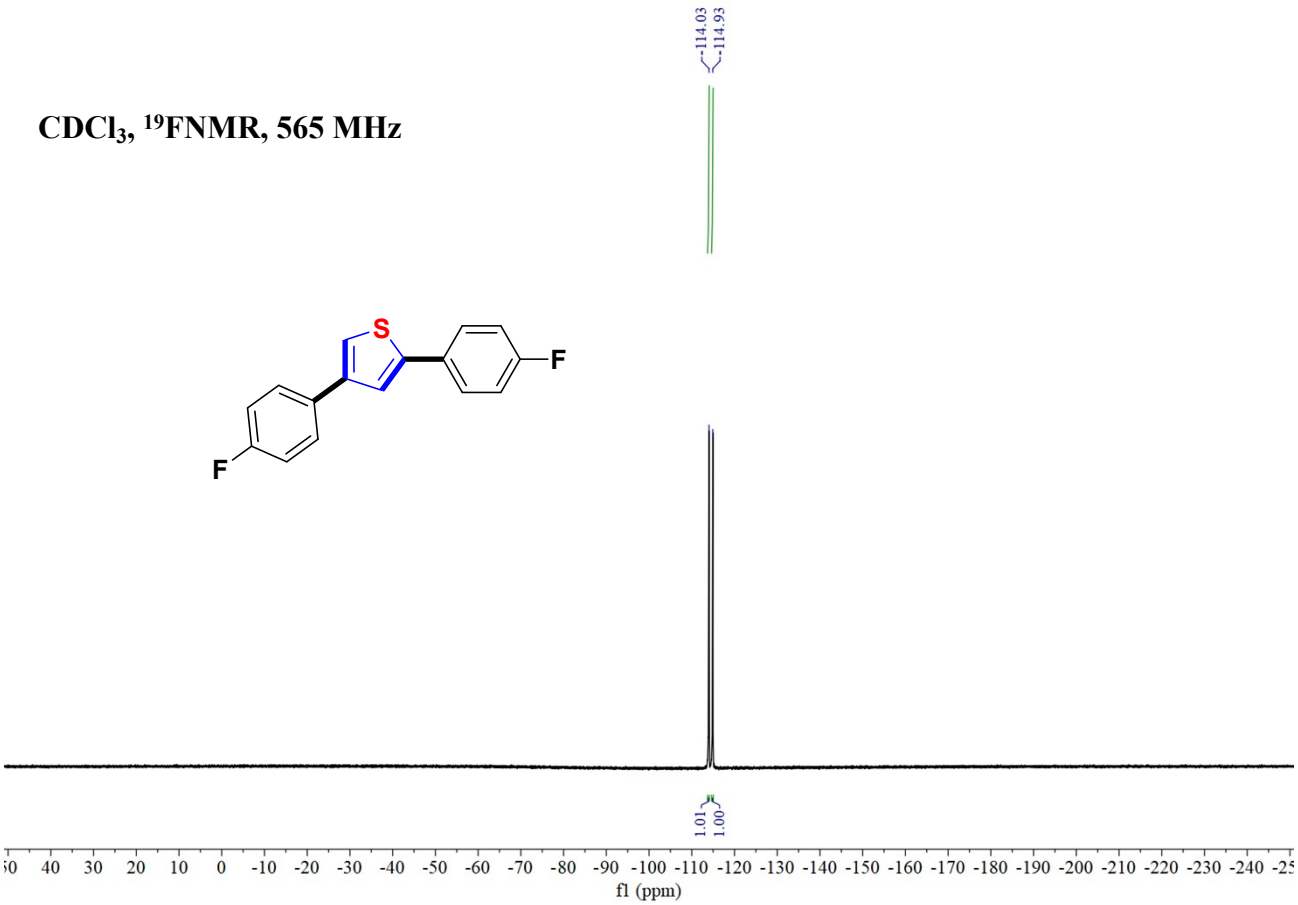


$CDCl_3$, ^{13}CNMR, 101 MHz



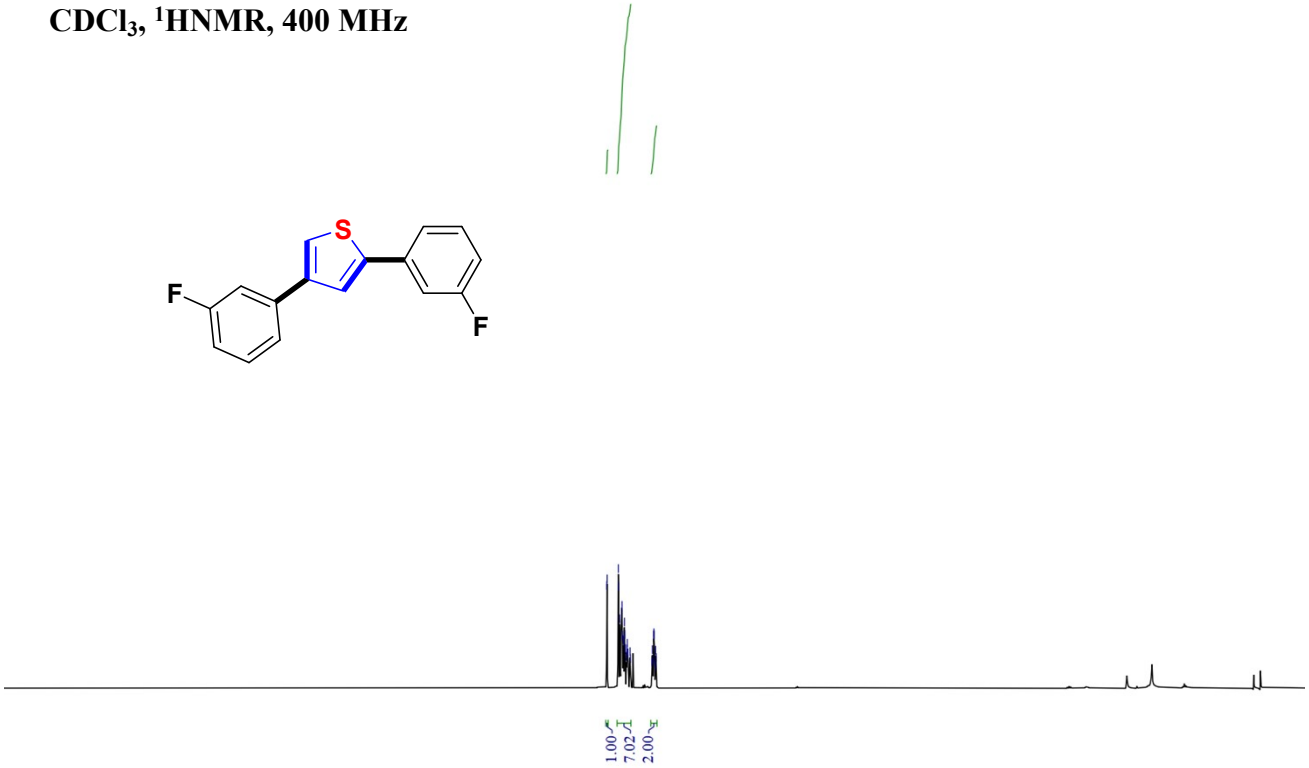


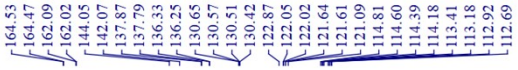
$CDCl_3$, ^{19}FNMR, 565 MHz



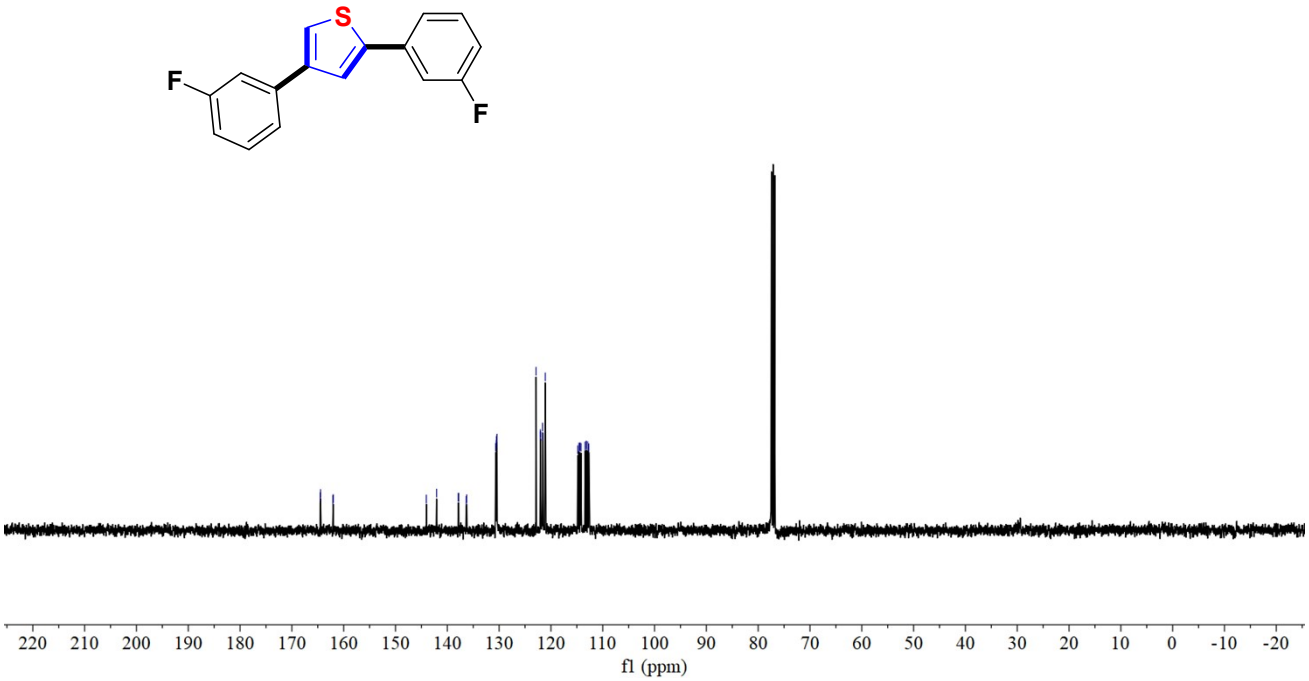
2,4-Di-(3-fluorophenyl)-thiophene (2l)

$CDCl_3$, ^{1}HNMR, 400 MHz

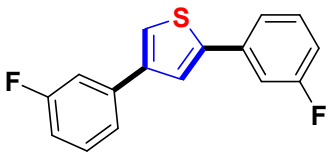




$CDCl_3$, ^{13}CNMR, 101 MHz

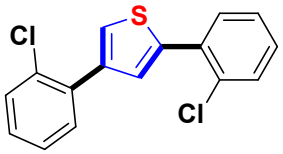


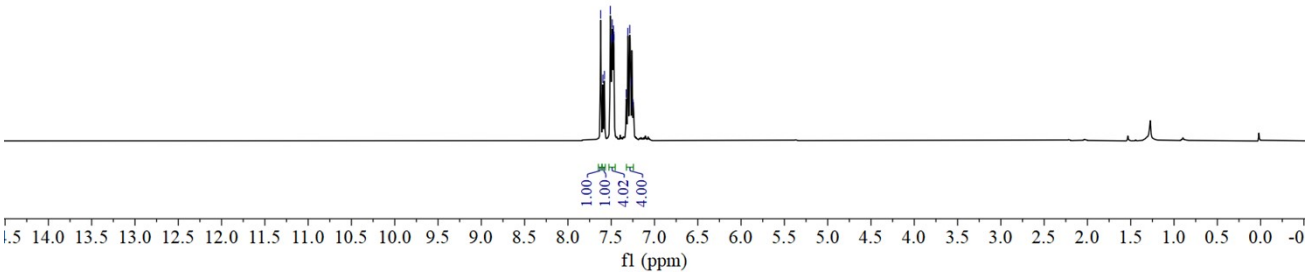
$CDCl_3$, ^{19}FNMR, 565 MHz



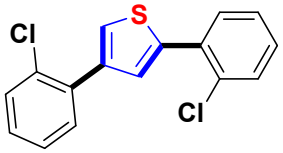
2,4-Di-(2-chlorophenyl)-thiophene (2m)

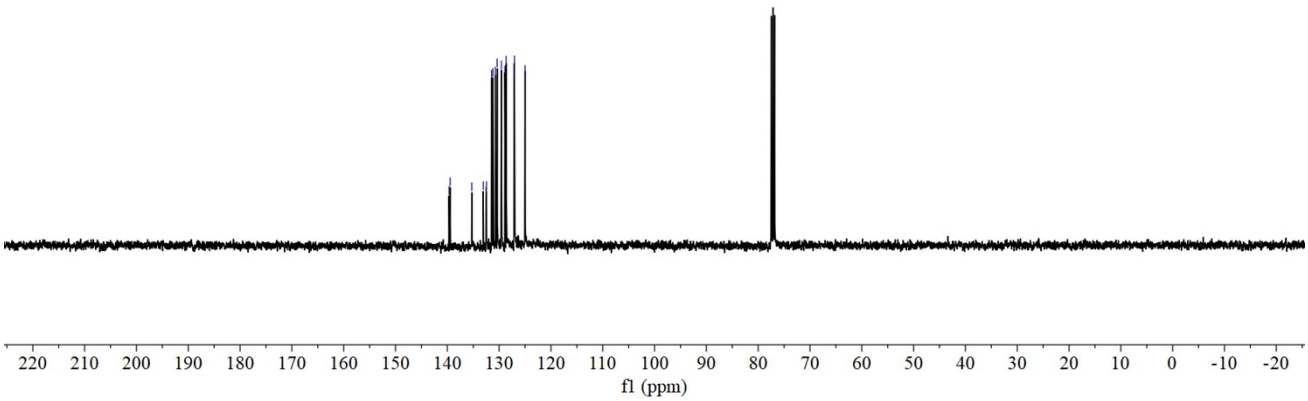
$CDCl_3$, ^{1}HNMR, 400 MHz





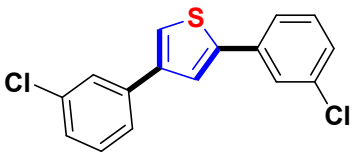
$CDCl_3$, ^{13}CNMR, 101 MHz

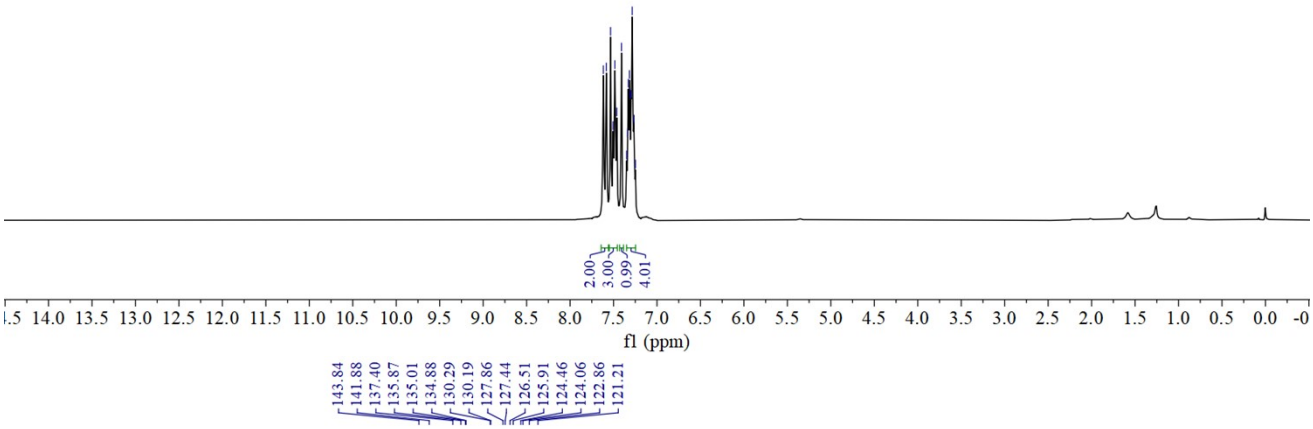




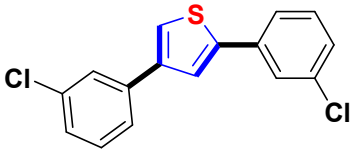
2,4-Di-(3-chlorophenyl)-thiophene (2n)

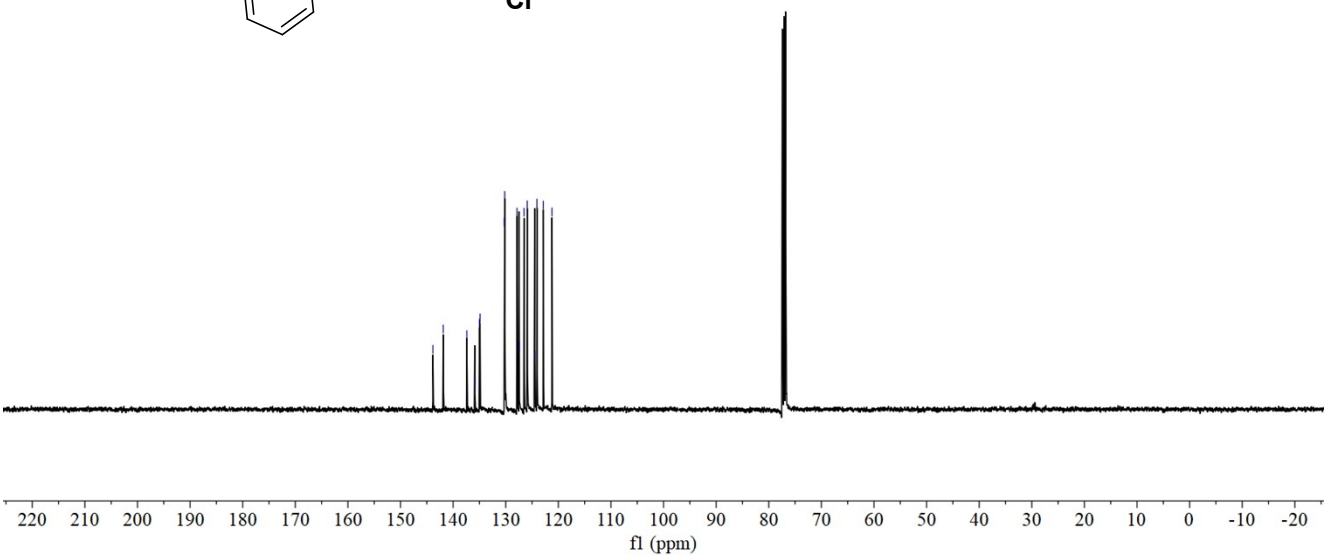
$CDCl_3$, ^{1}HNMR, 400 MHz





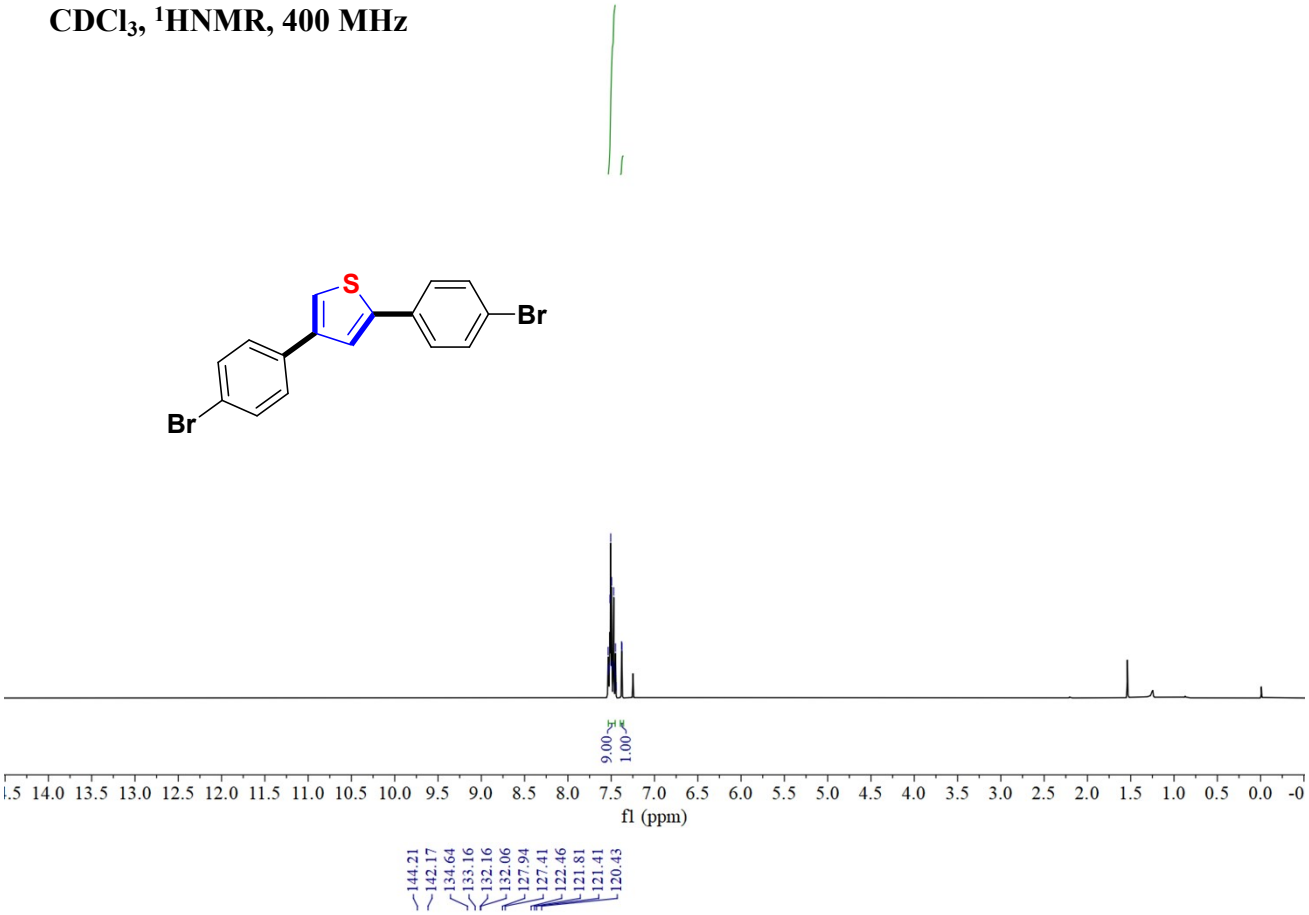
$CDCl_3$, ^{13}CNMR, 101 MHz



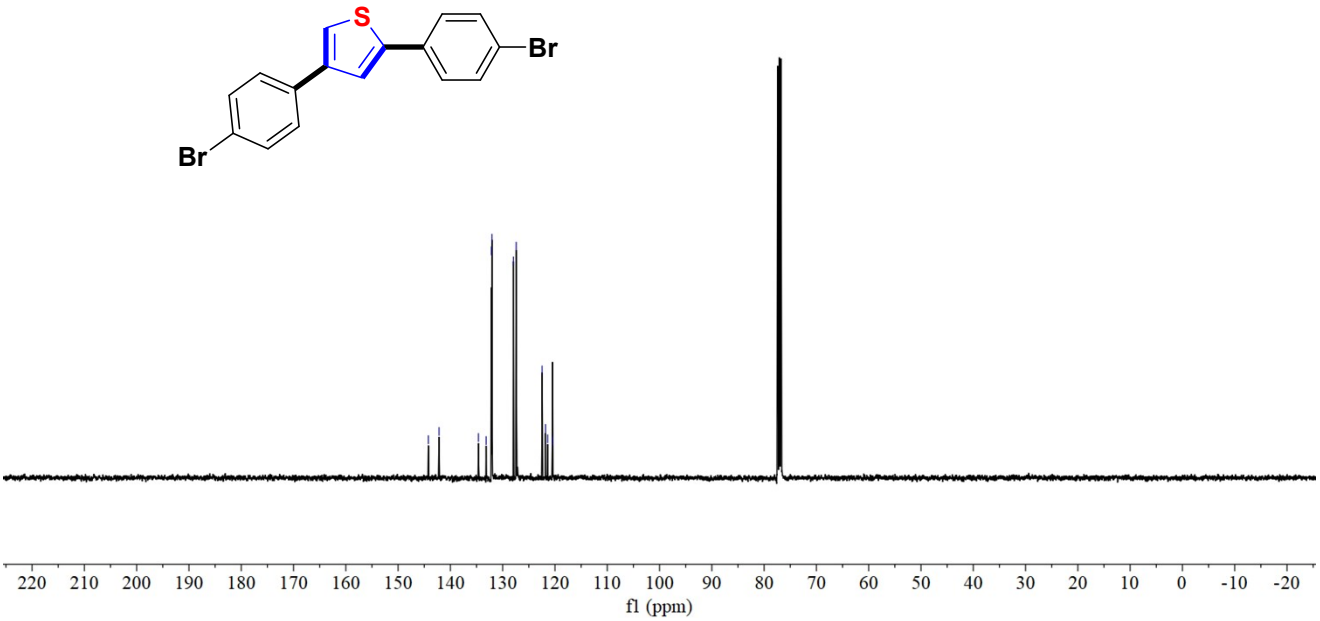


2,4-Di-(4-bromophenyl)-thiophene (2o)

$CDCl_3$, ^{1}HNMR, 400 MHz

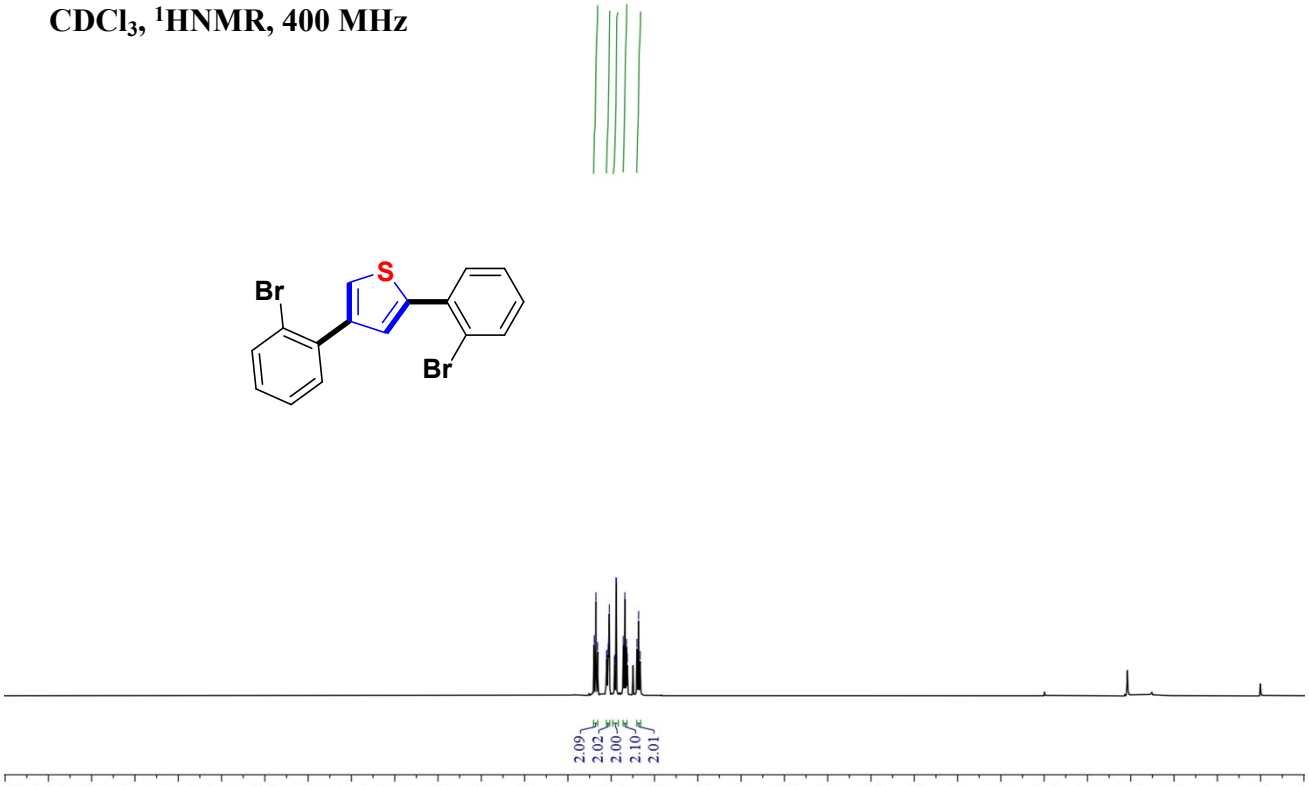


$CDCl_3$, ^{13}CNMR, 101 MHz

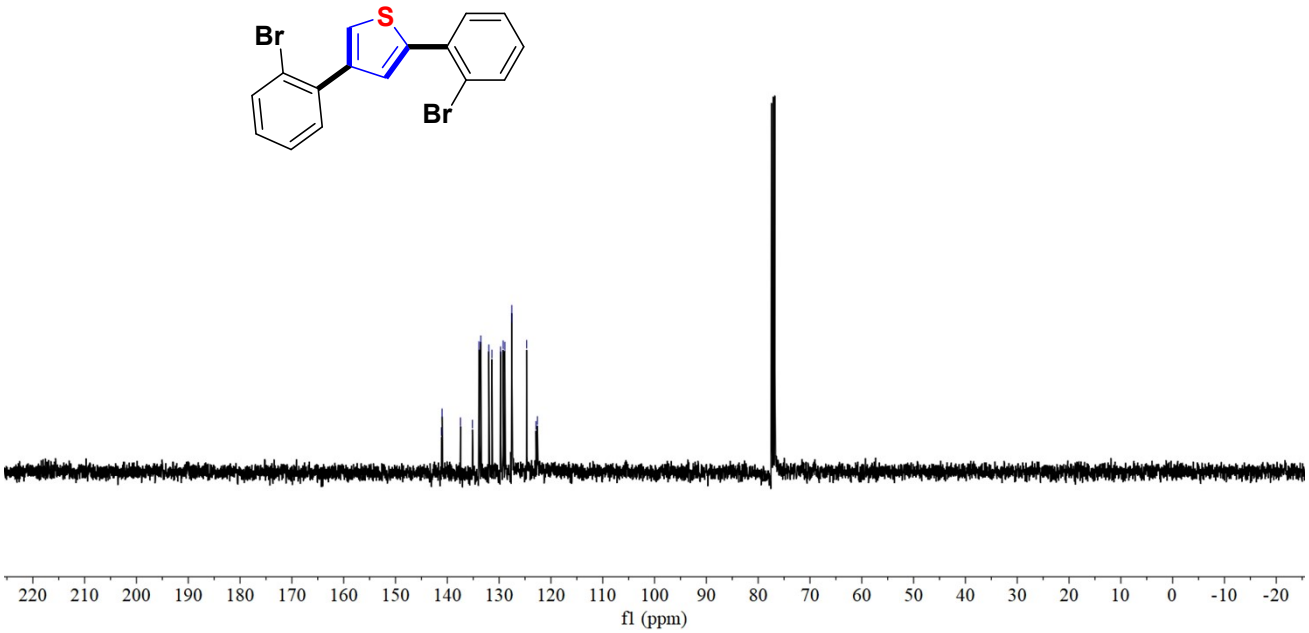


2,4-Di-(2-bromophenyl)-thiophene (2p)

$CDCl_3$, ^{1}HNMR, 400 MHz

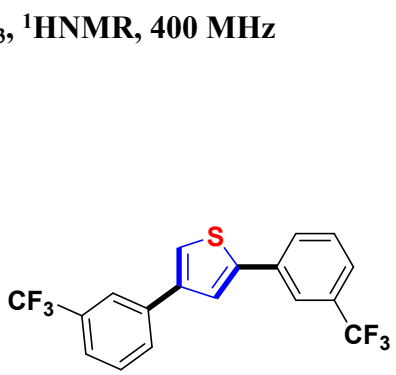


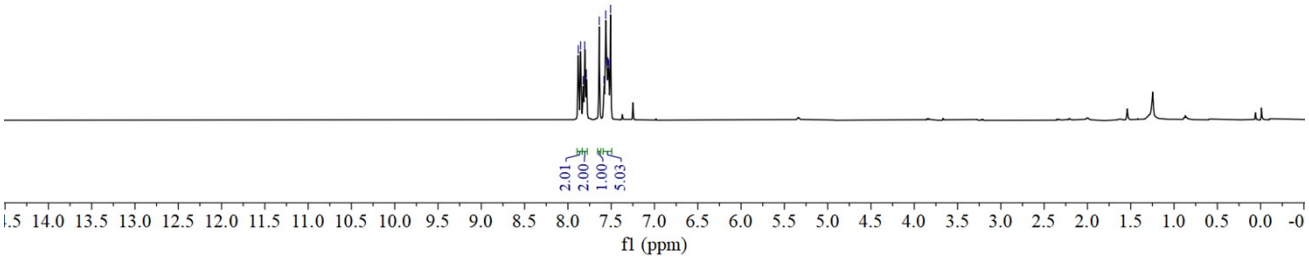
$CDCl_3$, ^{13}CNMR, 101 MHz



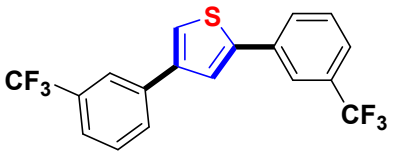
2,4-Di-(3-trifluoromethyl)-thiophene (2q)

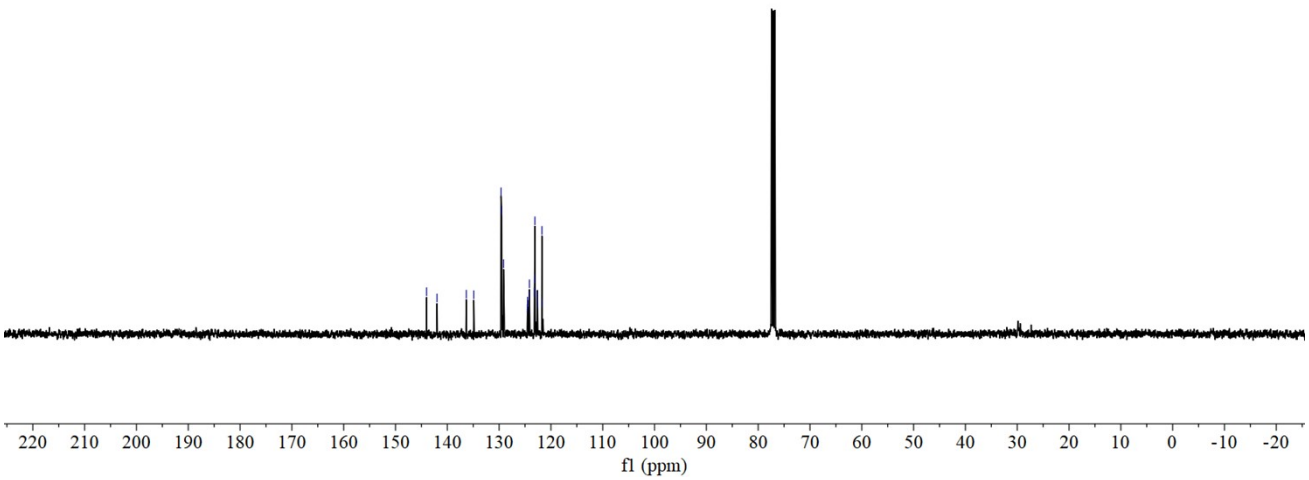
$CDCl_3$, ^{1}HNMR, 400 MHz



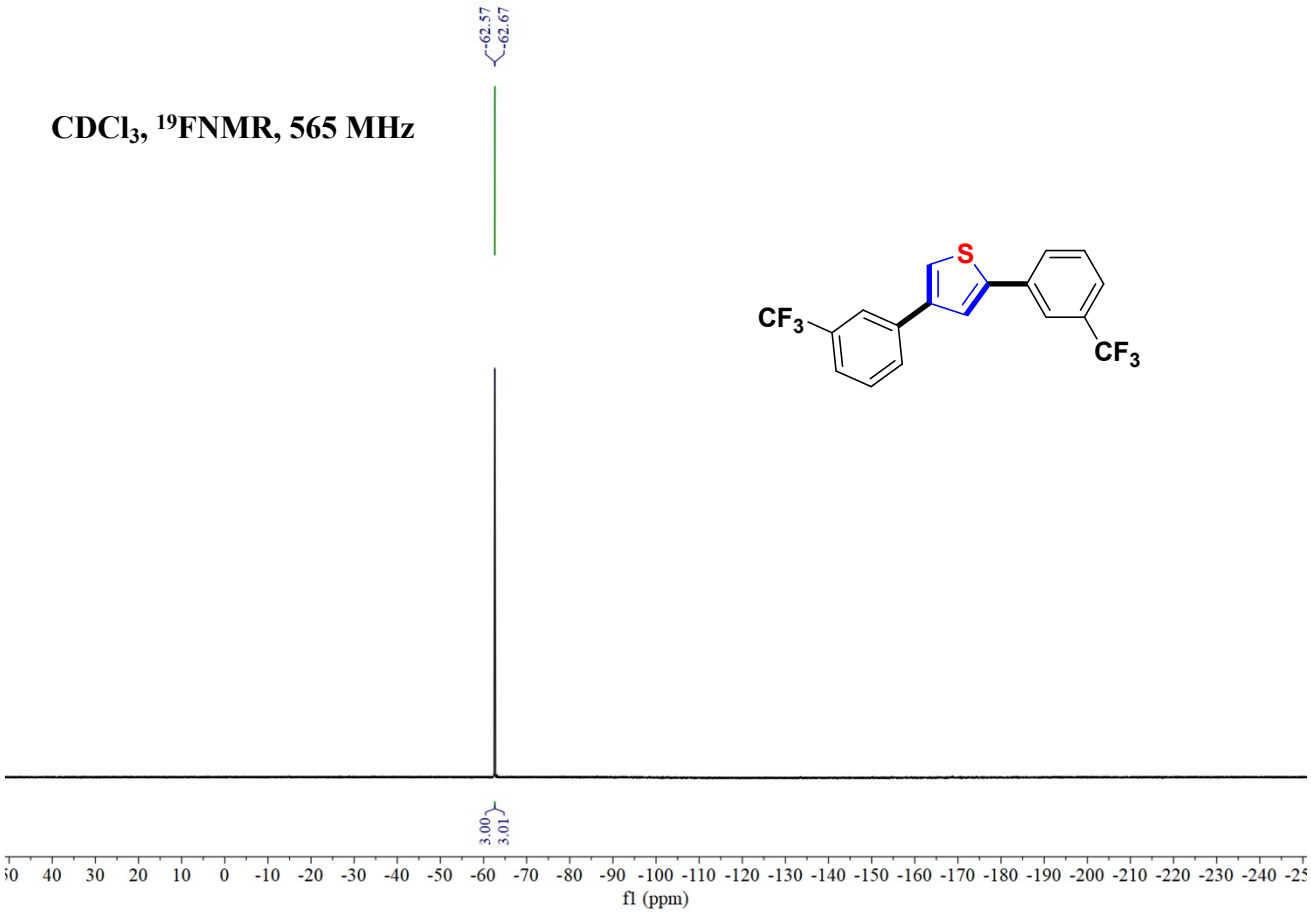


$CDCl_3$, ^{13}CNMR, 101 MHz



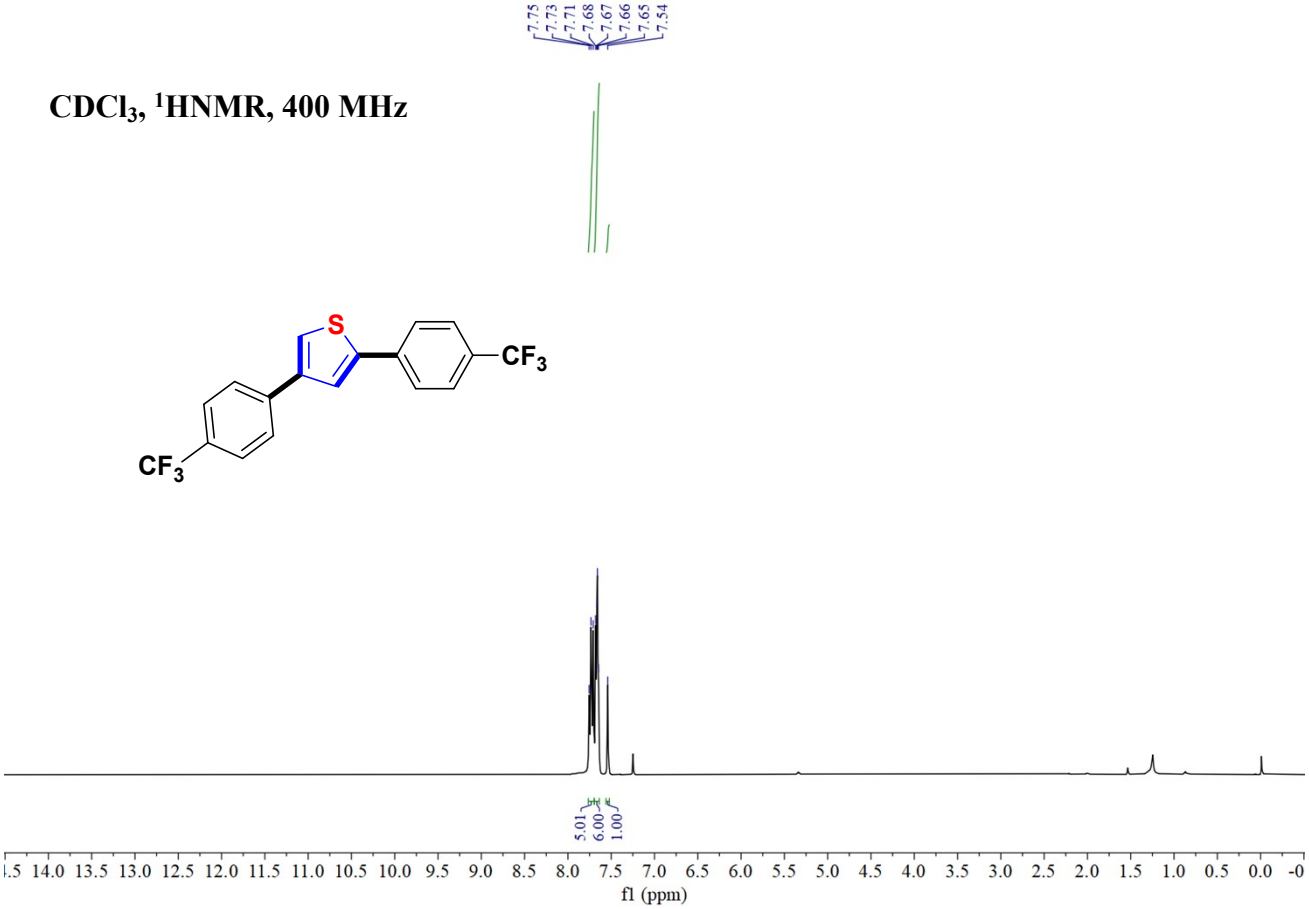


$CDCl_3$, ^{19}FNMR, 565 MHz

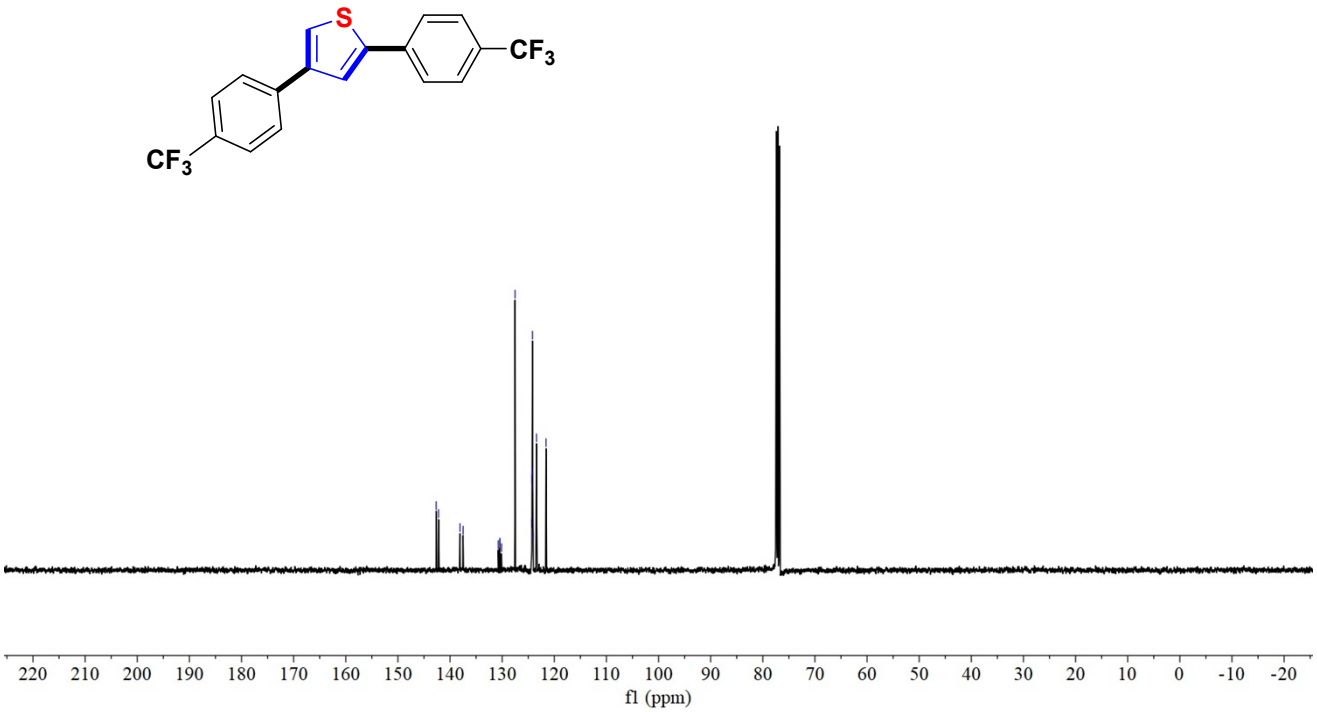


2,4-Di-(4-trifluoromethyl)-thiophene (2r)

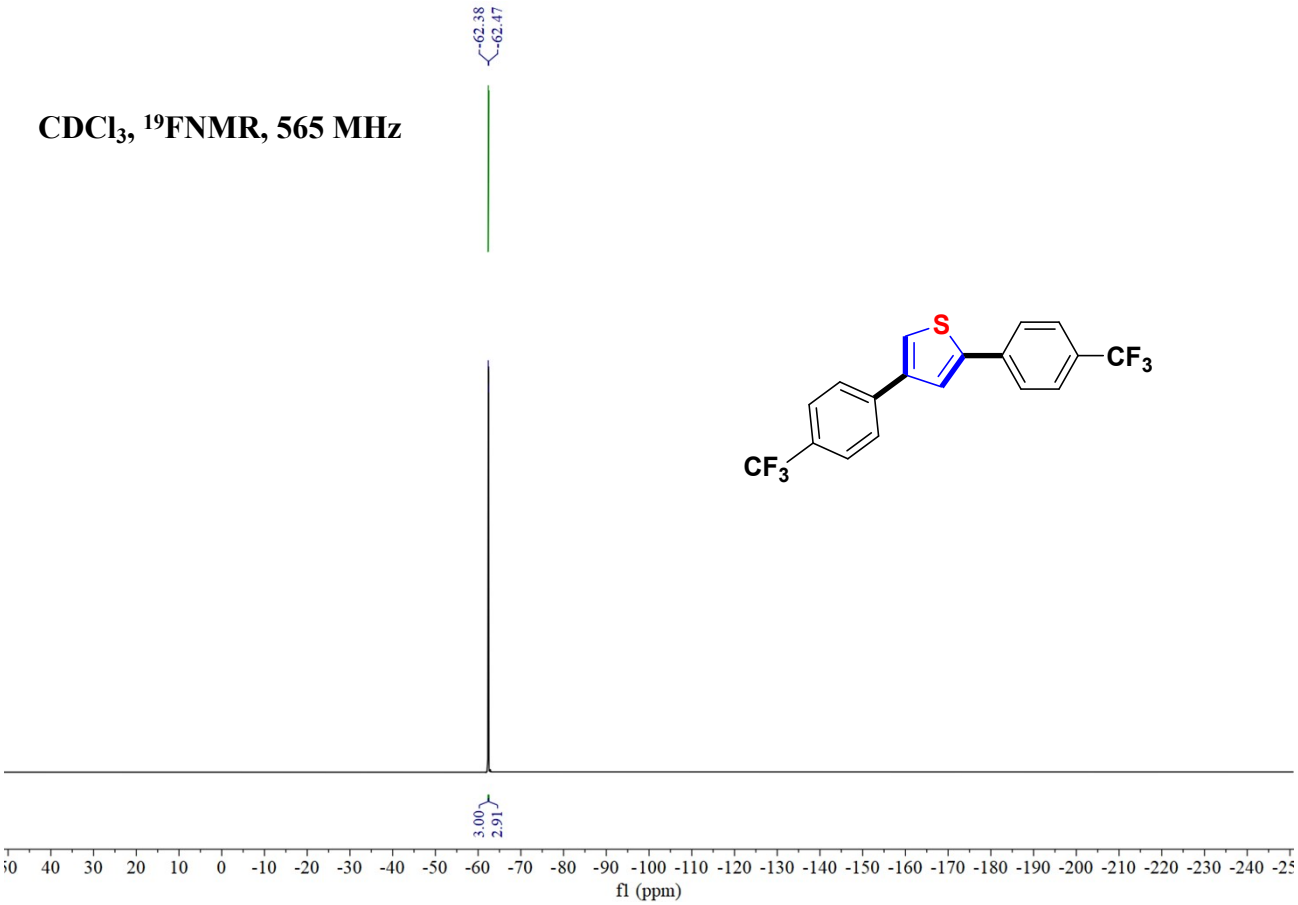
$CDCl_3$, ^{1}HNMR, 400 MHz



$CDCl_3$, ^{13}CNMR, 101 MHz

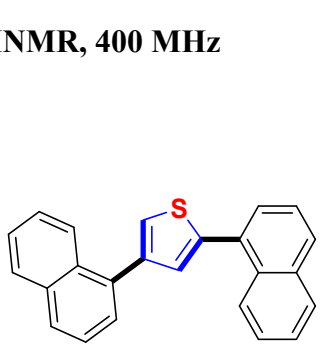


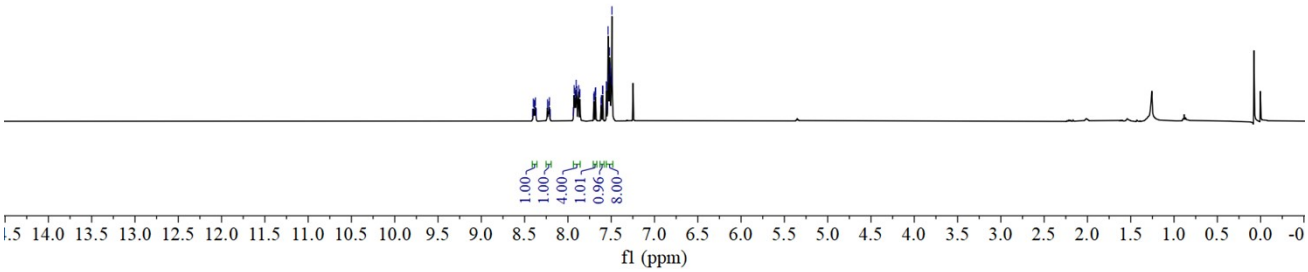
$CDCl_3$, ^{19}FNMR, 565 MHz



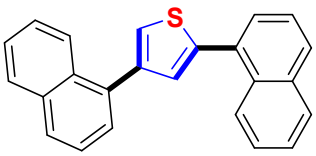
2,4-Di-(naphthalen-1-yl)-thiophene (2s)

$CDCl_3$, ^{1}HNMR, 400 MHz



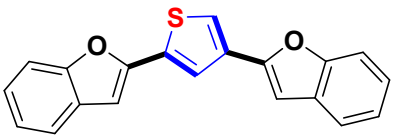


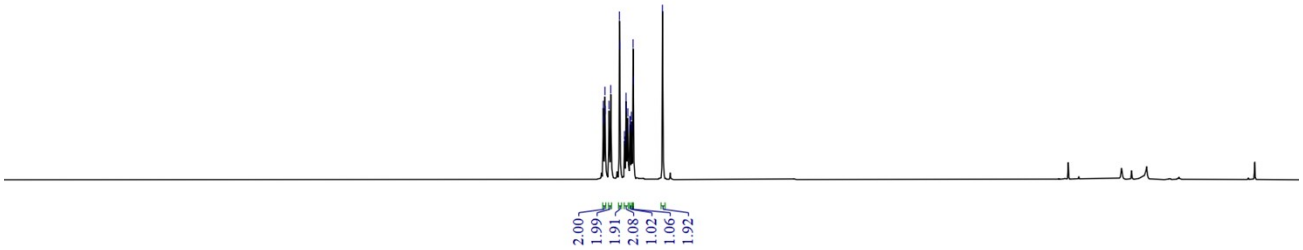
$CDCl_3$, ^{13}CNMR, 101 MHz



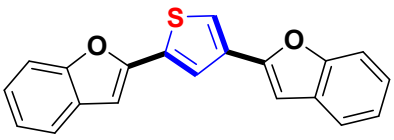
2,4-Di-(benzofuran-2-yl)-thiophene (2t)

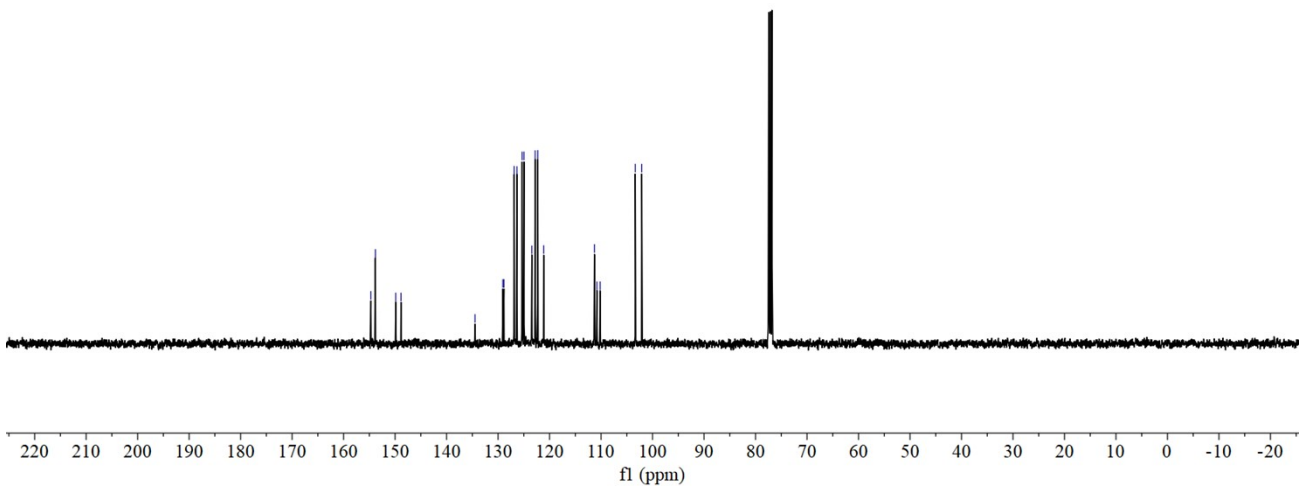
$CDCl_3$, ^{1}HNMR, 400 MHz





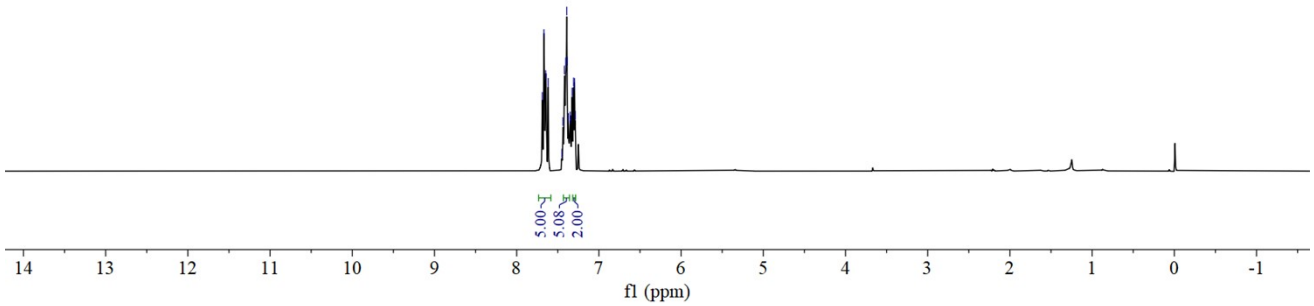
$CDCl_3$, ^{13}CNMR, 101 MHz



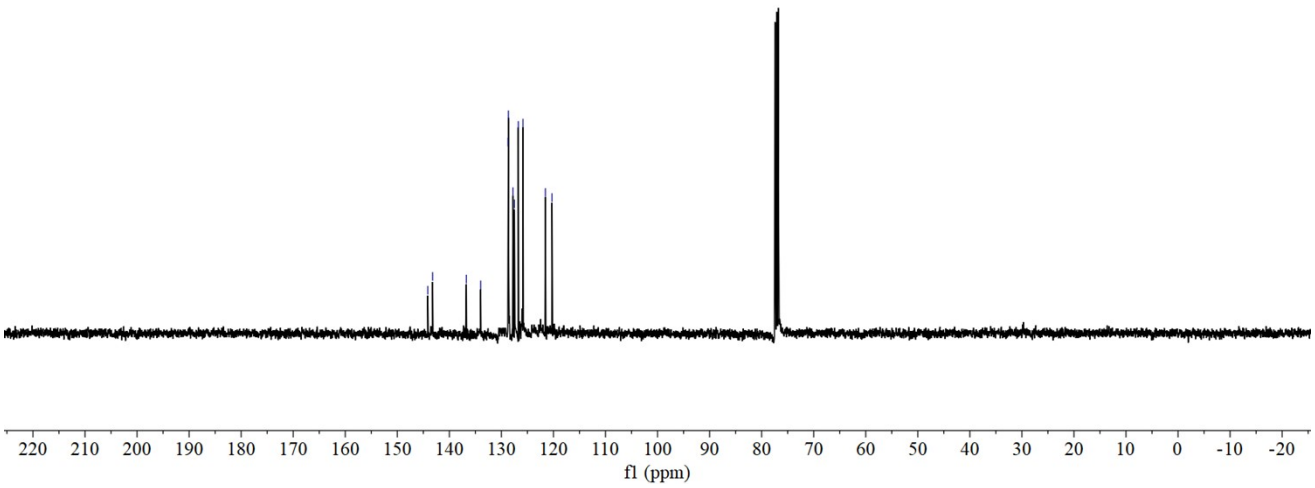


2,4-Diphenylselenophen (3a)

$CDCl_3$, ^{1}HNMR, 400 MHz

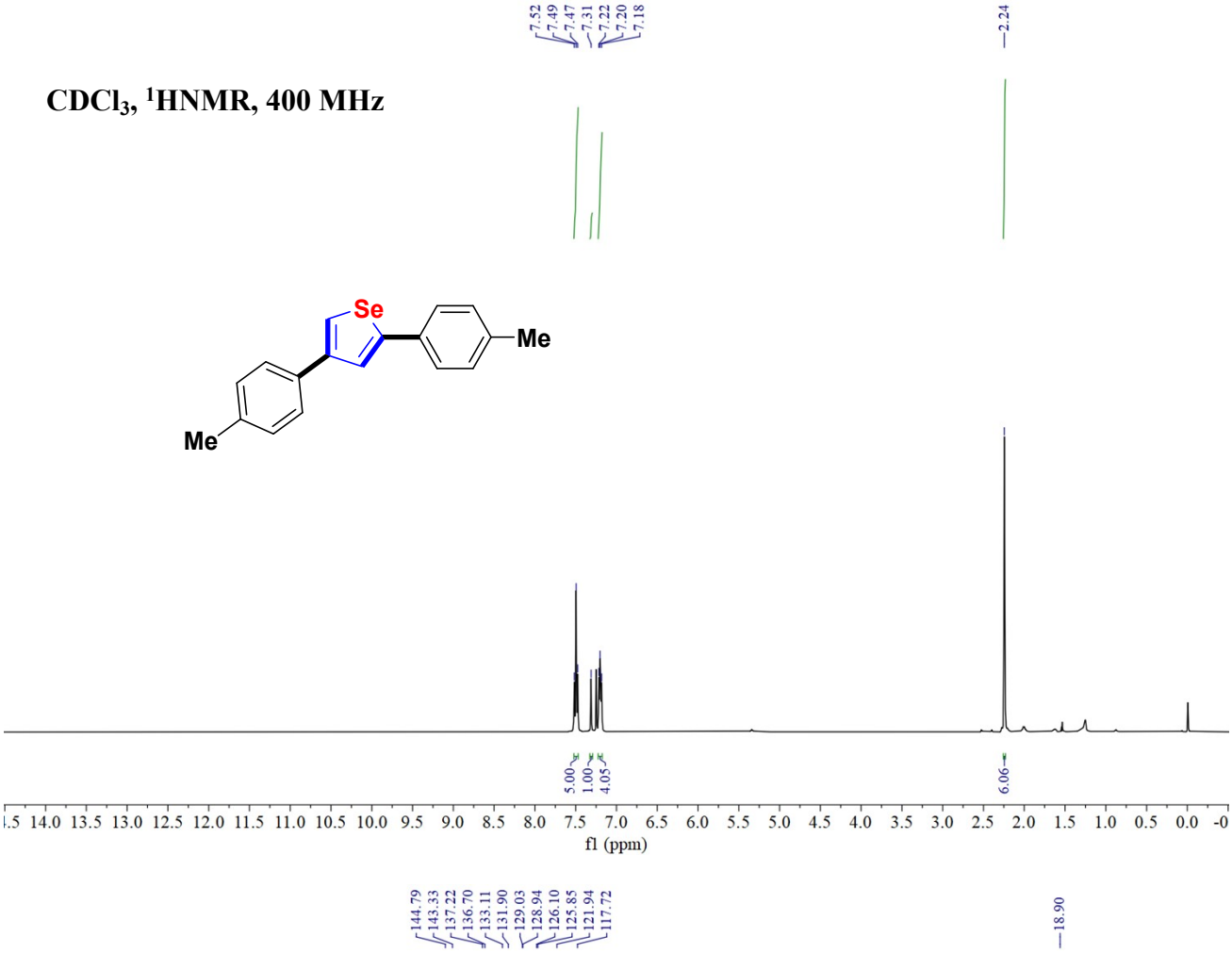


$CDCl_3$, ^{13}CNMR, 101 MHz

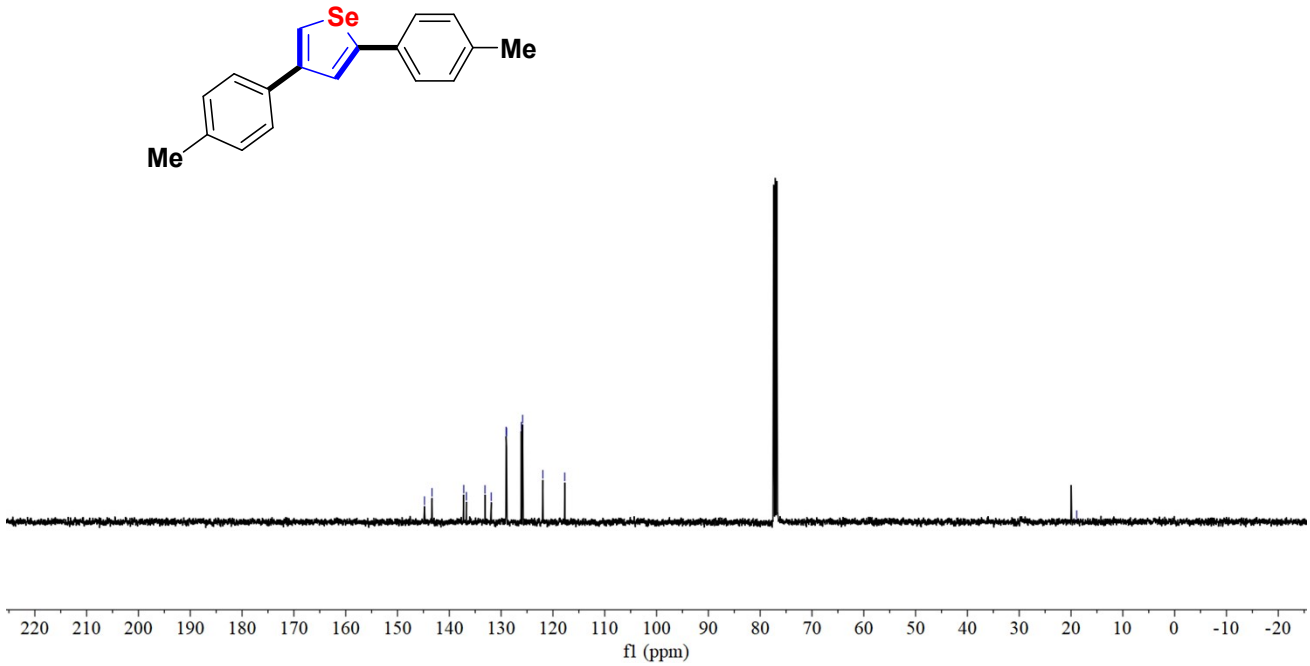


2,4-Di-*p*-tolylselenophen (3b)

$CDCl_3$, ^{1}HNMR, 400 MHz

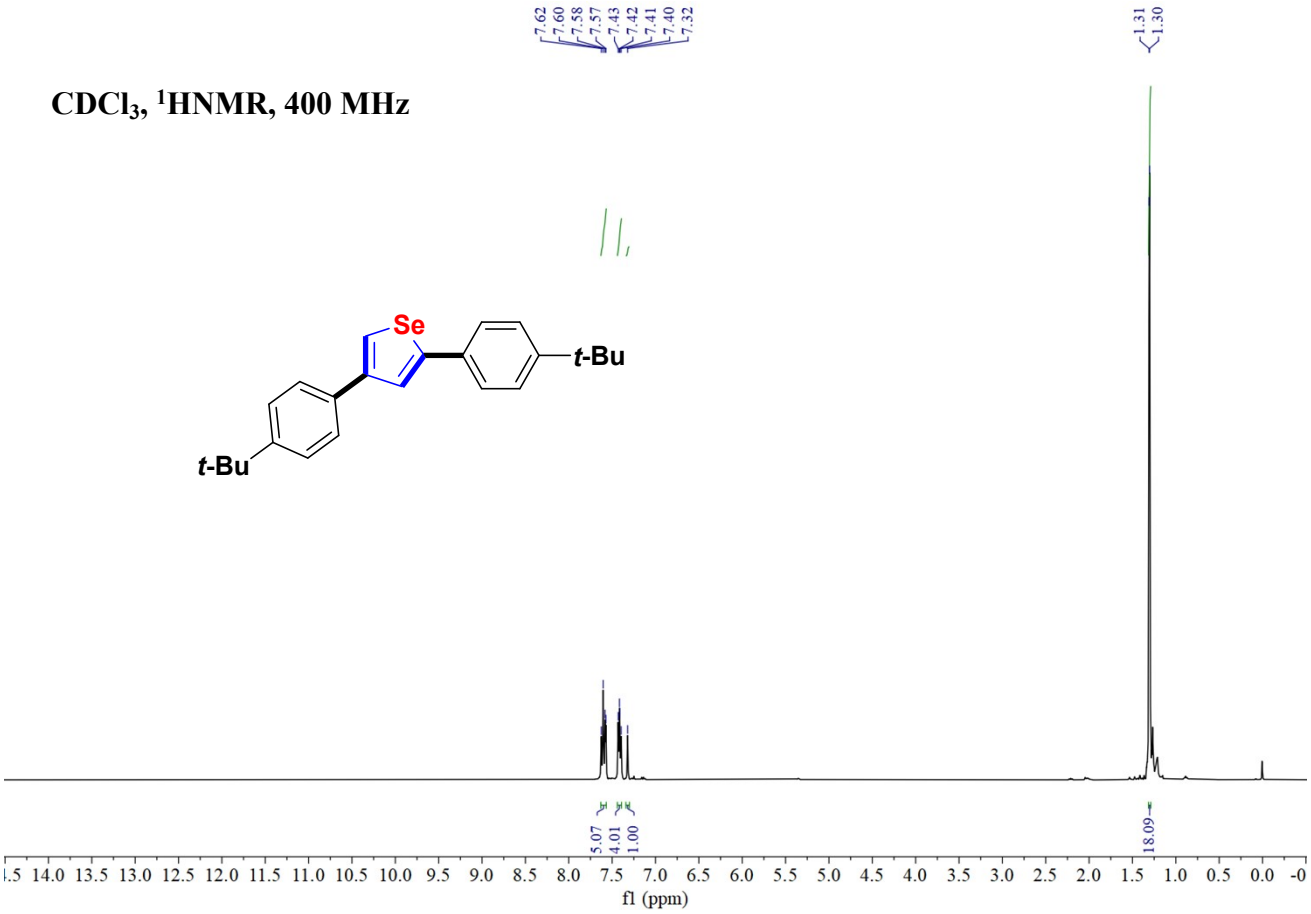


$CDCl_3$, ^{13}CNMR, 101 MHz

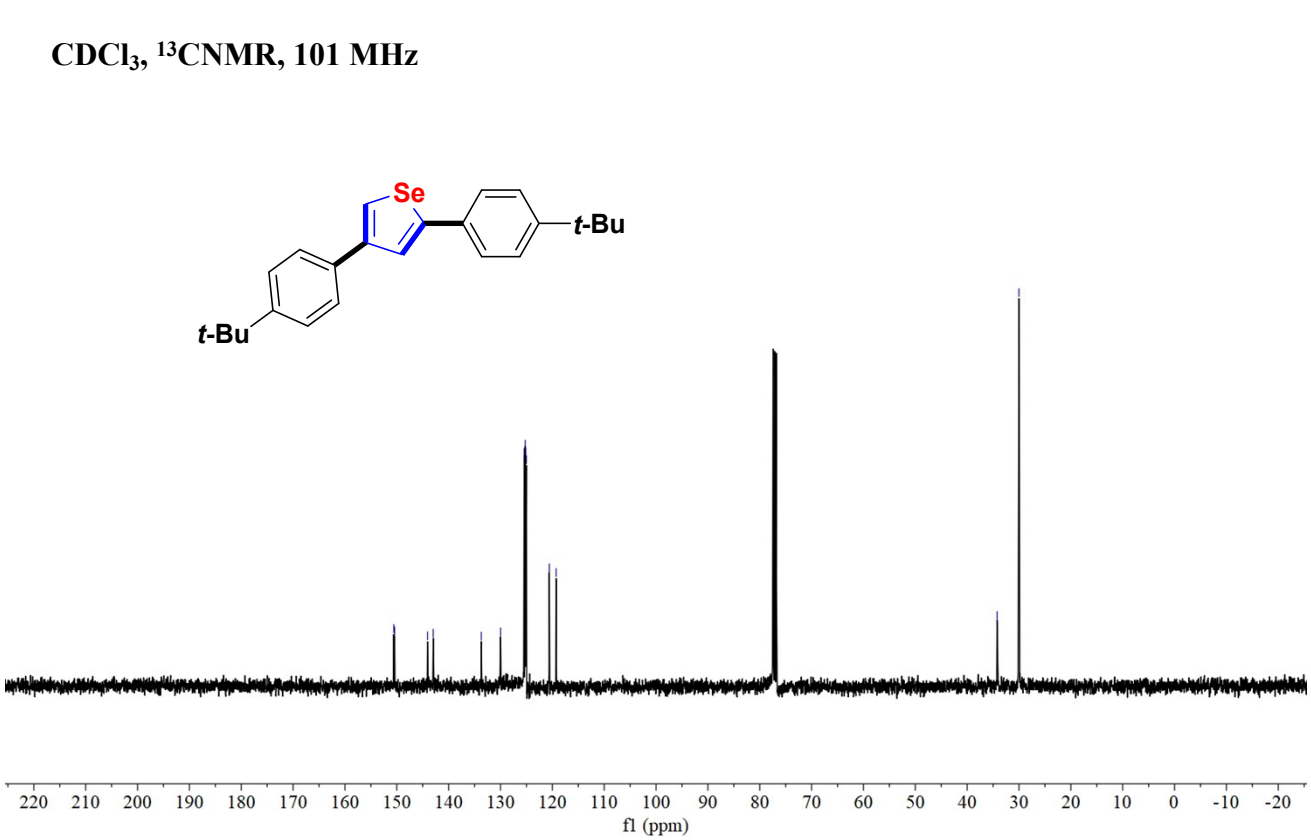


2,4-Di-(4-(tert-butylphenyl)-selenophen (3c)

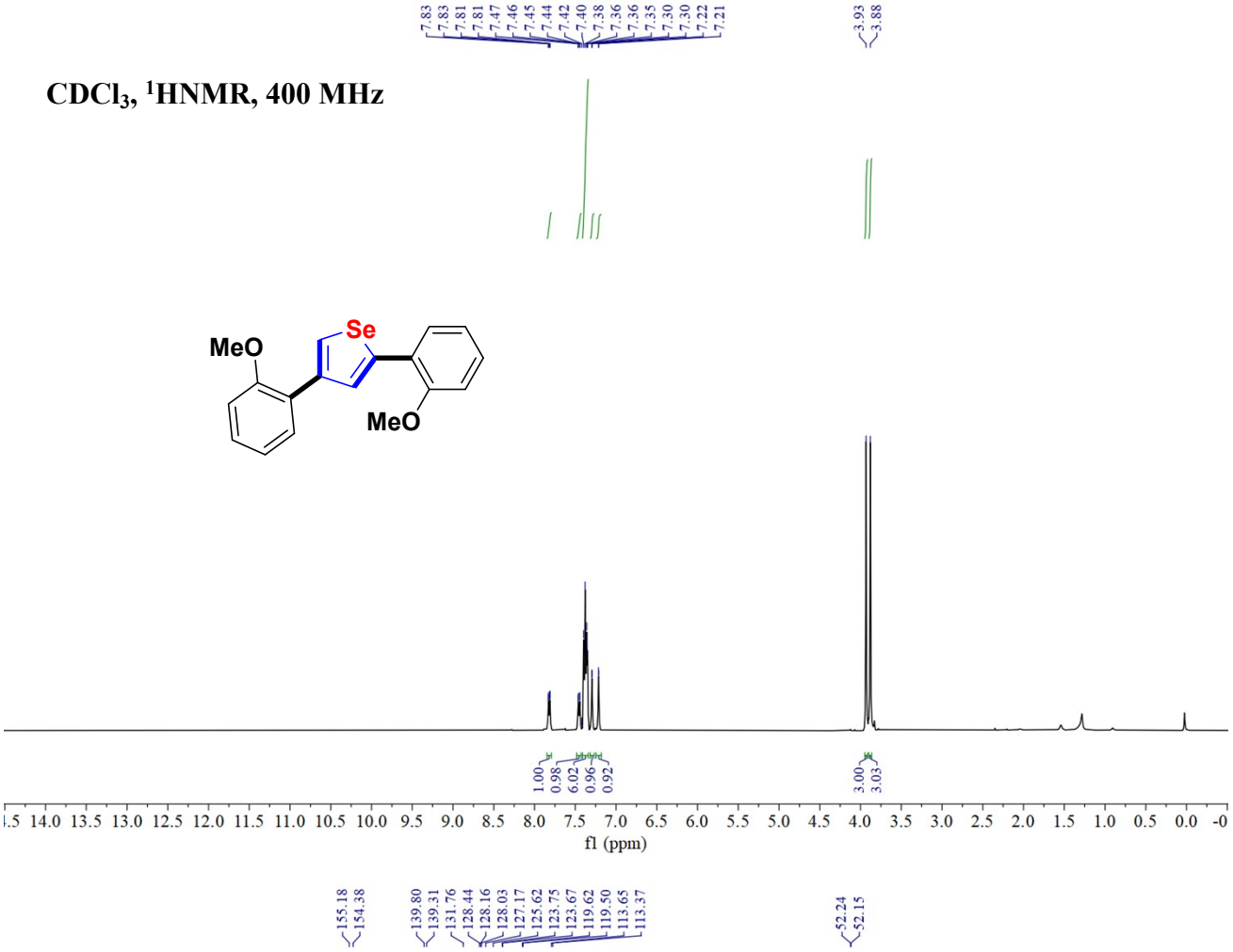
$CDCl_3$, ^{1}HNMR, 400 MHz



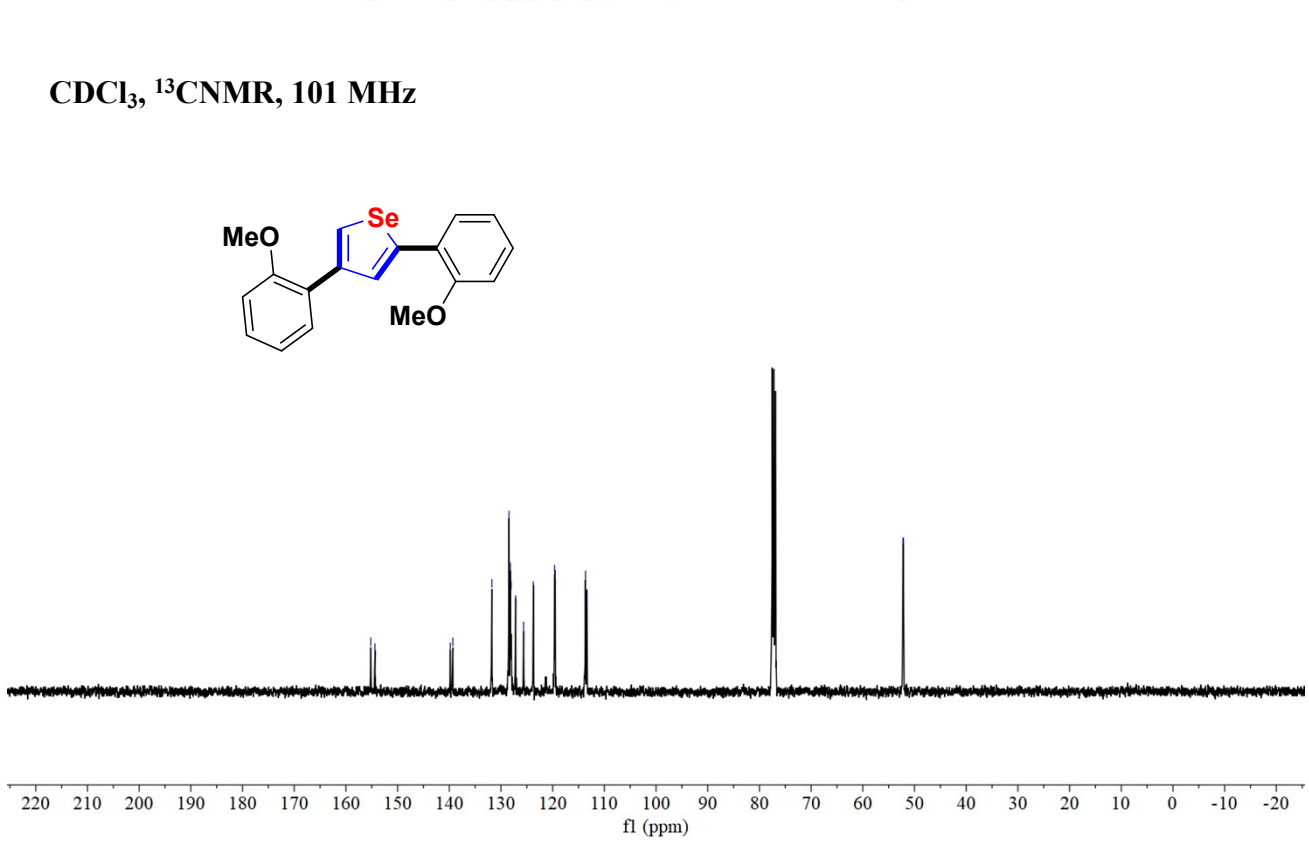
$CDCl_3$, ^{13}CNMR, 101 MHz



2,4-Di-(2-methoxyphenyl)-selenophen (3d)

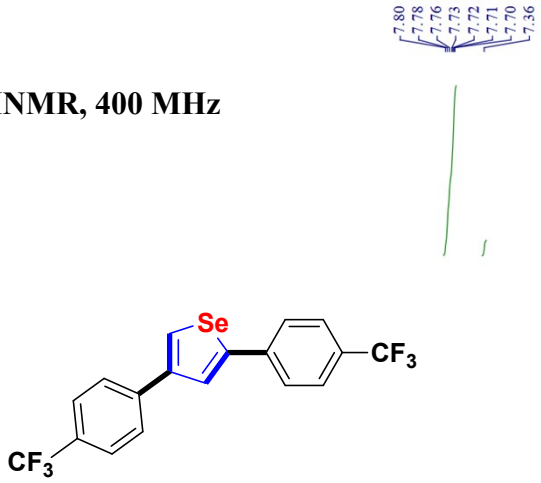


$CDCl_3$, ^{1}HNMR, 400 MHz

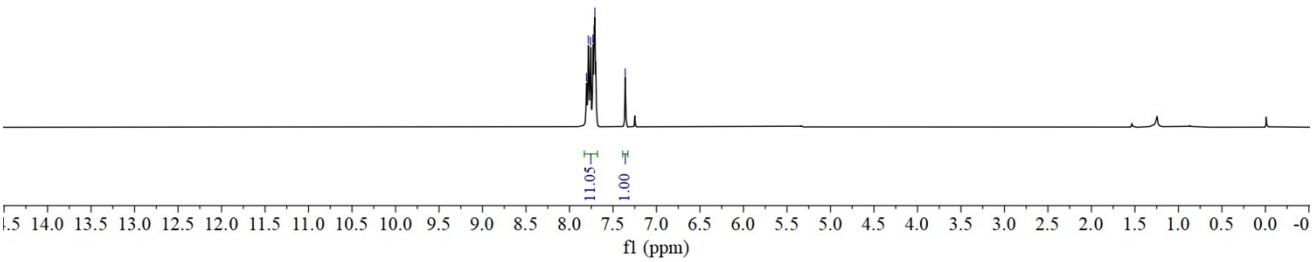


$CDCl_3$, ^{13}CNMR, 101 MHz

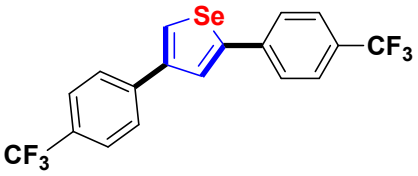
2,4-Di-(4-trifluoromethylphenyl)-selenophen (3e)

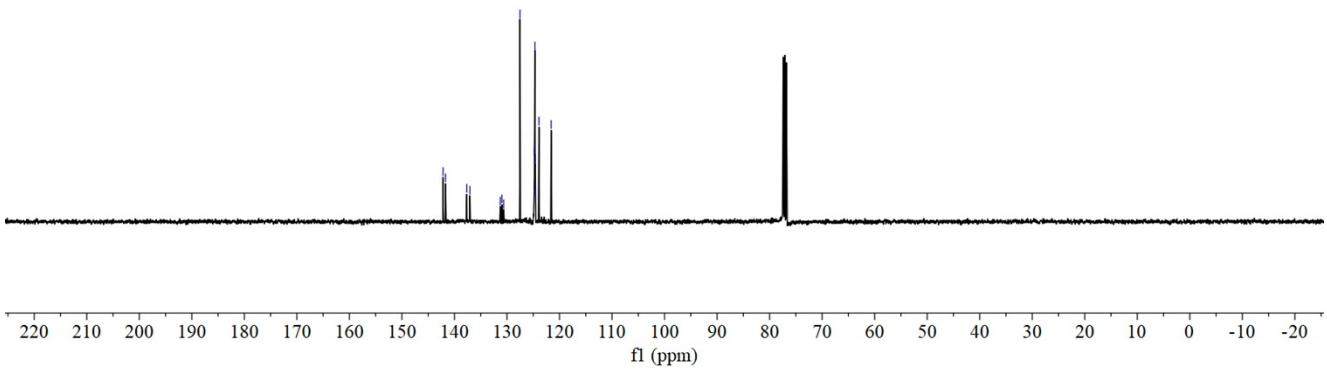


$CDCl_3$, ^{1}HNMR, 400 MHz

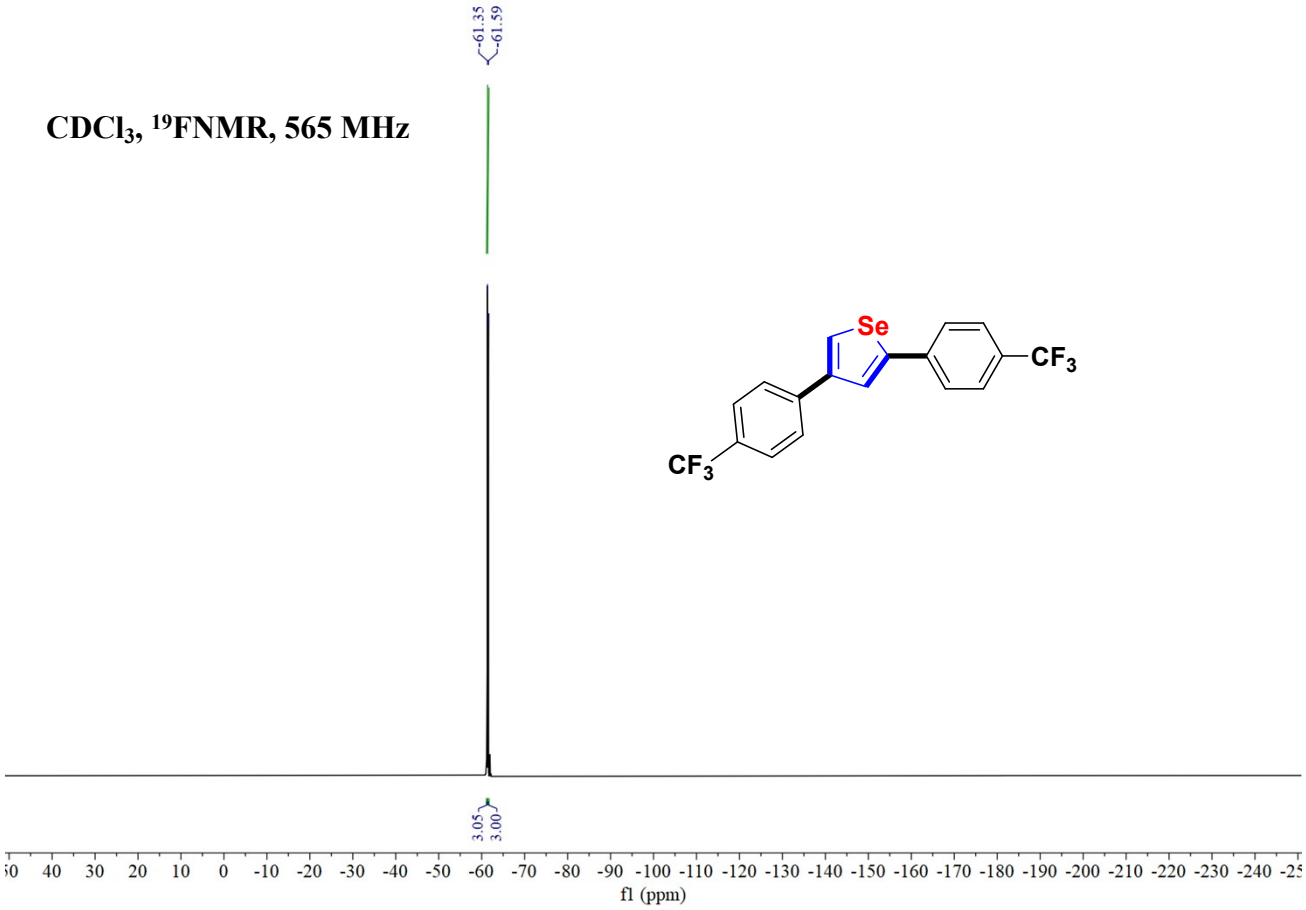


$CDCl_3$, ^{13}CNMR, 101 MHz



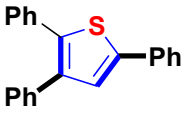


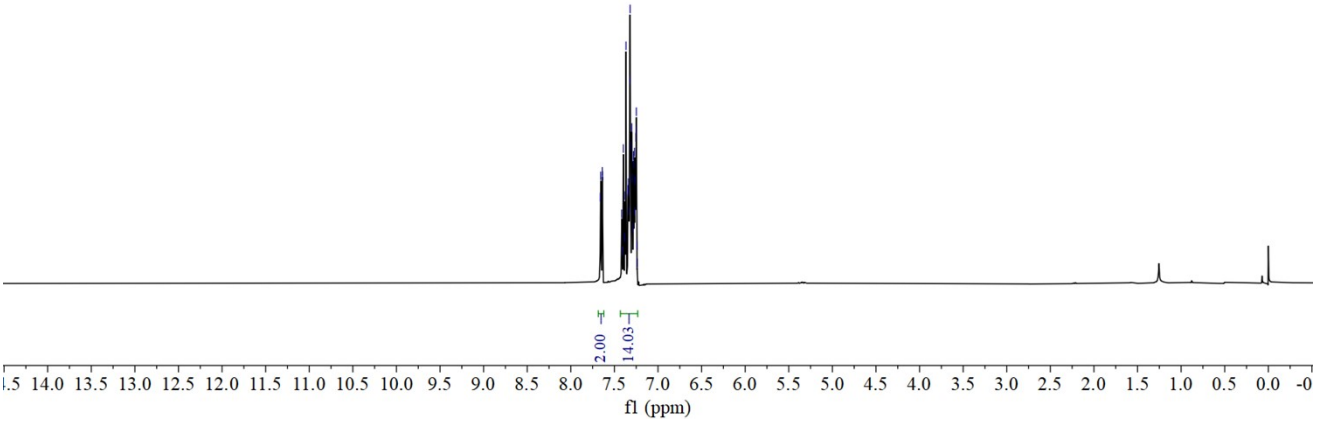
$CDCl_3$, ^{19}FNMR, 565 MHz



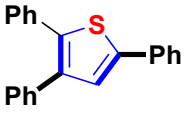
2,3,5-triphenylthiophene (4)

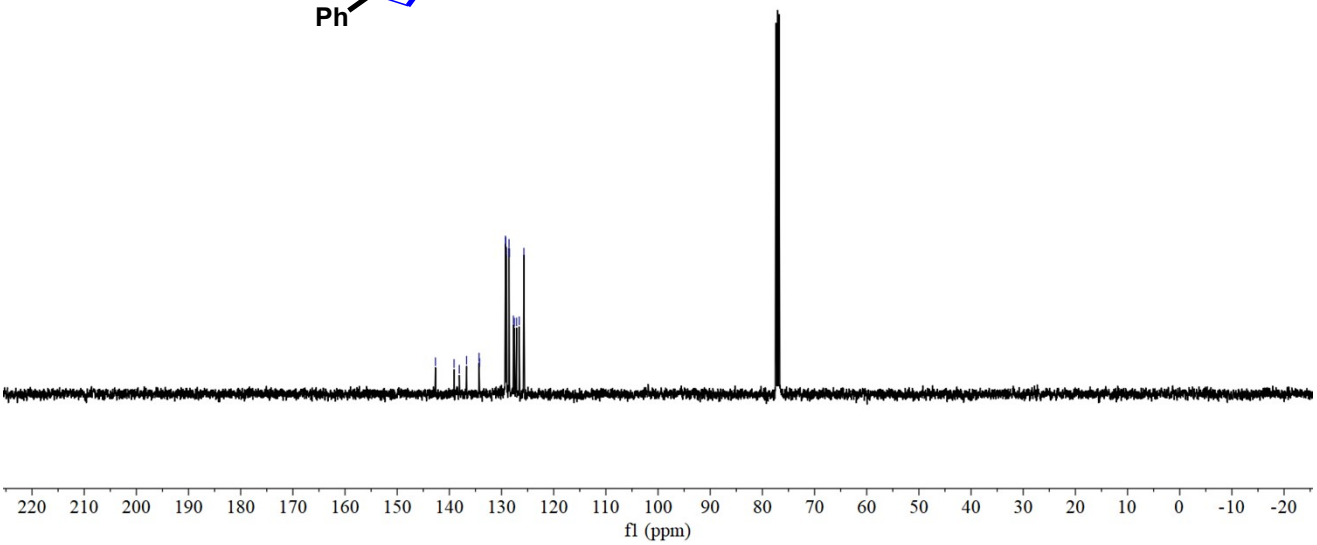
$CDCl_3$, ^{1}HNMR, 400 MHz



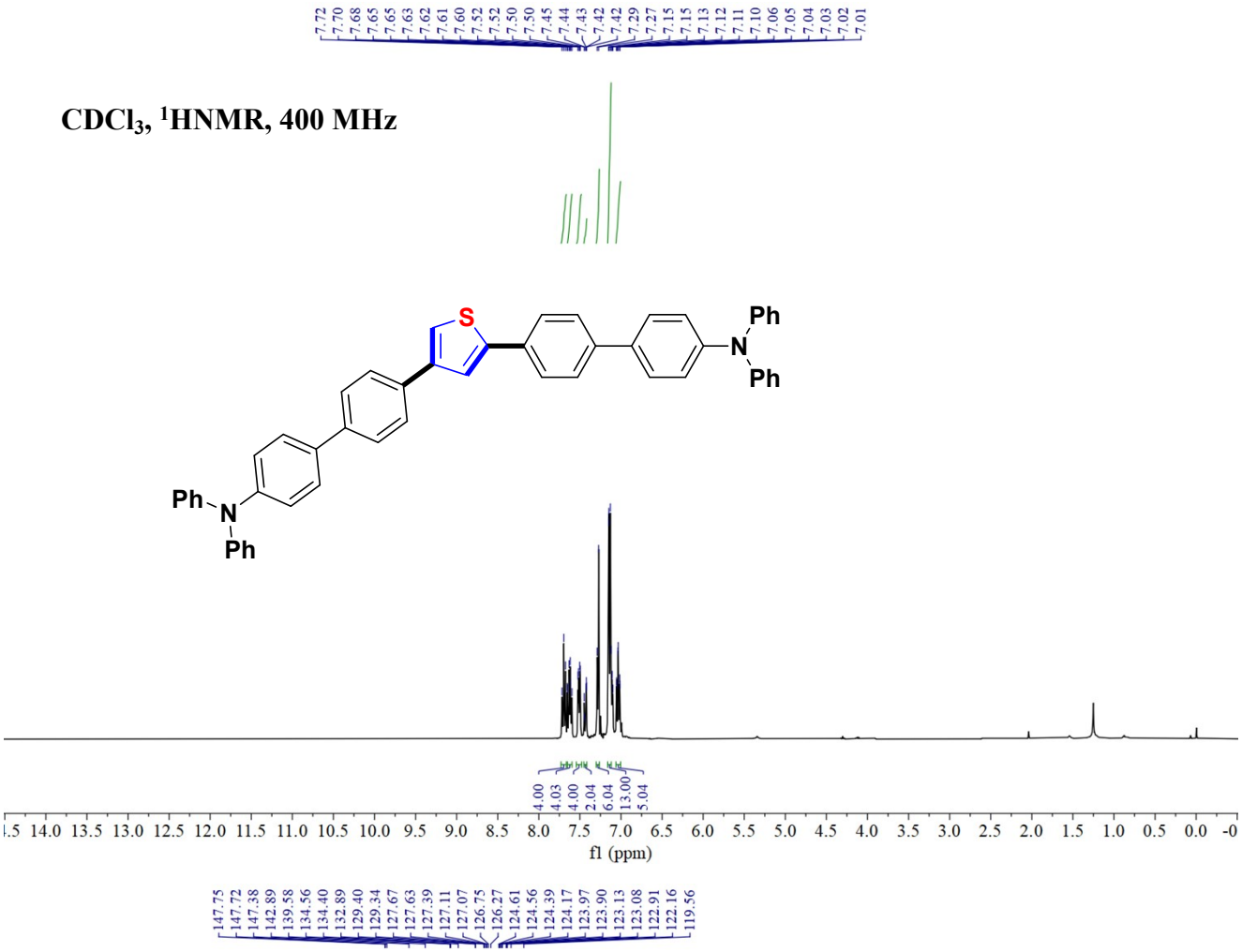


$CDCl_3$, ^{13}CNMR, 101 MHz

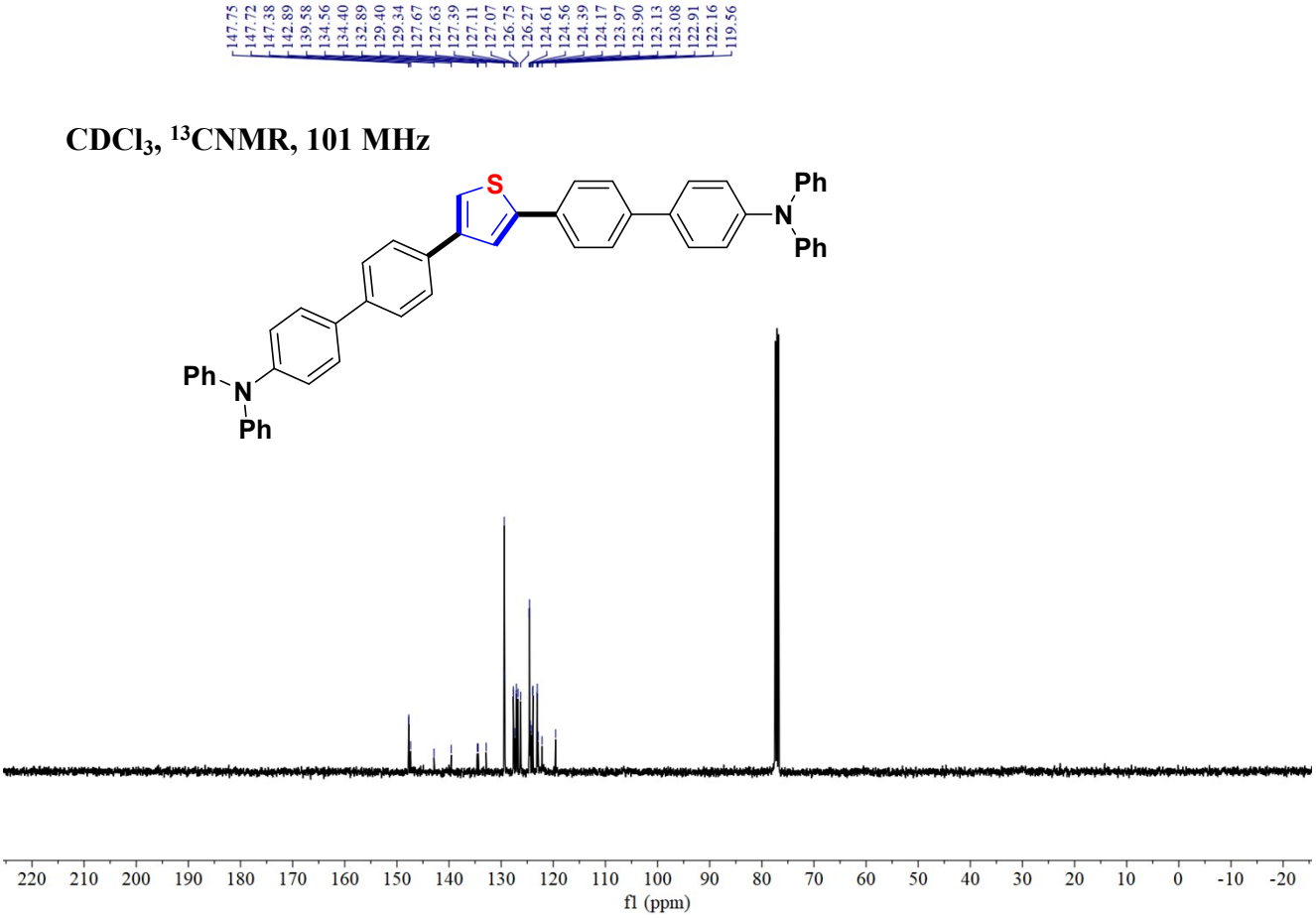




2,4-Di-(4-(4-diphenylaminophenyl)-phenyl)-thiophene (5)



$CDCl_3$, ^{1}HNMR, 400 MHz



$CDCl_3$, ^{13}CNMR, 101 MHz