Supporting Information

Sulfurative Self-Condensation of Ketones and Elemental Sulfur: a Three-Component Access to Thiophenes Catalyzed by Aniline Acid-Base Conjugate Pairs

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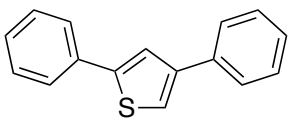
General information

Reagents were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference ($CDCl_3$, δ 7.26 ppm for ^1H and δ 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

General procedure for the reaction of ketone 1 with elemental sulfur catalyzed by aniline and PTSA•H_2O

A mixture of ketone **1** (2 mmol), sulfur (96 mg, 3 mmol), aniline (1 mmol 93 mg), and monohydrated *p*-toluenesulfonic acid (18 mg, 0.1 mmol) in a closed test tube was heated at 120 ºC (for acetophenones **1a-p**) or 100 ºC (for cyclopentanone **1q**) under an argon atmosphere for 16 h. The crude reaction mixture was purified by column chromatography on silica gel (eluent heptane:toluene, heptane:CH_2Cl_2 or hexane:EtOAc) to afford the product **2a-p** as white or pale yellow solid.

2,4-Diphenylthiophene (2a)[1]



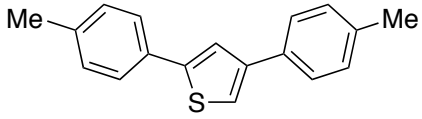
Eluent heptane:toluene 9:1. 177 mg, 75%.

^1H NMR (300 MHz, $CDCl_3$) δ 7.69-7.61 (m, 5H), 7.46-7.39 (m, 5H), 7.35-7.30 (m, 2H).

[1] D. D. Tang, K. D. Collins, J. B. Ernst and F. Glorius, *Angew. Chem. Int. Ed.* **2014**, *53*, 1809.

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 143.3, 136.1, 134.5, 129.1, 129.1, 127.9, 127.5, 126.5, 126.1, 122.5, 119.9.

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

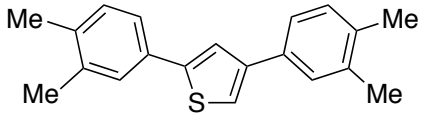


Eluent heptane:toluene 9:1. 190 mg, 72%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.54 (m, 5H), 7.34 (s, 1H), 7.27-7.23 (m, 4H), 2.42 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 143.3, 137.8, 137.2, 133.5, 131.9, 129.9, 129.8, 126.5, 126.0, 122.1, 118.9, 21.5, 21.5.

2,4-bis(3,4-Dimethylphenyl)thiophene (2c)



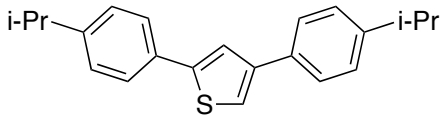
Eluent heptane:toluene 9:1. 199 mg, 68%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, J = 1.2 Hz, 1H), 7.43 (d, J = 1.9 Hz, 1H), 7.40 (d, J = 1.9 Hz, 1H), 7.38 (dd, J = 7.7, 1.9 Hz, 1H), 7.36 (dd, J = 7.7, 1.9 Hz, 1H), 7.29 (d, J = 1.2 Hz, 1H), 7.16 (d, J = 7.7 Hz, 1H), 7.15 (d, J = 7.7 Hz, 1H), 2.32 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.3, 137.3, 136.4, 135.8, 133.9, 132.3, 130.3, 130.2, 127.8, 127.3, 123.9, 123.5, 122.0, 118.6, 20.1, 20.1, 19.7, 19.7.

HRMS (ESI^+) calcd for $C_{20}H_{21}S$ $[M + H]^+$ 293.1364. Found 293.1356.

2,4-bis(4-Isopropylphenyl)thiophene (2d)



Eluent heptane:toluene 9:1. 247 mg, 77%.

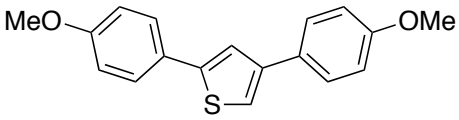
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.58 (m, 5H), 7.34-7.28 (m, 5H), 2.98 (septet, J = 6.9 Hz, 1H), 2.97 (septet, J = 6.9 Hz, 1H), 1.33 (d, J = 6.9 Hz, 6H), 1.32 (d, J = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 148.1, 145.2, 143.3, 133.8, 132.3, 127.2, 127.0, 126.5, 126.1, 122.1, 118.9, 34.1, 34.1, 24.2, 24.1.

HRMS (ESI^+) calcd for $C_{22}H_{25}S$ $[M + H]^+$ 321.1677. Found 321.1659.

2,4-bis(4-Methoxyphenyl)thiophene (2e)[3]

[2] M. Arisawa, T. Ichikawa, and M. Yamaguchi, *Chem. Commun*. **2015**, *51*, 8821.
[3] J. Meneyrol WO2016066742 A1, 2106.

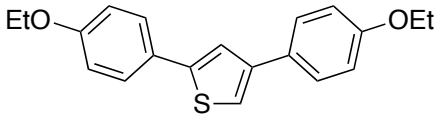


Eluent heptane:CH_2Cl_2 2:1. 260 mg, 88%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.63 (m, 4H), 7.53 (s, 1H), 7.31 (s, 1H), 7.07-7.00 (m, 4H), 3.94 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 159.1, 145.0, 142.9, 129.1, 127.6, 127.3, 123.1, 121.5, 117.7, 114.5, 114.4, 55.6, 55.5.

2,4-bis(4-Ethoxyphenyl)thiophene (2f)



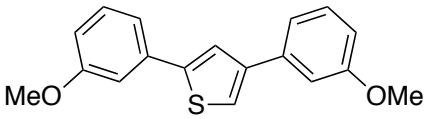
Eluent heptane:CH_2Cl_2 2:1. 261 mg, 81%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.62 (m, 4H), 7.54 (d, J = 1.4 Hz, 1H), 7.31 (d, J = 1.4 Hz, 1H), 7.06-7.00 (m, 4H), 4.17 (q, J = 7.0 Hz, 4H), 1.54 (t, J = 7.0 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 158.6, 145.1, 143.0, 127.6, 127.3, 121.5, 117.6, 115.1, 115.0, 129.0, 123.0, 63.8, 63.8, 15.1 (2C).

HRMS (ESI$^+$) calcd for $C_{20}H_{21}O_2S$ $[M + H]^+$ 325.1262. Found 325.1255.

2,4-bis(3-Methoxyphenyl)thiophene (2g)[4]

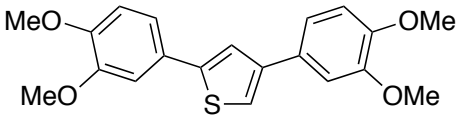


Eluent heptane:CH_2Cl_2 2:1. 210 mg, 71%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.42-7.20 (m, 7H), 6.92-6.89 (m, 2H), 3.90 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (2C), 145.0, 143.1, 137.4, 135.8, 130.1, 130.0, 122.8, 120.2, 119.1, 118.6, 113.4, 112.8, 112.3, 111.7, 55.5 (2C).

2,4-bis(3,4-Dimethoxyphenyl)thiophene (2h)



Eluent heptane:CH_2Cl_2 2:1. 288 mg, 81%.

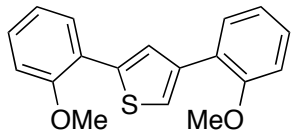
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 1.5 Hz, 1H), 7.29 (d, J = 1.5 Hz, 1H), 7.27 (dd, J = 8.2, 2.0 Hz, 1H), 7.24 (dd, J = 8.2, 2.0 Hz, 1H), 7.19 7.24 (d, J = 2.0 Hz, 1H), 7.18 (d, J = 2.0 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.96 (d, J = 2.0 Hz, 1H), 4.02 (s, 3H), 4.01 (s, 3H), 3.98 (s, 6H).

[4] E. Bey, S. Marchais-Oberwinkler, R. Werth, M. Negri, Y. A. Al-Soud, P. Kruchten, A. Oster, M. Frotscher, B. Birk and R. W. Hartmann, *J. Med. Chem.* **2008**, *51*, 6725.

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4 (2C), 149.2, 148.8, 145.2, 143.1, 129.4, 127.7, 121.8, 119.0, 118.7, 118.0, 111.7 (2C), 110.1, 109.7, 56.2 (4C).

HRMS (ESI$^+$) calcd for $C_{20}H_{21}O_4S$ $[M + H]^+$ 357.1161. Found 357.1176.

2,4-bis(2-Methoxyphenyl)thiophene (2i)



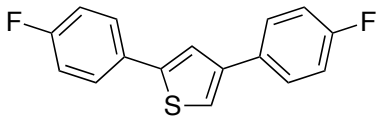
Eluent heptane:CH_2Cl_2 2:1. 152 mg, 51%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.67 (s, 1H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.37-7.28 (m, 2H), 7.10-7.03 (m, 4H), 3.99 (s, 3H), 3.93 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 155.9, 138.5, 138.1, 129.9, 128.7, 128.5, 128.3, 127.2, 125.9, 125.7, 123.8, 121.1, 121.0, 111.9, 111.6, 55.8, 55.7.

HRMS (ESI$^+$) calcd for $C_{18}H_{17}O_2S$ $[M + H]^+$ 297.0949. Found 297.0942.

2,4-bis(4-Fluorophenyl)thiophene (2j)[5]



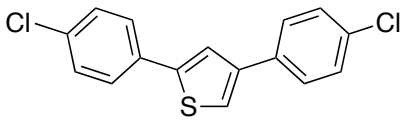
Eluent heptane:toluene 9:1. 200 mg, 74%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.53 (m, 4H), 7.43 (s, 1H), 7.29 (s, 1H), 7.11-7.05 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (d, *J* = 245 Hz), 162.4 (d, *J* = 245 Hz), 144.3, 142.3, 132.1 (d, *J* = 3Hz), 130.7 (d, *J* = 3 Hz), 128.1 (d, *J* = 8 Hz), 127.7 (d, *J* = 8 Hz), 122.5, 119.6, 116.1 (d, *J* = 21 Hz), 115.9 (d, *J* = 21 Hz).

HRMS (ESI$^+$) calcd for $C_{16}H_{11}F_2S$ $[M + H]^+$ 273.0550. Found 273.0558.

2,4-bis(4-Chlorophenyl)thiophene (2k)[5]



Eluent heptane:toluene 9:1. 210 mg, 69%.

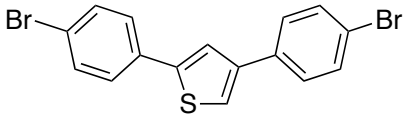
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.49 (m, 6H), 7.38-7.34 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 142.2, 134.3, 133.8, 133.4, 132.8, 129.3, 129.2, 127.7, 127.2, 122.6, 120.5.

HRMS (ESI$^+$) calcd for $C_{16}H_{11}Cl_2S$ $[M + H]^+$ 304.9959. Found 304.9948.

2,4-bis(4-Bromophenyl)thiophene (2l)[5]

[5] E. Campaigne, W. B, Reid Jr. and J. D. Pera, *J. Org. Chem*. **1959**, *24*, 1229.



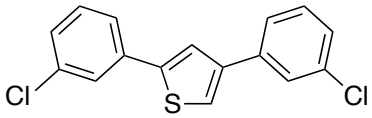
Eluent heptane:toluene 9:1. 189 mg, 48%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.36 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.3, 142.3, 134.8, 133.3, 132.3, 132.2, 128.1, 127.5, 122.6, 121.9, 121.5, 120.6.

HRMS (ESI^+) calcd for $C_{16}H_{11}Br_2S$ $[M + H]^+$ 392.8948. Found 392.8935.

2,4-bis(3-Chlorophenyl)thiophene (2m)



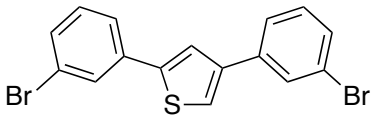
Eluent heptane:toluene 9:1. 209 mg, 69%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (t, J = 1.8 Hz, 1H), 7.58 (t, J = 1.8 Hz, 1H), 7.54 (d, J = 1.5 Hz, 1H), 7.51-7.45 (m, 2H), 7.41 (d, J = 1.5 Hz, 1H), 7.36-7.25 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 141.9, 137.4, 135.9, 135.1, 134.9, 130.3, 130.2, 127.9, 127.5, 126.5, 125.9, 124.5, 124.1, 122.9, 121.3.

HRMS (ESI^+) calcd for $C_{16}H_{11}Cl_2S$ $[M + H]^+$ 304.9959. Found 304.9942.

2,4-bis(3-Bromophenyl)thiophene (2n)



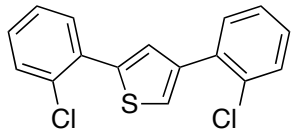
Eluent heptane:toluene 9:1. 315 mg, 80%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.57-7.42 (m, 6H), 7.32-7.25 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8, 141.8, 137.7, 136.2, 130.9, 130.6, 130.6, 130.5, 129.5, 128.9, 125.0, 124.6, 123.3, 123.2, 122.9, 121.4.

HRMS (ESI^+) calcd for $C_{16}H_{11}Br_2S$ $[M + H]^+$ 392.8948. Found 392.8957.

2,4-bis(2-Chlorophenyl)thiophene (2o)



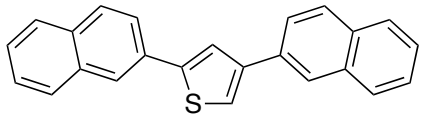
Eluent heptane:toluene 9:1. 224 mg, 73%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66-7.61 (m, 2H), 7.55-7.51 (m, 3H), 7.37-7.27 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.1, 139.8, 139.5, 135.3, 133.1, 132.6, 132.5, 132.4, 131.5, 131.4, 131.3, 130.8, 130.8, 130.4, 129.6, 129.0, 128.9, 128.7, 127.9, 127.2, 127.1, 125.1. We note that the ^{13}C displays a mixture of two rotamers.

HRMS (ESI$^+$) calcd for $C_{16}H_{11}Cl_2S$ $[M + H]^+$ 304.9959. Found 304.9965.

2,4-Di(naphthalen-2-yl)thiophene (2p)



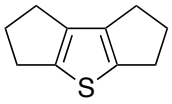
Eluent heptane:toluene 9:1. 266 mg, 79%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.07 (s, 1H), 7.86-7.40 (m, 14H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 143.4, 133.9, 133.8, 133.4, 133.1, 132.9, 131.9, 128.9, 128.7, 128.3 (2C), 128.0, 127.9, 126.9, 126.6, 126.3, 126.1, 125.1, 125.0, 124.5, 124.5, 123.0, 120.5.

HRMS (ESI$^+$) calcd for $C_{24}H_{17}S$ $[M + H]^+$ 337.1051. Found 337.1043.

1,2,3,5,6,7-Hexahydrodicyclopenta[*b*,*d*]thiophene (2q)[6]



Eluent hexane:EtOAc 99:1. 95 mg, 58%.

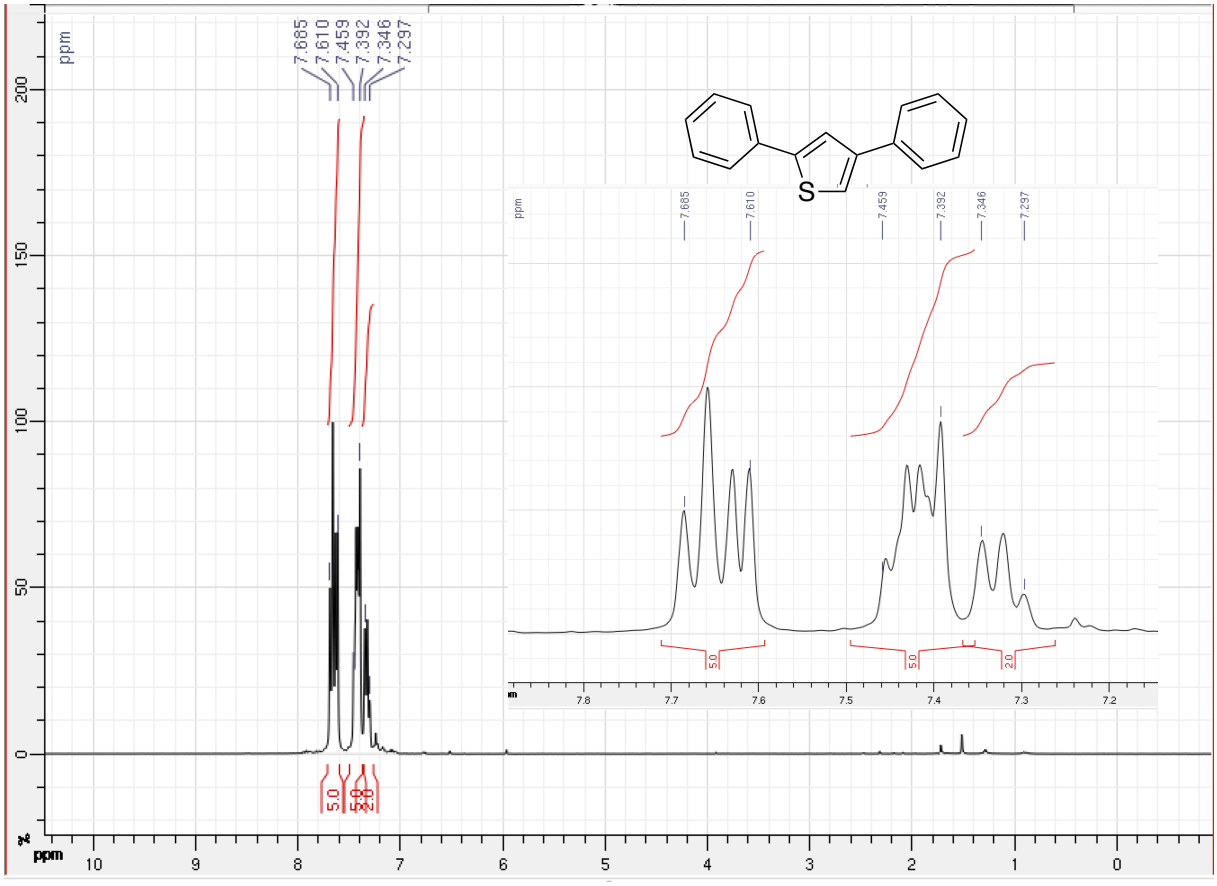
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94-2.91 (m, 4H), 2.69-2.67 (m, 4H), 2.51-2.45 (m, 4H).

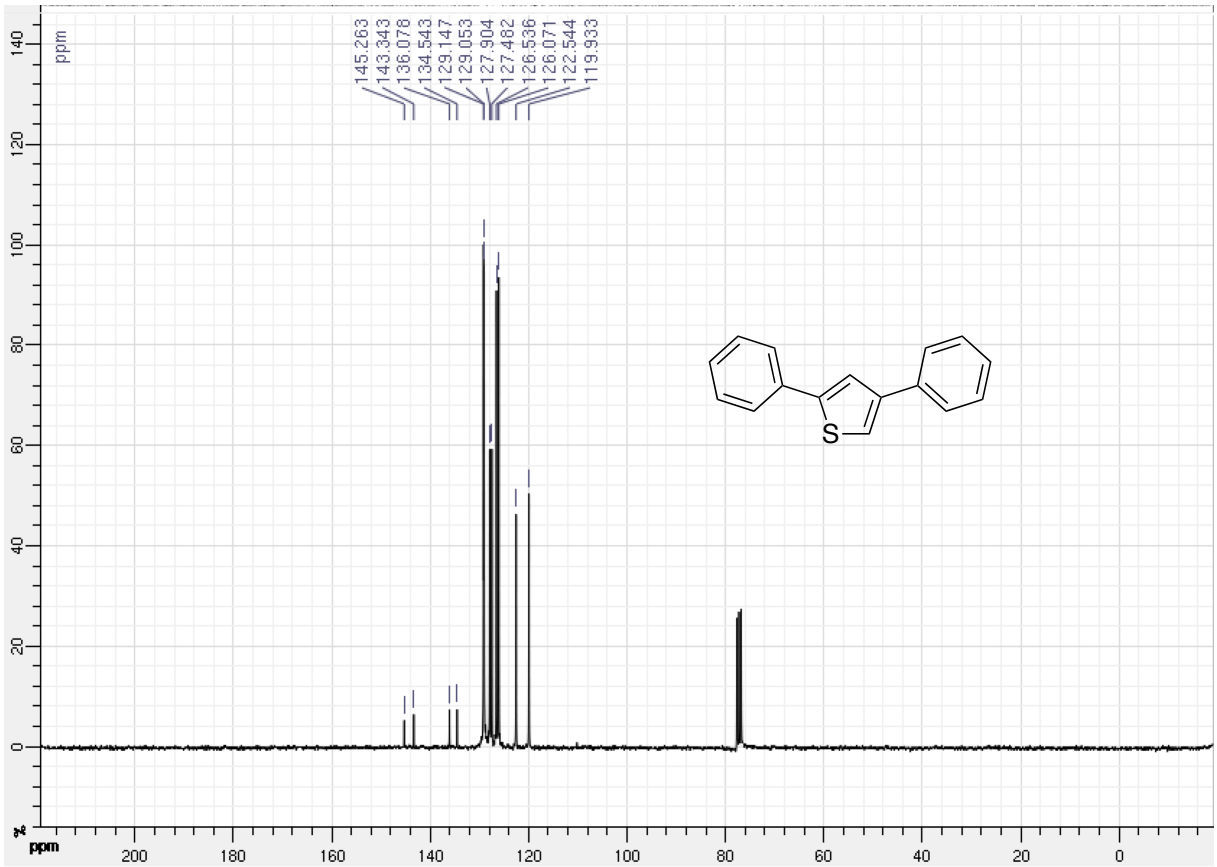
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 140.5, 29.8, 29.4, 27.6.

HRMS (ESI$^+$) calcd for $C_{10}H_{13}S$ $[M + H]^+$ 165.0738. Found 165.0742.

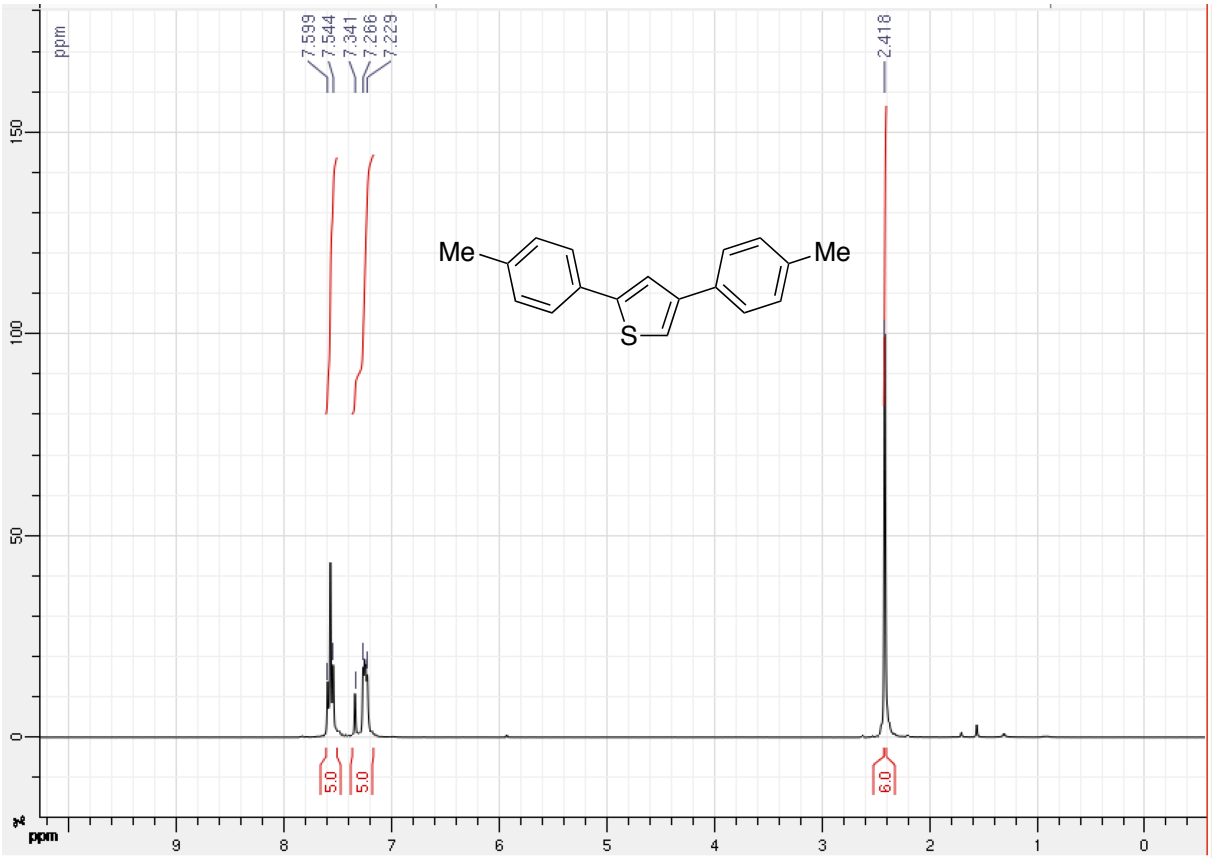
[6] J. R. Grunwell, D. L. Foerst, and M. J. Sanders, *J. Org. Chem*. **1977**, *42*, 1142.

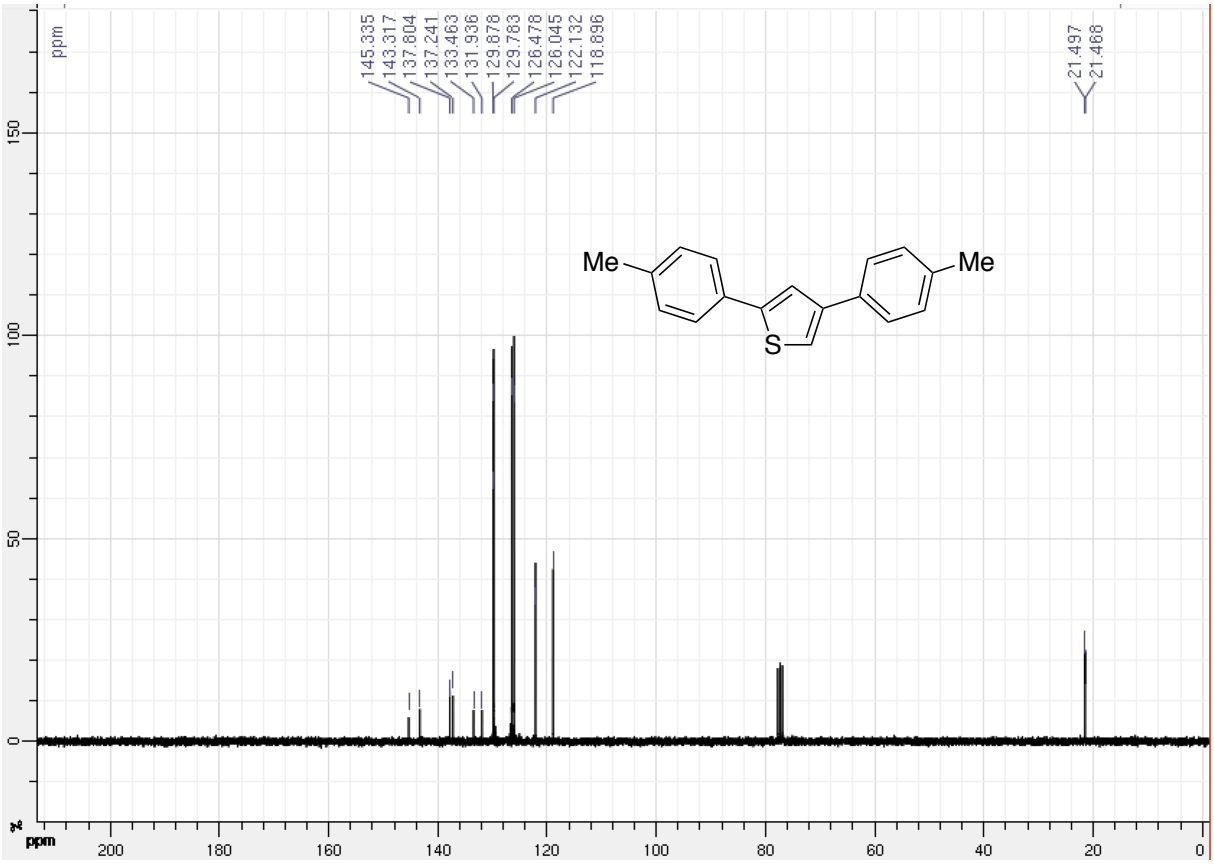
2,4-Diphenylthiophene (2a)



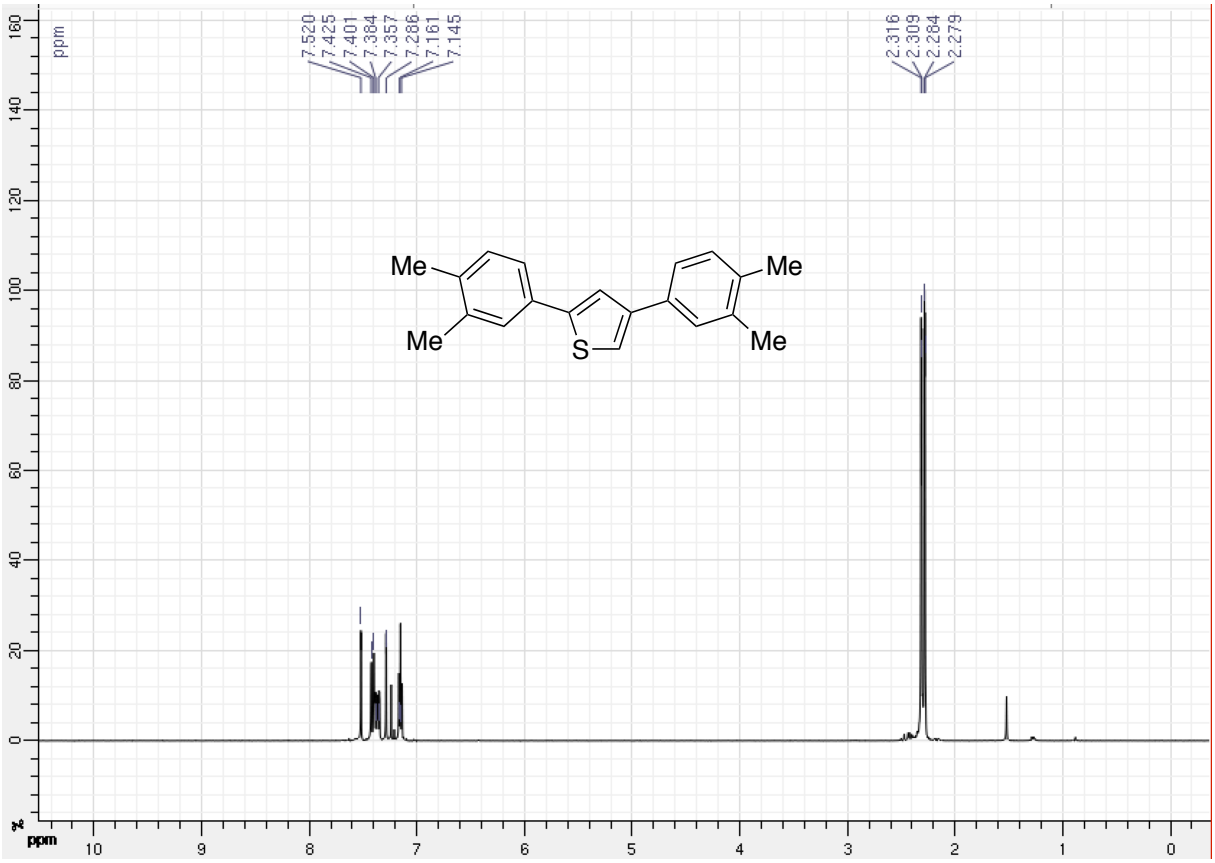


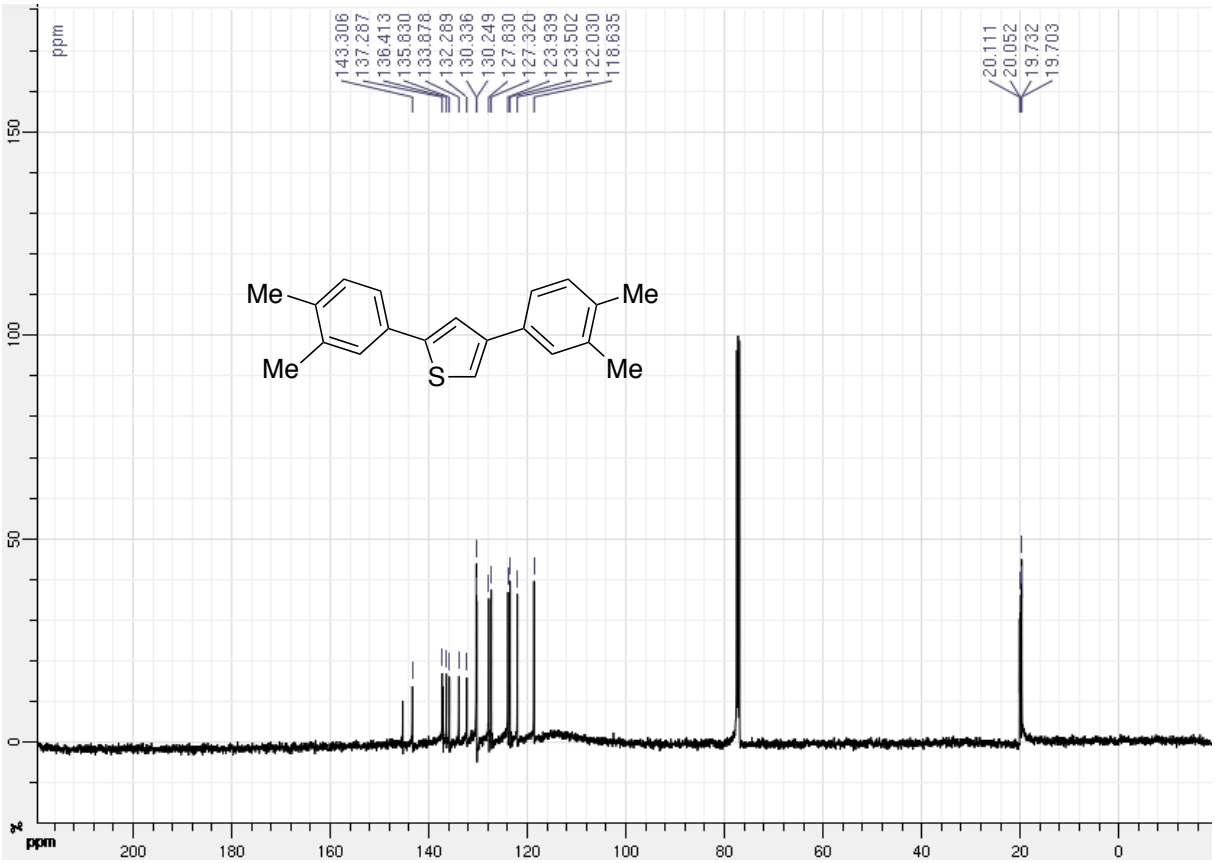
2,4-Di-*p*-tolylthiophene (2b)



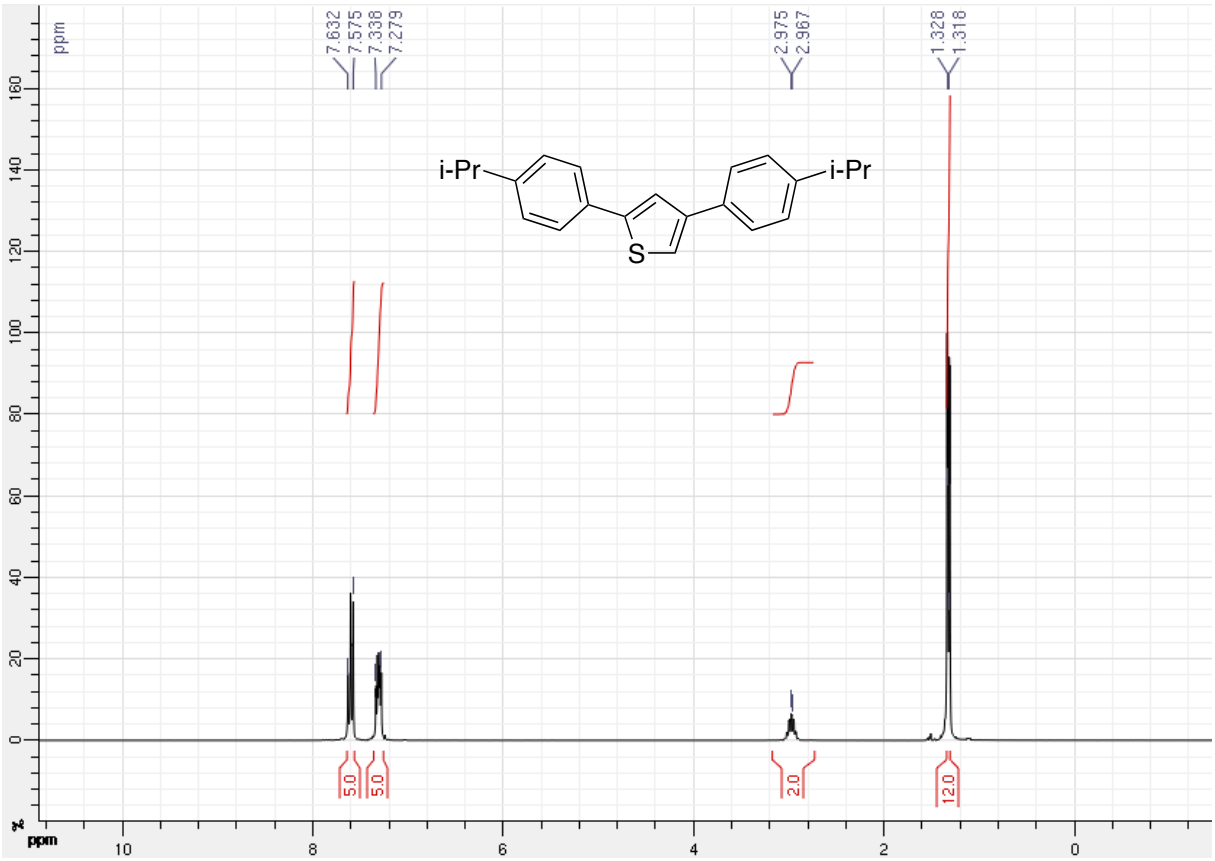


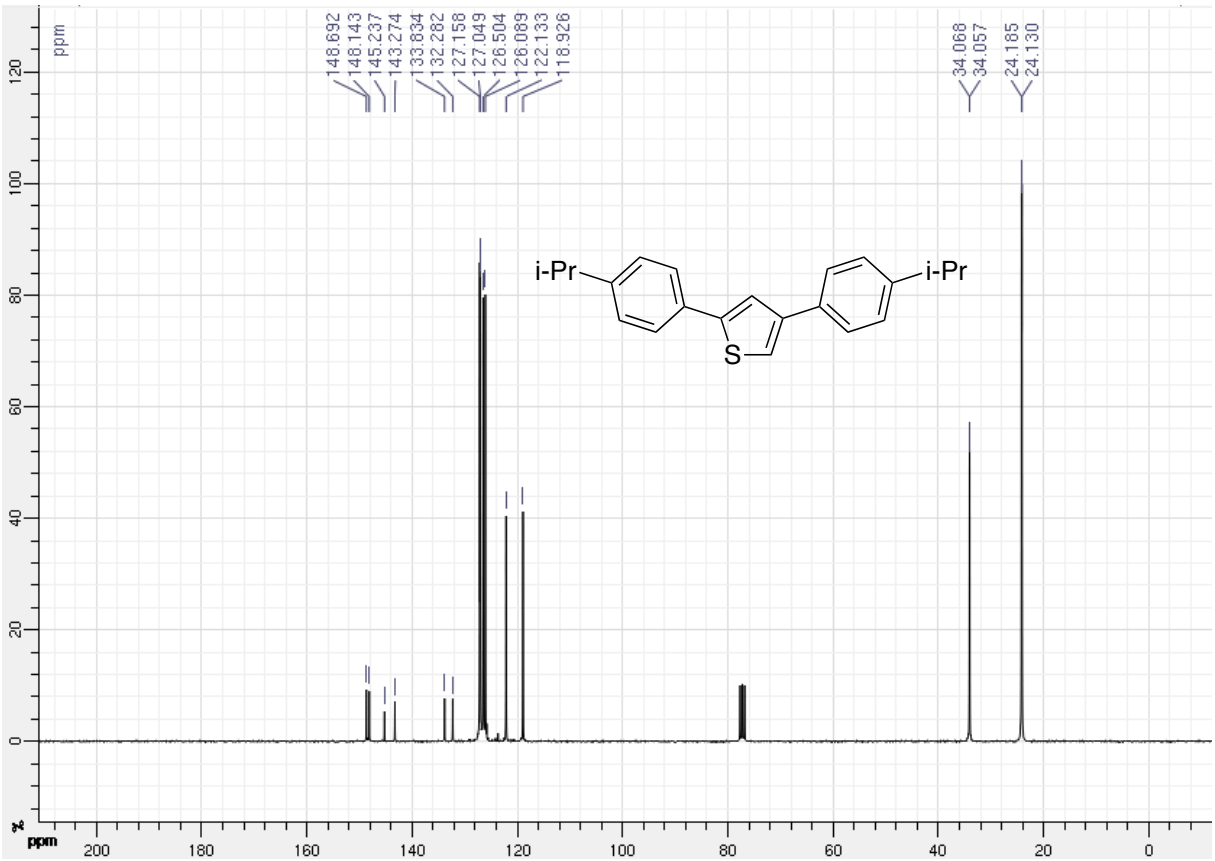
2,4-bis(3,4-Dimethylphenyl)thiophene (2c)



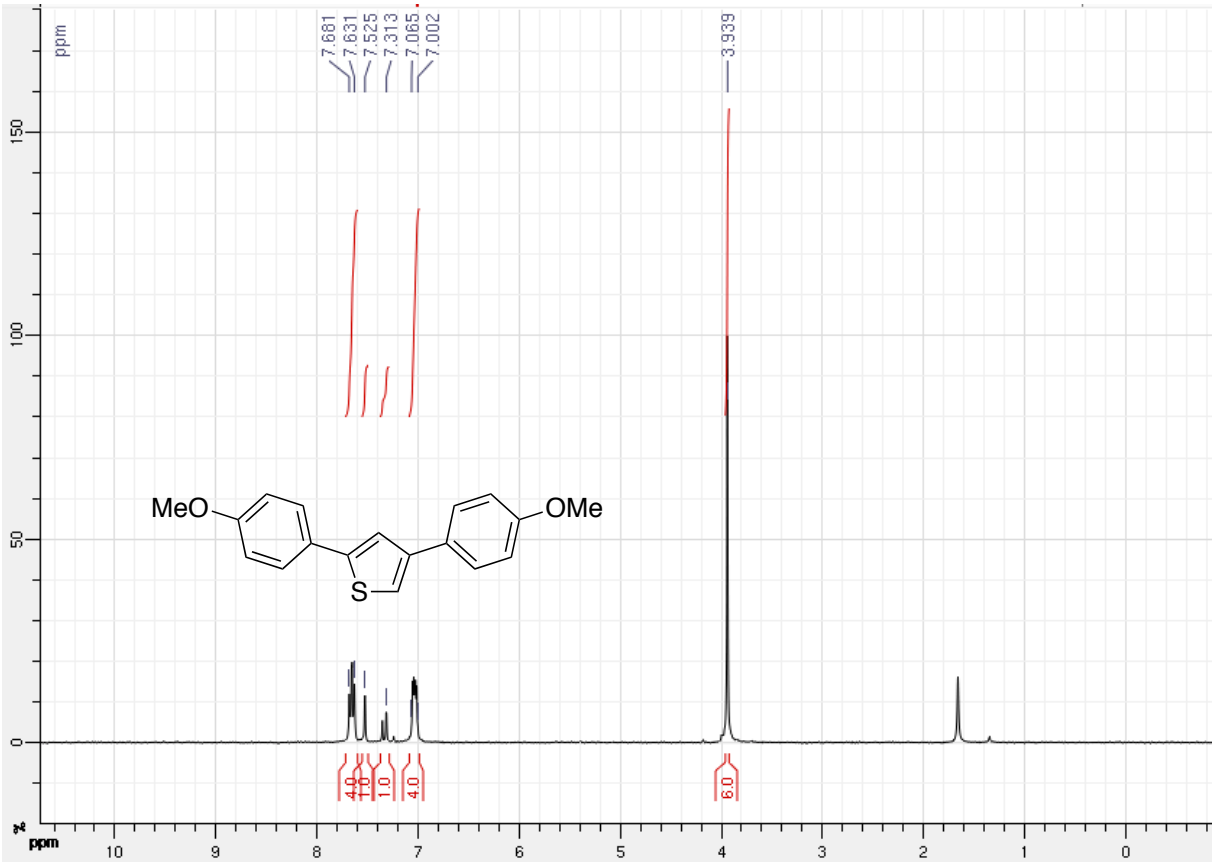


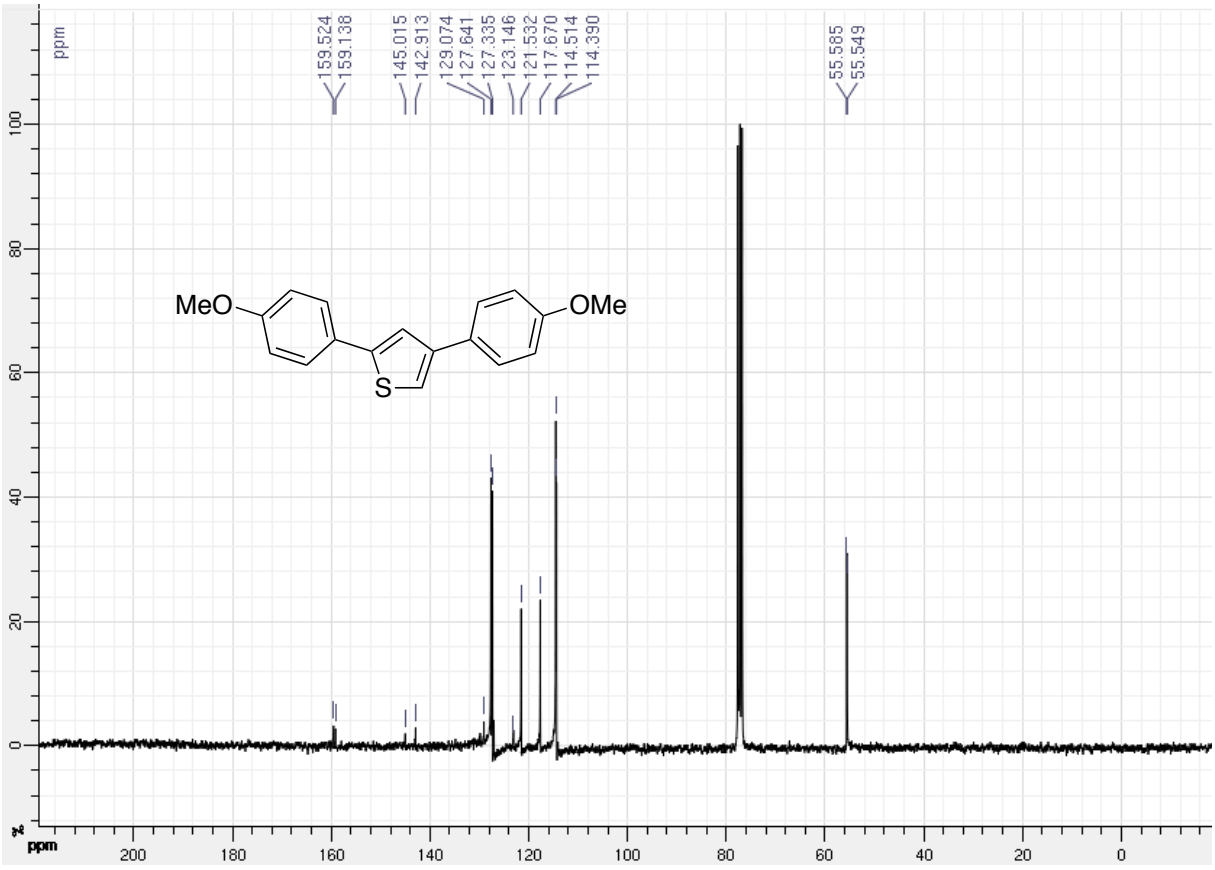
2,4-bis(4-Isopropylphenyl)thiophene (2d)



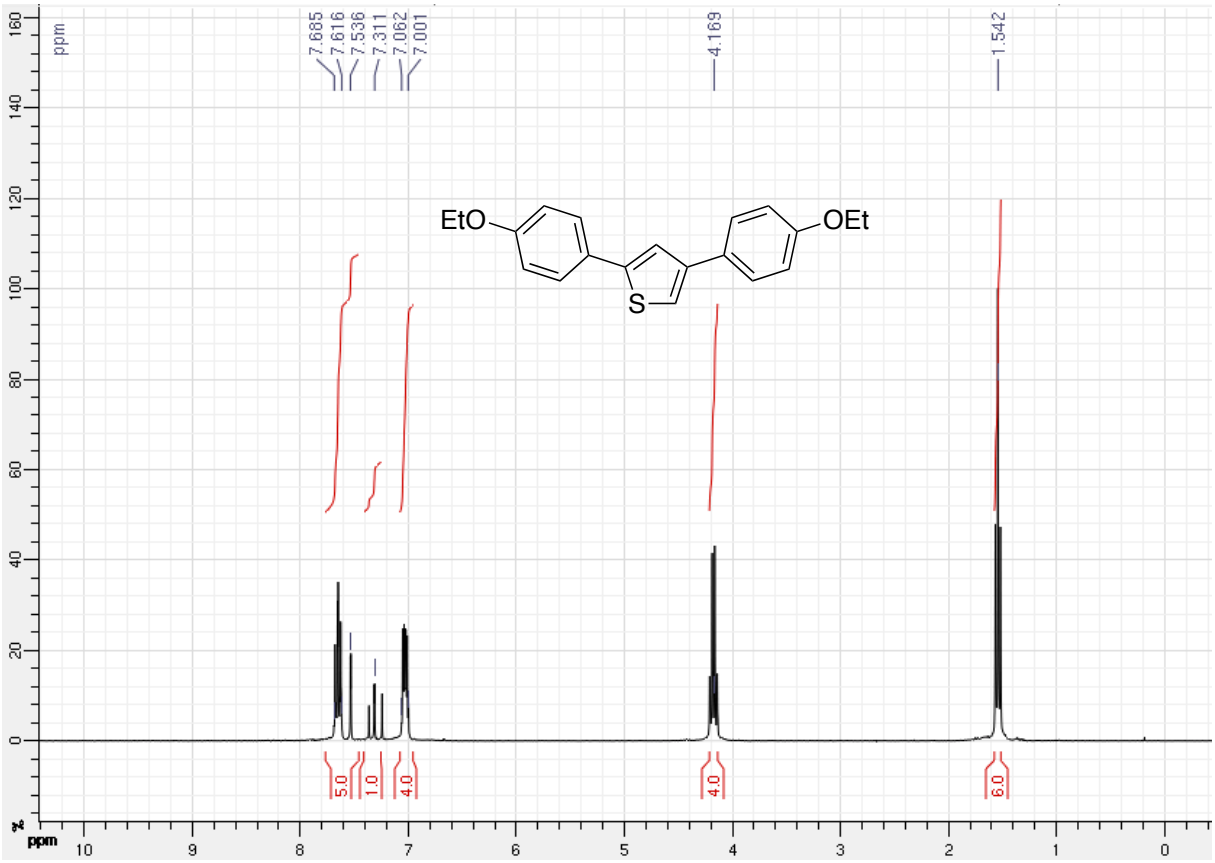


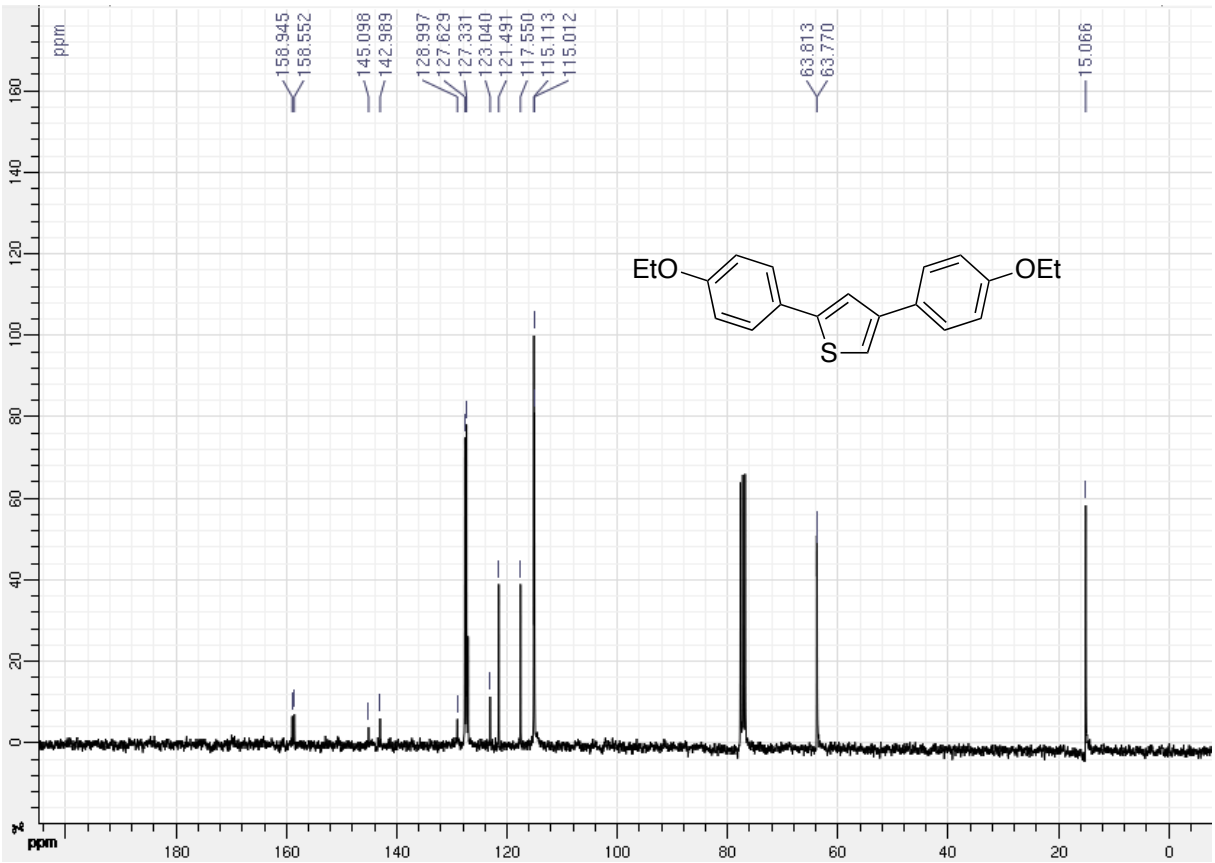
2,4-bis(4-Methoxyphenyl)thiophene (2e)



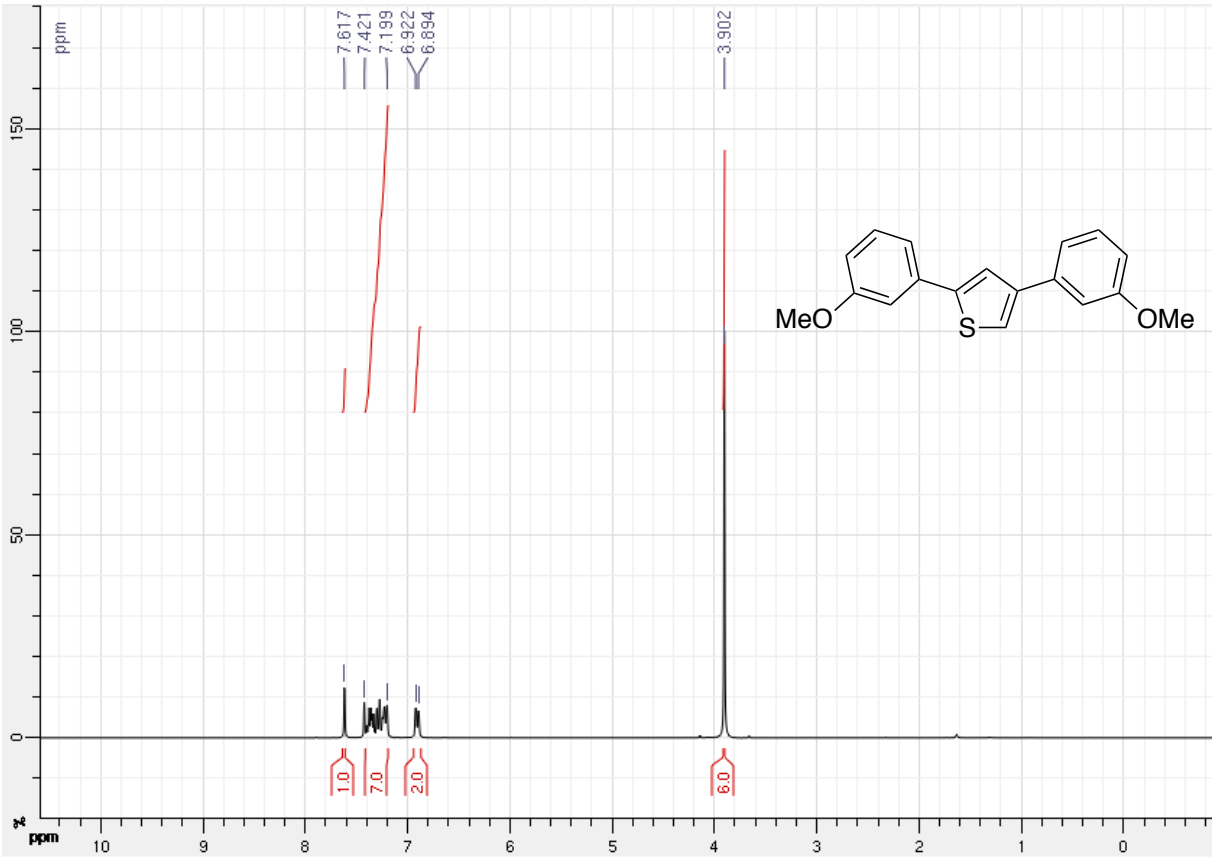


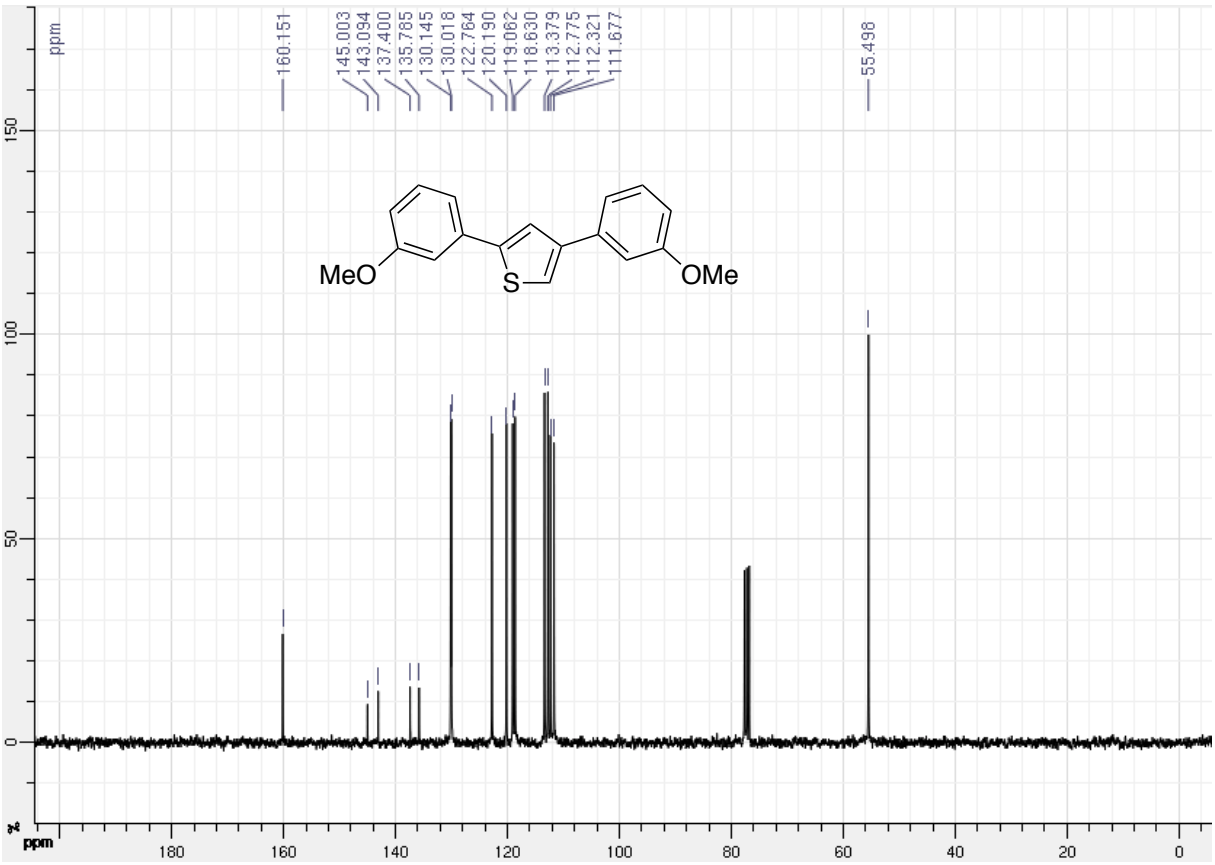
2,4-bis(4-Ethoxyphenyl)thiophene (2f)



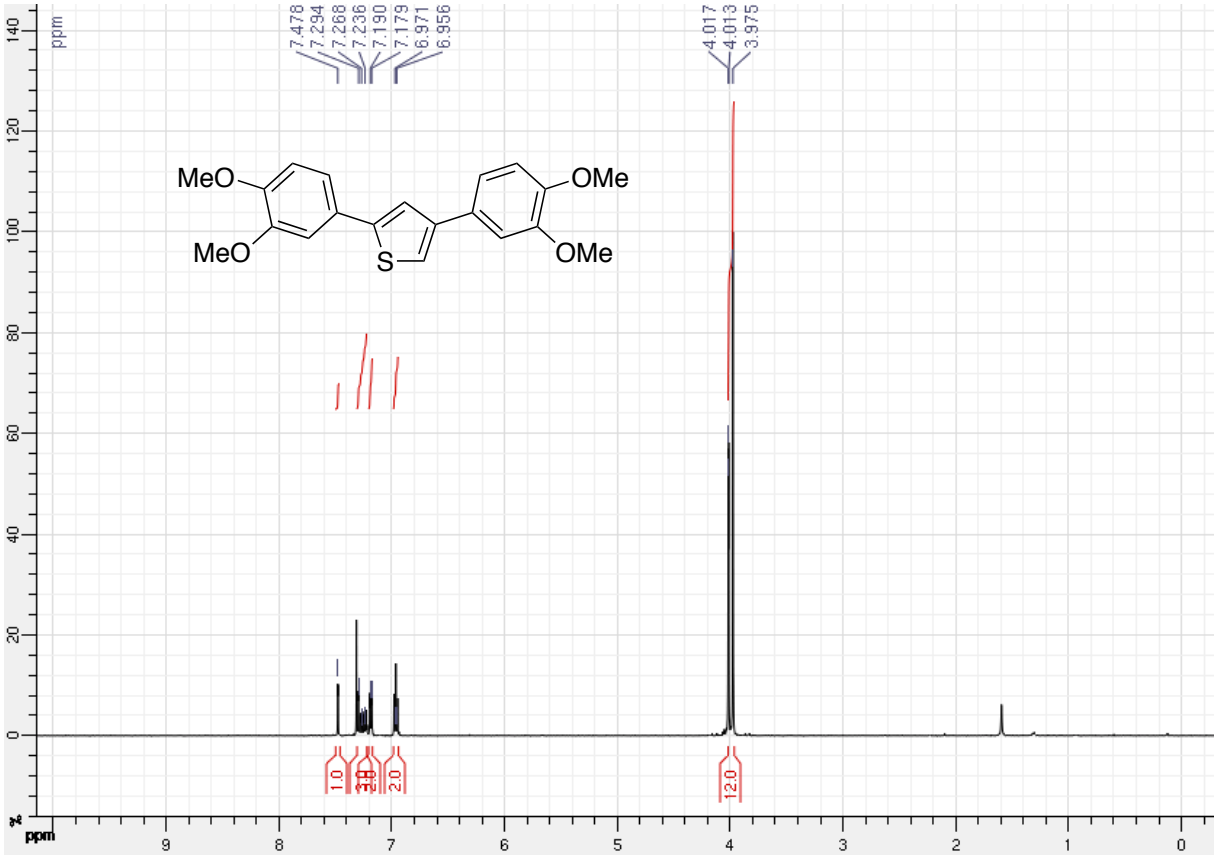


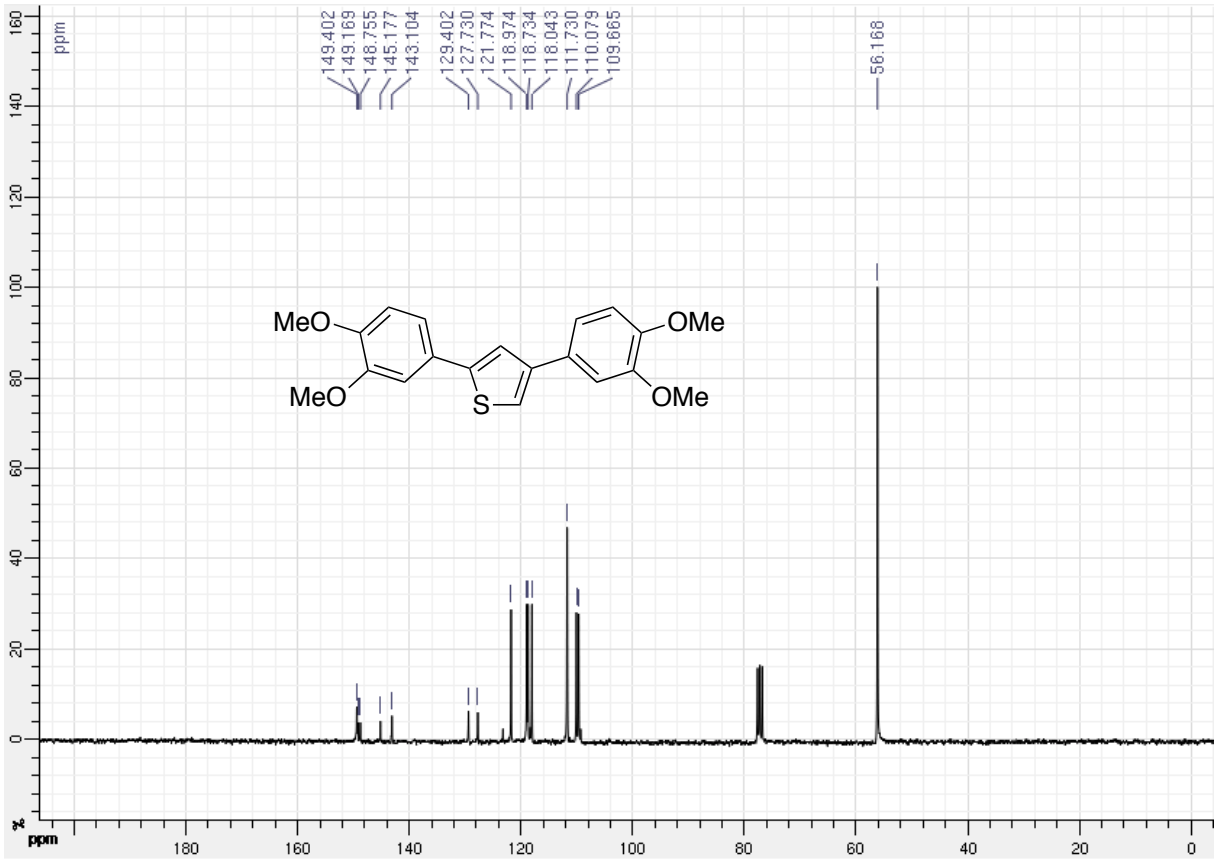
2,4-bis(3-Methoxyphenyl)thiophene (2g)



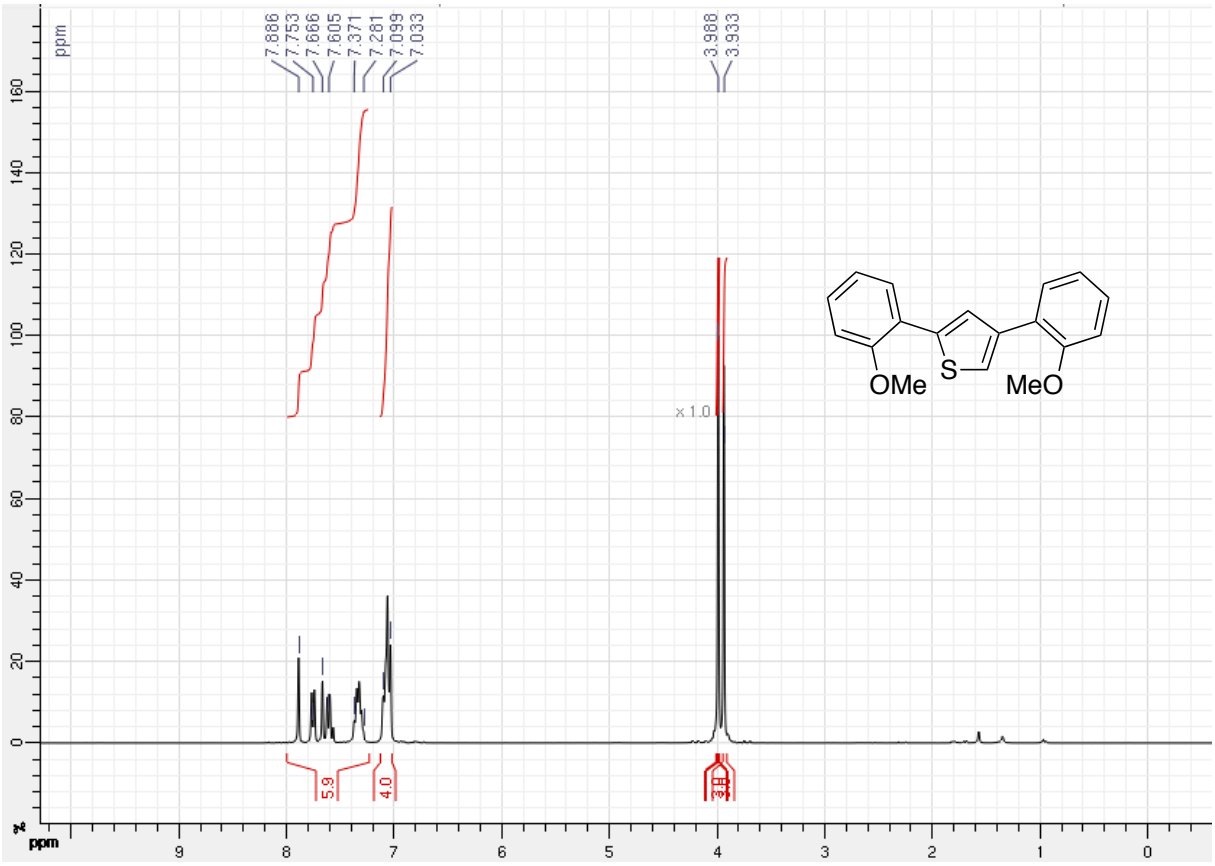


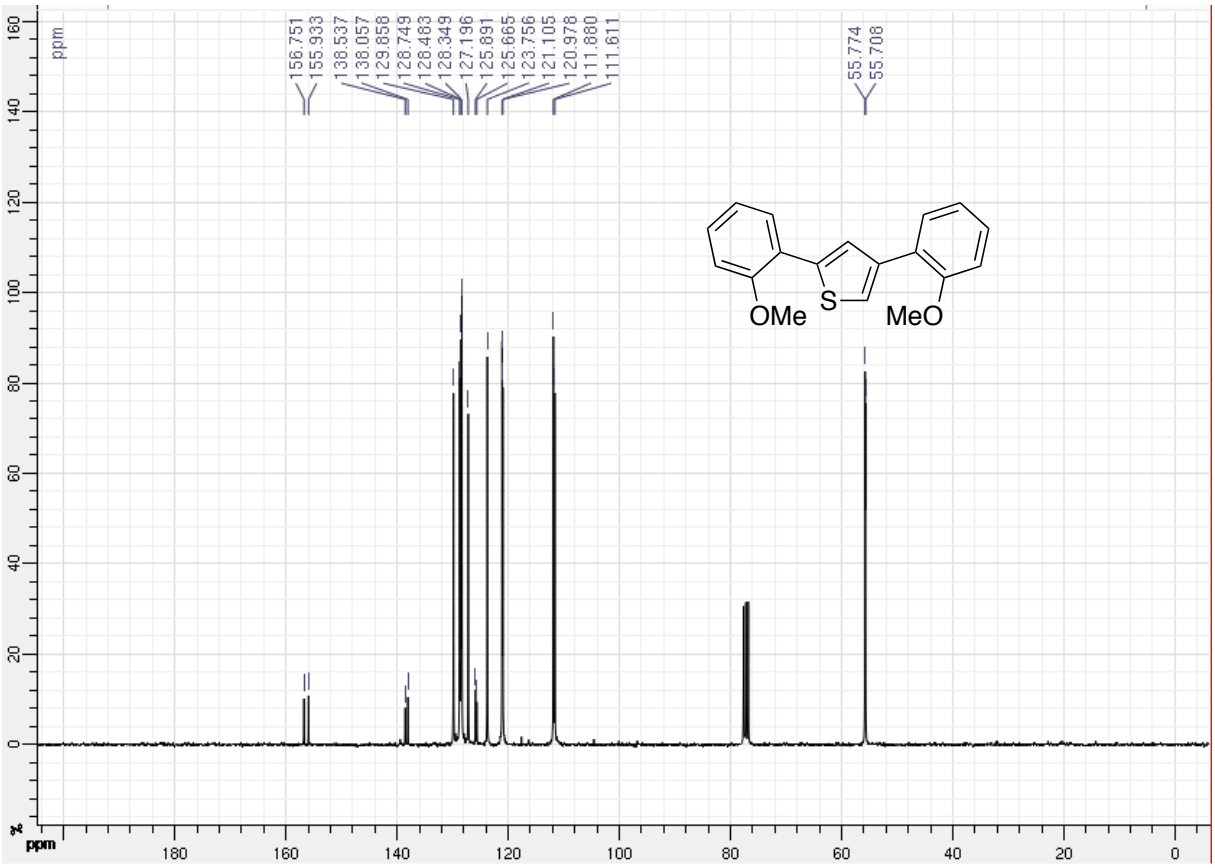
2,4-bis(3,4-Dimethoxyphenyl)thiophene (2h)



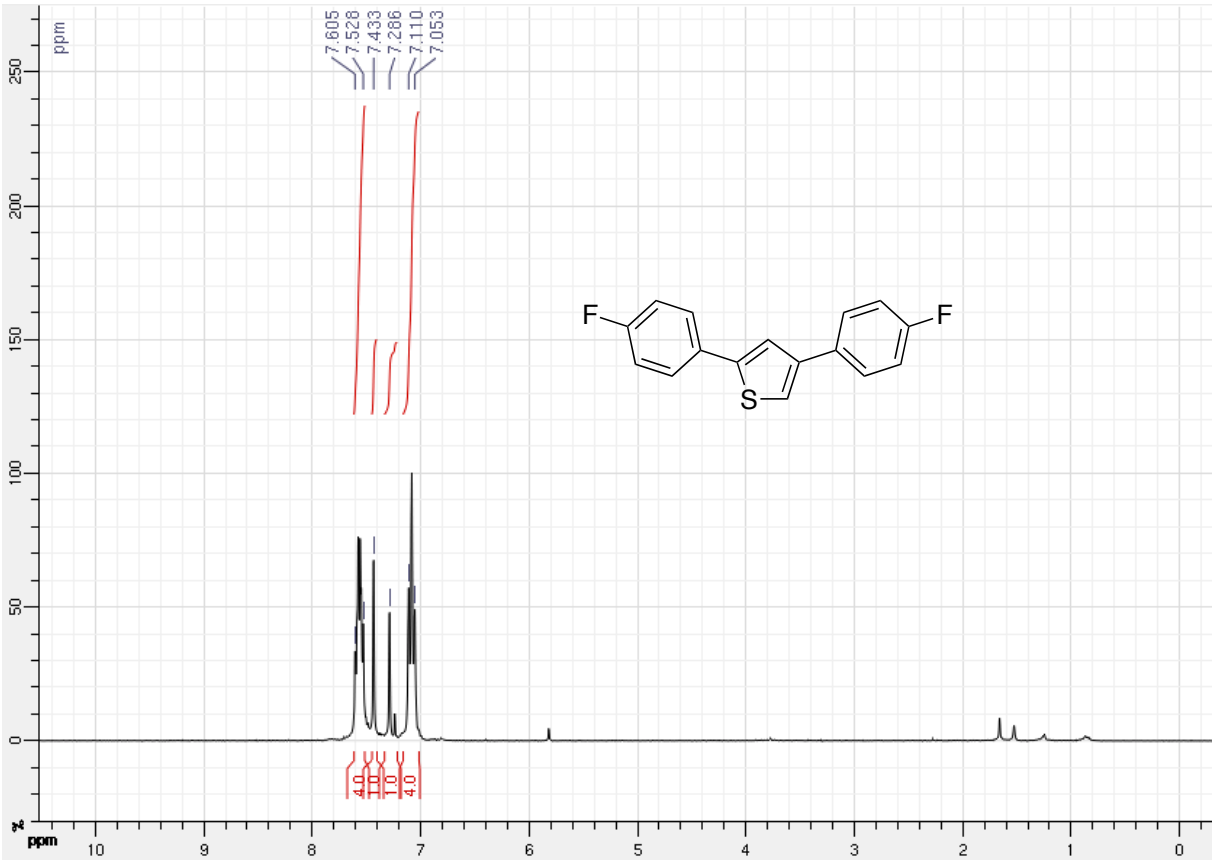


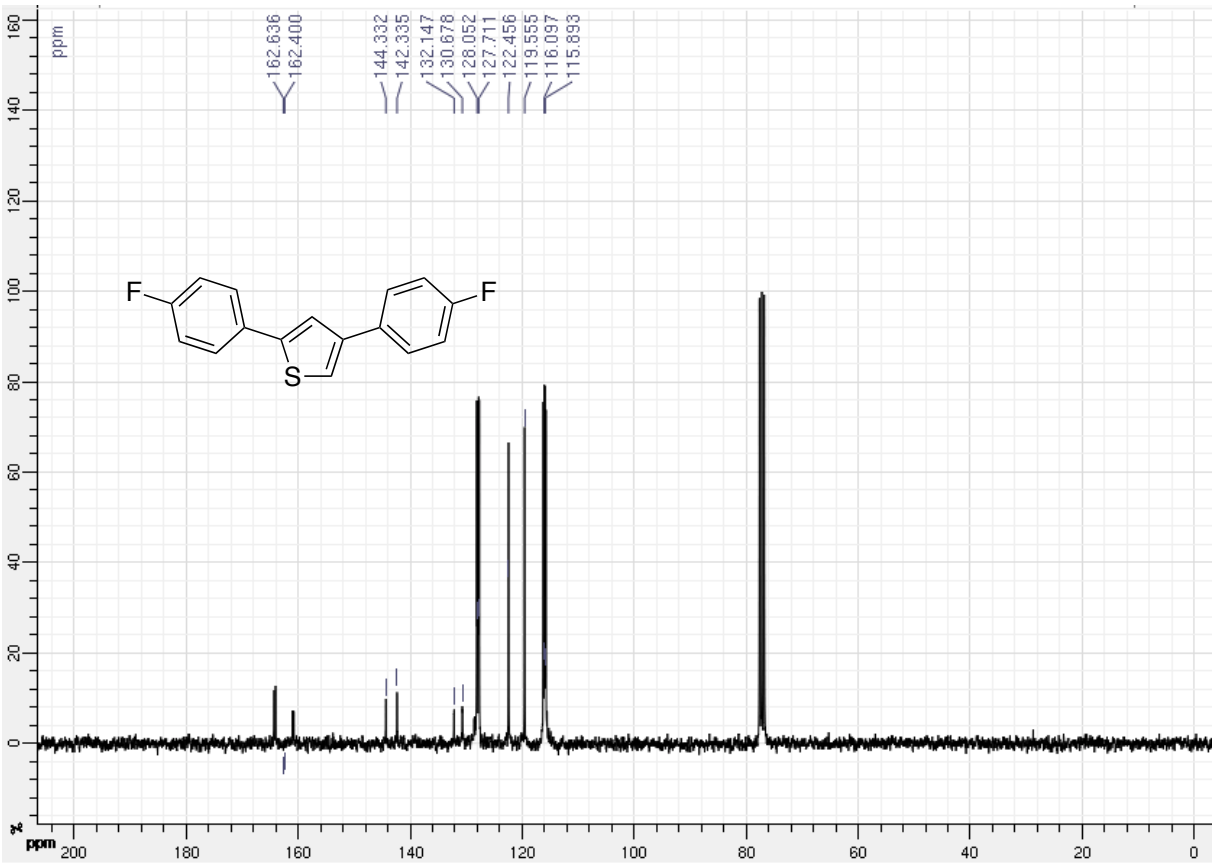
2,4-bis(2-Methoxyphenyl)thiophene (2i)



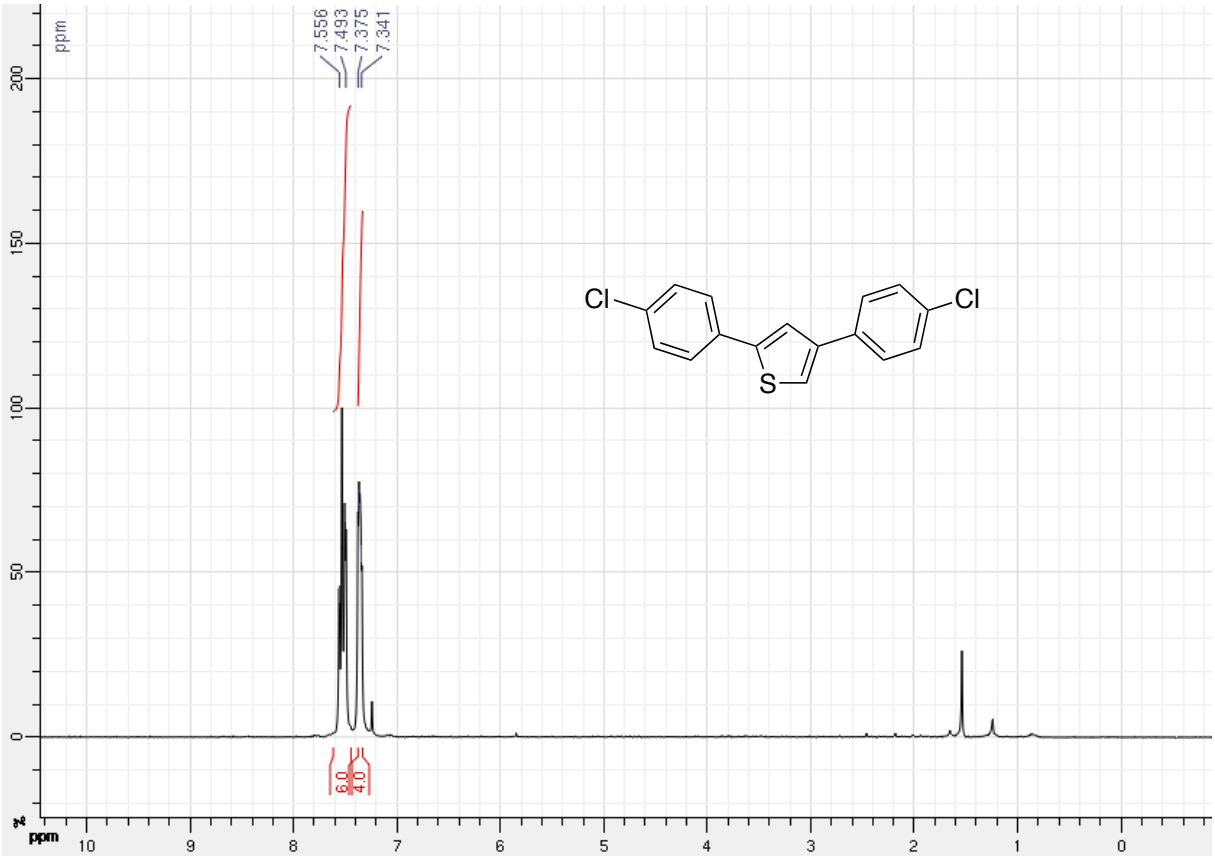


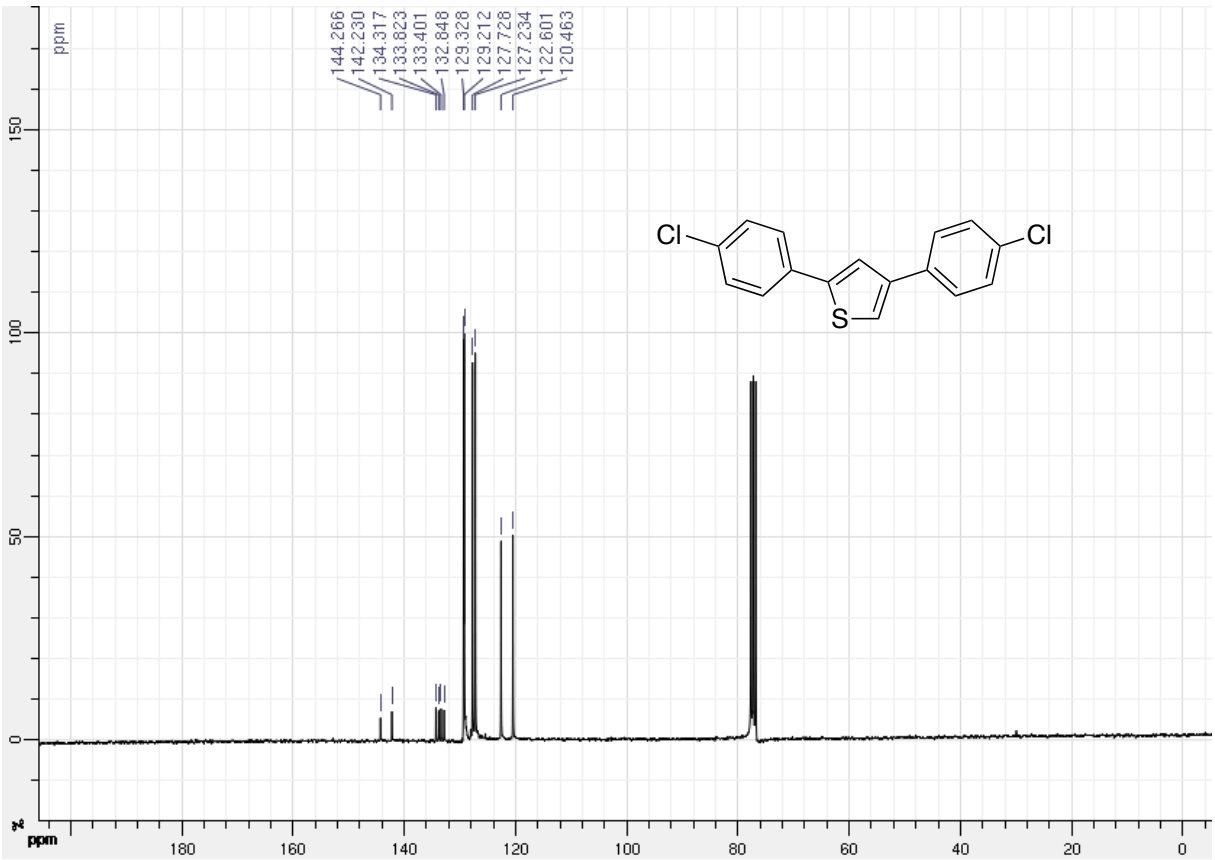
2,4-bis(4-Fluorophenyl)thiophene (2j)



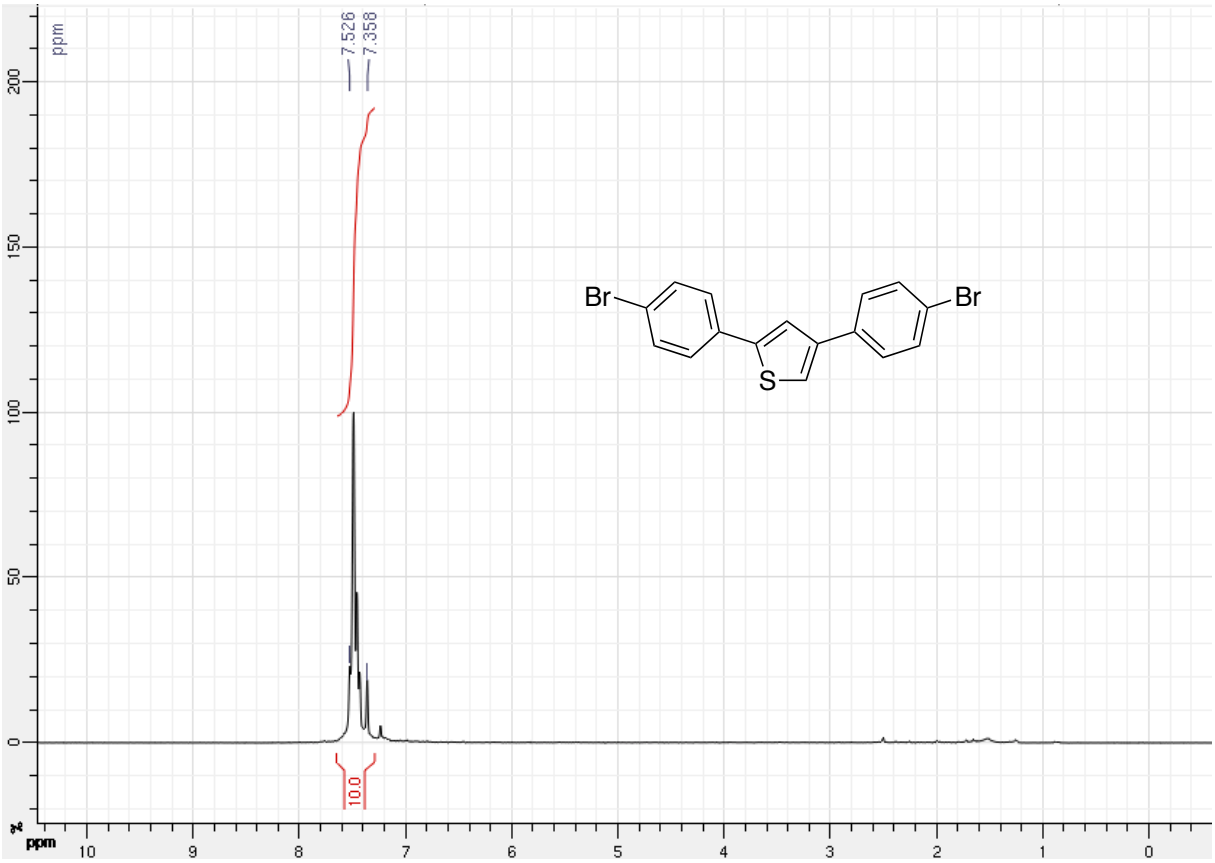


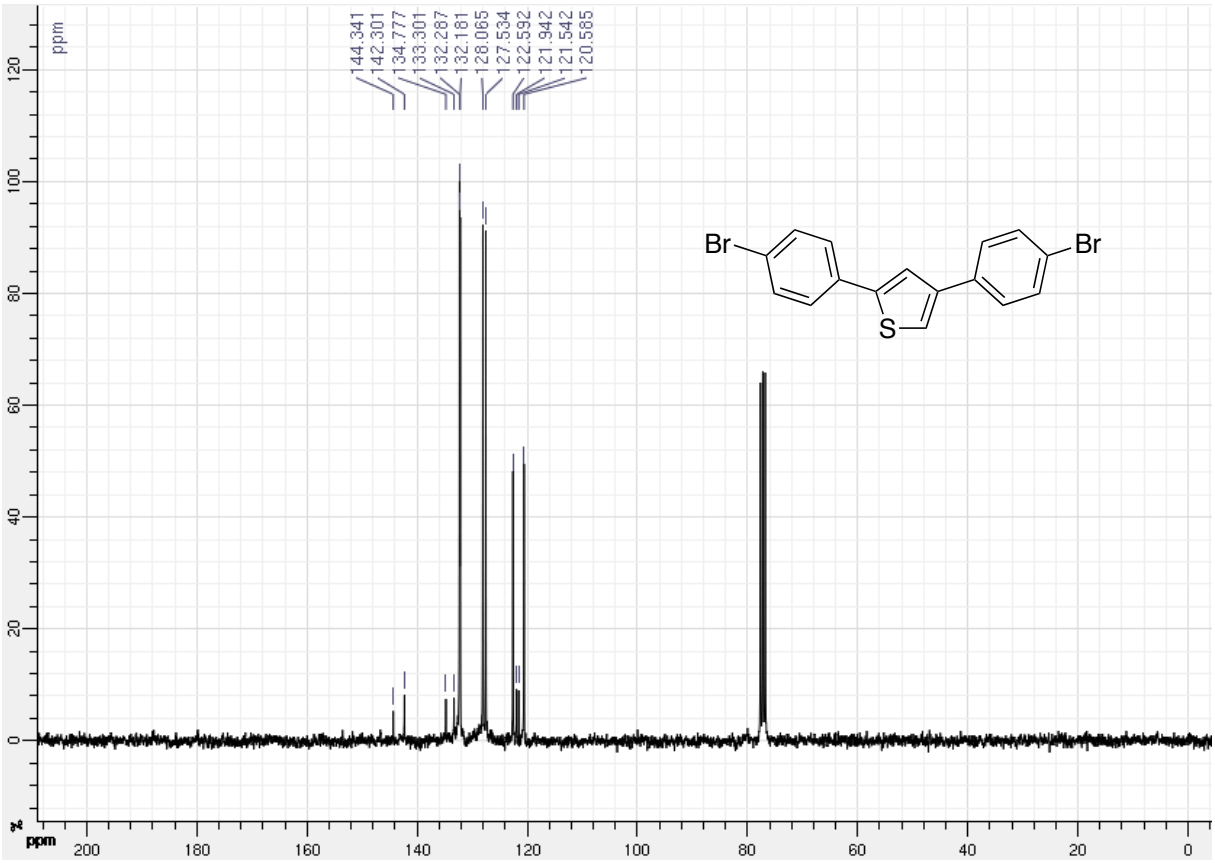
2,4-bis(4-Chlorophenyl)thiophene (2k)



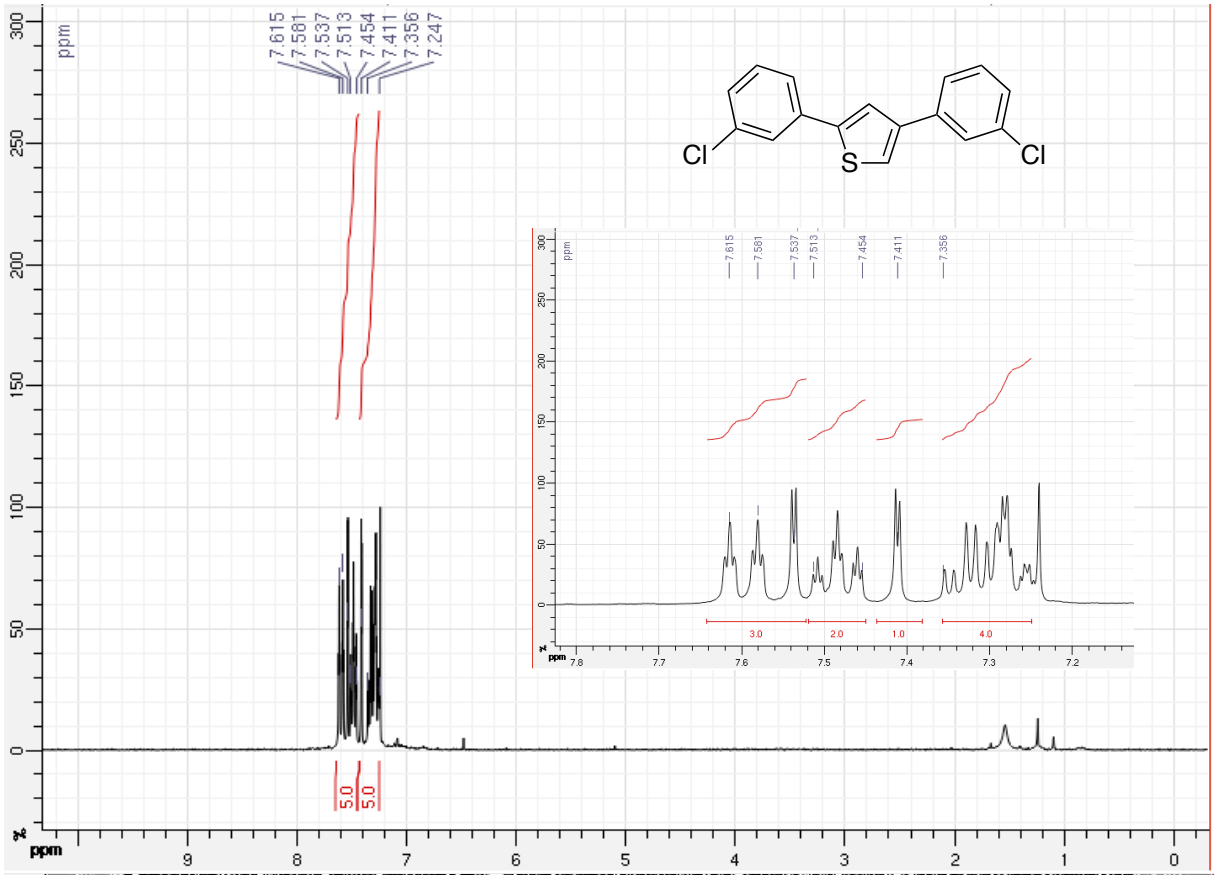


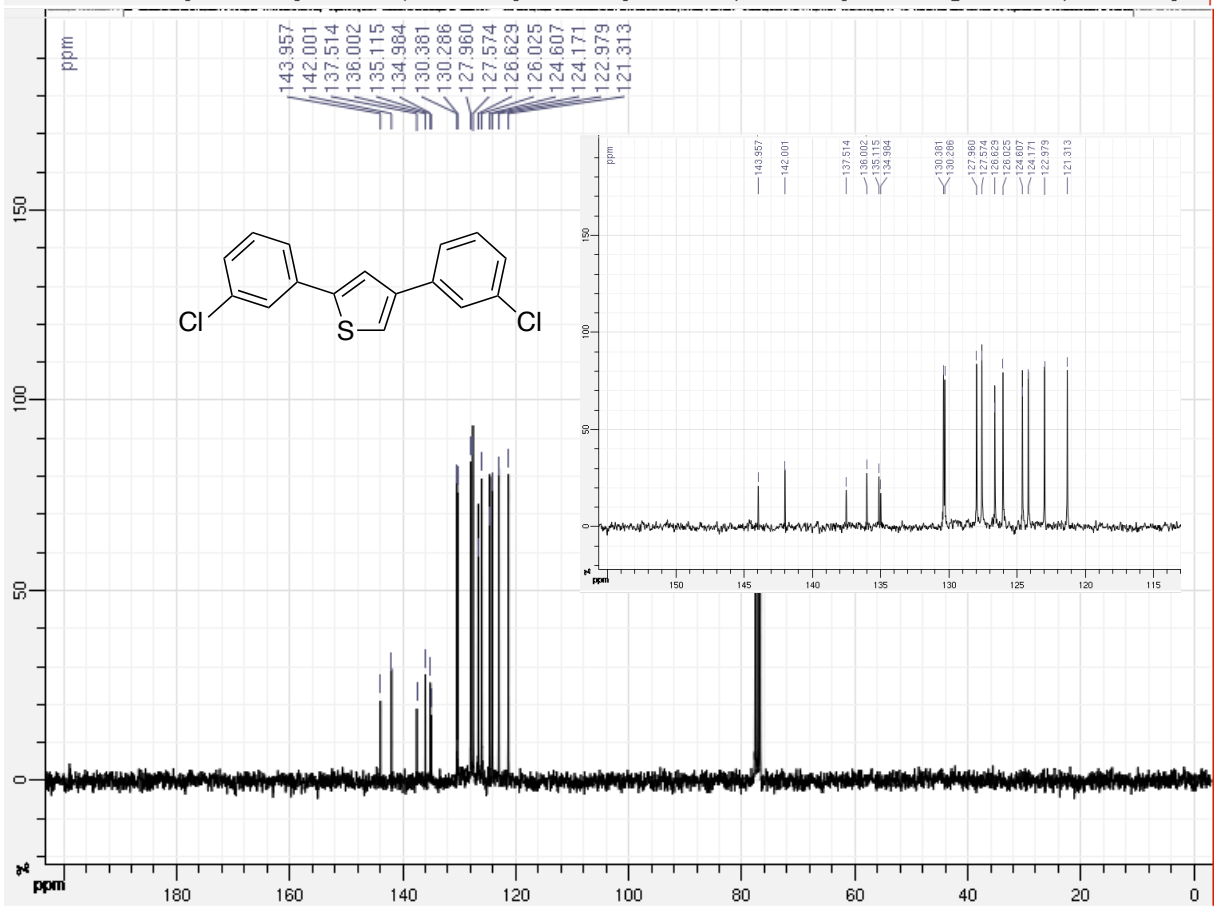
2,4-bis(4-Bromophenyl)thiophene (2l)



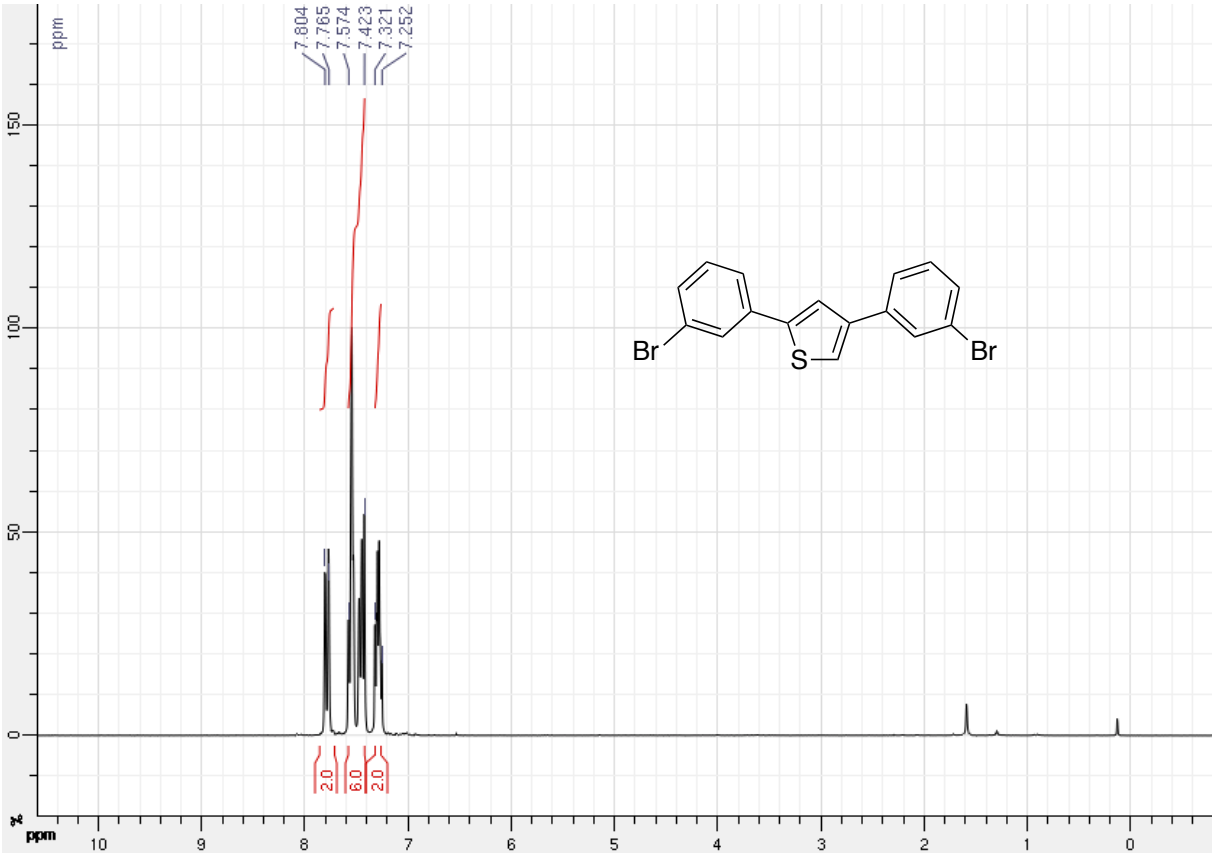


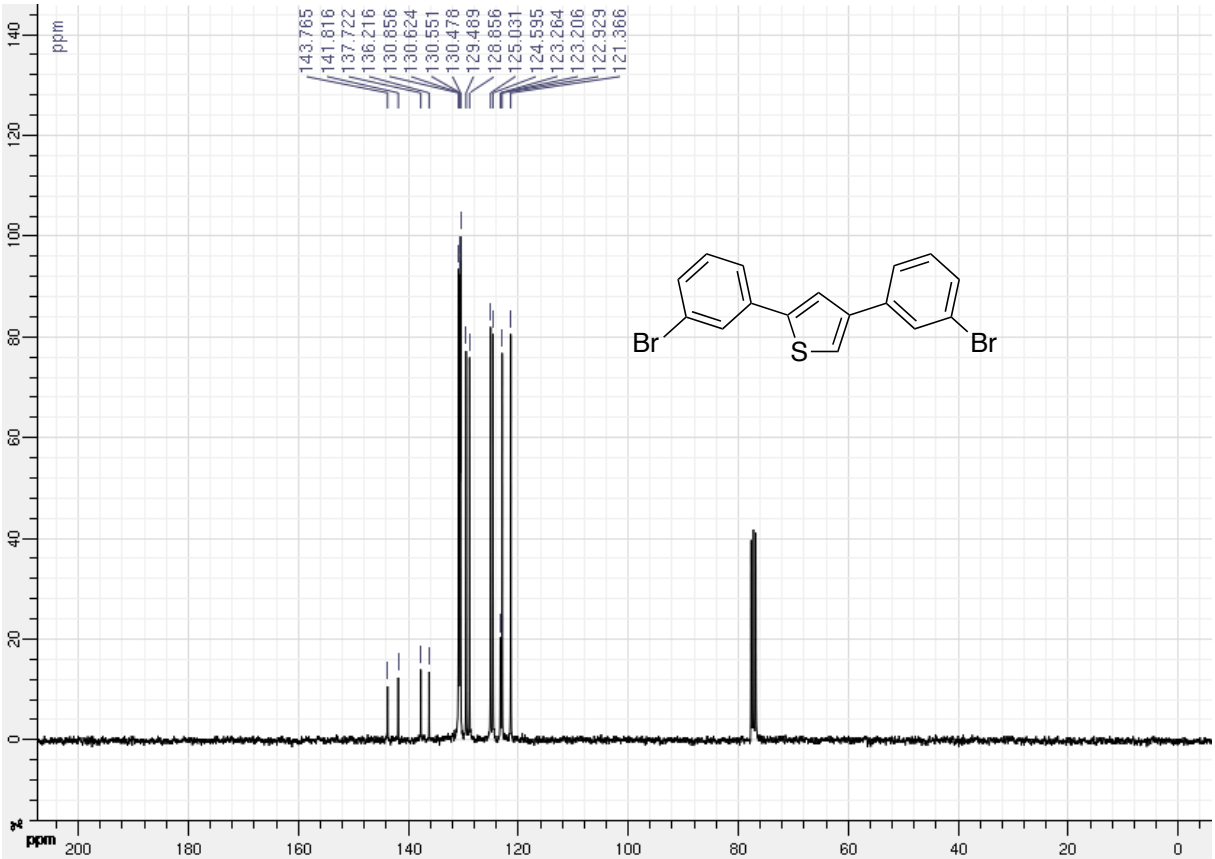
2,4-bis(3-Chlorophenyl)thiophene (2m)



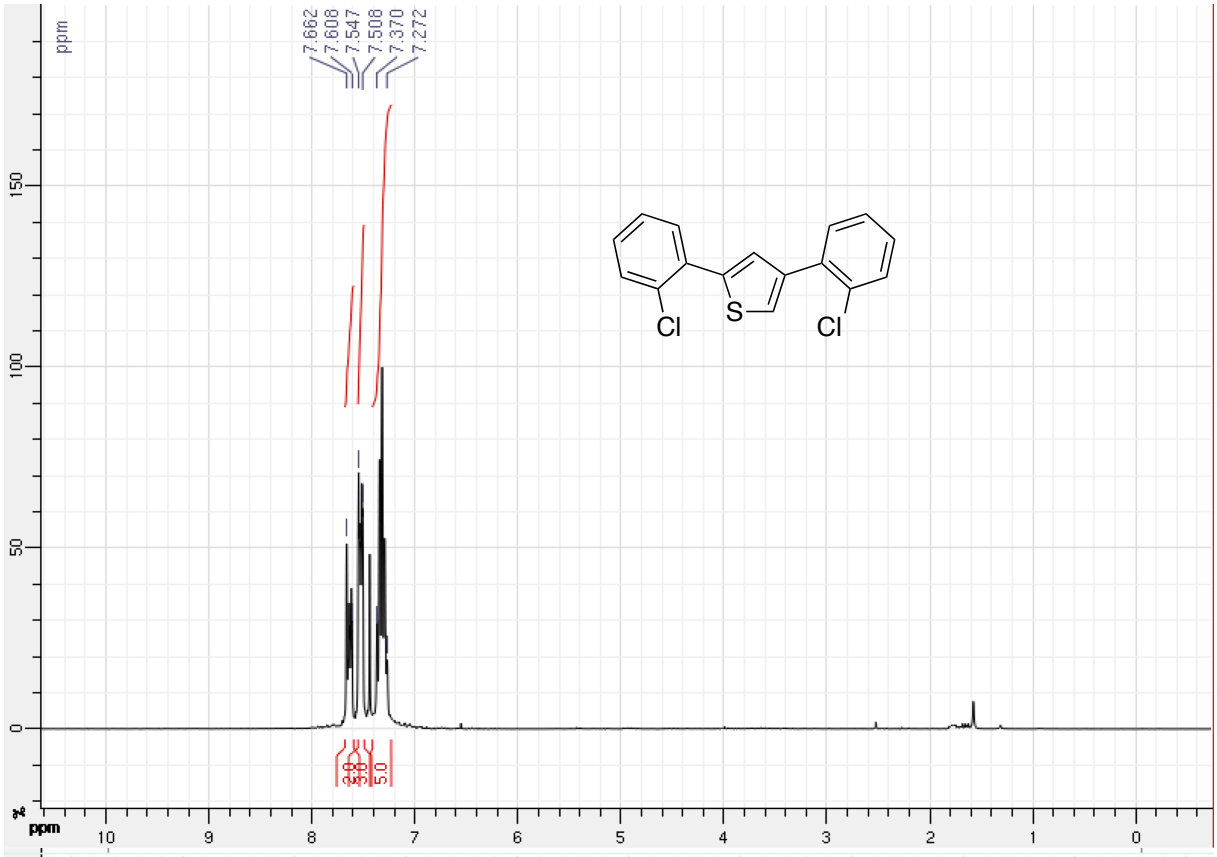


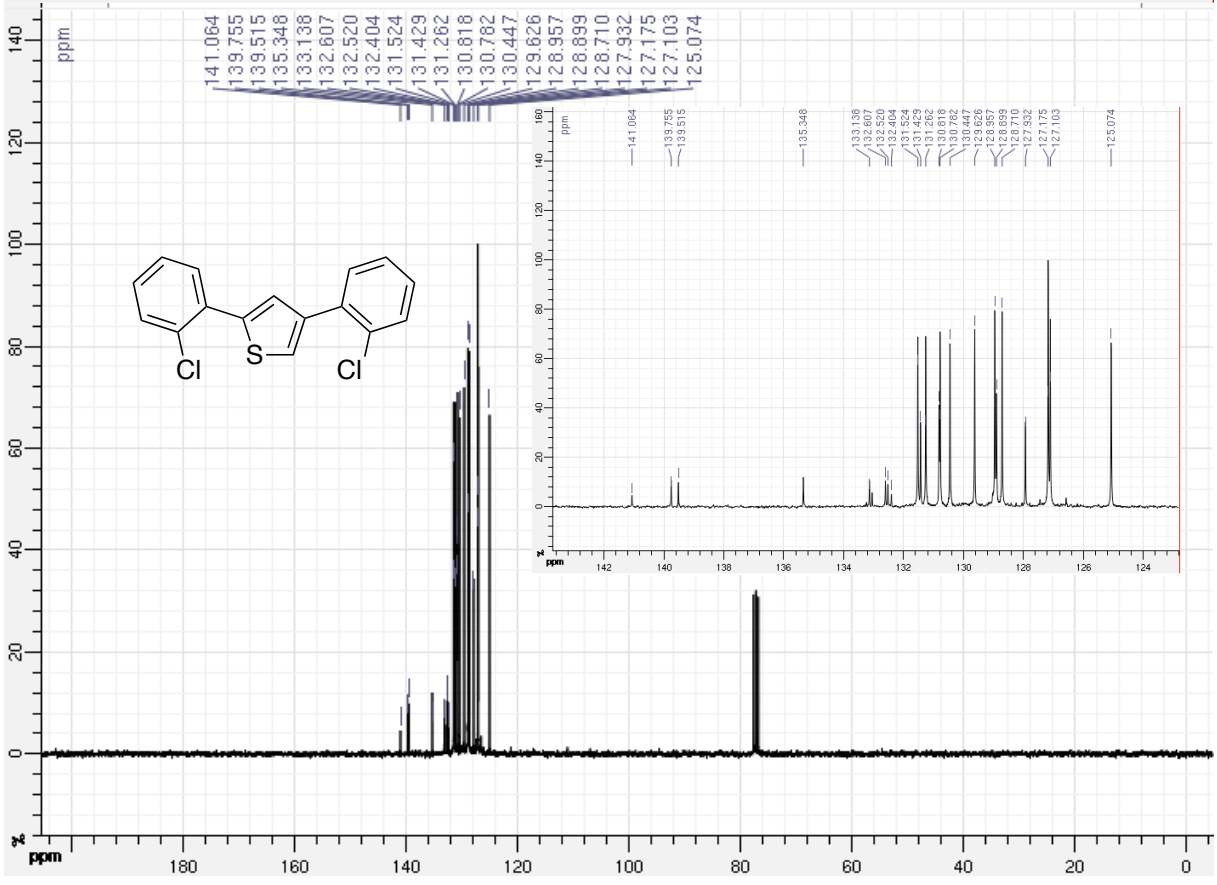
2,4-bis(3-Bromophenyl)thiophene (2n)



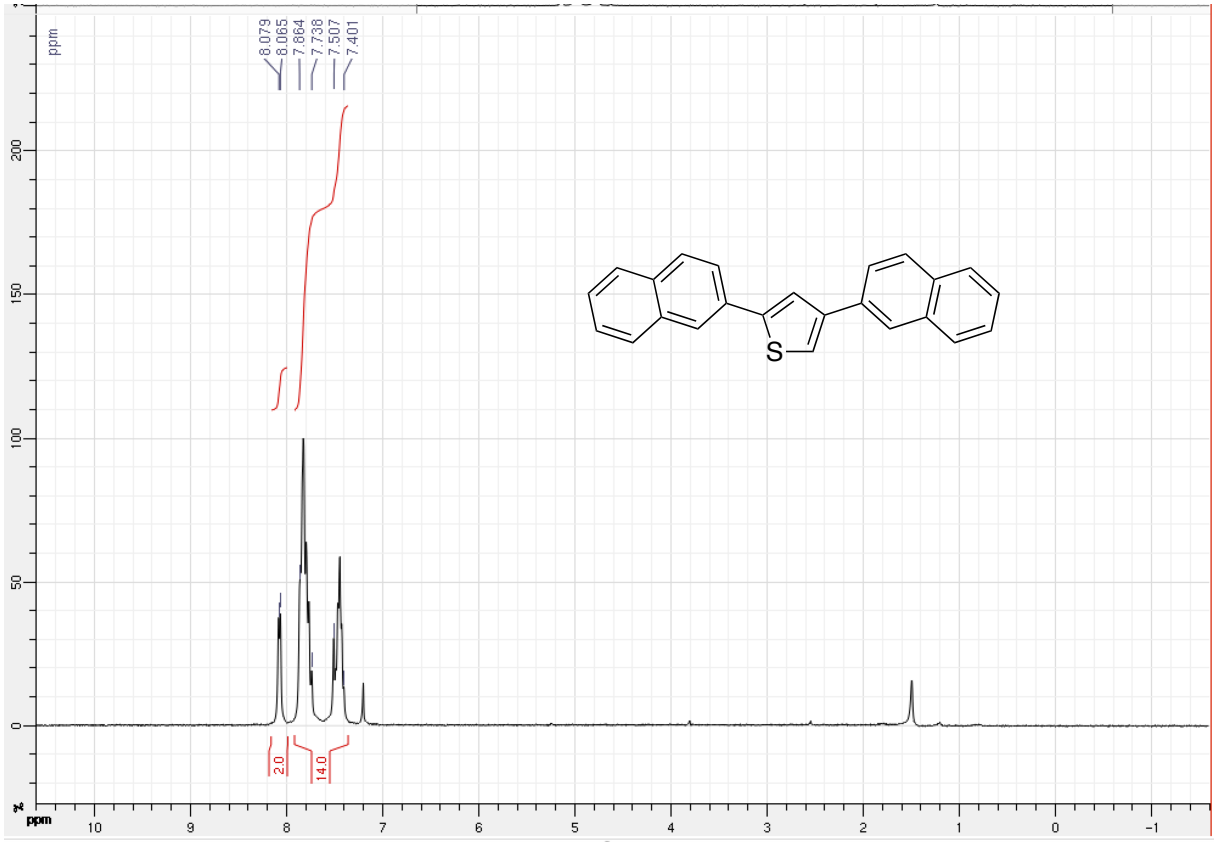


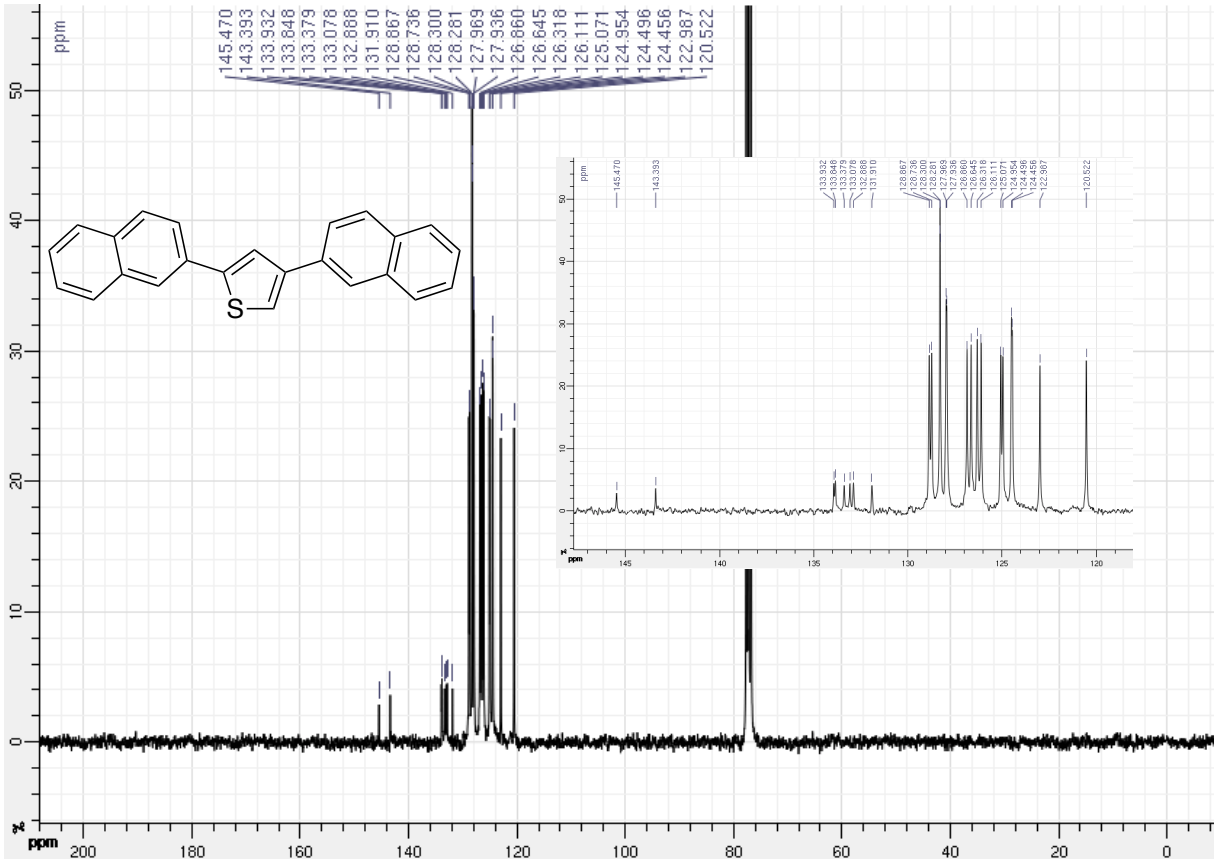
2,4-bis(2-Chlorophenyl)thiophene (2o)





2,4-Di(naphthalen-2-yl)thiophene (2p)





1,2,3,5,6,7-Hexahydrodicyclopenta[*b*,*d*]thiophene (2q)