Supplementary material

Benzenesulfonyl chlorides: New reagents for access to alternative regioisomers in palladium-catalysed direct arylations of thiophenes

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CONTENT

General:

All reactions were carried out under an inert atmosphere with standard Schlenk techniques. HPLC grade solvents (acetonitrile, dimethylsulfoxide, 1,4-dioxane and *N*-methyl-2-pyrrolidone) were used and stored under argon without further purification. Toluene was dried and purified by solvent purification system equipped with a series of activated filter columns. ^{1}H NMR spectra were recorded on Bruker GPX (300 MHz, 400 MHz) spectrometer. Chemical shifts (δ) were reported in parts per million relative to residual chloroform (7.26 ppm for ^{1}H; 77.0 ppm for ^{13}C), constants were reported in Hertz. ^{1}H NMR assignment abbreviations were the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). ^{13}C NMR spectra were recorded at 75 MHz, 100 MHz on the same spectrometer and reported in ppm. All reagents were weighed and handled in air, and refilled with an inert atmosphere of argon at room temperature.

General procedure:

To a 25 mL oven dried Schlenk tube, arylsulfonyl chloride (1 mmol), thiophene derivative (1.5 mmol), Li_2CO_3 (6 mmol, 0.444 g), 1,4–dioxane (2 mL) and bis(acetonitrile)dichloropalladium(II) (0.05 mmol, 12.9 mg) were successively added. The reaction mixture was evacuated by vacuum-argon cycles (5 times) and stirred at 140 °C (oil bath temperature) for 40 hours. After cooling the reaction at room temperature, the crude mixture was filtrated with a short column, the filtrate was analysed by GC and GC-MS to determine the regioselectivity, and purified by silica column chromatography (Et_2O/PE) to afford the corresponding C3 or C4 arylated products.

2-Methyl-4-*p*-tolylthiophene (1b)[1]

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **1b** in 75% (0.141 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.15 (s, 1H), 7.04 (s, 1H), 2.52 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 140.3, 136.6, 133.3, 129.4, 126.1, 124.6, 117.3, 21.1, 15.4.

2-Methyl-4-(4-nitrophenyl)-thiophene (2)

The reaction of 4-nitrobenzenesulfonyl chloride (0.222 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **2** in 78% (0.171 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.38 (s, 1H), 7.10 (s, 1H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 142.2, 141.7, 139.6, 126.5, 124.3, 124.2, 121.1, 15.4. Elemental analysis: calcd (%) for $C_{11}H_9NO_2S$ (219.26): C 60.26, H 4.14; found: C 60.04, H 4.17.

2-Methyl-4-(4-cyanophenyl)-thiophene (3)

The reaction of 4-cyanobenzenesulfonyl chloride (0.202 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **3** in 71% (0.141 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.60 (m, 4H), 7.32 (s, 1H), 7.06 (s, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 140.2, 140.0, 132.6, 126.6, 124.0, 120.4, 119.0, 110.2, 15.4. Elemental analysis: calcd (%) for $C_{12}H_9NS$ (199.27): C 72.33, H 4.55; found: C 72.19, H 4.48.

2-Methyl-4-(4-trifluoromethylphenyl)-thiophene (4)

The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **4** in 80% (0.194 g) yield as a white solid (regioselectivity 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.28 (s, 1H), 7.07 (s, 1H), 2.54 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 62.42 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 140.5, 139.4, 128.6 (q, *J* = 32.6 Hz), 126.5, 125.7 (q, *J* = 3.2 Hz), 124.3, 124.0 (q, *J* = 271.8 Hz), 119.6, 15.4. Elemental analysis: calcd (%) for $C_{12}H_9F_3S$ (242.26): C 59.49, H 3.74; found: C 59.34, H 3.79.

4-(4-Chlorophenyl)-2-methylthiophene (5)

The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **5** in 67% (0.139 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 (s, 1H), 7.02 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.8, 140.7, 134.6, 132.6, 128.8, 127.4, 124.3, 118.3, 15.4. Elemental analysis: calcd (%) for $C_{11}H_9ClS$ (208.71): C 63.30, H 4.35; found: C 63.18, H 4.17.

4-(4-Bromophenyl)-2-methylthiophene (6)

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **6** in 88% (0.223 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.18 (s, 1H), 7.02 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.8, 135.0, 131.8, 127.7, 124.3, 120.7, 118.4, 15.4. Elemental analysis: calcd (%) for $C_{11}H_9BrS$ (253.16): C 52.19, H 3.58; found: C 52.27, H 3.44.

4-(4-Fluorophenyl)-2-methylthiophene (7)[1]

The reaction of 4-fluorobenzenesulfonyl chloride (0.195 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **7** in 88% (0.169 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.48 (m, 2H), 7.13 (d, *J* = 1.4 Hz, 1H), 7.11-7.03 (m, 2H), 7.02 (m, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, *J* = 245.4 Hz), 141.0, 140.7, 132.3 (d, *J* = 3.3 Hz), 127.6 (d, *J* = 8.1 Hz), 124.5, 117.7, 115.5 (d, *J* = 21.3 Hz), 15.3.

2-Methyl-4-phenylthiophene (8)[2]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **8** in 81% (0.141 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 6.98 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 140.5, 136.1, 128.7, 126.9, 126.2, 124.6, 118.0, 15.5.

2-Methyl-4-naphthalen-1-ylthiophene (9)

The reaction of naphthalene-1-sulfonyl chloride (0.227 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **9** in 31% (0.069 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.49-7.47 (m, 4H), 7.13 (s, 1H), 6.97 (s, 1H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 139.5, 135.3, 133.8, 131.7, 128.2, 127.9, 127.5, 126.7, 126.0, 125.9, 125.7, 125.4, 121.2, 15.3. Elemental analysis: calcd (%) for $C_{15}H_{12}S$ (224.32): C 80.31, H 5.39; found: C 80.47, H 5.28.

4-(4-Methoxyphenyl)-2-methylthiophene (10)

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and 2-methylthiophene (0.147 g, 1.5 mmol), affords **10** in 41% (0.086 g) yield as a white solid (regioselectivity 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 7.01 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 141.7, 140.3, 129.1, 127.3, 124.6, 116.6, 114.1, 55.3, 15.4. Elemental analysis: calcd (%) for $C_{12}H_{12}OS$ (204.29): C 70.55, H 5.92; found: C 70.59, H 6.02.

2-*n*Butyl-4-(4-chlorophenyl)-thiophene (11)

The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and 2-*n*-butylthiophene (0.210 g, 1.5 mmol), affords **11** in 62% (0.155 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.20 (s, 1H), 7.03 (s, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 1.72 (quint., *J* = 7.6 Hz, 2H), 1.43 (sext., *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 140.5, 134.7, 132.6, 128.8, 127.4, 123.1, 118.0, 33.7, 29.8, 22.2, 13.8. Elemental analysis: calcd (%) for $C_{14}H_{15}ClS$ (250.79): C 67.05, H 6.03; found: C 67.19, H 6.00.

2-*n*Butyl-4-*p*-tolylthiophene (12)

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-*n*-butylthiophene (0.210 g, 1.5 mmol), affords **12** in 63% (0.145 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.18 (s, 1H), 7.06 (s, 3H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.72 (quint., *J* = 7.6 Hz, 2H), 1.43 (sext., *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 141.7, 136.6, 133.4, 129.4, 126.1, 123.4, 117.1, 33.7, 29.9, 22.2, 21.1, 13.8. Elemental analysis: calcd (%) for $C_{15}H_{18}S$ (230.37): C 78.21, H 7.88; found: C 78.02, H 7.67.

2-*n*Butyl-4-(4-methoxyphenyl)-thiophene (13)

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and 2-*n*-butylthiophene (0.210 g, 1.5 mmol), affords **13** in 43% (0.106 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.11 (s, 1H), 7.03 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 2.84 (t, *J* = 7.6 Hz, 2H), 1.72 (quint., *J* = 7.6 Hz, 2H), 1.43 (sext., *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 146.5, 141.4, 129.1, 127.3, 123.3, 116.3, 114.1, 55.3, 33.7, 29.9, 22.2, 13.8. Elemental analysis: calcd (%) for $C_{15}H_{18}OS$ (246.37): C 73.13, H 7.36; found: C 73.24, H 7.38.

3-*p*-Tolylthiophene (14)[3a]

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and thiophene (0.504 g, 6 mmol), affords **14** in 48% (0.084 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.9 Hz, 2H), 7.41 (s, 1H), 7.37 (s, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 136.8, 133.1, 129.5, 129.4, 126.3, 126.0, 119.6, 21.1. The formation of **3,4-di-*p*-tolylthiophene[3b]** in low yield was also observed. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 2H), 7.09 (d, *J* = 7.9 Hz, 4H), 7.06 (d, *J* = 7.9 Hz, 4H), 2.33 (s, 6H).

3-(4-Methoxyphenyl)-thiophene (15)[4]

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and thiophene (0.504 g, 6 mmol), affords **15** in 34% (0.065 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.41-7.35 (m, 3H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 142.0, 128.7, 127.5, 126.2, 126.0, 118.9, 114.2, 55.3.

2-Chloro-4-(4-trifluoromethylphenyl)-thiophene (16)[5]

The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.490 g, 2 mmol) and 2-chlorothiophene (0.119 g, 1 mmol), affords **16** in 41% (0.108 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 1.8 Hz, 1H), 7.23 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 138.4, 131.5, 129.5 (q, *J* = 33.0 Hz), 126.3, 126.0 (q, *J* = 3.6 Hz), 125.2, 124.1 (q, *J* = 273.0 Hz), 120.0.

2-Chloro-4-phenylthiophene (17)[2]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 2-chlorothiophene (0.178 g, 1.5 mmol), affords **17** in 69% (0.134 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.8 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (s, 1H), 7.19 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 135.1, 130.7, 128.7, 127.6, 126.1, 125.5, 118.4.

2-Chloro-4-*p*-tolylthiophene (18)[6]

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-chlorothiophene (0.178 g, 1.5 mmol), affords **18** in 56% (0.117 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 1H), 7.14 (d, *J* = 1.5 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 137.4, 132.4, 130.5, 129.5, 125.9, 125.5, 117.8, 21.3.

2-Bromo-4-*p*-tolylthiophene (19)

The reaction of 4-methylbenzenesulfonyl chloride (0.382 g, 2 mmol) and 2-bromothiophene (0.163 g, 1 mmol), affords **19** in 53% (0.134 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 1H), 7.18 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 137.4, 132.2, 129.5, 129.1, 126.0, 120.7, 112.7, 21.1. Elemental analysis: calcd (%) for $C_{11}H_9BrS$ (253.16): C 52.19, H 3.58; found: C 52.04, H 3.77.

2-Bromo-4-(4-chlorophenyl)-3-methylthiophene (20)

The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and 2-bromo-3-methylthiophene (0.266 g, 1.5 mmol), affords **20** in 80% (0.230 g) yield as a colorless oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.13 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 135.5, 135.3, 133.5, 129.8, 128.6, 122.5, 110.8, 14.8. Elemental analysis: calcd (%) for $C_{11}H_8BrClS$ (287.60): C 45.94, H 2.80; found: C 46.08, H 3.04.

2-Bromo-3-methyl-4-phenylthiophene (21)[7]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 2-bromo-3-methylthiophene (0.266 g, 1.5 mmol), affords **21** in 67% (0.170 g) yield as a colourless oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.4 Hz, 2H), 7.40-7.30 (m, 3H), 7.15 (s, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 136.9, 135.7, 128.5, 128.4, 127.4, 122.2, 110.5, 14.8.

2-Bromo-3-methyl-4-*p*-tolylthiophene (22)

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 2-bromo-3-methylthiophene (0.266 g, 1.5 mmol), affords **22** in 71% (0.190 g) yield as a colourless oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 4H), 7.11 (s, 1H), 2.40 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 137.2, 135.7, 134.0, 129.1, 128.4, 121.9, 110.3, 21.1, 14.8. Elemental analysis: calcd (%) for $C_{12}H_{11}BrS$ (267.19): C 53.94, H 4.15; found: C 53.99, H 4.31.

1-(4-Phenylthiophen-2-yl)-ethanone (23)[8]

The reaction of benzenesulfonyl chloride (0.354 g, 2 mmol) and 2-methyl-2-(thiophen-2-yl)-1,3-dioxolane (0.170 g, 1 mmol), affords **23** in 61% (0.123 g) yield as a yellow oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.73 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.7, 144.9, 143.4, 134.8, 131.1, 129.0, 128.3, 127.8, 126.3, 26.9.

1-[4-(4-Bromophenyl)-thiophen-2-yl]-ethanone (24)

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and 2-methyl-2-(thiophen-2-yl)-1,3-dioxolane (0.255 g, 1.5 mmol), affords **24** in 29% (0.082 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.64 (s, 1H), 7.48 (d,

J = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5, 145.2, 142.1, 133.7, 132.1, 130.6, 128.4, 127.8, 121.8, 26.9. Elemental analysis: calcd (%) for $C_{12}H_9BrOS$ (281.17): C 51.26, H 3.23; found: C 51.21, H 3.08.

4-(4-Trifluoromethylphenyl)-[2,2']bithiophenyl (25)

The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and [2,2']bithiophenyl (0.249 g, 1.5 mmol), affords **25** in 78% (0.242 g) yield as a white solid (regioselectivity 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.44 (s, 1H), 7.39 (s, 1H), 7.26 (d, *J* = 3.6 Hz, 1H), 7.22 (d, *J* = 2.7 Hz, 1H), 7.07 (dd, *J* = 3.6, 2.7 Hz, 1H). ^{19}F NMR (376 MHz, $CDCl_3$): δ. 62.4 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.3, 138.8, 138.7, 136.8, 129.2 (q, *J* = 32.3 Hz), 127.9, 126.4, 125.8 (q, *J* = 3.6 Hz), 124.9, 124.2, 124.1 (q, *J* = 272.0 Hz), 122.5, 120.5. Elemental analysis: calcd (%) for $C_{15}H_9F_3S_2$ (310.36): C 58.05, H 2.92; found: C 58.04, H 3.00.

4-(4-Bromophenyl)-[2,2']bithiophenyl (26)

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and [2,2']bithiophenyl (0.249 g, 1.5 mmol), affords **26** in 60% (0.193 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 1.2 Hz, 1H), 1H), 7.30 (d, *J* = 1.2 Hz, 1H), 7.25-7.20 (m, 2H), 7.0 (dd, *J* = 5.2, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 138.4, 137.0, 134.4, 131.9, 127.9, 127.8, 124.7, 124.0, 122.5, 121.2, 119.4. Elemental analysis: calcd (%) for $C_{14}H_9BrS_2$ (321.26): C 52.34, H 2.82; found: C 52.17, H 3.01.

3-Methyl-4-phenylthiophene (27)[1]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 3-methylthiophene (0.147 g, 1.5 mmol), affords **27** in 86% (0.150 g) yield as a colorless oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.30 (m, 5H), 7.20 (d, *J* = 3.2 Hz, 1H), 7.03 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 137.1, 136.1, 128.6, 128.3, 126.9, 122.9, 121.9, 15.5.

3-Methyl-4-*p*-tolylthiophene (28)[9]

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 3-methylthiophene (0.147 g, 1.5 mmol), affords **28** in 55% (0.103 g) yield as a colorless oil (regioselectivity >98%). ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 3.3 Hz, 1H), 7.03 (dq, *J* = 3.3 and 0.7 Hz, 1H), 2.41 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 136.6, 136.2, 134.2, 129.0, 128.5, 122.6, 121.8, 21.1, 15.5.

3-Chloro-4-phenylthiophene (29)[5]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and 3-chlorothiophene (0.178 g, 1.5 mmol), affords **29** in 62% (0.121 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.24 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 134.4, 128.8, 128.3, 127.7, 124.5, 123.3, 121.2.

3-Chloro-4-*p*-tolylthiophene (30)

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and 3-chlorothiophene (0.178 g, 1.5 mmol), affords **30** in 43% (0.089 g) yield as a white solid (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.28-7.22 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 137.6, 131.8, 129.0, 128.6, 124.8, 122.9, 121.1, 21.2. Elemental analysis: calcd (%) for $C_{11}H_9ClS$ (208.71): C 63.30, H 4.35; found: C 63.17, H 4.20.

3-Chloro-4-(4-methoxyphenyl)-thiophene (31)

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and 3-chlorothiophene (0.178 g, 1.5 mmol), affords **31** in 61% (0.137 g) yield as a white solid (regioselectivity 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 140.0, 129.9, 127.0, 124.8, 122.5, 121.1, 113.7, 55.3. Elemental analysis: calcd (%) for $C_{11}H_9ClOS$ (224.71): C 58.80, H 4.04; found: C 58.64, H 4.19.

3-Phenylbenzo[*b*]thiophene (32)[2]

The reaction of benzenesulfonyl chloride (0.177 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **32** in 83% (0.174 g) yield as a colorless oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.93 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.45-7.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 138.1, 137.9, 136.0, 128.7, 128.5, 127.5, 124.4, 124.3, 123.4, 122.9.

3-*p*-Tolylbenzo[b]thiophene (33)[10]

The reaction of 4-methylbenzenesulfonyl chloride (0.191 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **33** in 50% (0.112 g) yield as a colorless oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.90 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 2H), 7.37 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 138.1, 138.0, 137.3, 133.1, 129.4, 128.6, 124.3, 124.2, 123.1, 123.0, 122.9, 21.2.

3-(4-Methoxyphenyl)-benzo[b]thiophene (34)[10]

The reaction of 4-methoxybenzenesulfonyl chloride (0.207 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **34** in 62% (0.149 g) yield as a colorless oil (regioselectivity 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.88 (m, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.42-7.38 (m, 2H), 7.34 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 140.6, 138.1, 137.7, 129.8, 128.5, 124.3, 124.2, 122.9, 122.8, 122.5, 114.1, 55.3.

3-(4-Chlorophenyl)-benzo[b]thiophene (35)[1]

The reaction of 4-chlorobenzenesulfonyl chloride (0.211 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **35** in 88% (0.215 g) yield as a colorless oil (regioselectivity 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94-7.84 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.42-7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 137.6, 136.8, 134.4, 133.5, 129.9, 128.9, 124.5, 124.4, 123.7, 123.0, 122.6.

3-(4-Bromophenyl)-benzo[b]thiophene (36)[1]

The reaction of 4-bromobenzenesulfonyl chloride (0.256 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **36** in 83% (0.240 g) yield as a white solid (regioselectivity 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96-7.84 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.42-7.39 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 137.5, 136.8, 134.8, 131.9, 130.2, 124.6, 124.5, 123.7, 123.0, 122.6, 121.6.

3-(4-Trifluoromethylphenyl)-benzo[b]thiophene (37)[1]

The reaction of 4-(trifluoromethyl)benzenesulfonyl chloride (0.245 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **37** in 88% (0.245 g) yield as a colorless oil (regioselectivity 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.67 (m, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.39 (s, 1H), 7.38-7.31 (m, 2H). ^{19}F NMR (376 MHz, $CDCl_3$): δ 62.4 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 139.6, 137.4, 136.6, 129.5 (q, J = 32.6 Hz), 128.8, 125.7 (q, J = 4.0 Hz), 124.7, 124.6 (m), 124.1 (q, J = 271.8 Hz), 123.1, 122.5,

4-Benzo[b]thiophen-3-ylbenzonitrile (38)

The reaction of 4-cyanobenzenesulfonyl chloride (0.202 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **38** in 83% (0.195 g) yield as a colorless oil (regioselectivity >98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.90 (m, 1H), 7.89-7.83 (m, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.50 (s, 1H), 7.46-7.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 140.5, 137.0, 136.1, 132.5, 129.1, 125.3, 124.8, 124.7, 123.1, 122.3, 118.8, 111.1. Elemental analysis: calcd (%) for $C_{15}H_9NS$ (235.30): C 76.56, H 3.86; found: C 76.38, H 3.70.

Methyl 3-benzo[b]thiophen-3-ylthiophene-2-carboxylate (39)

The reaction of methyl 3-chlorosulfonylthiophene-2-carboxylate (0.241 g, 1 mmol) and benzo[b]thiophene (0.201 g, 1.5 mmol), affords **39** in 51% (0.140 g) yield as a colorless oil (regioselectivity 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 5.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.40-7.32 (m, 2H), 7.19 (d, J = 5.0 Hz, 1H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2, 141.4, 139.5, 138.5, 131.5, 130.9, 130.4, 129.0, 125.6, 124.3, 124.2, 122.8, 122.7, 51.9. Elemental analysis: calcd (%) for $C_{14}H_{10}O_2S_2$ (274.36): C 61.29, H 3.67; found: C 61.09, H 3.54.

[1] K. Funaki, T. Sato, S. Oi, *Org. Lett.* **2012**, *14*, 6186-6189.

[2] S. Kirchberg, S. Tani, K. Ueda, J. Yamaguchi, A. Studer, K. Itami, *Angew. Chem. Int. Ed.* **2011**, *50*, 2387-2391.

[3] a) T. Hatakeyama, S. Hashimoto, K. Ishizuka, M. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 11949-11963; b) Y. Dang, Y. Chen, *Eur. J. Org. Chem.* **2007**, 5661.

[4] N. Mejias, R. Pleixats, A. Shafir, M. Medio-Simon, G. Asensio, *Eur. J. Org. Chem.* **2010**, 5090-5099.

[5] K. Ueda, S. Yanagisawa, J. Yamaguchi, K. Itami, *Angew. Chem. Int. Ed.* **2010**, *49*, 8976-8949.

[6] T. Sone, M. Inoue, K. Sato, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3779-3781.

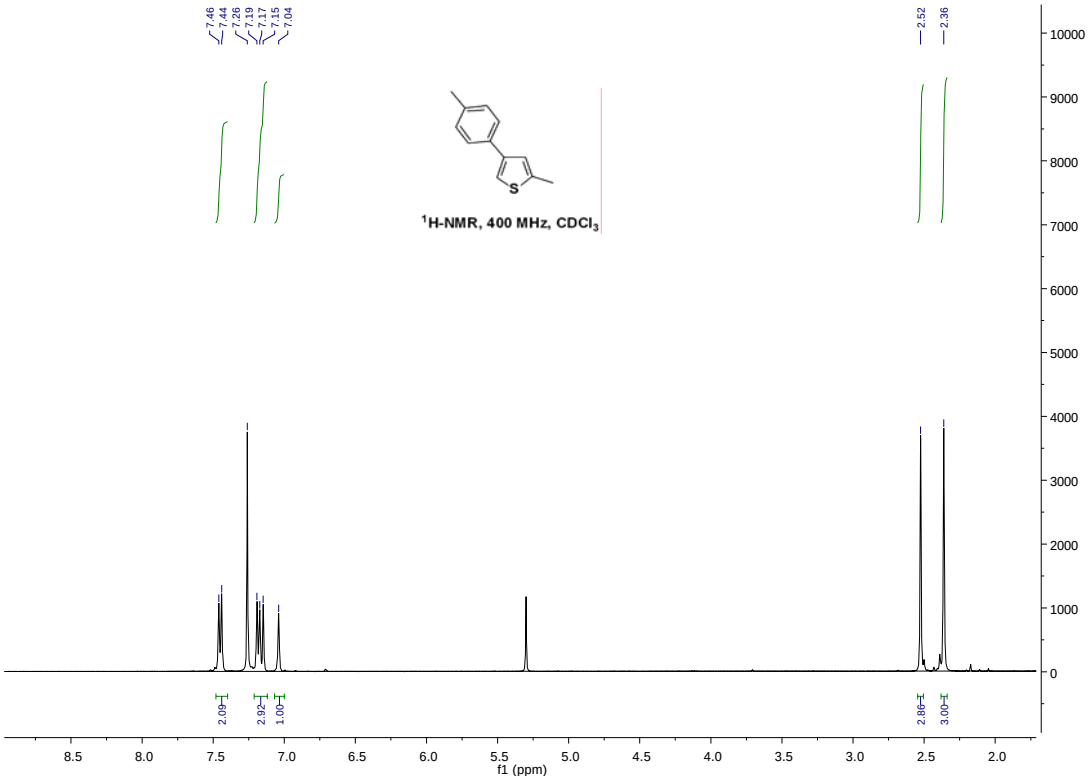
[7] I. Schnapperelle, T. Bach, *ChemCatChem* **2013**, DOI: 10.1002/cctc.201300167.

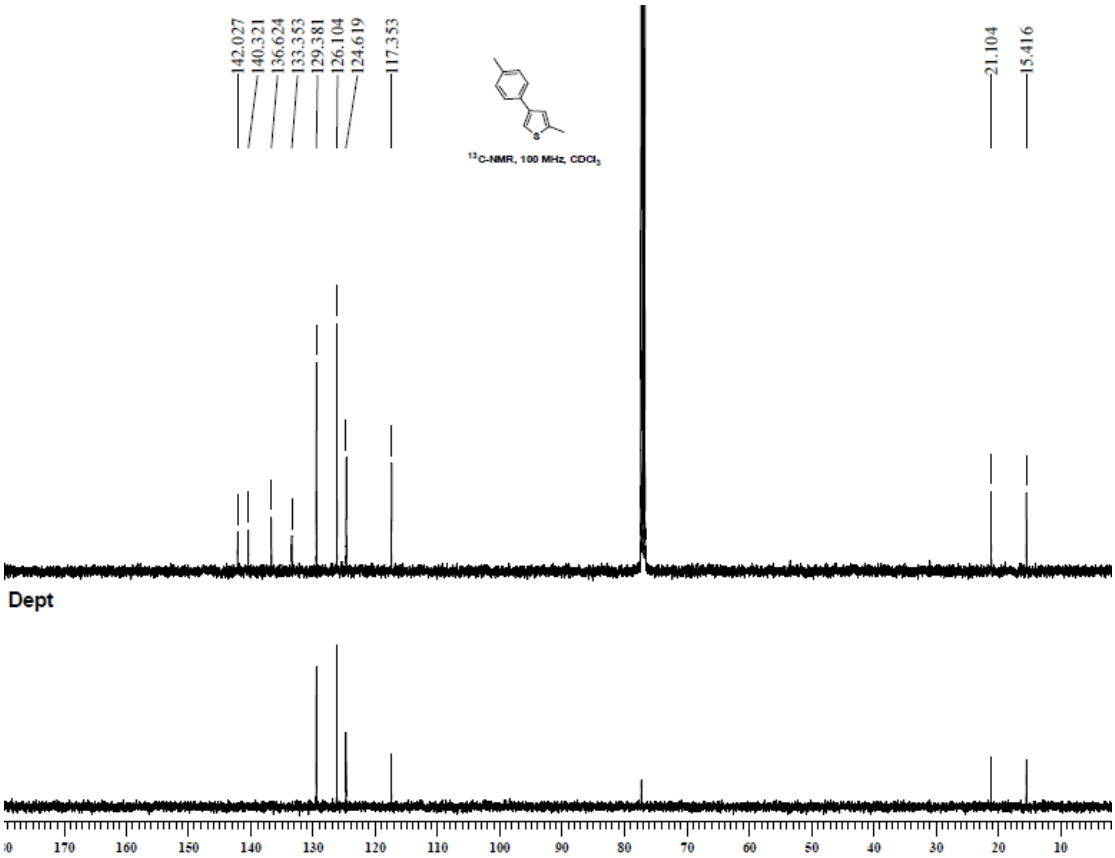
[8] T. Itahara, *J. Org. Chem.* **1985**, *50*, 5272-5275.

[9] K. Morimoto, T. Nakae, N. Yamaoka, T. Dohi, Y. Kita, *Eur. J. Org. Chem.* **2011**, 6326-6334.

[10] D.-T. D. Tang, K. D. Collins, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 7450-7453.

2-Methyl-4-*p*-tolylthiophene (1b)





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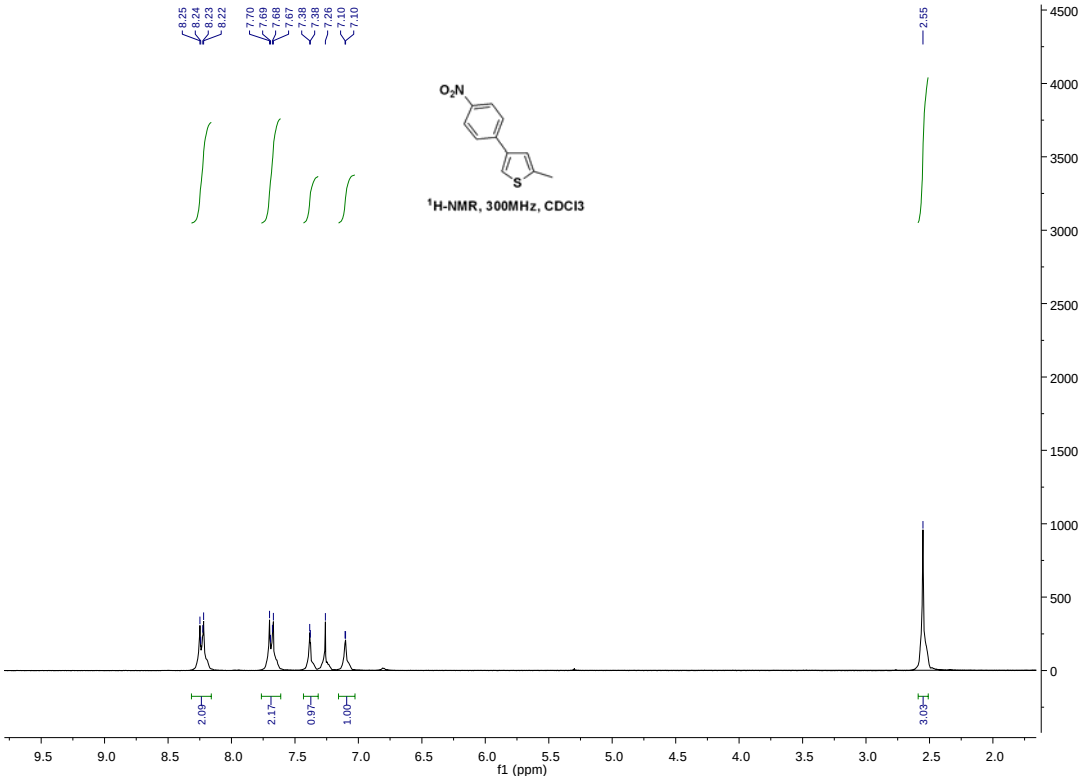

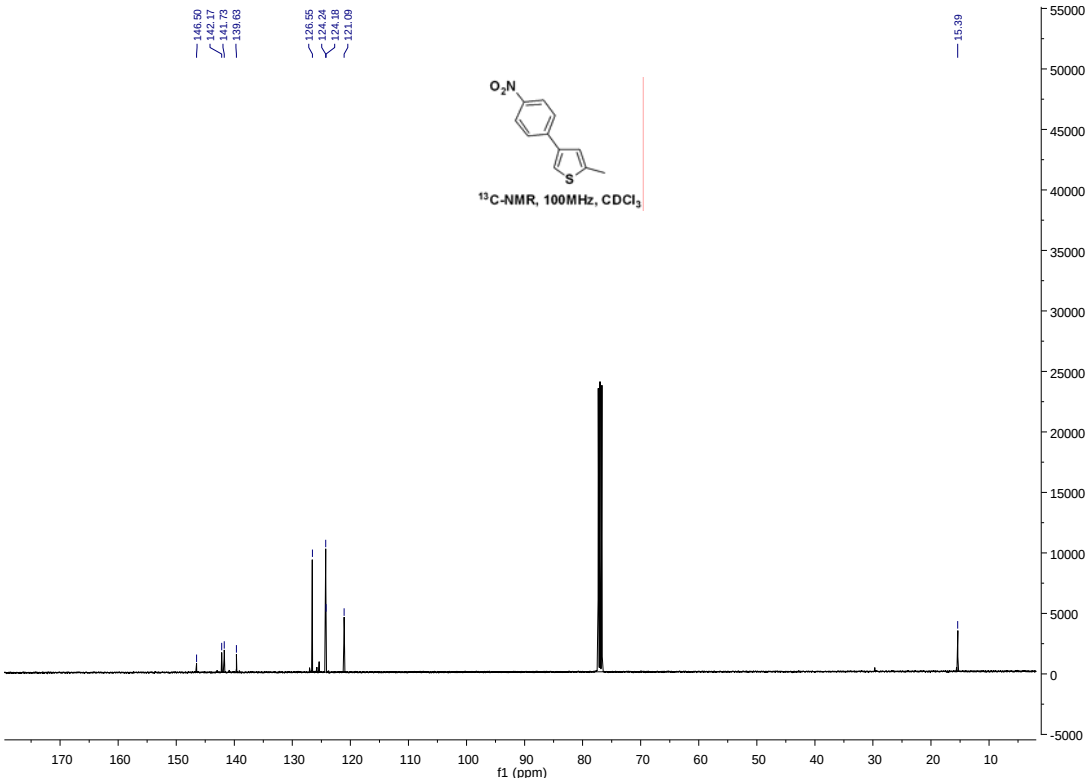

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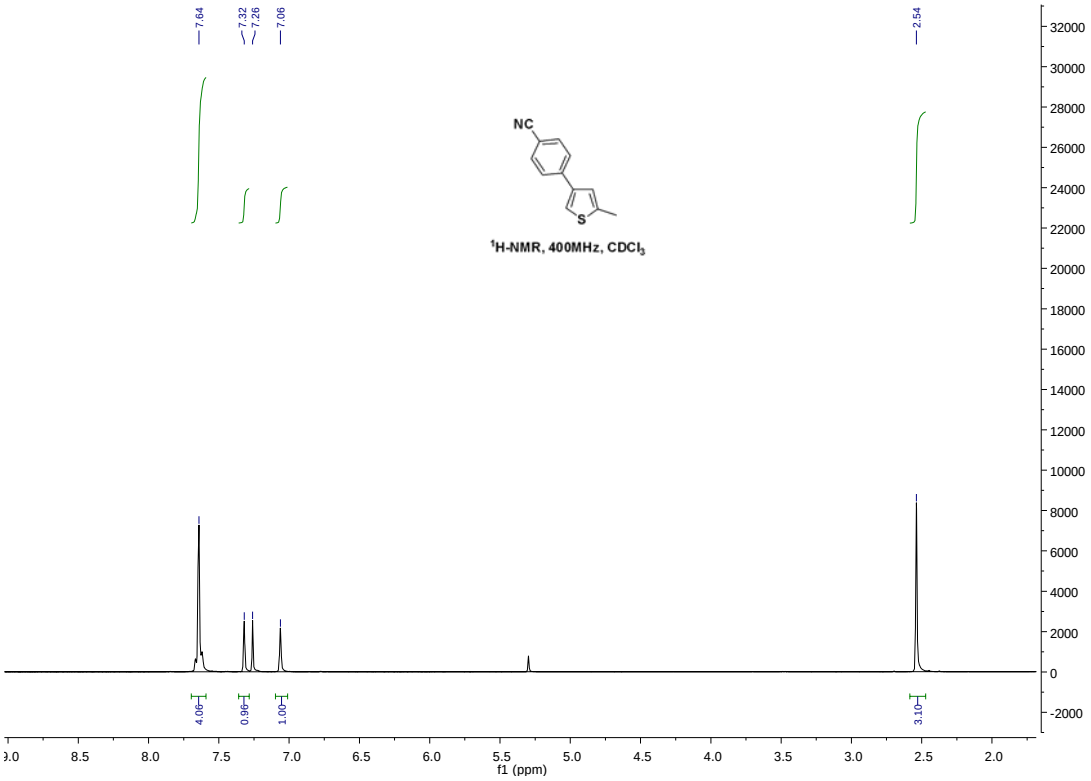
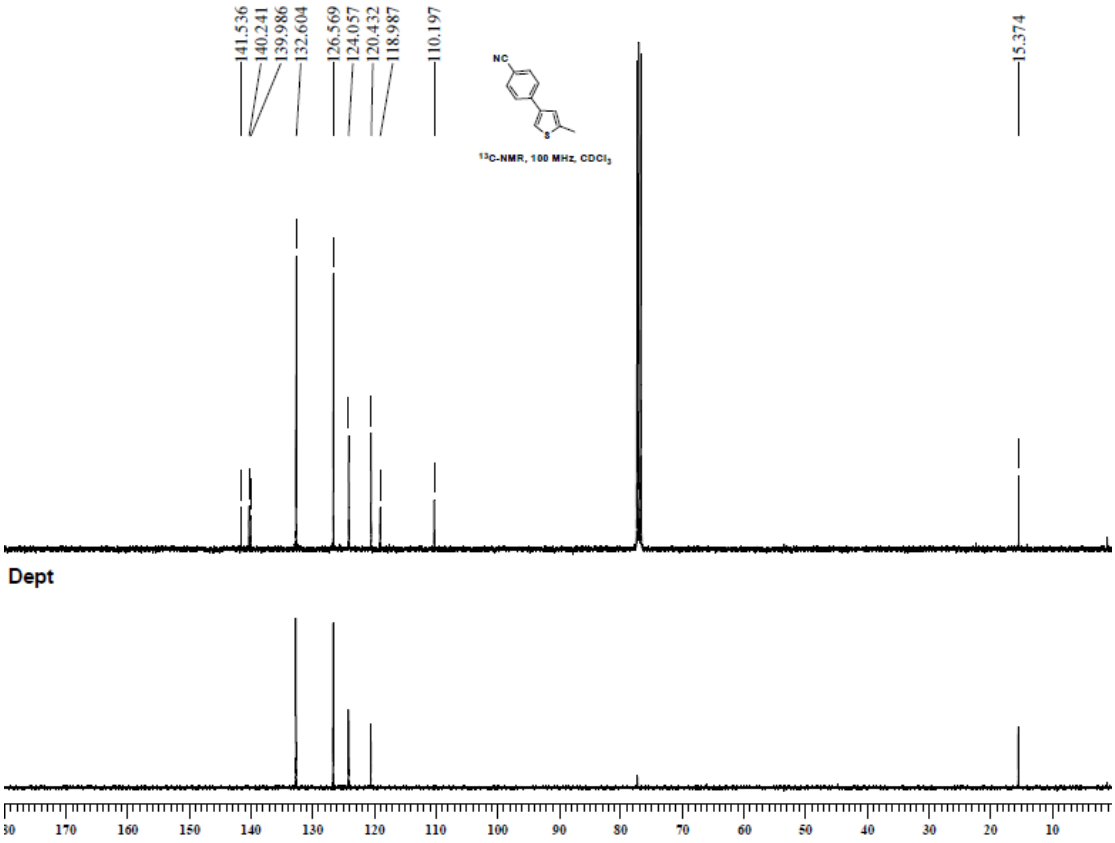
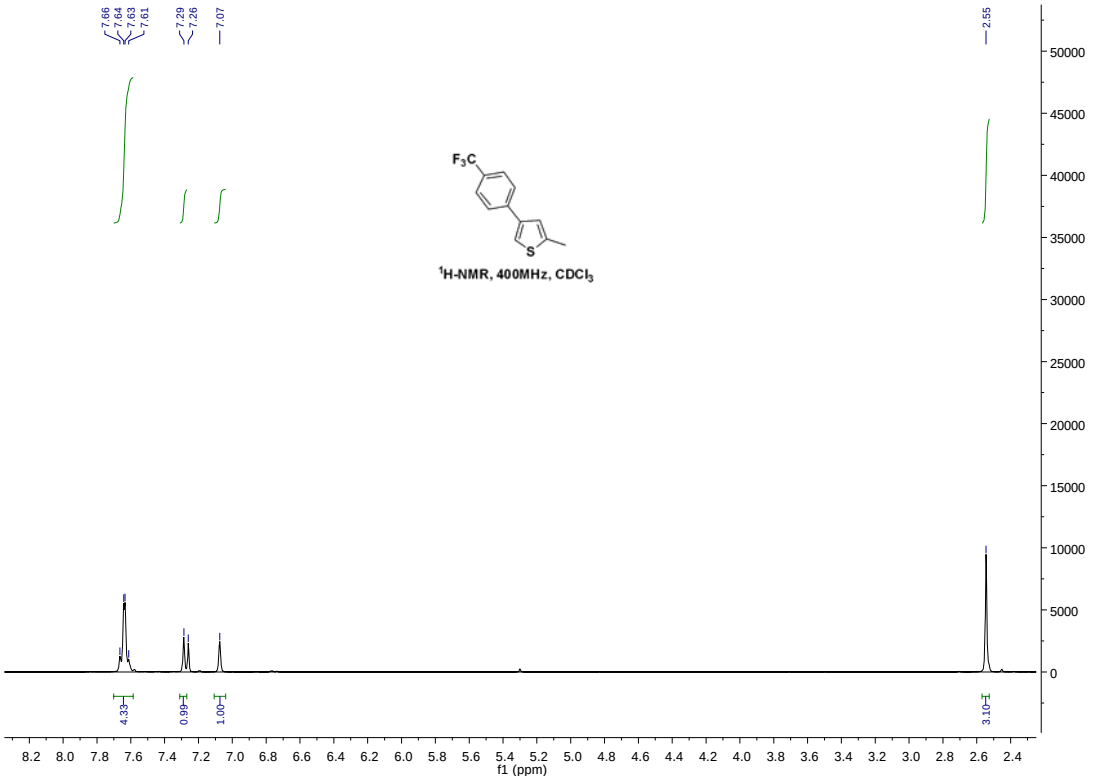
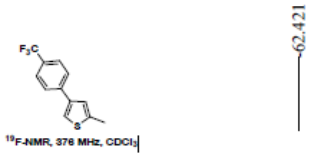


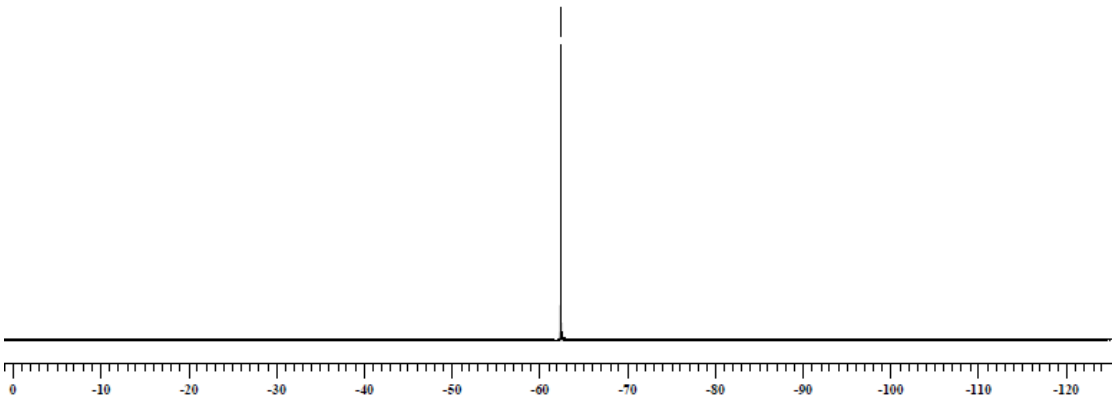


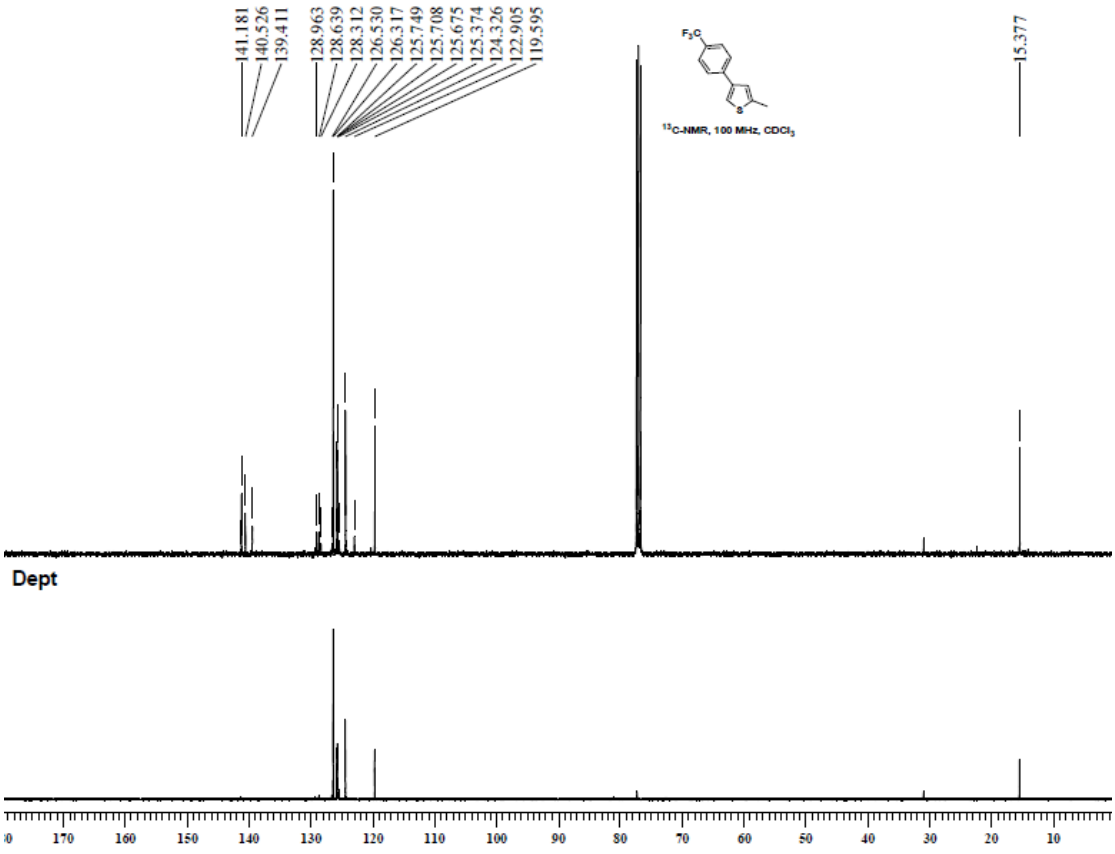
Dept

2-Methyl-4-(4-trifluoromethylphenyl)-thiophene (4)





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160
150
140
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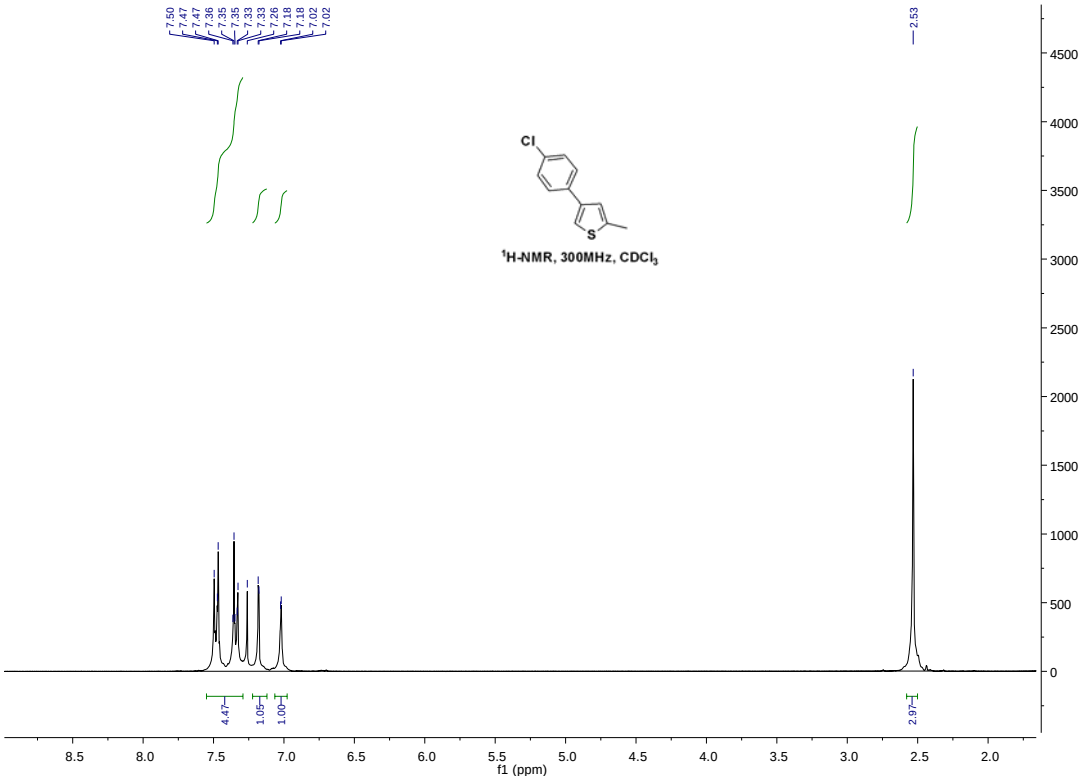
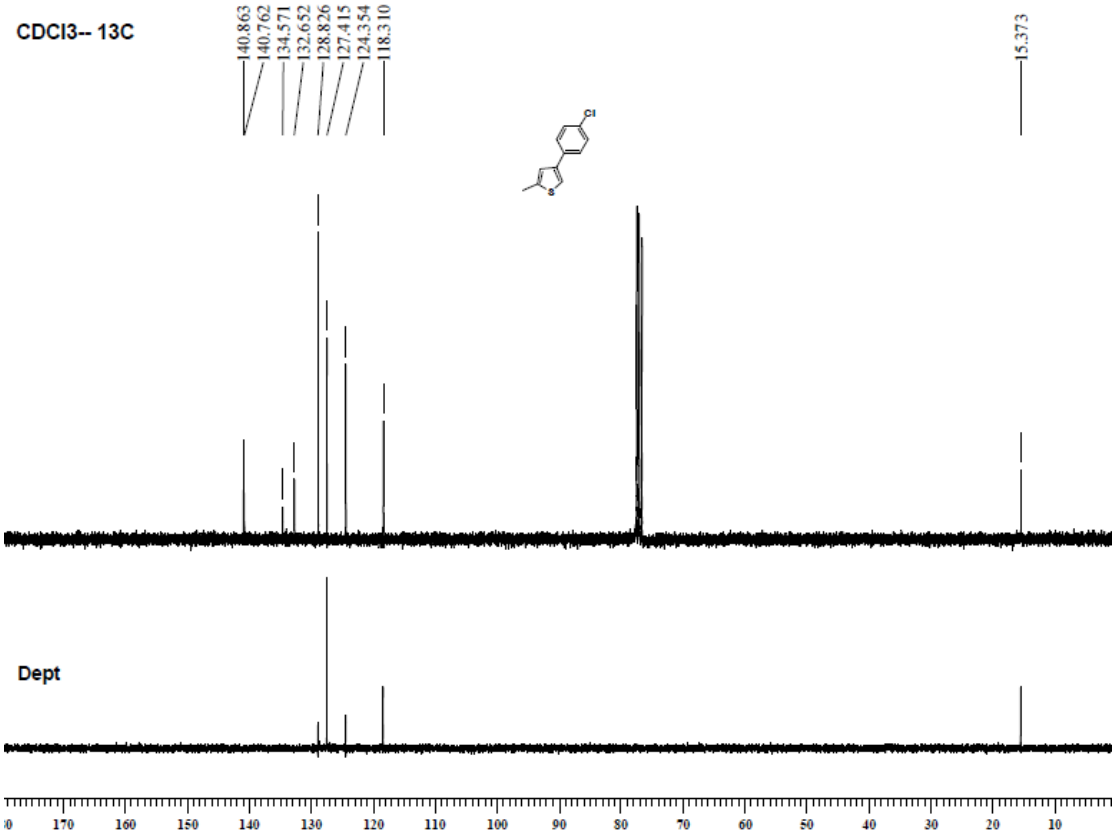
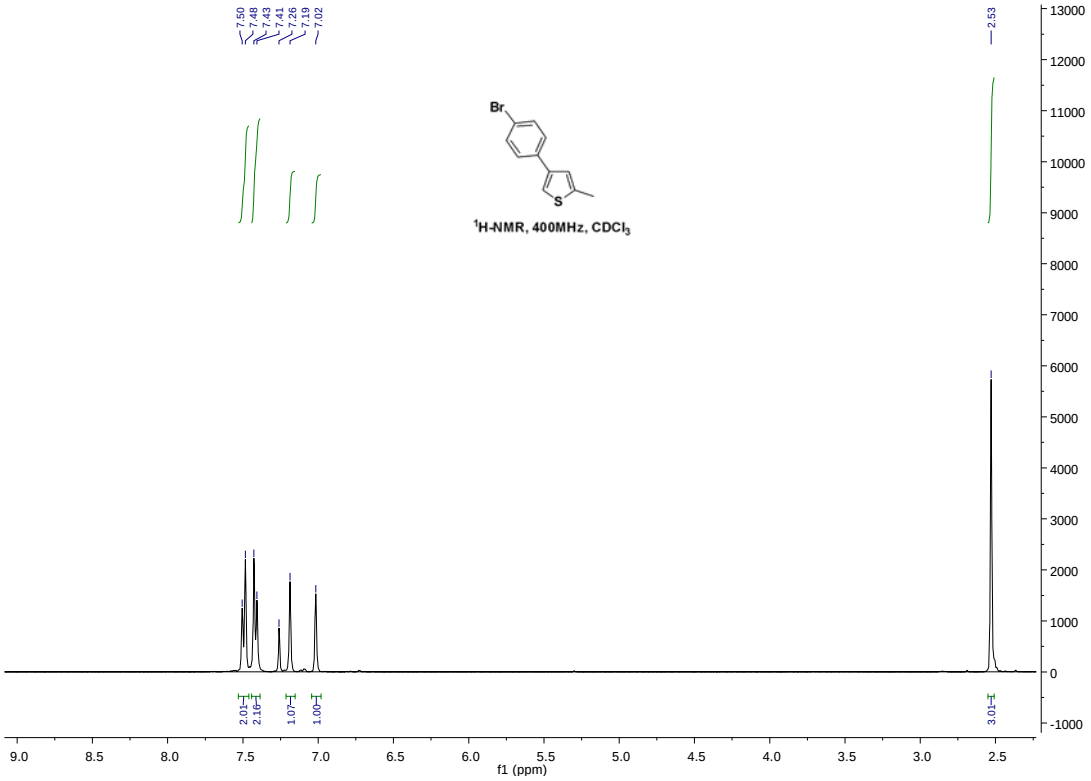
100
90
80
70
60
50
40
30
20
10

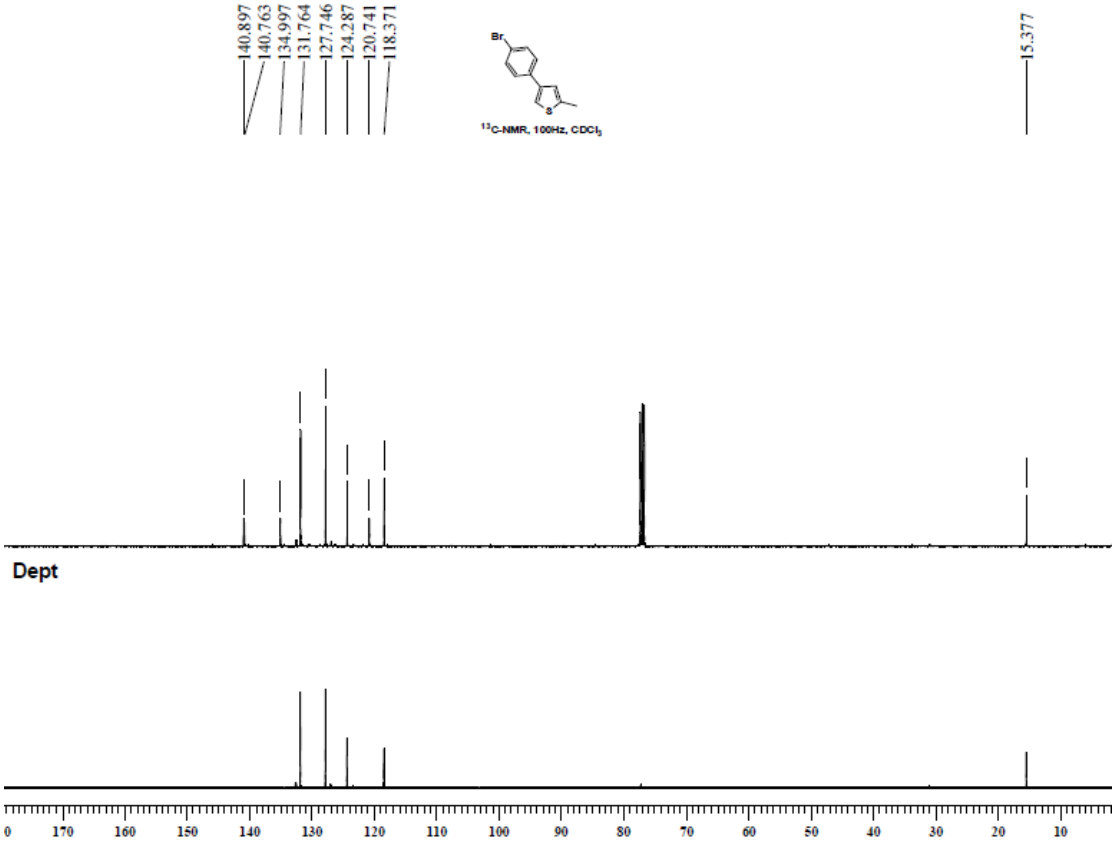
4-(4-Chlorophenyl)-2-methylthiophene (5)



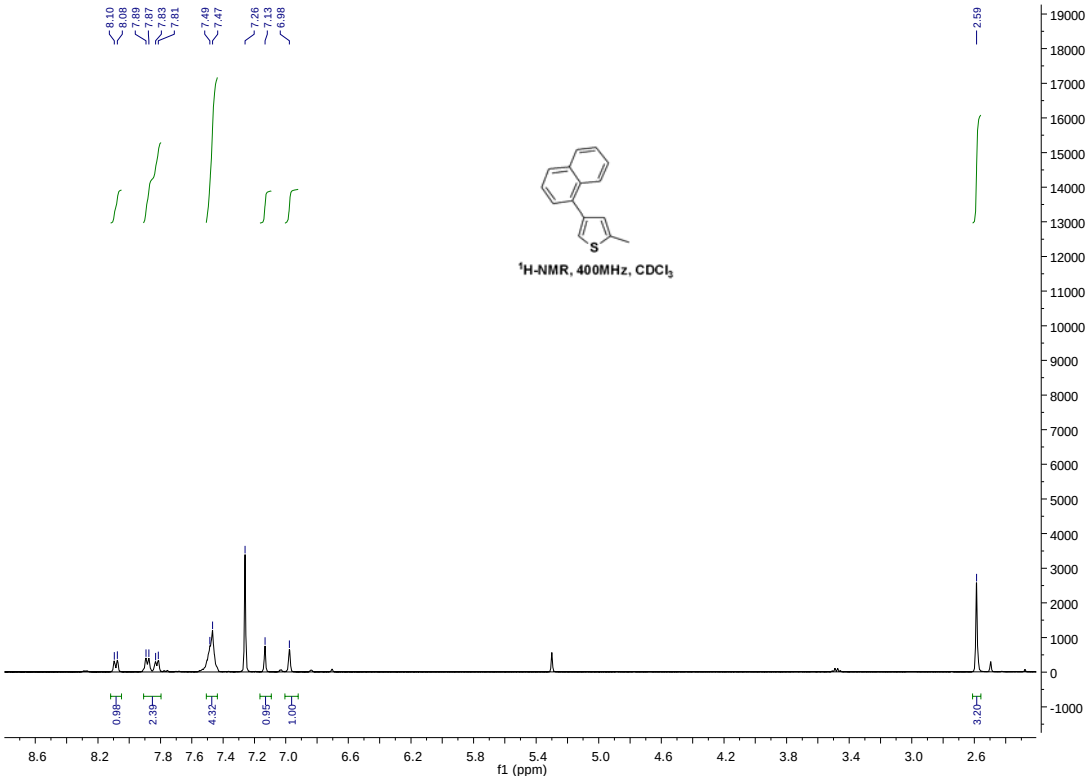


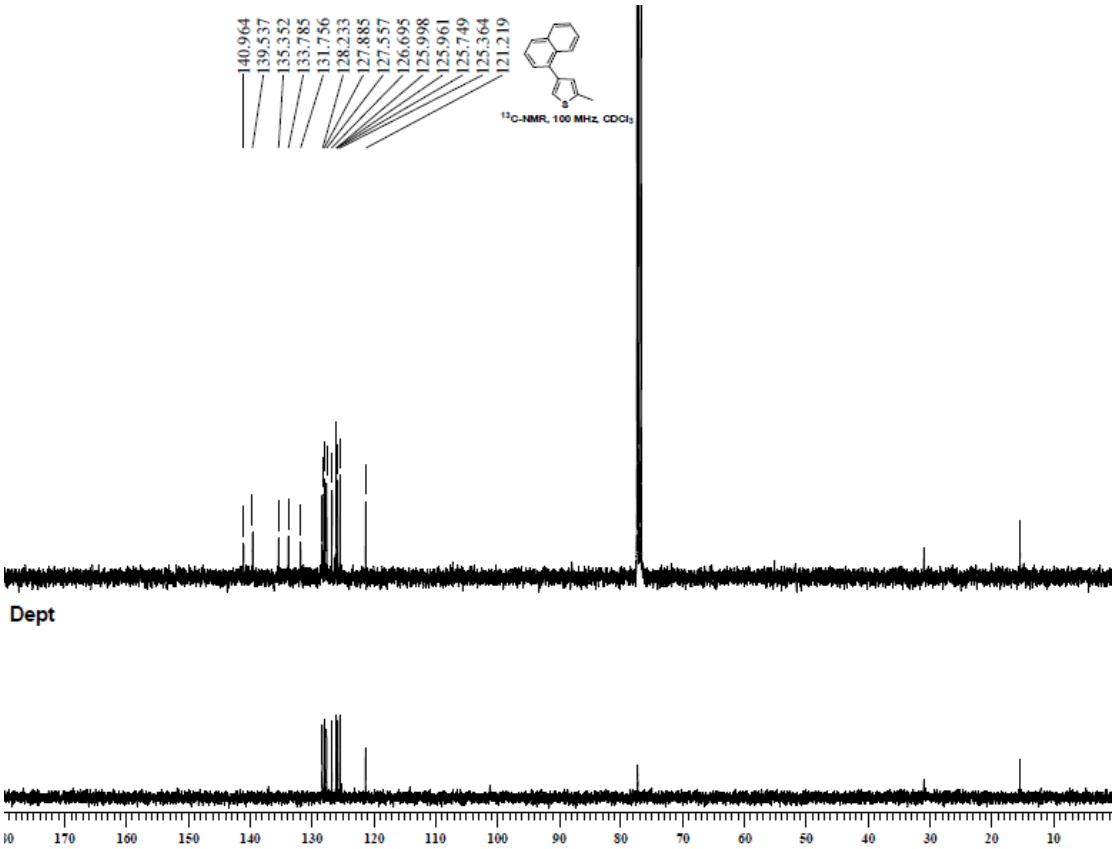
4-(4-Bromophenyl)-2-methylthiophene (6)



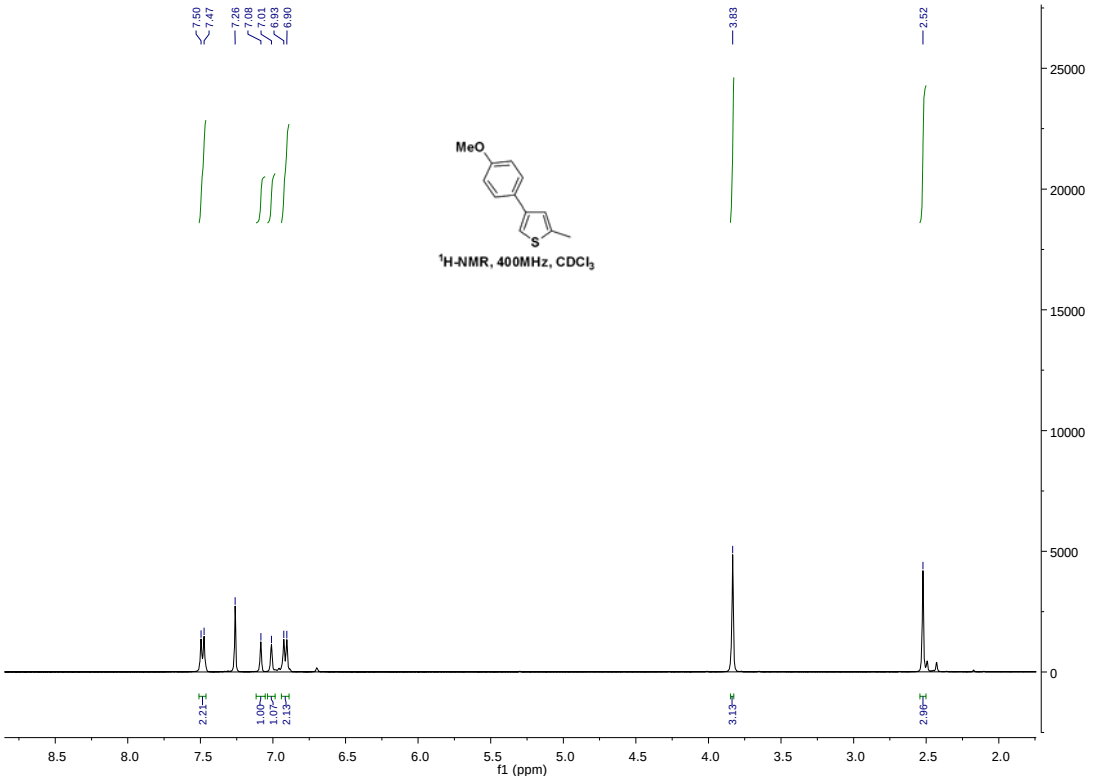


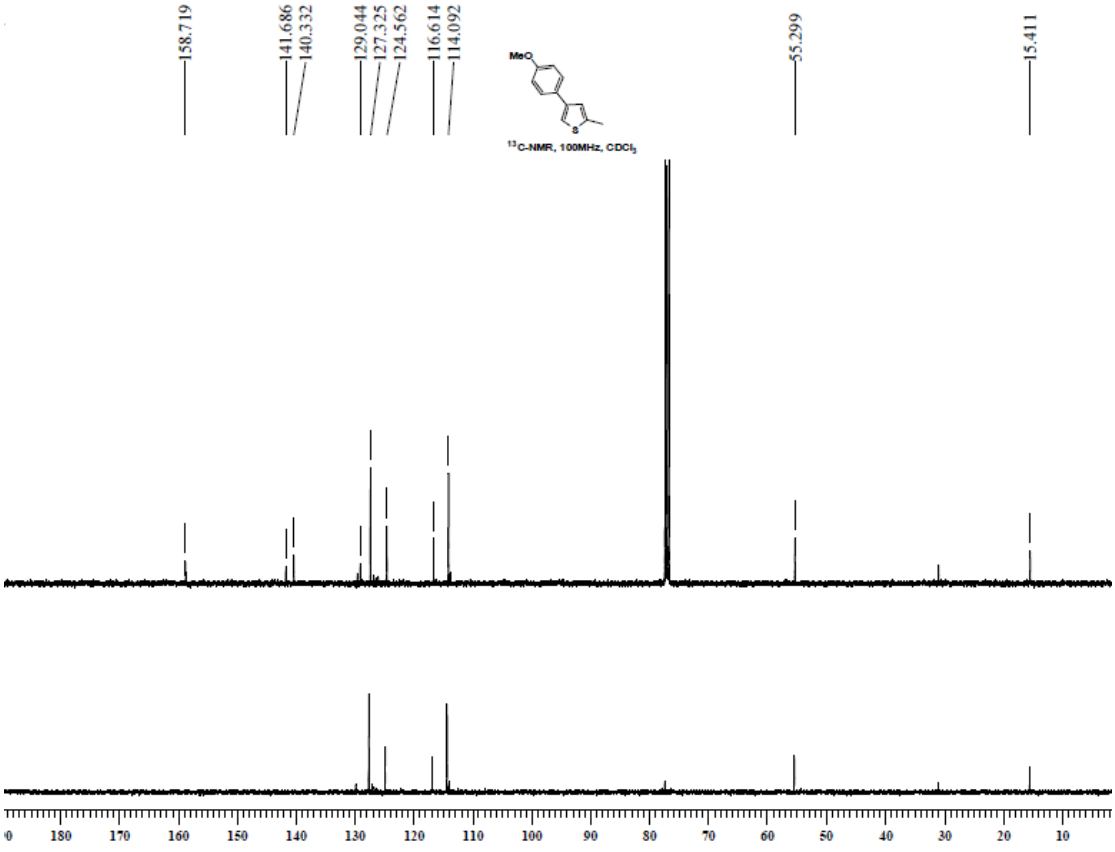
2-Methyl-4-naphthalen-1-ylthiophene (9)



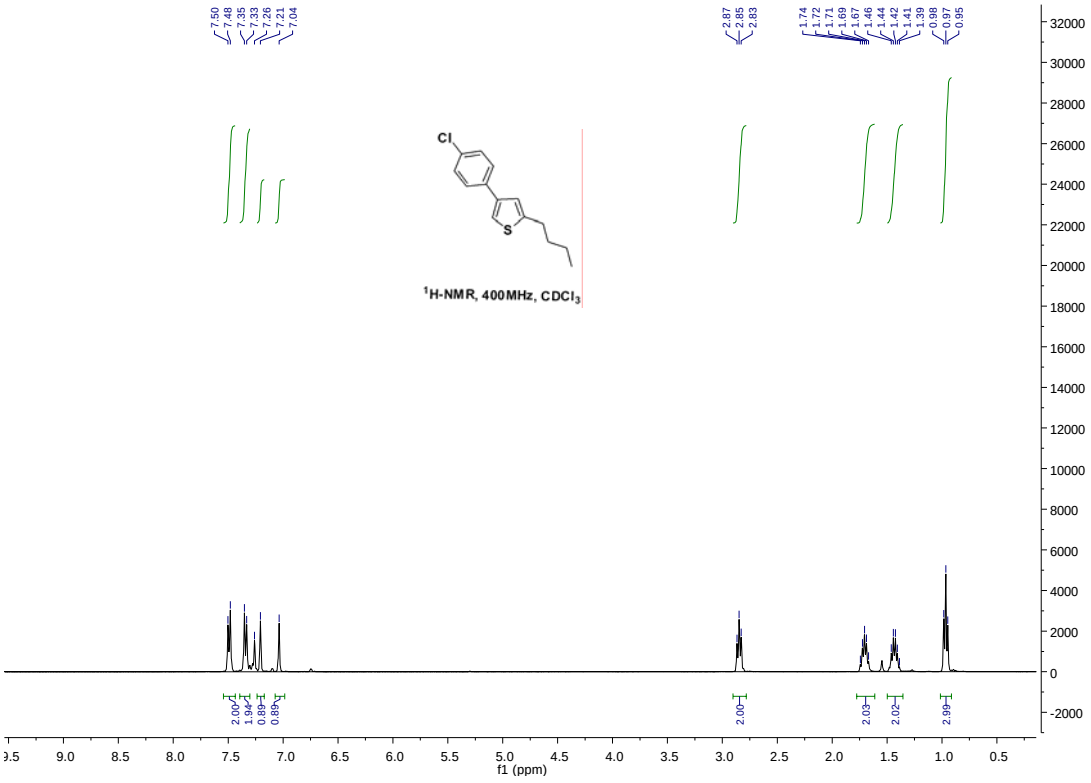


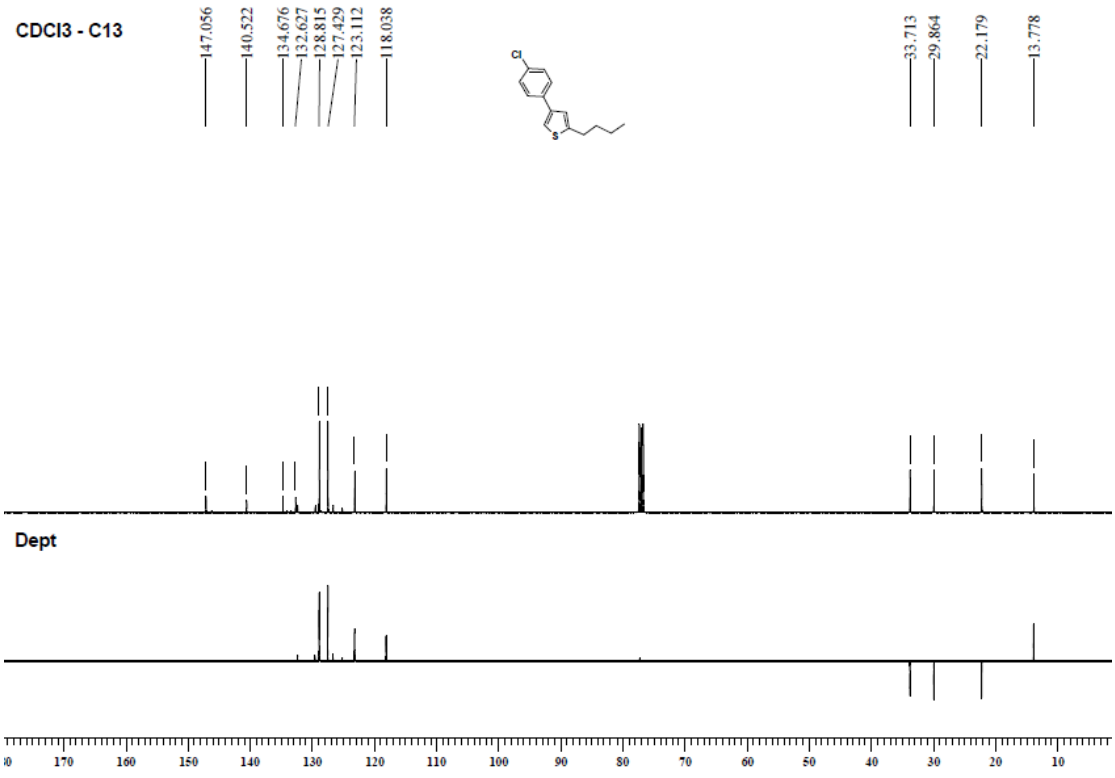
4-(4-Methoxyphenyl)-2-methylthiophene (10)



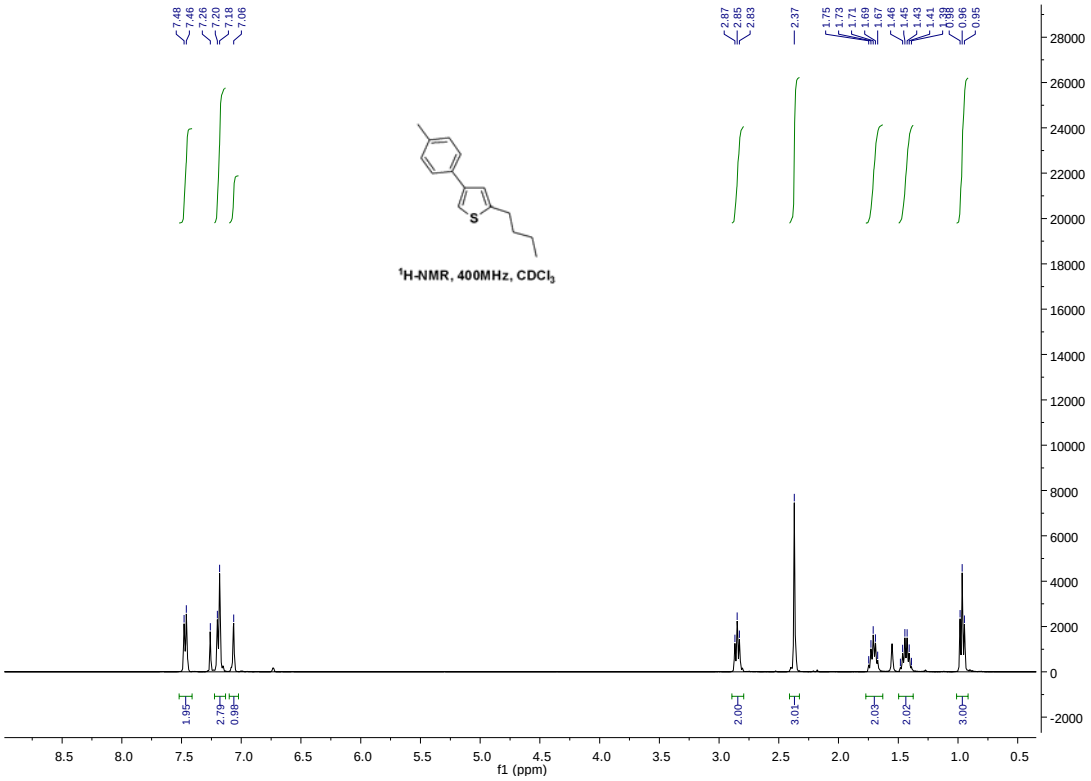


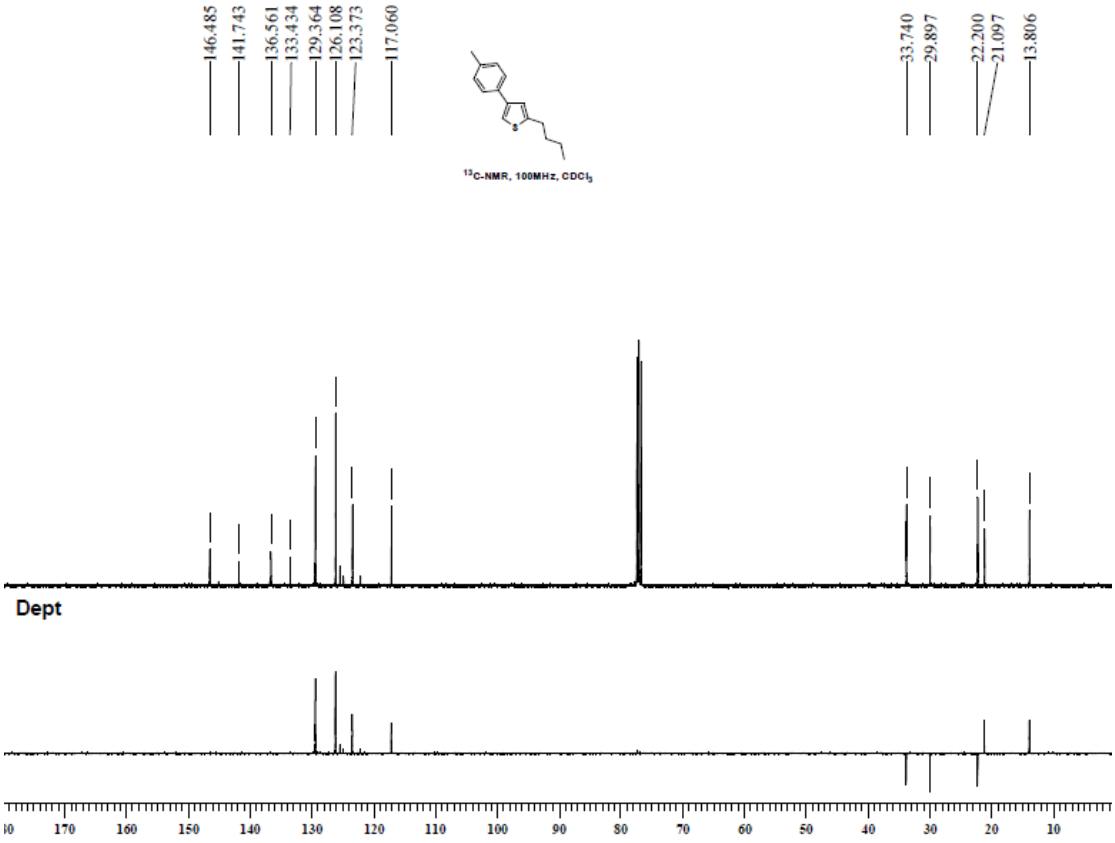
2-*n*Butyl-4-(4-chlorophenyl)-thiophene (11)





2-*n*Butyl-4-*p*-tolylthiophene (12)





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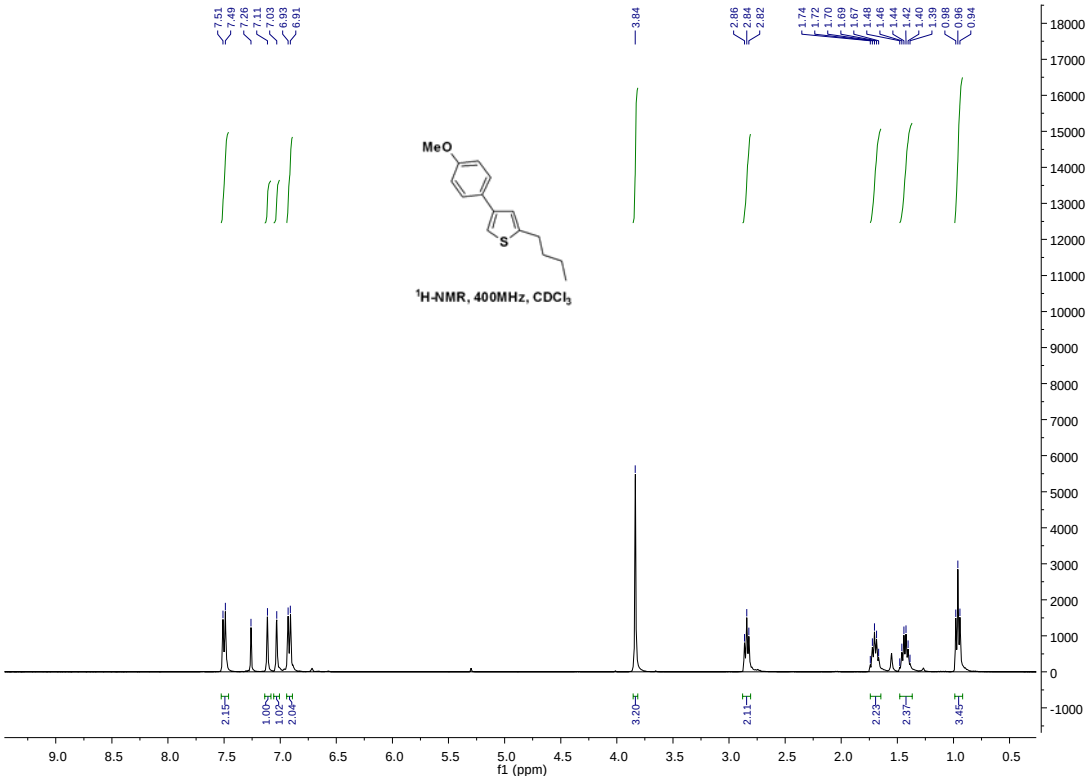
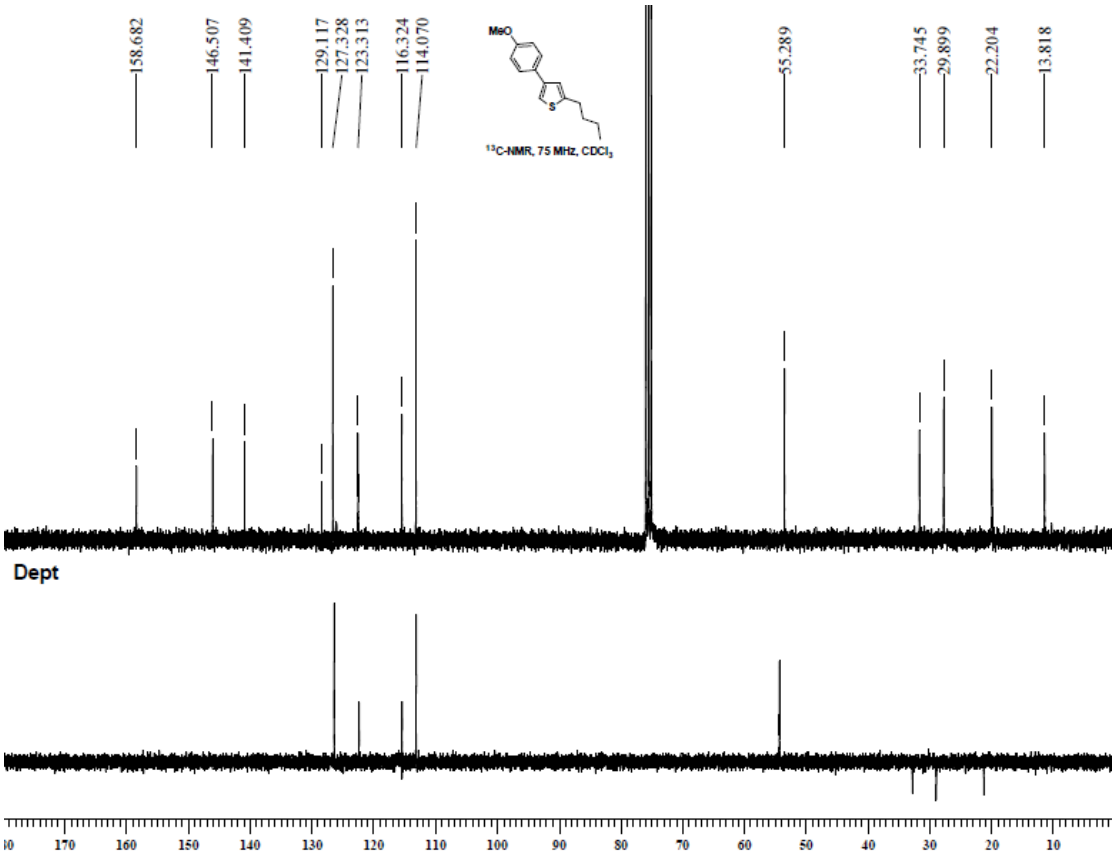
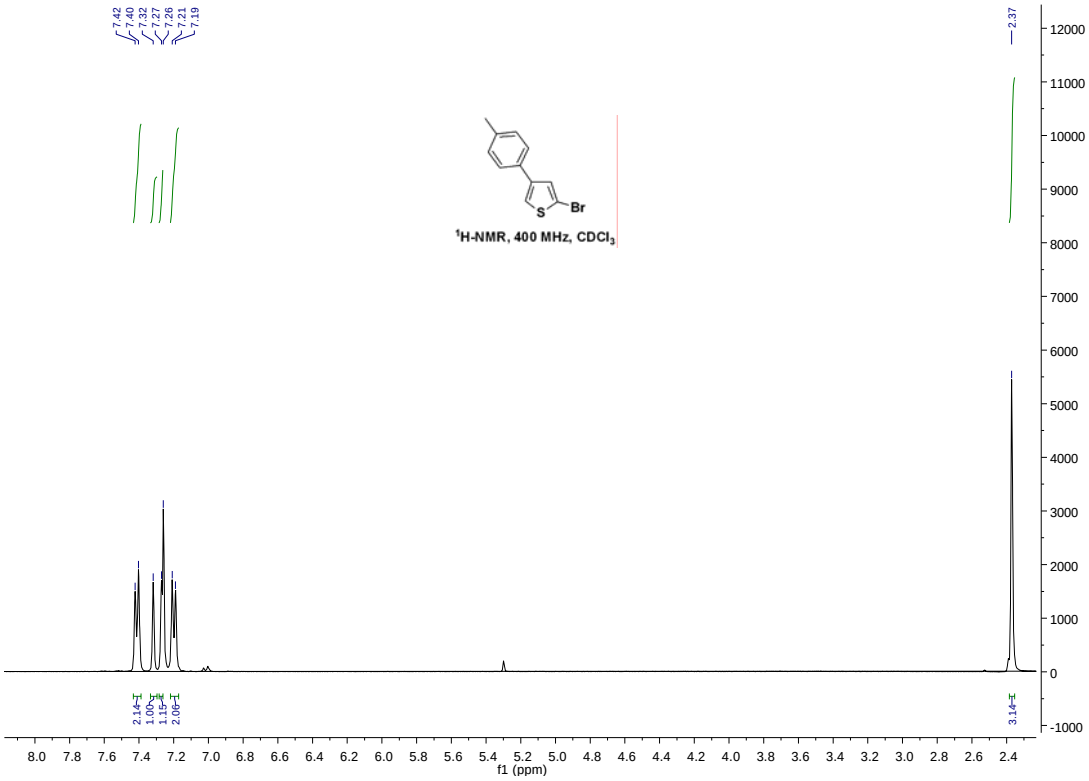
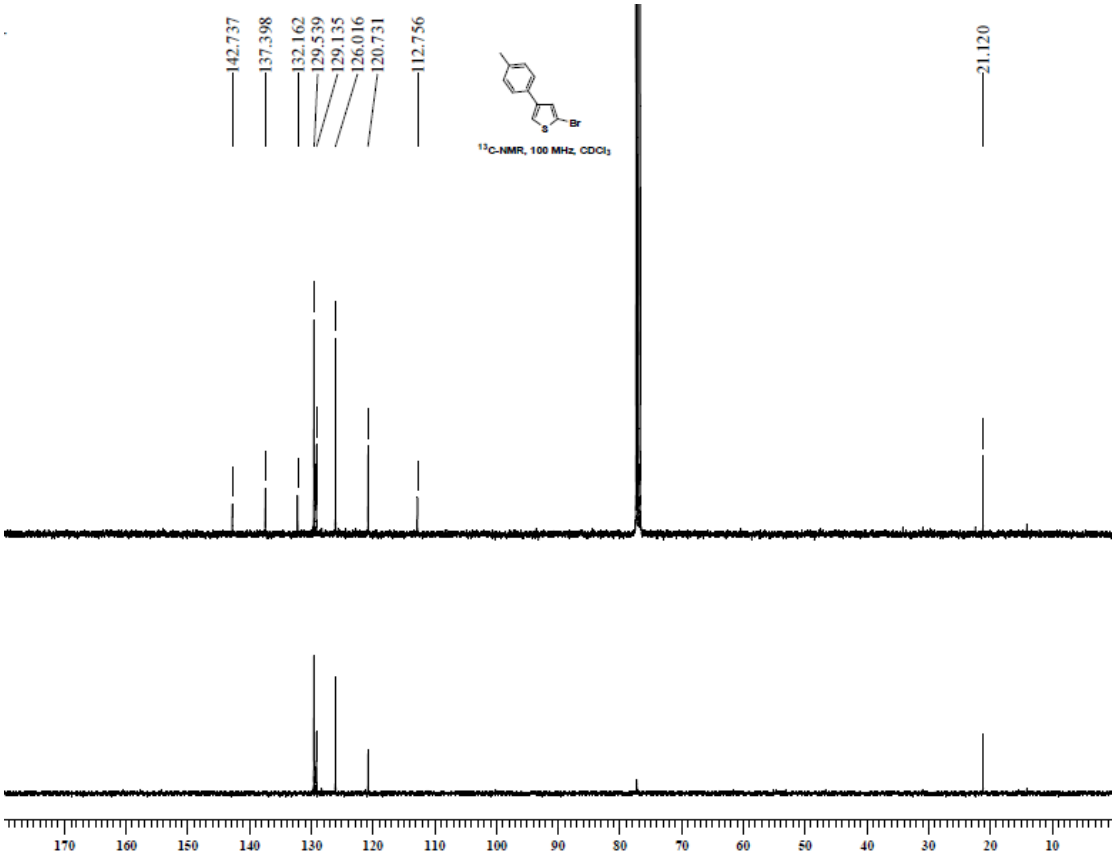


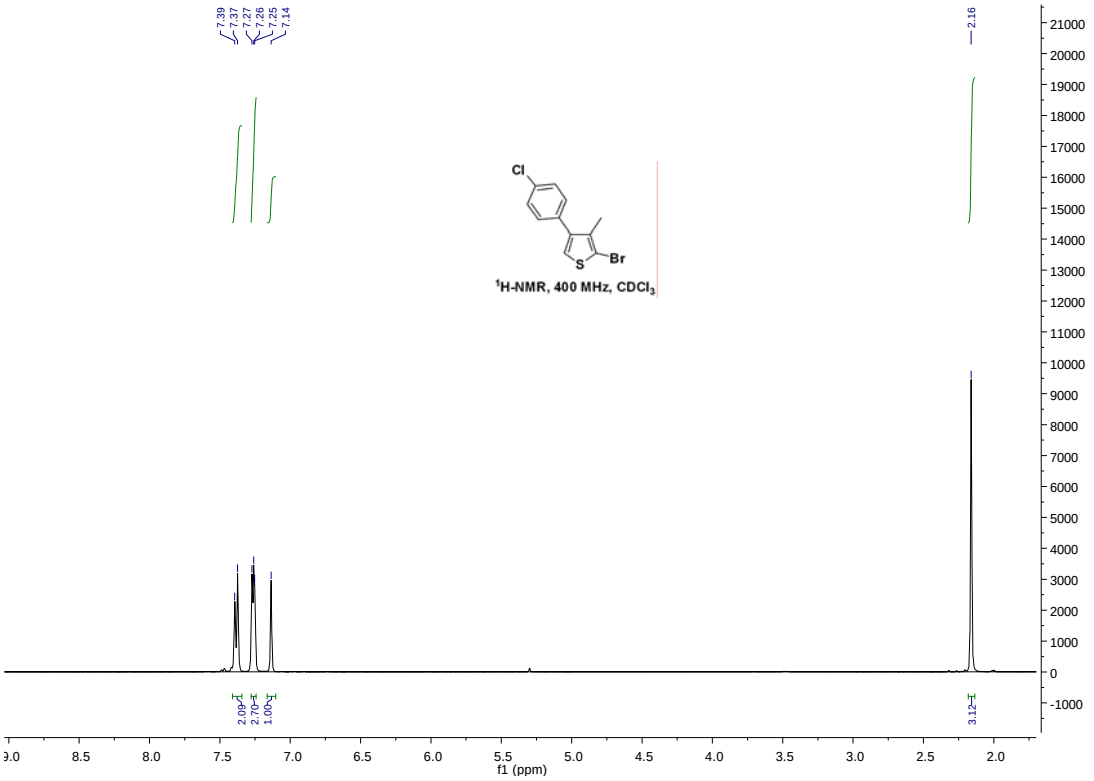


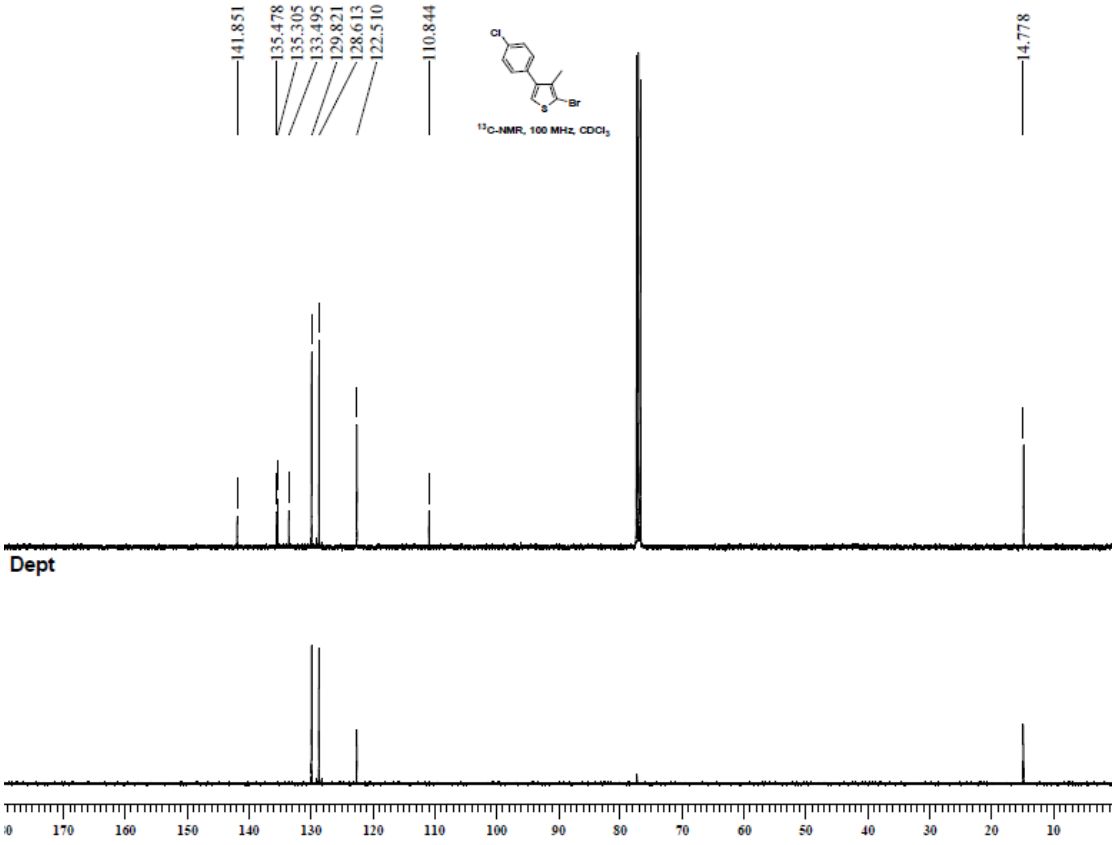
2-Bromo-4-*p*-tolylthiophene (19)



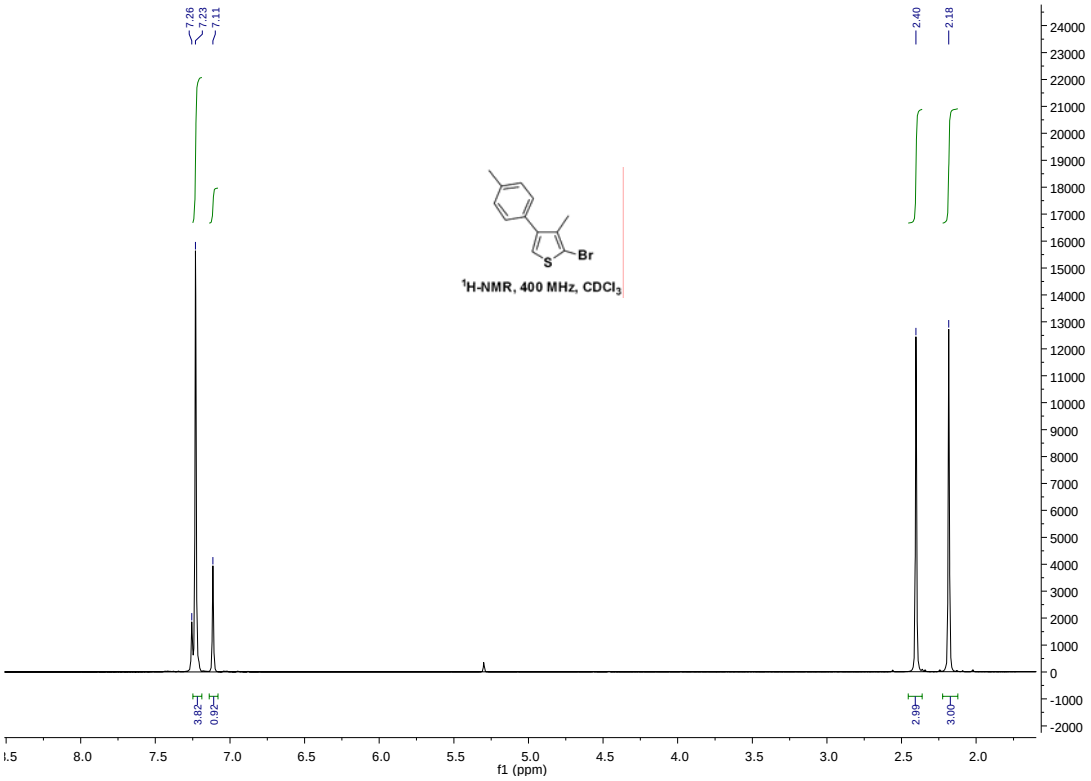


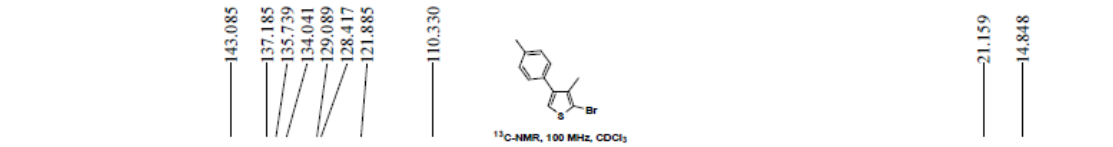
2-Bromo-4-(4-chlorophenyl)-3-methylthiophene (20)

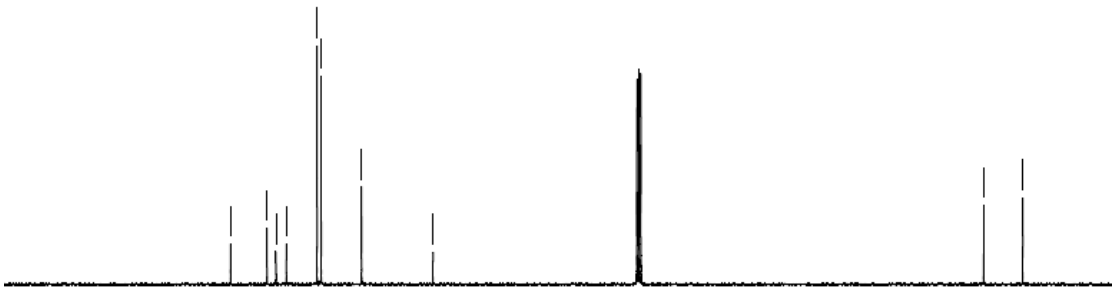




2-Bromo-3-methyl-4-*p*-tolylthiophene (22)







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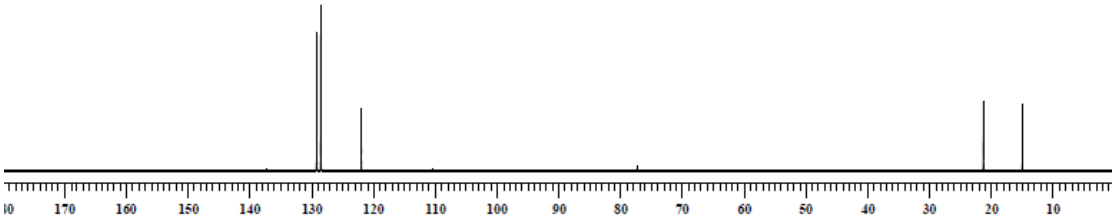
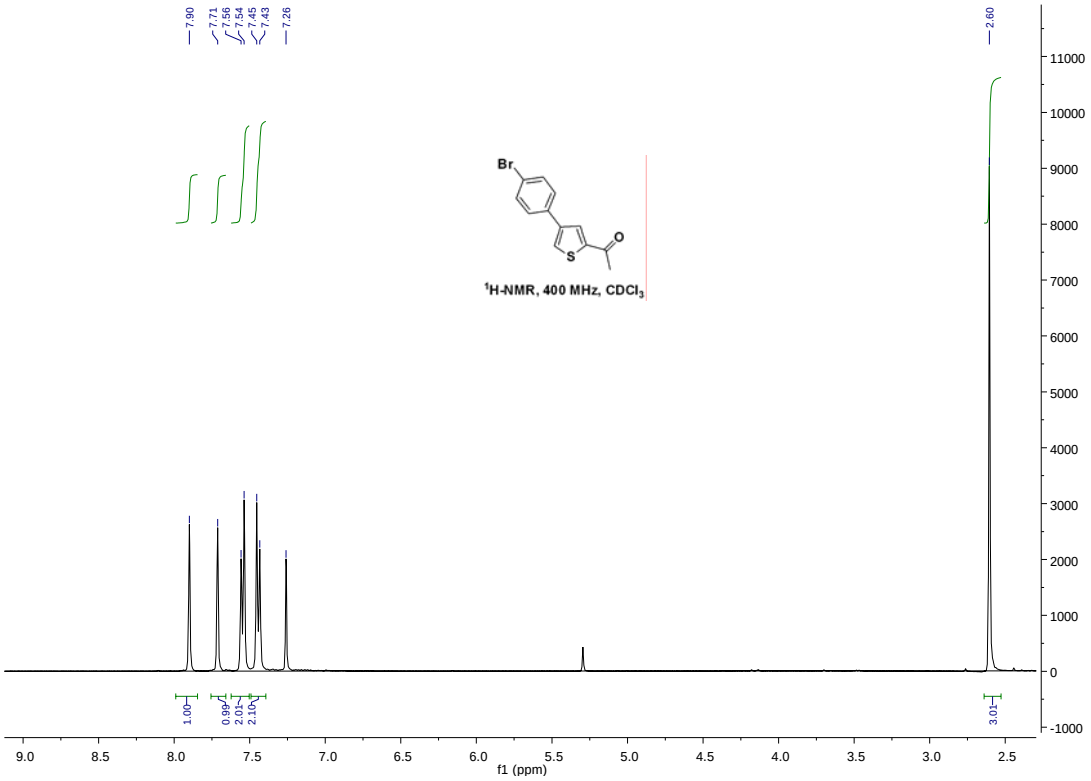
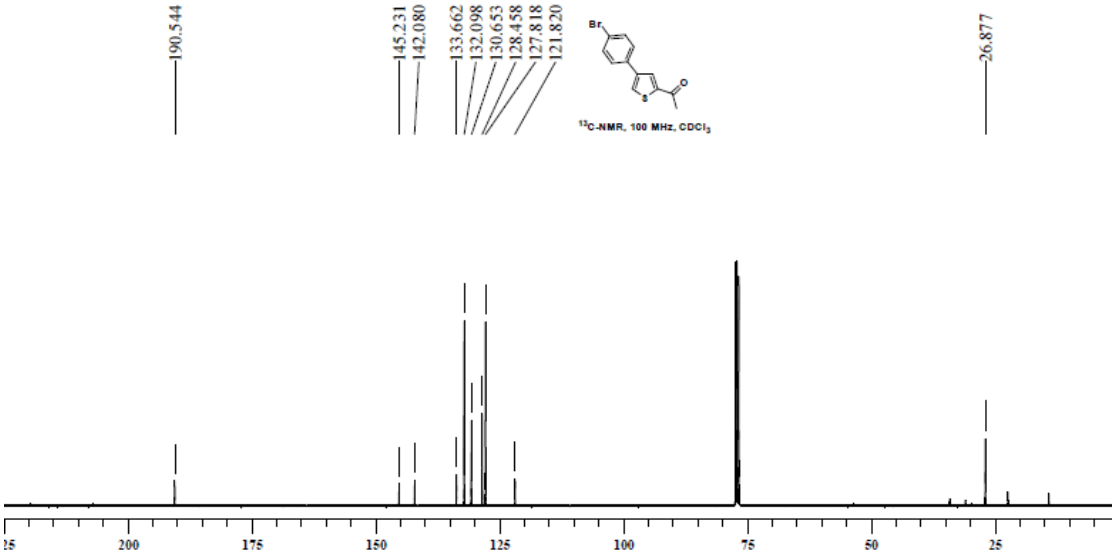
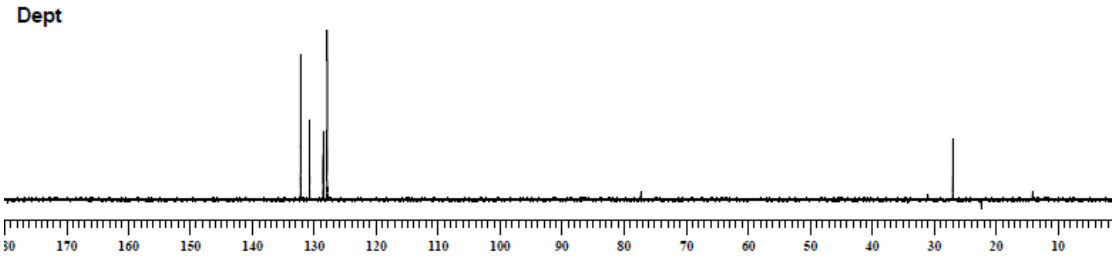


1-[4-(4-Bromophenyl)-thiophen-2-yl]-ethanone (24)







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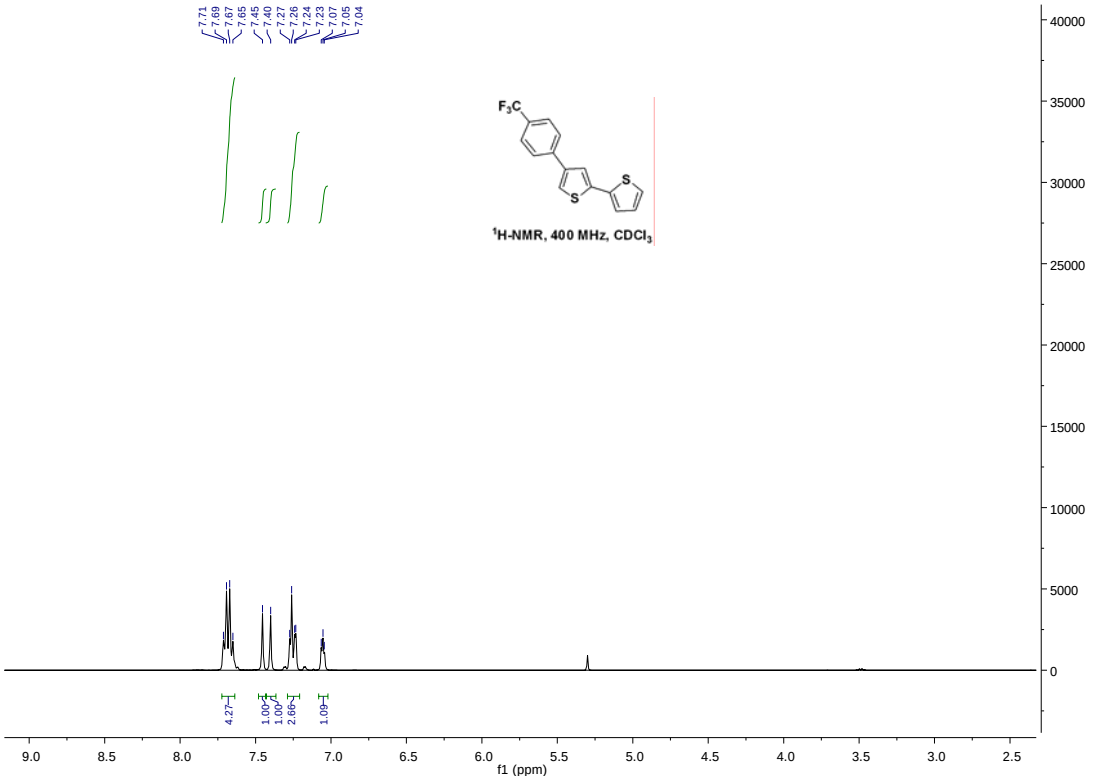
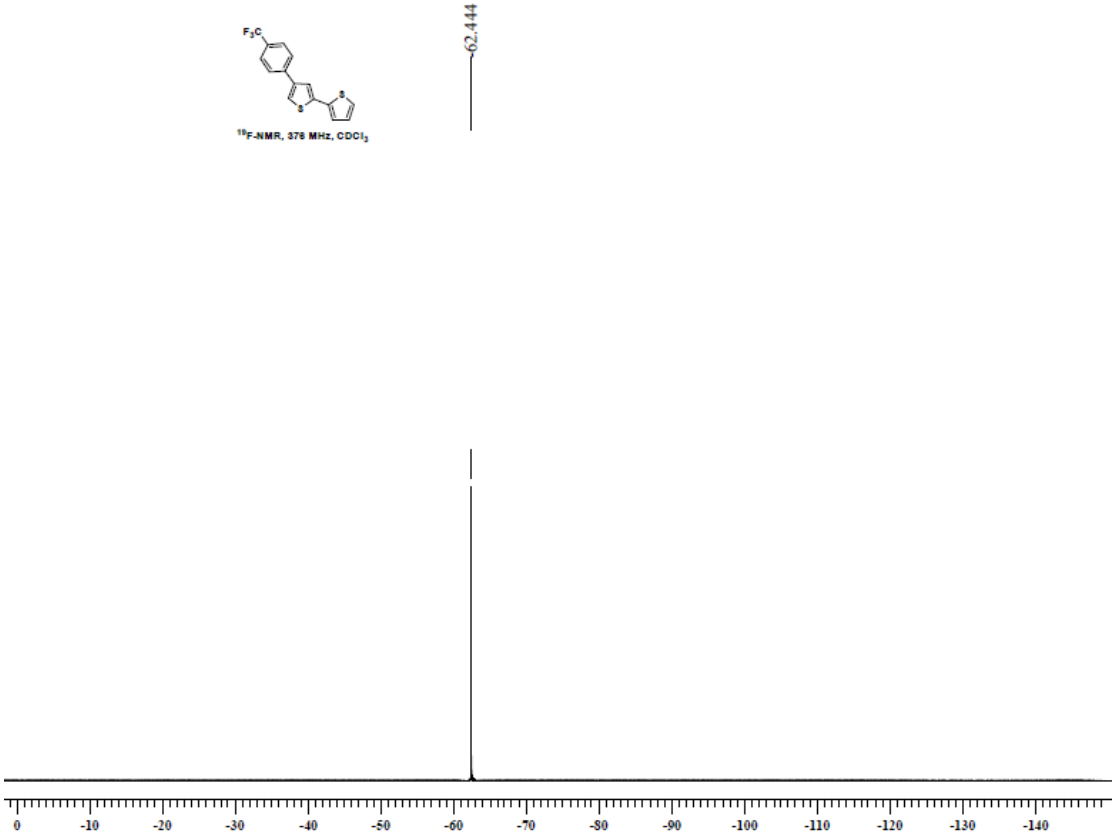
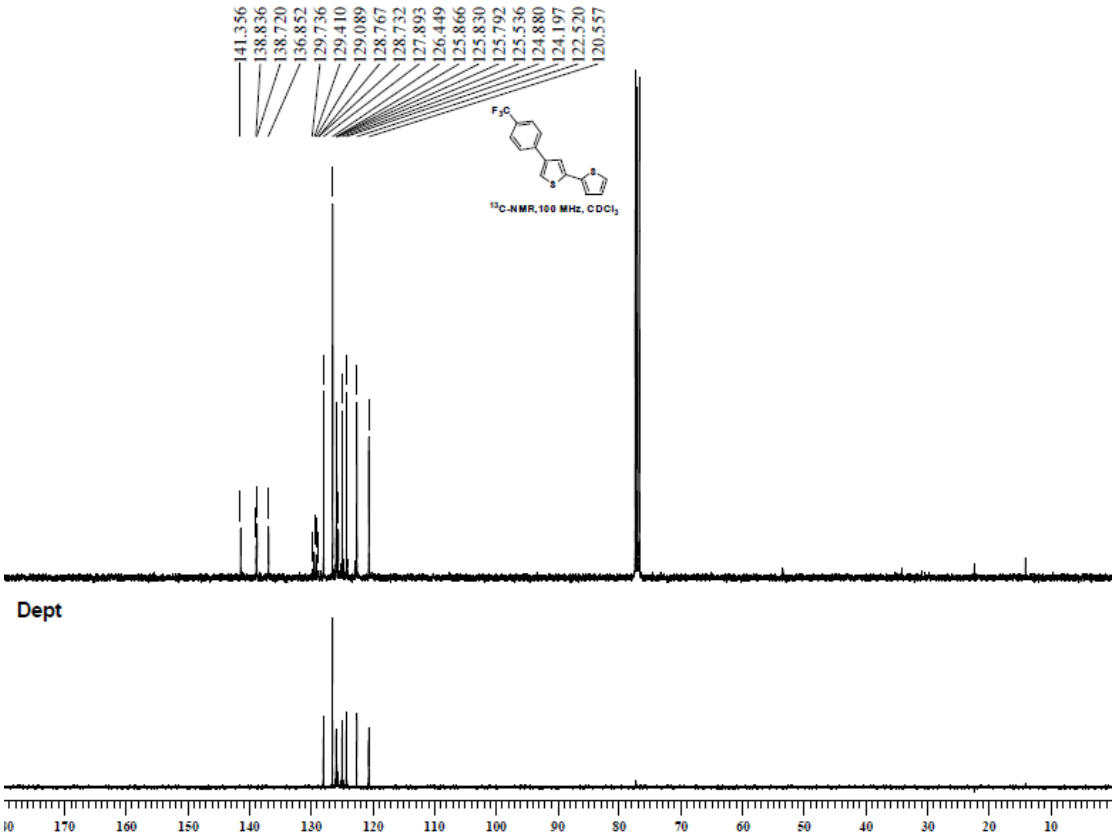
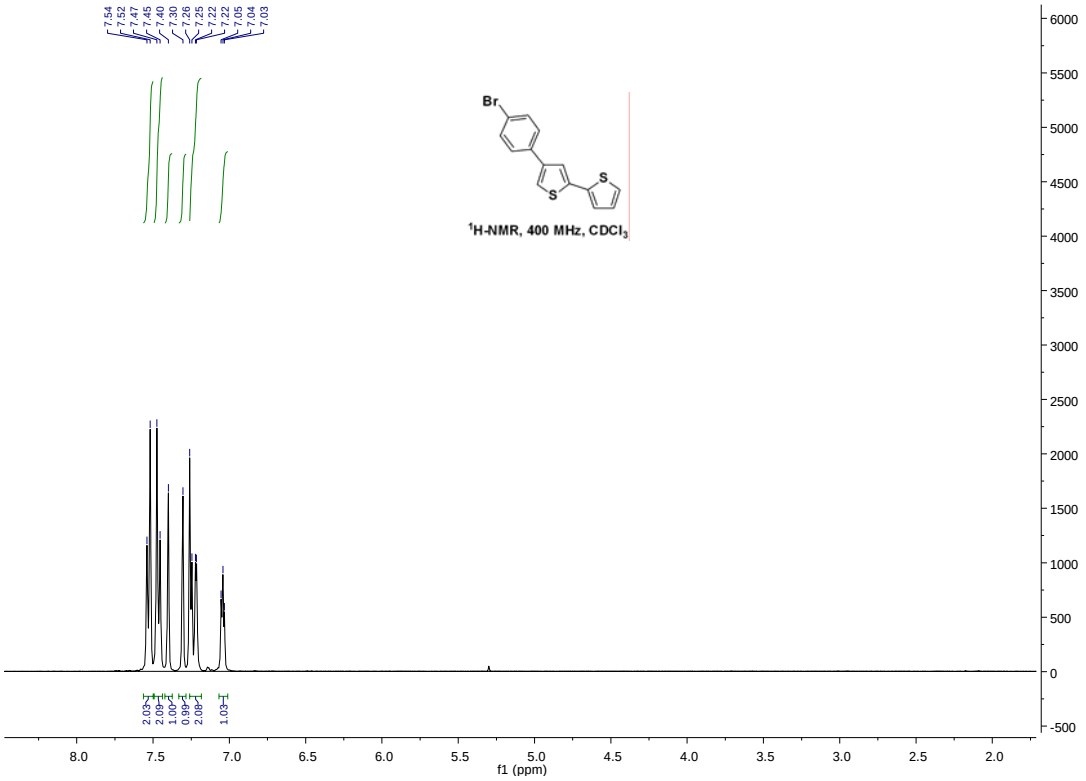
4-(4-Trifluoromethylphenyl)-[2,2']bithiophenyl (25)

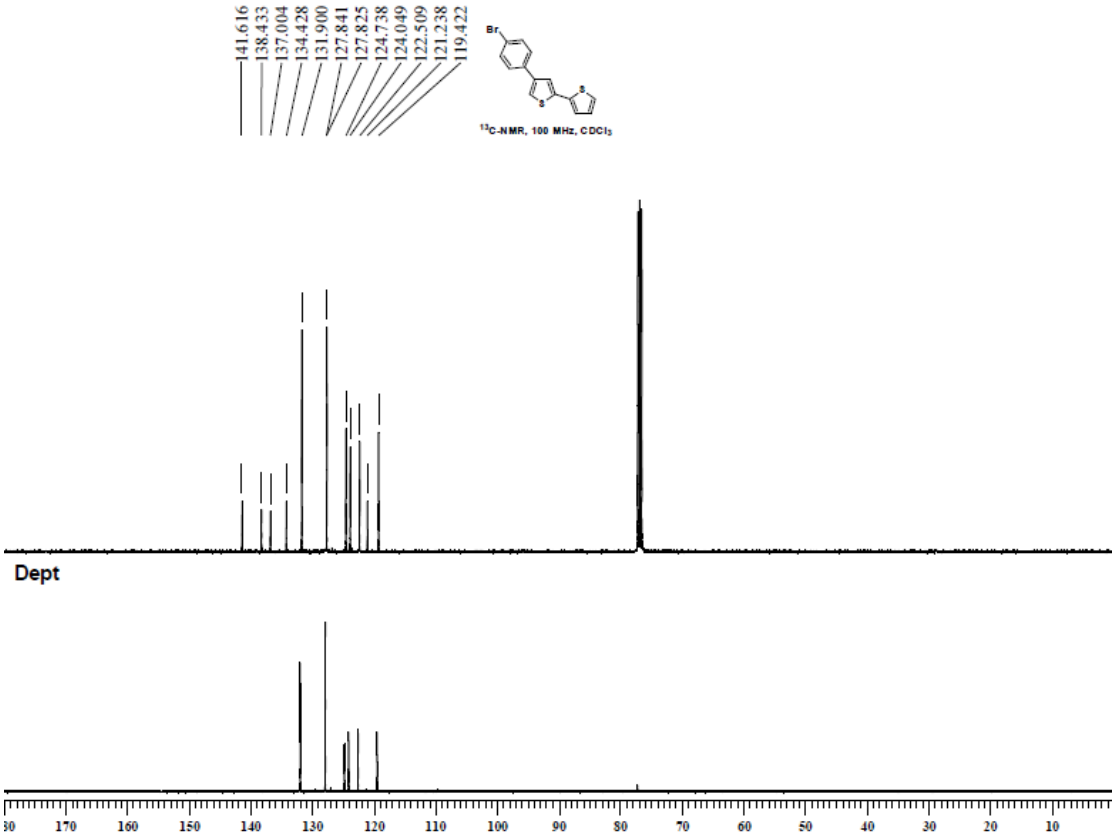




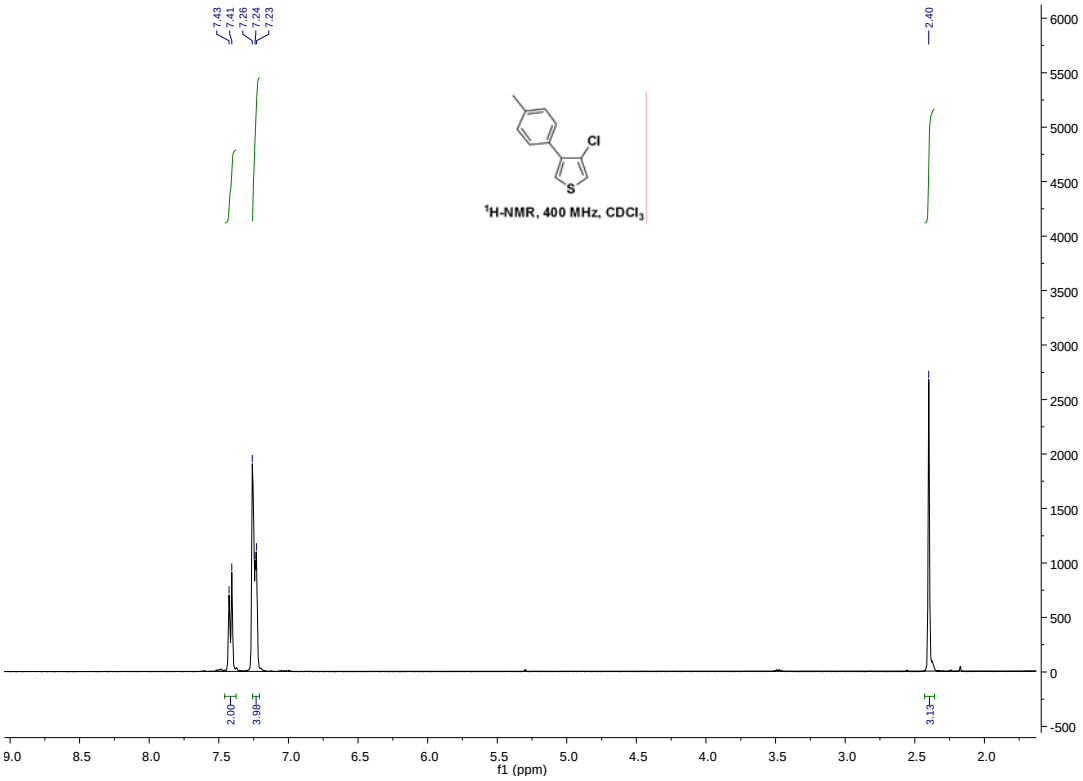

141.356
138.836
138.720
136.852
129.736
129.410
129.089
128.767
128.732
127.893
126.449
125.866
125.830
125.792
125.536
124.880
124.197
122.520
120.557
F3C
S
S
13C-NMR,100 MHz, CDCl3
Dept
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

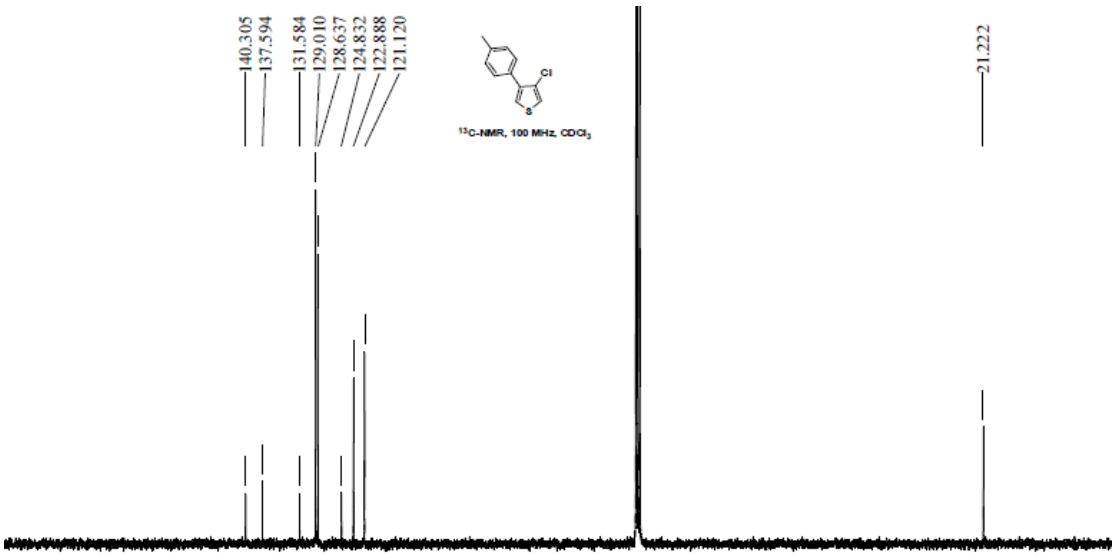
4-(4-Bromophenyl)-[2,2']bithiophenyl (26)





3-Chloro-4-*p*-tolylthiophene (30)





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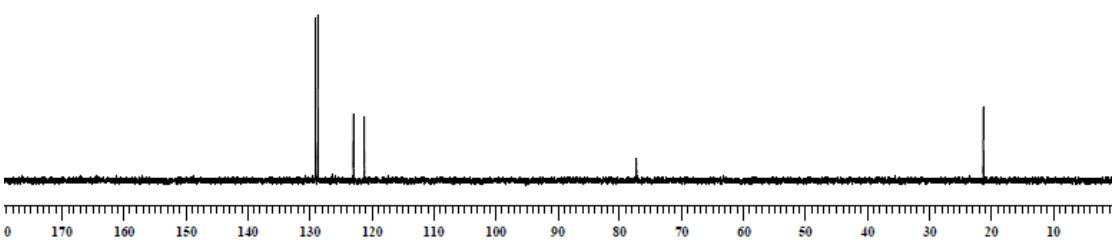
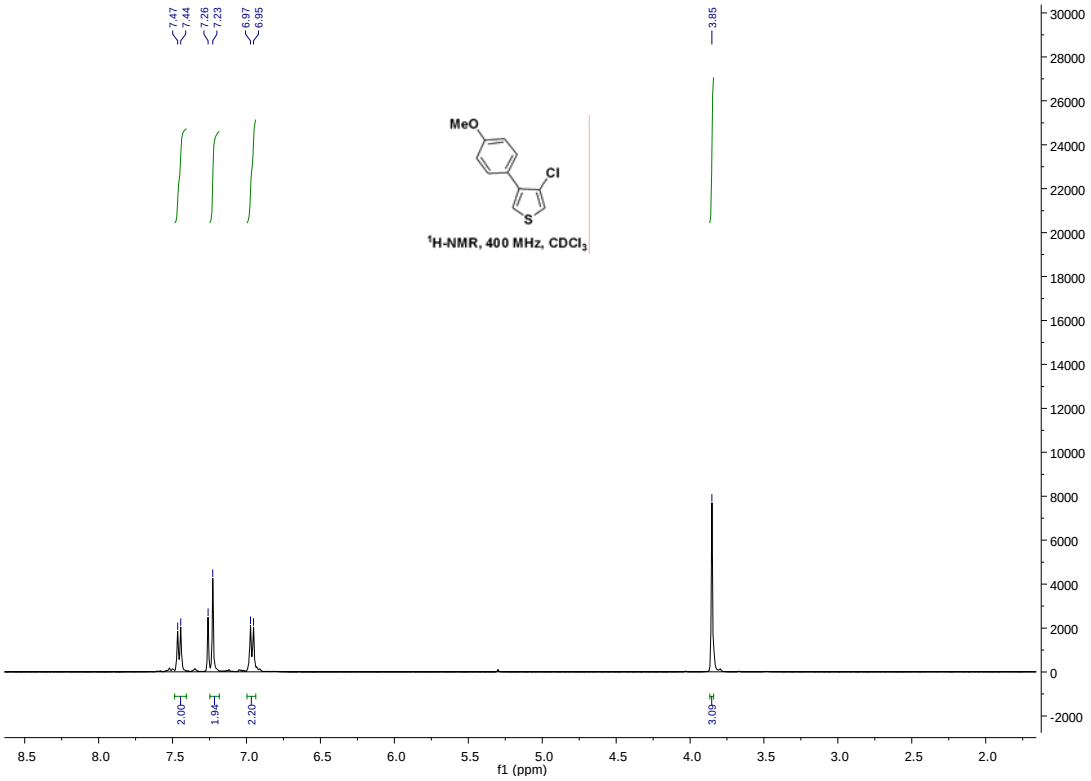
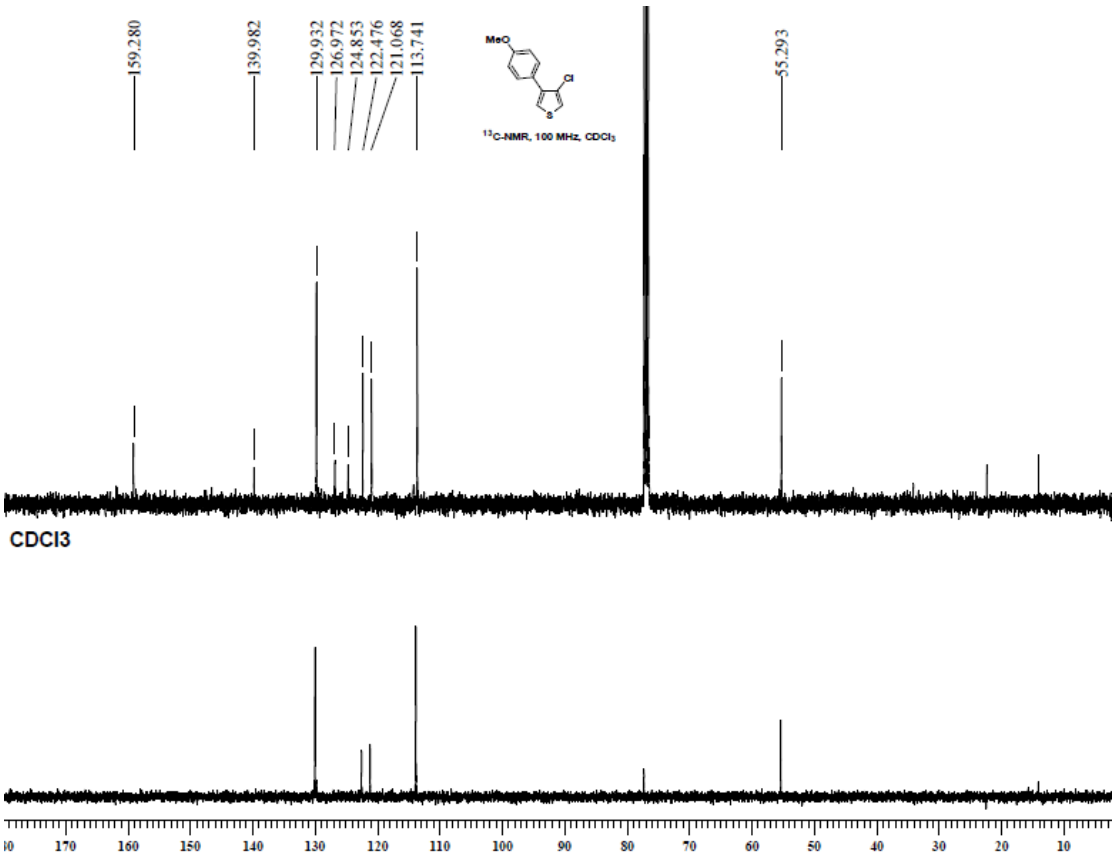
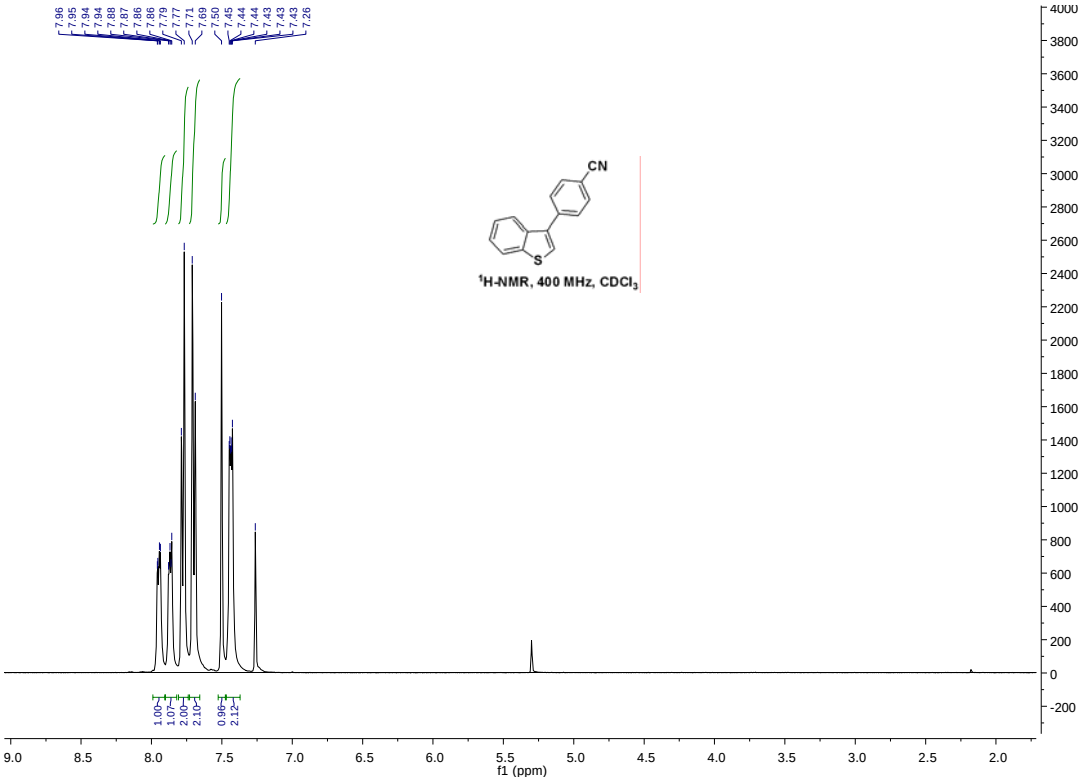


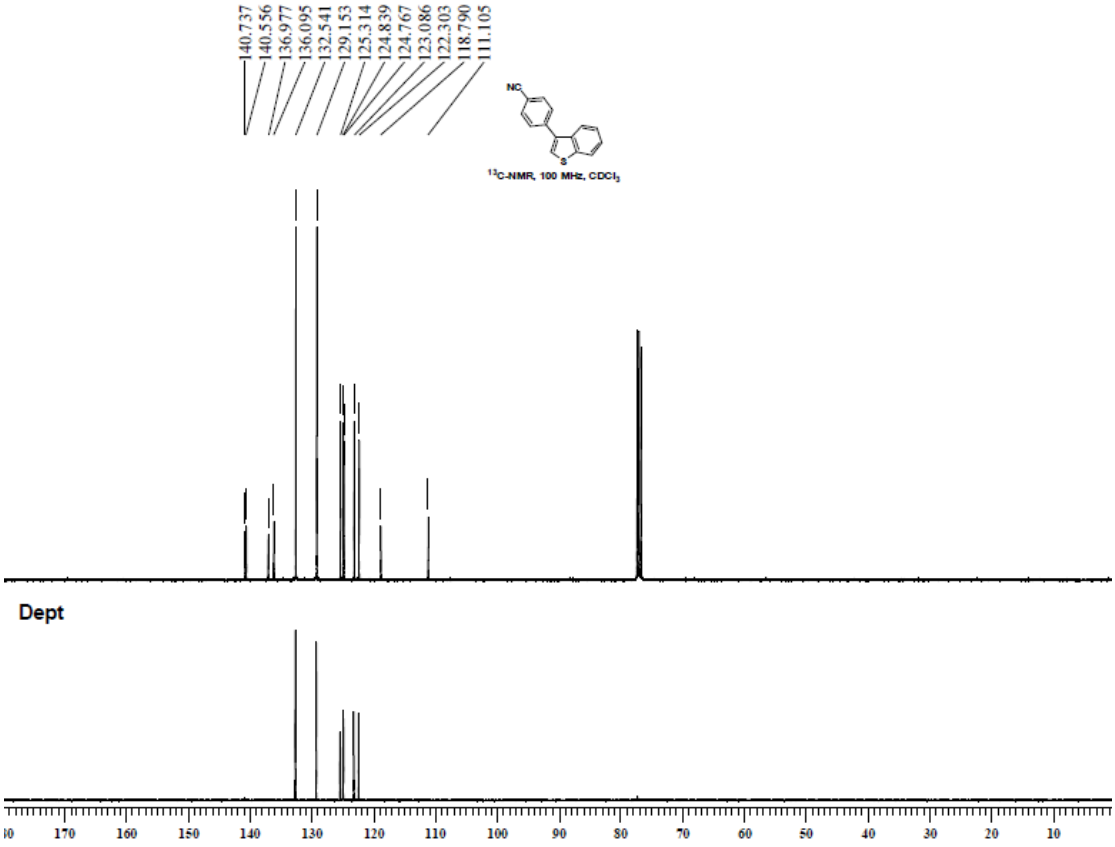
3-Chloro-4-(4-methoxyphenyl)-thiophene (31)



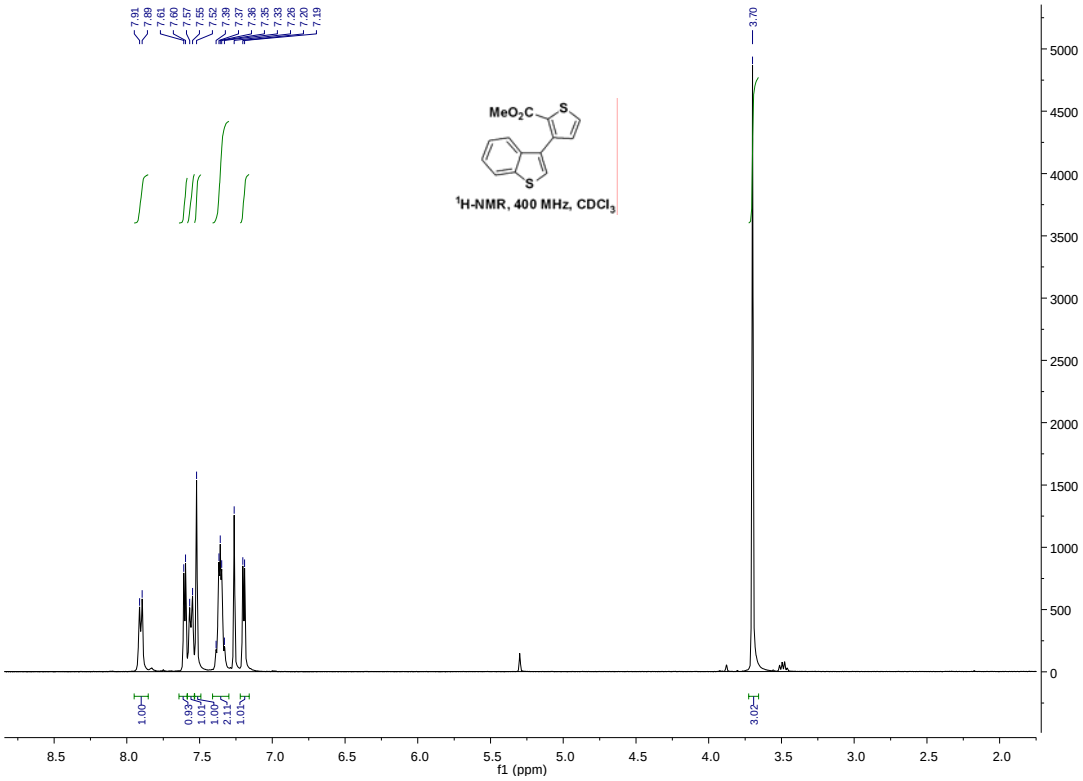


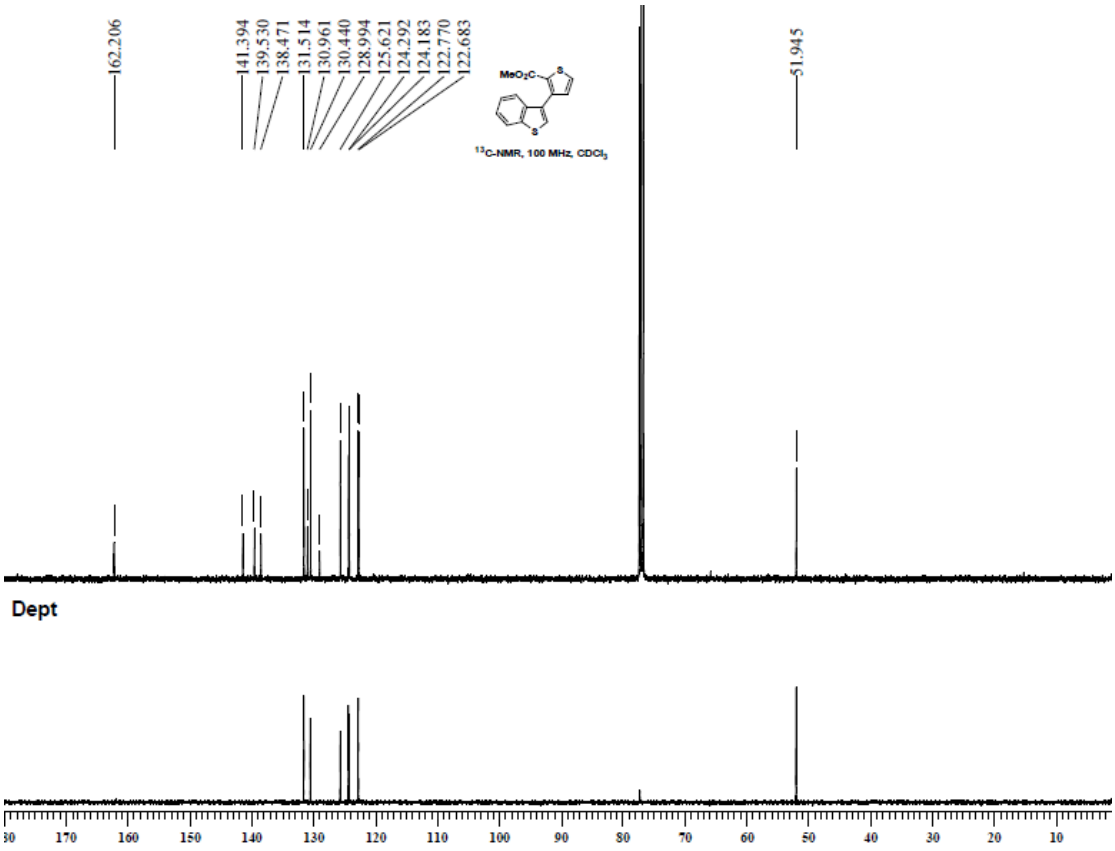
4-Benzo[b]thiophen-3-ylbenzonitrile (38)





Methyl 3-benzo[b]thiophen-3-ylthiophene-2-carboxylate (39)





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