Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Application of DIB/BBr_3 Protocol in Metal-free Aryl Coupling Reactions

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1) General Information

Commercially available reagents were used as received. The solvents were dried over a solvent purification system from Innovative Technology. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker AMX500 (500 MHz) spectrometer or a Bruker AMX400 (400 MHz) spectrometer. Proton and carbon chemical shifts are reported in parts per million (ppm) values downfield from TMS (δ 0.00) and referenced to residual protons in NMR solvents ($CDCl_3$ at 7.26) or carbon signals in NMR solvent (CDCl3 at 77.0). High resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer (ionization mode: ESI or APCI/DIP). Analytical thin layer chromatography (TLC) was performed with Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. Products **2a-i**,[1] **7a-e** and **7h**,[2] **7f-g**,[3] and **7i**[4] are known compounds and their analytical data are in accordance with the literature reported values.

2) General procedure

2.1 General procedure for the oxidative self-coupling of alkylthiophene in synthesizing **2a-2d** and **2j**

To a stirred solution of thiophene **1** (0.4 mmol, 2 equiv) in HFIP (2 mL) was added DIB (0.2 mmol, 1.0 equiv) at room temperature. The resultant mixture was cooled to 0 °C and BBr_3 (0.4 mmol, 2.0 equiv, 1 M in CH_2Cl_2) was added and the reaction mixture was stirred at the same temperature for 30 minutes. Upon completion, the reaction was quenched with water (2 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexanes and CH_2Cl_2 to yield the pure product **2a-2d** and **2j**.

2.1 General procedure for the oxidative self-coupling of alkoxythiophene in synthesizing **2e-2i**

To a stirred solution of alkoxythiophene **1** (0.4 mmol, 2 equiv) in CH_2Cl_2/HFIP (1:5 v/v, 2 mL) was added DIB (0.2 mmol, 1.0 equiv) at room temperature. The resultant mixture was cooled to 0 °C and BBr_3 (0.4 mmol, 2.0 equiv, 1 M in CH_2Cl_2) was added and the reaction mixture was stirred at the same temperature for 10 minutes. Upon completion, the reaction was quenched with water (2 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexanes and CH_2Cl_2 to yield the pure product **2e-2i**.

2.3 General procedure for the oxidative cross-coupling of arenes in synthesizing **7a-7i**

To a stirred solution of arene Ar^1 (0.2 mmol, 1.0 equiv) in HFIP (2 mL) was added DIB (0.2 mmol, 1.0 equiv) at room temperature. The resultant mixture was cooled to 0 °C, and arene Ar^2 (0.3 mmol, 1.5 equiv) and BBr_3 (0.4 mmol, 2.0 equiv, 1 M in CH_2Cl_2)

were sequentially added. The reaction mixture was then allowed to warm to room temperature and stirred for additional 3 h. Upon completion, the reaction was quenched with water (2 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexanes and CH_2Cl_2 to yield the pure product **7a-7i**.

2.7 Representative procedure for the synthesis of **8**

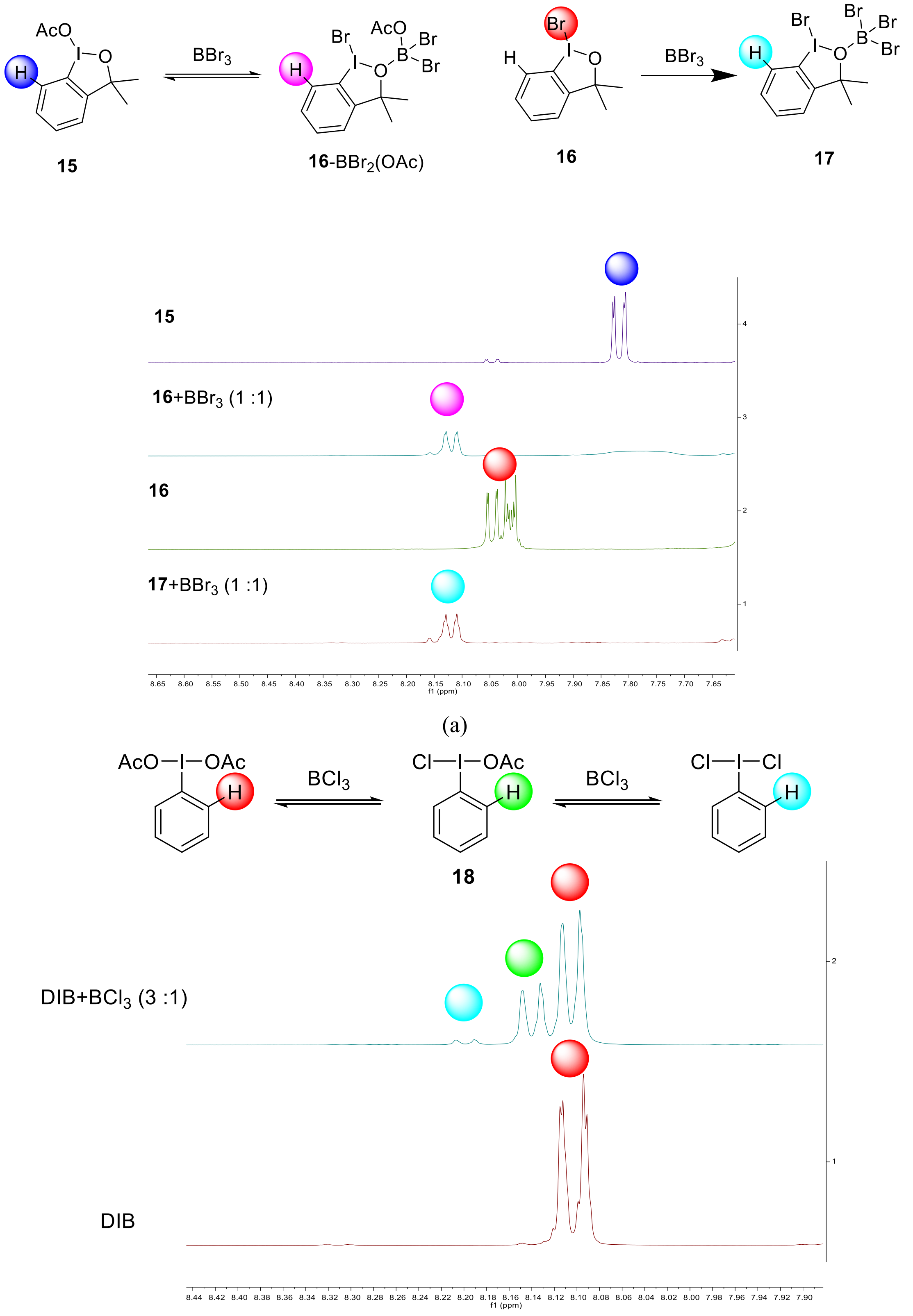
To a stirred solution of **2a** (0.2 mmol, 1.0 equiv) and mesitylene (1.2 mmol, 6.0 equiv) in CH_2Cl_2 (2 mL) was added successively boron trifluoride etherate (0.4 mmol, 2.0 equiv) and PIFA (0.2 mmol, 1.0 equiv) under nitrogen atmosphere at -78 °C. The reaction mixture was stirred at -78 °C for 1 h and then at -40 °C for 20 h. Upon completion, the reaction was quenched with water (4 mL). The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexanes to yield the cross-coupling product **8**. According the same procedure but using 1,3,5-triethylbenzene instead of mesitylene, product **9** was synthesized.

2.8 Representative procedure for the synthesis of **11**

In a 10 mL round-bottom flask was charged with substrate **10** (0.2 mmol, 1.0 equiv), 3-thienylboronic acid (0.48 mmol, 2.4 equiv) and $Pd(PPh_3)_4$ (0.012 mmol, 6 mol%). Then, the flask was purged with argon and degassed 1,2-dimethoxyethane (5 mL) and Na_2CO_3 (1.2 mmol, 6.0 equiv, 1 M in degassed H_2O) were added. The resultant mixture was heated at 80 °C under argon atmosphere for 12 h. The organic solvent was removed under reduced pressure and the aqueous layer was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over anhydrous

Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography eluted with hexanes to yield the cross-coupling product **11**. For the synthesis of **13**, the same procedure was used in which substrate **12**, 3-thienylboronic acid (0.24 mmol, 1.2 equiv), $Pd(PPh_3)_4$ (0.006 mmol, 3 mol%) and Na_2CO_3 (0.6 mmol, 3.0 equiv) were utilized.

3) NMR study to probe the reactive species



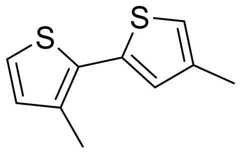
(a)

(b)

Figure S1 (a) ^{1}H NMR study on reaction between BBr$_3$ and **15** and **16**; (b) ^{1}H NMR study on reaction between BCl$_3$ and DIB.

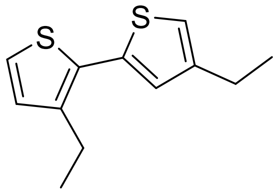
4) Analytical data

3,4'-dimethyl-2,2'-bithiophene



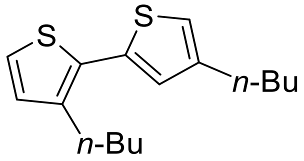
2a, 97% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 5.1 Hz, 1H), 6.95 (s, 1H), 6.90 – 6.78 (m, 2H), 2.39 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 138.00, 136.35, 133.73, 131.31, 127.79, 123.03, 120.44, 15.76, 15.34.

3,4'-diethyl-2,2'-bithiophene



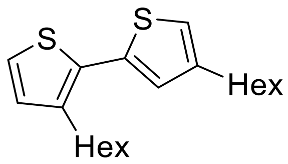
2b, 96% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.16 (d, *J* = 5.2 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.90 (d, *J* = 1.2 Hz, 1H), 2.79 (q, *J* = 7.6 Hz, 2H), 2.65 (q, *J* = 8.0 Hz, 2H), 1.40 – 1.15 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.96, 140.60, 135.92, 130.67, 129.38, 127.01, 123.60, 119.33, 23.66, 22.42, 15.15, 14.59.

3,4'-dibutyl-2,2'-bithiophene



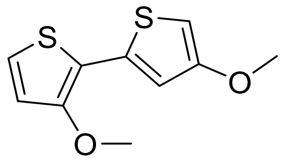
2c, 90% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 5.2 Hz, 1H), 6.95 (d, *J* = 1.4 Hz, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 6.89 (d, *J* = 1.2 Hz, 1H), 2.76 (t, J **= 7.5 Hz**,2H), 2.62 (t, J **= 7.5 Hz,** 2H), 1.69 – 1.57 (m, 4H), 1.48 – 1.31 (m, 4H), 0.94 (q, *J* = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.49, 139.31, 135.85, 130.99, 129.91, 127.33, 123.40, 119.90, 32.92, 32.59, 30.21, 28.88, 22.65, 22.42, 13.98, 13.97.

1,1'-([2,2'-bithiophene]-3,4'-diyl)bis(hexan-1-one)



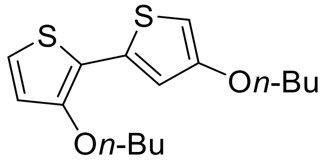
2d,95% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 5.2 Hz, 1H), 6.95 (s, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 6.89 (s, 1H), 2.76 (t, *J* = 7.7 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.73 – 1.55 (m, 4H), 1.42 – 1.22 (m, 12H), 1.00 – 0.76 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.55, 139.37, 135.86, 131.00, 129.91, 127.32, 123.40, 119.90, 31.73, 31.70, 30.74, 30.54, 30.43, 29.26, 29.18, 29.05, 22.67, 14.15, 14.13.

3,4'-dimethoxy-2,2'-bithiophene



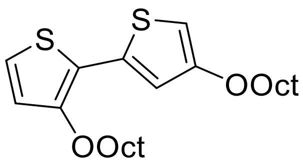
2e,88% yield, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 6.50 (m, 3H), 6.13 (s, 1H), 3.94 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.98, 153.72, 133.98, 121.71, 116.82, 115.13, 114.71, 95.01, 58.85, 57.22.

3,4'-dibutoxy-2,2'-bithiophene



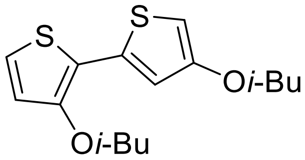
2f,86% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 5.2 Hz, 1H), 6.95 (d, *J* = 1.3 Hz, 1H), 6.93 (d, *J* = 5.2 Hz, 1H), 6.89 (d, *J* = 1.2 Hz, 1H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.62 (t, *J* = 6.4 Hz, 2H), 1.71 – 1.55 (m, 4H), 1.47 – 1.32 (m, 4H), 0.94 (q, *J* = 7.4 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.49, 139.31, 135.85, 130.99, 129.91, 127.33, 123.40, 119.90, 32.92, 32.59, 30.21, 28.88, 22.65, 22.42, 13.98, 13.97.

[2,2'-bithiophene]-3,4'-diyl dioctanoate



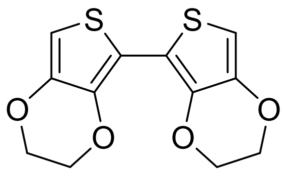
2g,84% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 5.5 Hz, 1H), 6.89 (d, *J* = 1.6 Hz, 1H), 6.82 (d, *J* = 5.6 Hz, 1H), 6.10 (d, *J* = 1.7 Hz, 1H), 4.08 (t, *J* = 6.5 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 1.95 – 1.68 (m, 4H), 1.54 – 1.40 (m, 4H), 1.37 – 1.23 (m, 16H), 0.89 (t, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.15, 152.97, 133.92, 121.43, 117.36, 115.37, 114.58, 95.37, 71.88, 70.03, 31.84, 31.83, 29.65, 29.39, 29.32, 29.29, 29.26, 29.23, 26.08, 26.02, 22.68, 14.15, 14.13.

3,4'-diisobutoxy-2,2'-bithiophene



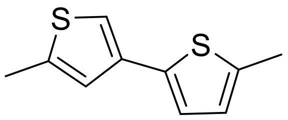
2h,90% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 5.6 Hz, 1H), 6.89 (d, *J* = 1.7 Hz, 1H), 6.81 (d, *J* = 5.5 Hz, 1H), 6.10 (d, *J* = 1.6 Hz, 1H), 3.87 (d, *J* = 6.4 Hz, 2H), 3.71 (d, *J* = 6.6 Hz, 2H), 2.15 (dt, *J* = 13.2, 6.6 Hz, 1H), 2.08 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.08 (d, *J* = 6.7 Hz, 6H), 1.01 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.23, 153.01, 133.91, 121.40, 117.12, 114.98, 114.46, 95.37, 78.17, 76.42, 28.69, 28.28, 19.36, 19.28.

2,2',3,3'-tetrahydro-5,5'-bithieno[3,4-b][1,4]dioxine



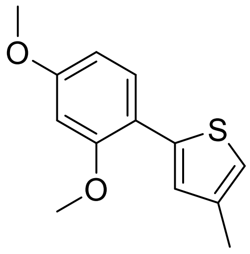
2i,74% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 6.27 (s, 2H), 4.44 – 4.29 (m, 4H), 4.29 – 4.15 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.23, 137.03, 109.91, 97.54, 65.02, 64.62.

5,5'-dimethyl-2,3'-bithiophene



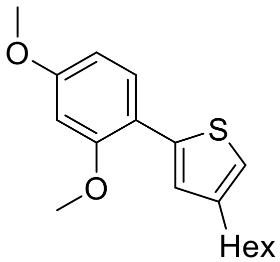
2j, 42% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.03 (s, 1H), 6.95 – 6.87 (m, 2H), 6.65 (d, *J* = 1.5 Hz, 1H), 2.49 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 140.43, 138.20, 137.32, 135.59, 125.67, 124.23, 122.63, 116.47, 15.37, 15.35. HRMS (EI) calculated for $C_{10}H_{10}S_2$ [M+H]$^+$ 195.02967, found 195.02976.

2-(2,4-dimethoxyphenyl)-4-methylthiophene



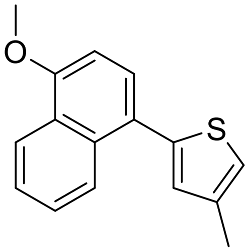
7a, 86% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.6 Hz, 1H), 7.20 (d, *J* = 1.4 Hz, 1H), 6.84 (s, 1H), 6.57 – 6.49 (m, 2H), 3.90 (s, 3H), 3.84 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.06, 156.80, 139.41, 137.36, 129.32, 126.93, 119.69, 116.72, 104.92, 98.99, 55.55, 55.45, 15.89.

1-(5-(2,4-dimethoxyphenyl)thiophen-3-yl)hexan-1-one



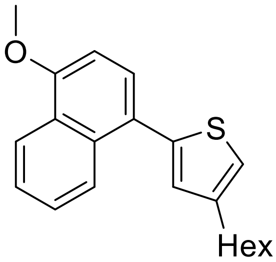
7b, 85% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.9 Hz, 1H), 7.21 (d, *J* = 1.4 Hz, 1H), 6.84 (d, *J* = 1.3 Hz, 1H), 6.62 – 6.46 (m, 2H), 3.89 (s, 3H), 3.84 (s, 3H), 2.61 (t, *J* = 7.5 Hz,2H), 1.64 (p, *J* = 7.9, 7.4 Hz, 2H), 1.45 – 1.22 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 160.01, 156.75, 142.98, 139.19, 129.27, 125.96, 118.98, 116.82, 104.92, 98.98, 55.55, 55.44, 31.75, 30.66, 30.49, 29.11, 22.66, 14.15.

2-(4-methoxynaphthalen-1-yl)-4-methylthiophene



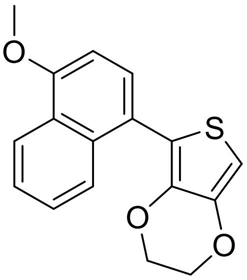
7c, 90% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.38 – 8.31 (m, 1H), 8.24 – 8.11 (m, 1H), 7.55 – 7.50 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 6.98 (s, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 4.04 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.45, 141.96, 137.79, 132.73, 129.41, 128.17, 126.87, 125.70, 125.61, 125.33, 125.06, 122.20, 120.41, 103.31, 55.62, 15.96.

1-(5-(4-methoxynaphthalen-1-yl)thiophen-3-yl)hexan-1-one



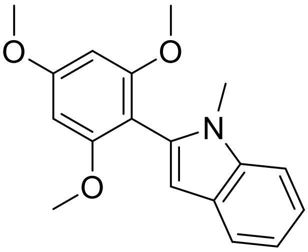
7d, 82% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 – 8.29 (m, 1H), 8.23 – 8.15 (m, 1H), 7.58 – 7.43 (m, 3H), 7.03 (s, 1H), 6.97 (s, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 3H), 1.80 – 1.61 (m, 2H), 1.47 – 1.19 (m, 6H), 0.91 (t, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.40, 143.47, 141.73, 132.72, 128.50, 128.14, 126.85, 125.70, 125.60, 125.30, 125.18, 122.18, 119.60, 103.31, 55.61, 31.75, 30.72, 30.52, 29.13, 22.68, 14.15.

5-(4-methoxynaphthalen-1-yl)-2,3-dihydrothieno[3,4-b][1,4]dioxine



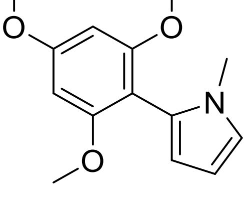
7e, 91% yield, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.44 – 8.23 (m, 1H), 8.07 – 7.83 (m, 1H), 7.56 – 7.50 (m, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.45 (s, 1H), 4.31 – 4.24 (m, 2H), 4.23 – 4.17 (m, 2H), 4.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.83, 141.40, 138.05, 132.84, 129.25, 126.78, 126.06, 125.74, 125.34, 122.24, 121.98, 115.50, 103.48, 98.47, 64.74, 64.67, 55.63.

1-methyl-2-(2,4,6-trimethoxyphenyl)-1H-indole



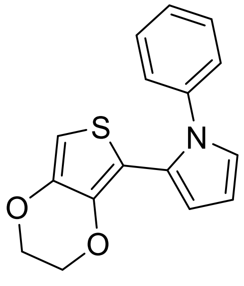
7f, 54% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.45 (s, 1H), 6.24 (s, 2H), 3.89 (s, 3H), 3.73 (s, 6H), 3.50 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.90, 160.03, 137.16, 133.19, 128.06, 120.58, 120.39, 118.92, 109.24, 103.03, 102.42, 90.66, 55.87, 55.45, 30.13.

1-methyl-2-(2,4,6-trimethoxyphenyl)-1H-pyrrole



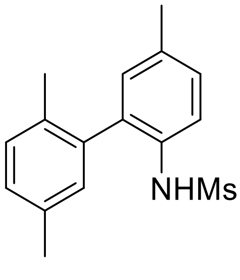
7g, 72% yield, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.74 – 6.71 (m, 1H), 6.25 (dd, *J* = 3.5, 2.7 Hz, 1H), 6.21 (s, 2H), 6.08 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.87 (s, 3H), 3.75 (s, 6H), 3.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.31, 159.99, 125.28, 121.51, 109.45, 107.22, 103.55, 90.60, 55.86, 55.39, 34.05.

2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-1-phenyl-1H-pyrrole



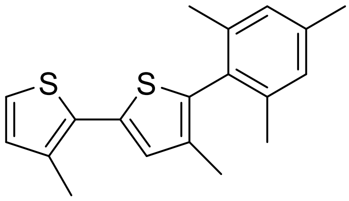
7h, 84% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.33 – 7.22 (m, 3H), 6.92 (t, *J* = 2.3 Hz, 1H), 6.51 (dd, *J* = 3.6, 1.7 Hz, 1H), 6.35 (t, *J* = 3.2 Hz, 1H), 6.19 (s, 1H), 4.09 – 4.00 (m, 2H), 3.92 – 3.79 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.18, 140.46, 137.94, 128.66, 126.90, 125.79, 124.30, 123.59, 111.77, 109.30, 108.87, 98.35, 64.39, 64.34.

N-(2',5,5'-trimethyl-[1,1'-biphenyl]-2-yl)methanesulfonamide



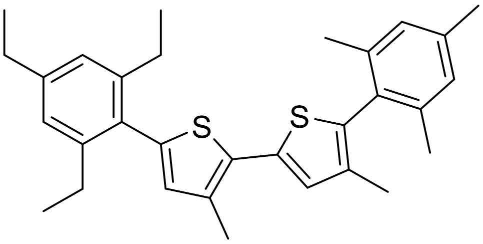
7i, 36% yield, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.10 (m, 3H), 6.98 (d, *J* = 2.1 Hz, 1H), 6.93 (d, *J* = 1.9 Hz, 1H), 6.04 (s, 1H), 2.85 (s, 3H), 2.34 (s, 6H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)δ 19.2, 20.7, 20.9, 39.4, 119.2, 129.3, 129.6, 130.1, 130.8, 130.9, 131.8, 132.4, 133.1, 134.2, 136.2, 136.2

5'-mesityl-3,4'-dimethyl-2,2'-bithiophene



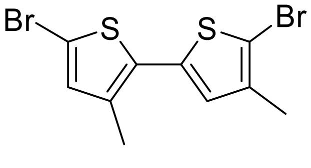
8, colorless oil, 48% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 5.1 Hz, 1H), 7.00 (s, 1H), 6.94 (s, 2H), 6.87 (d, *J* = 5.2 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H), 2.11 (s, 6H), 1.93 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 138.60, 137.87, 135.76, 134.93, 134.38, 133.27, 131.55, 131.43, 129.77, 128.05, 127.63, 122.57, 21.15, 20.40, 15.54, 13.87. HRMS (EI) calculated for $C_{19}H_{20}S_2$ [M+H]$^+$ 313.10792, found 313.10754.

5'-mesityl-3,4'-dimethyl-5-(2,4,6-triethylphenyl)-2,2'-bithiophene



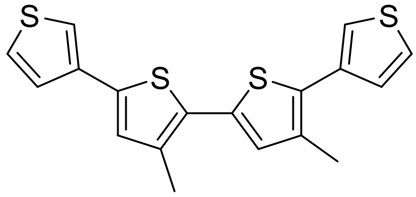
9, colorless oil, 80% yield, ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.04 (s, 1H), 6.99 (s, 2H), 6.95 (s, 1H), 6.59 (s, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 2.53 (q, *J* = 7.5 Hz, 4H), 2.44 (s, 3H), 2.33 (s, 3H), 2.13 (s, 6H), 1.94 (s, 3H), 1.29 (t, *J* = 7.6 Hz, 4H), 1.15 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 144.54, 144.51, 138.63, 137.85, 135.36, 135.18, 134.38, 132.74, 131.74, 131.38, 129.83, 129.56, 128.06, 127.11, 125.20, 28.77, 26.95, 21.17, 20.42, 16.24, 15.89, 15.47, 13.87. HRMS (EI) calculated for $C_{31}H_{36}S_2$ [M+H]$^+$ 473.23312, found 473.23266.

5,5'-dibromo-3,4'-dimethyl-2,2'-bithiophene



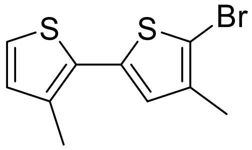
10, yellow oil, 81% yield (two steps), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.83 (s, 1H), 6.74 (s, 1H), 2.29 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.68, 134.79, 134.53, 133.87, 131.82, 127.69, 110.32, 109.47, 15.22, 15.14. HRMS (EI) calculated for $C_{10}H_8Br_2S_2$ [M+H]$^+$ 352.84858, found 352.84867.

3',3''-dimethyl-3,2':5',2'':5'',3'''-quaterthiophene



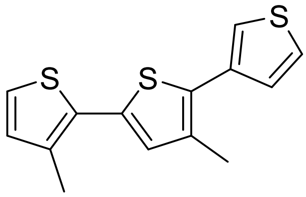
11, yellow solid, m.p. 203-204 °C, 68% yield (two steps), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 4H), 7.31 – 7.27 (m, 2H), 6.99 (s, 1H), 6.96 (s, 1H), 2.42 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.15, 136.11, 135.29, 134.80, 134.29, 133.67, 133.55, 132.39, 129.65, 129.21, 127.85, 127.63, 126.38, 125.82, 121.64, 119.42, 15.73, 15.44. HRMS (EI) calculated for $C_{18}H_{14}S_4$ [M+H]$^+$ 359.00514, found 359.00511.

5'-bromo-3,4'-dimethyl-2,2'-bithiophene



12, yellow oil, 54% yield (two steps), ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 5.1 Hz, 1H), 6.87 (d, *J* = 5.1 Hz, 1H), 6.81 (s, 1H), 2.36 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.55, 135.90, 134.26, 131.35, 130.40, 127.30, 123.53, 108.84, 15.26, 15.25. HRMS (EI) calculated for $C_{10}H_9BrS_2$ [M+H]$^+$ 274.93801, found 274.93822.

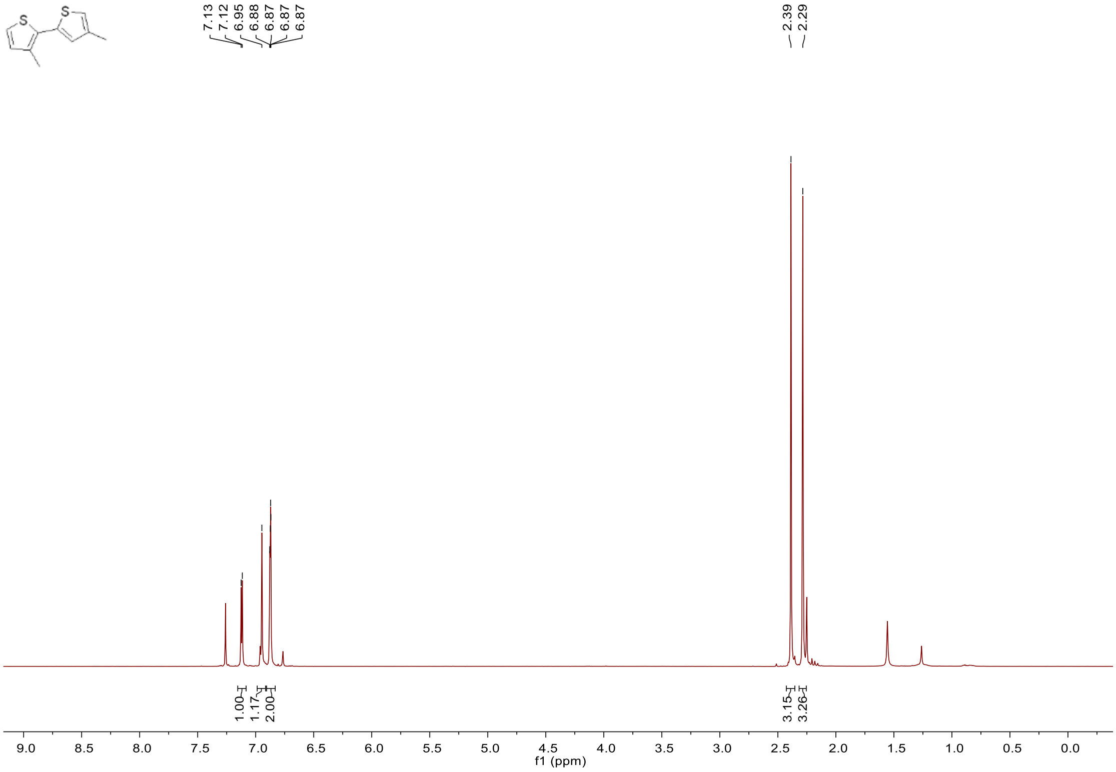
3,4'-dimethyl-2,2':5',3''-terthiophene



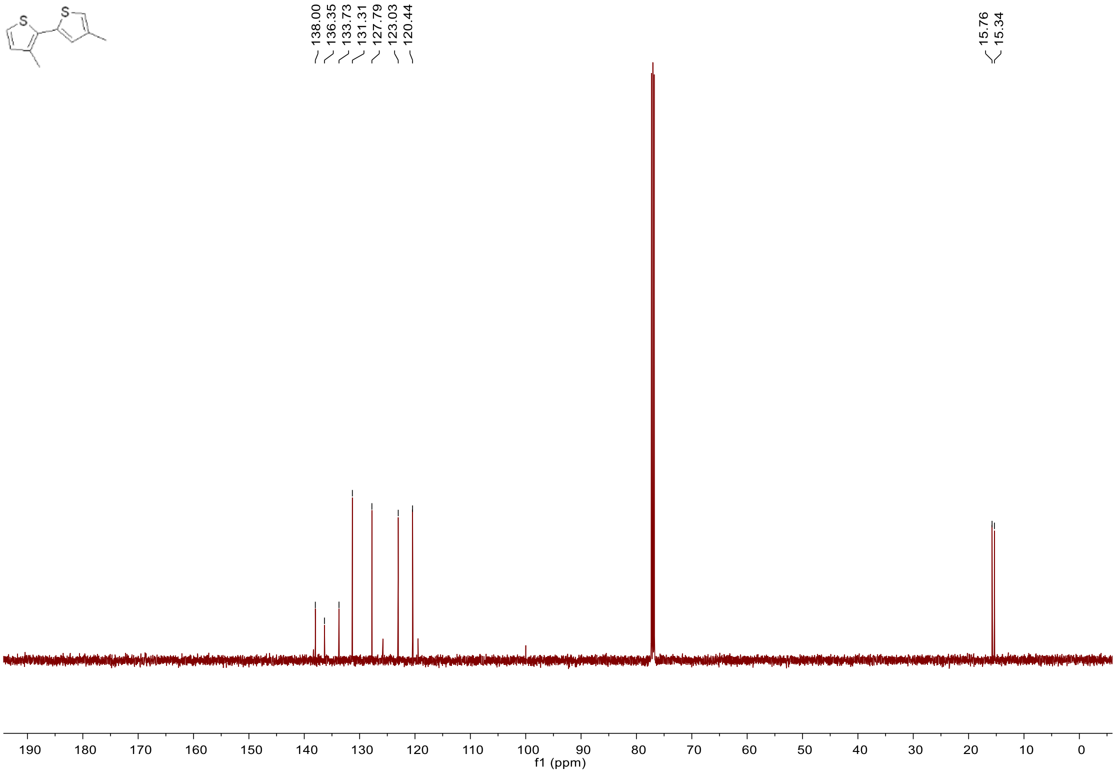
13, yellow solid, m.p. 92-93 °C, 76% yield, ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.29 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.14 (d, *J* = 5.2 Hz, 1H), 6.96 (s, 1H), 6.90 (d, *J* = 5.1 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.83, 133.78, 133.61, 133.59, 132.48, 131.48, 131.12, 129.48, 127.88, 125.80, 123.06, 121.65, 15.50, 15.44. HRMS (EI) calculated for $C_{14}H_{12}S_3$ $[M+H]^+$ 277.01739, found 277.01713.

5) NMR spectrum

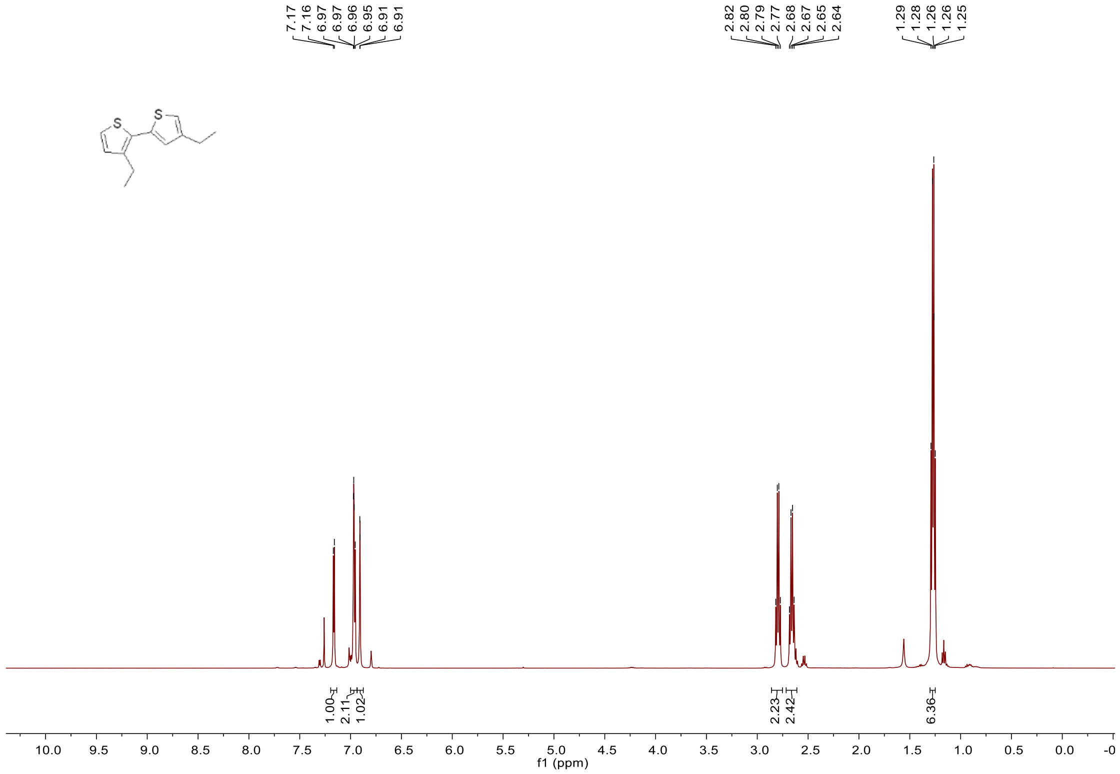
2a, ^{1}H NMR (400 MHz, CDCl$_3$)



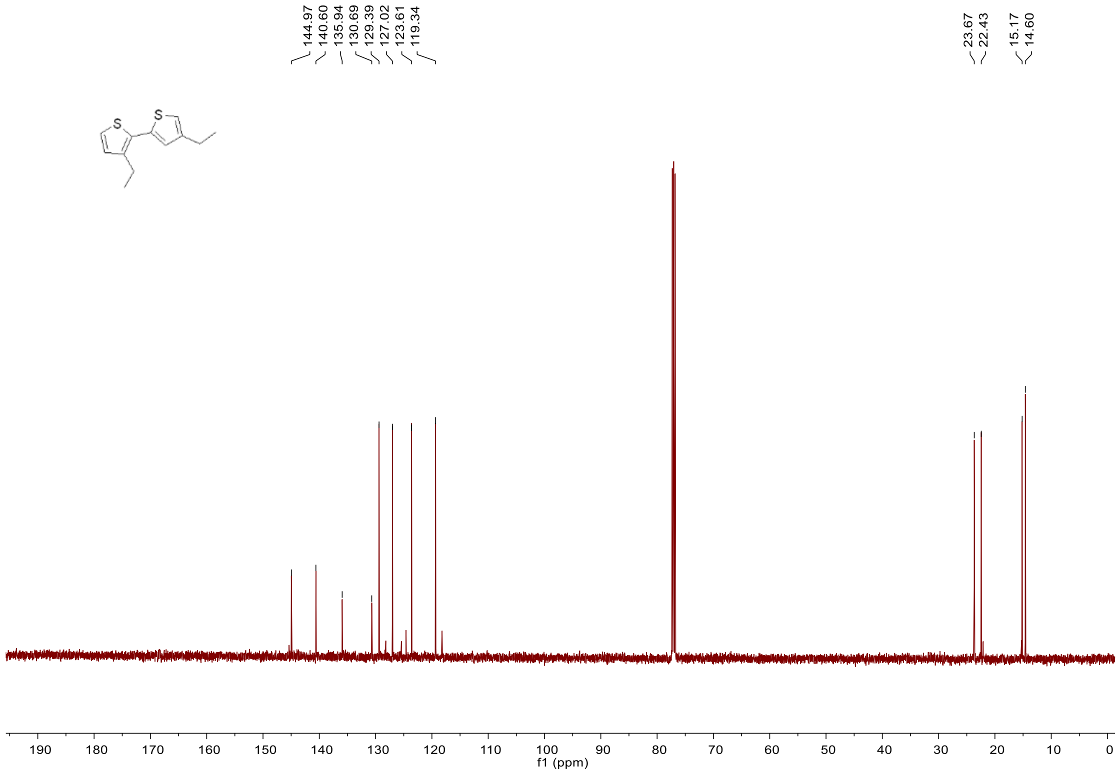
2a, ^{13}C NMR (101 MHz, CDCl$_3$)



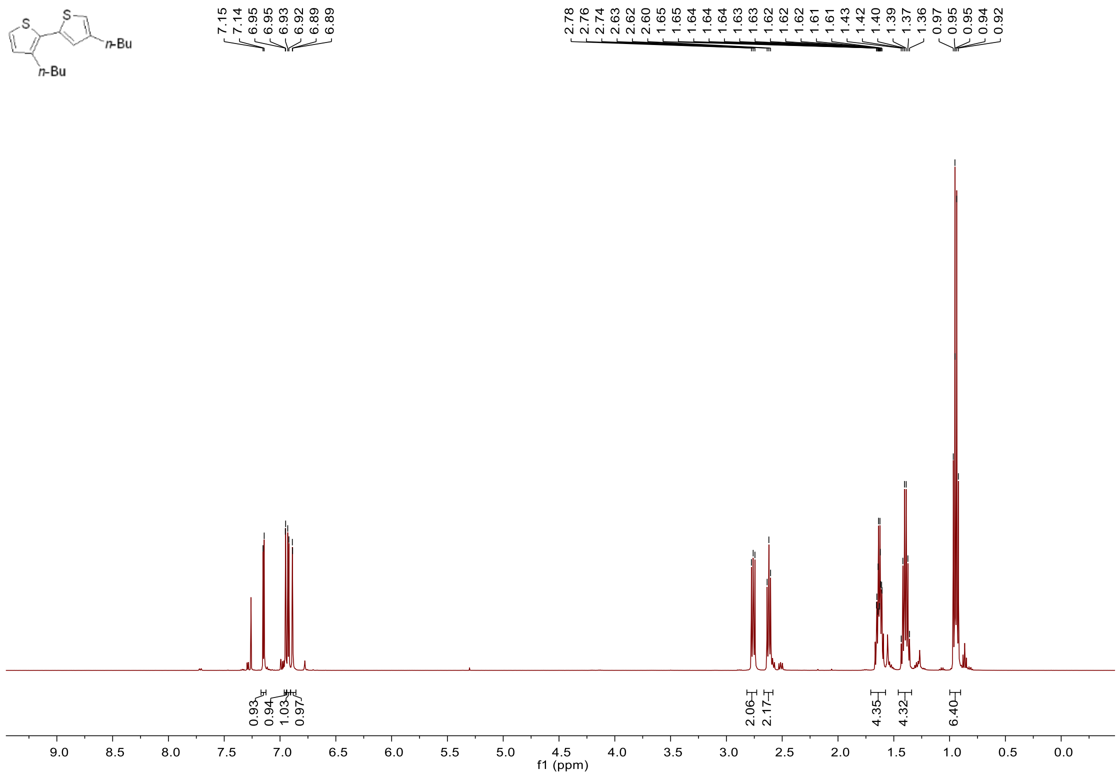
2b, ^{1}H NMR (400 MHz, CDCl$_3$)



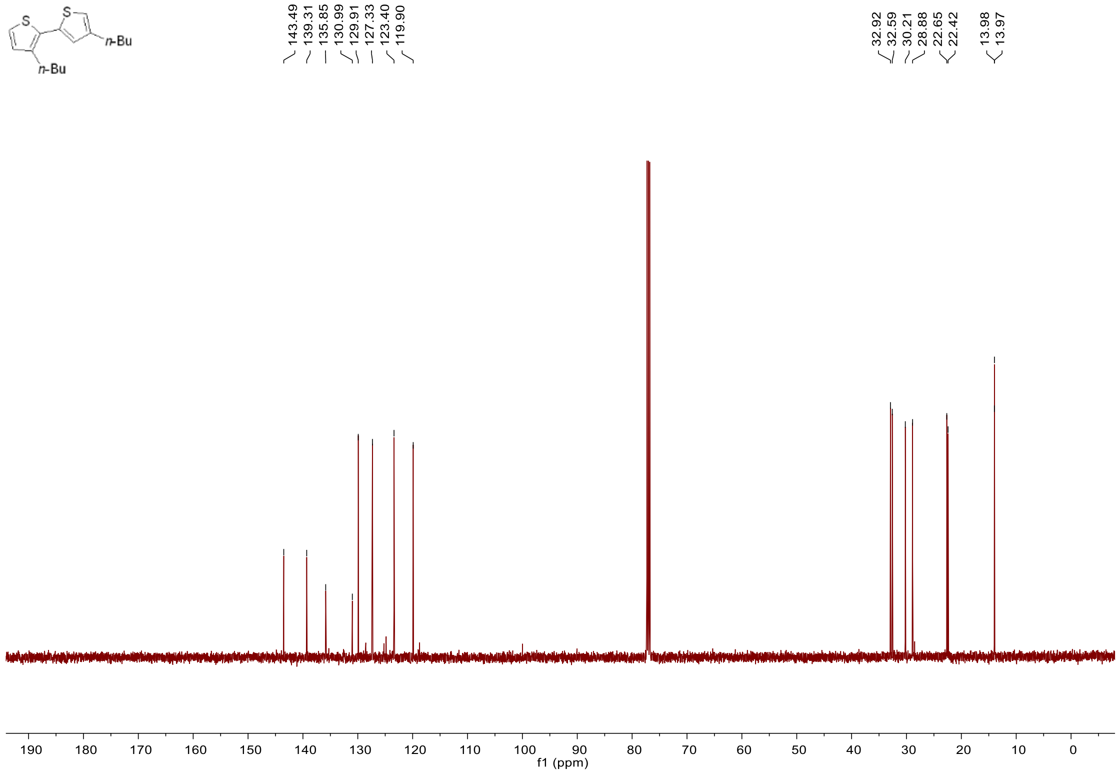
2b, ^{13}C NMR (101 MHz, CDCl$_3$)



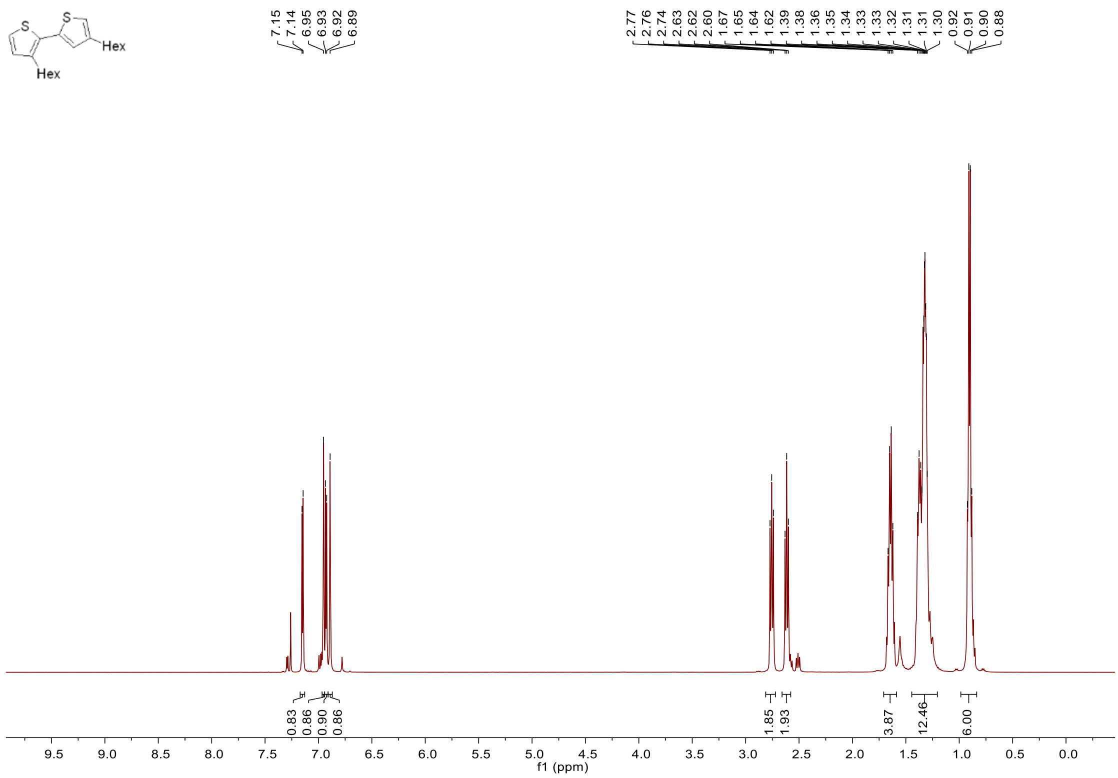
2c, ^{1}H NMR (400 MHz, CDCl$_3$)



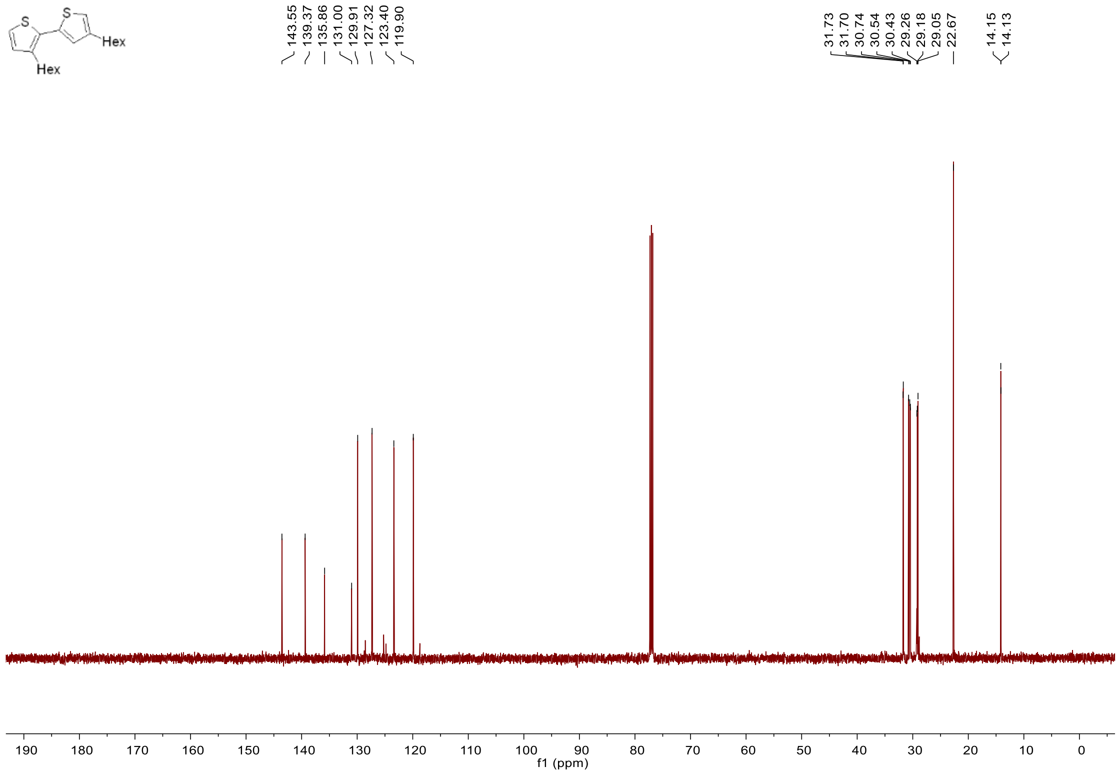
2c, ^{13}C NMR (101 MHz, CDCl$_3$)



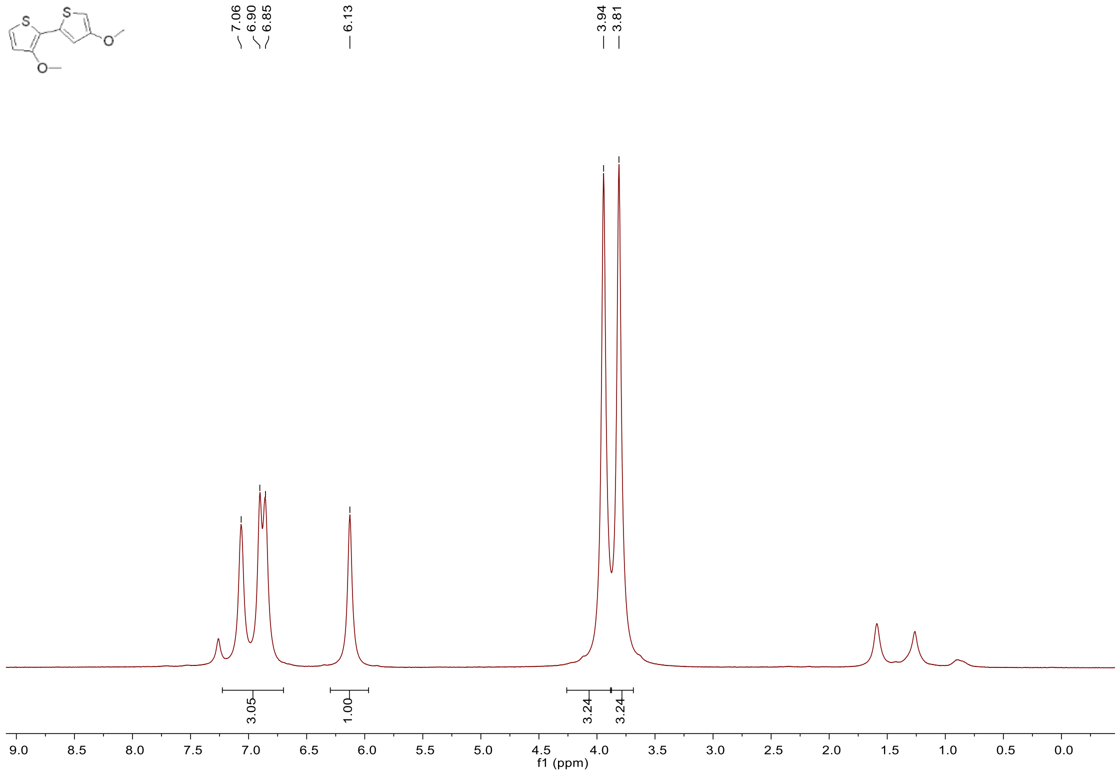
2d, ^{1}H NMR (400 MHz, CDCl$_3$)



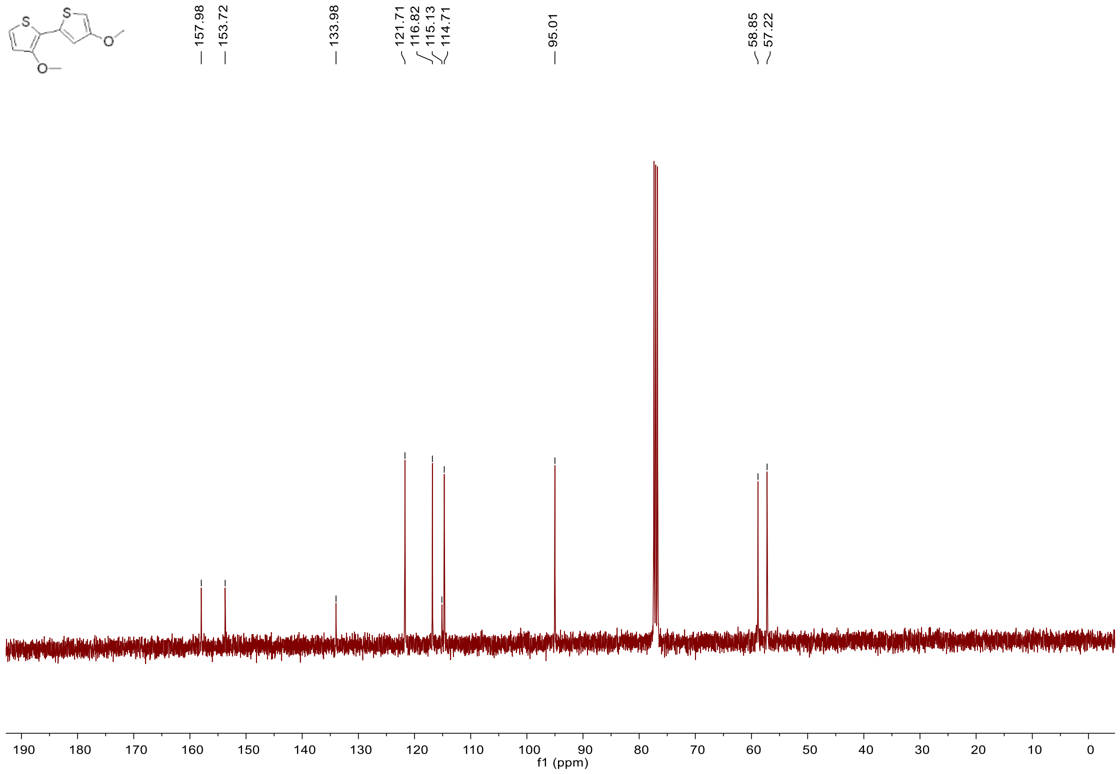
2d, ^{13}C NMR (101 MHz, CDCl$_3$)



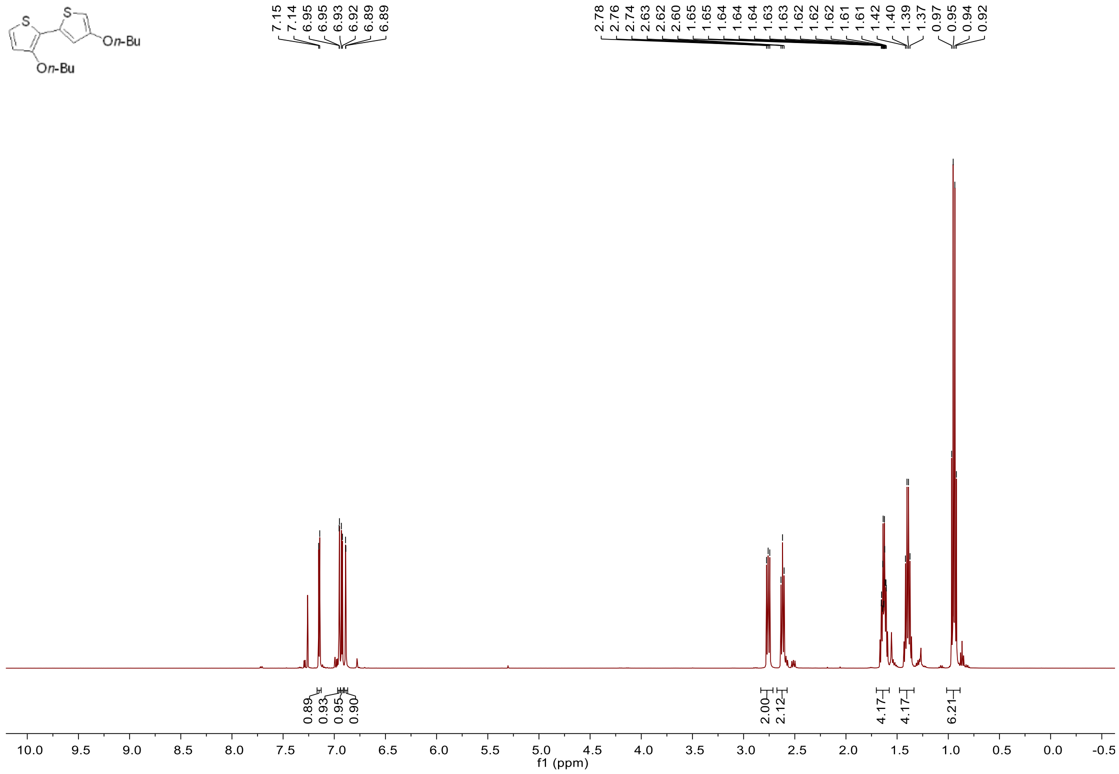
2e, ^{1}H NMR (400 MHz, CDCl$_3$)



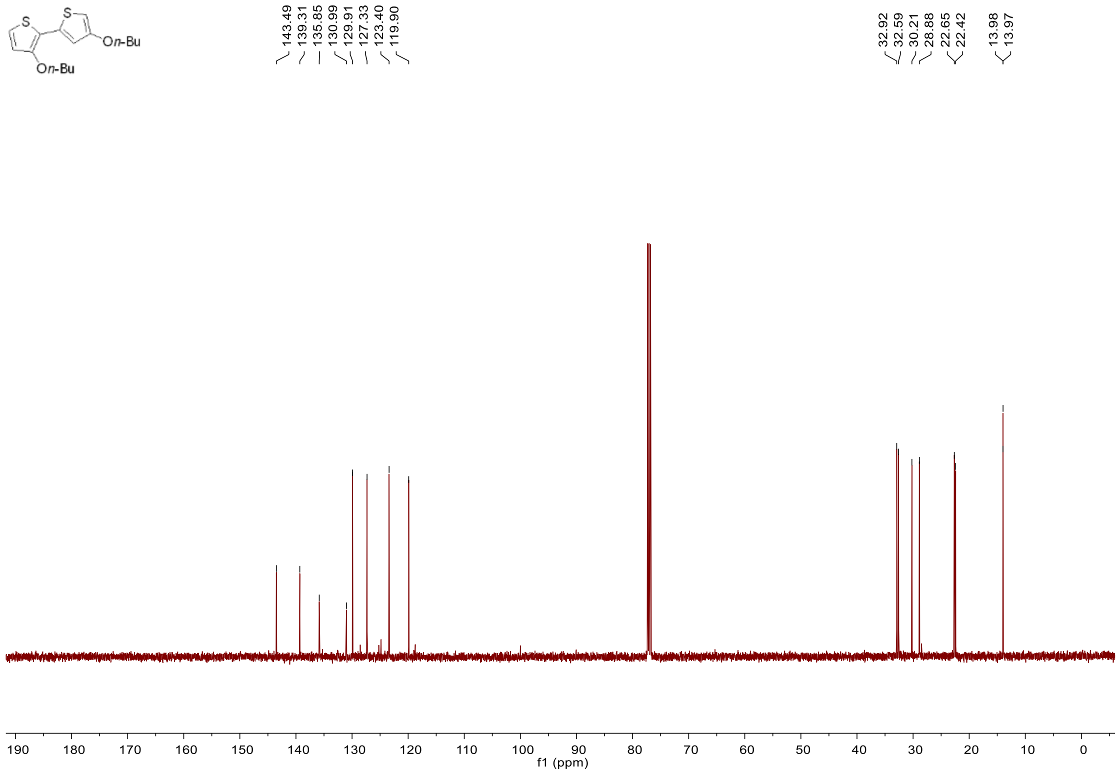
2e, ^{13}C NMR (101 MHz, CDCl$_3$)



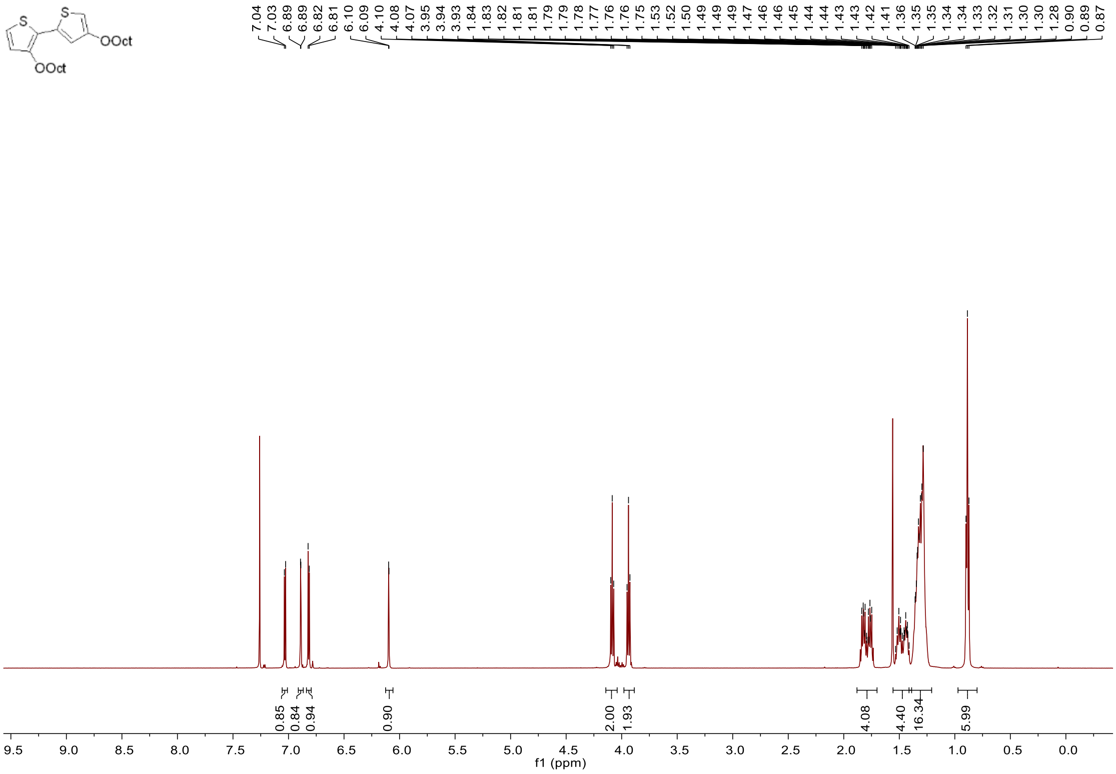
2f, ^{1}H NMR (400 MHz, CDCl$_3$)



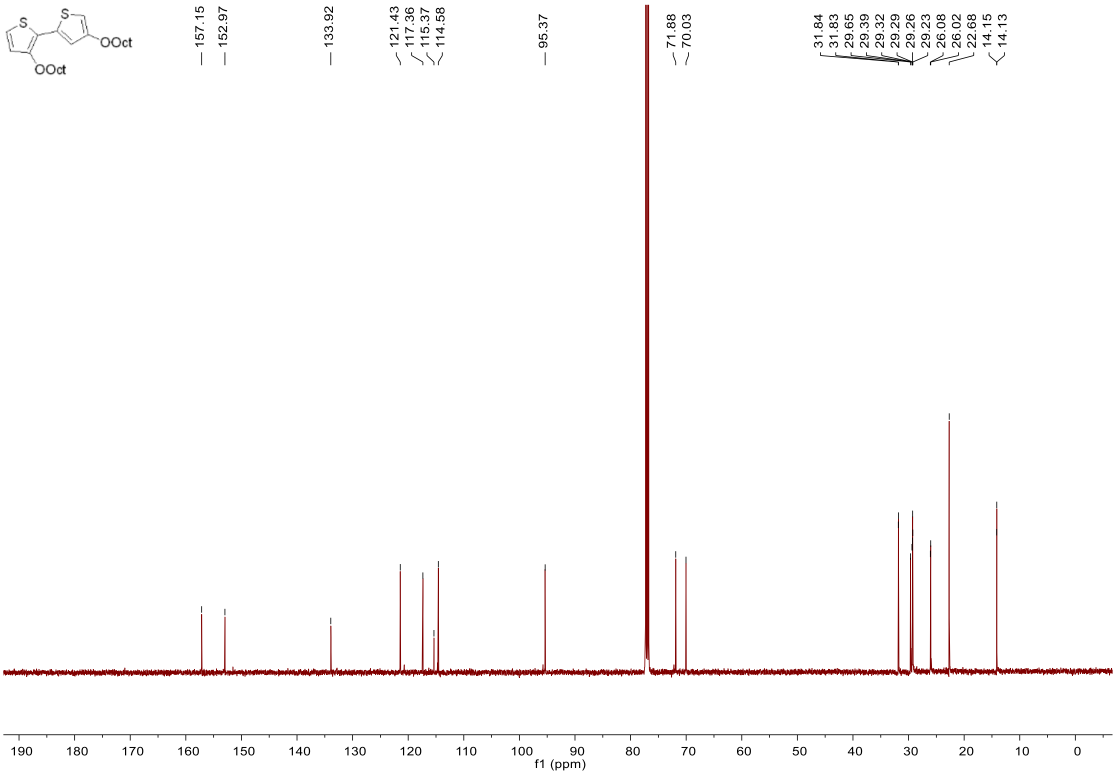
2f, ^{13}C NMR (101 MHz, CDCl$_3$)



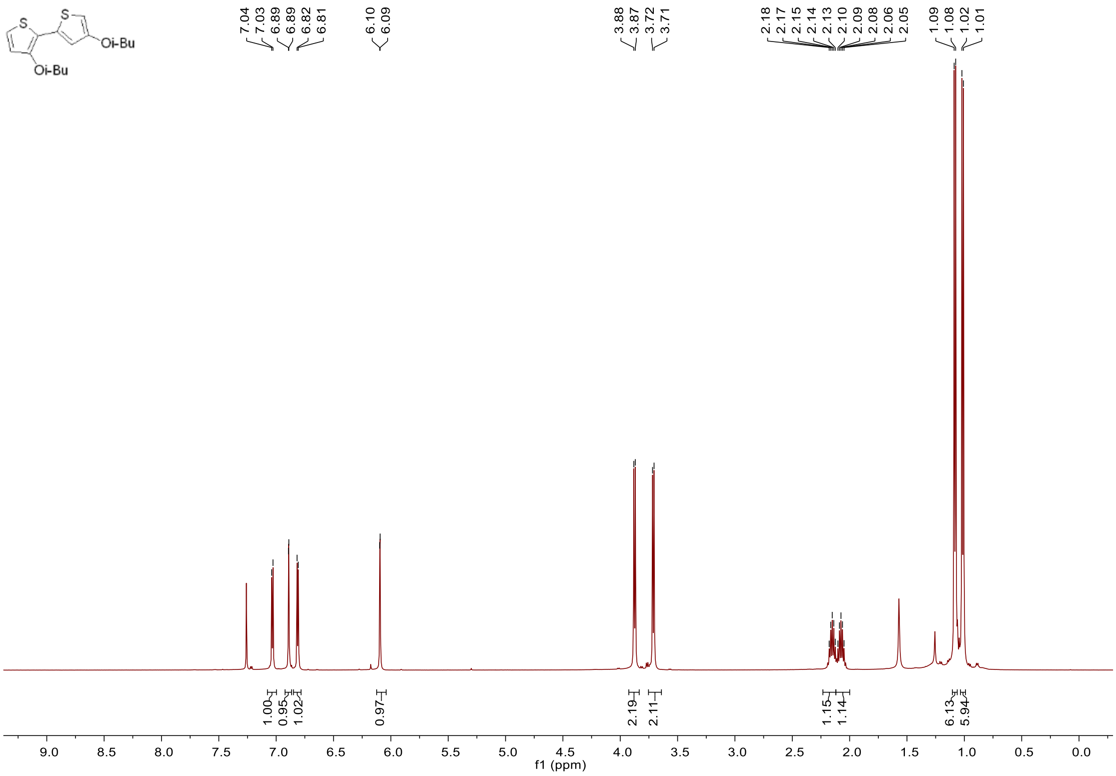
2g, ^{1}H NMR (400 MHz, CDCl$_3$)



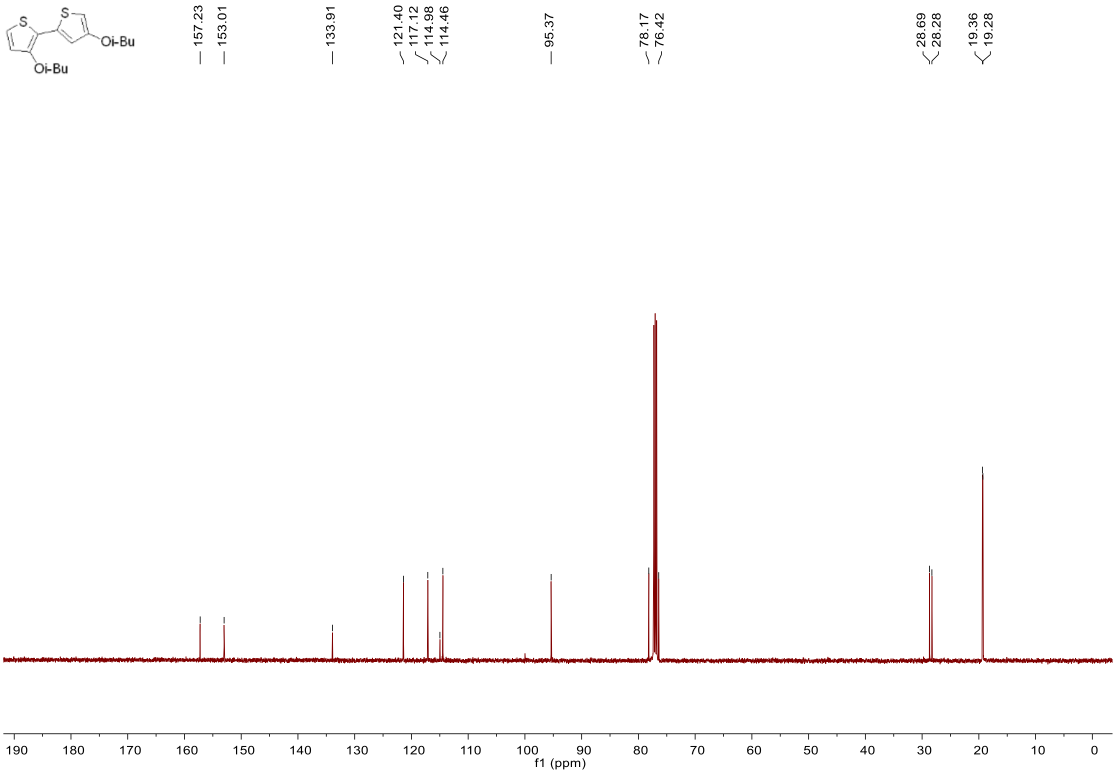
2g, ^{13}C NMR (101 MHz, CDCl$_3$)



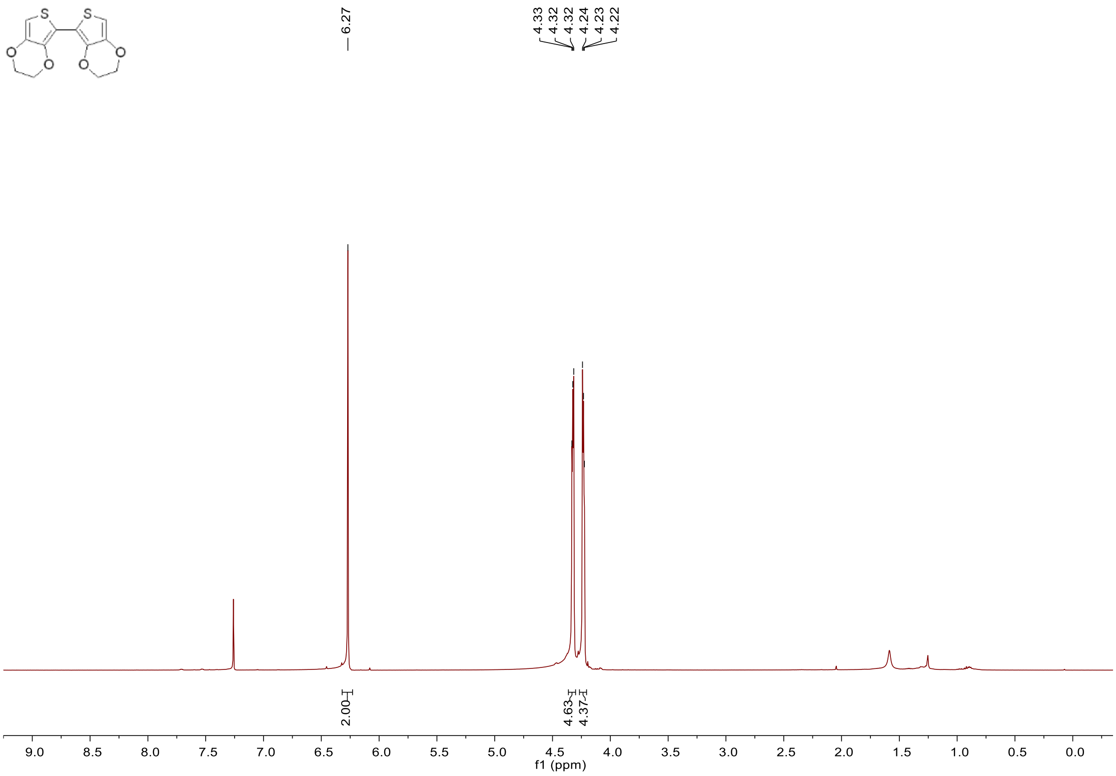
2h, ^{1}H NMR (400 MHz, CDCl$_3$)



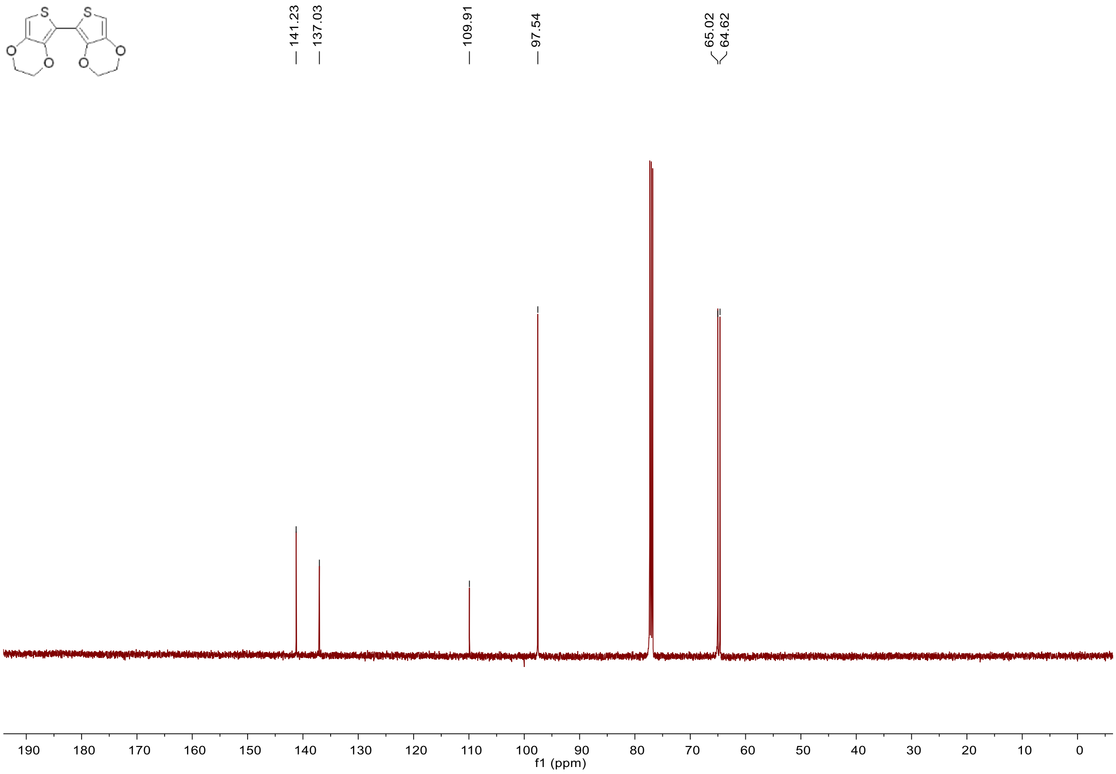
2h, ^{13}C NMR (101 MHz, CDCl$_3$)



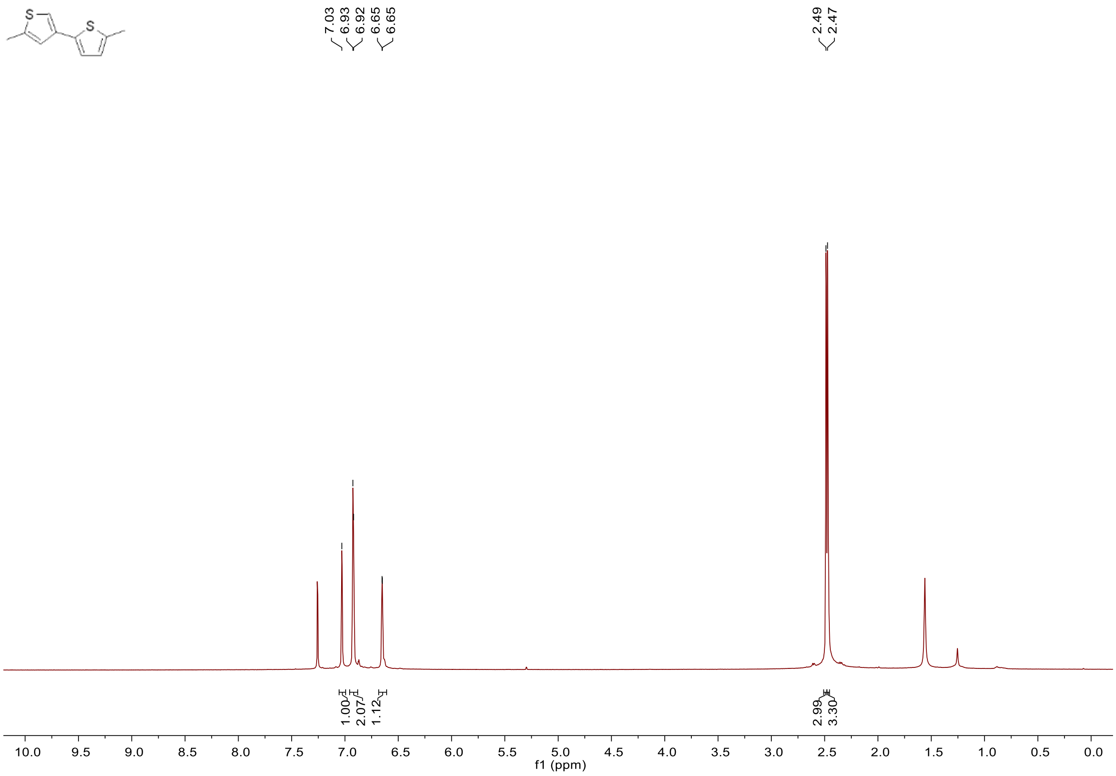
2i, ^{1}H NMR (400 MHz, CDCl$_3$)



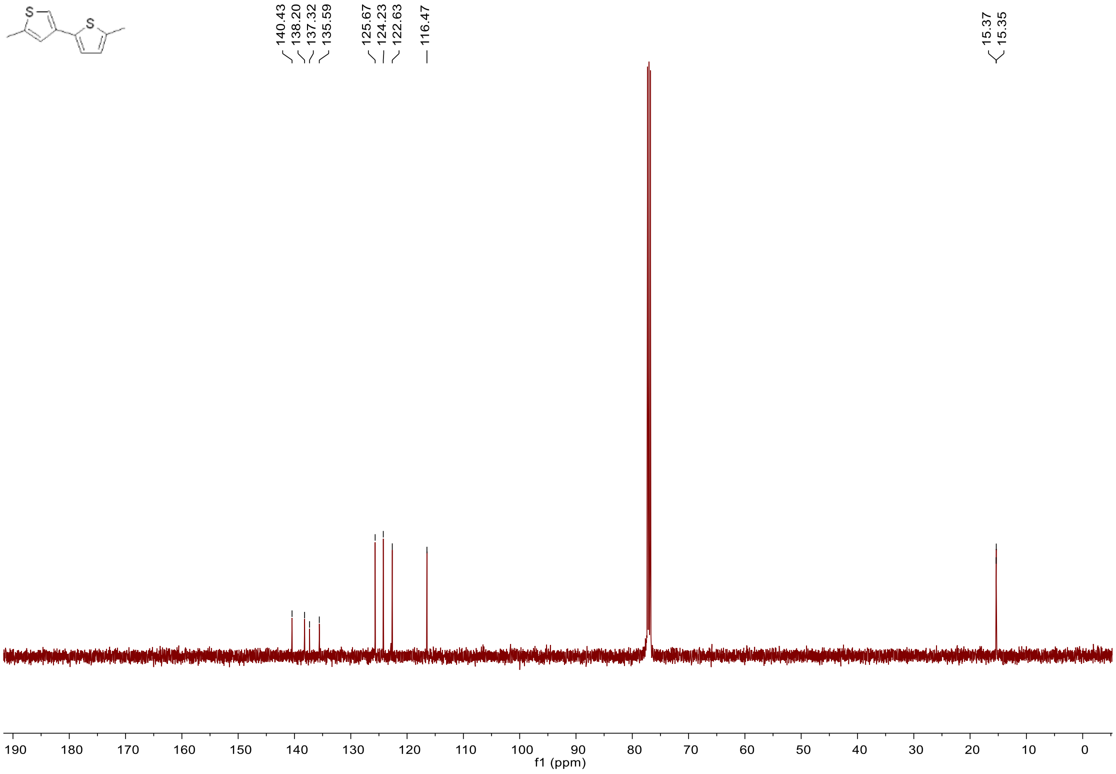
2i, ^{13}C NMR (101 MHz, CDCl$_3$)



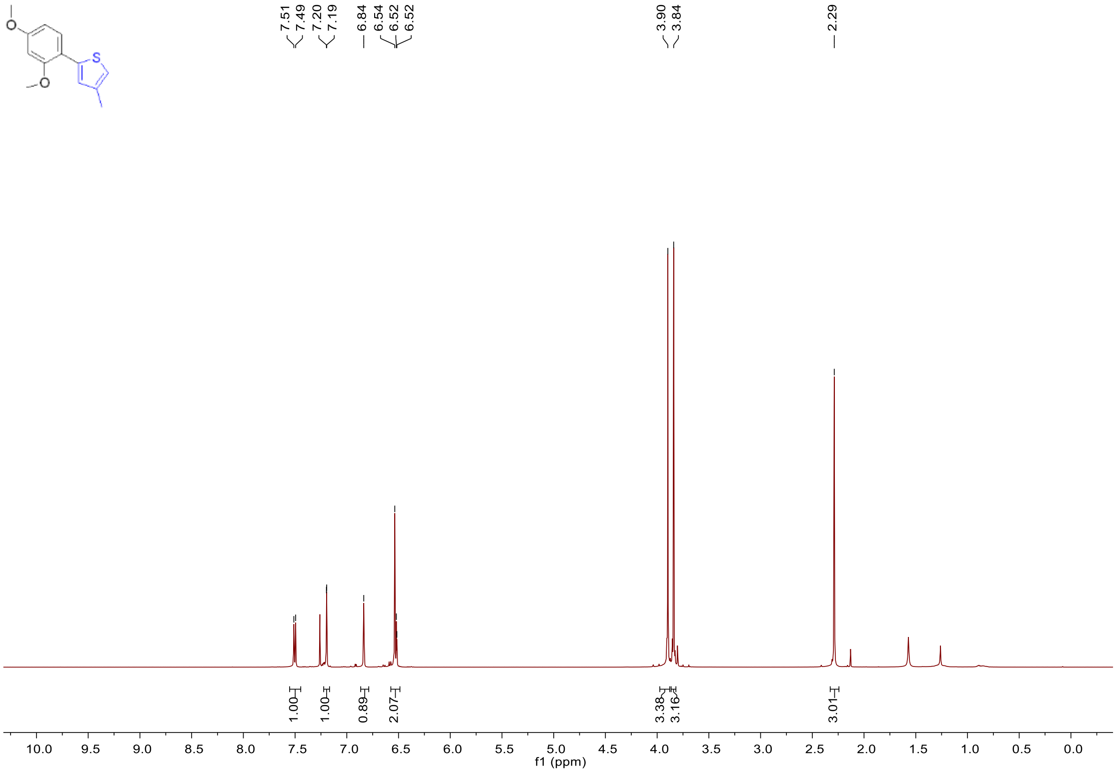
2j, ^{1}H NMR (400 MHz, CDCl$_3$)



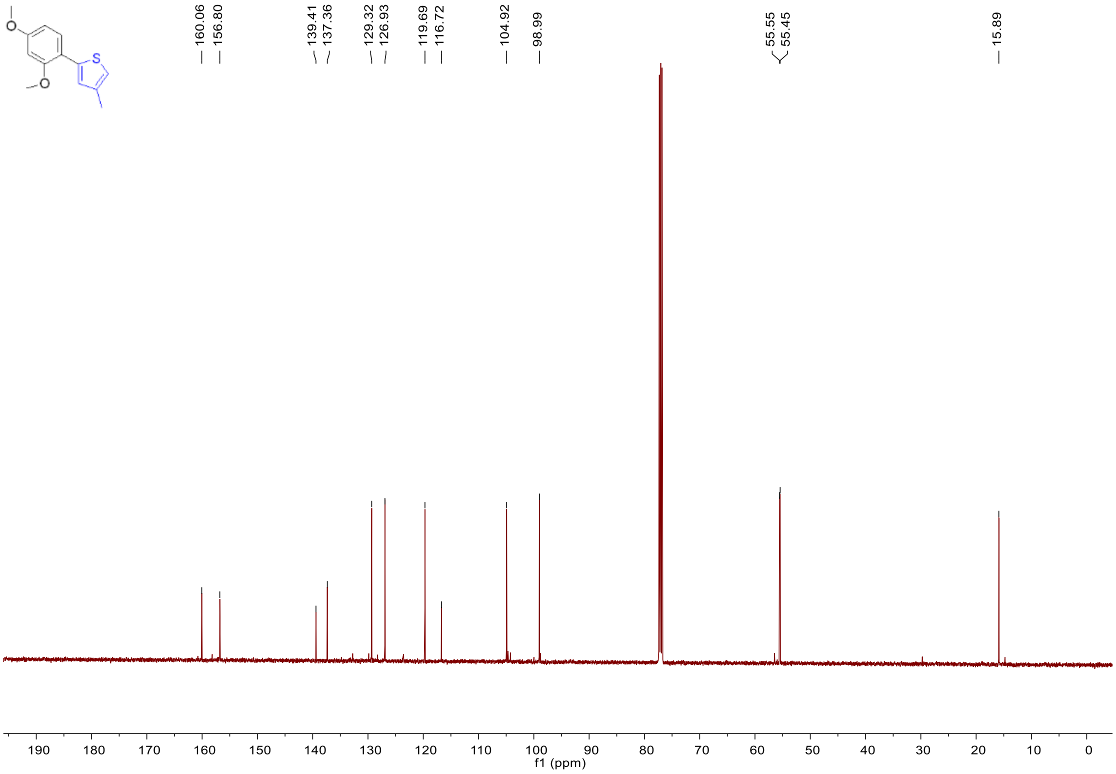
2j, ^{13}C NMR (101 MHz, CDCl$_3$)



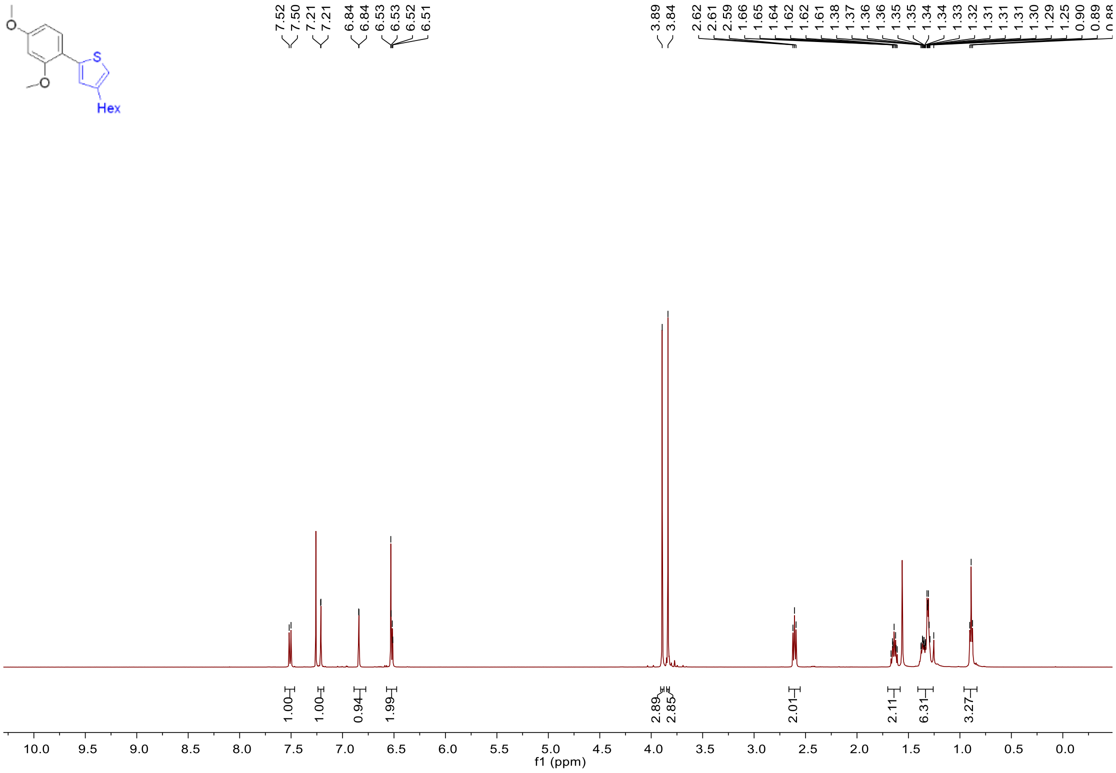
7a, ^{1}H NMR (400 MHz, CDCl$_3$)



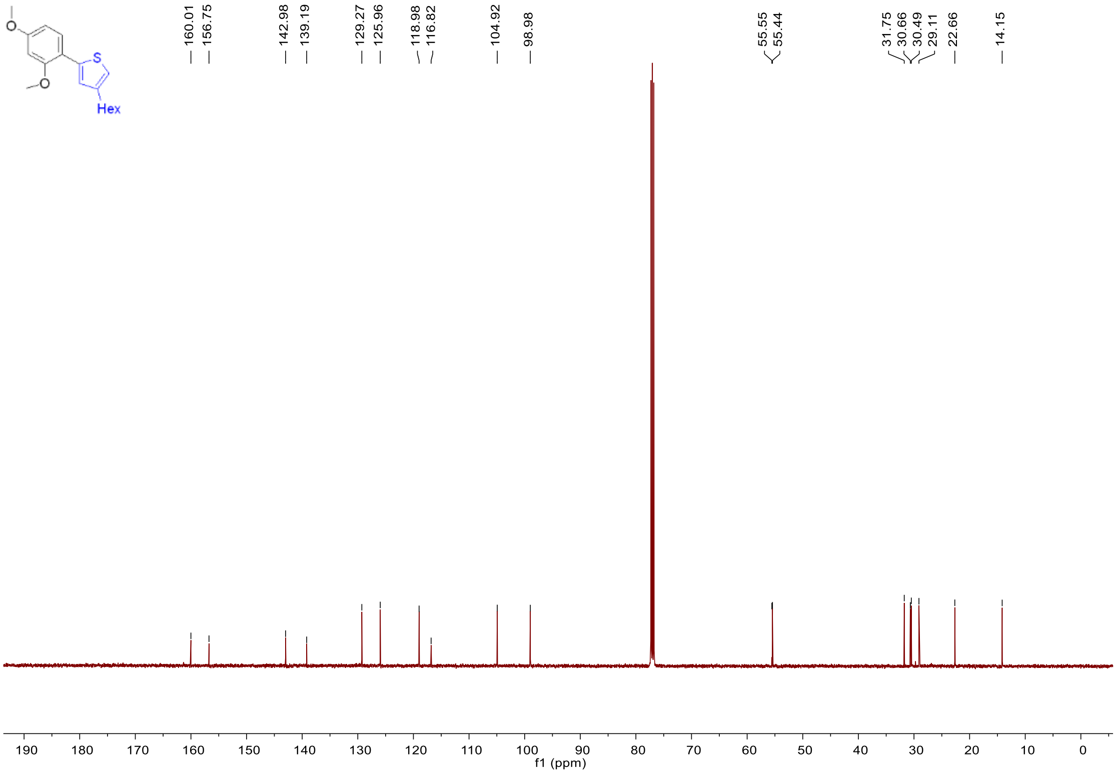
7a, ^{13}C NMR (101 MHz, CDCl$_3$)



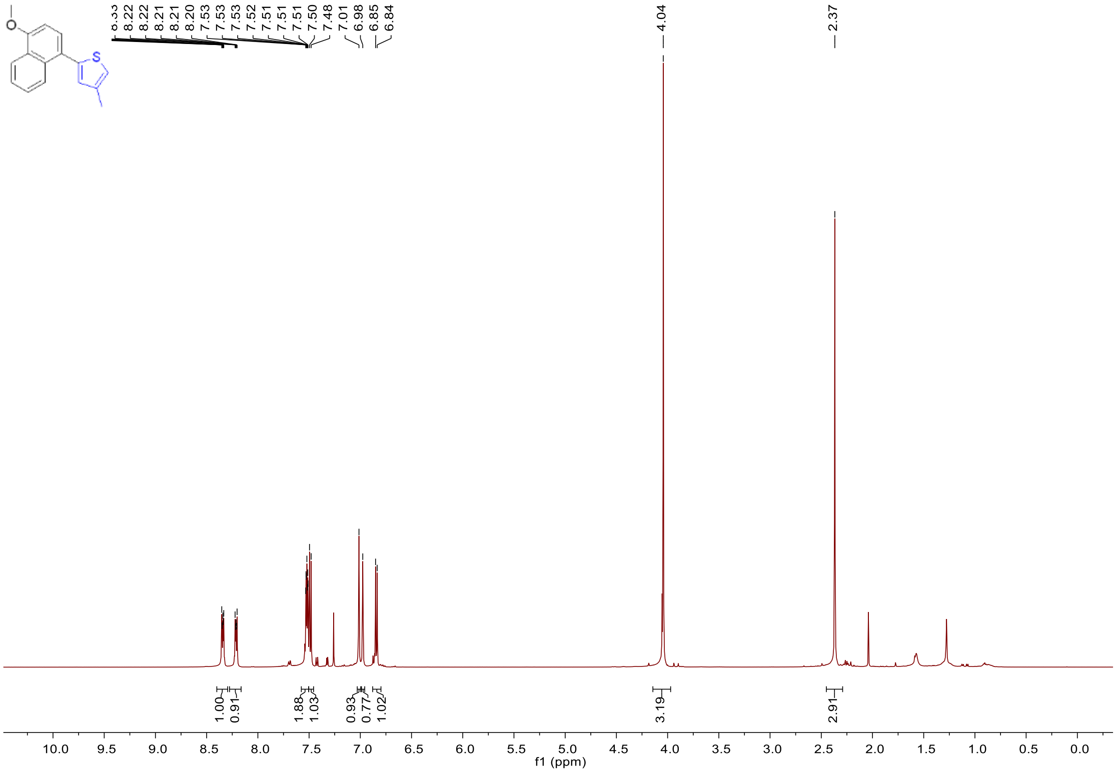
7b, ^{1}H NMR (400 MHz, CDCl$_3$)



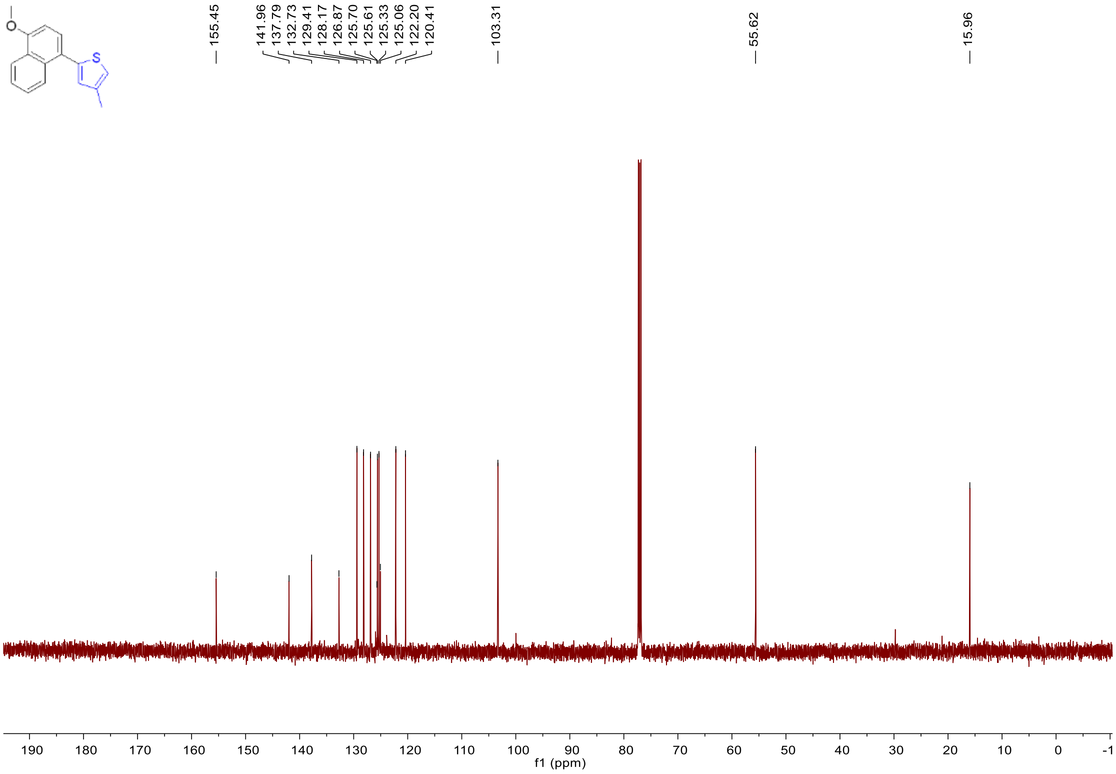
7b, ^{13}C NMR (101 MHz, CDCl$_3$)



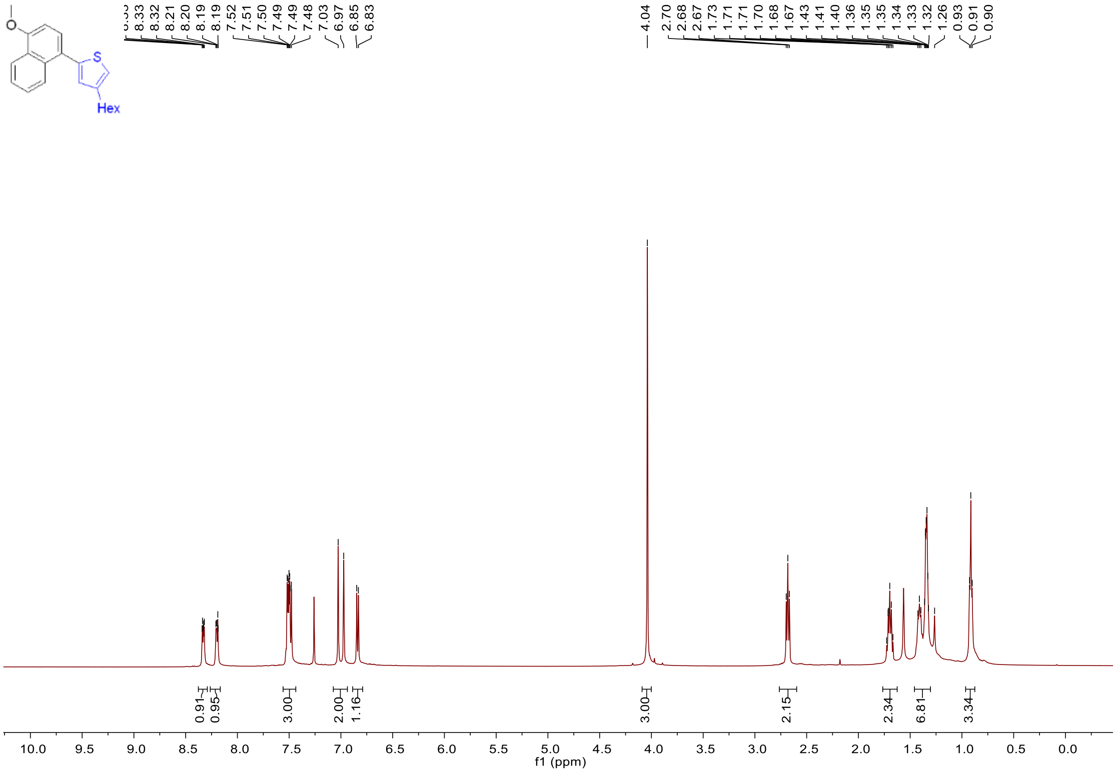
7c, ^{1}H NMR (400 MHz, CDCl$_3$)



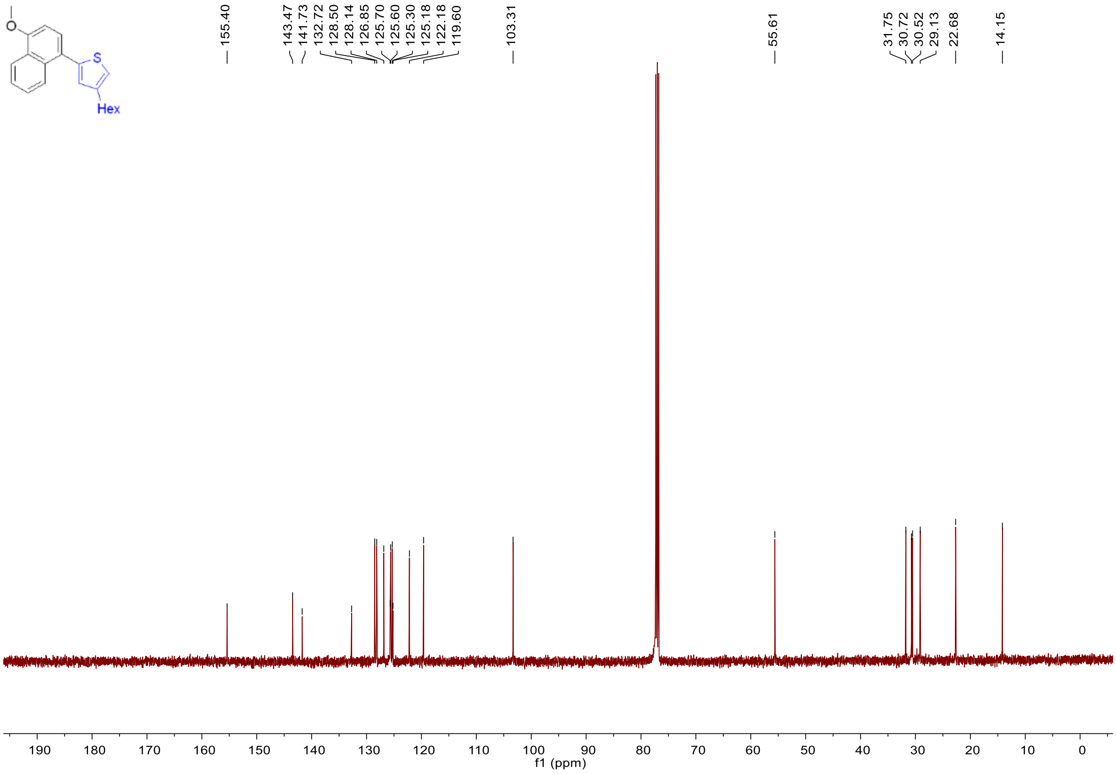
7c, ^{13}C NMR (101 MHz, CDCl$_3$)



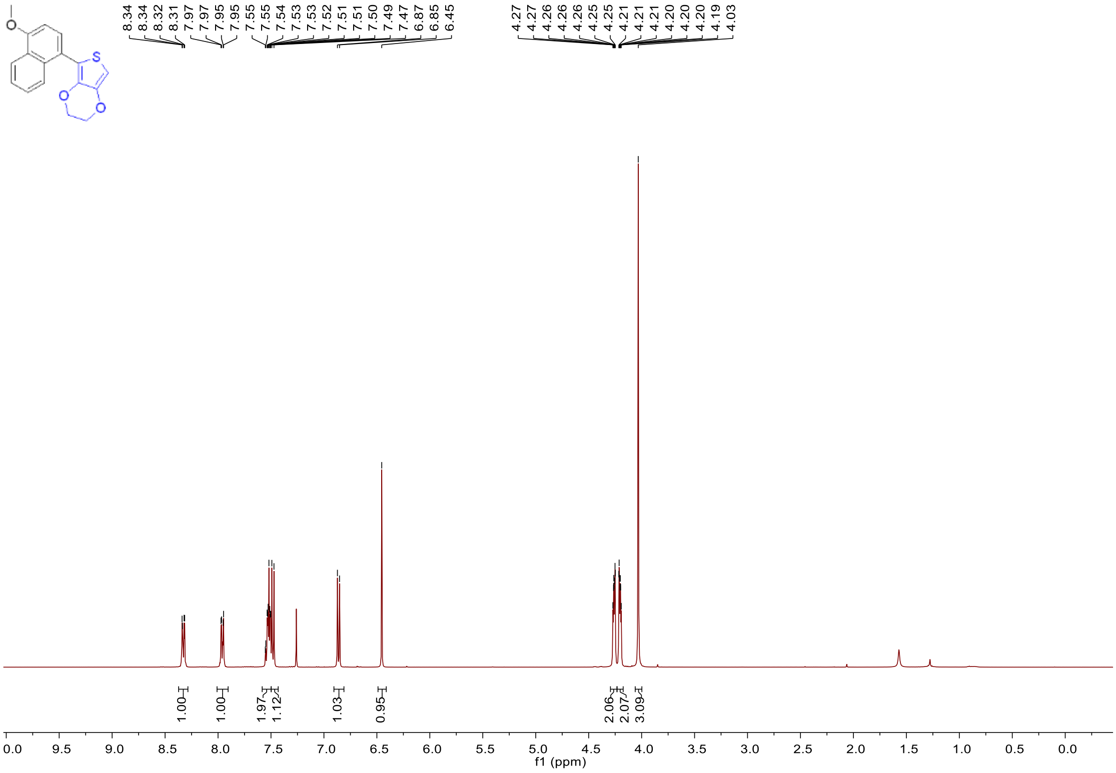
7d, ^{1}H NMR (400 MHz, CDCl$_3$)



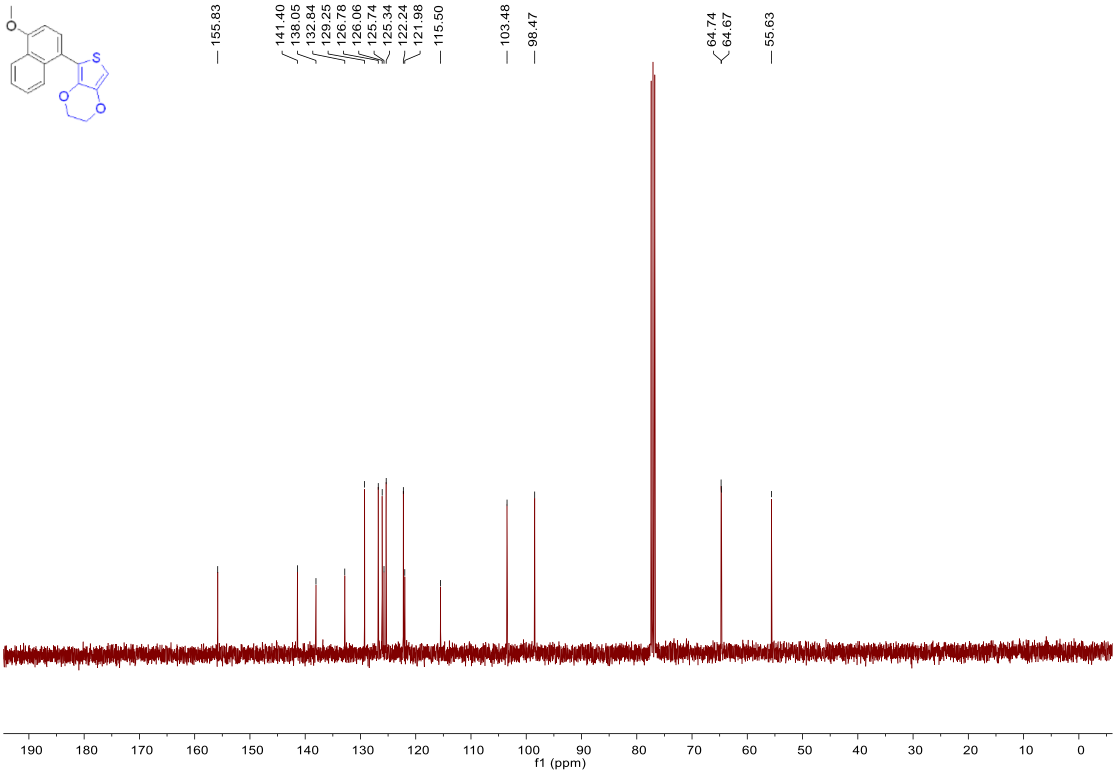
7d, ^{13}C NMR (101 MHz, CDCl$_3$)



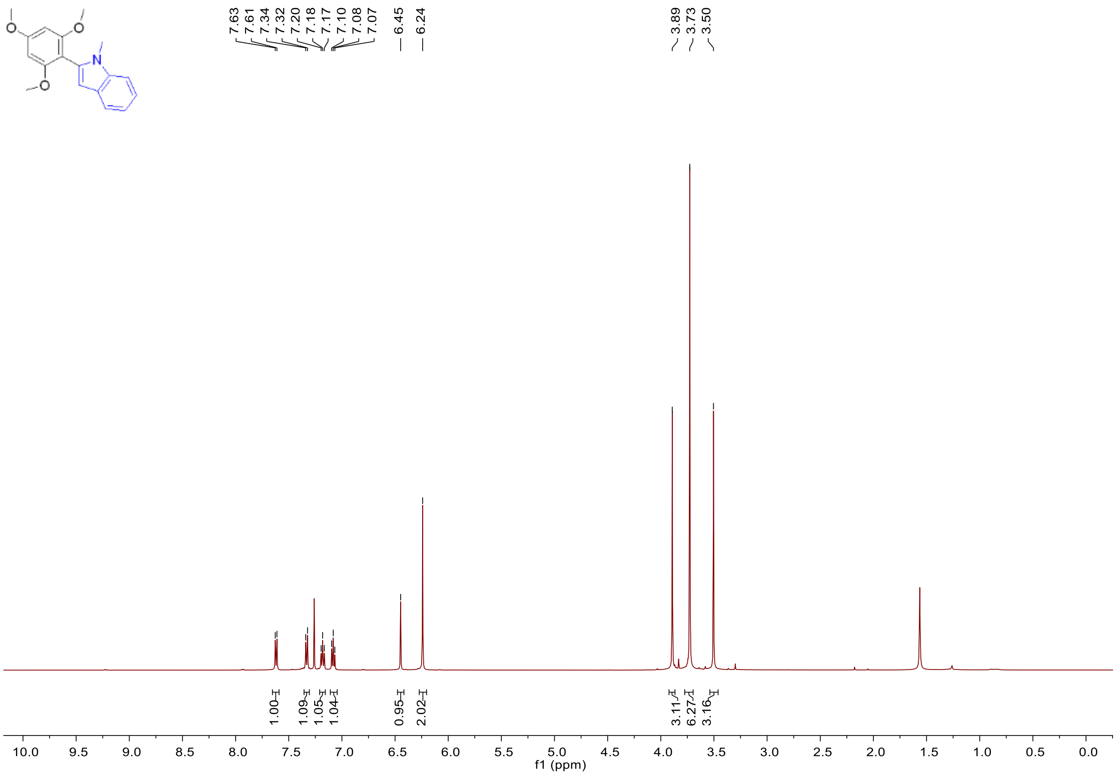
7e, ^{1}H NMR (400 MHz, CDCl$_3$)



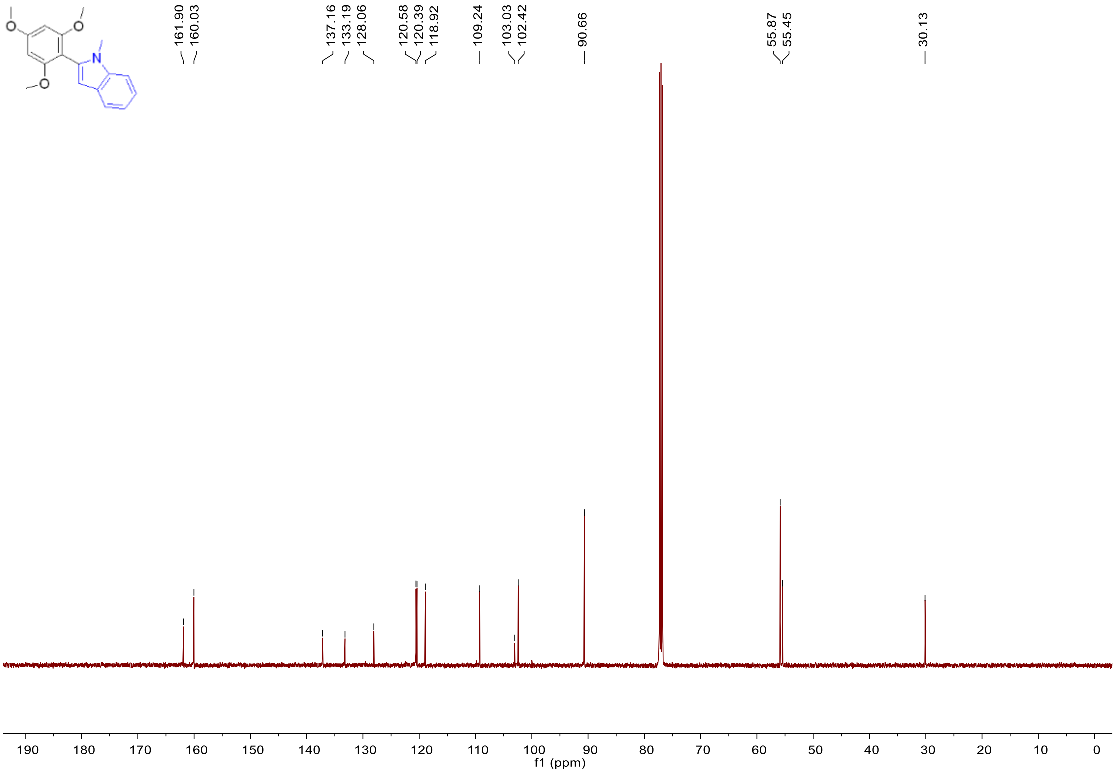
7e, ^{13}C NMR (101 MHz, CDCl$_3$)



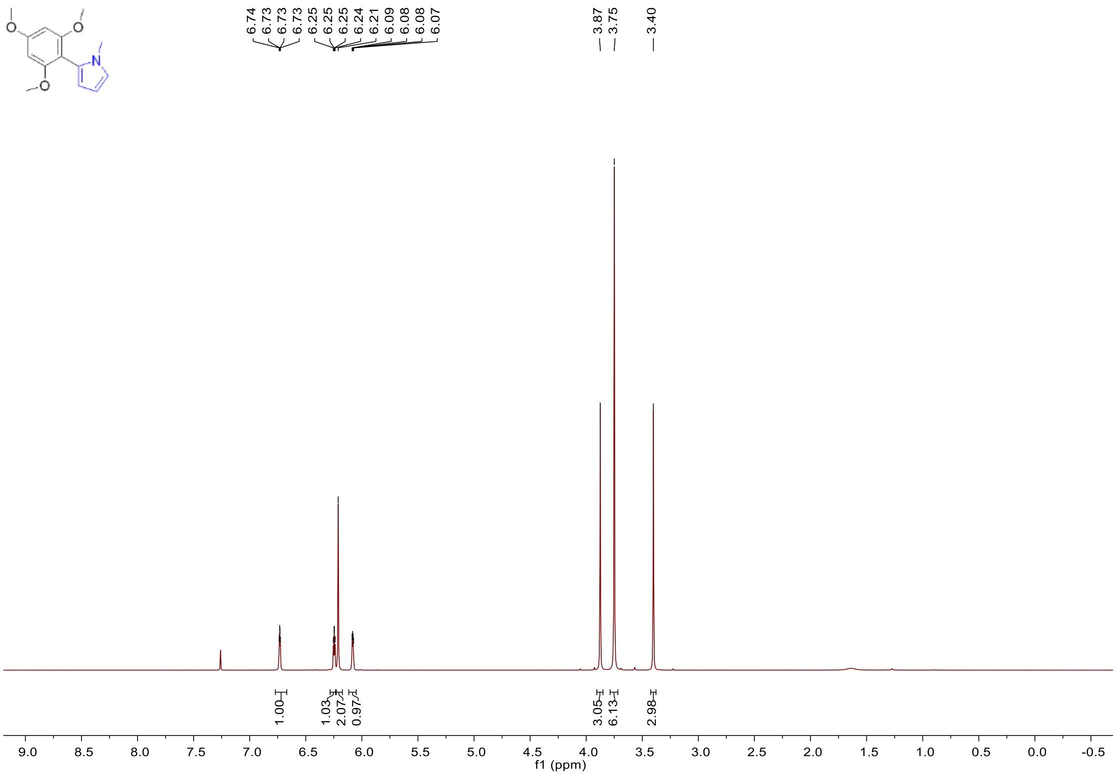
7f, ^{1}H NMR (400 MHz, CDCl$_3$)



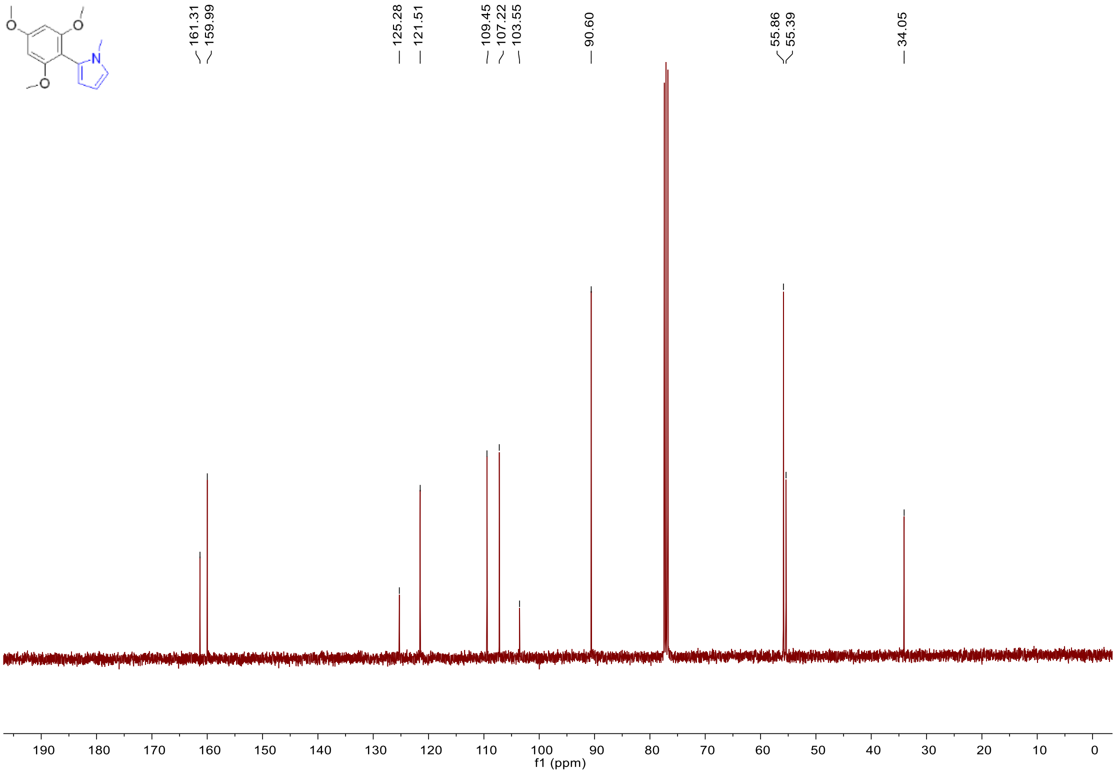
7f, ^{13}C NMR (101 MHz, CDCl$_3$)



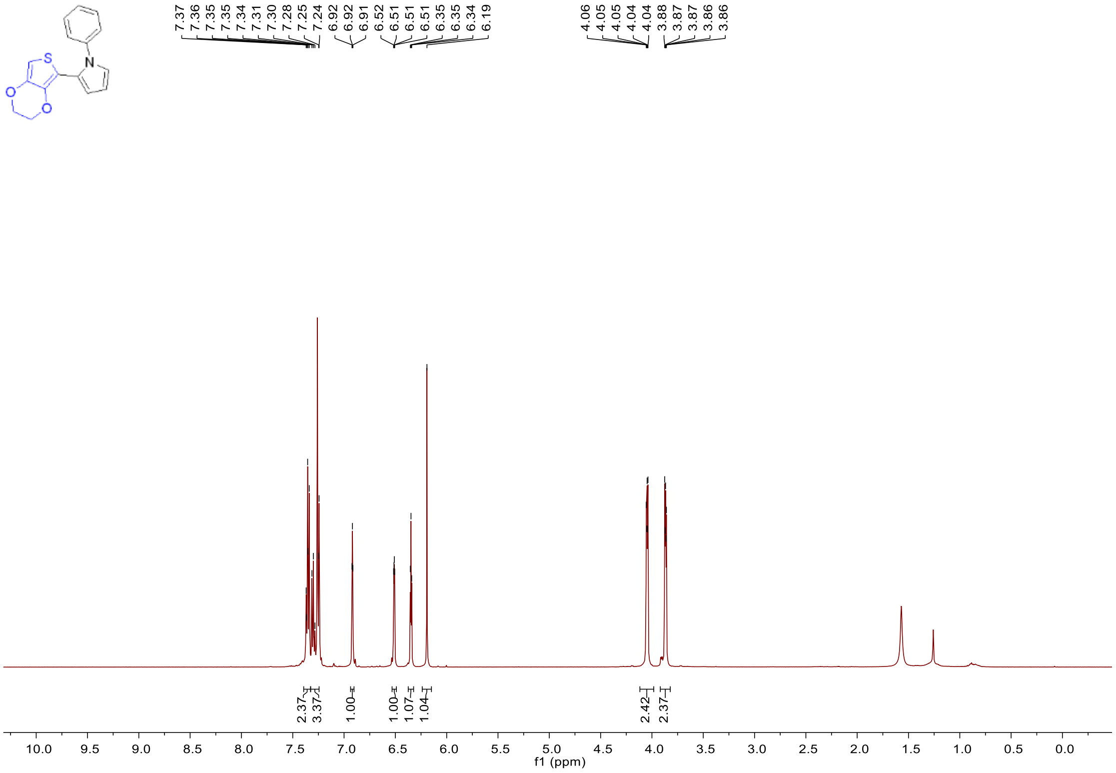
7g, ^{1}H NMR (400 MHz, CDCl$_3$)



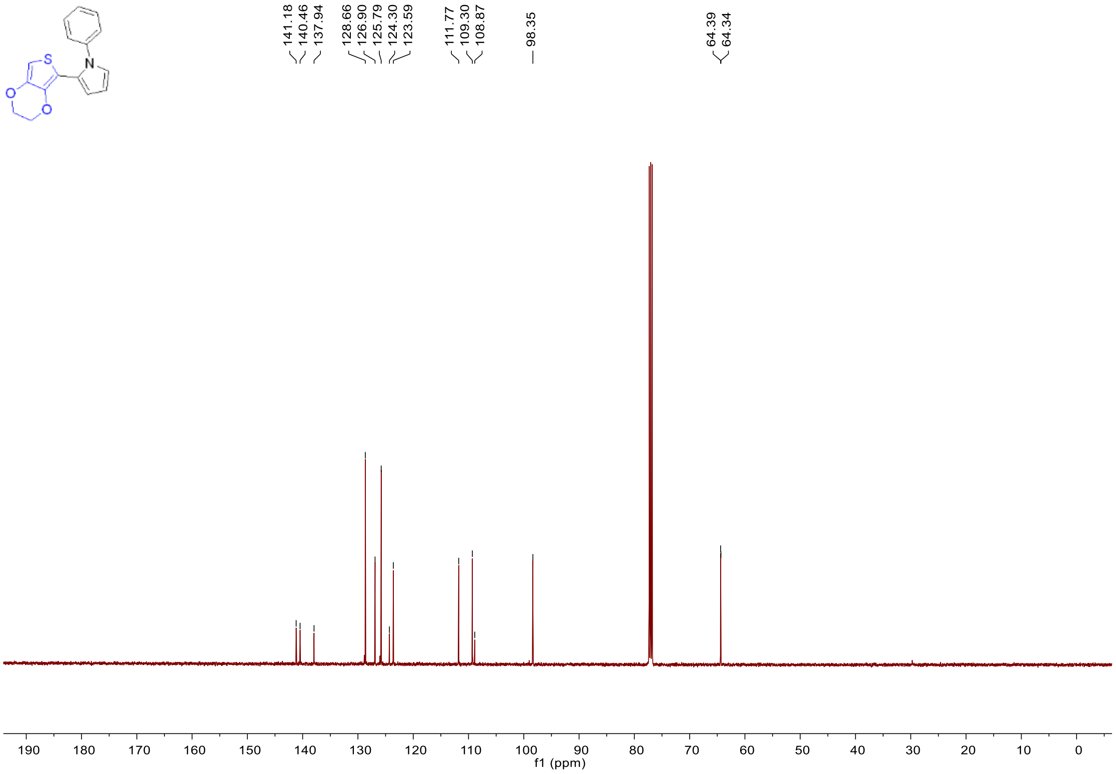
7g, ^{13}C NMR (101 MHz, CDCl$_3$)



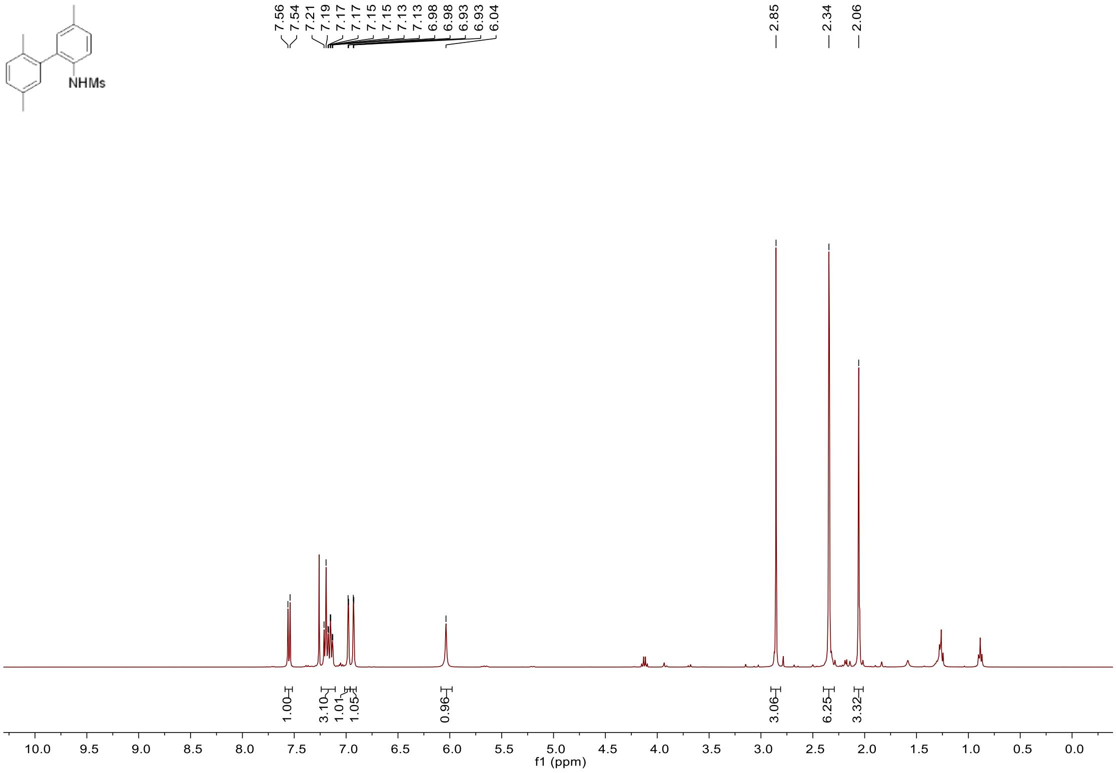
7h, ^{1}H NMR (400 MHz, CDCl$_3$)



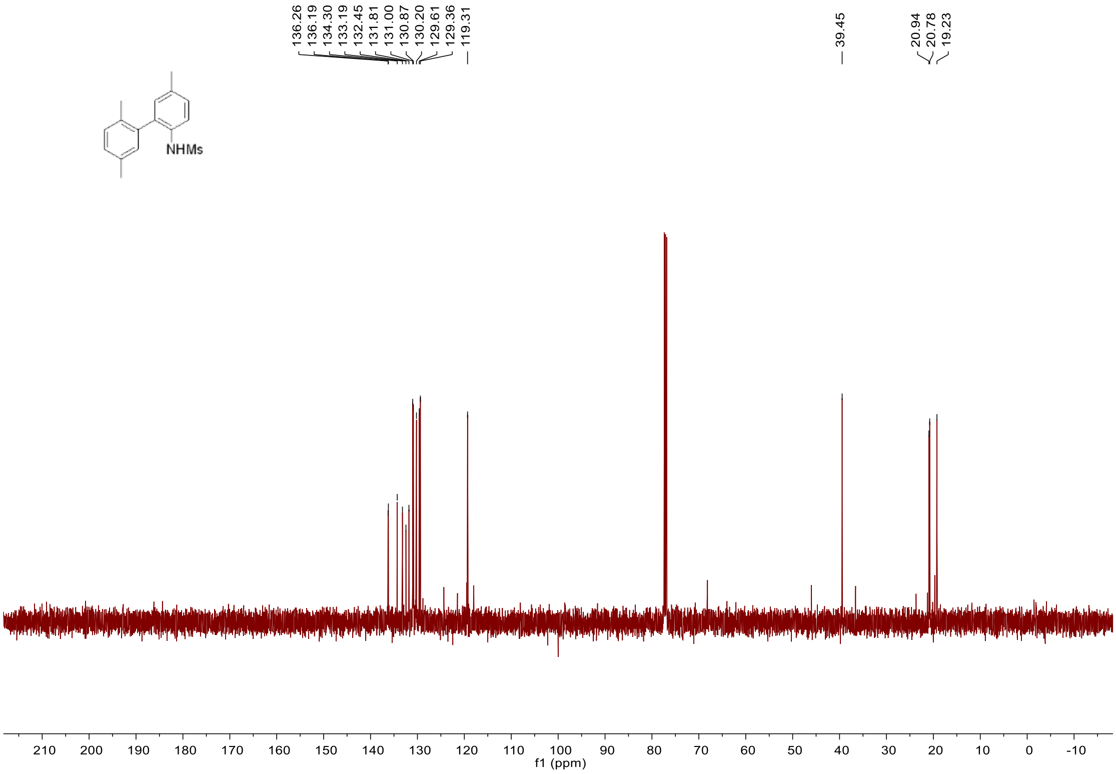
7h, ^{13}C NMR (101 MHz, CDCl$_3$)



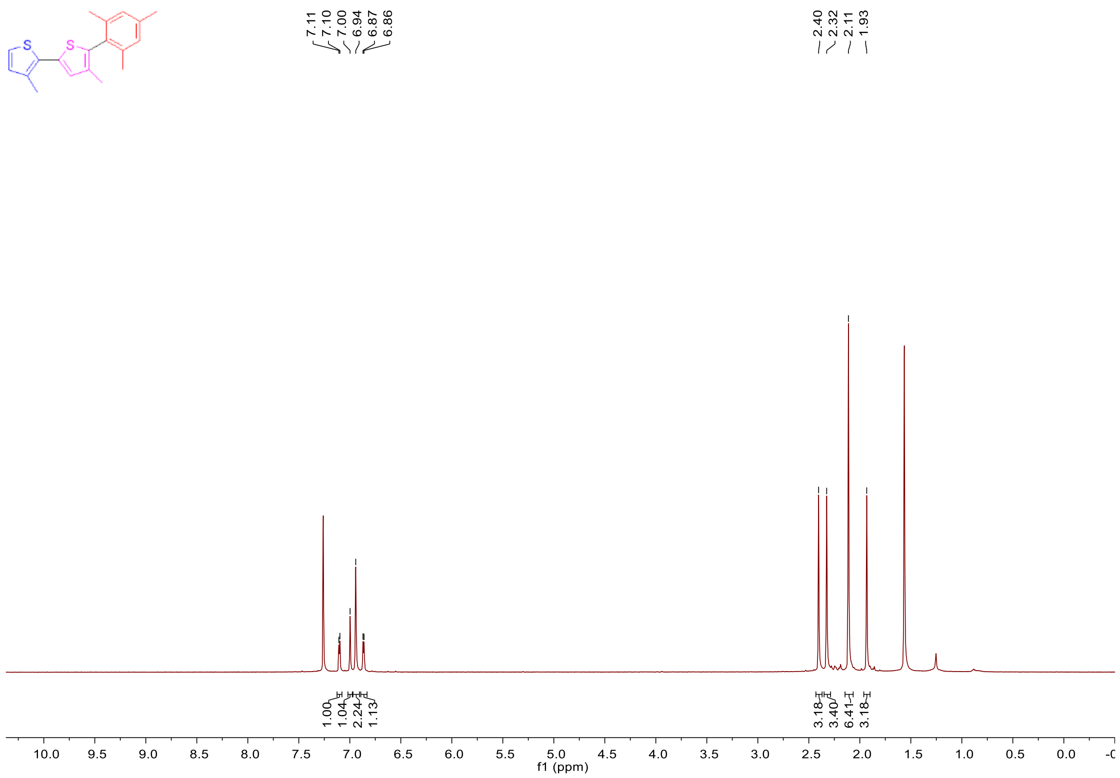
7i, ^{1}H NMR (400 MHz, CDCl$_3$)



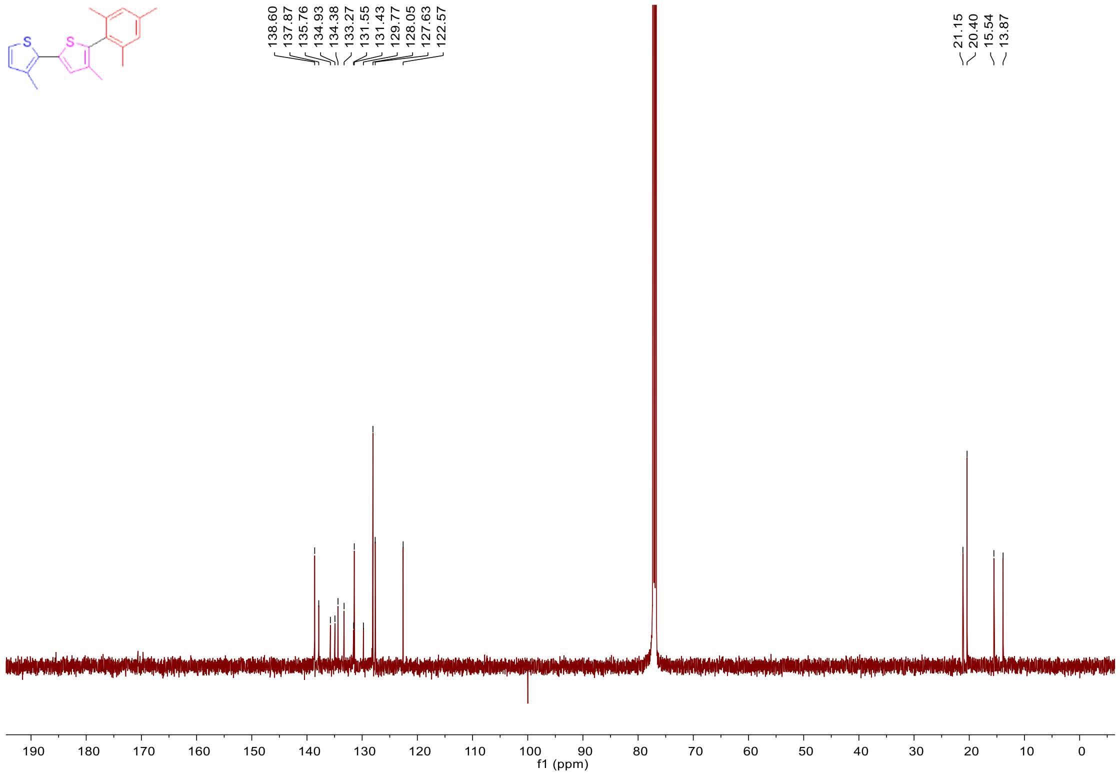
7i, ^{13}C NMR (101 MHz, CDCl$_3$)



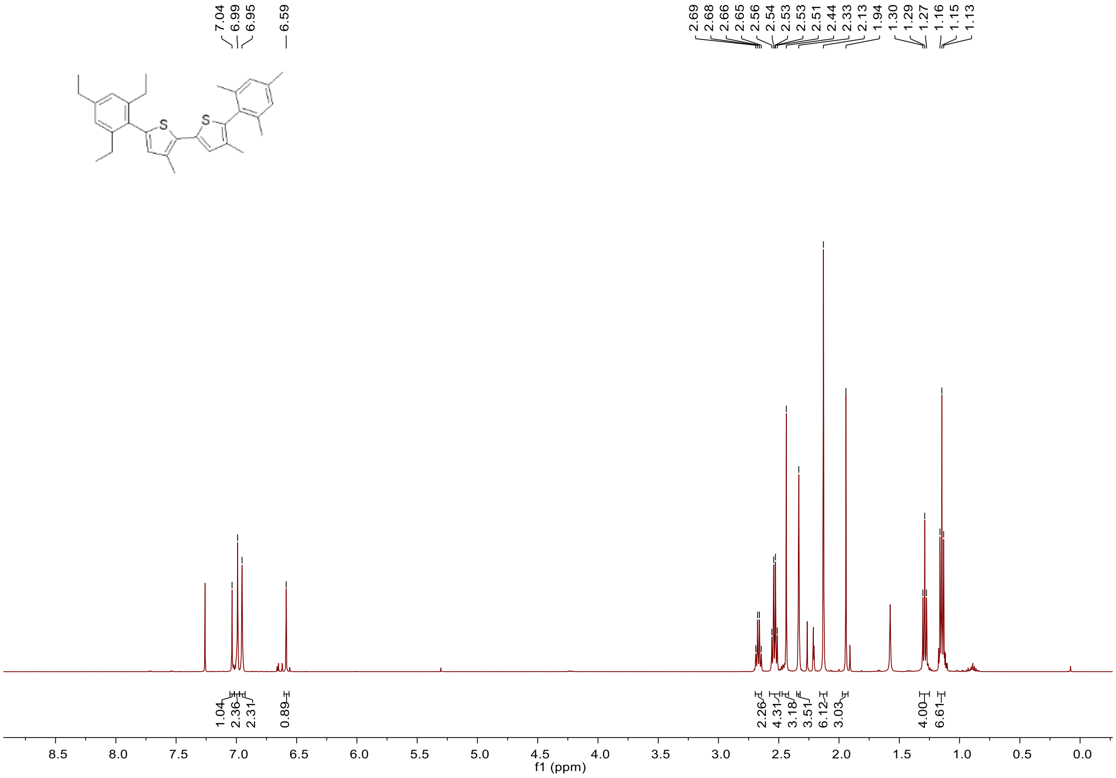
8, ^{1}H NMR (400 MHz, CDCl$_3$)



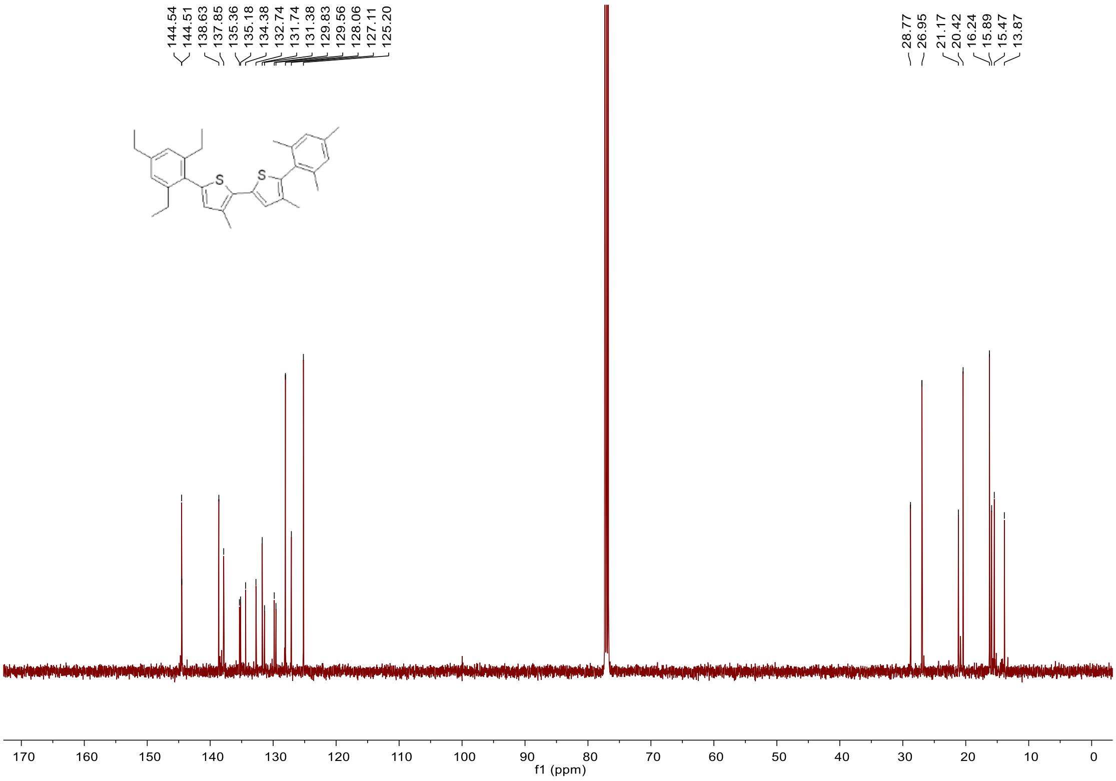
8, ^{13}C NMR (101 MHz, CDCl$_3$)



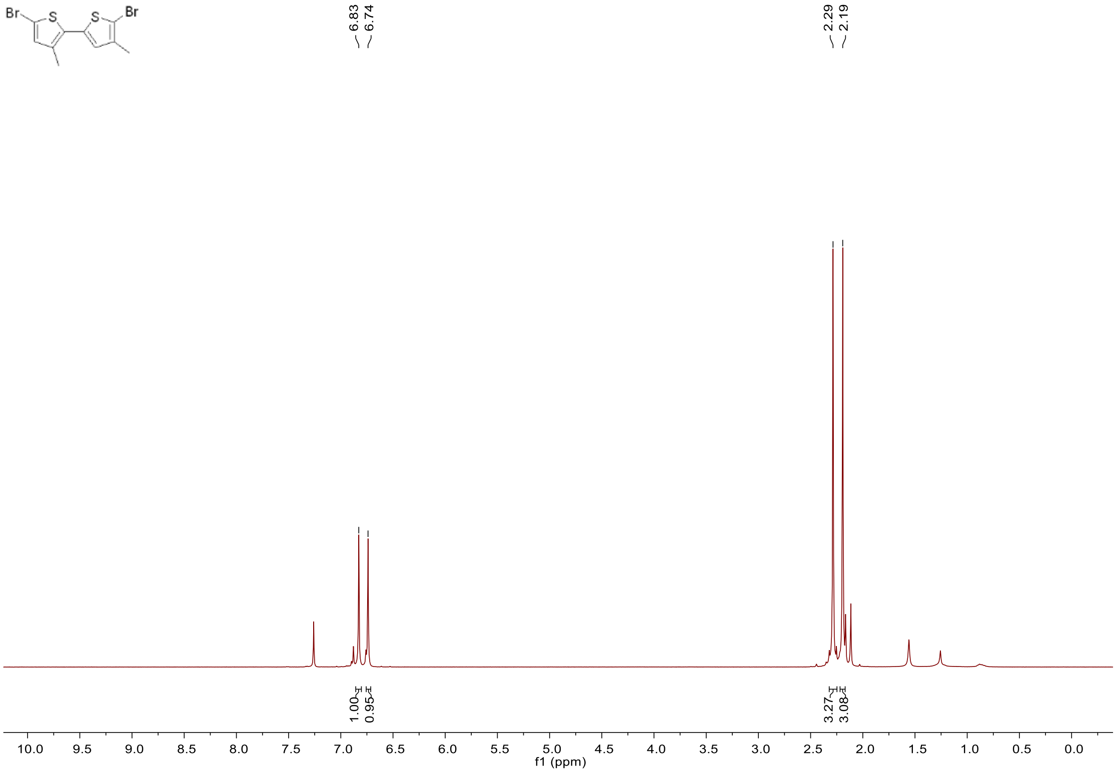
9, ^{1}H NMR (500 MHz, $CDCl_3$)



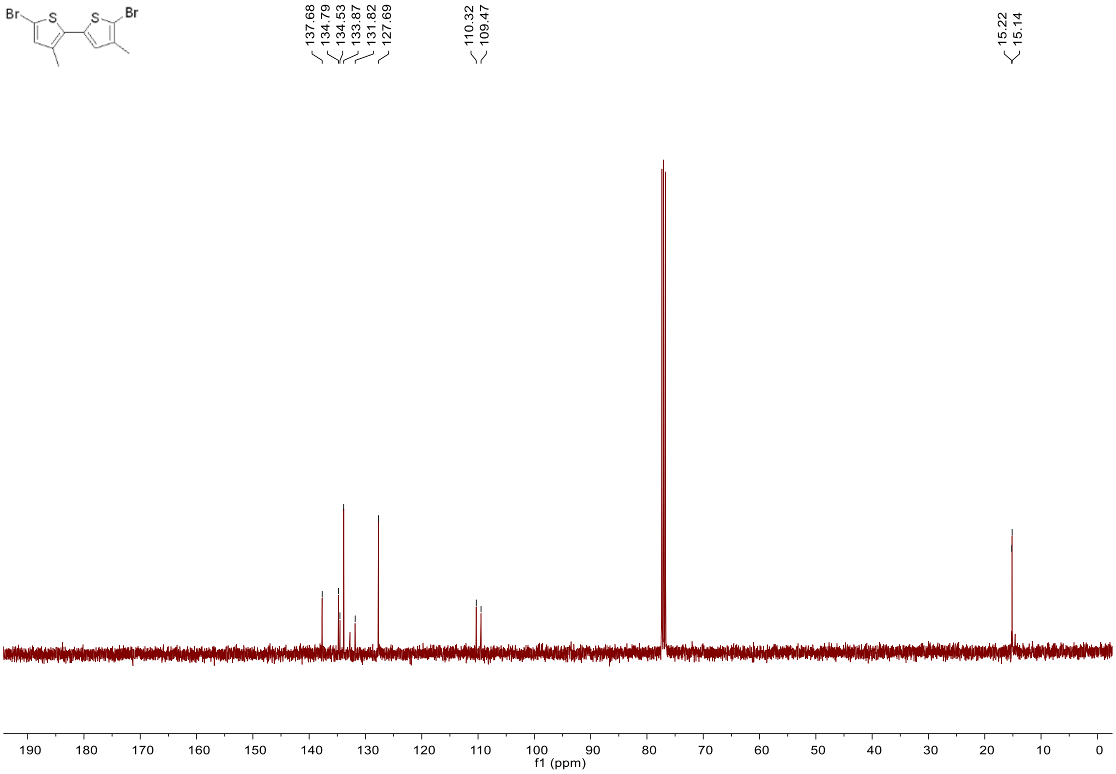
9, ^{13}C NMR (126 MHz, $CDCl_3$)



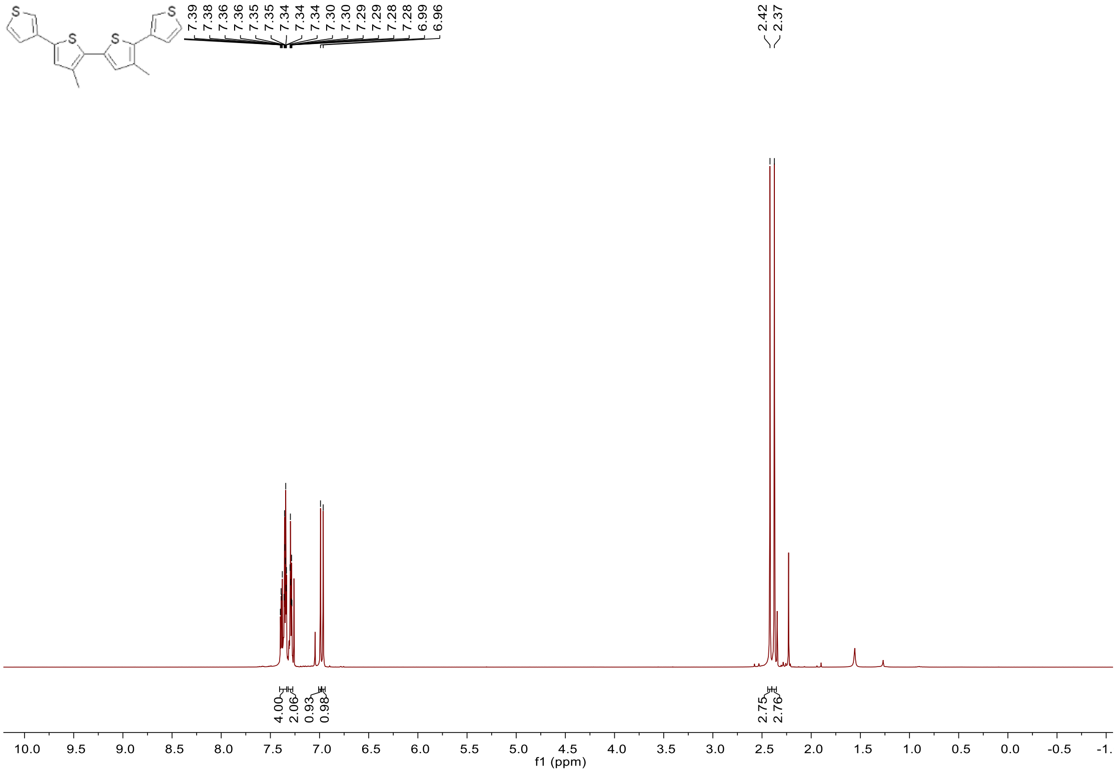
10, ^{1}H NMR (400 MHz, CDCl$_3$)



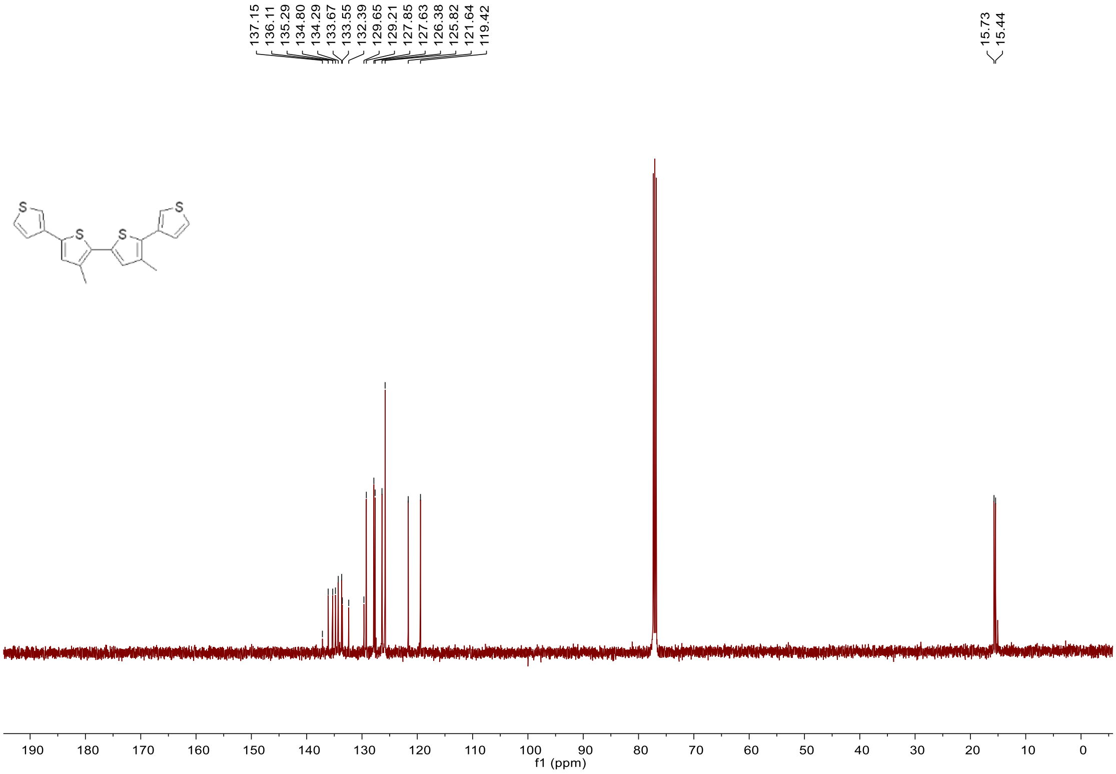
10, ^{13}C NMR (101 MHz, CDCl$_3$)



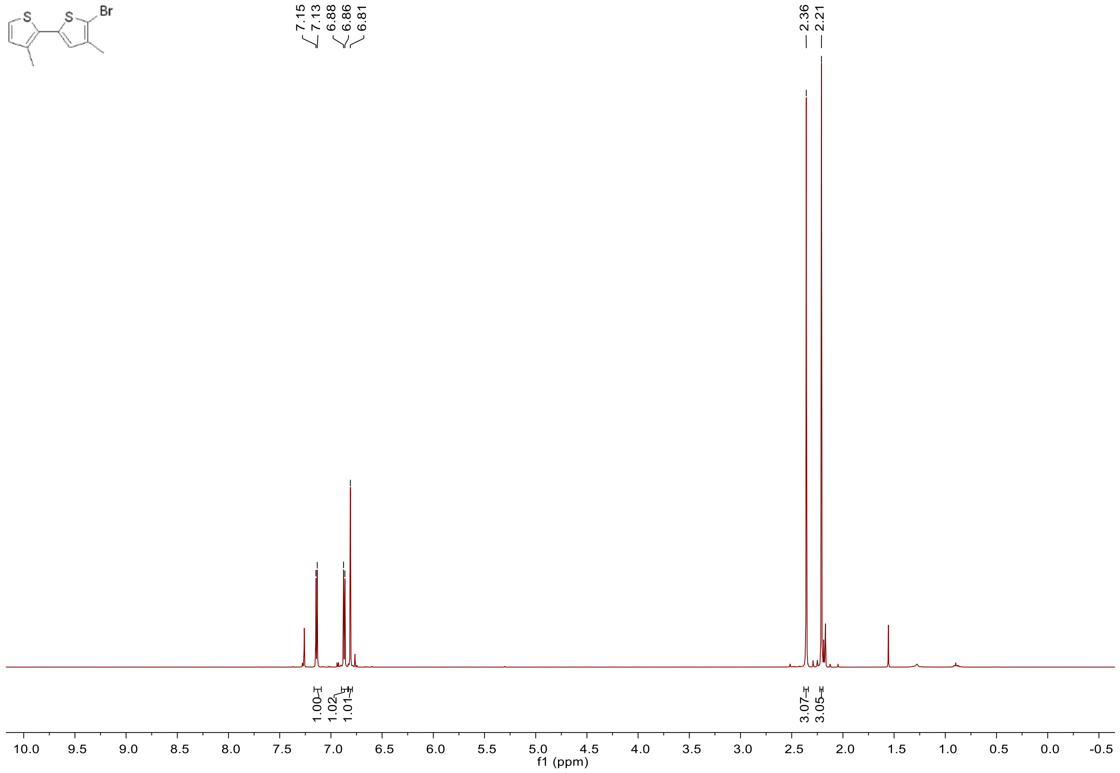
11, ^{1}H NMR (400 MHz, CDCl$_3$)



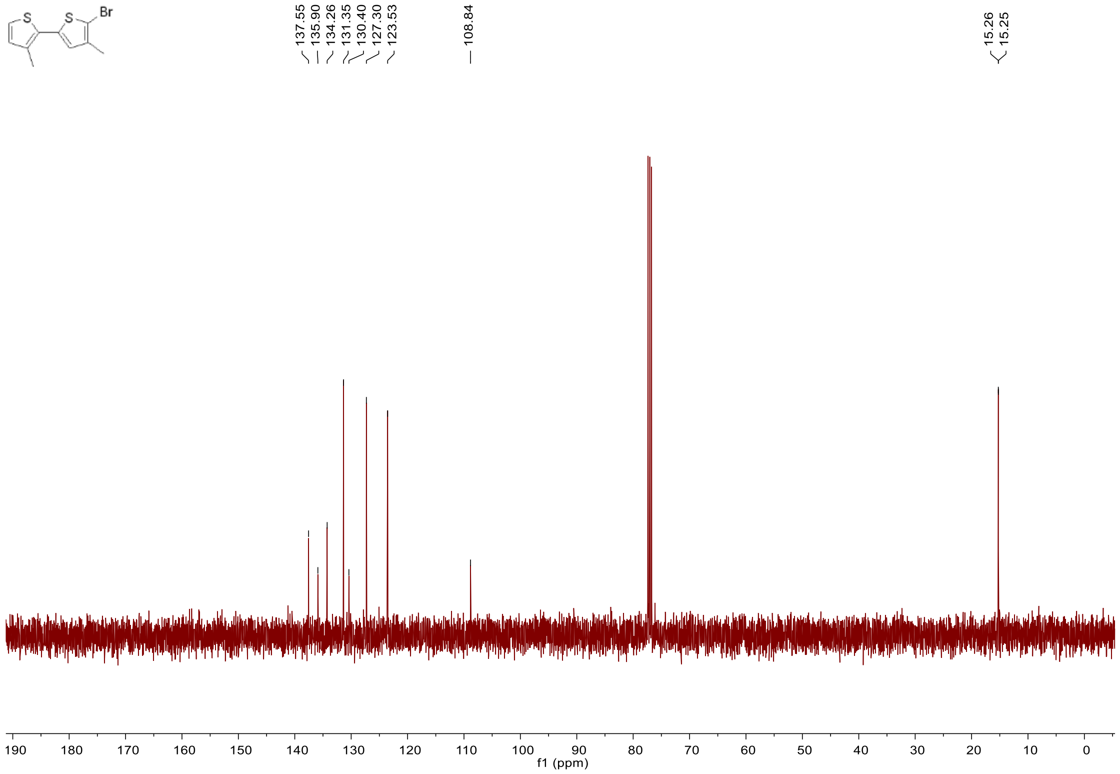
11, ^{13}C NMR (101 MHz, CDCl$_3$)



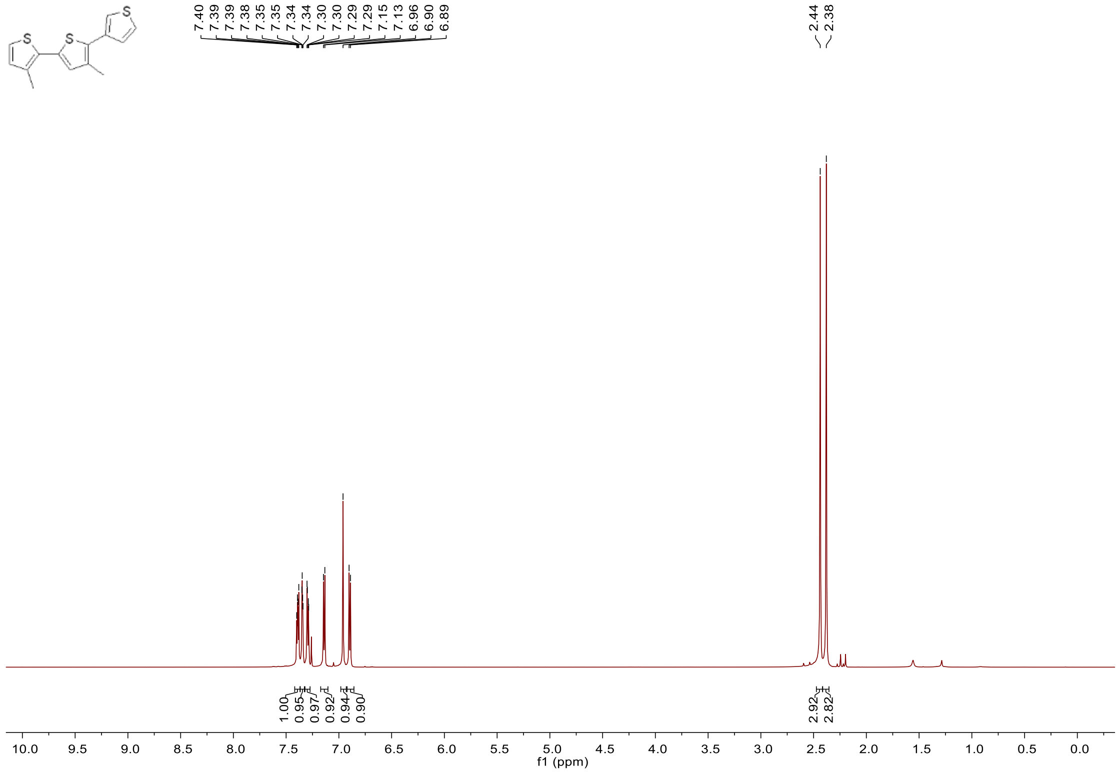
12, ^{1}H NMR (400 MHz, CDCl$_3$)



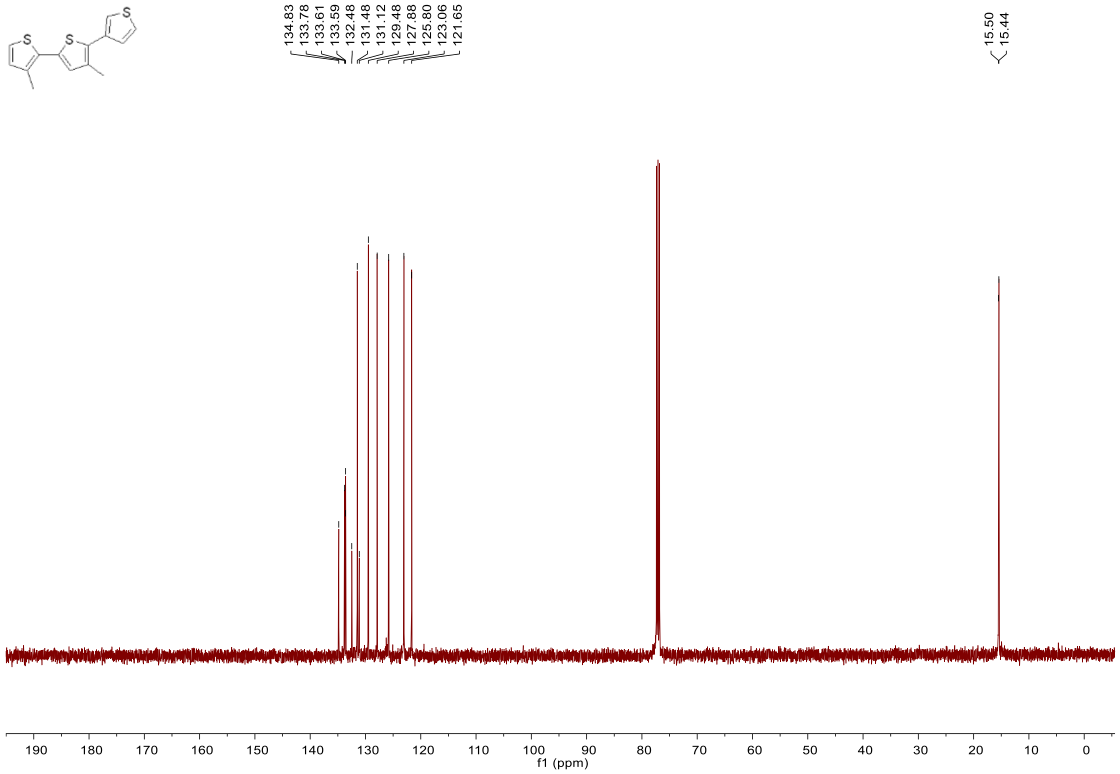
12, ^{13}C NMR (101 MHz, CDCl$_3$)



13, ^{1}H NMR (400 MHz, CDCl$_3$)



13, ^{13}C NMR (101 MHz, CDCl$_3$)



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