Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Highly Selective Synthesis of *6*-Substituted Benzothiophenes by $Sc(OTf)_3$-Catalyzed Intermolecular Cyclization and Sulfur Migration

Xiaoming Wang, Tobias Gensch, Frank Glorius*

Table of content

1. General information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Flash chromatography was either performed on Merck silica gel (40-63 mesh) by standard technique eluting with solvents as indicated.

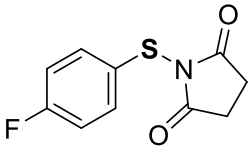
GC-MS Spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5975C VL MSD or an Agilent 5975 inert Mass Selective Detector (EI) and a HP-5MS column (0.25 mm × 30 m, Film: 0.25 µm). The major signals are quoted in m/z with the relative intensity in parentheses.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker AV 300 or AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicate. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). ESI mass spectra were recorded on a Bruker Daltonics MicroTof. No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of *N*-(arylthio)succinimides

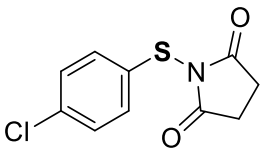
The *N*-(arylthio)succinimides derivatives (**1a**-**1i**)[1] were synthesized according to the reported procedures without optimization of the reaction conditions.

1-((4-fluorophenyl)thio)pyrrolidine-2,5-dione (**1a**)[2]



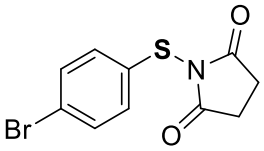
^{1}H NMR (300 MHz, Chloroform-d) δ 7.77-7.72 (m, 2H), 7.07-7.01 (m, 2H), 2.81 (s, 4H) ppm. ^{13}C NMR (75 MHz, CDCl3) δ 176.17, 165.65, 162.31, 136.57, 136.45, 129.11, 129.06, 116.60, 116.31, 28.51 ppm. ^{19}F NMR (282 MHz, CDCl3) δ -108.67 ppm.

1-((4-chlorophenyl)thio)pyrrolidine-2,5-dione (**1b**)[3]



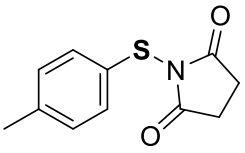
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55-7.49 (m, 2H), 7.28-7.21 (m, 2H), 2.75 (s, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.14, 136.55, 134.27, 132.15, 129.55, 28.56 ppm.

1-((4-bromophenyl)thio)pyrrolidine-2,5-dione (**1c**)[3]



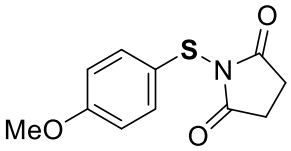
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52-7.46 (m, 4H), 2.83 (s, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.14, 134.17, 132.76, 132.49, 124.71, 28.54 ppm.

1-(p-tolylthio)pyrrolidine-2,5-dione (**1d**)[3]



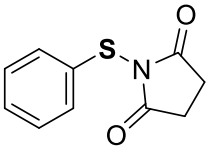
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 2.78 (s, 4H), 2.34 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.43, 140.83, 133.64, 130.31, 130.00, 28.52, 21.29 ppm.

1-((4-methoxyphenyl)thio)pyrrolidine-2,5-dione (**1e**)[3]



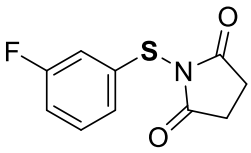
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.74 (s, 3H), 2.69 (s, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.51, 161.73, 137.36, 124.43, 114.66, 55.41, 28.53 ppm.

1-(phenylthio)pyrrolidine-2,5-dione (**1f**)[3]



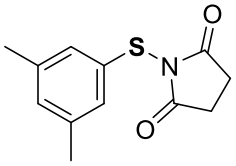
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 6.8, 2.0 Hz, 2H), 7.45-7.29 (m, 3H), 2.82 (s, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.35, 133.84, 132.23, 129.87, 129.30, 28.54 ppm.

1-((3-fluorophenyl)thio)pyrrolidine-2,5-dione (**1g**)



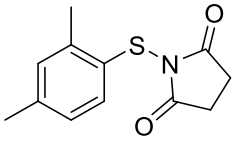
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.35-7.28 (m, 2H), 7.26-7.19 (m, 1H), 7.09-6.98 (m, 1H), 2.87 (s, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.10, 164.18, 160.87, 135.92, 135.82, 130.76, 130.65, 126.50, 126.45, 117.88, 117.58, 116.78, 116.50, 28.57 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.66 ppm.

1-((3,5-dimethylphenyl)thio)pyrrolidine-2,5-dione (**1h**)[4]



^{1}H NMR (300 MHz, Chloroform-d) δ 7.16 (s, 2H), 6.95-6.87 (m, 1H), 2.74 (s, 4H), 2.21 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl3) δ 176.40, 139.07, 133.37, 131.72, 129.82, 28.58, 21.06 ppm.

1-((2,4-dimethylphenyl)thio)pyrrolidine-2,5-dione (**1i**)



^{1}H NMR (400 MHz, Chloroform-d) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.04 (s, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 2.78 (s, 4H), 2.60 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.53, 140.93, 140.78, 134.69, 131.48, 129.63, 127.55, 28.57, 21.15, 20.63 ppm.

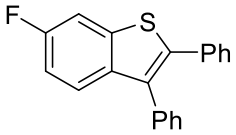
3. $Sc(OTf)_3$-Catalyzed cyclization of *N*-(arylthio)succinimides 1 with alkynes 2

General procedure:

To a 50 mL screw-capped vial equipped with a 10 x 5 mm Teflon stirring bar were charged with *N*-(arylthio)succinimides **1** (1.5 or 2.0 equiv), alkynes **2** (0.2 mmol), $Sc(OTf)_3$ (10 mol% or 20 mol%) and DCE (5 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C or 130 °C for 12 h in an oil bath. The reaction was cooled to room temperature, and the solvent was removed under vacuum. Then the resulting crude product was purified by flash chromatography on silica gel using an appropriate eluent.

The structures of the benzo[b]thiophenes with sulfur migration were determined through XRD-analysis or the analysis of NMR spectra. The ratio of the isomers (product with sulfur migration/product without sulfur migration) was determined by GC-MS or NMR.

6-fluoro-2,3-diphenylbenzo[b]thiophene (**3a/3g**)

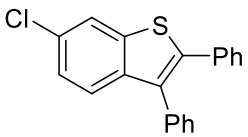


For **3a**: following the general procedure, the cyclization reaction was carried out with 1.5 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 130 °C. White solid, 82% yield. The ratio of the isomers was >99/1 determined by ^{19}F-NMR and GC.

For **3g**: following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 100 °C. White solid, 61% yield. The ratio of the isomers was 68/29/2/1 determined by ^{19}F-NMR.

^{1}H NMR (300 MHz, Chloroform-d) δ 7.47-7.42 (m, 2H), 7.35-7.25 (m, 3H), 7.25-7.17 (m, 4H), 7.17-7.10 (m, 3H), 6.98 (td, *J* = 8.9, 2.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl3) δ 162.22, 158.98, 139.67, 139.53, 139.05, 139.00, 137.44, 137.42, 135.24, 133.94, 132.68, 130.32, 129.47, 128.72, 128.38, 127.75, 127.54, 124.49, 124.37, 113.48, 113.17, 108.30, 107.96 ppm. ^{19}F NMR (282 MHz, CDCl3) δ -117.23 ppm. HRMS m/z (APCI) calcd for $[C_{20}H_{13}SF]^{\cdot+}$: 304.0716, found: 304.0713.

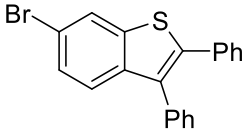
6-chloro-2,3-diphenylbenzo[b]thiophene (**3b**)[5]



Following the general procedure, the cyclization reaction was carried out with 1.5 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 130 °C. White solid, 79% yield. ^{1}H NMR

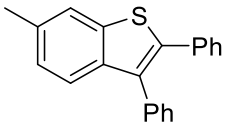
(300 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 3.0 Hz, 1H), 7.41-7.38 (m, 1H), 7.33-7.22 (m, 3H), 7.20-7.13 (m, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.94, 139.72, 139.35, 135.01, 133.76, 132.79, 130.53, 130.29, 129.49, 128.74, 128.40, 127.91, 127.59, 125.22, 124.15, 121.59 ppm. The ratio of the isomers was 93/7 determined by GC-MS.

6-bromo-2,3-diphenylbenzo[b]thiophene (**3c**)[5]



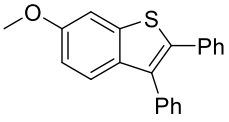
Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 130 °C. White solid, 74% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (t, *J* = 1.2 Hz, 1H), 7.34-7.27 (m, 4H), 7.25-7.12 (m, 8H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.19, 140.02, 139.69, 134.98, 133.73, 132.90, 130.31, 129.51, 128.75, 128.42, 127.95, 127.85, 127.61, 124.53, 124.48, 118.34 ppm. The ratio of the isomers was 95/5 determined by GC-MS.

6-methyl-2,3-diphenylbenzo[b]thiophene (**3d**)[5]



Following the general procedure, the cyclization reaction was carried out with 1.5 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 100 °C. White solid, 67% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.61-7.54 (m, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.34-7.18 (m, 7H), 7.17-7.10 (m, 3H), 7.06 (d, *J* = 9.3 Hz, 1H), 2.39 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.08, 138.72, 138.27, 135.67, 134.51, 134.36, 132.98, 130.37, 129.52, 128.59, 128.28, 127.49, 127.27, 126.12, 122.96, 121.87, 21.52 ppm. The ratio of the isomers was >99/1 determined by ^{1}H-NMR

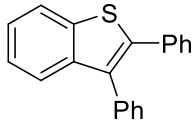
6-methoxy-2,3-diphenylbenzo[b]thiophene (**3e**)[6]



Following the general procedure, the cyclization reaction was carried out with 1.5 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 100 °C. White solid, 56% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.9 Hz, 1H), 7.35-7.17 (m, 8H), 7.17-7.09 (m, 3H),

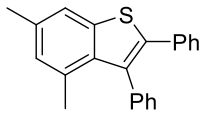
6.87 (dd, J = 8.9, 2.4 Hz, 1H), 3.80 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.55, 140.13, 136.75, 135.64, 135.00, 134.36, 132.80, 130.33, 129.41, 128.61, 128.29, 127.36, 127.31, 124.03, 114.37, 104.51, 55.63 ppm. The ratio of the isomers was >99/1 determined by ^{1}H-NMR.

2,3-diphenylbenzo[b]thiophene (**3f**)[7]



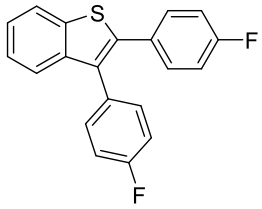
Following the general procedure, the cyclization reaction was carried out with 1.5 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 100 °C. White solid, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79-7.77 (m, 1H), 7.54-7.46 (m, 1H), 7.33-7.20 (m, 9H), 7.18-7.10 (m, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.87, 139.53, 138.83, 135.50, 134.22, 133.22, 130.42, 129.60, 128.63, 128.32, 127.68, 127.36, 124.51, 124.42, 123.33, 122.05 ppm.

5,7-dimethyl-2,3-diphenylbenzo[b]thiophene (**3h**)



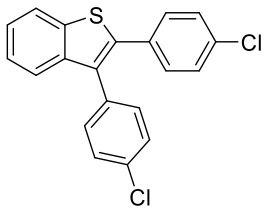
Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 100 °C. White solid, 70% yield. ^{1}H NMR (600 MHz, Benzene-d_6) δ 7.42 – 7.38 (m, 2H), 7.32 (s, 1H), 7.12 – 7.07 (m, 2H), 7.05 – 6.99 (m, 3H), 6.99 – 6.95 (m, 2H), 6.92 – 6.88 (m, 1H), 6.79 (s, 1H) ppm; ^{13}C NMR (151 MHz, Benzene-d_6) δ 140.30, 138.99, 138.84, 137.24, 135.37, 135.07, 134.24, 134.24, 131.45, 130.02, 129.45, 128.50, 128.35, 127.62, 127.50, 120.48, 21.69, 21.22 ppm; HRMS m/z (APCI) calcd for $[C_{22}H_{18}S]^{\cdot+}$: 314.1123, found: 314.1120. The ratio of the isomers was 88/12 determined by ^{1}H-NMR.

2,3-bis(4-fluorophenyl)benzo[b]thiophene (**3i**)[8]



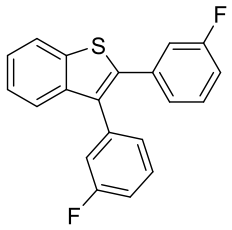
Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 130 °C. White solid, 53% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.94-7.84 (m, 1H), 7.60-7.54 (m, 1H), 7.44-7.35 (m, 2H), 7.35-7.23 (m, 4H), 7.17-7.09 (m, 2H), 7.04-6.93 (m, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.98, 163.82, 160.68, 160.55, 140.58, 138.66, 138.60, 132.17, 132.06, 131.96, 131.34, 131.23, 131.12, 131.08, 130.10, 130.05, 124.72, 124.63, 123.11, 122.12, 115.95, 115.66, 115.37 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.45, -114.23 ppm.

2,3-bis(4-chlorophenyl)benzo[b]thiophene (**3j**)[8]



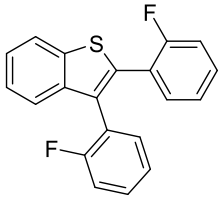
Following the general procedure, the cyclization reaction was carried out with 1.5 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 130 °C. White solid, 56% yield. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.93-7.85 (m, 1H), 7.61-7.53 (m, 1H), 7.44-7.35 (m, 4H), 7.28-7.22 (m, 6H) ppm. ^{13}C NMR (75 MHz, CDCl3) δ 140.34, 138.78, 138.55, 133.97, 133.58, 132.39, 132.28, 131.66, 130.78, 129.09, 128.75, 124.91, 124.73, 123.12, 122.18 ppm.

2,3-bis(3-fluorophenyl)benzo[b]thiophene (**3k**)



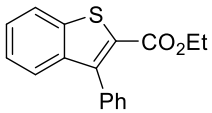
Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 130 °C. White solid, 61% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.84-7.73 (m, 1H), 7.53-7.45 (m, 1H), 7.35-7.22 (m, 3H), 7.18-7.09 (m, 1H), 7.06-6.79 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.57, 164.13, 161.30, 160.87, 140.30, 138.80, 138.57, 138.54, 137.31, 137.20, 136.00, 135.89, 132.56, 132.53, 130.38, 130.27, 130.03, 129.92, 126.16, 126.13, 125.32, 125.28, 125.01, 124.77, 123.23, 122.15, 117.34, 117.06, 116.55, 116.25, 115.03, 114.83, 114.75, 114.55 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.45, -112.55. HRMS m/z (APCI) calcd for $[C_{20}H_{12}SF_2]^{\cdot+}$: 322.0622, found: 322.0618.

2,3-bis(2-fluorophenyl)benzo[b]thiophene (**3l**)[8]



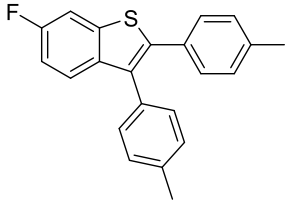
Following the general procedure, the cyclization reaction was carried out with 1.5 equiv of the corresponding substrate and $Sc(OTf)_3$ (10 mol%) at 100 °C. White solid, 60% yield. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.85-7.74 (m, 1H), 7.49-7.40 (m, 1H), 7.35-7.09 (m, 6H), 7.07-6.86 (m, 4H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.84, 161.34, 158.55, 158.03, 139.49, 139.44, 134.54, 132.23, 132.19, 130.20, 130.10, 129.78, 129.65, 129.55, 124.75, 124.48, 124.06, 124.01, 123.95, 123.90, 123.28, 123.26, 122.89, 122.68, 122.04, 121.91, 121.71, 116.02, 116.00, 115.73, 115.71 ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.47, -112.92 ppm.

ethyl 3-phenylbenzo[b]thiophene-2-carboxylate (**3m**)[9]



Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 130 °C. Colorless oil, 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.79 (m, 1H), 7.47-7.41 (m, 5H), 7.38-7.17 (m, 3H), 4.15 (dd, *J* = 12.0 Hz, 6.0 Hz, 2H), 1.11 (t, *J* = 9.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.61, 143.75, 140.35, 140.13, 134.67, 129.65, 128.61, 127.95, 127.09, 125.24, 124.72, 122.43, 61.22, 13.94 ppm.

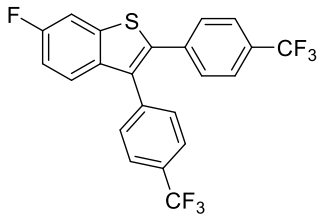
6-fluoro-2,3-di-p-tolylbenzo[b]thiophene (**3n**)



Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 130 °C. White solid, 64% yield. ^{1}H NMR (600 MHz, Benzene-d_6) δ 7.39 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.20 (dd, *J* =

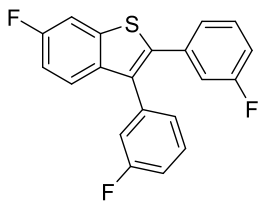
8.6, 2.4 Hz, 1H), 7.13 – 7.10 (m, 2H), 6.96 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.88 (td, *J* = 8.8, 2.4 Hz, 1H), 6.81 (dt, *J* = 7.8, 0.8 Hz, 2H), 2.11 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR (151 MHz, Benzene-d_6) δ 161.89, 160.27, 140.22, 140.15, 139.56, 139.54, 138.24, 138.23, 137.82, 137.23, 133.00, 132.92, 131.90, 130.65, 129.82, 129.79, 129.56, 124.83, 124.77, 113.56, 113.41, 108.66, 108.49, 21.07, 21.02 ppm. ^{19}F NMR (564 MHz, Benzene-d_6) δ -117.39 (td, *J* = 8.8, 5.3 Hz) ppm. The ratio of the isomers was >99/1 determined by ^{19}F-NMR. HRMS m/z (APCI) calcd for $[C_{22}H_{17}SF]^{\cdot+}$: 332.1029, found: 332.1027.

6-fluoro-2,3-bis(4-(trifluoromethyl)phenyl)benzo[b]thiophene (**3o**)



Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 130 °C. White solid, 68% yield. ^{1}H NMR (600 MHz, Benzene-d_6) δ 7.35 (d, *J* = 8.0 Hz, 2H), 7.23 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.17 (s, 1H), 7.14 (dd, *J* = 8.9, 5.0 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.96 (td, *J* = 8.8, 2.4 Hz, 1H), 6.93 (d, *J* = 12.0 Hz, 2H) ppm; ^{13}C NMR (151 MHz, Benzene-d_6) δ 162.25, 160.63, 140.49, 140.42, 138.74, 138.48, 138.45, 137.32, 137.09, 137.09, 132.75, 132.74, 130.87, 130.24, 130.17, 129.96, 126.05, 125.85, 124.84, 124.78, 124.56, 116.49, 116.34, 114.30, 114.14, 108.82, 108.65 ppm; ^{19}F NMR (564 MHz, Benzene-d_6) δ -62.35, -62.57, -115.44 ppm. The ratio of the isomers was 87/13 determined by ^{1}H-NMR. HRMS m/z (APCI) calcd for $[C_{22}H_{11}SF_7]^{\cdot+}$: 440.0464, found: 440.0459.

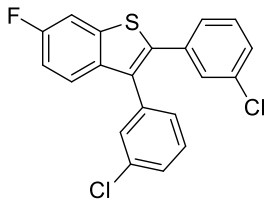
6-fluoro-2,3-bis(3-fluorophenyl)benzo[b]thiophene (**3p**)



Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and $Sc(OTf)_3$ (20 mol%) at 130 °C. White solid, 82% yield. ^{1}H NMR (600 MHz, Benzene-d_6) δ 7.14 (dd, *J* = 9.0, 5.0 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.02 (ddd, *J* = 9.9, 2.5, 1.8 Hz, 1H), 6.93 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 6.87 – 6.80 (m, 1H), 6.79 –

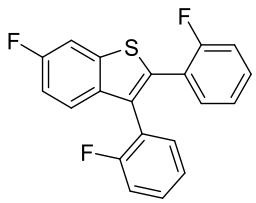
6.76 (m, 1H), 6.75 – 6.67 (m, 3H), 6.60 (tdd, *J* = 8.4, 2.6, 0.9 Hz, 1H) ppm; ^{13}C NMR (151 MHz, Benzene-d_6) δ 164.21, 163.89, 162.57, 162.25, 162.09, 160.46, 140.22, 140.15, 138.44, 138.42, 138.41, 138.40, 137.46, 137.41, 137.31, 137.30, 136.27, 136.22, 132.53, 132.52, 132.52, 132.51, 130.69, 130.63, 130.45, 130.39, 126.30, 126.28, 125.45, 125.43, 124.80, 124.74, 117.49, 117.34, 116.70, 116.55, 115.28, 115.14, 115.04, 114.90, 114.04, 113.88, 108.68, 108.51 ppm; ^{19}F NMR (564 MHz, Benzene-d_6) δ -111.92 (ddd, *J* = 9.6, 8.6, 6.0 Hz), -112.04 (ddd, *J* = 9.9, 8.5, 6.0 Hz), -116.16 (td, *J* = 8.7, 5.1 Hz) ppm. The ratio of the isomers was >99/1 determined by ^{19}F-NMR. HRMS m/z (APCI) calcd for $[C_{20}H_{11}SF_3]^{\cdot+}$: 340.0528, found: 340.0525.

2,3-bis(3-chlorophenyl)-6-fluorobenzo[b]thiophene (**3q**)



Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and Sc(OTf)$_3$ (20 mol%) at 130 °C. White solid, 91% yield. ^{1}H NMR (600 MHz, Benzene-d_6) δ 7.35 (t, *J* = 1.9 Hz, 1H), 7.13 – 7.07 (m, 3H), 7.05 (ddd, *J* = 7.7, 2.1, 1.4 Hz, 1H), 6.93 (ddd, *J* = 7.7, 1.7, 1.0 Hz, 1H), 6.88 (ddd, *J* = 8.0, 2.1, 1.0 Hz, 1H), 6.81 (td, *J* = 8.8, 2.5 Hz, 1H), 6.76 (td, *J* = 7.7, 0.5 Hz, 1H), 6.73 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.61 (t, *J* = 7.9 Hz, 1H) ppm; ^{13}C NMR (151 MHz, Benzene-d_6) δ 162.08, 160.45, 140.22, 140.15, 138.31, 138.29, 137.21, 137.04, 135.83, 135.02, 134.89, 132.39, 130.44, 130.34, 130.03, 129.77, 128.74, 128.39, 127.79, 124.77, 124.71, 116.49, 116.34, 114.09, 113.93, 108.68, 108.51 ppm; ^{19}F NMR (564 MHz, Benzene-d_6) δ -116.01 ppm. The ratio of the isomers was 95/5 determined by ^{19}F-NMR. HRMS m/z (APCI) calcd for $[C_{20}H_{11}SCl_2F]^{\cdot+}$: 371.9937, found: 371.9934.

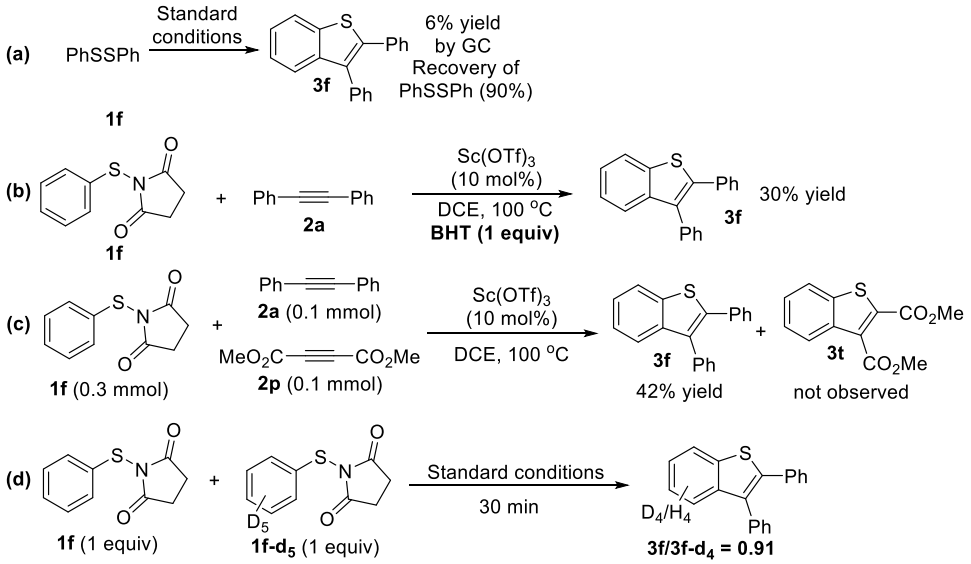
6-fluoro-2,3-bis(2-fluorophenyl)benzo[b]thiophene (**3r**)



Following the general procedure, the cyclization reaction was carried out with 2.0 equiv of the corresponding substrate and Sc(OTf)$_3$ (20 mol%) at 130 °C. White solid, 91% yield. ^{1}H NMR

(600 MHz, Benzene-d_6) δ 7.27 (ddd, J = 8.8, 5.1, 1.6 Hz, 1H), 7.23 (td, J = 7.5, 1.8 Hz, 1H), 7.09 (dd, J = 8.7, 2.4 Hz, 1H), 7.02 (td, J = 7.4, 1.8 Hz, 1H), 6.88 – 6.79 (m, 3H), 6.76 – 6.61 (m, 4H) ppm; ^{13}C NMR (151 MHz, Benzene-d_6) δ 161.18, 160.73, 160.22, 140.99, 136.55, 134.69, 132.50, 132.47, 130.54, 130.02, 129.88, 124.86, 124.35, 124.24, 123.18, 122.17, 116.20, 116.18, 113.79, 108.53 ppm; ^{19}F NMR (564 MHz, Benzene-d_6) δ -112.16 – -112.24 (m), -112.52 (q, J = 7.3 Hz), -115.43 – -119.51 (m) ppm. The ratio of the isomers was >99/1 determined by ^{19}F-NMR. HRMS m/z (APCI) calcd for $[C_{20}H_{11}SF_3]^{\cdot+}$: 340.0528, found: 304.0524.

4. Preliminary mechanism studies



(a) To a 50 mL screw-capped vial equipped with a 10 x 5 mm Teflon stirring bar were charged with 1,2-diphenyldisulfane (0.3 mmol), **2a** (0.2 mmol), $Sc(OTf)_3$ (10 mol%) and DCE (5.0 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 12 h in an oil bath. The reaction was cooled to room temperature, and 20 μL *p*-xylene was added as an internal standard. Then the solution was analyzed by GC after a rapid filtration with silica. The GC yield of **3f** was 6% and 90% of 1,2-diphenyldisulfane was recovered based on GC.

(b) To a 50 mL screw-capped vial equipped with a 10 x 5 mm Teflon stirring bar were charged with *N*-(phenylthio)succinimides **1f** (0.3 mmol), **2a** (0.2 mmol), $Sc(OTf)_3$ (10 mol%), BHT (2,6-Di-tert-butyl-4-methylphenol, 0.2 mmol) and DCE (5 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 12 h in an oil bath. The reaction was cooled to room temperature, and the solvent was

removed under vacuum. Then the resulting crude product was purified by flash chromatography on silica gel to give the final product **3f** in 30% yield.

(c) To a 50 mL screw-capped vial equipped with a 10 x 5 mm Teflon stirring bar were charged with *N*-(phenylthio)succinimides **1f** (0.3 mmol), **2a** (0.1 mmol), dimethyl but-2-ynedioate (0.1 mmol), $Sc(OTf)_3$ (0.02 mmol), and DCE (5 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 12 h in an oil bath. The reaction was cooled to room temperature, and the solution was analyzed by GCMS. The product **3a**, was detected, but the product **3t** was not detected. Then the solvent was removed under vacuum and the resulting crude product was purified by flash chromatography on silica gel to give the final product **3f** in 42% yield.

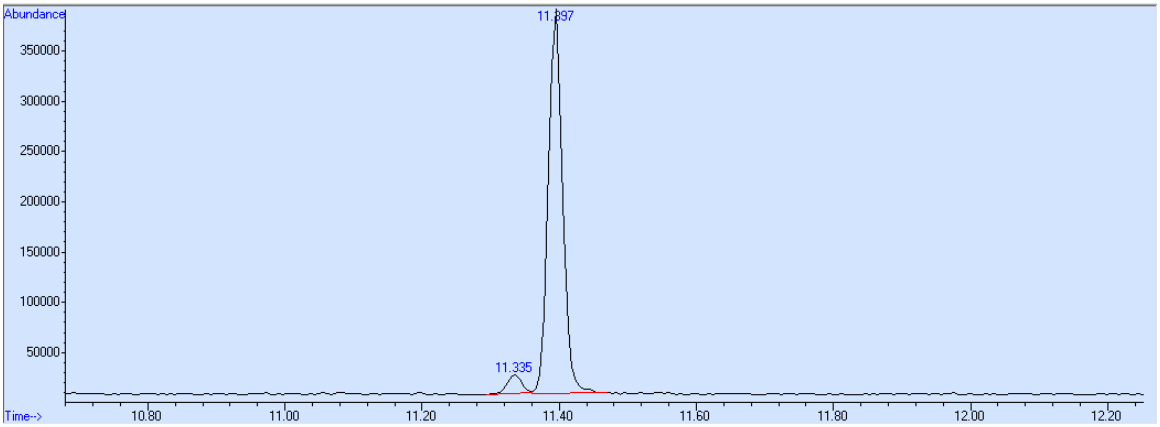
(d) To a 50 mL screw-capped vial equipped with a 10 x 5 mm Teflon stirring bar were charged with *N*-(phenylthio)succinimides **1f** (0.1 mmol), *N*-(D_5-phenylthio)succinimides **1f-*d*$_5$** (0.1 mmol), **2a** (0.1 mmol), $Sc(OTf)_3$ (10 mol%) and DCE (2.5 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 0.5 h in an oil bath. The reaction was cooled to room temperature. Because 2,3-diphenylbenzo[b]thiophene can't be detected by HRMS-ESI, the crude product was oxidized by MCPBA directly. So MCPBA (0.4 mmol) was added into the above solution and then stirred at rt for 4 h. The ratio of 2,3-diphenylbenzo[*b*]thiophene 1,1-dioxide and 2,3-diphenylbenzo[*b*]thiophene 1,1-dioxide-4,5,6,7-d_4 was determined by HRMS-ESI of the resulting solution directly.

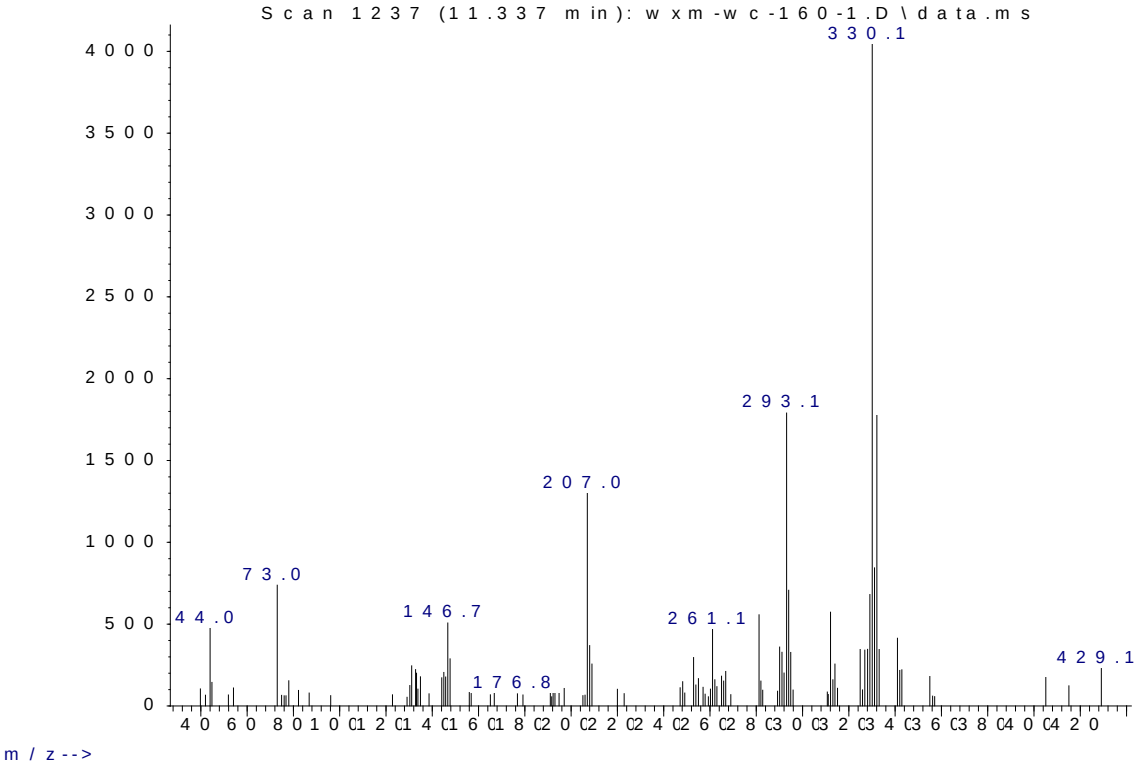
Product	m/z	Res	S/N	I	FWHM
3f-dioxide $+Na^+$	341.0603	7213	2291.9	387225	0.0473
3f-*d*$_4$-dioxide $+Na^+$	345.0857	7616	2540.4	425837	0.0453

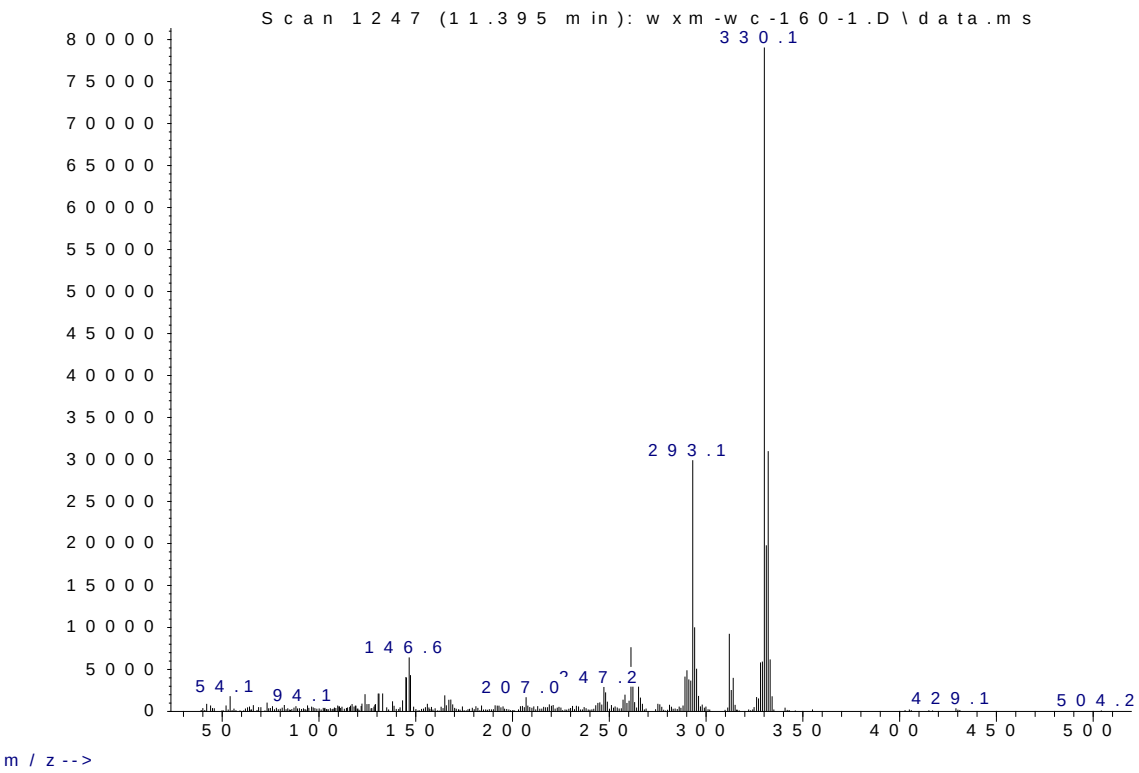
(e) The reaction between **1b** with **2a-d$_{10}$**

To a 50 mL screw-capped vial equipped with a 10 x 5 mm Teflon stirring bar were charged with **1b** (0.2 mmol), **2a-d$_{10}$** (0.1 mmol), $Sc(OTf)_3$ (10 mol%) and DCE (2.5 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 12 h in an oil bath. The reaction was cooled to room temperature, and the solution

was analyzed by GCMS after a rapid filtration with silica. Two products (retention time: 11.335 min and 11.397 min) were detected by GCMS (96/4, m/z: 330.1 for each).

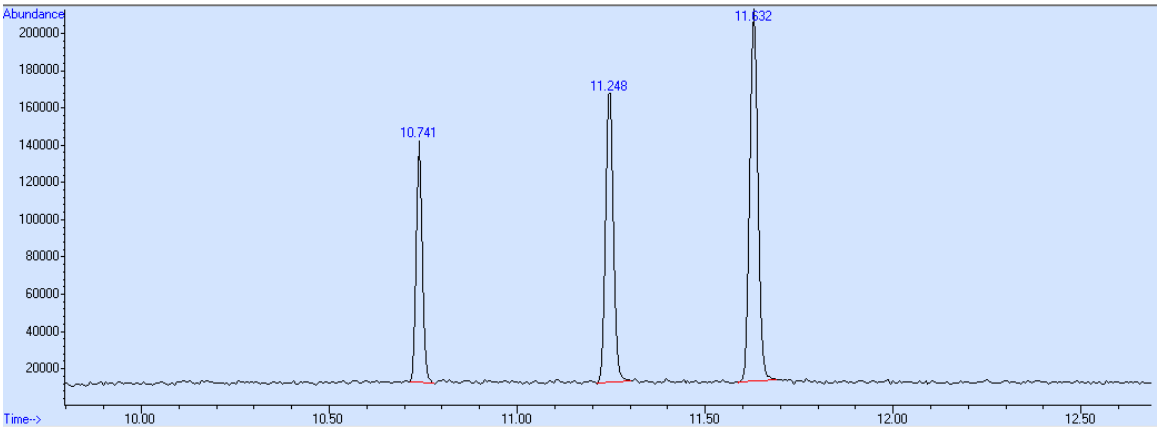




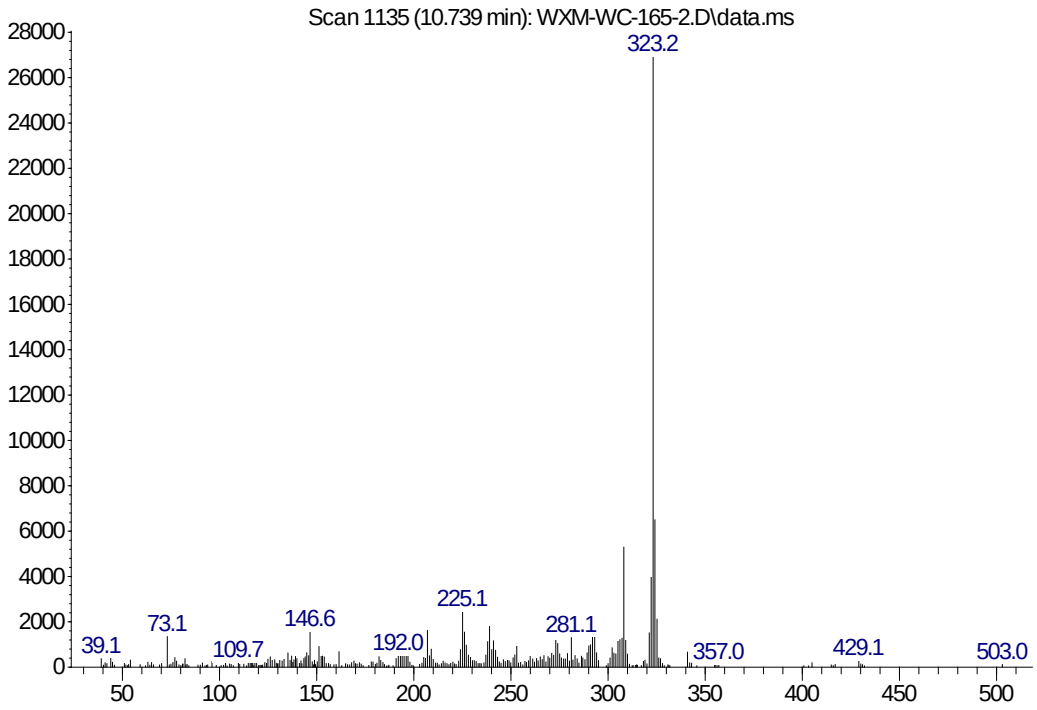


(f) The reaction between **1i** with **2a-d$_{10}$**

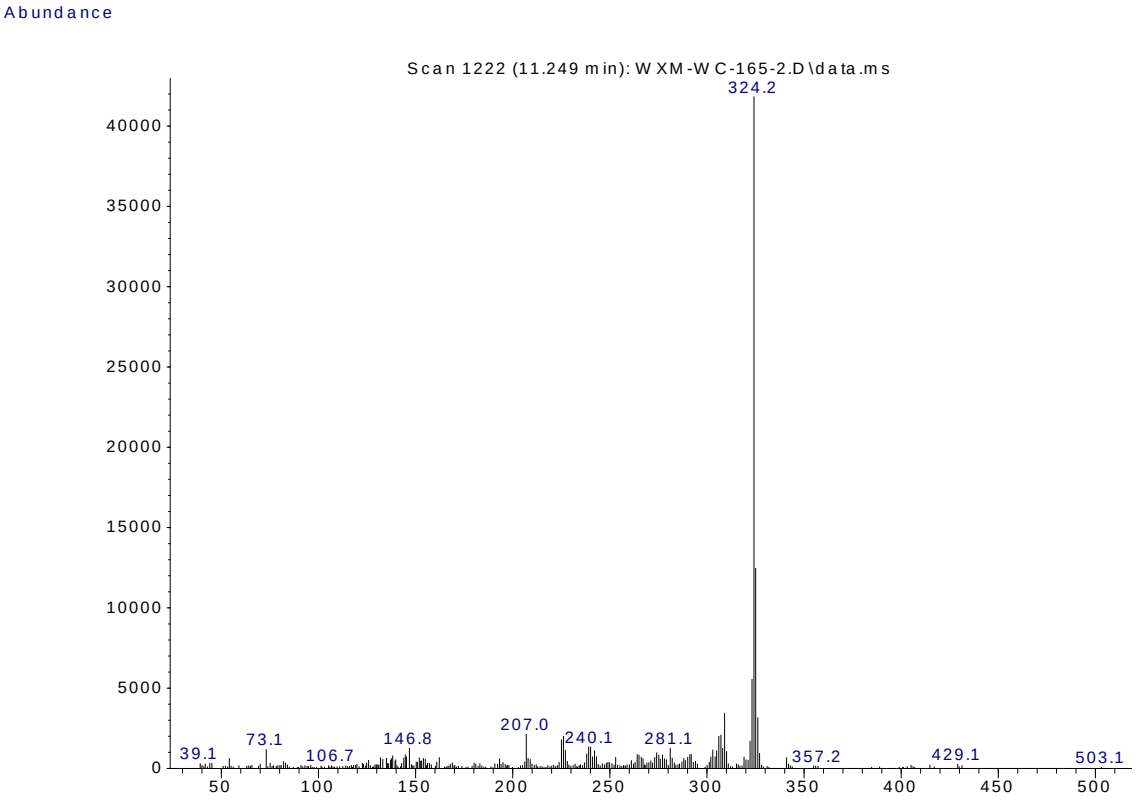
To a 50 mL screw-capped vial equipped with a 10 x 5 mm Teflon stirring bar were charged with **1i** (0.3 mmol), **2a-d$_{10}$** (0.2 mmol), $Sc(OTf)_3$ (10 mol%) and DCE (5.0 mL) under the Argon atmosphere. The resulting mixture was sealed with a Teflon-lined cap and stirred at 100 °C for 12 h in an oil bath. The reaction was cooled to room temperature, and the solution was analyzed by GCMS after a rapid filtration with silica. Three products (retention time: 10.741 min, 11.248 min and 11.632 min) were detected by GCMS (ratio: 21/33/45). This reaction was repeated twice, and the three reactions were combined. The solvent was removed under vacuum. Then the resulting crude products were purified by flash chromatography on silica gel to give the pure **3s''-d$_9$** in 9% yield and mixture of two isomers of **3s-d$_{10}$** (41% yield). The prodcut **3q''-d$_9$** was characterized by ^{1}H-NMR, ^{13}C-NMR, 2D-NMR and HRMS.

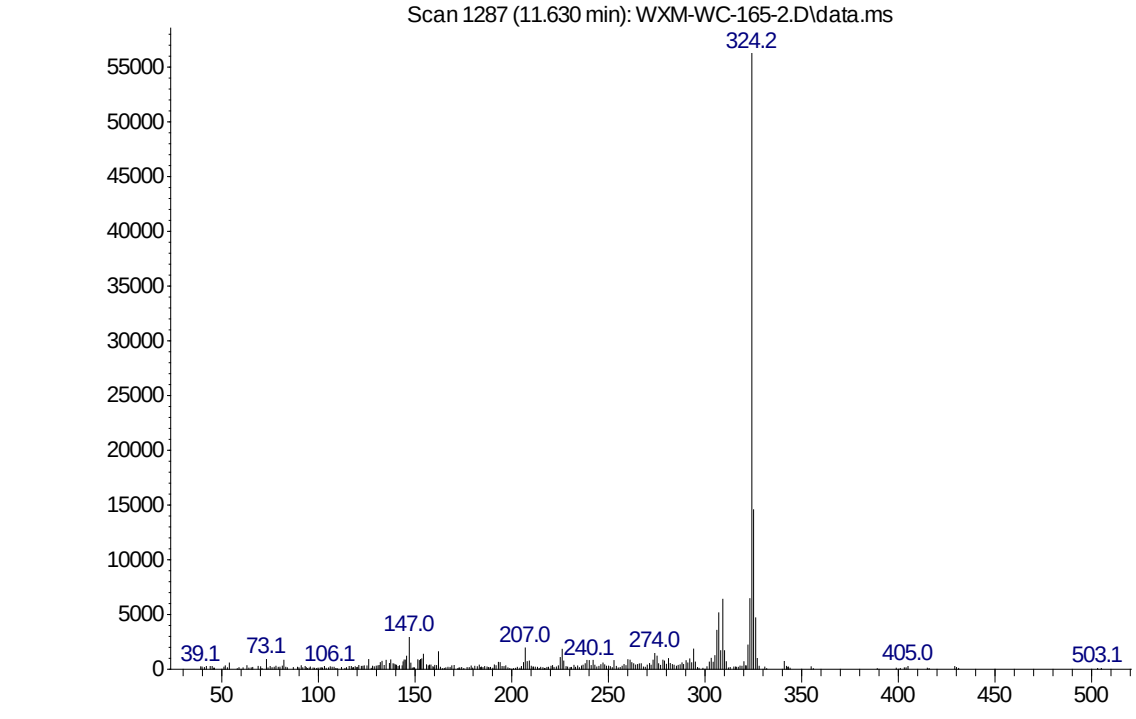


Abundance

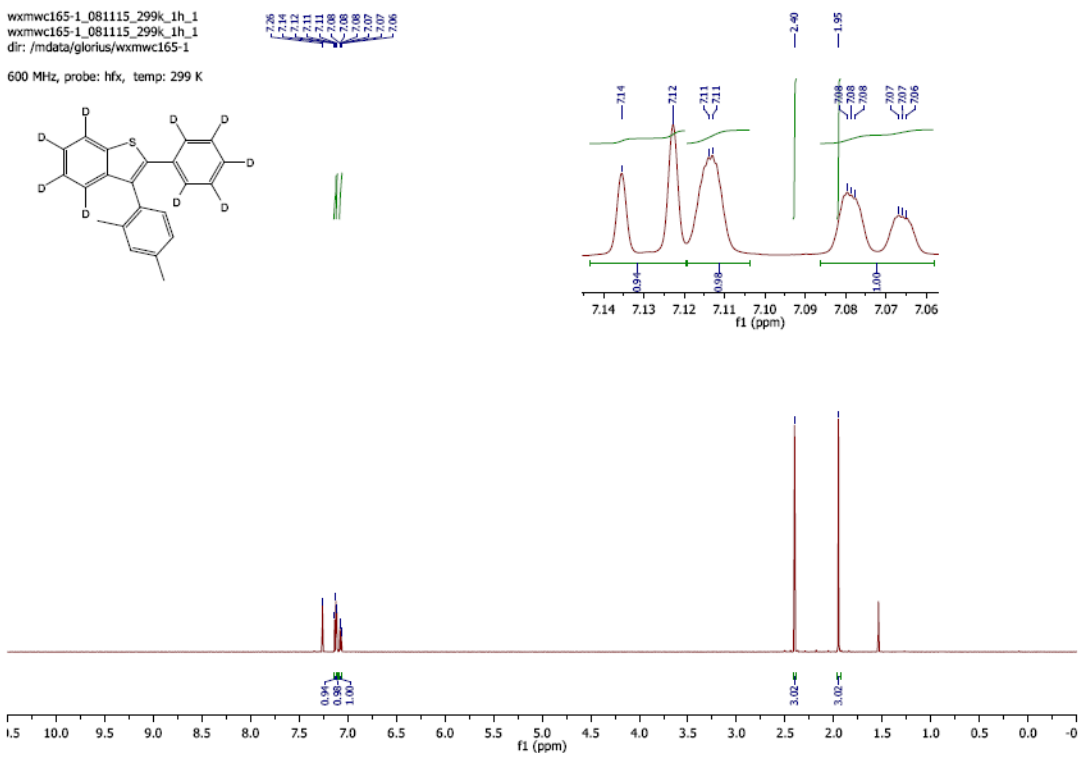


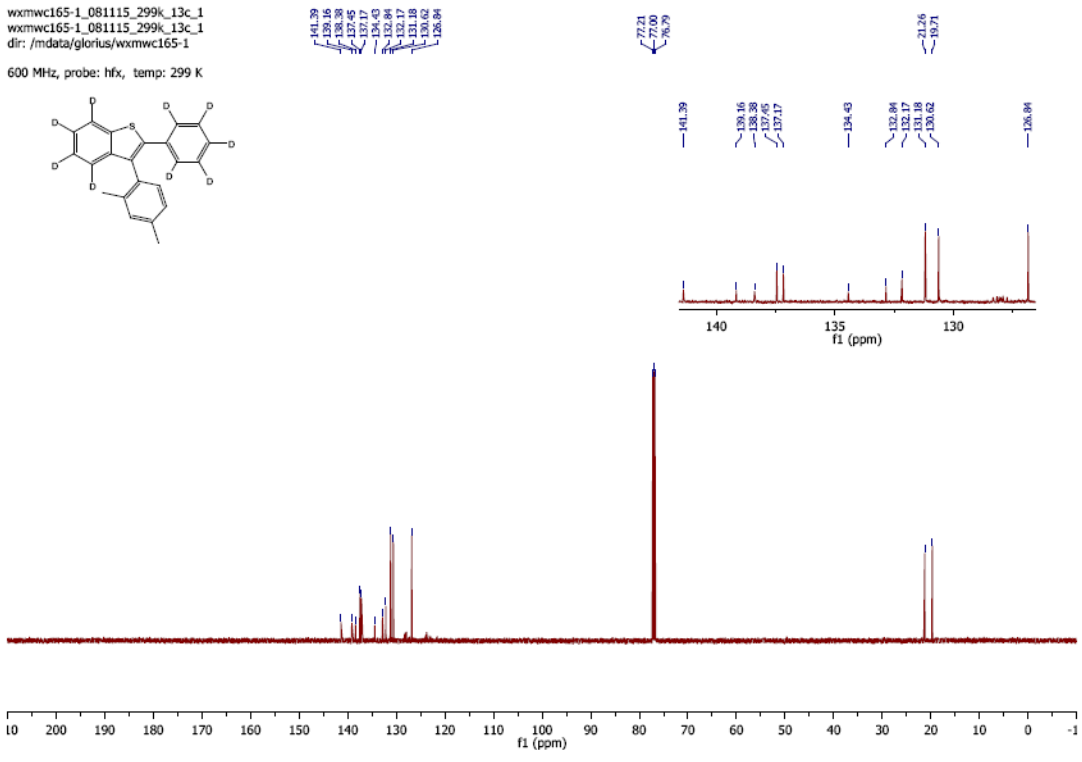
m/z-->

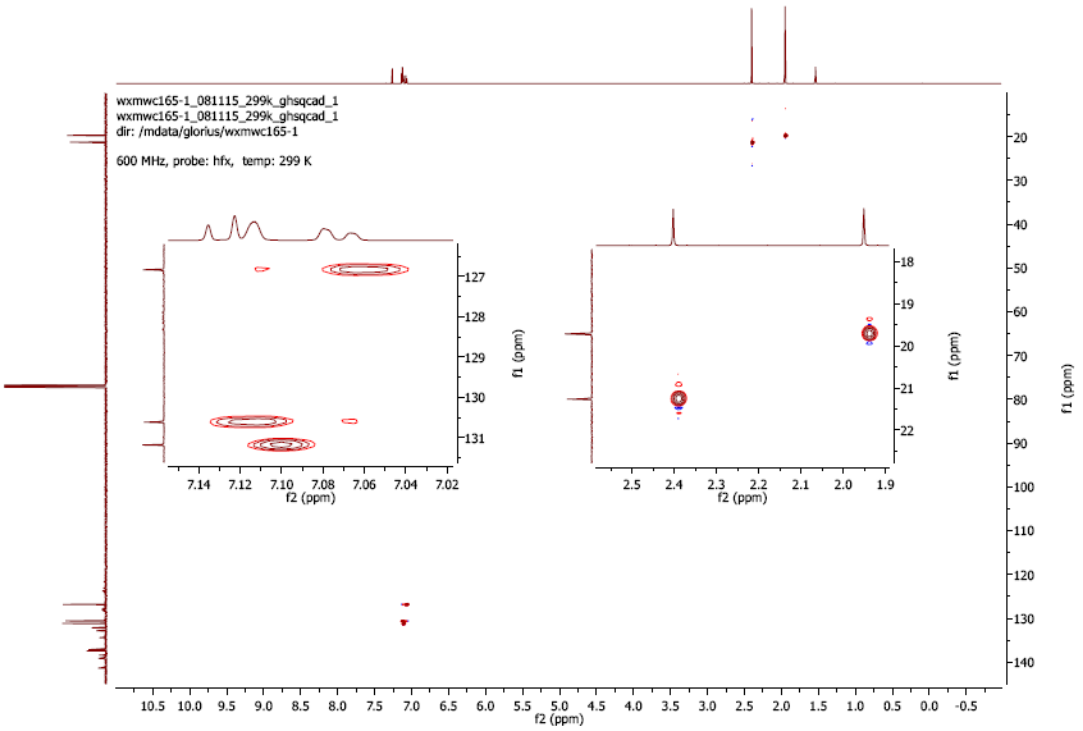


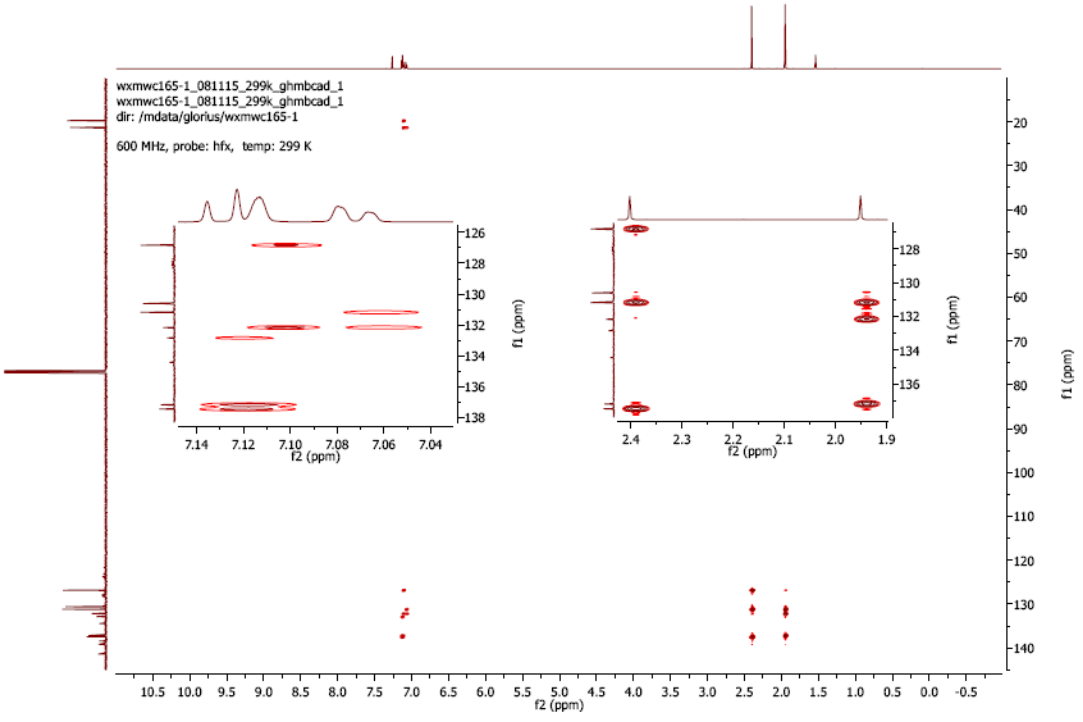


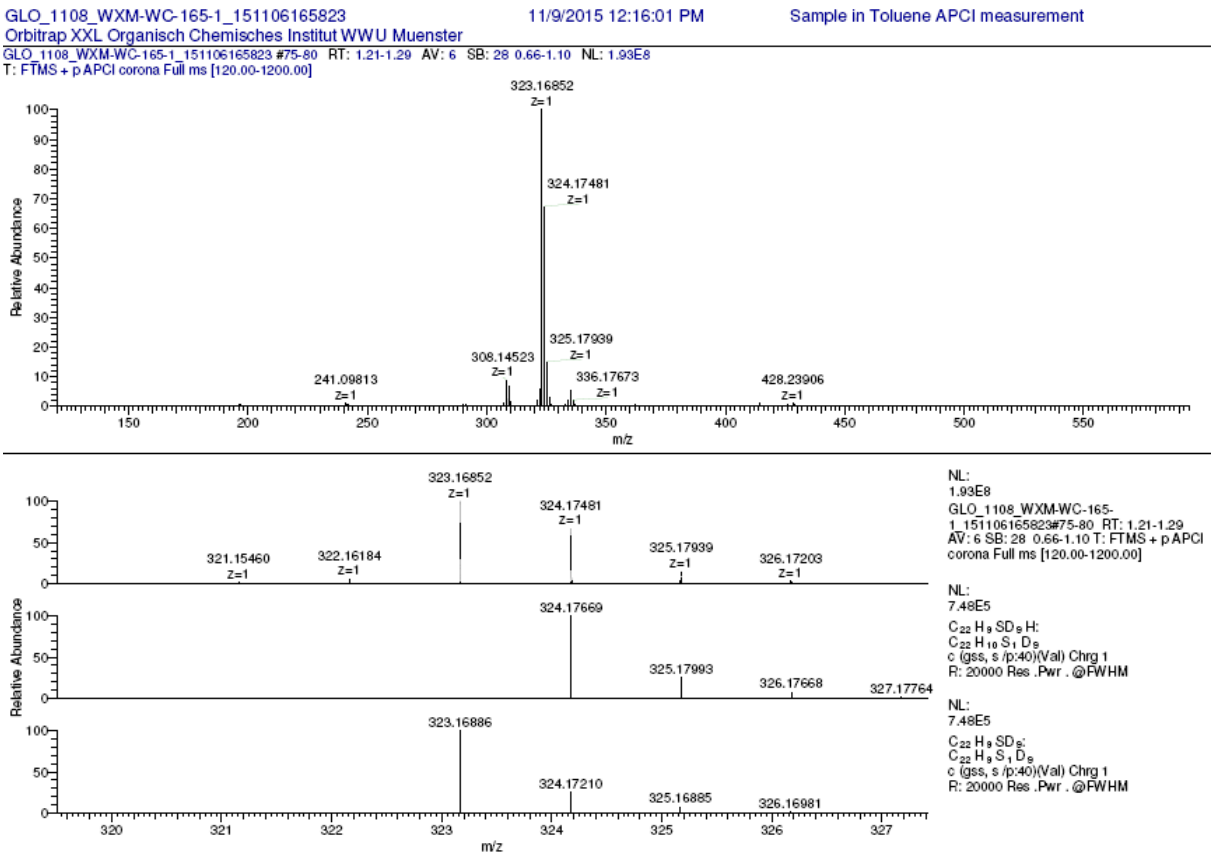
3-(2,4-dimethylphenyl)-2-(phenyl-d_5)benzo[b]thiophene-4,5,6,7-d_4 (**3q''-d$_9$**)


wxmwc165-1_081115_299k_1h_1
wxmwc165-1_081115_299k_1h_1
dir: /mdata/glorius/wxmwc165-1
600 MHz, probe: hfx, temp: 299 K
f1 (ppm)


wxmwc165-1_081115_299k_13c_1
wxmwc165-1_081115_299k_13c_1
dir: /mdata/glorius/wxmwc165-1
600 MHz, probe: hfx, temp: 299 K
f1 (ppm)


wxmwc165-1_081115_299k_ghsqcad_1
wxmwc165-1_081115_299k_ghsqcad_1
dir: /mdata/glorius/wxmwc165-1
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)


wxmwc165-1_081115_299k_ghmbcad_1
wxmwc165-1_081115_299k_ghmbcad_1
dir: /mdata/glorius/wxmwc165-1
600 MHz, probe: hfx, temp: 299 K
f2 (ppm)
f1 (ppm)



5. X-ray crystal structure analysis of compound 3a (CCDC number: 1498887):

X-Ray diffraction: Data sets for the compound **3a** were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: *APEX2 V2014.5-0* (Bruker AXS Inc., 2014); cell refinement: *SAINT V8.34A* (Bruker AXS Inc., 2013); data reduction: *SAINT V8.34A* (Bruker AXS Inc., 2013); absorption correction, *SADABS V2014/2* (Bruker AXS Inc., 2014); structure solution *SHELXT-2014* (Sheldrick, 2014); structure refinement *SHELXL-2014* (Sheldrick, 2014). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

X-ray crystal structure analysis of 3a: A colorless prism-like specimen of $C_{20}H_{13}FS$, approximate dimensions 0.110 mm x 0.170 mm x 0.183 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 638 frames were collected. The total exposure time was 7.97 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 29243 reflections to a maximum θ angle of

26.42° (0.80 Å resolution), of which 3020 were independent (average redundancy 9.683, completeness = 99.7%, R_{int} = 6.07%, R_{sig} = 2.92%) and 2433 (80.56%) were greater than $2\sigma(F^2)$. The final cell constants of a = 6.0149(4) Å, b = 13.4117(9) Å, c = 18.2153(12) Å, β = 91.601(2)°, volume = 1468.86(17) $Å^3$, are based upon the refinement of the XYZ-centroids of 9967 reflections above 20 σ(I) with 5.408° < 2θ < 52.64°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.912. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9600 and 0.9760. The final anisotropic full-matrix least-squares refinement on F^2 with 199 variables converged at R1 = 3.97%, for the observed data and wR2 = 8.61% for all data. The goodness-of-fit was 1.076. The largest peak in the final difference electron density synthesis was 0.220 $e^-/Å^3$ and the largest hole was -0.289 $e^-/Å^3$ with an RMS deviation of 0.051 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.376 g/cm^3 and F(000), 632 e^-.

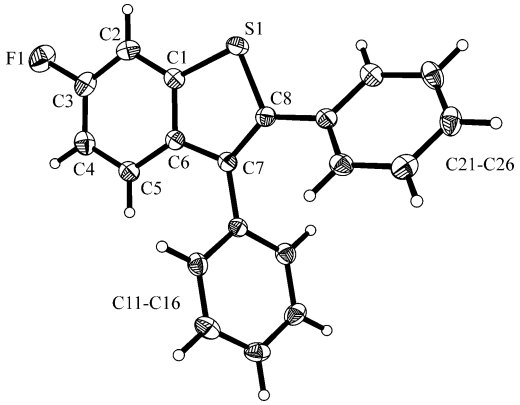


Figure S1. Crystal structure of compound **3a**.
(Thermals ellipsoids are shown with 50% probability)

6. For details on the calculations

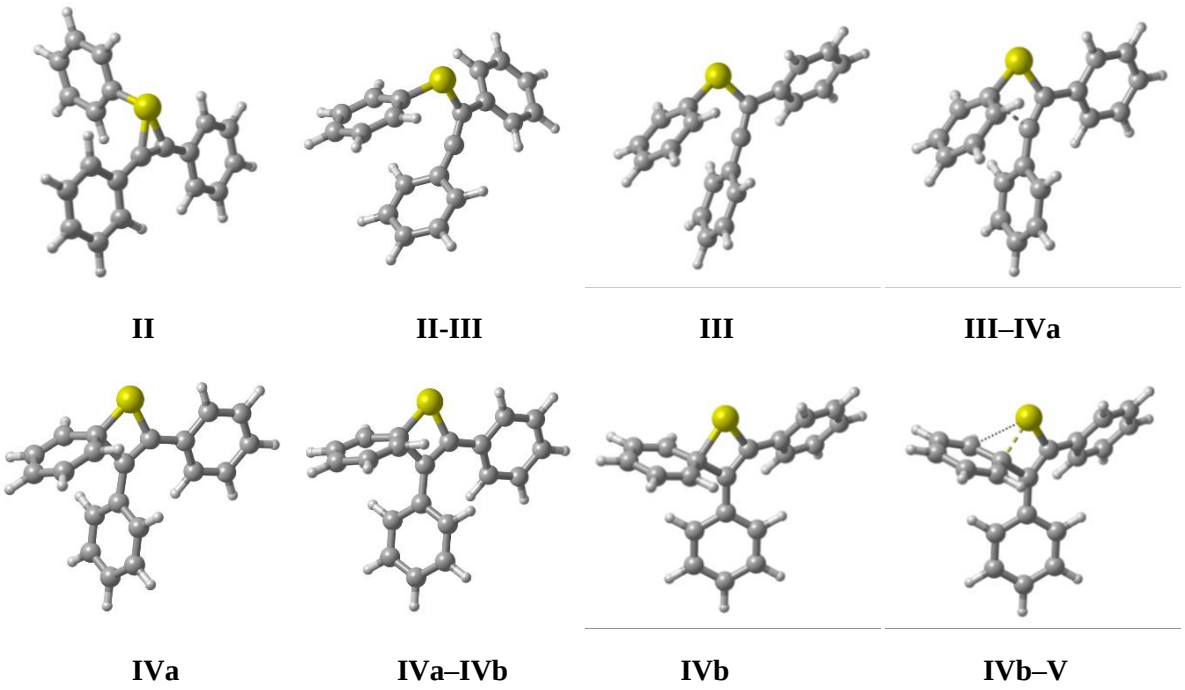
Computational Details

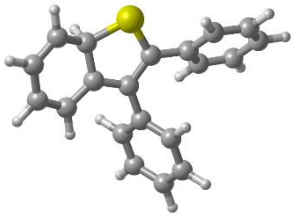
All calculations were carried out with the Gaussian 09 suite. The geometries of all stationary points were optimized using the M06-2X hybrid functional with the 6-311G** basis on all atoms, the "ultrafine" setting for the integration grid and the IEFPCM solvation model with the presets for 1,2-dichloroethane. Frequencies were calculated at the same level to confirm the absence of imaginary frequencies for minima and the presence of a single imaginary frequency for the transition states. Free energies are reported at 100 °C in kcal mol^{-1}.

Full authorship for manuscript reference 12a (Gaussian 09):

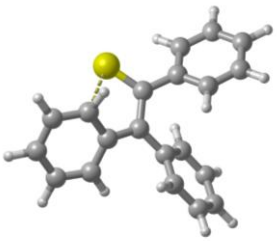
Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2013.

Minimum energy structures of the relevant intermediates and transition states.

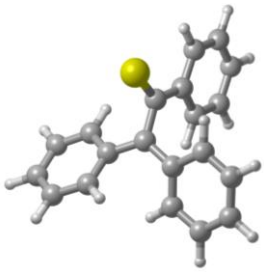




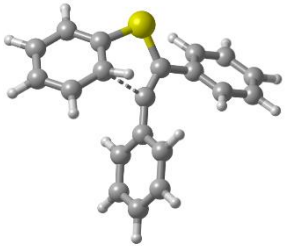
V



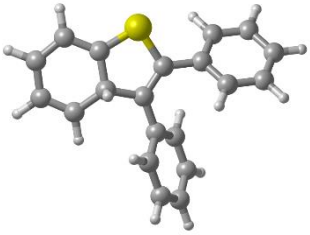
V–VI



VI



III–V‘



V‘

Cartesian coordinates and energies in Hartee of minimum energy structures

II
E_elec = 1168.955965
E_elec + E_ZPE = -1168.668276
H(298.15 K) = -1168.650199
G(298.15 K) = -1168.715602
H(373.15 K) = -1168.640860
G(373.15 K) = -1168.733099
Number of imaginary frequencies = 0
1 1
C 0.035725 4.248841 1.366394
C -0.049873 2.965592 1.901128
C -0.059127 1.856238 1.064770
C 0.018934 2.065895 -0.306342
C 0.105630 3.336567 -0.862496
C 0.113745 4.435196 -0.009344
H -0.110513 2.824991 2.972691
H -0.125763 0.857561 1.480226
H 0.166625 3.471016 -1.936306
H 0.180734 5.432783 -0.423893
S 0.009617 0.706537 -1.487281
C 0.642763 -0.723488 -0.584982
C -0.654299 -0.711669 -0.591758
C -1.982825 -1.151235 -0.256944
C -3.094161 -0.424000 -0.692837
C -2.142701 -2.306758 0.519447
C -4.367411 -0.858871 -0.356090
H -2.957708 0.470979 -1.288627
C -3.420426 -2.730770 0.846915
H -1.275721 -2.859782 0.857881
C -4.530402 -2.009427 0.410420
H -5.231737 -0.300167 -0.691015
H -3.552205 -3.623822 1.444229
H -5.526215 -2.345888 0.670987
C 1.961719 -1.191628 -0.252060
C 2.104764 -2.419985 0.407102
C 3.081714 -0.420070 -0.575397
C 3.373990 -2.867037 0.737050
H 1.232883 -3.015344 0.646276
C 4.346046 -0.878224 -0.236190
H 2.958786 0.529052 -1.083814
C 4.492061 -2.098319 0.417899
H 3.492901 -3.816446 1.243166
H 5.216508 -0.283970 -0.482272
H 5.480930 -2.453455 0.680050
H 0.041422 5.106811 2.026817

II-III
E_elec = 1168.936738
E_elec + E_ZPE = -1168.650257
H(298.15 K) = -1168.632560
G(298.15 K) = -1168.696773
H(373.15 K) = -1168.623384
G(373.15 K) = -1168.713952
Number of imaginary frequencies = 1
C 3.535793 -1.996832 0.600216
C 2.415034 -2.387170 1.329765
C 1.145742 -2.268399 0.775433
C 1.009364 -1.746371 -0.510911
C 2.126958 -1.360506 -1.249465
C 3.393355 -1.489772 -0.687612
H 2.528456 -2.789902 2.328618
H 0.266664 -2.570272 1.332401
H 2.002559 -0.957708 -2.247504
H 4.265298 -1.190771 -1.255954
S -0.619223 -1.560060 -1.221175
C -1.203168 -0.052447 -0.395374
C -0.265734 0.809899 -0.199477
C 0.877204 1.504742 0.044886
C 1.662180 1.162382 1.187925
C 1.348246 2.466488 -0.898369
C 2.891312 1.753323 1.358576
H 1.278892 0.430609 1.887911
C 2.580104 3.043776 -0.705720
H 0.732266 2.707344 -1.755417
C 3.342682 2.683916 0.414206
H 3.508697 1.501618 2.210235
H 2.964648 3.767720 -1.411114
H 4.314948 3.142120 0.553525
C -2.639323 0.092306 -0.078099
C -3.229228 1.358775 -0.131570
C -3.393223 -1.022781 0.289164
C -4.569521 1.506042 0.194738
H -2.641939 2.214703 -0.443506
C -4.735290 -0.864497 0.612572
H -2.931442 -2.001249 0.331123
C -5.323227 0.395556 0.566775
H -5.028089 2.485818 0.150017
H -5.320918 -1.728345 0.900724
H -6.370699 0.512423 0.815890
H 4.522654 -2.093724 1.035898

III
E_elec = 1168.937213
E_elec + E_ZPE = -1168.650582
H(298.15 K) = -1168.631978
G(298.15 K) = -1168.699450
H(373.15 K) = -1168.622578
G(373.15 K) = -1168.717476
Number of imaginary frequencies = 0
1 1
C 3.755053 -1.555492 0.097128
C 2.947569 -1.909333 1.175277
C 1.583259 -2.104107 0.990041
C 1.039372 -1.939822 -0.282432
C 1.842645 -1.604163 -1.369837

C 3.206198 -1.409829 -1.173522
H 3.378189 -2.031877 2.161375
H 0.942093 -2.366821 1.822827
H 1.400423 -1.480946 -2.351331
H 3.836635 -1.143376 -2.012724
S -0.734239 -2.057338 -0.502722
C -1.163009 -0.356857 -0.153112
C -0.211204 0.510802 -0.034300
C 0.848202 1.350472 0.095906
C 1.528940 1.442550 1.348554
C 1.323304 2.073327 -1.041565
C 2.652548 2.228194 1.445500
H 1.149145 0.881019 2.192840
C 2.445103 2.856029 -0.918981
H 0.790721 1.980963 -1.979844
C 3.101509 2.927389 0.317817
H 3.189076 2.308322 2.381054
H 2.825211 3.410957 -1.765758
H 3.988472 3.544337 0.403750
C -2.600586 -0.004124 -0.028254
C -3.069959 1.188239 -0.583594
C -3.470301 -0.864032 0.644099
C -4.411795 1.521632 -0.456583
H -2.390283 1.837079 -1.123838
C -4.811559 -0.522442 0.761475
H -3.099623 -1.783775 1.079917
C -5.282275 0.667700 0.214370
H -4.778410 2.443900 -0.889325
H -5.488722 -1.187584 1.282297
H -6.329489 0.927616 0.307187
H 4.816304 -1.399222 0.247205

III–IVa
E_elec = 1168.928578
E_elec + E_ZPE = -1168.642685
H(298.15 K) = -1168.624839
G(298.15 K) = -1168.689518
H(373.15 K) = -1168.615640
G(373.15 K) = -1168.706818
Number of imaginary frequencies = 1
1 1
C 3.578056 -1.200190 -0.019815
C 2.925895 -1.492091 1.181655
C 1.611118 -1.917170 1.163762
C 0.937792 -2.004752 -0.072118
C 1.624610 -1.798471 -1.285961
C 2.941241 -1.376746 -1.249803
H 3.446981 -1.382125 2.123786
H 1.073923 -2.134109 2.079220
H 1.096626 -1.925008 -2.223572
H 3.472392 -1.178903 -2.171725
S -0.817831 -2.444370 -0.110678
C -1.081658 -0.698159 -0.043029
C 0.084400 -0.081267 -0.004471
C 0.973779 0.996953 0.045992
C 1.420699 1.600060 -1.153232
C 1.416996 1.489012 1.295348
C 2.256893 2.697415 -1.094736
H 1.088383 1.196584 -2.102463
C 2.252760 2.588384 1.337728
H 1.081238 1.003830 2.203897
C 2.668077 3.187352 0.147075
H 2.593947 3.174055 -2.005685
H 2.586184 2.981860 2.288869
H 3.326231 4.047082 0.186786
C -2.412205 -0.066551 -0.027332
C -2.564557 1.284269 -0.355933
C -3.527237 -0.830717 0.321282
C -3.824933 1.862003 -0.326420
H -1.703036 1.876052 -0.642984
C -4.787154 -0.245353 0.345223
H -3.415015 -1.877284 0.582142
C -4.937036 1.099278 0.023988
H -3.941441 2.907200 -0.583955
H -5.649627 -0.841166 0.615931
H -5.920043 1.553357 0.042068
H 4.603333 -0.851071 0.003305

IVa
E_elec = 1168.933601
E_elec + E_ZPE = -1168.646295
H(298.15 K) = -1168.628245
G(298.15 K) = -1168.693259
H(373.15 K) = -1168.618932
G(373.15 K) = -1168.710655
Number of imaginary frequencies = 0
C -3.845999 -1.159942 0.046811
C -3.225055 -1.383908 -1.194611
C -1.892553 -1.692860 -1.223971
C -1.124813 -1.684869 0.004780
C -1.834629 -1.585544 1.264053
C -3.166411 -1.269003 1.271312
H -3.800077 -1.317037 -2.107793
H -1.360693 -1.863623 -2.153565
H -1.259485 -1.672061 2.179266
H -3.696184 -1.116156 2.201190
S 0.488585 -2.564731 0.010556
C 0.951217 -0.844946 -0.038612
C -0.267666 -0.294580 -0.048497
C -0.842580 1.050249 -0.002107
C -0.761112 1.786120 1.186473
C -1.449735 1.615275 -1.128122
C -1.267608 3.077483 1.239292
H -0.289824 1.342507 2.056335
C -1.959286 2.906821 -1.067597
H -1.504343 1.051123 -2.052080
C -1.868410 3.636517 0.113812
H -1.194986 3.647370 2.157162
H -2.421689 3.344316 -1.943517
H -2.265338 4.643371 0.157812

C 2.306608 -0.305898 -0.061559
C 2.532324 1.046394 -0.348752
C 3.387808 -1.149975 0.202262
C 3.828327 1.539996 -0.361415
H 1.698004 1.701829 -0.568229
C 4.683119 -0.648337 0.189219
H 3.218551 -2.198389 0.425294
C 4.904013 0.696027 -0.090979
H 4.001721 2.584983 -0.586163
H 5.517246 -1.306538 0.397163
H 5.913894 1.087289 -0.102397
H -4.899506 -0.903403 0.059874

IVa-IVb
E_elec = 1168.933415
E_elec + E_ZPE = -1168.646143
H(298.15 K) = -1168.628953
G(298.15 K) = -1168.691474
H(373.15 K) = -1168.619888
G(373.15 K) = -1168.708215
Number of imaginary frequencies = 1
C 3.996374 -1.240186 -0.069764
C 3.369142 -1.429177 1.176492
C 2.015342 -1.605504 1.214466
C 1.231288 -1.522910 -0.008671
C 1.944243 -1.432019 -1.273544
C 3.297545 -1.242493 -1.289904
H 3.959152 -1.438424 2.082410
H 1.479254 -1.748858 2.146487
H 1.353722 -1.439725 -2.183277
H 3.831671 -1.111170 -2.220467
S -0.320946 -2.534112 -0.039834
C -0.900789 -0.850508 0.045245
C 0.287889 -0.233955 0.067277
C 0.754572 1.154165 0.006666
C 0.352712 1.955119 -1.069547
C 1.584995 1.690554 0.994713
C 0.766489 3.278033 -1.144543
H -0.286221 1.533452 -1.837401
C 2.002605 3.013653 0.909909
H 1.886567 1.082863 1.839820
C 1.594169 3.807246 -0.157368
H 0.447804 3.894689 -1.975780
H 2.640634 3.425827 1.681693
H 1.919747 4.838356 -0.220023
C -2.290405 -0.410504 0.082859
C -2.617533 0.884748 0.503919
C -3.304417 -1.295567 -0.291142
C -3.945274 1.284180 0.534535
H -1.835660 1.567398 0.814427
C -4.632068 -0.888076 -0.260301
H -3.056553 -2.301112 -0.615118
C -4.953122 0.401507 0.150252
H -4.196611 2.284780 0.863586
H -5.413374 -1.577177 -0.555142
H -5.988337 0.718857 0.176213
H 5.070811 -1.093789 -0.089379

IVb
E_elec = 1168.935789
E_elec + E_ZPE = -1168.648051
H(298.15 K) = -1168.630000
G(298.15 K) = -1168.695666
H(373.15 K) = -1168.620720
G(373.15 K) = -1168.713223
Number of imaginary frequencies = 0
1 1
C -4.116172 -1.766080 0.214072
C -3.635185 -1.436296 -1.076737
C -2.342151 -1.042887 -1.223477
C -1.448674 -0.985725 -0.068505
C -2.016844 -1.295892 1.240048
C -3.324334 -1.697354 1.363984
H -4.300274 -1.495275 -1.926970
H -1.925900 -0.781455 -2.189983
H -1.360452 -1.203666 2.098905
H -3.740321 -1.947089 2.329818
S -0.083821 -2.340863 -0.194251
C 0.760386 -0.768385 -0.088554
C -0.318278 0.034684 -0.068899
C -0.548449 1.477892 -0.075610
C -1.776763 1.988265 0.356257
C 0.424024 2.359768 -0.566191
C -2.024160 3.355202 0.317612
H -2.543029 1.320865 0.739994
C 0.172616 3.723204 -0.600855
H 1.365009 1.971972 -0.937823
C -1.049061 4.225731 -0.156470
H -2.977469 3.738280 0.659797
H 0.928449 4.396535 -0.986003
H -1.240735 5.291160 -0.186702
C 2.208202 -0.622885 0.013020
C 2.762264 0.373124 0.825906
C 3.046006 -1.511940 -0.665964
C 4.140260 0.484460 0.938706
H 2.110712 1.045015 1.372742
C 4.425310 -1.395291 -0.548192
H 2.618281 -2.283475 -1.297737
C 4.972682 -0.396694 0.250877
H 4.567003 1.253385 1.570562
H 5.071062 -2.082366 -1.080392
H 6.048060 -0.306849 0.343089
H -5.149344 -2.080636 0.312562

IVb–V
E_elec = 1168.935755
E_elec + E_ZPE = -1168.647886
H(298.15 K) = -1168.630824
G(298.15 K) = -1168.692523
H(373.15 K) = -1168.621791

G(373.15 K) = -1168.709053
Number of imaginary frequencies = 1
1 1
C -4.066987 -1.870673 0.296173
C -3.692387 -1.418790 -1.000600
C -2.443580 -0.933161 -1.207386
C -1.476242 -0.908554 -0.113290
C -1.933323 -1.328102 1.206429
C -3.208597 -1.831256 1.386578
H -4.414299 -1.456663 -1.804787
H -2.116141 -0.575570 -2.176785
H -1.239488 -1.218641 2.032679
H -3.536895 -2.166678 2.360178
S -0.138699 -2.309423 -0.255993
C 0.733666 -0.753149 -0.140902
C -0.327101 0.076439 -0.121468
C -0.527255 1.522568 -0.092302
C -1.755854 2.037211 0.335349
C 0.465252 2.403052 -0.543562
C -1.985134 3.407675 0.328304
H -2.534731 1.367794 0.689841
C 0.231229 3.769842 -0.547063
H 1.407415 2.012543 -0.909421
C -0.991202 4.276451 -0.108600
H -2.938100 3.794971 0.666578
H 1.001341 4.443460 -0.902146
H -1.168143 5.344852 -0.113366
C 2.182818 -0.643154 -0.013326
C 2.745274 0.326945 0.824752
C 3.011776 -1.539121 -0.693967
C 4.123340 0.405196 0.961865
H 2.099940 1.004126 1.372392
C 4.391160 -1.456590 -0.550764
H 2.577695 -2.288537 -1.347796
C 4.947135 -0.483689 0.273606
H 4.556642 1.154007 1.613105
H 5.030179 -2.149136 -1.083964
H 6.022563 -0.419565 0.384750
H -5.072720 -2.251026 0.435671

V
E_elec = 1168.988236
E_elec + E_ZPE = -1168.699673
H(298.15 K) = -1168.682451
G(298.15 K) = -1168.744450
H(373.15 K) = -1168.673310
G(373.15 K) = -1168.761067
Number of imaginary frequencies = 0
1 1
C 4.589963 -0.728165 0.362756
C 4.196917 0.660330 0.338573
C 2.921777 1.063304 0.070206
C 1.931061 0.078234 -0.173577
C 2.366518 -1.311915 -0.428349
C 3.713755 -1.699798 0.053104
H 2.636364 2.104508 0.144899
H 2.460178 -1.366255 -1.536262
H 3.994769 -2.745166 0.032625
S 0.910446 -2.374068 -0.187583
C -0.118546 -1.004303 -0.114374
C 0.544504 0.232541 -0.124594
C -0.126690 1.545464 0.019112
C 0.092772 2.548383 -0.927021
C -0.976624 1.787602 1.101018
C -0.539364 3.780189 -0.796084
H 0.745233 2.356947 -1.772191
C -1.604188 3.019722 1.229113
H -1.142996 1.010337 1.838524
C -1.389068 4.015703 0.279900
H -0.370796 4.552395 -1.536425
H -2.260485 3.203522 2.070725
H -1.882711 4.974571 0.380152
C -1.563818 -1.228154 -0.083506
C -2.420073 -0.407918 -0.832413
C -2.093051 -2.286906 0.666602
C -3.784049 -0.653250 -0.829224
H -2.014168 0.399116 -1.429311
C -3.461660 -2.512411 0.678780
H -1.437147 -2.909597 1.264627
C -4.306536 -1.698169 -0.069695
H -4.441907 -0.028120 -1.419428
H -3.867971 -3.320475 1.273439
H -5.374647 -1.877390 -0.061979
H 4.942430 1.405662 0.588502
H 5.605112 -0.977870 0.641466

V–VI
E_elec = 1168.956198
E_elec + E_ZPE = -1168.667962
H(298.15 K) = -1168.651047
G(298.15 K) = -1168.712349
H(373.15 K) = -1168.642077
G(373.15 K) = -1168.728772
Number of imaginary frequencies = 1
1 1
C -1.154688 3.976110 -0.281924
C -1.584294 2.968735 -1.145826
C -1.037978 1.700504 -1.056349
C -0.028919 1.435259 -0.113892
C 0.403840 2.460283 0.745137
C -0.165696 3.721051 0.665092
H -2.347436 3.175831 -1.884914
H -1.368355 0.917322 -1.728018
H 1.158092 2.247854 1.494023
H 0.155523 4.502503 1.341592
S 0.639375 -2.496486 -0.582188
C -0.192120 -1.108200 -0.196490
C 0.574872 0.113887 -0.025967
C 1.953874 -0.071757 0.193096
C 2.911026 0.872395 -0.282284

C 2.422316 -1.333729 0.704618
C 4.230051 0.521005 -0.352833
H 2.565747 1.813868 -0.688960
C 3.784363 -1.665305 0.619615
H 1.820261 -1.849425 1.445661
C 4.666824 -0.752406 0.094904
H 4.948536 1.207857 -0.780857
H 4.133339 -2.604618 1.026613
C -1.643588 -1.147285 0.033267
C -2.218097 -0.403521 1.076356
C -2.457752 -1.969712 -0.757317
C -3.577618 -0.497532 1.326462
H -1.596995 0.223941 1.704044
C -3.821491 -2.040181 -0.516211
H -2.019939 -2.527308 -1.576976
C -4.381402 -1.308195 0.527047
H -4.012727 0.062790 2.144170
H -4.447273 -2.662509 -1.143064
H -5.446275 -1.365916 0.716363
H -1.596559 4.962990 -0.345693
H 5.722928 -0.989839 0.052010

VI
E_elec = 1168.974451
E_elec + E_ZPE = -1168.686056
H(298.15 K) = -1168.668036
G(298.15 K) = -1168.733117
H(373.15 K) = -1168.658809
G(373.15 K) = -1168.750520
Number of imaginary frequencies = 0
1 1
C 3.659557 -2.587202 -0.679702
C 3.977079 -1.294058 -0.263783
C 2.967765 -0.411523 0.069319
C 1.618362 -0.827314 0.003820
C 1.316590 -2.156387 -0.374363
C 2.331986 -3.017264 -0.737005
H 5.011445 -0.985846 -0.188532
H 3.208086 0.576710 0.440068
H 0.285188 -2.487290 -0.413539
H 2.100521 -4.025254 -1.054742
S -0.487979 -0.855547 2.495241
C -0.695051 -0.511330 0.914611
C 0.550093 0.064021 0.340238
C 0.609229 1.487236 0.157465
C 1.456320 2.039070 -0.833789
C -0.248114 2.347130 0.883614
C 1.458230 3.402079 -1.065282
H 2.050611 1.387692 -1.460446
C -0.218753 3.707271 0.658532
H -0.898810 1.944028 1.648959
C 0.633971 4.236251 -0.313637
H 2.090951 3.814732 -1.839912
H -0.857535 4.363120 1.235120
C -1.897313 -0.632763 0.103537
C -1.855838 -0.324063 -1.266467
C -3.096664 -1.084018 0.677039
C -2.995232 -0.460920 -2.044140
H -0.936139 0.020282 -1.726704
C -4.230301 -1.213577 -0.104019
H -3.123792 -1.325521 1.732440
C -4.181042 -0.902227 -1.463765
H -2.959992 -0.223634 -3.099489
H -5.155435 -1.557742 0.340224
H -5.071396 -1.006192 -2.071815
H 4.454701 -3.273160 -0.945493
H 0.644030 5.304354 -0.493334

III–V'
E_elec = 1168.920212
E_elec + E_ZPE = -1168.634463
H(298.15 K) = -1168.616628
G(298.15 K) = -1168.681957
H(373.15 K) = -1168.607445
G(373.15 K) = -1168.699418
Number of imaginary frequencies = 1
1 1
C 4.143770 -0.873075 0.234616
C 3.772671 -2.122480 0.746904
C 2.524423 -2.672551 0.472666
C 1.655321 -1.967069 -0.346004
C 2.030487 -0.742788 -0.915820
C 3.280529 -0.185000 -0.595029
H 4.452182 -2.655871 1.400278
H 2.220038 -3.608578 0.923067
H 1.488616 -0.363186 -1.778962
H 3.562513 0.770540 -1.020923
S -0.038337 -2.465859 -0.560521
C -0.659057 -0.842930 -0.276720
C 0.134546 0.198210 -0.162506
C 0.410364 1.558509 0.006317
C 0.306366 2.453691 -1.083902
C 0.793417 2.028396 1.283388
C 0.558557 3.795661 -0.885969
H 0.030368 2.072523 -2.060087
C 1.030777 3.376161 1.467451
H 0.884689 1.322316 2.099324
C 0.917518 4.252261 0.385831
H 0.477575 4.492553 -1.709623
H 1.309707 3.751789 2.443001
H 1.114216 5.307245 0.534029
C -2.122563 -0.665392 -0.068268
C -2.810740 0.349468 -0.734836
C -2.799648 -1.528132 0.797249
C -4.176699 0.500289 -0.533830
H -2.282580 1.005330 -1.416502
C -4.165438 -1.370140 0.990948
H -2.258601 -2.307612 1.320167
C -4.853570 -0.357419 0.327902
H -4.712360 1.283917 -1.054599

H -4.691490 -2.036918 1.662496
H -5.918885 -0.238078 0.482100
H 5.111221 -0.456244 0.482225

V'
E_elec = 1168.978939
E_elec + E_ZPE = -1168.691080
H(298.15 K) = -1168.673794
G(298.15 K) = -1168.736044
H(373.15 K) = -1168.664612
G(373.15 K) = -1168.752729
Number of imaginary frequencies = 0
1 1
C 4.275529 0.460901 0.390242
C 4.563411 -0.932132 0.234333
C 3.600068 -1.872882 -0.043380
C 2.279088 -1.429952 -0.176301
C 1.969016 0.008076 -0.271264
C 3.023060 0.931113 0.199176
H 5.584930 -1.264183 0.378145
H 3.837654 -2.927841 -0.072081
H 2.103095 0.130969 -1.384552
H 2.782402 1.984179 0.283367
S 0.879243 -2.371280 -0.207852
C -0.185644 -0.952110 -0.113628
C 0.495244 0.212537 -0.096708
C -0.090343 1.561183 0.023454
C 0.304556 2.589078 -0.838054
C -1.039626 1.822458 1.016441
C -0.252616 3.856661 -0.715023
H 1.029685 2.398630 -1.622430
C -1.590337 3.091053 1.137113
H -1.337732 1.030018 1.693091
C -1.200230 4.109383 0.271416
H 0.051935 4.644355 -1.392890
H -2.322597 3.285923 1.910868
H -1.632446 5.097808 0.367197
C -1.640427 -1.190120 -0.098815
C -2.477139 -0.444483 -0.934772
C -2.187600 -2.163461 0.740600
C -3.847206 -0.665362 -0.918221
H -2.049702 0.301146 -1.594829
C -3.560440 -2.380004 0.752813
H -1.543862 -2.738410 1.397491
C -4.390757 -1.631090 -0.074370
H -4.491538 -0.086871 -1.568535
H -3.979661 -3.131159 1.410471
H -5.460400 -1.800921 -0.064545
H 5.074695 1.131765 0.674556

7. References

(1) H. Shimada, S. Kikuchi, S. Okuda, K. Haraguchi and H. Tanaka, *Tetrahedron* 2009, **65**, 6008.

(2) M. Xu, B. Qiao, S. Duan, H. Liu and Z. Jiang, *Tetrahedron* 2014, **70**, 8696.

(3) Y. You, Z.-J. Wu, Z.-H. Wang, X.-Y. Xu, X.-M. Zhang and W.-C. Yuan, *J. Org. Chem.* 2015, **80**, 8470.

(4) F. Piscitelli, A. Coluccia, A. Brancale, G. L. Regina, A. Sansone, C. Giordano, J. Balzarini, G. Maga, S. Zanoli, A. Samuele, R. Cirilli, F. L. Torre, A. Lavecchia, E. Novellino and R. Silvestri, *J. Med. Chem.* 2009, **52**, 1922.

(5) F. Effenberger and W. Russ, *Chem. Ber.* 1982, **115**, 3719.

(6) K. Inamoto, Y. Arai, K. Hiroya and T. Doi, *Chem. Comm.* 2008, 5529.

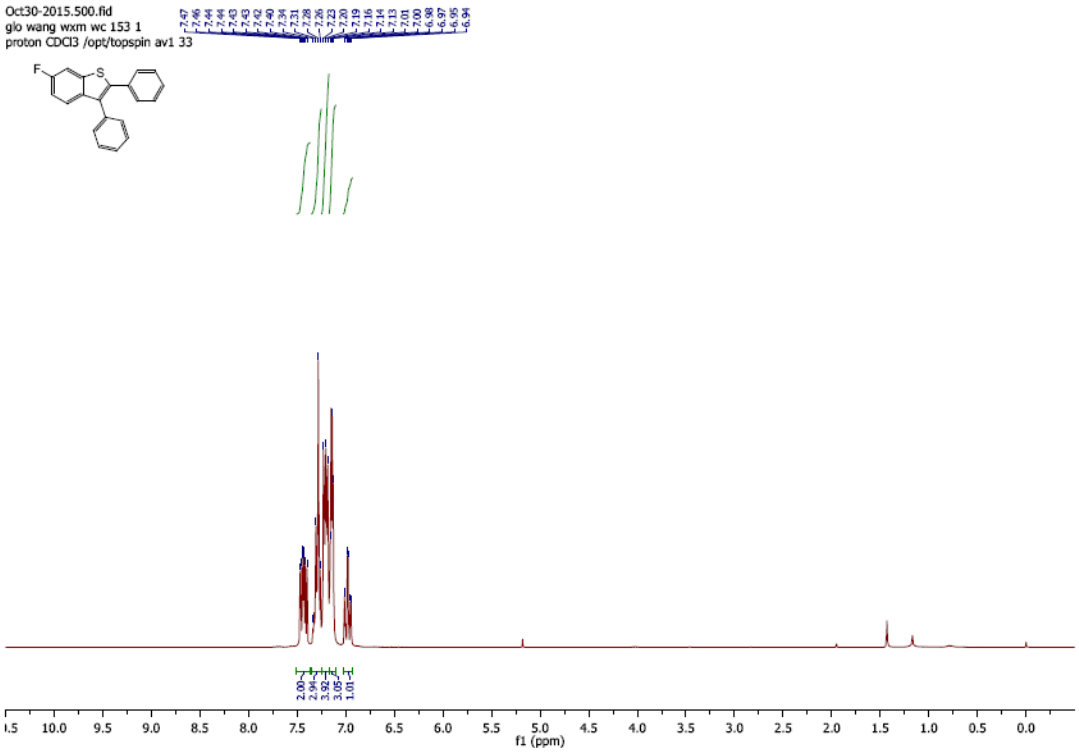
(7) K. Nobushige, K. Hirano, T. Satoh and M. Miura, *Org. Lett.* **2014**, *16*, 1188.

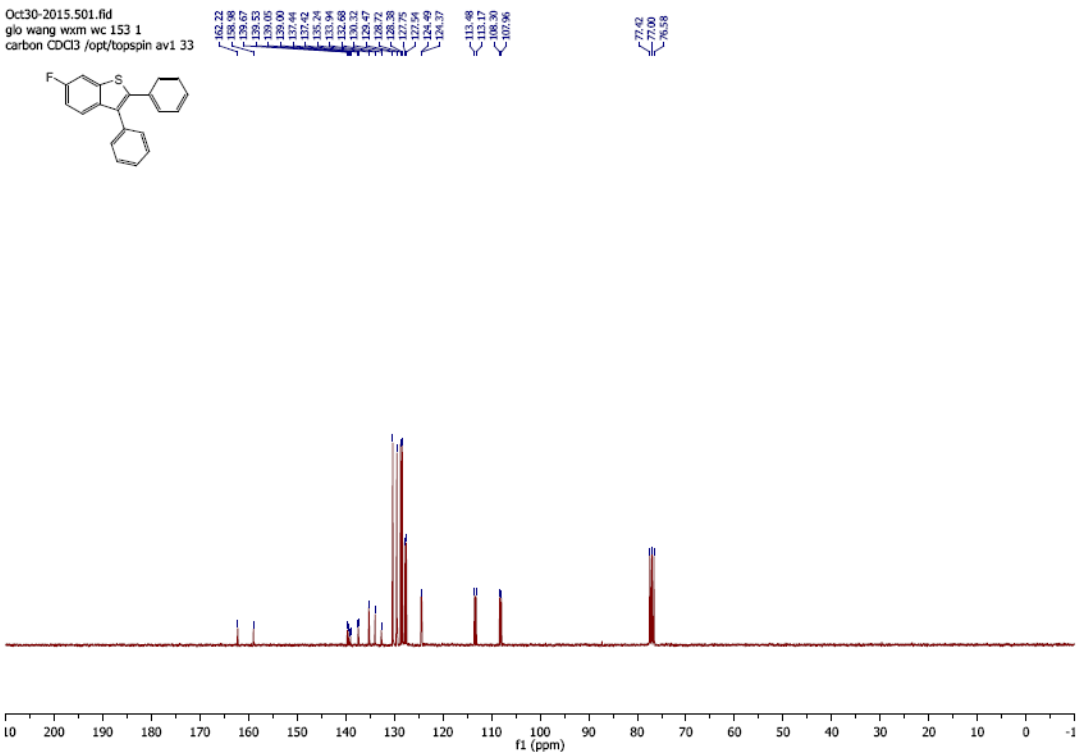
(8) A. B. Bíró and A. Kotschy, *Eur. J. Org. Chem.* 2007, 1364.

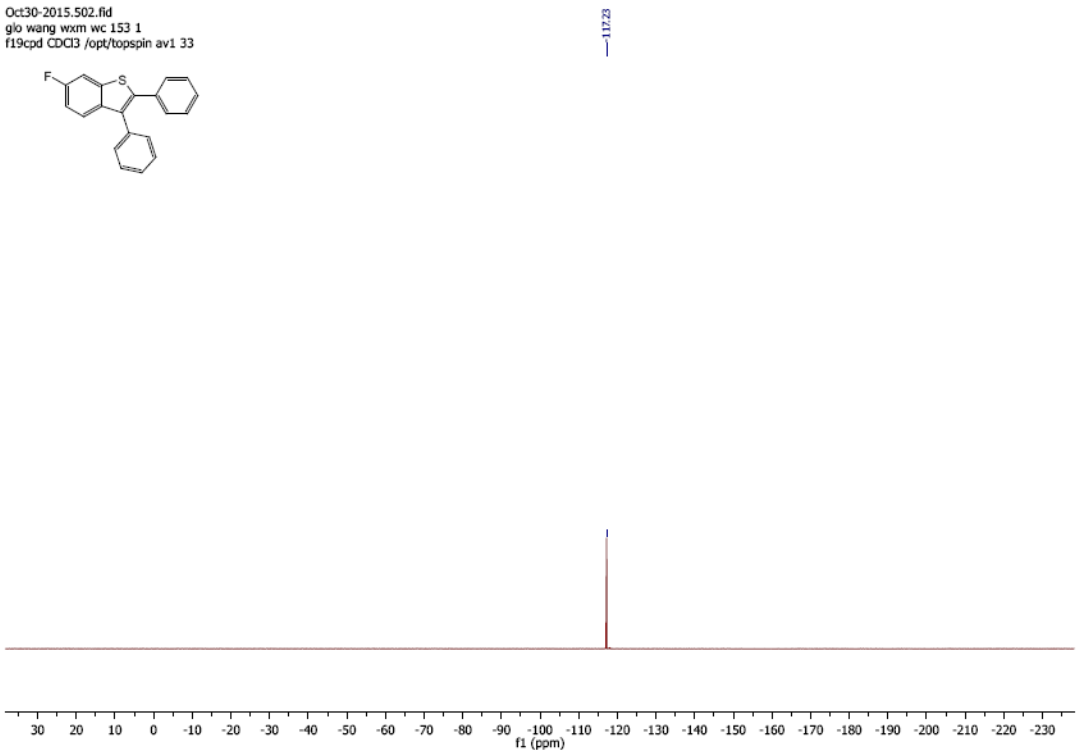
(9) D. Yang, K. Yan, W. Wei, L. Tian, Q. Li, J. You and H. Wang, *RSC Adv.* 2014, **4**, 48547.

8. NMR spectra of the Benzo[b]thiophenes 3

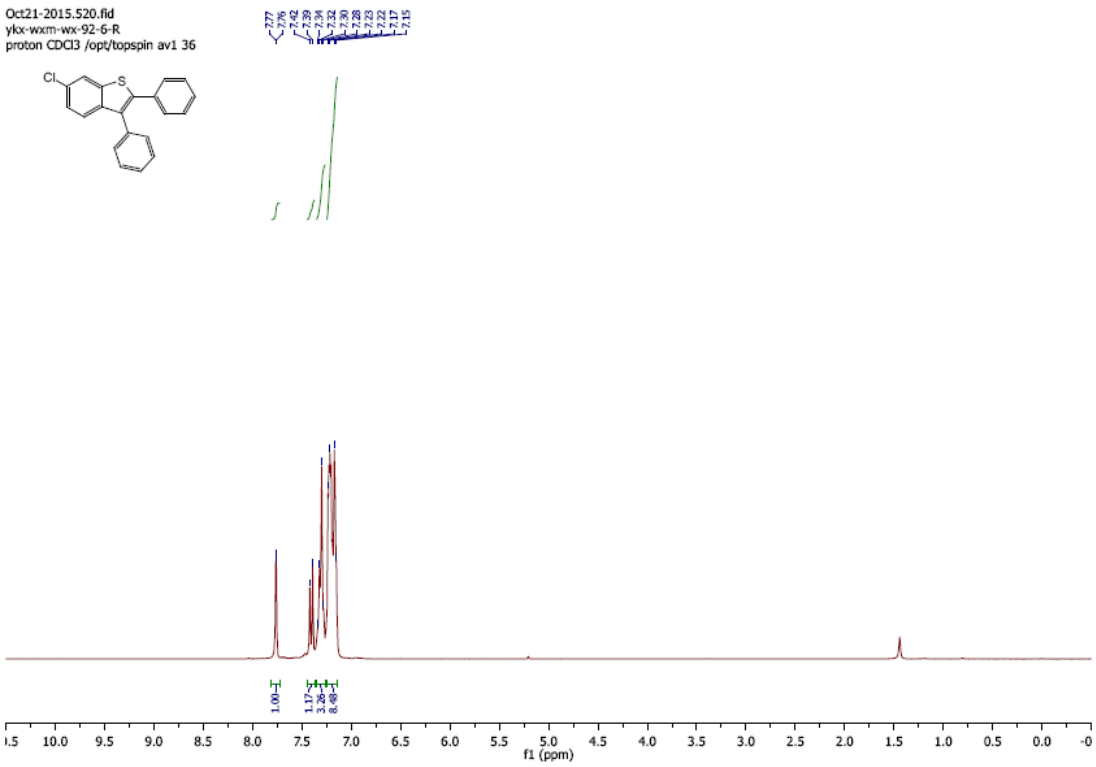
6-fluoro-2,3-diphenylbenzo[b]thiophene (**3a/3g**)

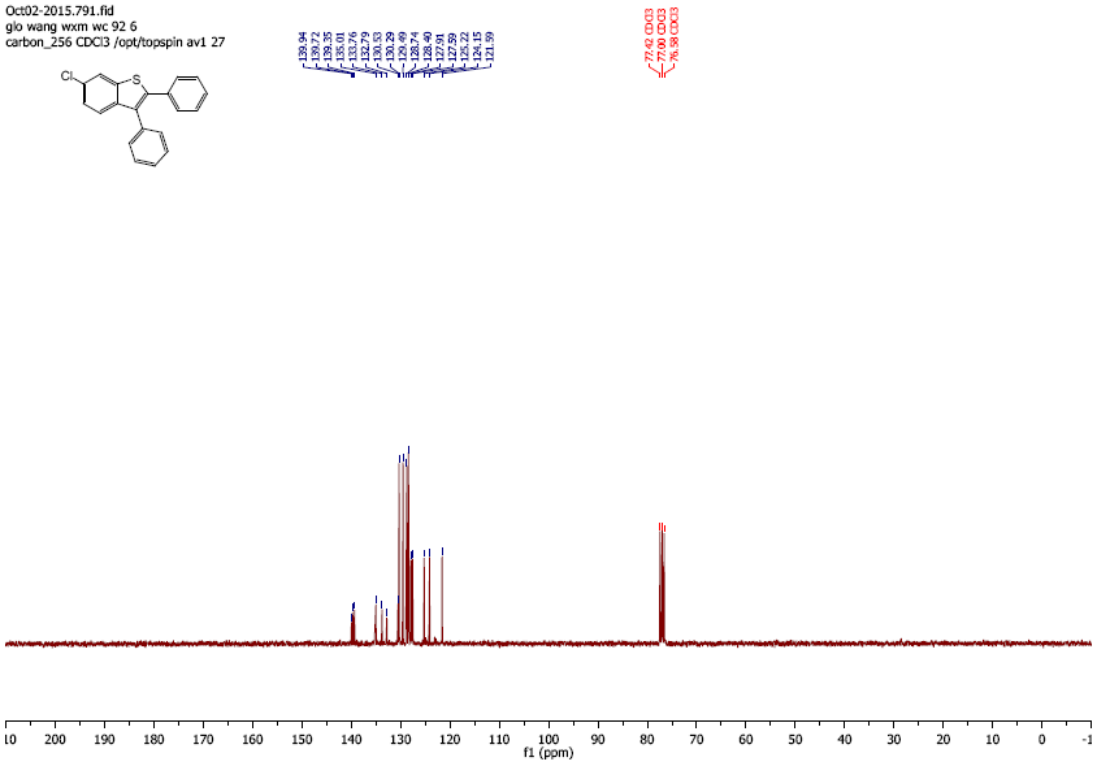




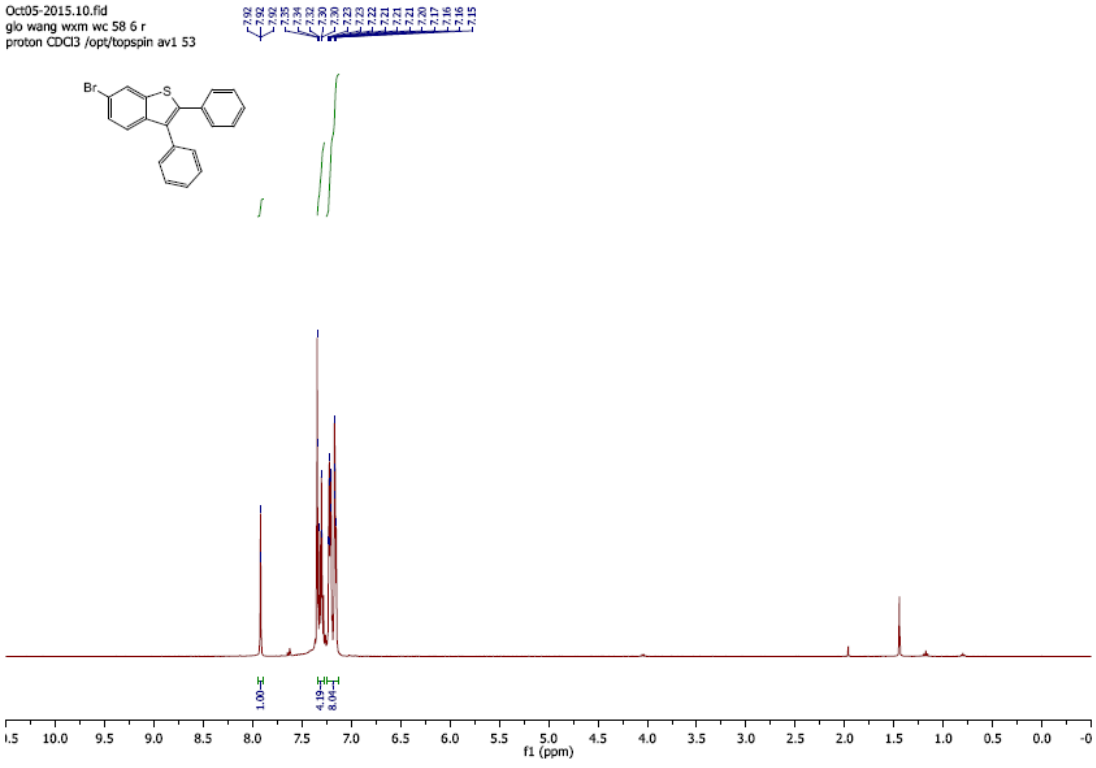


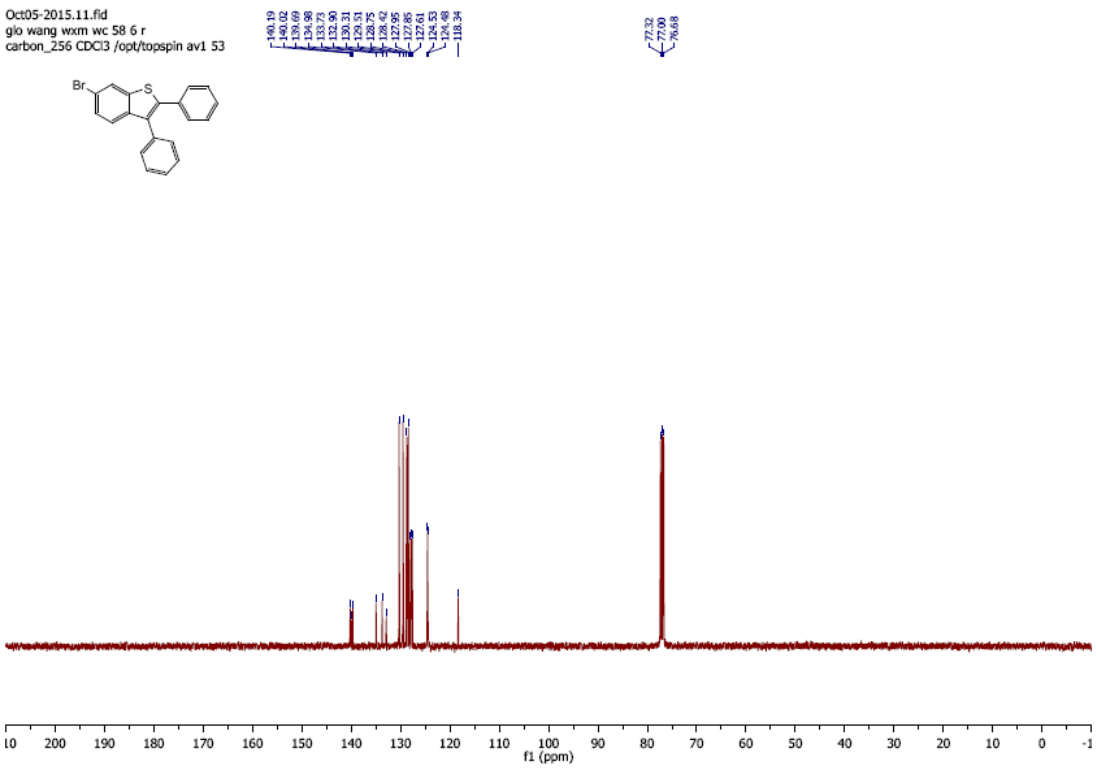
6-chloro-2,3-diphenylbenzo[b]thiophene (**3b**)



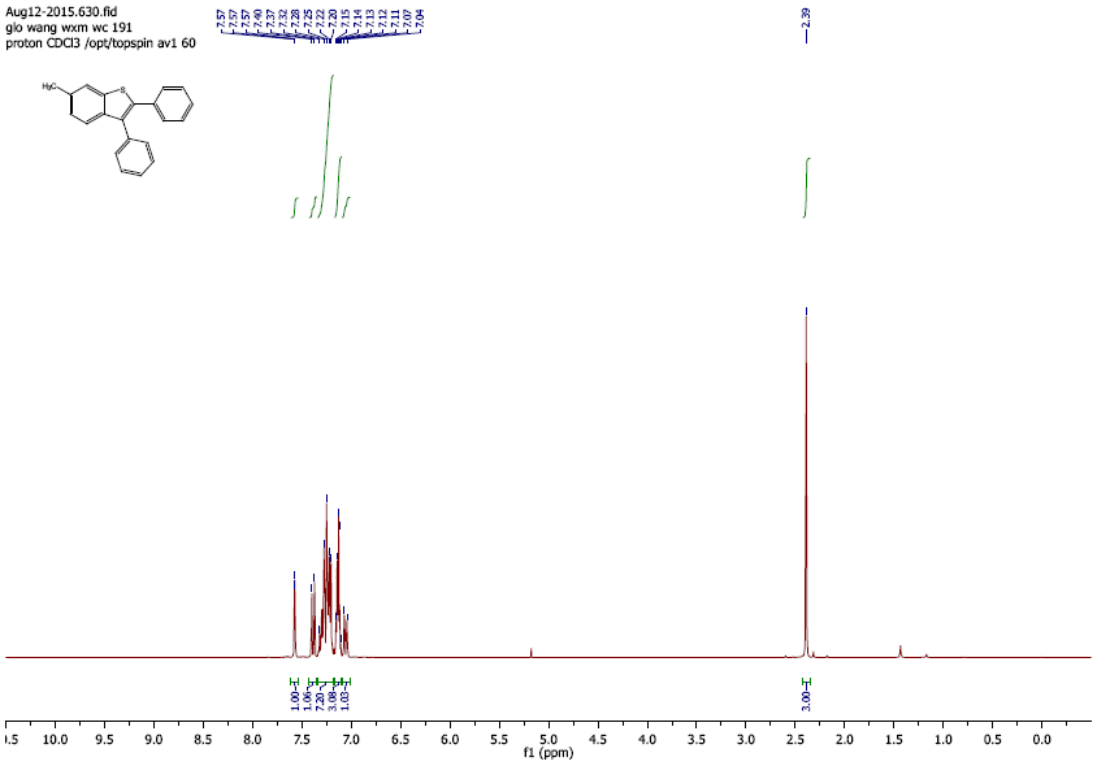


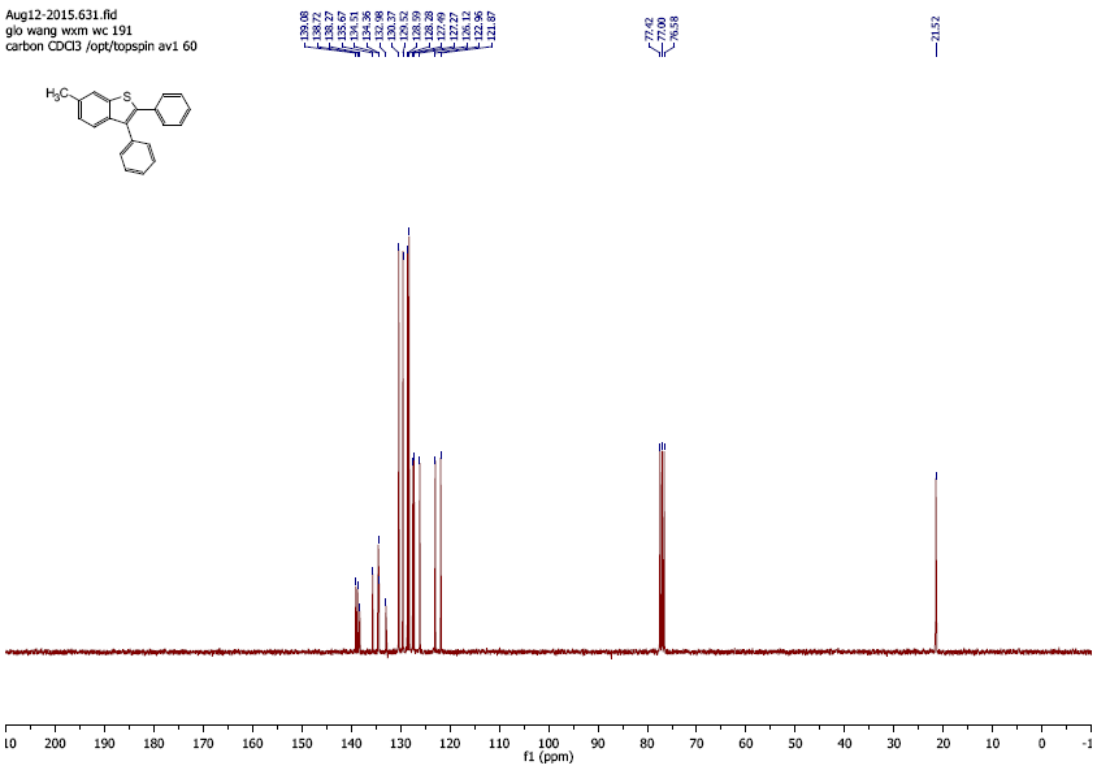
6-bromo-2,3-diphenylbenzo[b]thiophene (**3c**)



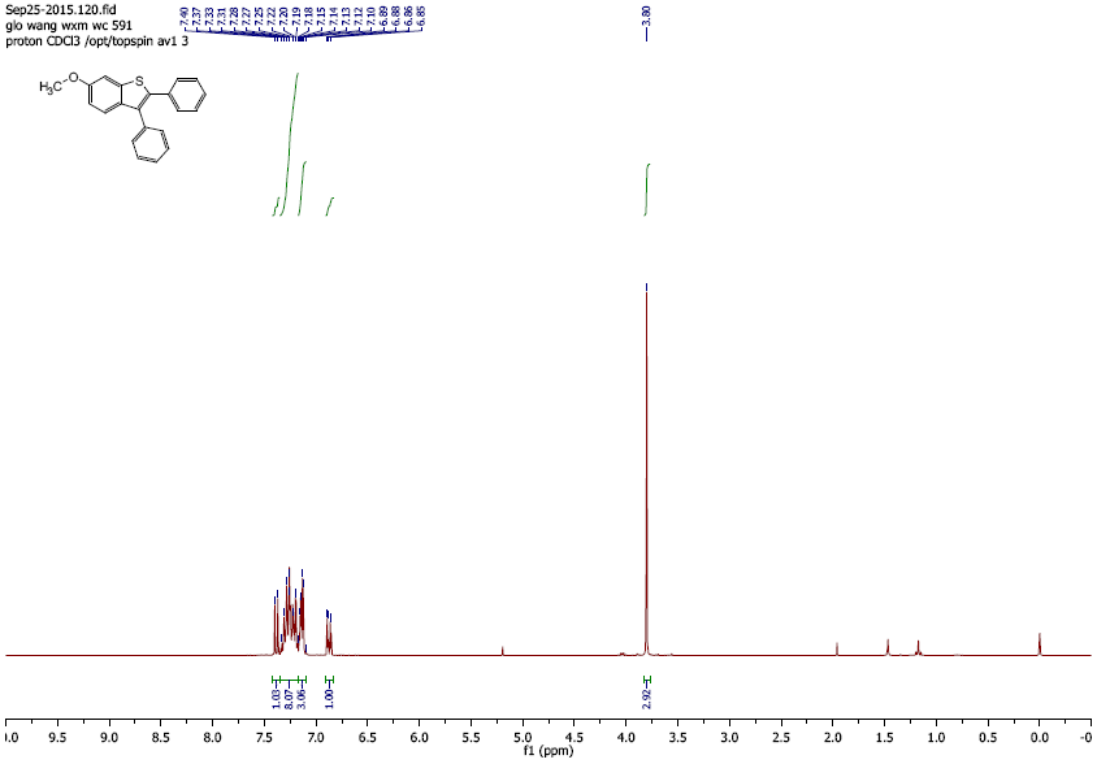


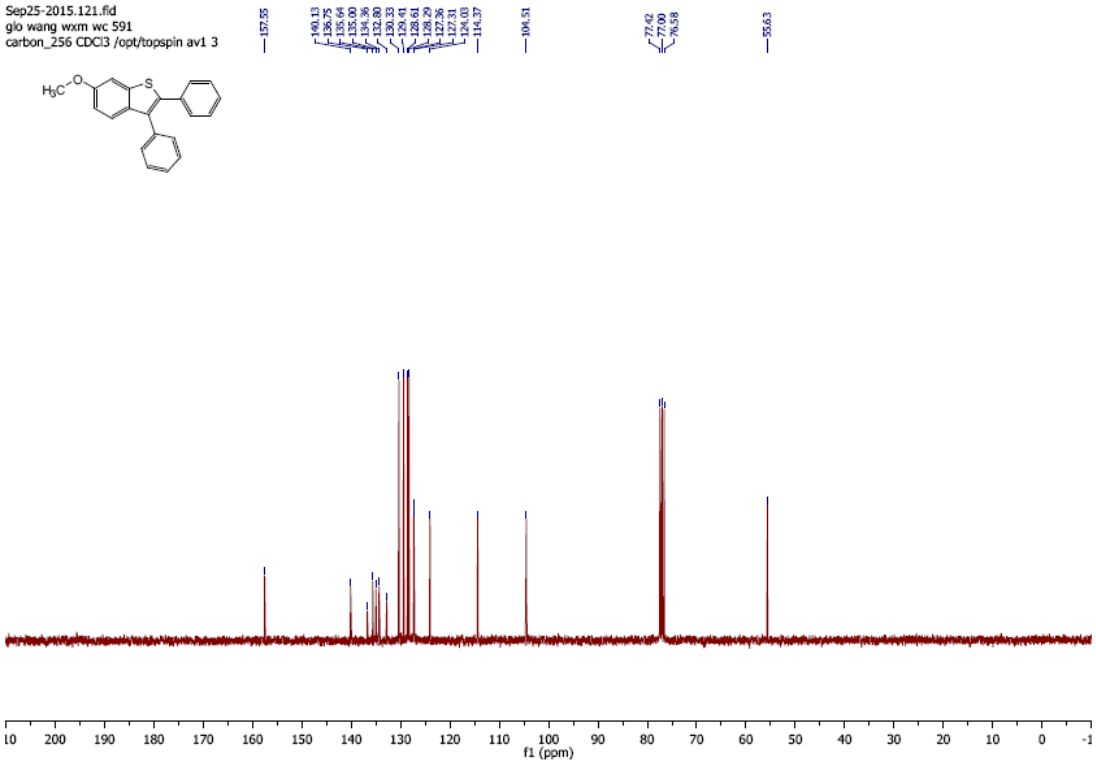
6-methyl-2,3-diphenylbenzo[b]thiophene (**3d**)



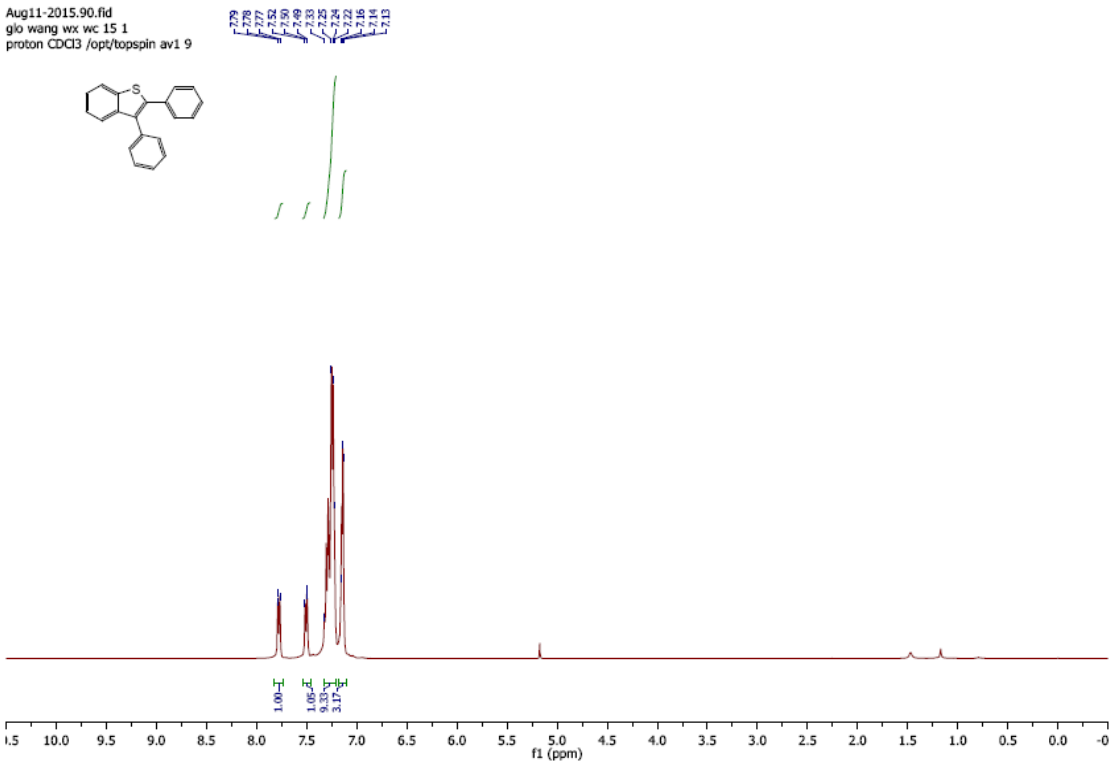


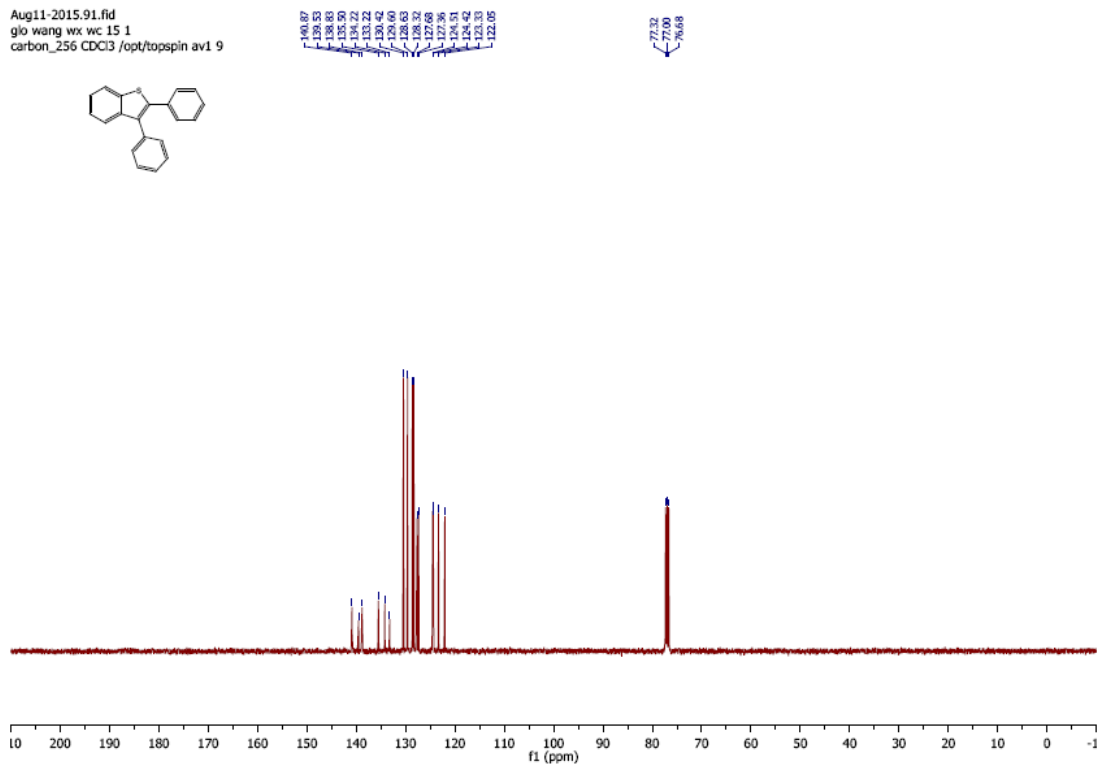
6-methoxy-2,3-diphenylbenzo[b]thiophene (**3e**)



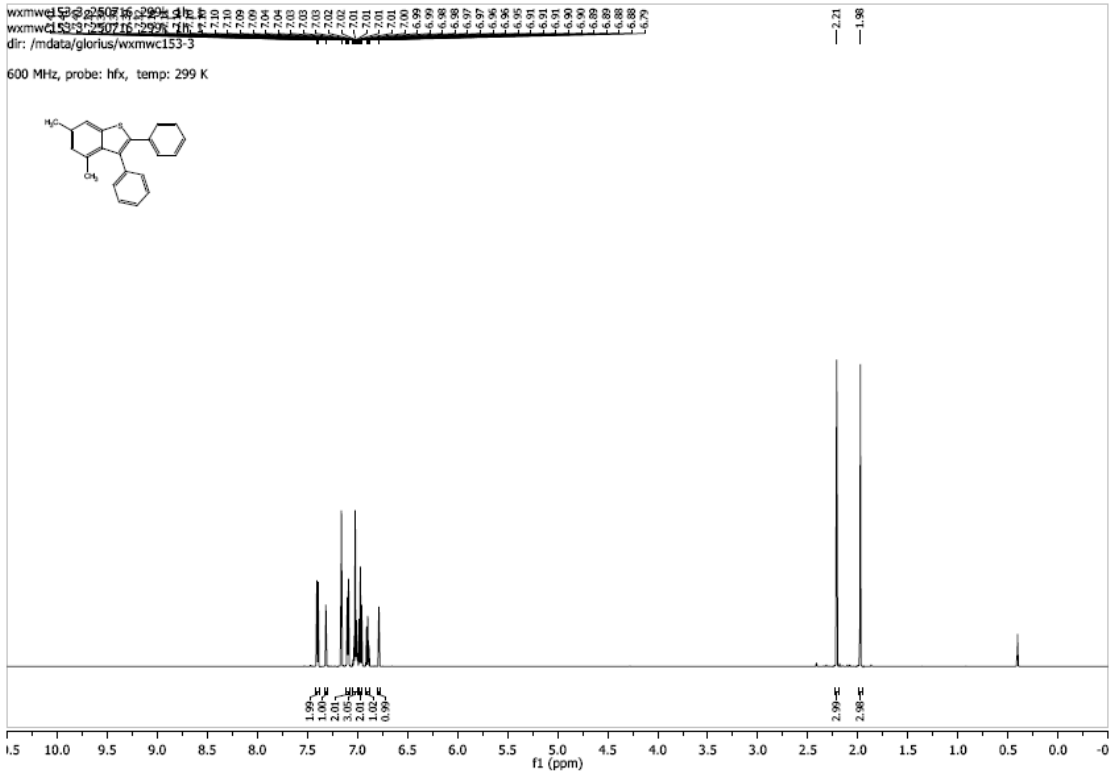


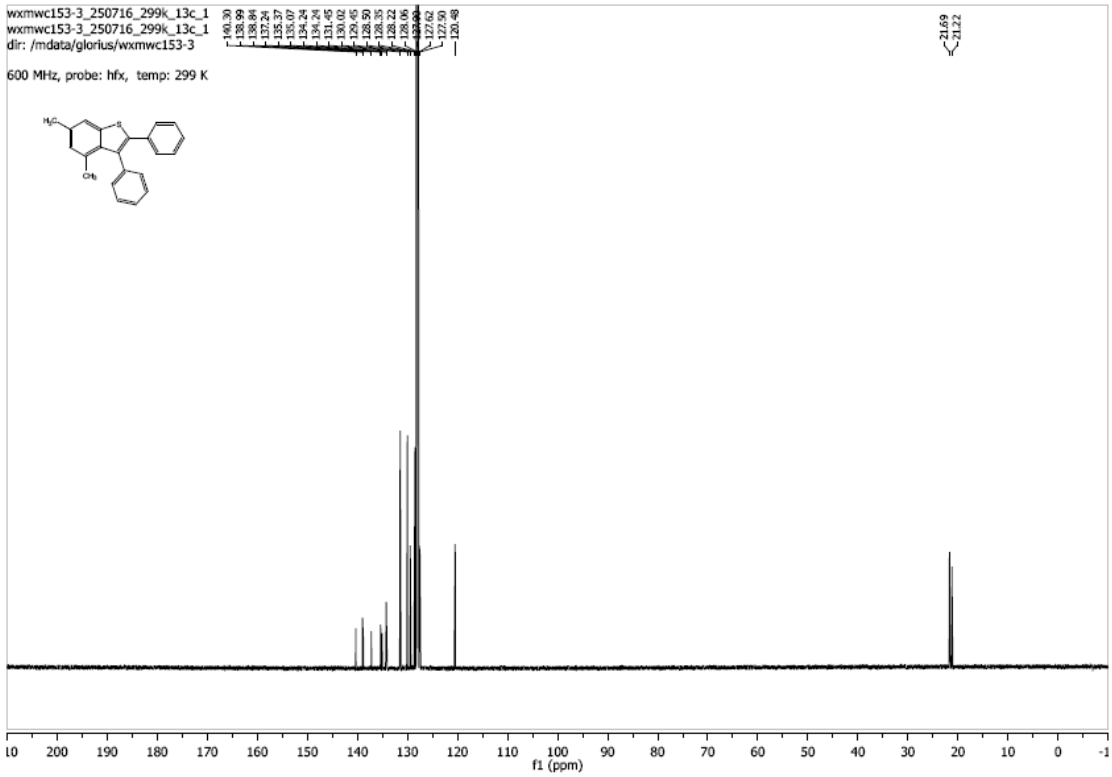
2,3-diphenylbenzo[b]thiophene (**3f**)



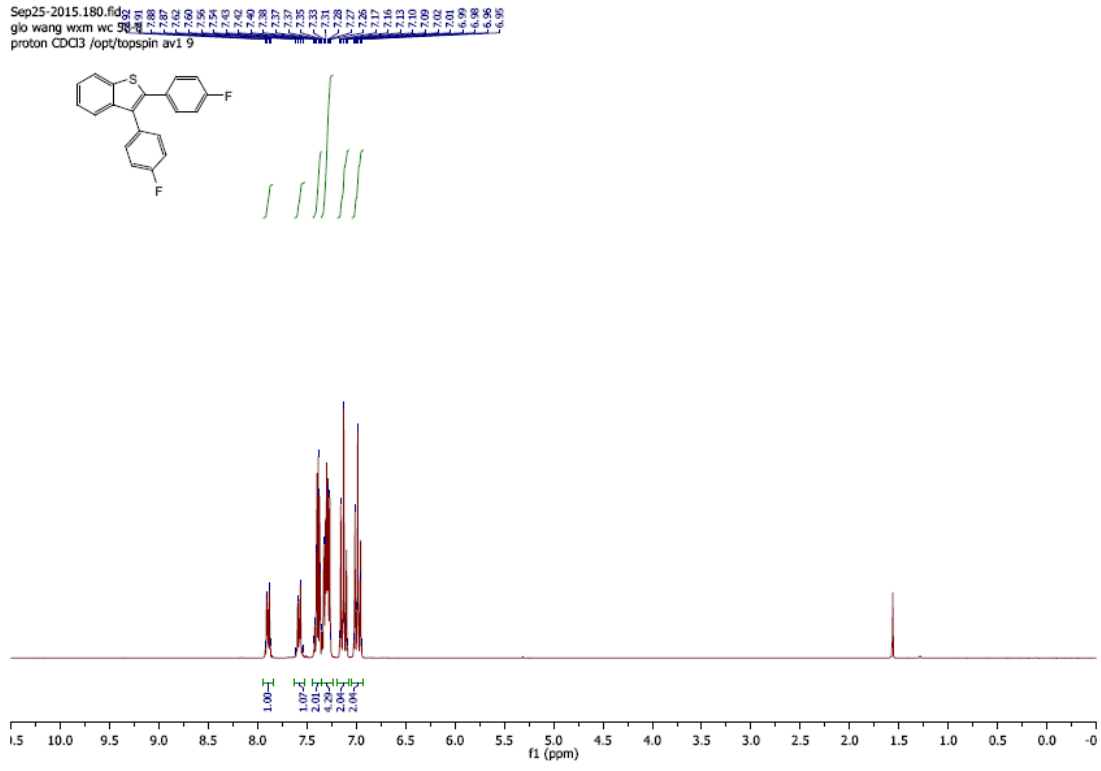


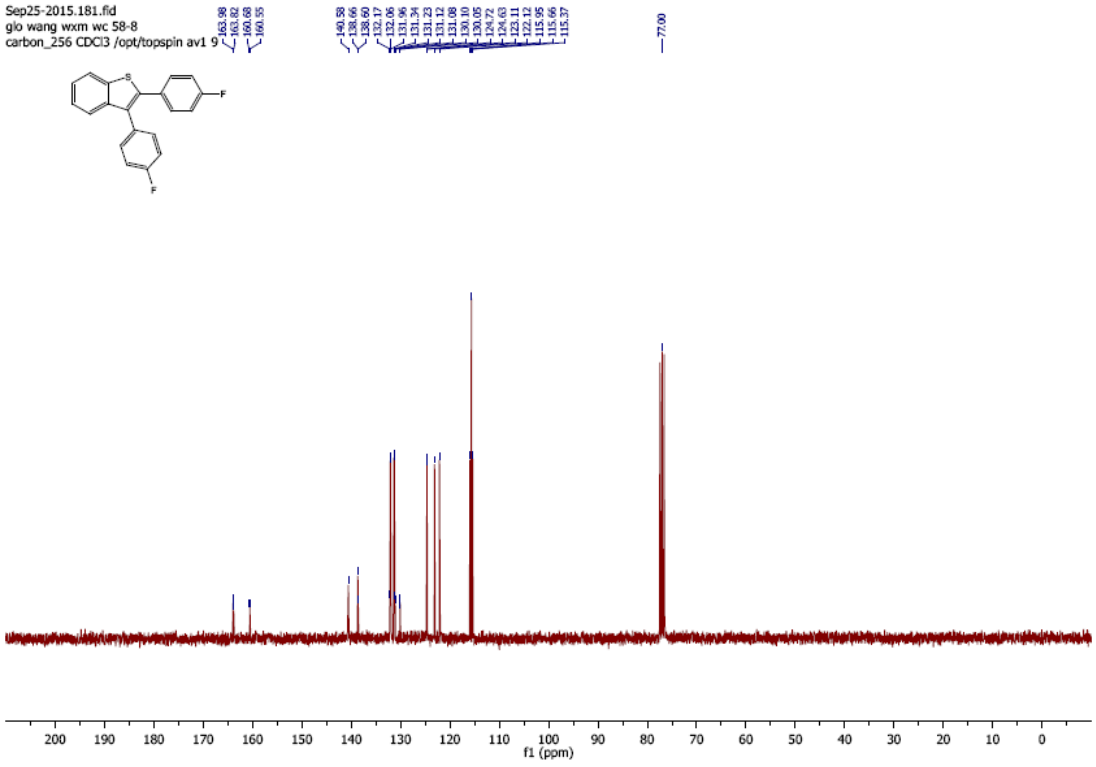
5,7-dimethyl-2,3-diphenylbenzo[b]thiophene (**3h**)

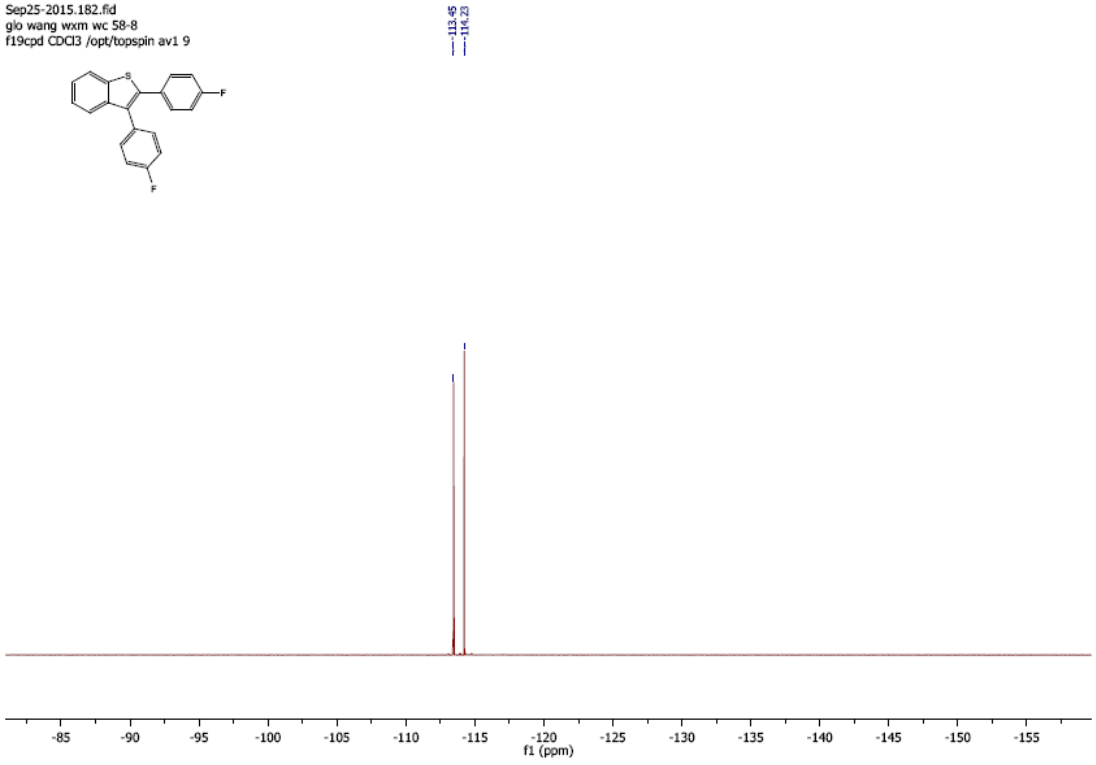




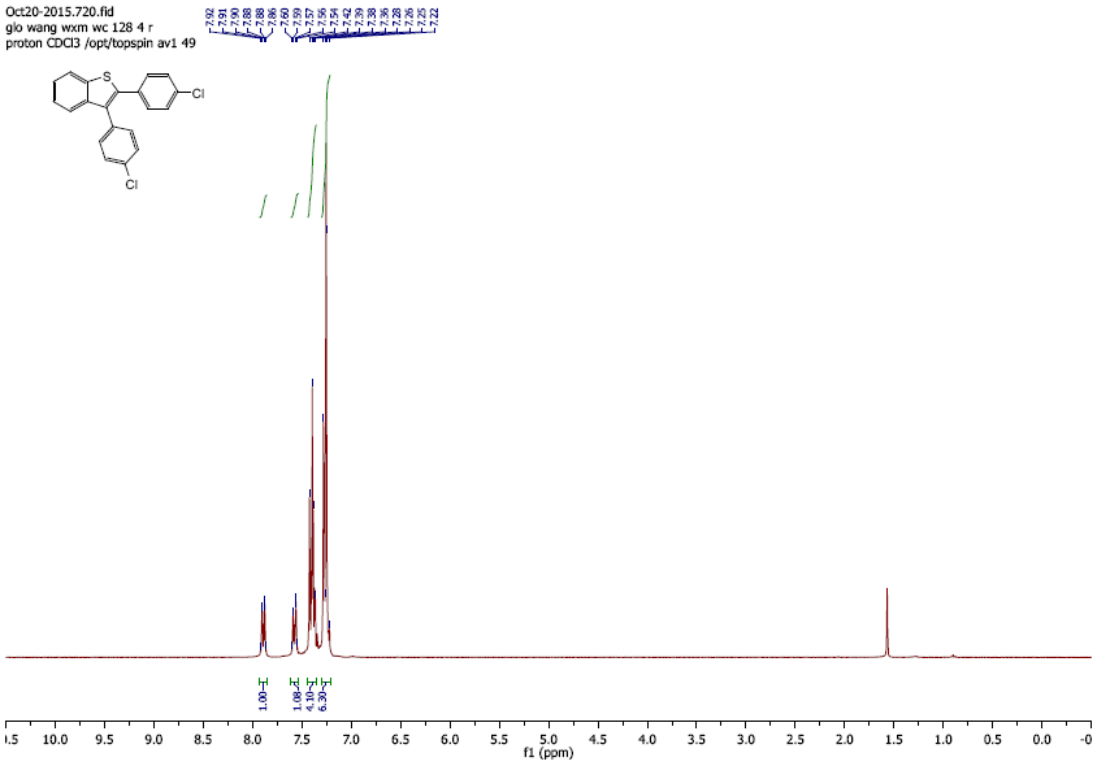
2,3-bis(4-fluorophenyl)benzo[b]thiophene (**3i**)

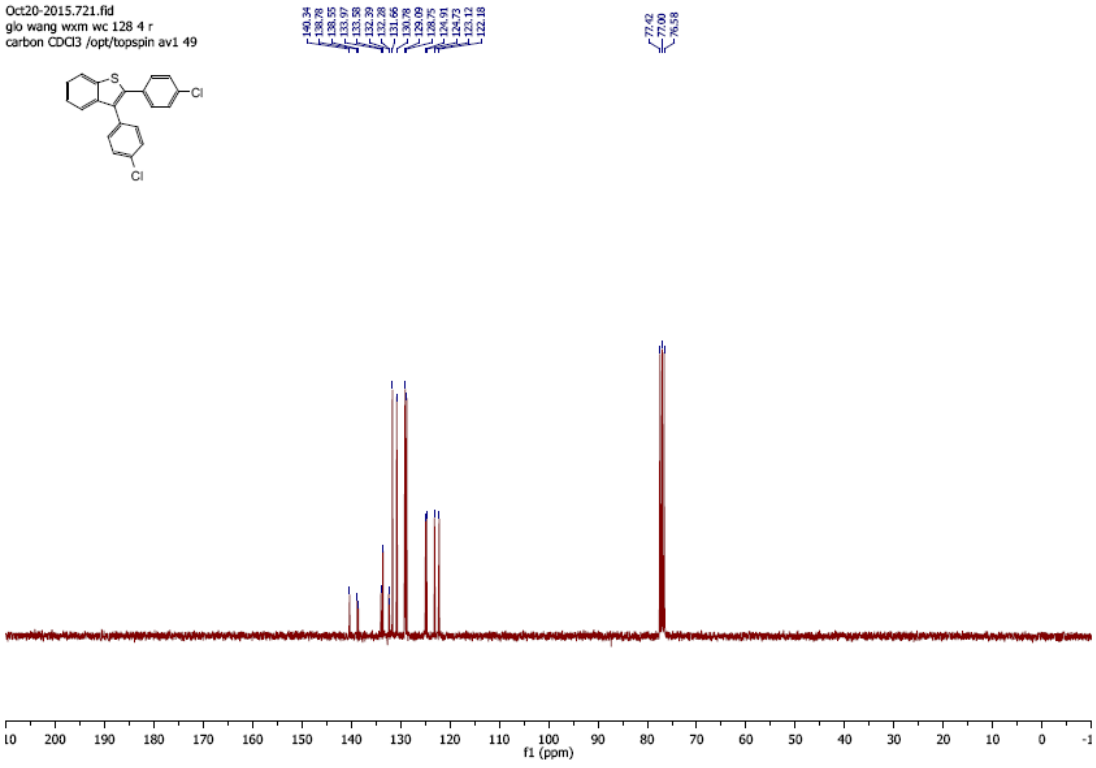



Sep25-2015.181.fid
glo wang wxm wc 58-8
carbon_256 CDCl3 /opt/topspin av1 9
163.98
163.82
160.68
160.55
140.58
138.66
138.60
132.17
132.06
131.96
131.34
131.23
131.12
131.08
130.10
130.05
124.72
124.63
123.11
122.12
115.95
115.66
115.37
77.00
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

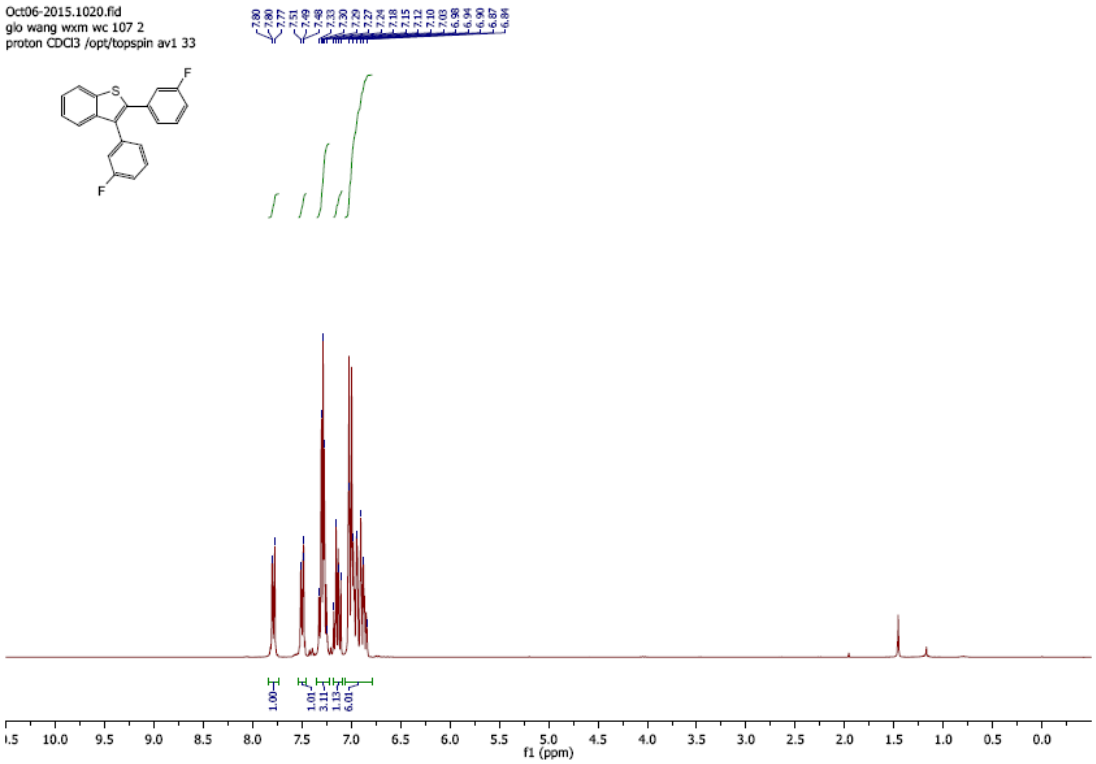

Sep25-2015.182.fid
glo wang wxm wc 58-8
f19cpd CDCl3 /opt/topspin av1 9
-113.45
-114.23
F
F
-85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)

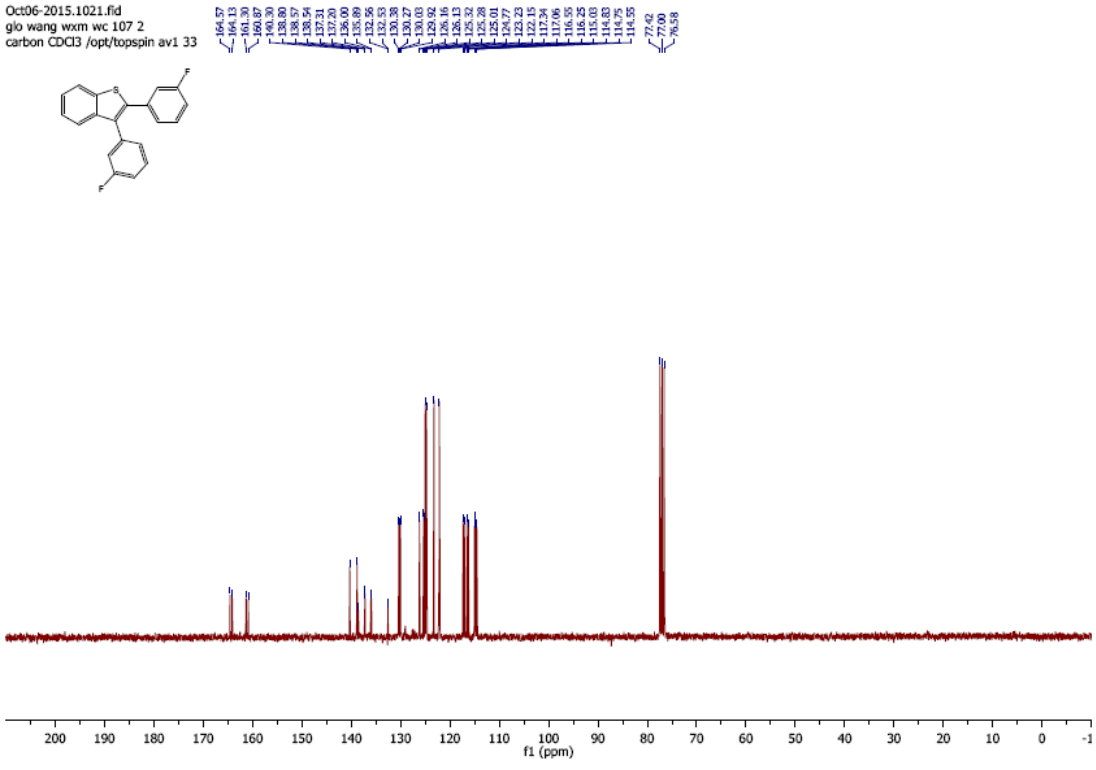
2,3-bis(4-chlorophenyl)benzo[b]thiophene (**3j**)

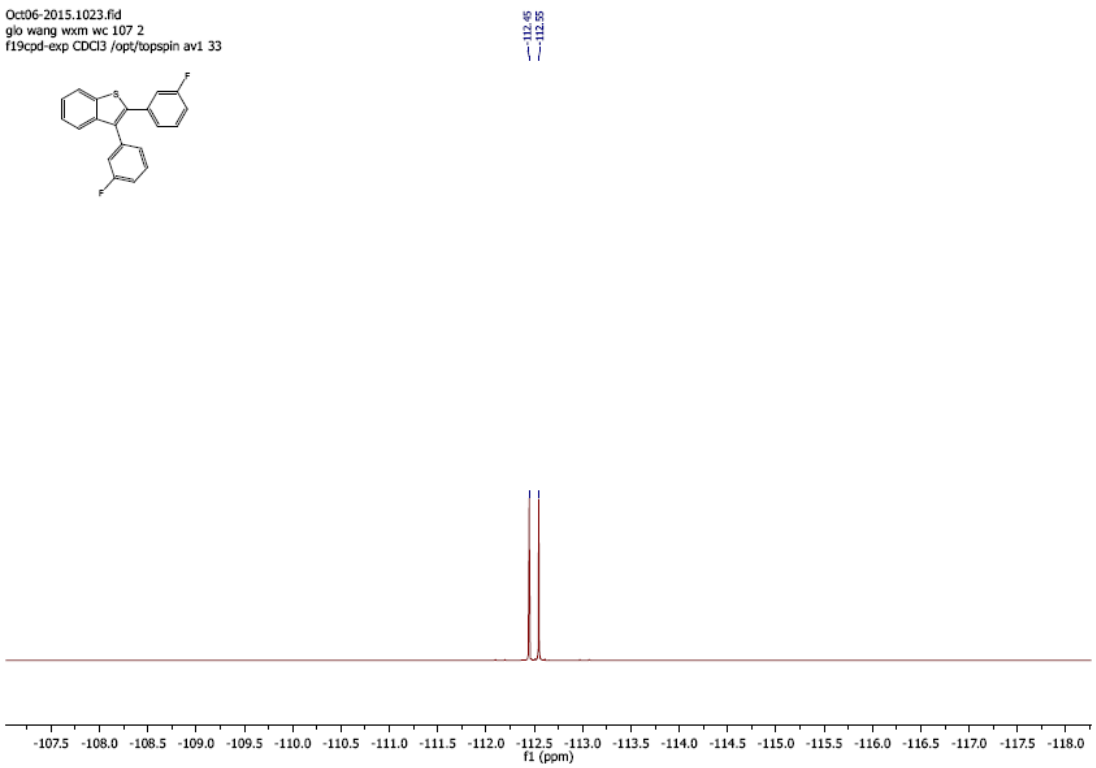




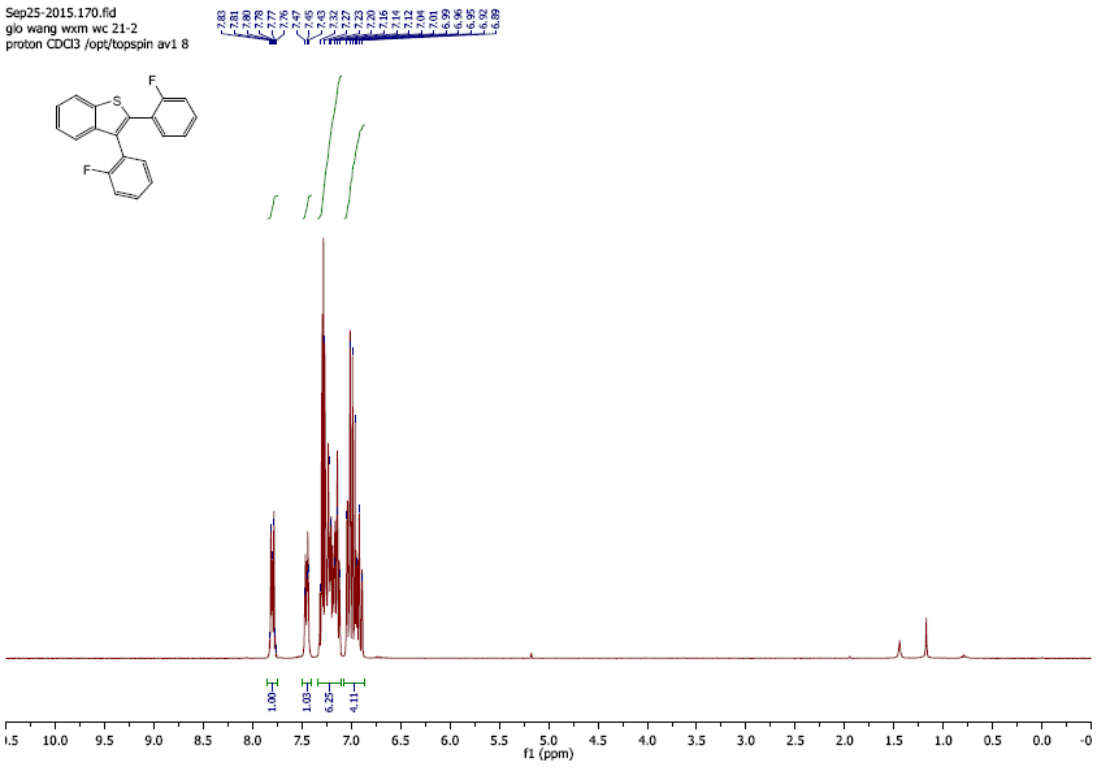
2,3-bis(3-fluorophenyl)benzo[b]thiophene (**3k**)

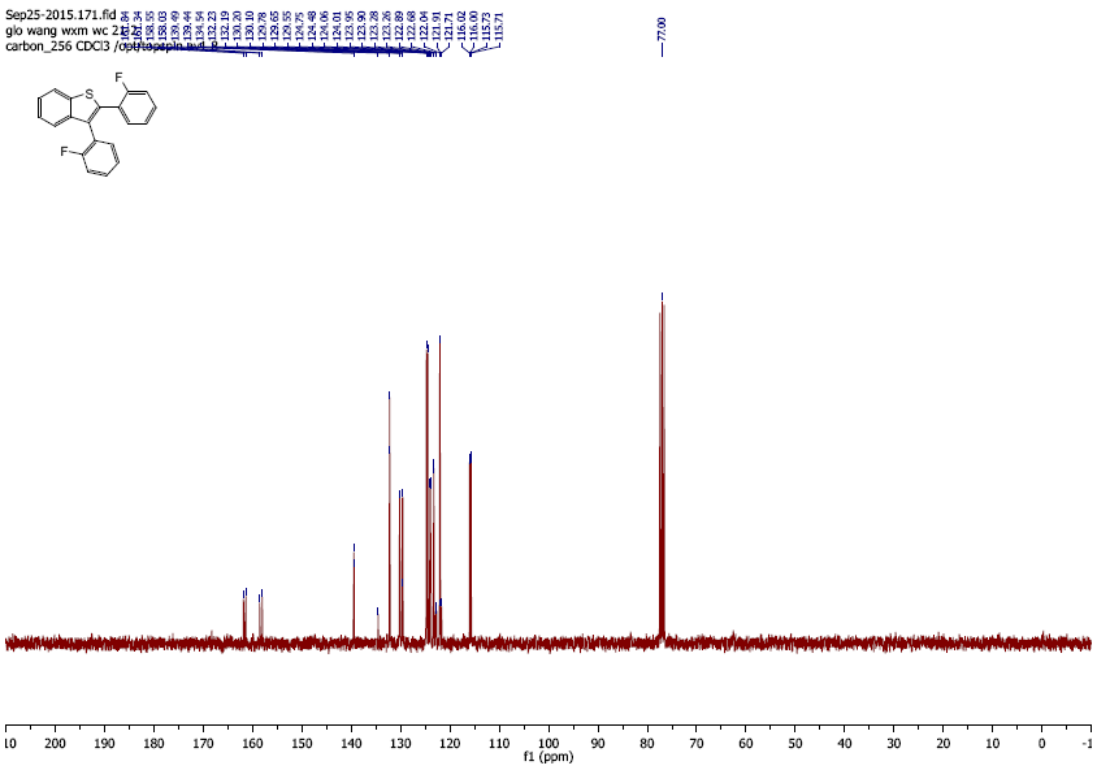


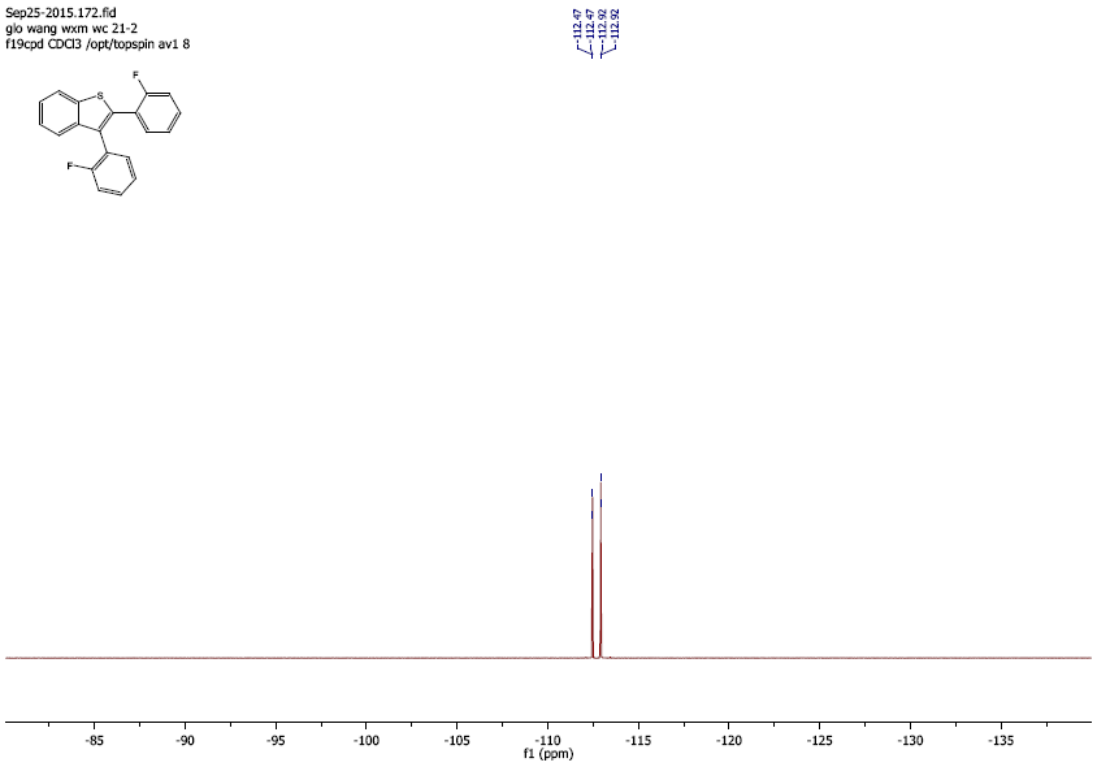




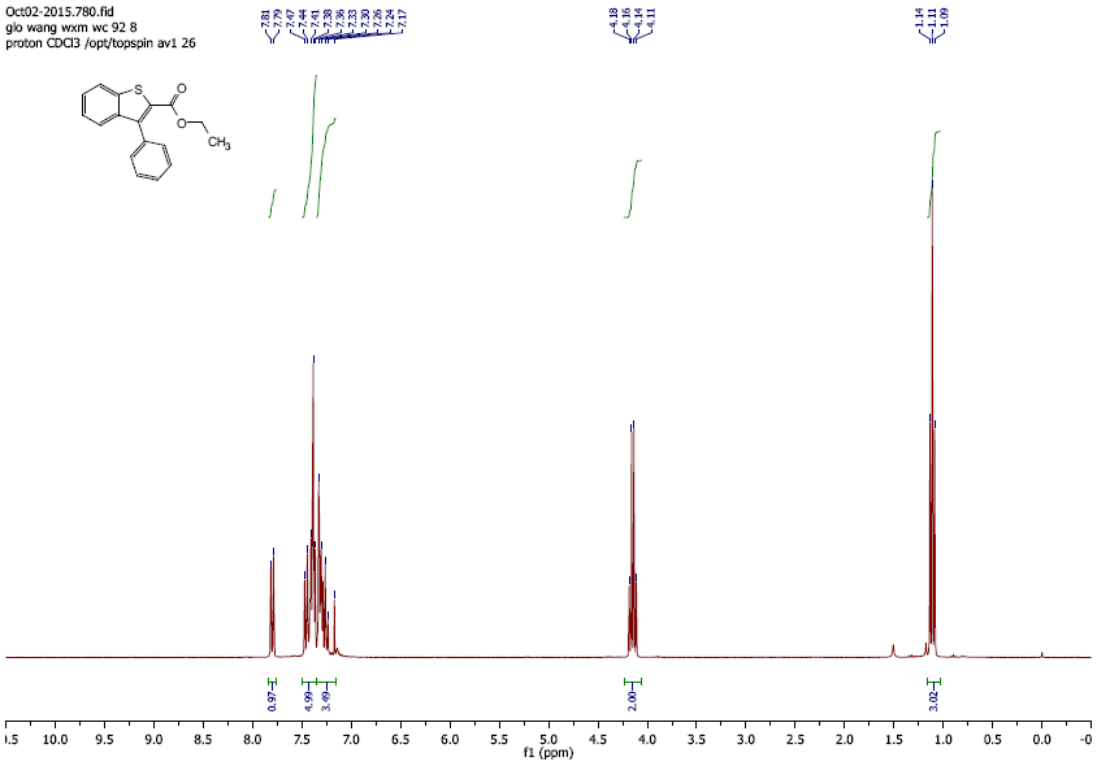
2,3-bis(2-fluorophenyl)benzo[b]thiophene (**3l**)

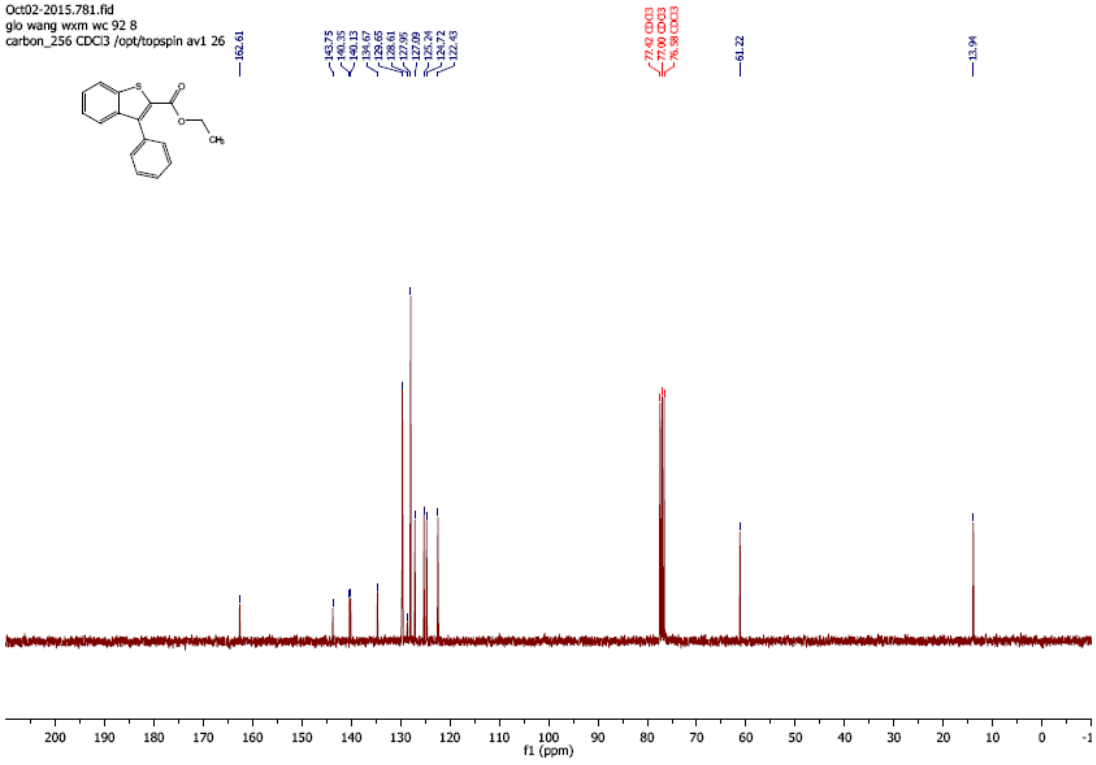



Sep25-2015.171.fid
glo wang wxm wc 21-2
carbon_256 CDCl3 /opt/topspin av1 8
F
S
F
f1 (ppm)

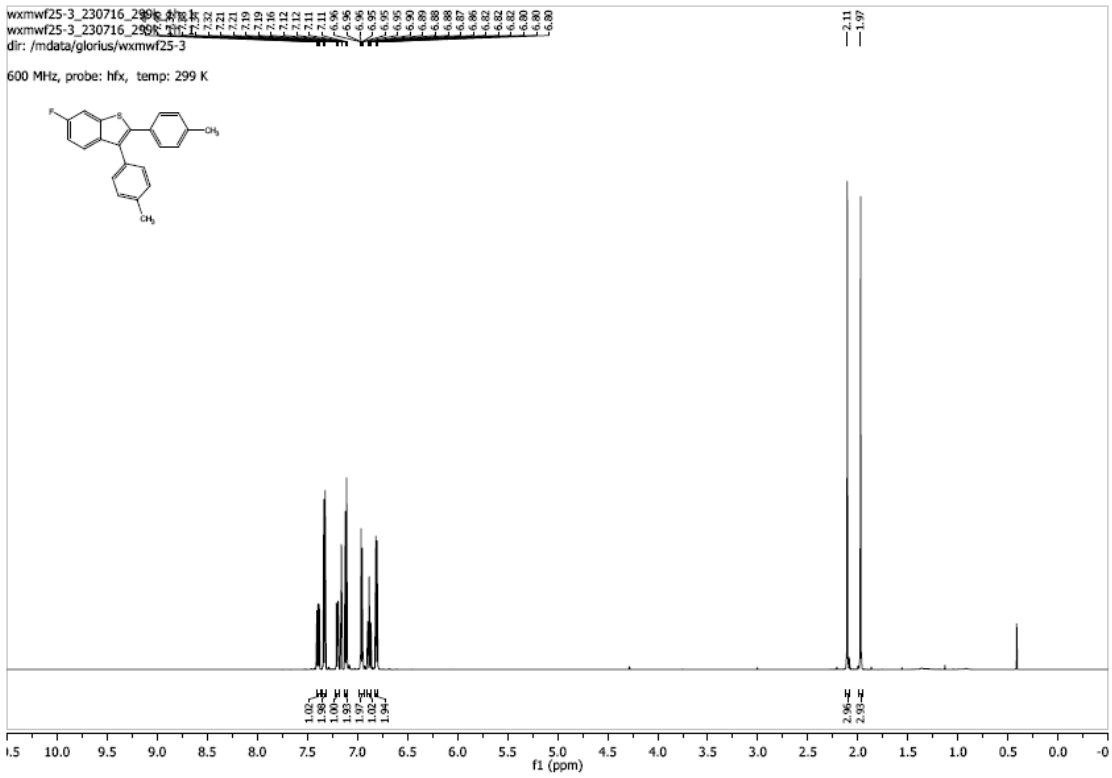

Sep25-2015.172.fid
glo wang wxm wc 21-2
f19cpd CDCl3 /opt/topspin av1 8
F
S
F
f1 (ppm)

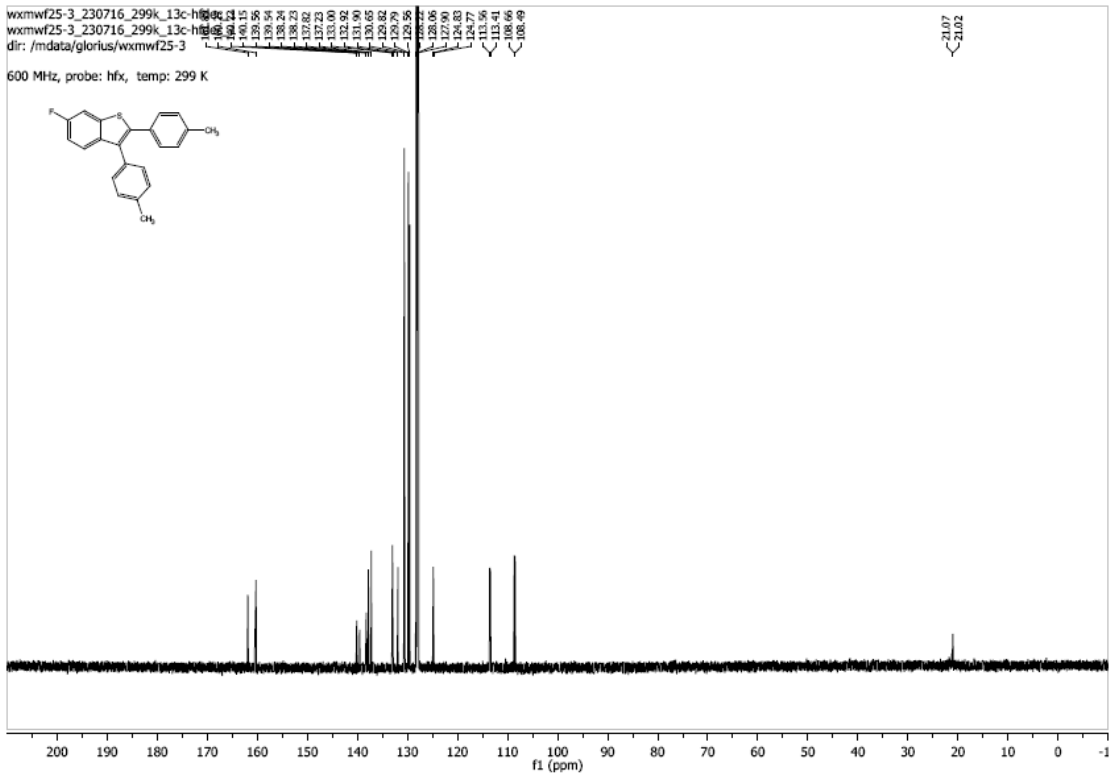
ethyl 3-phenylbenzo[b]thiophene-2-carboxylate (**3m**)

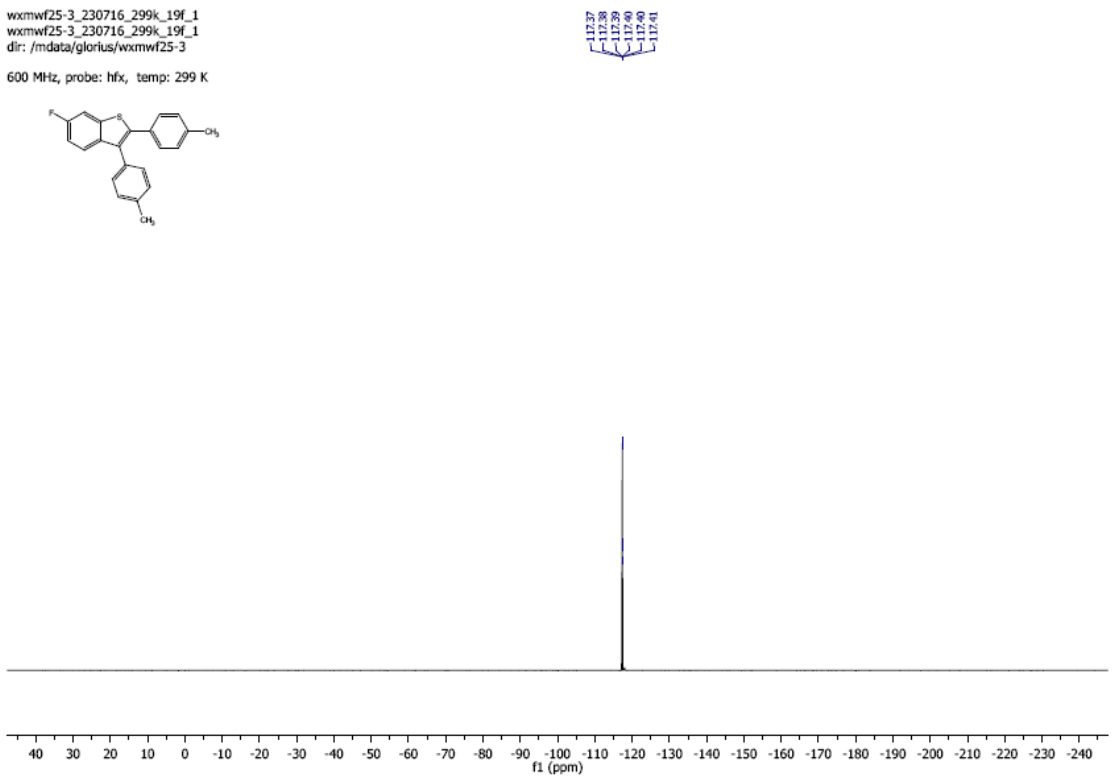




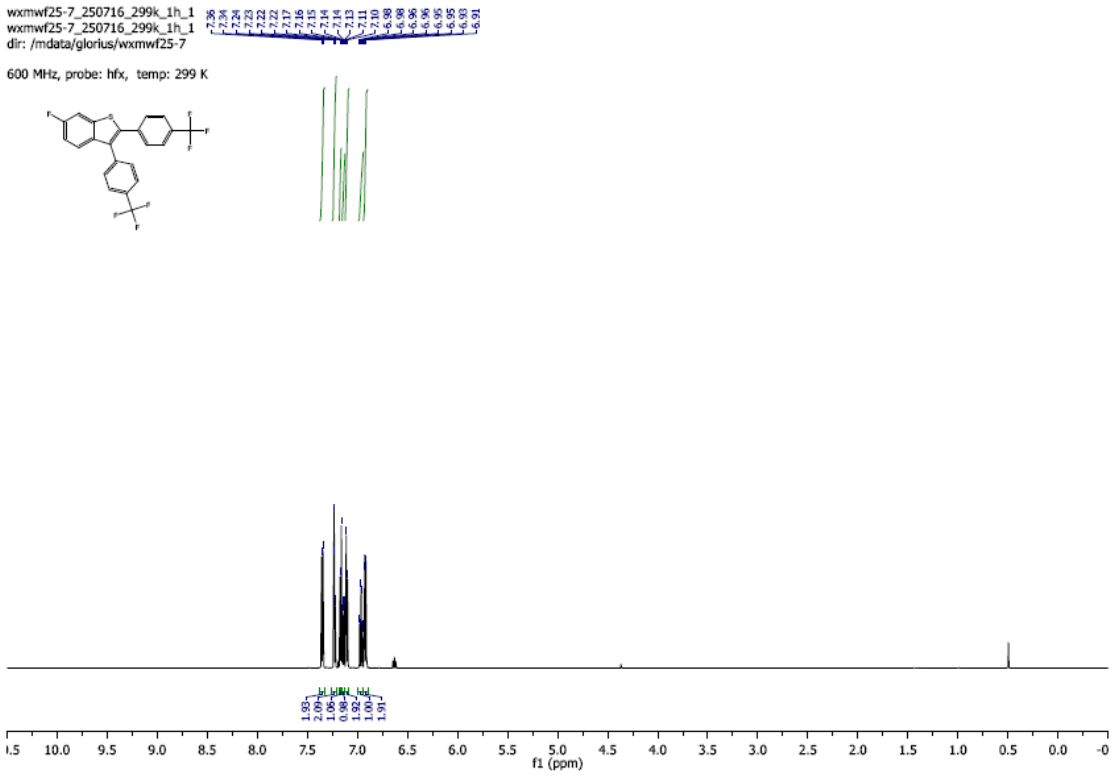
6-fluoro-2,3-di-p-tolylbenzo[b]thiophene (**3n**)

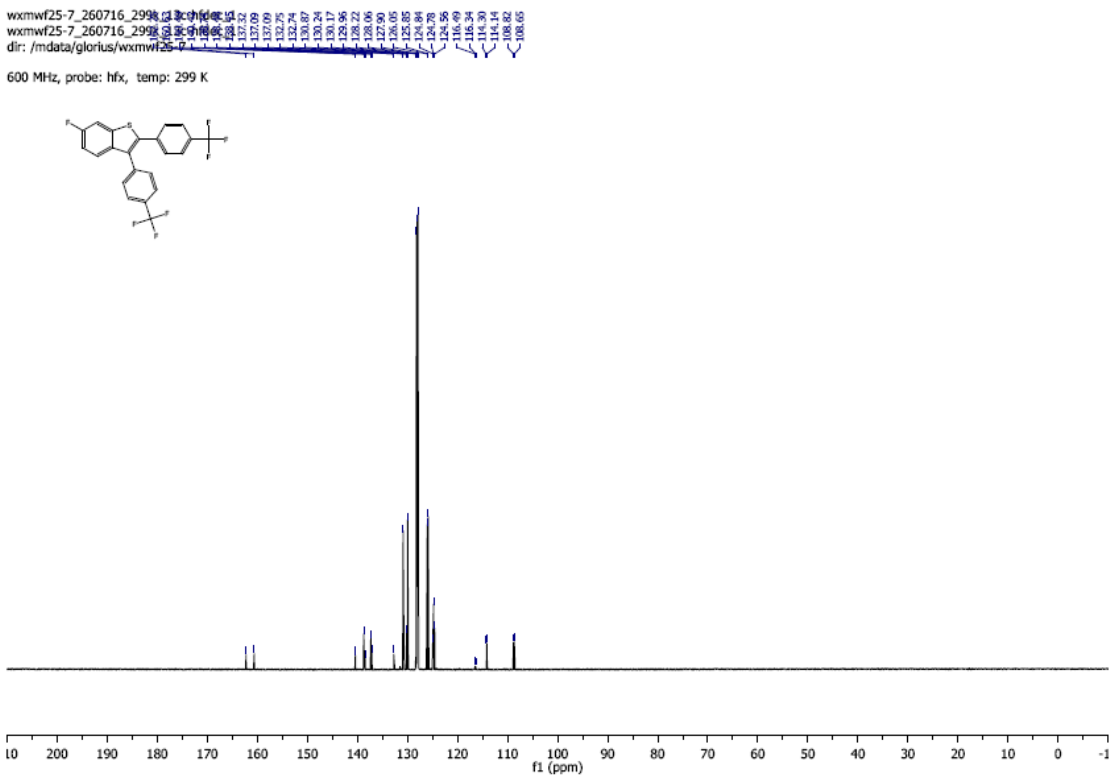


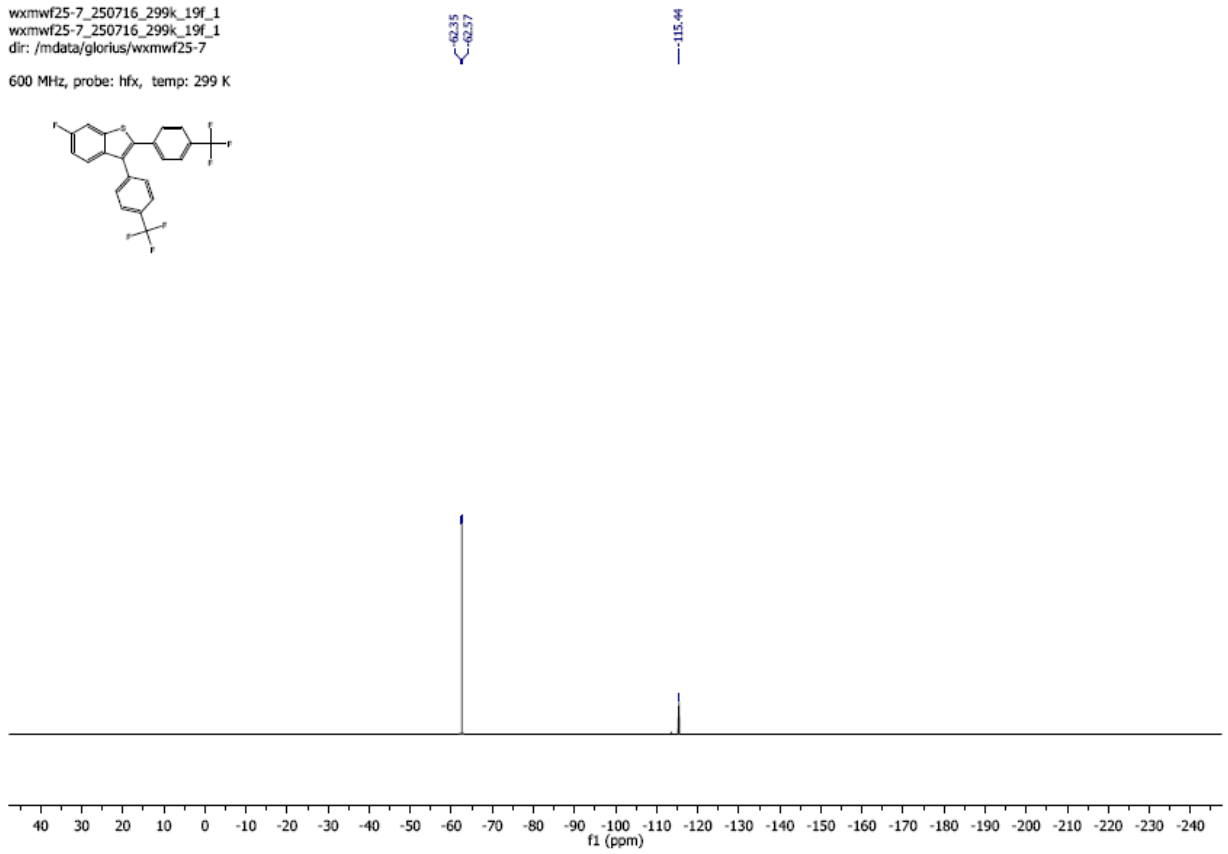




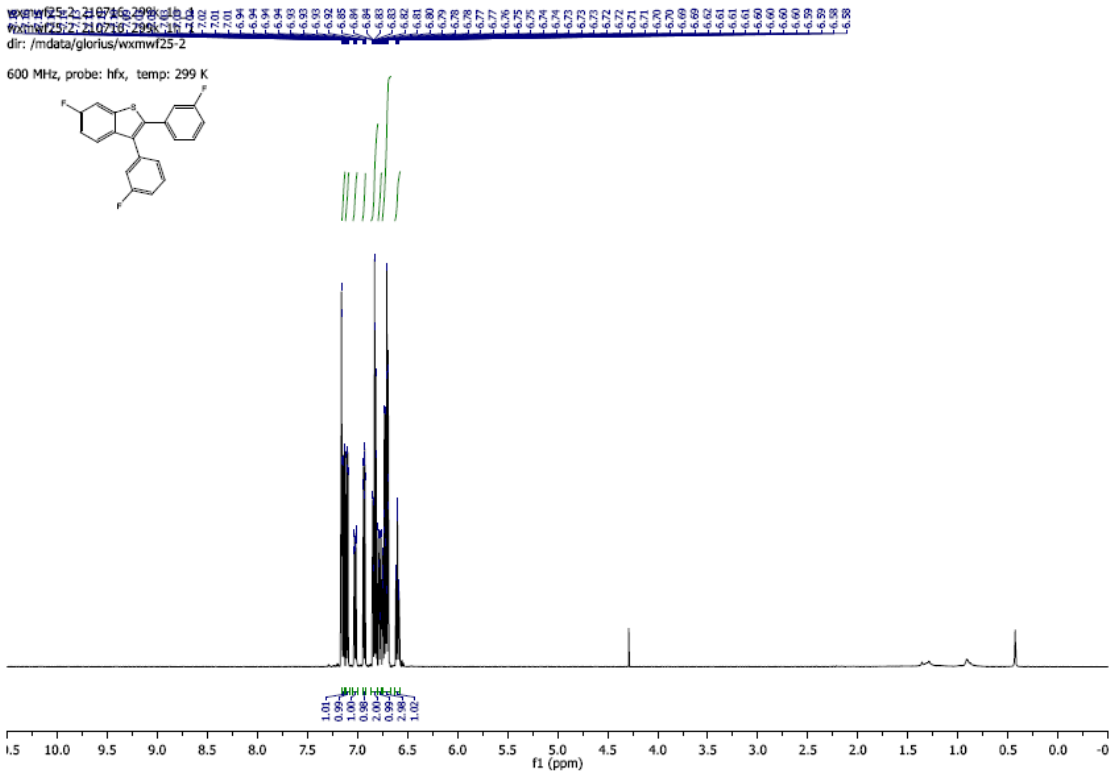
6-fluoro-2,3-bis(4-(trifluoromethyl)phenyl)benzo[b]thiophene (**3o**)

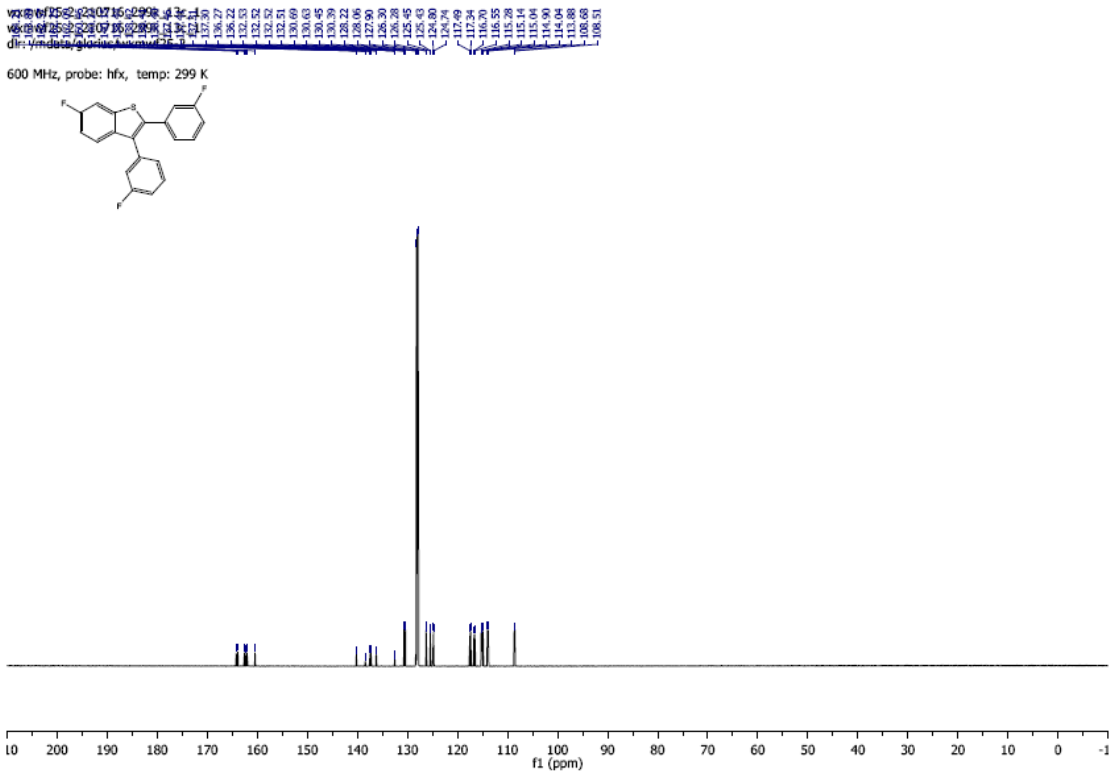


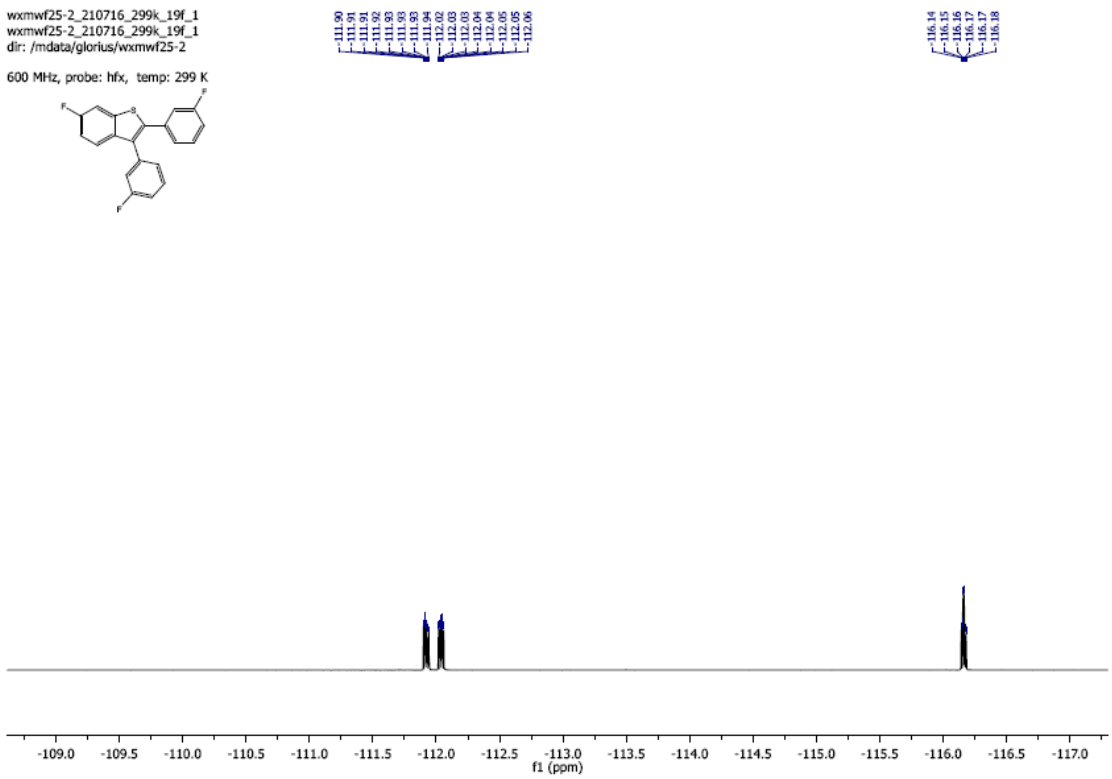

wxmwf25-7_260716_299k_13c_chfx_1
wxmwf25-7_260716_299k_13c_chfx_1
dir: /mdata/glorius/wxmwf25-7
137.32
137.09
137.09
132.74
130.87
130.24
130.17
129.96
128.22
128.06
127.90
126.05
125.85
124.84
124.78
124.55
116.49
116.34
114.30
114.14
108.82
108.65
600 MHz, probe: hfx, temp: 299 K
f1 (ppm)


wxmwf25-7_250716_299k_19f_1
wxmwf25-7_250716_299k_19f_1
dir: /mdata/glorius/wxmwf25-7
-62.35
-62.57
-115.44
600 MHz, probe: hfx, temp: 299 K
f1 (ppm)

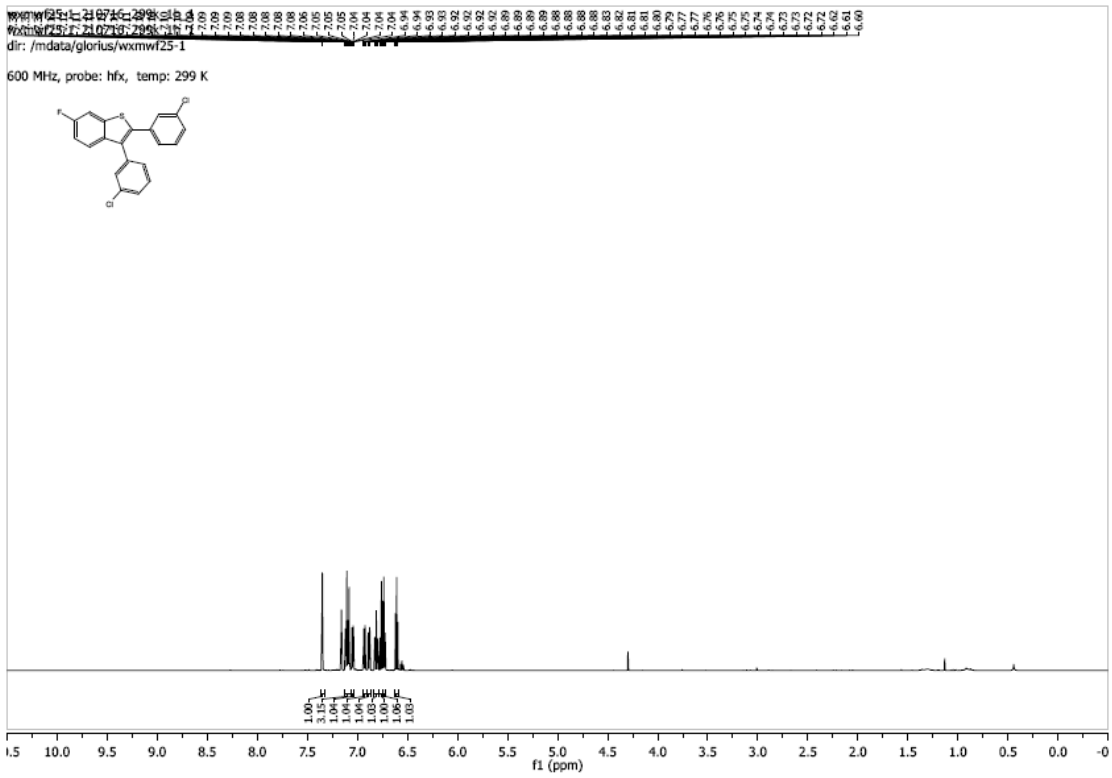
6-fluoro-2,3-bis(3-fluorophenyl)benzo[b]thiophene (**3p**)

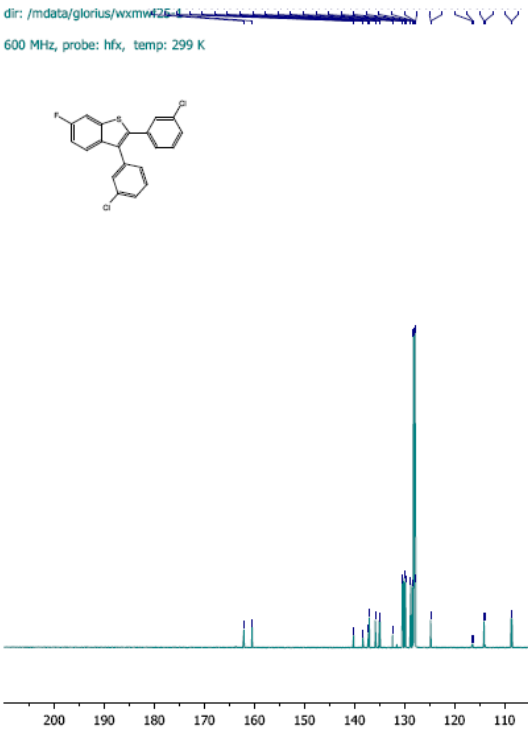


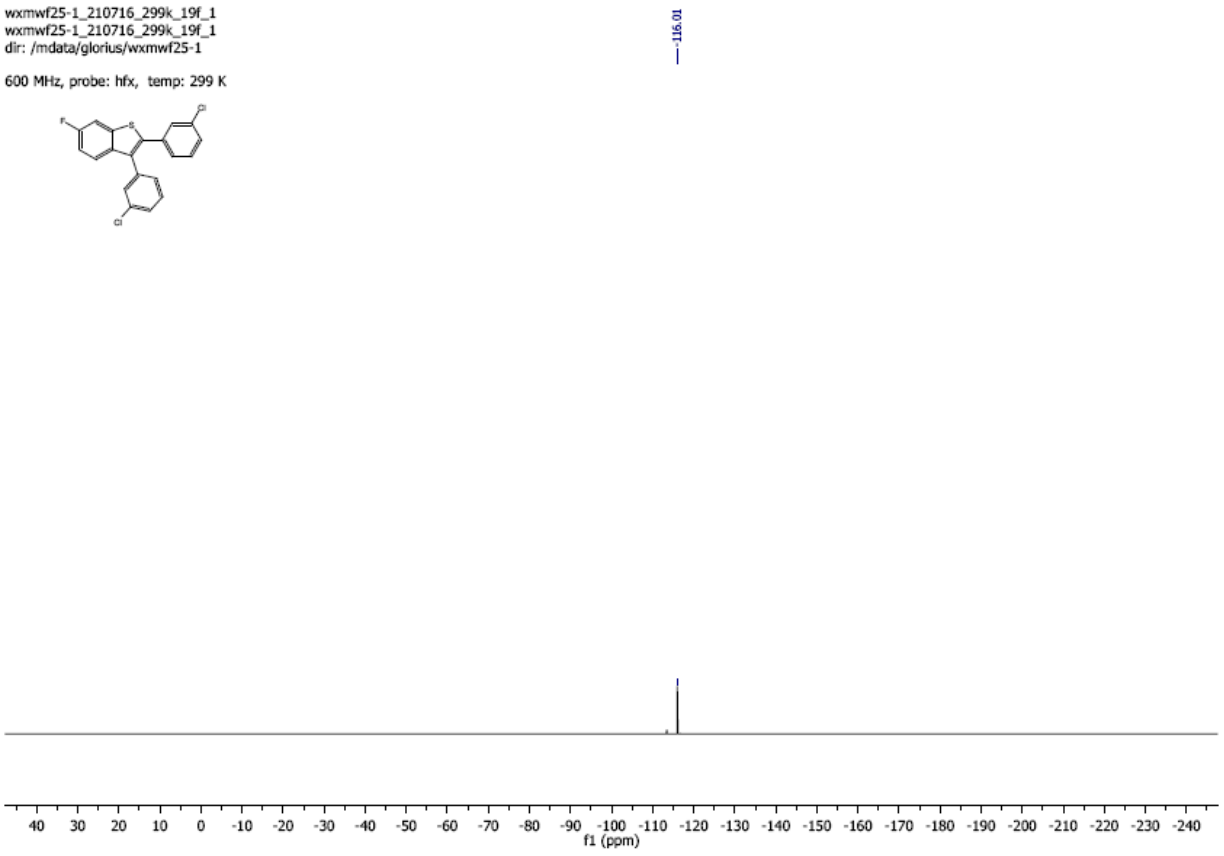




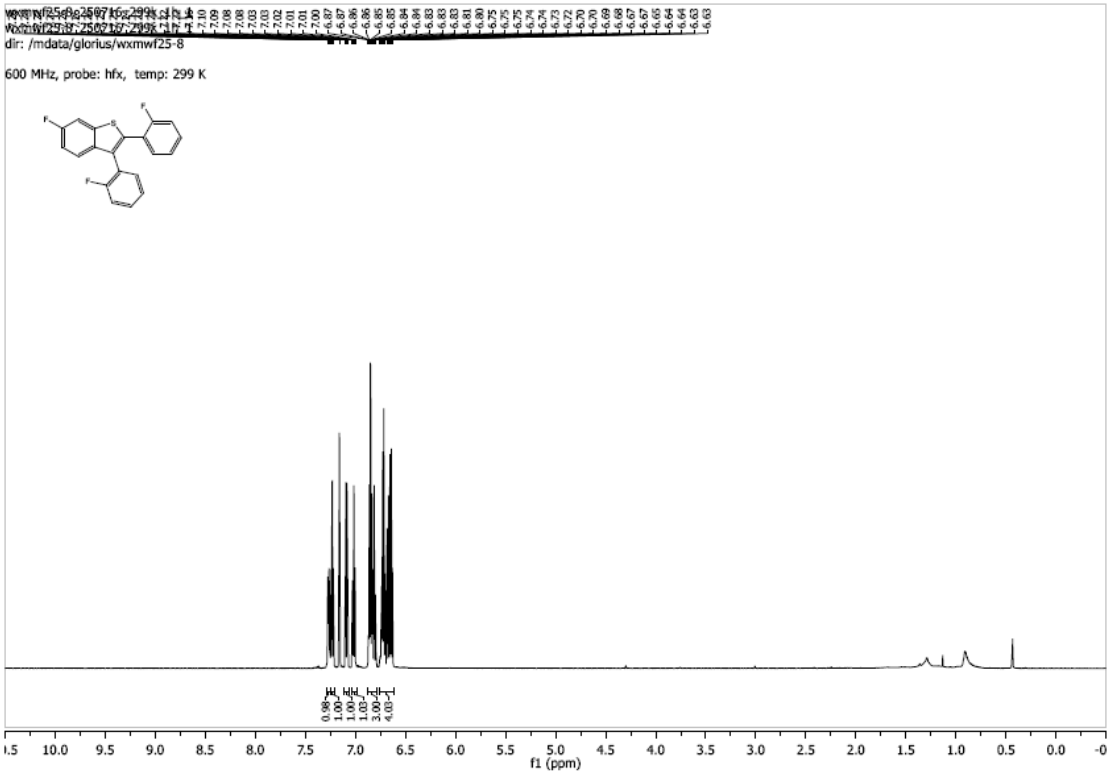
2,3-bis(3-chlorophenyl)-6-fluorobenzo[b]thiophene (**3q**)

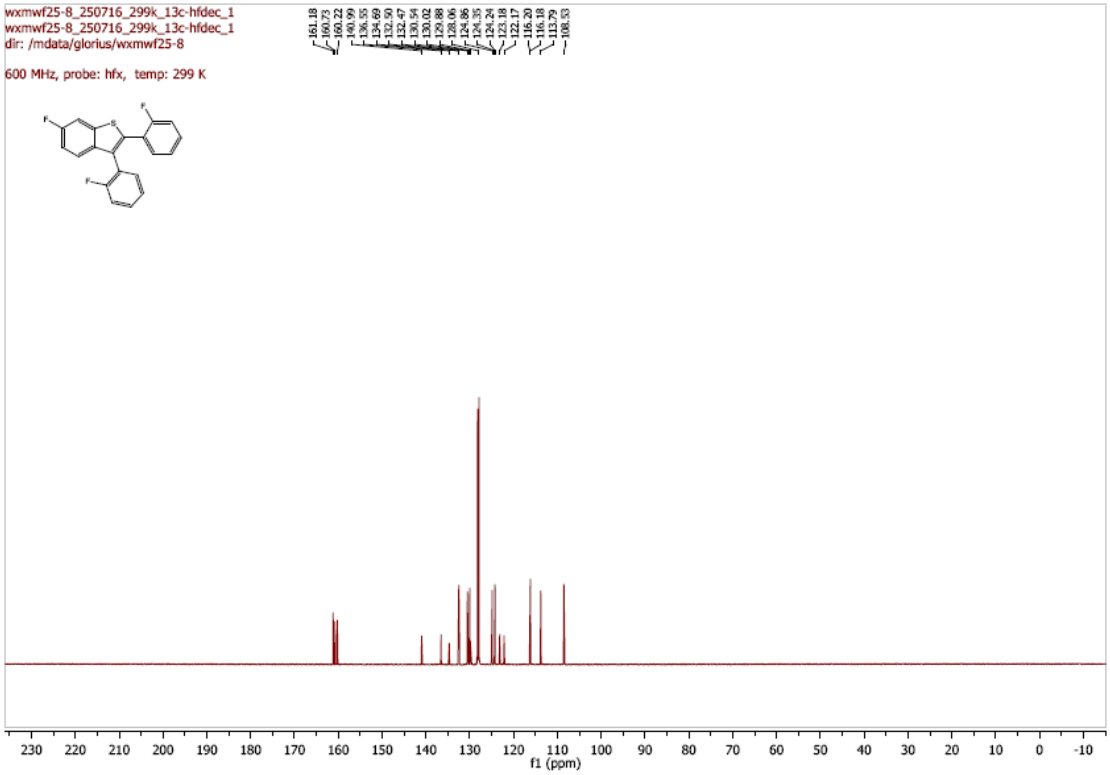



dir: /mdata/glorius/wxmwf25-1
600 MHz, probe: hfx, temp: 299 K
F
S
Cl
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


wxmwf25-1_210716_299k_19f_1
wxmwf25-1_210716_299k_19f_1
dir: /mdata/glorius/wxmwf25-1
600 MHz, probe: hfx, temp: 299 K
F
S
Cl
Cl
-116.01
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

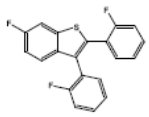
6-fluoro-2,3-bis(2-fluorophenyl)benzo[b]thiophene (**3r**)





wxmwf25-8_250716_299k_19f_1
wxmwf25-8_250716_299k_19f_1
dir: /mdata/glorius/wxmwf25-8

600 MHz, probe: hfx, temp: 299 K



-112.18
-112.19
-112.20
-112.22
-112.50
-112.51
-112.53
-112.54
-116.67
-116.67
-116.67
-116.68
-116.68
-116.68
-116.69
-116.69
-116.71
-116.71