Supplementary Information

Divergent Synthesis of 3-Substituted Thieno[3,4-b]thiophene Derivatives via Hydroxy-based Transformations

Yue Zhou, Jie Hao and Dongbing Zhao*

State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, 94 Weijin Road, Tianjin 300071 (China).
E-mail: dongbing.chem@nankai.edu.cn

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1. Materials and instrumentation methods

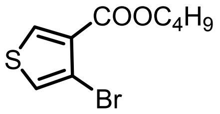
All reactions were carried out in a dry reaction vessel under a positive pressure of nitrogen, unless otherwise stated. Dry solvents (<50 ppm H_2O) were purchased from Acros Organics, Sigma-Aldrich or Carl Roth and stored over molecular sieves under argon atmosphere and were transferred under argon. Starting materials were obtained from Acros Organics, Aldrich Chemical Co., J&K and Energy Chemical and were used without further purification. Anhydrous THF and toluene were distilled over Na/benzophenone prior to use. Anhydrous DMF was distilled over CaH_2 prior to use. These dry solvents stored over molecular sieves under argon atmosphere and were transferred under argon.

UV-vis was recorded with SPECORD® 210 PLUS spectrometers. Fluorescence spectrometry was recorded with Spectrofluorometer FS5. Cyclicvoltammetry (CV) was performed with a CHI660E potentiostat. All measurements were carried out in a one-compartment cell under a nitrogen atmosphere, equipped with a glassy-carbon electrode, a platinumcounter-electrode, and an Ag/Ag+ reference electrode with a scan rate of 100 mV s-1. The supporting electrolyte was a 0.1 mol/L acetonitrile solution of tetrabutylammoniumhexafluorophosphate. All potentials were corrected against Fc/Fc^+.

^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300, Bruker AV 400, Varian 500 MHz INOVA or Varian Unity plus 600 in solvents as indicated. Chemical shifts (δ) for ^1H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm; $(CD_3)_2SO$: $\delta_H = 2.50$ ppm, $\delta_C = 39.52$ ppm). Elemental analyses were performed with vario EL CUBE from elementar.. HRMS spectra were recorded on Varian 7.0T FTMS. GPC spectra were performed with Waters 1525.

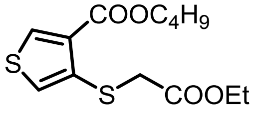
2. Detailed experimental procedures

Compound **1a** was synthesized according to the procedure in the literature.[1]



1a

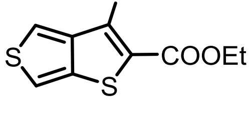
^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 3.6 Hz, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 4.30 (t, *J* = 6.6 Hz, 2H), 1.74 (dt, *J* = 14.6, 6.7 Hz, 2H), 1.47 (dt, *J* = 14.6, 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.37, 134.06, 131.48, 125.20, 110.76, 64.82, 30.62, 19.21, 13.66. HRMS (ESI): calcd.for $C_9H_{11}BrO_2S$ [M+Na]$^+$: 284.9561, found: 284.9558. Anal. Calca. for $C_9H_{11}BrO_2S$: C: 41.08; H: 4.21; Found: C: 41.09; H: 4.57.



3a

Butyl 4-((2-ethoxy-2-oxoethyl)thio)thiophene-3-carboxylate (3a)

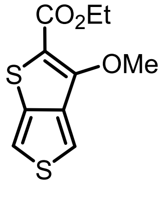
In a Schlenk flask equipped with a magnetic stirrer were placed butyl 4-bromothiophene-3-carboxylate (**1a**, 1.31g, 5 mmol，1.0 eq), Pd_2dba_3 (0.46 g, 10 mol%), XantPhos (0.58 g, 20 mol%), DIPEA (1.2 mL, 1.5 eq) and anhydrous toluene (28 mL), After stirring for a few minutes, ethyl 2-mercaptoacetate (1.1 mL, 2.0 eq) was added drop by drop, then the reaction mixture was refluxed at 120 °C and stirred for 24 h. Then, it was cooled at room temperature and the precipitate was collected by filtration, washed with saturated $NaHCO_3$, extracted with CH_2Cl_2. After drying over $MgSO_4$, the residue was purified by column chromatography (PE:EA= 10:1) as eluent to obtain **3a** (1.45 g, 96%) as yellow oily liquid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.15 (d, *J* = 3.4 Hz, 1H), 7.04 (d, *J* = 3.4 Hz, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.67 (s, 2H), 1.75 – 1.67 (m, 2H), 1.46 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 169.52 (s), 162.13 (s), 134.57 (s), 133.86 (s), 131.25 (s), 119.50 (s), 64.75 (s), 61.60 (s), 35.82 (s), 30.65 (s), 19.20 (s), 14.04 (s), 13.68 (s). HRMS (ESI): calcd.for $C_{13}H_{18}O_4S_2$ [M+Na]$^+$: 325.0544, found: 325.0543.



4

Ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (4)

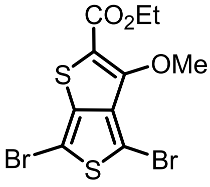
In a Schlenk flask equipped with a magnetic stirrer, to a solution of ^{t}BuOK (1.55 g, 2.1 eq), in THF (18 mL), after stirring for a few minutes, butyl 4-((2-ethoxy-2-oxoethyl)thio)thiophene-3-carboxylate (**3a**, 2 g, 6.6 mmol, 1.0 eq) of THF solution was added dropwise at 0 °C and stirred for 1 h. The reaction mixture was quenched with sat. NH_4Cl, and washed with H_2O, extracted with CH_2Cl_2. After drying over $MgSO_4$, the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (PE:acetone= 5:1) as eluent to obtain **4** (1.21 g, 80.1%) as green oily liquid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 10.29 (s, 1H), 7.73 (d, *J* = 2.6 Hz, 1H), 7.20 (d, *J* = 2.6 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.84 (s), 154.81 (s), 138.66 (s), 135.22 (s), 117.24 (s), 112.26 (s), 105.79 (s), 61.38 (s), 14.28 (s). HRMS (ESI): calcd.for $C_{10}H_8Br_2O_3S_2$ [M+Na]$^+$: 250.9813, found: 250.9843.



5

Ethyl 3-methoxythieno[3,4-b]thiophene-2-carboxylate (5)

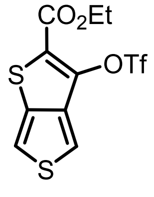
In a Schlenk flask equipped with a magnetic stirrer, were placed ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (**4**, 2.28 g, 10.0 mmol, 1.0 eq), DMF (50 mL), and DBU (1.64 mL, 1.1eq), after stirring for ten minutes, CH_3I (3.1 mL, 5eq) was added at r.t. and stirred for 12 h. The reaction mixture was quenched with H_2O, extracted with EA, dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE:EA= 20:1) as eluent to obtain **5** (507 mg, 20.9%) as yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 (d, *J* = 2.7 Hz, 1H), 7.21 (d, *J* = 2.7 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 4.26 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.41 (s), 151.58 (s), 139.93 (s), 135.61 (s), 116.64 (s), 111.88 (s), 60.99 (s), 60.75 (s), 14.30 (s). HRMS (ESI): calcd.for $C_{10}H_{10}O_3S_2$ [M+Na]$^+$: 264.9969, found: 264.9967. Anal. Calca. for $C_{10}H_{10}O_3S_2$: C: 49.57; H: 4.16; Found: C: 49.47; H: 4.59.



6

Ethyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate (6)

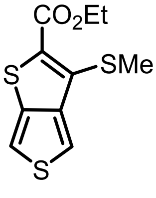
In a Schlenk flask equipped with a magnetic stirrer, were placed ethyl 3-methoxythieno[3,4-b]thiophene-2-carboxylate (**5**, 48 mg, 0.2 mmol, 1.0 eq), and DMF (1 mL), then NBS (88 mg, 0.5 mmol, 2.5 eq) in DMF (1 mL) was added at r.t. and stirred for 24 h and the reaction was protected from light. The reaction mixture was quenched with H_2O, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE:EA=50:1) as eluent to obtain **6** (47.8 mg, 60.3%) as light yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 4.36 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.46 (s), 151.80 (s), 139.01 – 138.81 (m), 136.43 (s), 101.86 (s), 98.01 (s), 63.03 (s), 61.56 (s), 14.13 (s). HRMS (ESI): calcd.for $C_{10}H_8Br_2O_3S_2$ [M+Na]$^+$: 420.8179, found: 420.8178.



7

Ethyl 3-(((trifluoromethyl)sulfonyl)oxy)thieno[3,4-b]thiophene-2-carboxylate (7)

In a Schlenk flask equipped with a magnetic stirrer, were added ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (**4**, 1.6 g, 7.0 mmol, 1.0 eq), dry CH_2Cl_2 (35 mL) and pyridine (2.37 mL, 2.0 eq), then Tf_2O (1.1 mL, 2.0 eq) at 0 °C was added dropwise. The reaction mixture was stirred for 5 h at room temperature, quenched with saturated $NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: CH_2Cl_2= 5:1) as eluent to obtain **7** (1.75 g, 70%) as yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.64 (d, *J* = 2.5 Hz, 1H), 7.38 (d, *J* = 2.7 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 160.70 (s), 137.63 (s), 134.72 (s), 133.80 (s), 128.71 (s), 123.32 (s), 120.13 (s), 116.94 (s), 116.34 (s), 113.61 (s), 62.52 (s), 14.06 (s). HRMS (ESI): calcd.for $C_{10}H_7F_3O_5S_3$ [M+Na]$^+$: 382.9305, found: 382.9305.

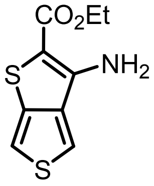


8

Ethyl 3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (8)

In a Schlenk flask equipped with a magnetic stirrer, were added ethyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (**7**, 36 mg, 0.1 mmol, 1.0 eq), $Pd_2(dba)_3$ (0.5 mg, 0.006mmol, 6mol%), XantPhos (7 mg, 0.012mmol, 12mol%), toluene (2 mL), DIPEA (31 mg, 1.2 eq) and NaSMe (aq., 20%) (55 mg, 0.15 mmol, 1.5 eq). The reaction mixture was stirred for 24 h at 100 °C. Then quenched with saturated

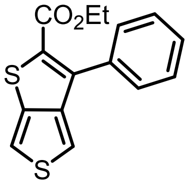
$NaHCO_3$, extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA= 20:1) as eluent to obtain **8** (23.5mg, 91%) as oily liquid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.75 (d, J = 2.7 Hz, 1H), 7.28 (d, J = 2.7 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.73 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.51 (s), 147.42 (s), 137.04 (s), 132.25 (d, *J* = 19.9 Hz), 117.29 (s), 111.55 (s), 61.51 (s), 17.57 (s), 14.28 (s). HRMS (ESI): calcd.for $C_{10}H_{10}O_2S_3$ $[M+Na]^+$: 280.9741, found: 280.9740.



9

Ethyl 3-aminothieno[3,4-b]thiophene-2-carboxylate (9)

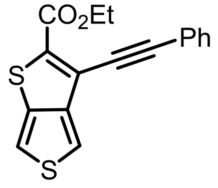
In a Schlenk flask equipped with a magnetic stirrer, were added (**7**, 180 mg, 0.5 mmol, 1.0 eq), $Pd_2(dba)_3$ (46 mg, 0.05 mmol, 10 mol%), XantPhos (29 mg, 0.05 mmol, 10 mol%), K_3PO_4 (212.2 mg, 1.0 mmol, 2.0 eq), toluene (10 mL) and diphenylmethanimine (0.125 mL,0.76 mmol, 1.52 eq). The reaction mixture was stirred for 24 h at 90 °C. Then, it was cooled at room temperature, quenched with H_2O, extracted with EA, dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was dissolved in methanol stirring for 1 h and was added ice water, extracted with EA, dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA= 5:1) as eluent to obtain 10 (98 mg, 86%) as light yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.49 (s, 1H), 7.16 (s, 1H), 5.83 (s, 2H), 4.32 (dd, *J* = 13.9, 6.9 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 165.89 (s), 143.22 (s), 140.95 (s), 136.40 (s), 115.04 (s), 111.88 (s), 102.42 (s), 60.35 (s), 14.46 (s). HRMS (ESI): calcd.for $C_9H_9NO_2S_2$ $[M+Na]^+$: 249.9972, found: 249.9972. Anal. Calca. for $C_9H_9NO_2S_2$: C: 47.56; H: 3.99; N: 6.16; Found: C: 47.89; H: 4.59; N: 6.17.



10

Ethyl 3-phenylthieno[3,4-b]thiophene-2-carboxylate (10)

In a Schlenk flask equipped with a magnetic stirrer, were added (**7**, 72 mg, 0.2 mmol, 1.0 eq), phenylboronic acid (32 mg, 0.26 mmol, 1.3 eq), Pd(PPh$_3$)$_4$ (7.0 mg, 0.006 mmol, 3 mol%), K$_3$PO$_4$ (68 mg, 0.32 mmol, 1.6 eq) and 1,4-dioxane (2 mL). The reaction mixture was stirred for 24 h at 110 °C. Then, it was cooled at room temperature, quenched with sat. NH$_4$Cl, and washed with H$_2$O, extracted with CH$_2$Cl$_2$, dried over MgSO$_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: CH$_2$Cl$_2$= 5:1) as eluent to obtain **10** (56 mg, 97%) as light yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.48 (dtd, *J* = 10.8, 3.8, 1.9 Hz, 5H), 7.39 (d, *J* = 2.7 Hz, 1H), 7.31 (d, *J* = 2.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.90 (s), 149.02 (s), 137.55 (s), 136.98 (s), 134.64 (s), 132.97 (s), 129.14 (s), 128.22 (s), 127.98 (s), 117.19 (s), 111.39 (s), 61.27 (s), 13.92 (s). HRMS (ESI): calcd.for C$_{15}$H$_{12}$O$_2$S$_2$ [M+Na]$^+$: 311.0176, found: 311.0175.

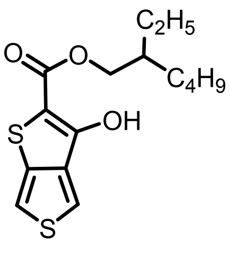


11

Ethyl 3-(phenylethynyl)thieno[3,4-b]thiophene-2-carboxylate (11)

In a Schlenk flask equipped with a magnetic stirrer, were added (**7**, 72 mg, 0.2 mmol, 1.0 eq), phenylacetylene (31 mg, 0.3 mmol, 1.5 eq), PdCl$_2$(PPh$_3$)$_2$ (4.2 mg, 0.006 mmol, 3 mol%), 0.12 mL Et$_3$N, 2 mL DMF, the reaction mixture was stirred for 24 h at 90 °C. Then, it was cooled at room temperature, quenched with H$_2$O, extracted with CH$_2$Cl$_2$, dried over MgSO$_4$, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: CH$_2$Cl$_2$= 3:1) as eluent to obtain **11** (57 mg, 91%) as yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.77 (d, *J* = 2.7 Hz, 1H), 7.63 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.32 (d, *J* = 2.7 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.42 (s), 147.33 (s), 139.70 (s), 136.48 (s), 131.92 (s), 129.00 (s), 128.45 (s), 122.75 (s), 117.08 (s), 116.88 (s), 112.22 (s), 98.11 (s), 82.92 (s), 61.70 (s), 14.34 (s). HRMS (ESI): calcd.for C$_{17}$H$_{12}$O$_2$S$_2$ [M+Na]$^+$: 335.0176, found: 335.0275.

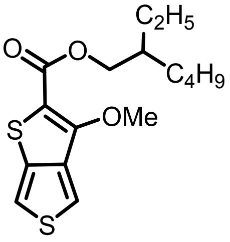
Compounds of **12, 13, 15** and **16** were synthesized with corresponding starting materials by similar procedure for preparation of **4, 5, 6, 7,** and **8.**



12

2-Ethylhexyl 3-hydroxythieno[3,4-b]thiophene-2-carboxylate (12)

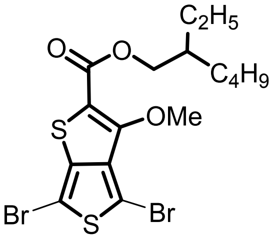
^{1}H NMR (400 MHz, CDCl$_3$) δ 10.26 (s, 1H), 7.73 (d, *J* = 2.6 Hz, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 4.24 (d, *J* = 5.3 Hz, 2H), 1.69 (dd, *J* = 11.8, 5.9 Hz, 1H), 1.44 – 1.30 (m, 8H), 0.94 (dd, *J* = 13.2, 5.7 Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 167.92 (s), 154.66 (s), 138.69 (s), 135.29 (s), 117.21 (s), 112.20 (s), 105.97 (s), 67.64 (s), 38.77 (s), 30.39 (s), 28.89 (s), 23.84 (s), 22.92 (s), 14.01 (s), 11.04 (s). HRMS (ESI): calcd.for $C_{15}H_{20}O_3S_2$ [M+Na]$^+$: 335.0752, found: 335.0750.



13

2-Ethylhexyl 3-methoxythieno[3,4-b]thiophene-2-carboxylate (13)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.69 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 4.26 (s, 3H), 4.20 (dd, *J* = 5.5, 2.9 Hz, 2H), 1.73 – 1.61 (m, 1H), 1.43 – 1.28 (m, 8H), 0.93 (dd, *J* = 13.6, 6.1 Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 162.59 (s), 151.50 (s), 139.83 (s), 135.70 (s), 116.66 (s), 116.24 (s), 111.86 (s), 67.21 (s), 60.67 (s), 38.85 (s), 30.49 (s), 28.92 (s), 23.91 (s), 22.97 (s), 14.05 (s), 11.09 (s). HRMS (ESI): calcd for $C_{16}H_{22}O_3S_2$ [M+Na]$^+$: 349.0908, found:349.0906.

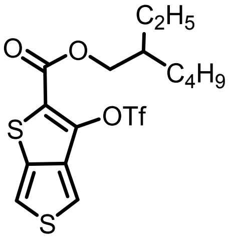


14

2-Ethylhexyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate (14)

^{1}H NMR (400 MHz, CDCl$_3$) δ 4.22 (s, 2H), 4.07 (s, 3H), 1.73 – 1.64 (m, 1H), 1.47 – 1.31 (m, 8H), 0.97 – 0.88 (m, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.57 (s), 151.75 (s), 138.94 (s), 136.50 (s), 122.62 (s), 101.80 (s), 98.00 (s), 67.77 (s), 63.11 (s), 38.85

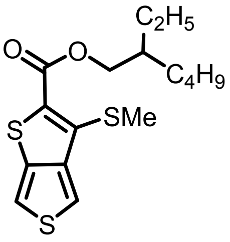
(s), 30.42 (s), 28.93 (s), 23.85 (s), 22.94 (s), 14.02 (s), 11.03 (s). HRMS (ESI): calcd.for $C_{16}H_{20}Br_2O_3S_2$ $[M+Na]^+$: 504.9118, found: 504.9118.



15

2-Ethylhexyl-3-(((trifluoromethyl)sulfonyl)oxy)thieno[3,4-b]thiophene-2-carboxylate (15)

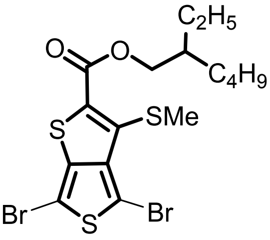
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.6 Hz, 1H), 7.38 (d, *J* = 2.7 Hz, 1H), 4.28 (dd, *J* = 6.0, 1.1 Hz, 2H), 1.74 (dt, *J* = 12.3, 6.1 Hz, 1H), 1.45 – 1.30 (m, 8H), 0.92 (dt, *J* = 10.4, 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.60 (s), 137.54 (s), 135.04 (s), 133.84 (s), 128.19 (s), 123.31 (s), 120.12 (s), 116.93 (s), 116.30 (s), 113.54 (s), 68.72 (s), 38.57 (s), 30.20 (s), 28.76 (s), 23.65 (s), 22.90 (s), 13.95 (s), 10.85 (s). HRMS (ESI): calcd.for $C_{16}H_{19}F_3O_5S_3$ $[M+Na]^+$: 467.0244, found: 467.0242. Anal. Calca. for $C_{16}H_{19}F_3O_5S_3$: C: 43.23; H: 4.31; Found: C: 43.21; H: 4.23.



16

2-Ethylhexyl 3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (16)

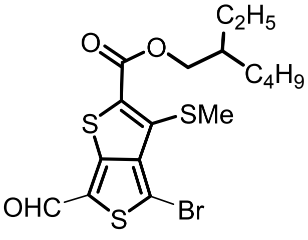
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.28 (s, 1H), 4.27 – 4.21 (m, 2H), 2.73 (s, 3H), 1.74 – 1.67 (m, 1H), 1.45 – 1.28 (m, 8H), 0.93 (dd, *J* = 14.5, 6.8 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.64 (s), 147.40 (s), 137.09 (s), 132.26 (d, *J* = 13.8 Hz), 117.26 (s), 111.50 (s), 67.73 (s), 38.82 (s), 30.47 (s), 28.90 (s), 23.91 (s), 22.95 (s), 17.53 (s), 14.03 (s), 11.08 (s). HRMS (ESI): calcd.for $C_{16}H_{22}O_2S_3$ $[M+Na]^+$: 365.0680, found: 365.0678.



17

2-Ethylhexyl 4,6-dibromo-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (17)

In a Schlenk flask equipped with a magnetic stirrer, were added (**16**, 1.24 g, 3.6 mmol, 1.0 eq), DMF (15 mL), then a solution of NBS (1.92 g, 10.8 mmol, 3.0 eq) in DMF (10 mL) was added at r.t. and stirred for 24 h and the reaction was protected from light. The reaction mixture was quenched with H_2O, extracted with saturated salt water and CH_2Cl_2, dried over Na_2SO_4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: CH_2Cl_2= 5:1) as eluent to obtain **17** (894 mg, 49%) as light yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 4.27 (d, *J* = 4.2 Hz, 2H), 2.52 (s, 3H), 1.75 – 1.65 (m, 1H), 1.40 (dd, *J* = 26.2, 14.5 Hz, 8H), 0.94 (dd, *J* = 14.6, 6.9 Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 161.49 (s), 143.10 (s), 139.42 (s), 138.43 (s), 131.64 (s), 103.13 (s), 97.42 (s), 72.07 – 71.87 (m), 68.16 (s), 38.82 (s), 30.44 (s), 29.63 – 29.43 (m), 28.92 (s), 23.88 (s), 22.94 (s), 21.60 – 21.40 (m), 20.39 (s), 14.40 – 14.20 (m), 14.03 (s), 11.06 (s). HRMS (ESI): calcd.for $C_{16}H_{20}Br_2O_2S_3$ $[M+Na]^+$: 520.8890, found: 520.8888.

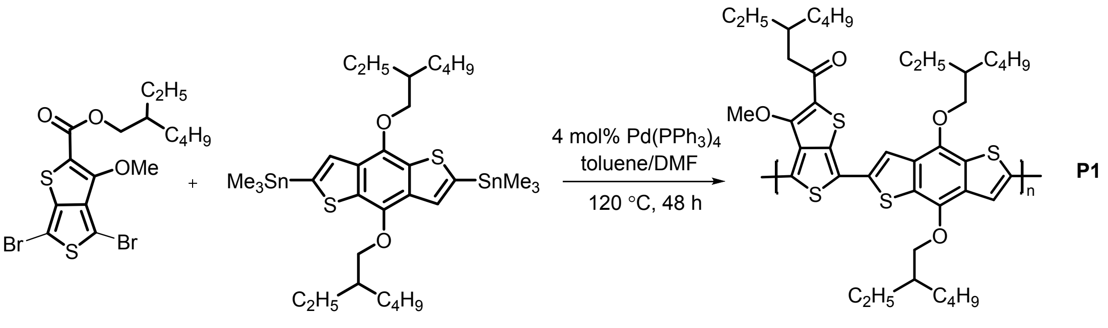


18

2-Ethylhexyl-4-bromo-6-formyl-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate(18)

A solution of **16** in 1,2-dichloroethane (DCE, 100 mL) was degassed with argon for 15 min and then the Vilsmerier reagent (was prepared according to the literature)[2] was added into the reaction slowly and stirred at room temperature for 1 h. The reaction solution was stirred at 100 °C for another 24 h. Then saturated sodiumacetate solution was added slowly to quench the reaction. The reaction solution was washed with water for three times and extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA=10:1) as eluent to obtain 2-ethylhexyl 6-formyl-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (5.3 g, 91%) as yellow solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.89 (s, 1H), 8.19 (s, 1H), 4.23 (dd, *J* = 10.4, 5.0 Hz, 2H), 2.71 (s, 3H), 1.68 (dt, *J* = 12.1, 6.0 Hz, 1H), 1.44 – 1.28 (m, 8H), 0.94 – 0.88 (m, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 179.63 (s), 162.07 (s), 148.11 (s), 143.12 (s), 133.55 (s), 132.25 (s), 127.58 (s), 127.02 (s), 68.05 (s), 53.41 (s), 38.81 (s), 30.41 (s), 28.93 (s), 23.85 (s), 22.94 (s), 17.96 (s), 14.05 (s), 11.05 (s). HRMS (ESI): calcd.for $C_{17}H_{22}O_3S_3$ $[M+Na]^+$: 393.0629, found: 393.0624.

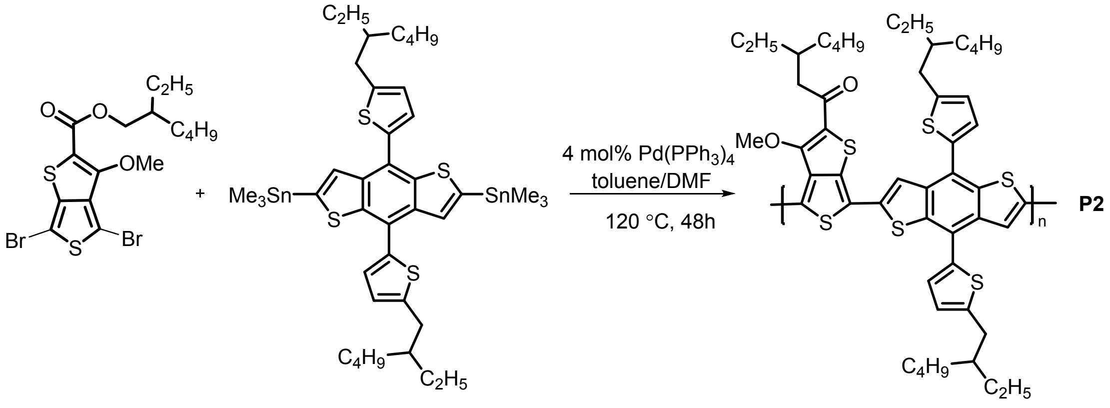
In a Schlenk flask equipped with a magnetic stirrer, were added 2-ethylhexyl 6-formyl-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate (5.0 g, 14 mmol, 1.0 eq), DMF (50 mL), then NBS (3.7 g,21mmol, 1.5eq) was added one-pot at 0 °C and then stirred for 24 h and the reaction was protected from light. The reaction solution was washed with water for three times and extracted with CH_2Cl_2, dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The crude product was purified by column chromatography (PE: EA=10:1) as eluent to obtain **18** (2.89 g, 91%) as yellow-brown viscous liquid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.81 (s, 1H), 4.28 (t, *J* = 4.5 Hz, 2H), 2.55 (s, 3H), 1.74 – 1.68 (m, 1H), 1.47 – 1.31 (m, 8H), 0.94 (dd, *J* = 15.1, 7.5 Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 178.31 (s), 161.30 (s), 144.44 (s), 143.04 (s), 139.71 (s), 131.04 (s), 126.72 (s), 117.14 (s), 68.34 (s), 38.85 (s), 30.43 (s), 28.93 (s), 23.87 (s), 22.93 (s), 20.42 (s), 14.02 (s), 11.04 (s). HRMS (ESI): calcd.for $C_{17}H_{21}BrO_3S_3$ $[M+Na]^+$: 470.9734, found: 470.9730.



The procedure for preparation and purification of Polymer P1

In a 100 mL Schlenk flask, 2-ethylhexyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate **14** (202 mg, 0.417 mmol) and (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (322 mg, 0.417 mmol) were dissolved in anhydrous toluene (10 mL) and DMF (2.5 mL).

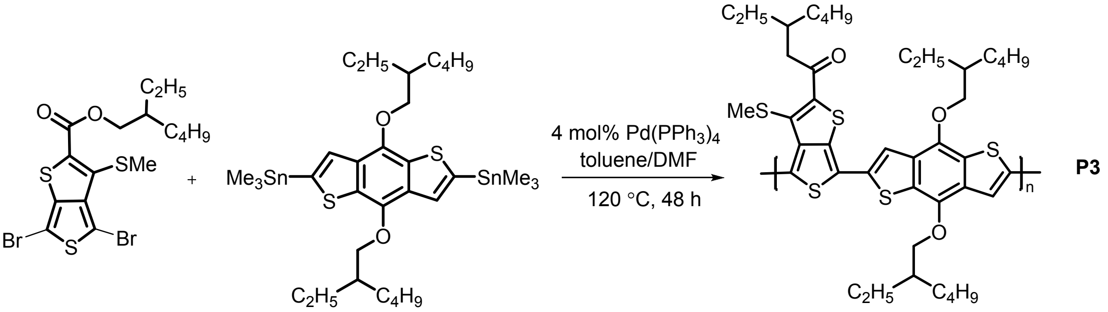
After being purged with nitrogen for 20 min, 21 mg (4.0 mol%) of $Pd(PPh_3)_4$ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 °C) for 48 h under an nitrogen atmosphere (according to the procedure in the literature)[3]. After the reaction mixture was cooled down to room temperature, 41 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer **P1** (276 mg, yield 87%). GPC: Mw = 30.1 KD, PDI= 2.1.



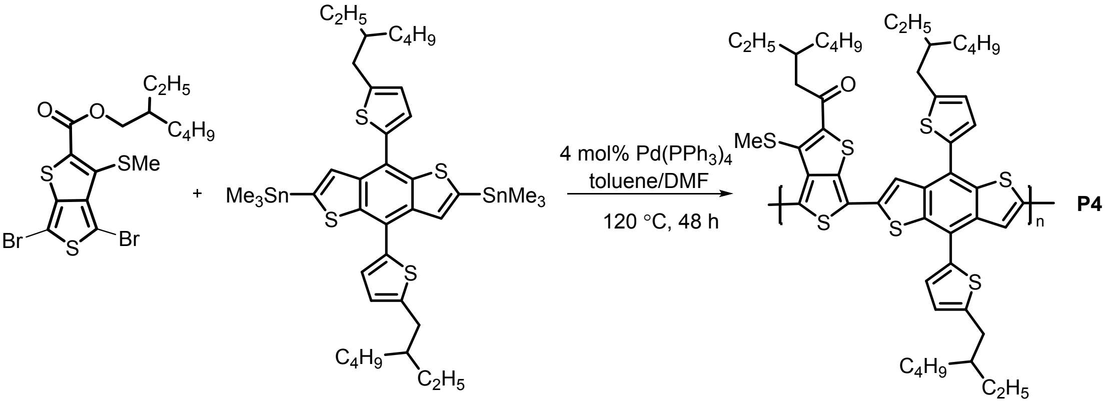
The procedure for preparation and purification of Polymer P2

In a 25 mL pressure tube, 2-ethylhexyl 4,6-dibromo-3-methoxythieno[3,4-b]thiophene-2-carboxylate **14** (97 mg, 0.2 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (181 mg, 0.2 mmol) were dissolved in anhydrous toluene (4 mL) and DMF (1.0 mL). After being purged with nitrogen for 20 min, 10 mg (4.0 mol%) of $Pd(PPh_3)_4$ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 °C) for 48 h under an nitrogen atmosphere. After the reaction mixture was cooled down to room temperature, 20 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by

Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer **P2** (148 mg, yield 84%). GPC: Mw = 20.4 KD, PDI= 1.9.



In a 100 mL Schlenk flask, 2-ethylhexyl 4,6-dibromo-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate **17** (200 mg, 0.4 mmol) and (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (309 mg, 0.4 mmol) were dissolved in anhydrous toluene (8 mL) and DMF (2 mL). After being purged with nitrogen for 20 min, 18.5 mg (4.0 mol%) of $Pd(PPh_3)_4$ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 ^{o}C) for 48 h under an nitrogen atmosphere. After the reaction mixture was cooled down to room temperature, 40 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer **P3** (152 mg, yield 48%). GPC: Mw = 39.8 KD, PDI= 1.9.



In a 25 mL pressure tube, 2-ethylhexyl 4,6-dibromo-3-(methylthio)thieno[3,4-b]thiophene-2-carboxylate **17** (150 mg, 0.3 mmol) and (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (272 mg, 0.3 mmol) were dissolved in anhydrous toluene (6 mL) and DMF (1.5 mL). After being purged with nitrogen for 20 min, 15 mg (4.0 mol%) of $Pd(PPh_3)_4$ was added into the flask as the catalyst, and then the reaction mixture was purged with nitrogen for another 30 min. The reaction mixture was stirred and heated to reflux (120 °C) for 48 h under an nitrogen atmosphere. After the reaction mixture was cooled down to room temperature, 31 mg of tributyl(thiophen-2-yl)stannane was added under nitrogen atmosphere and the reaction was refluxed for another 10 h. The reaction mixture was cooled to room temperature and added dropwise to 100 mL methanol. The precipitate was collected and further purified by Soxhlet extraction with methanol, acetone, hexane, and chloroform in sequence. The polymer was recovered as solid from the chloroform fraction by precipitation from methanol. The solid was dried under vacuum to get polymer **P4** (242 mg, yield 89%). GPC: Mw = 25.8 KD, PDI= 2.1.

3. Optoelectronic properties

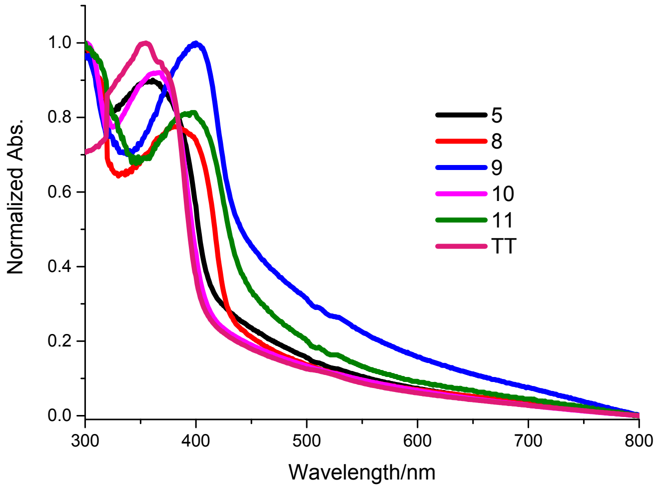


Figure S1. Normalized UV/Vis absorption spectra of **5**, **8**, **9**, **10**, **11** and TT as a film

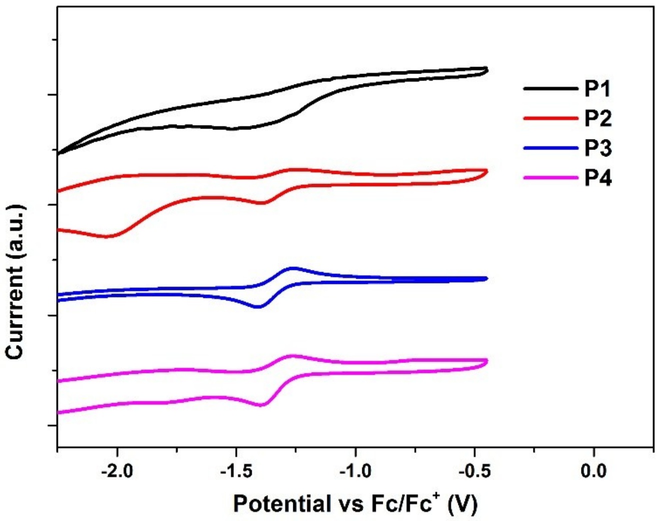


Figure S2. Reductive CV curves of **P1**, **P2**, **P3** and **P4** film in diluted CH_3CN solution with a scan rate of 100 mV s^{-1}.

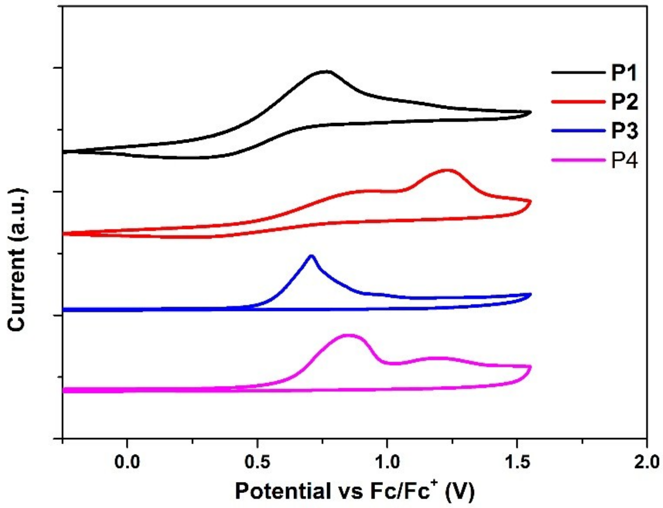


Figure S3. Oxidative CV curves of **P1**, **P2**, **P3** and **P4** in film in diluted CH_3CN solution with a scan rate of 100 mV s^{-1}.

4. References

1. WO 2008011337A1, Jan 24, 2008.

2. H. Gao, Y. Sun, X. Wan, B. Kan, X. Ke, H. Zhang, C. Li, and Y. Chen. *Sci. China Mater*. 2017, **60**, 819.

3. Q. V. Hoang, C. E. Song, S. J. Moon, S. K. Lee, J.C. Lee, B. J. Kim, and W. S. Shin. *Macromolecules*. 2015, **48**, 3918.

5.GPC and NMR spectra

Cirrus GPC Sample Injection Report

Generated by: Administrator Friday, November 03, 2017 9:48 AM
Workbook: F:\Cirrus Workbooks\20140701\20140701.plw

Sample Details

LWLP1
Acquired: 11/2/2017 6:33:27 PM
Batch Name: 20171102
Filename: F:\Cirrus Workbooks\20140701\20171102-0004.cgrm

Workbook Details

Eluent: TCB stabilised with 0.0125% BHT
Flow Rate: 1.00 ml/min
Column Set: 3 x PLgel MIXED-B LS 300 x 7.5 mm
Temperature: 150
Detector: RI
Injection Volume: 200.0 ul

Analysis Using Method: 20171022

Comments:

Calibration Used: 10/26/2017 2:28:28 PM

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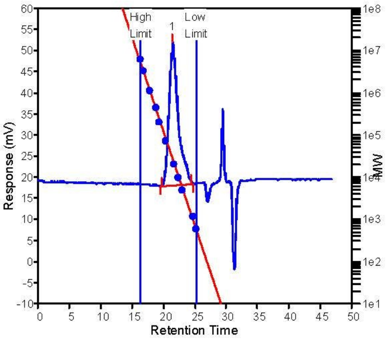
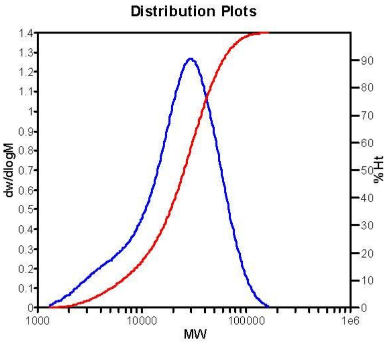
Low Limit MW RT: 25.32 mins
High Limit MW: 5198272
Low Limit MW: 529
K: 17.5000
Alpha: 0.6700





MW Averages

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Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
1		19.72	21.40	24.43	33.9192	100	3608.57	100

Sample Injection Report

Peak Detection

Peak No	Type	St Detect Code	End Detect Code	Is St Mod	Is Max Mod	Is End Mod
1	0	1	1	No	No	No

Baseline Detection

No	Start RT (mins)	End RT (mins)	Start Height	End Height	Is St Mod	Is End Mod
1	19.62	24.80	17.89	18.42	No	No

Cirrus GPC Version 3.4 Page 2 11/3/2017 9:48 AM

PDF created with pdfFactory Pro trial version www.pdffactory.com

Cirrus GPC Sample Injection Report

Generated by: Administrator
Friday, November 03, 2017 9:46 AM
Workbook: F:\Cirrus Workbooks\20140701\20140701.plw

Sample Details

LWLP2
Acquired: 11/2/2017 7:24:11 PM
Batch Name: 20171102
Filename: F:\Cirrus Workbooks\20140701\20171102-0005.cgrm

Workbook Details

Eluent: TCB stabilised with 0.0125% BHT
Flow Rate: 1.00 ml/min
Column Set: 3 x PLgel MIXED-B LS 300 x 7.5 mm
Temperature: 150
Detector: RI
Injection Volume: 200.0 ul

Analysis Using Method: 20171022

Comments:

Calibration Used: 10/26/2017 2:28:28 PM

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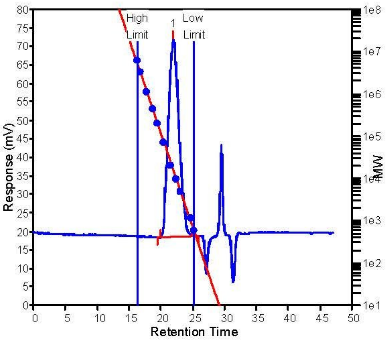
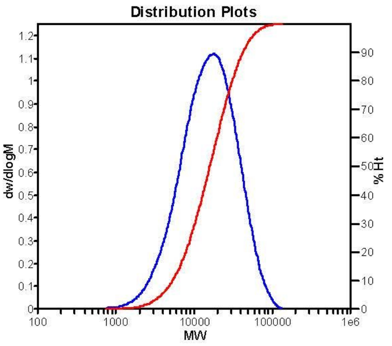
Low Limit MW: 529
K: 17.5000
Alpha: 0.6700





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
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Processed Peaks

Peak No	Name	Start RT (mins)	Max RT (mins)	End RT (mins)	Pk Height (mV)	% Height	Area (mV.secs)	% Area
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Sample Injection Report

Peak Detection

Peak No	Type	St Detect Code	End Detect Code	Is St Mod	Is Max Mod	Is End Mod
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Baseline Detection

No	Start RT (mins)	End RT (mins)	Start Height	End Height	Is St Mod	Is End Mod
1	19.48	25.97	18.34	18.68	No	No

Cirrus GPC Sample Injection Report

Generated by: Administrator Friday, November 03, 2017 10:06 AM
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Sample Details

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Acquired: 11/2/2017 8:14:55 PM
Batch Name: 20171102
Filename: F:\Cirrus Workbooks\20140701\20171102-0006.cgrm

Workbook Details

Eluent: TCB stabilised with 0.0125% BHT
Column Set: 3 x PLgel MIXED-B LS 300 x 7.5 mm
Detector: RI
Flow Rate: 1.00 ml/min
Temperature: 150
Injection Volume: 200.0 ul

Analysis Using Method: 20171022

Comments:

Calibration Used: 10/26/2017 2:28:28 PM

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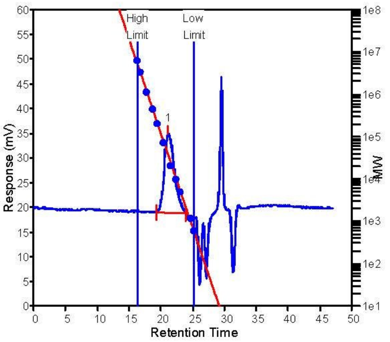
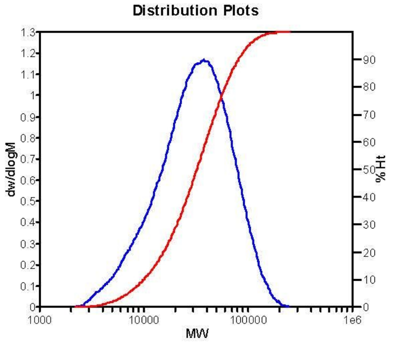
High Limit MW: 5198272
K: 17.5000
Low Limit MW RT: 25.32 mins
Low Limit MW: 529
Alpha: 0.6700





MW Averages

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Processed Peaks

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Sample Injection Report

Peak Detection

Peak No	Type	St Detect Code	End Detect Code	Is St Mod	Is Max Mod	Is End Mod
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Baseline Detection

No	Start RT (mins)	End RT (mins)	Start Height	End Height	Is St Mod	Is End Mod
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Cirrus GPC Sample Injection Report

Generated by: Administrator
Friday, November 03, 2017 10:07 AM
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Sample Details

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Batch Name: 20171102
Filename: F:\Cirrus Workbooks\20140701\20171102-0007.cgrm

Workbook Details

Eluent: TCB stabilised with 0.0125% BHT
Flow Rate: 1.00 ml/min
Column Set: 3 x PLgel MIXED-B LS 300 x 7.5 mm
Temperature: 150
Detector: RI
Injection Volume: 200.0 ul

Analysis Using Method: 20171022

Comments:

Calibration Used: 10/26/2017 2:28:28 PM

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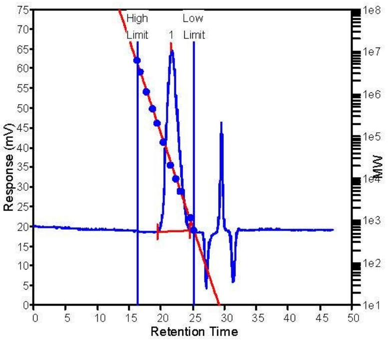
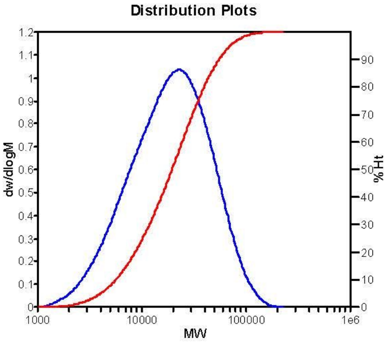
High Limit MW: 5198272
Low Limit MW: 529
K: 17.5000
Alpha: 0.6700





MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
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Processed Peaks

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Peak Detection

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Baseline Detection

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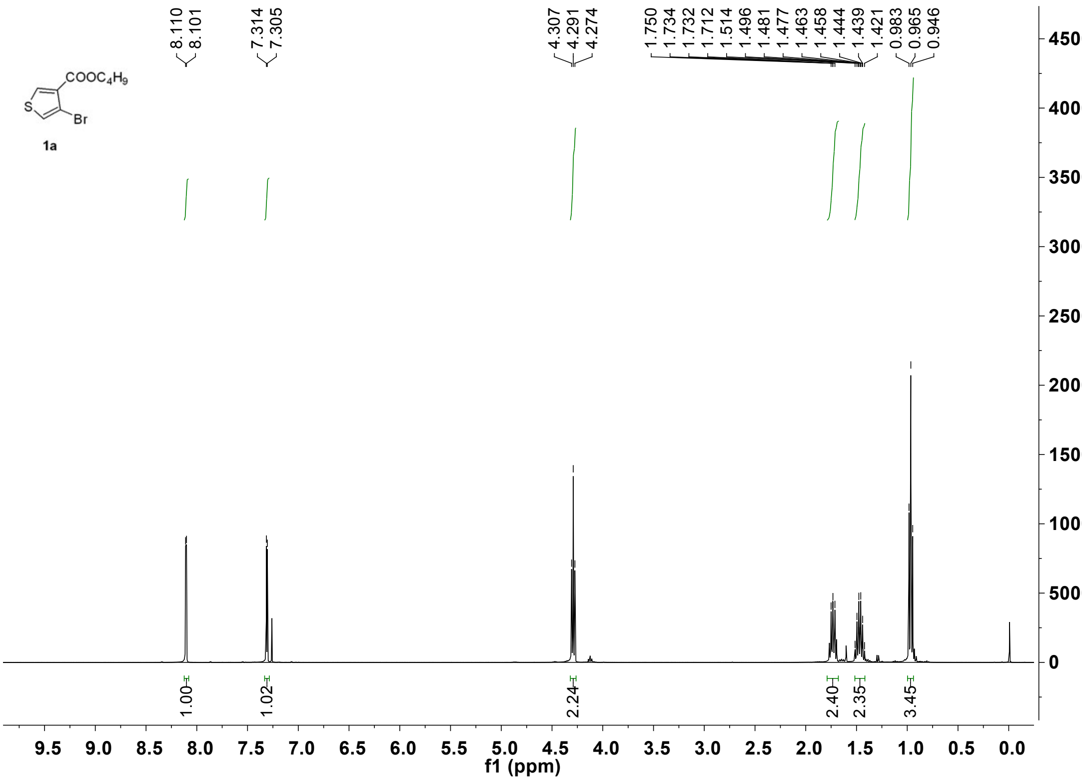
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4.307
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4.274
1.750
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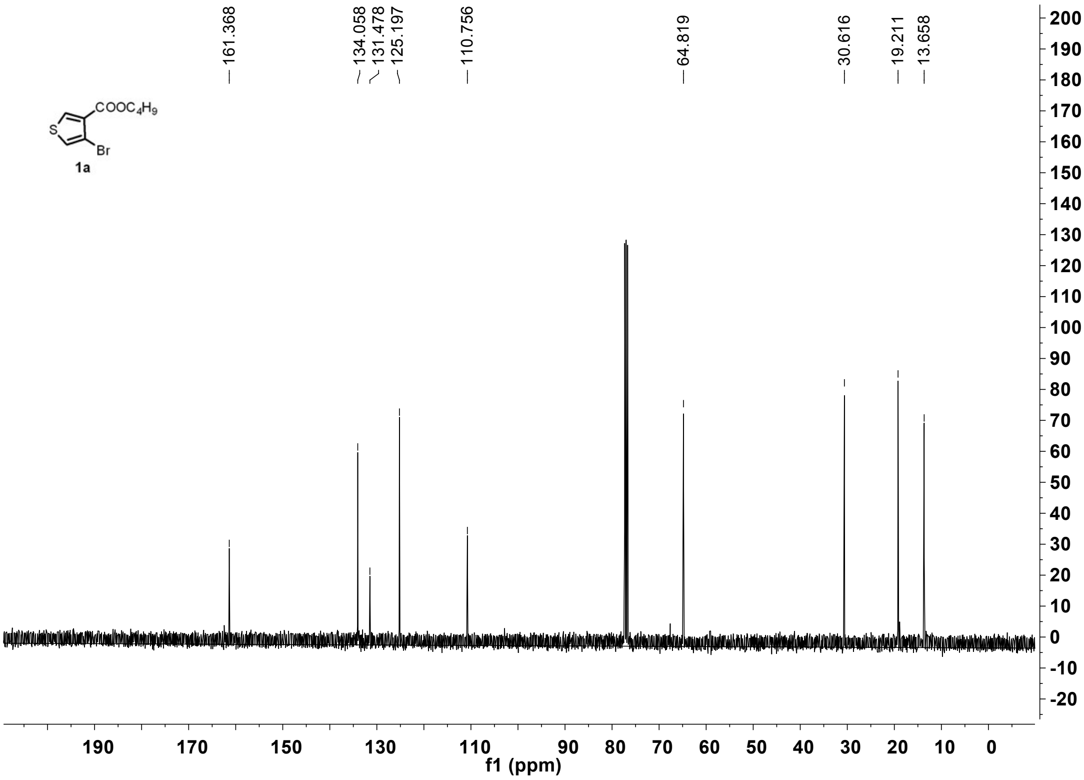
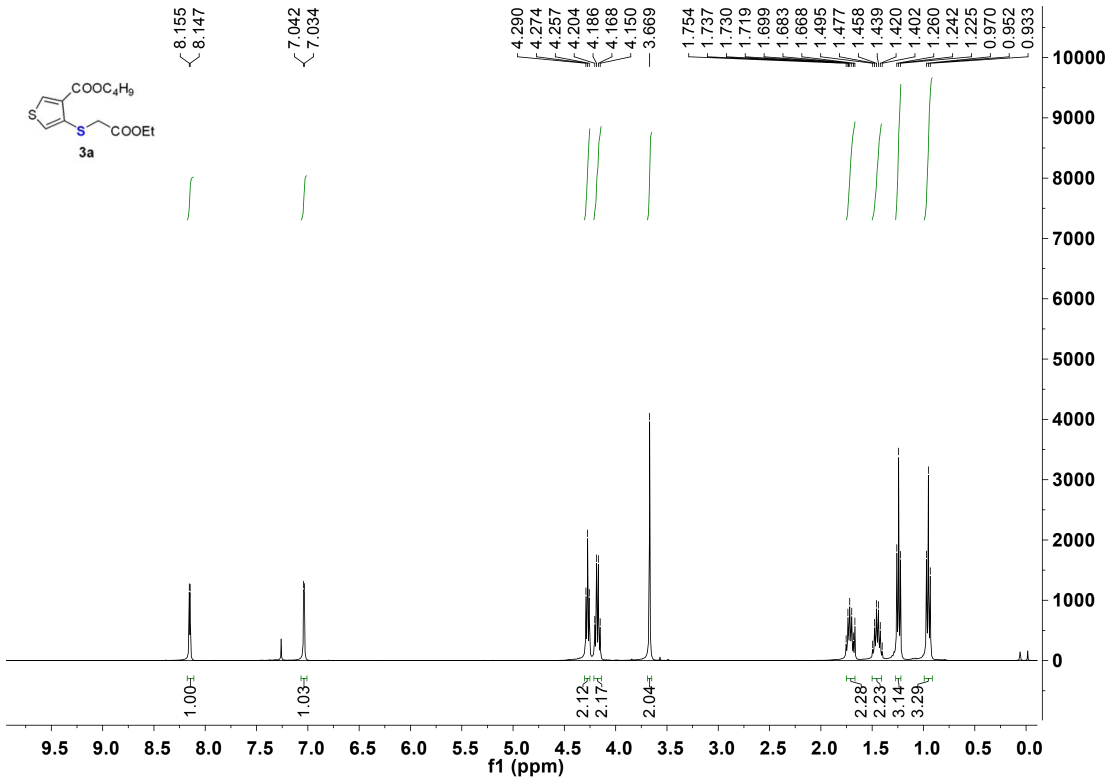
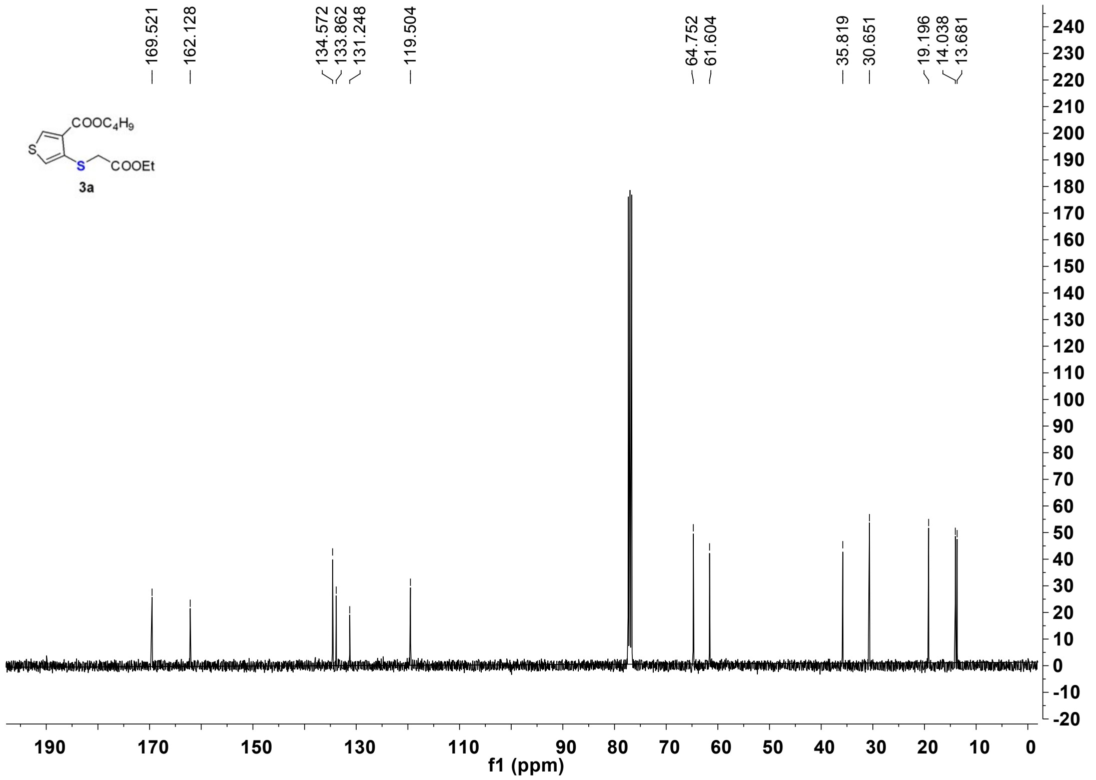
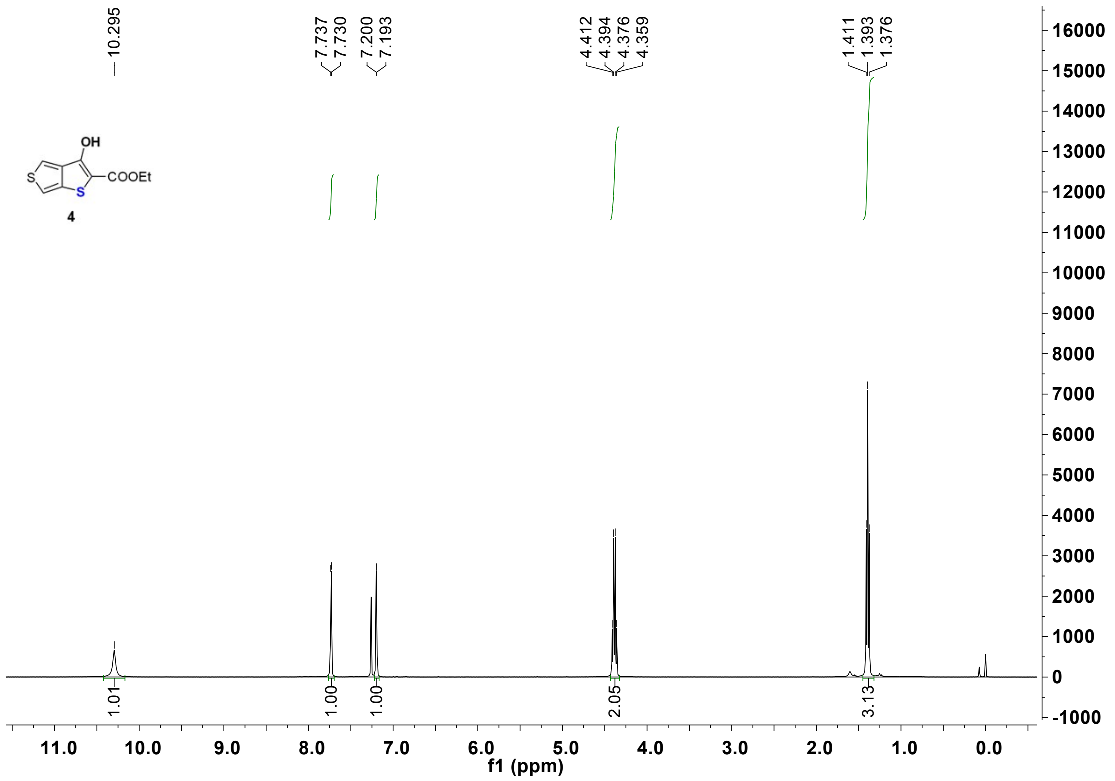
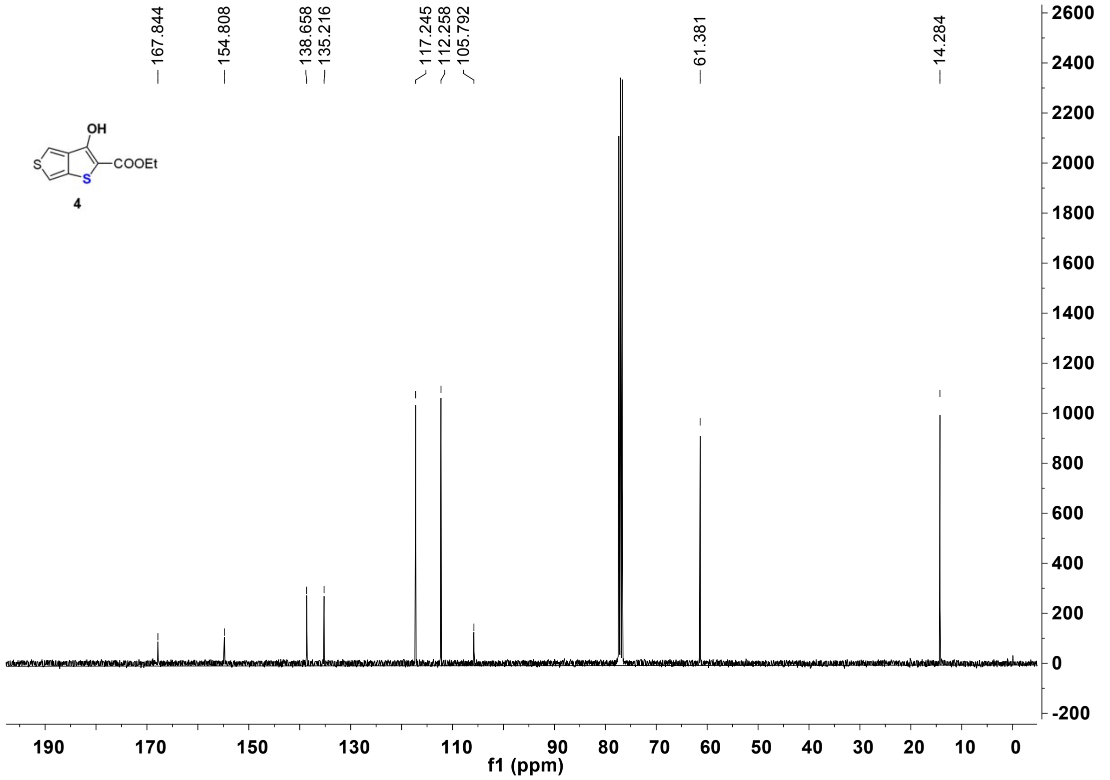
1.514
1.496
1.481
1.477
1.463
1.458
1.444
1.439
1.421
0.983
0.965
0.946
COOC4H9
S
Br
1a
1.00
1.02
2.24
2.40
2.35
3.45
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

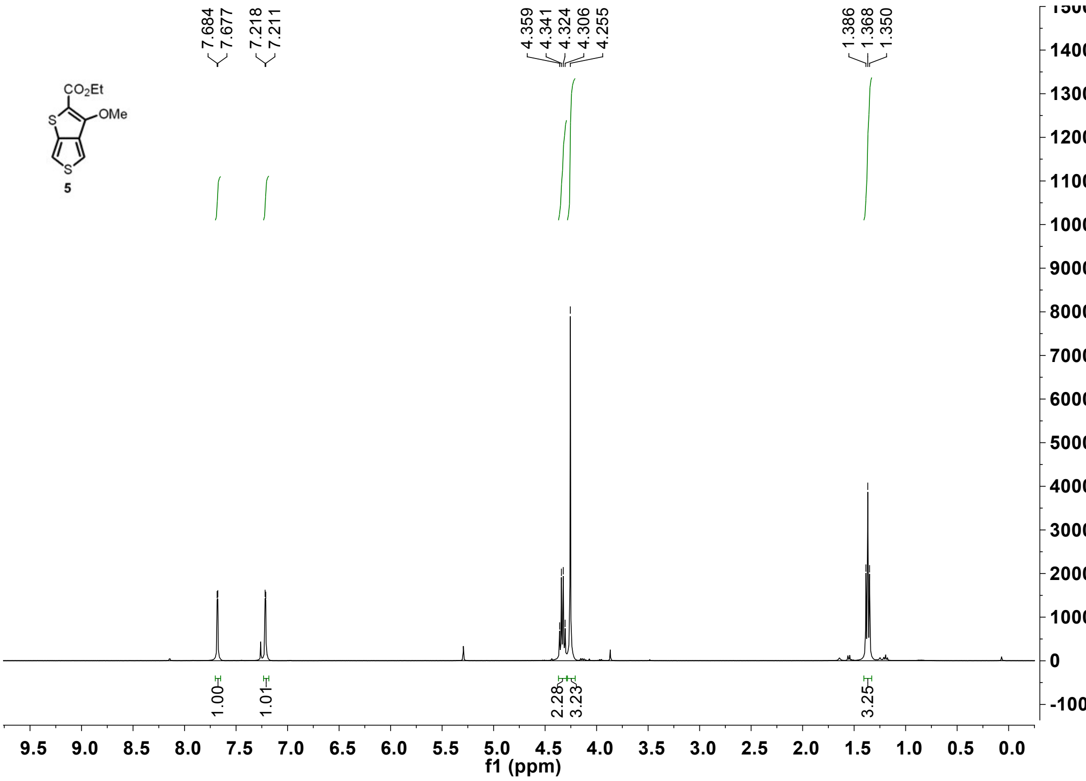

161.368
134.058
131.478
125.197
110.756
64.819
30.616
19.211
13.658
COOC4H9
S
Br
1a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

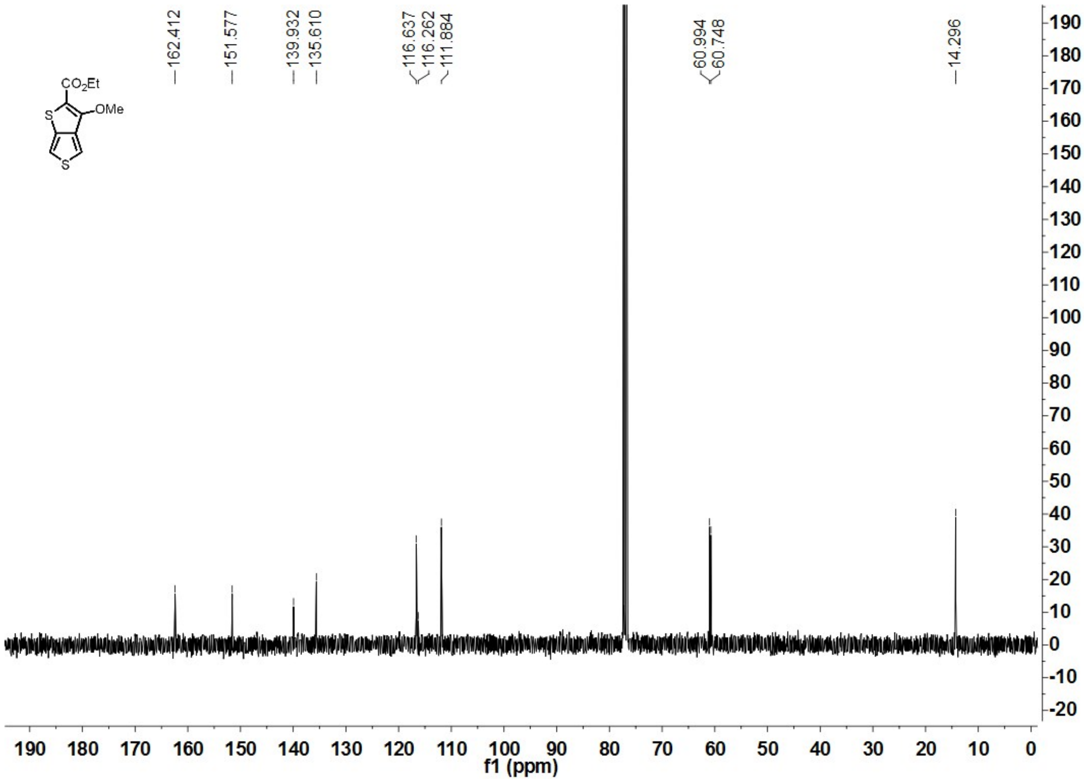

8.155
8.147
7.042
7.034
4.290
4.274
4.257
4.204
4.186
4.168
4.150
3.669
1.754
1.737
1.730
1.719
1.699
1.683
1.668
1.495
1.477
1.458
1.439
1.420
1.402
1.260
1.242
1.225
0.970
0.952
0.933
COOC4H9
S
S
COOEt
3a
1.00
1.03
2.12
2.17
2.04
2.28
2.23
3.14
3.29
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

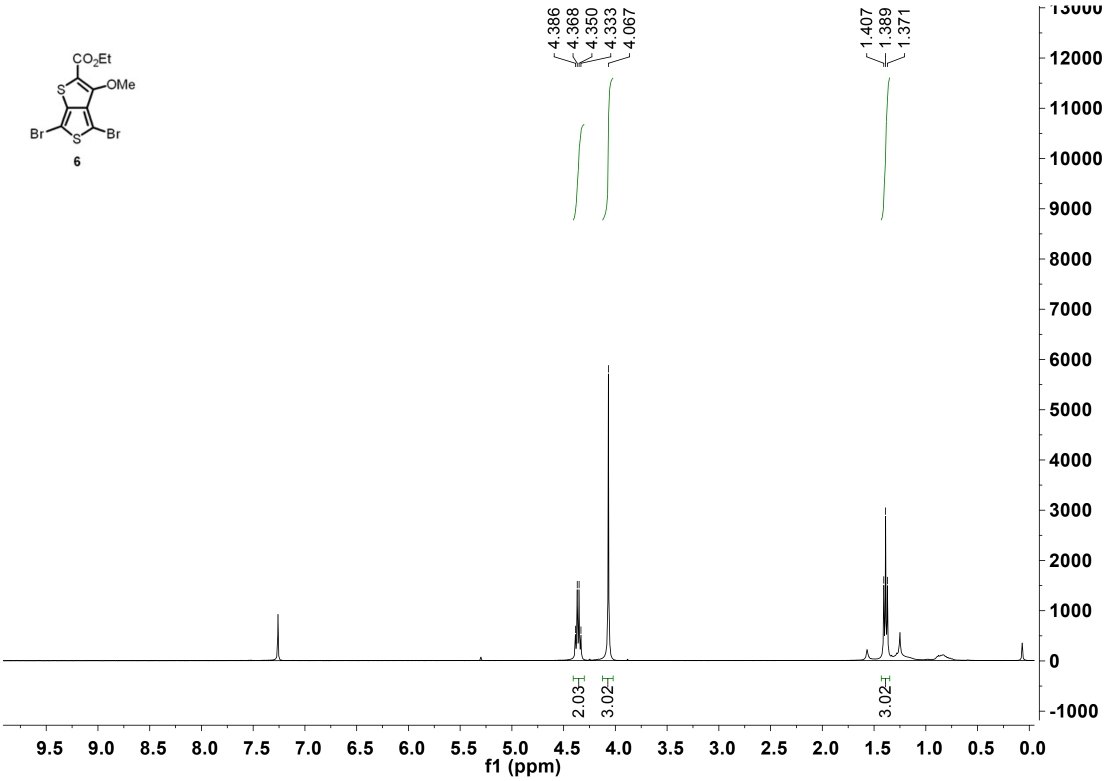

169.521
162.128
134.572
133.862
131.248
119.504
64.752
61.604
35.819
30.651
19.196
14.038
13.681
COOC4H9
S
S
COOEt
3a
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

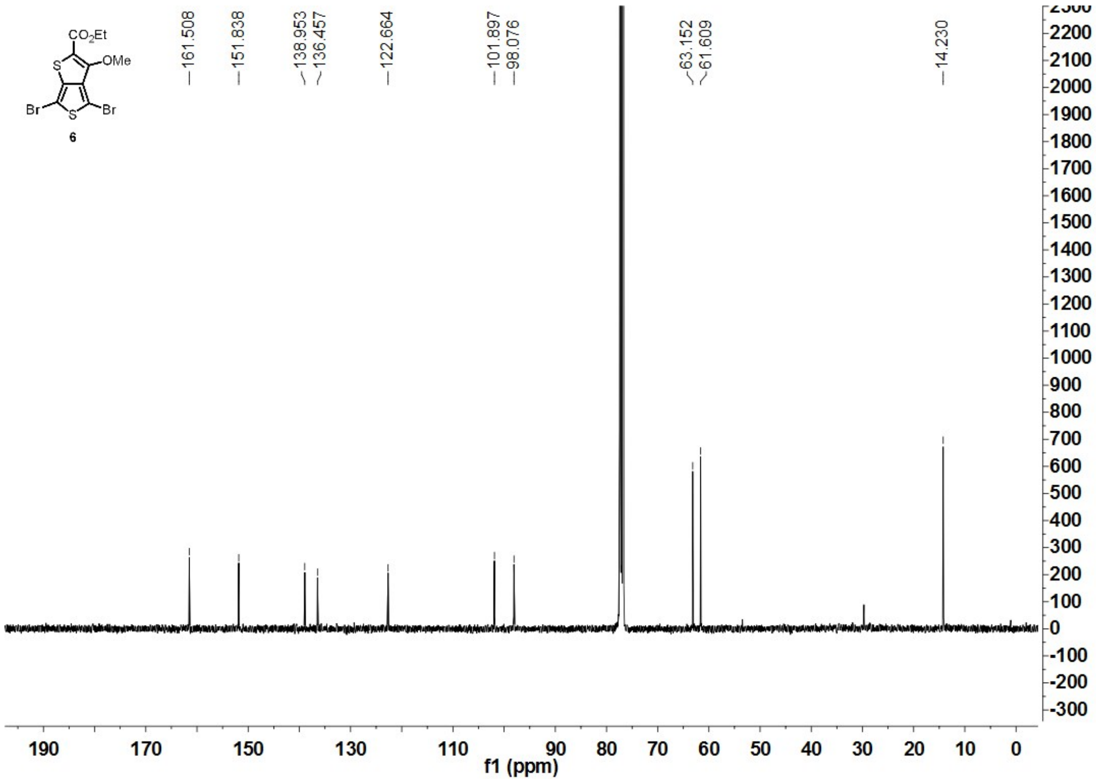

10.295
7.737
7.730
7.200
7.193
4.412
4.394
4.376
4.359
1.411
1.393
1.376
OH
S
COOEt
S
4
1.01
1.00
1.00
2.05
3.13
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

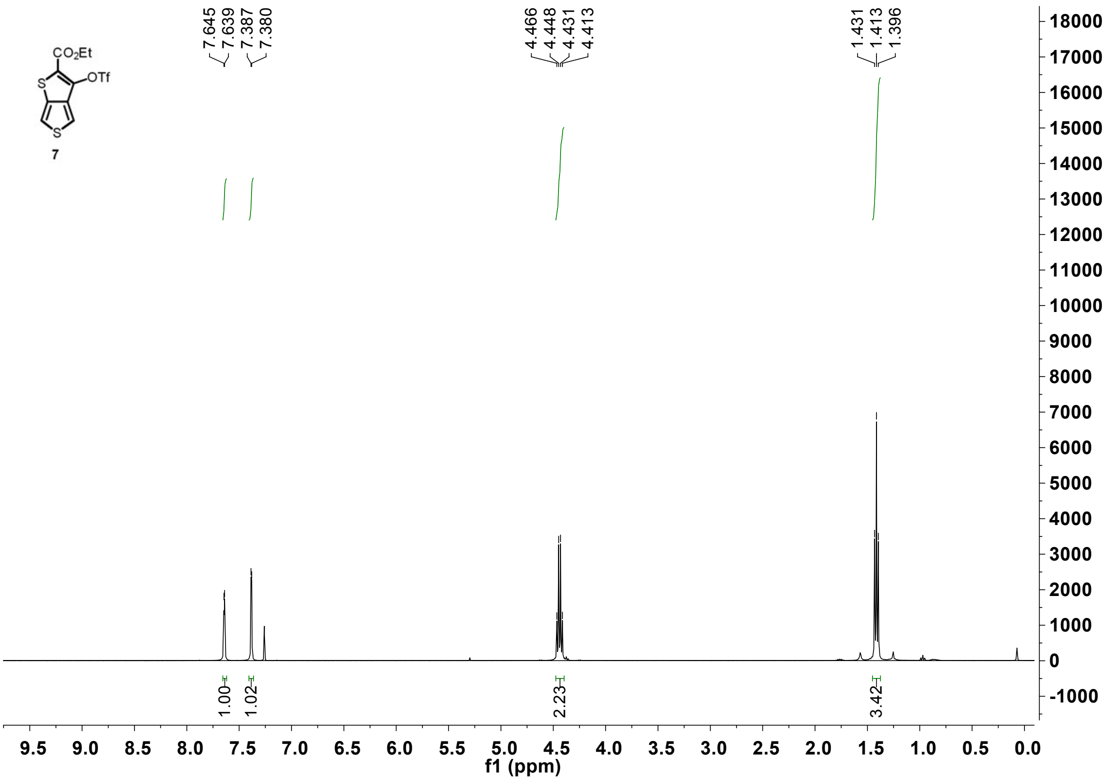

167.844
154.808
138.658
135.216
117.245
112.258
105.792
61.381
14.284
OH
S
COOEt
S
4
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

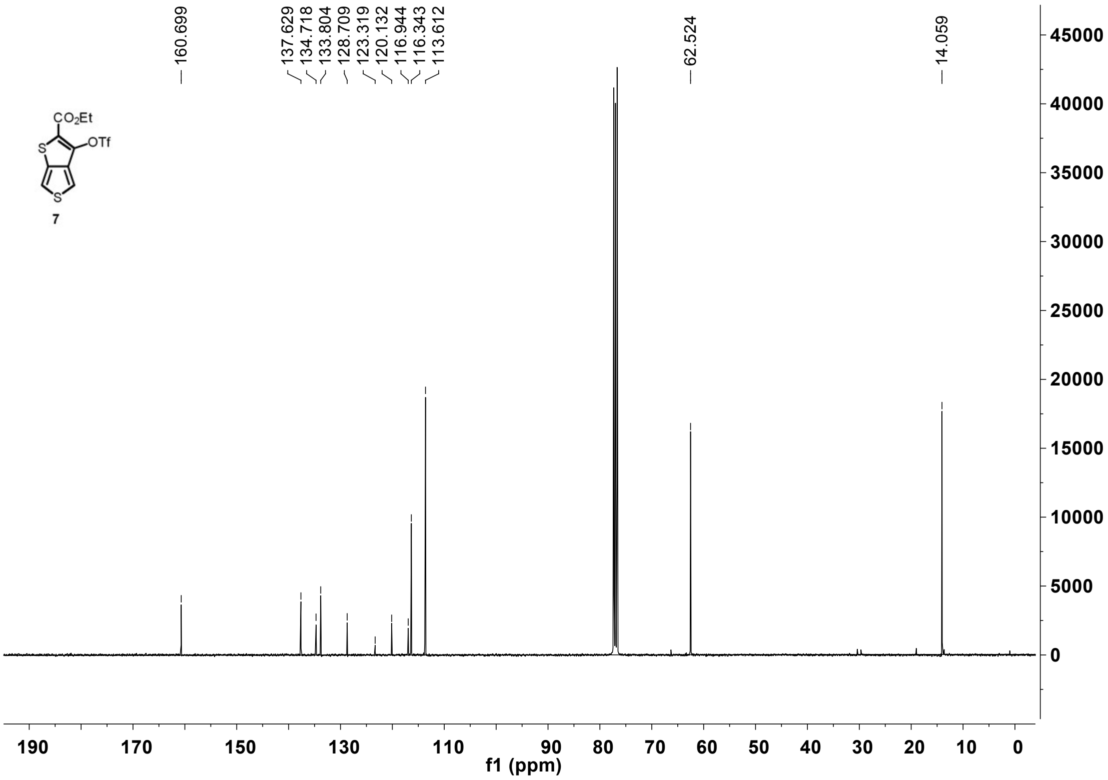

7.684
7.677
7.218
7.211
4.359
4.341
4.324
4.306
4.255
1.386
1.368
1.350
CO2Et
OMe
S
S
5
1.00
1.01
2.28
3.23
3.25
f1 (ppm)

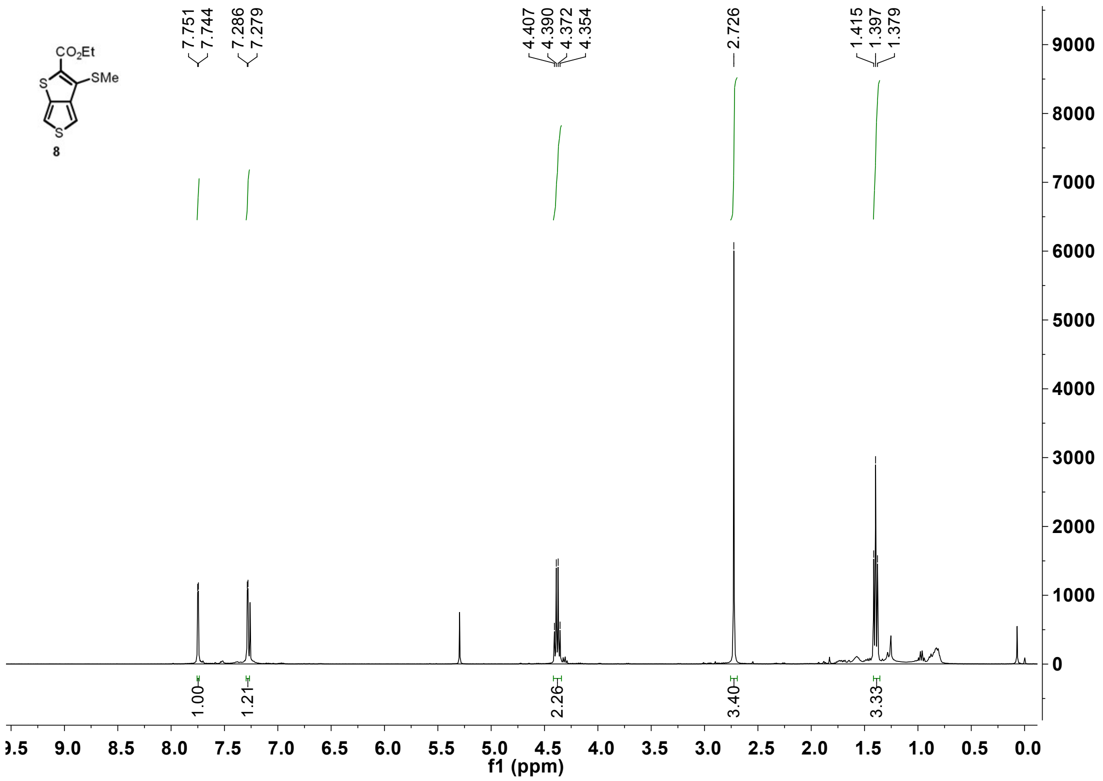

162.412
151.577
139.932
135.610
116.637
116.262
111.884
60.994
60.748
14.296
CO2Et
OMe
S
S
f1 (ppm)


CO2Et
OMe
S
Br
S
Br
6
4.386
4.368
4.350
4.333
4.067
1.407
1.389
1.371
2.03
3.02
3.02
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

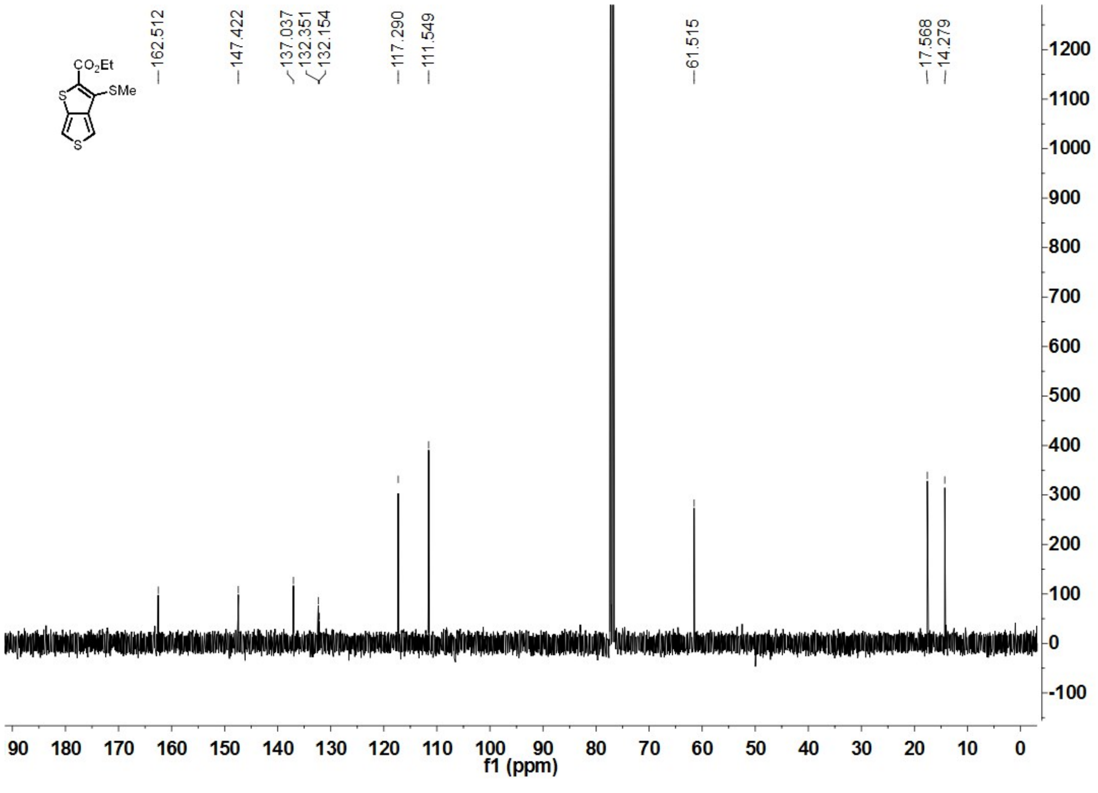

CO2Et
OMe
S
Br
S
Br
6
161.508
151.838
138.953
136.457
122.664
101.897
98.076
63.152
61.609
14.230
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-300
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


CO2Et
OTf
S
S
7
7.645
7.639
7.387
7.380
4.466
4.448
4.431
4.413
1.431
1.413
1.396
1.00
1.02
2.23
3.42
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

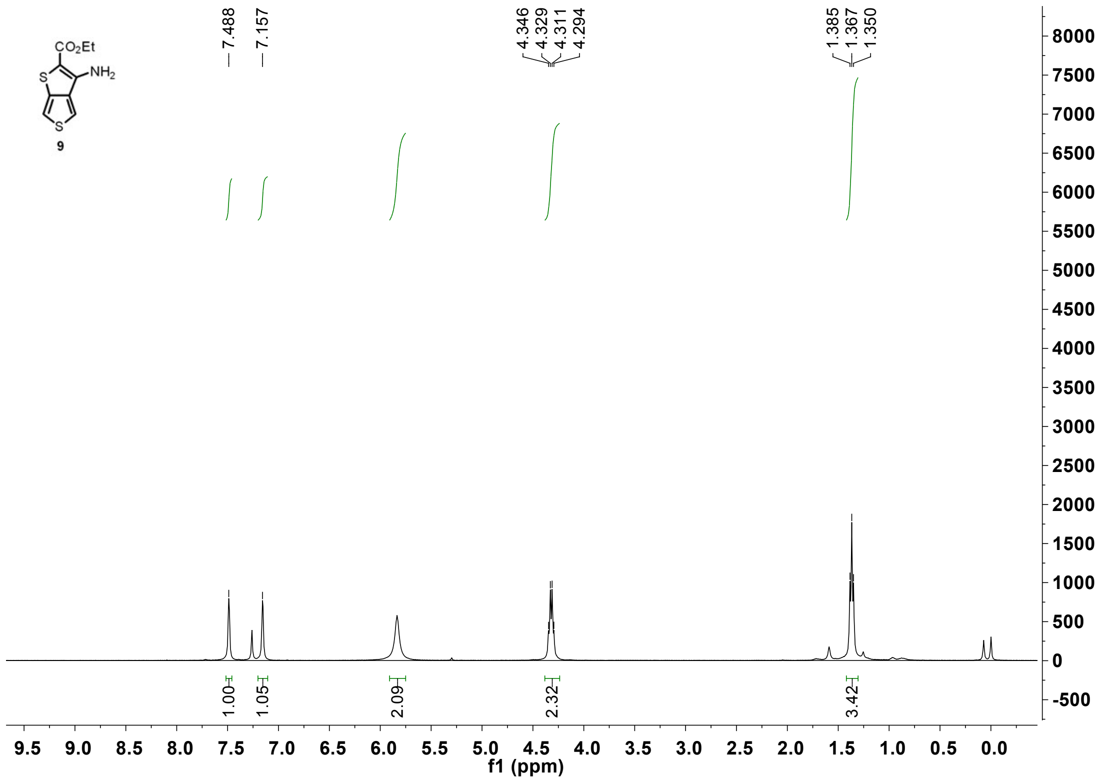

160.699
137.629
134.718
133.804
128.709
123.319
120.132
116.944
116.343
113.612
62.524
14.059
CO2Et
OTf
S
S
7
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

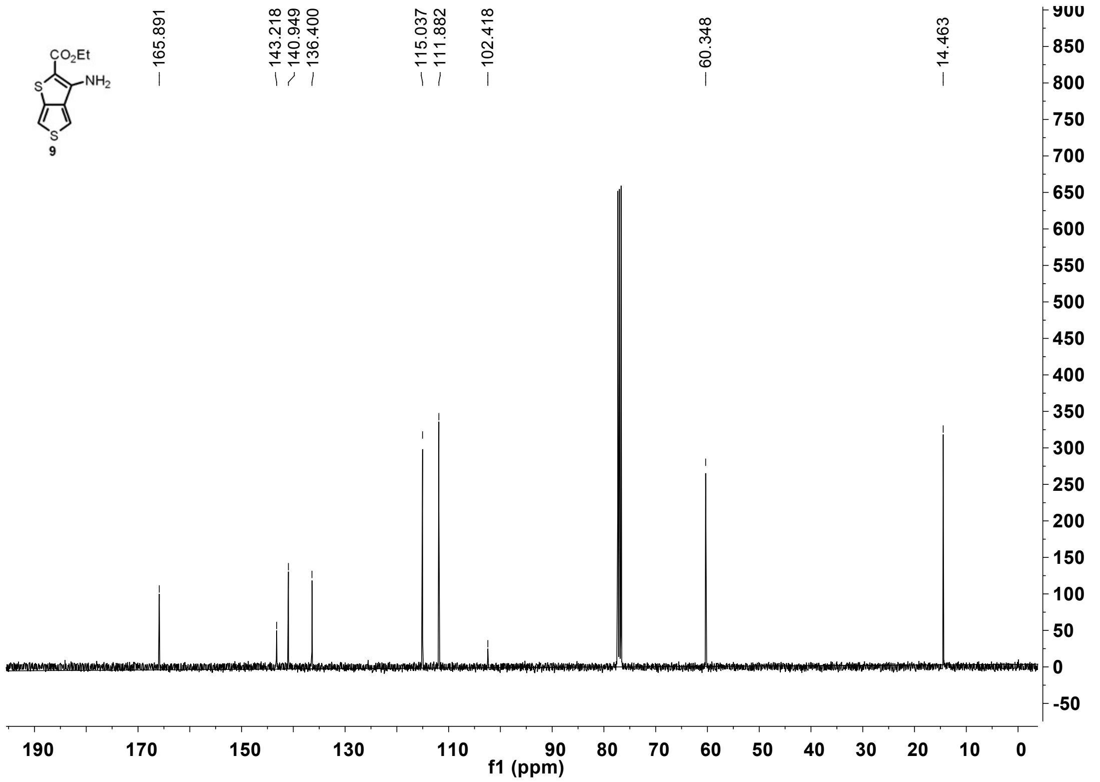


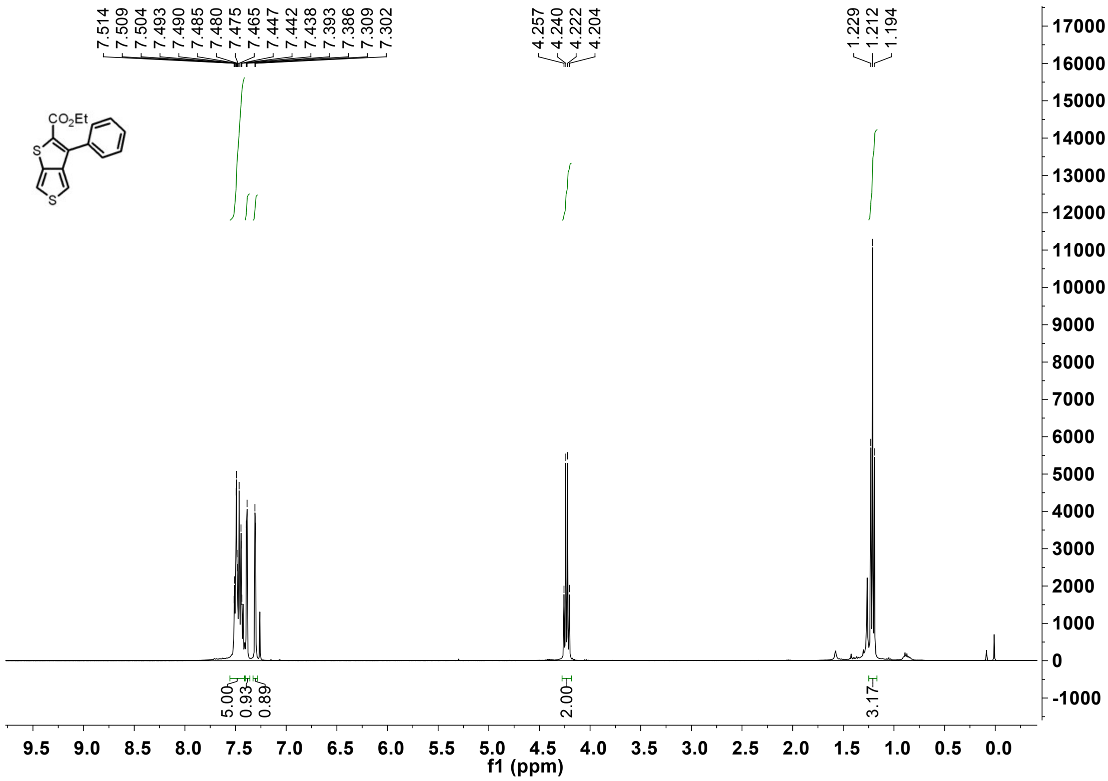
CO2Et
SMe
S
S
8
7.751
7.744
7.286
7.279
4.407
4.390
4.372
4.354
2.726
1.415
1.397
1.379
1.00
1.21
2.26
3.40
3.33
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

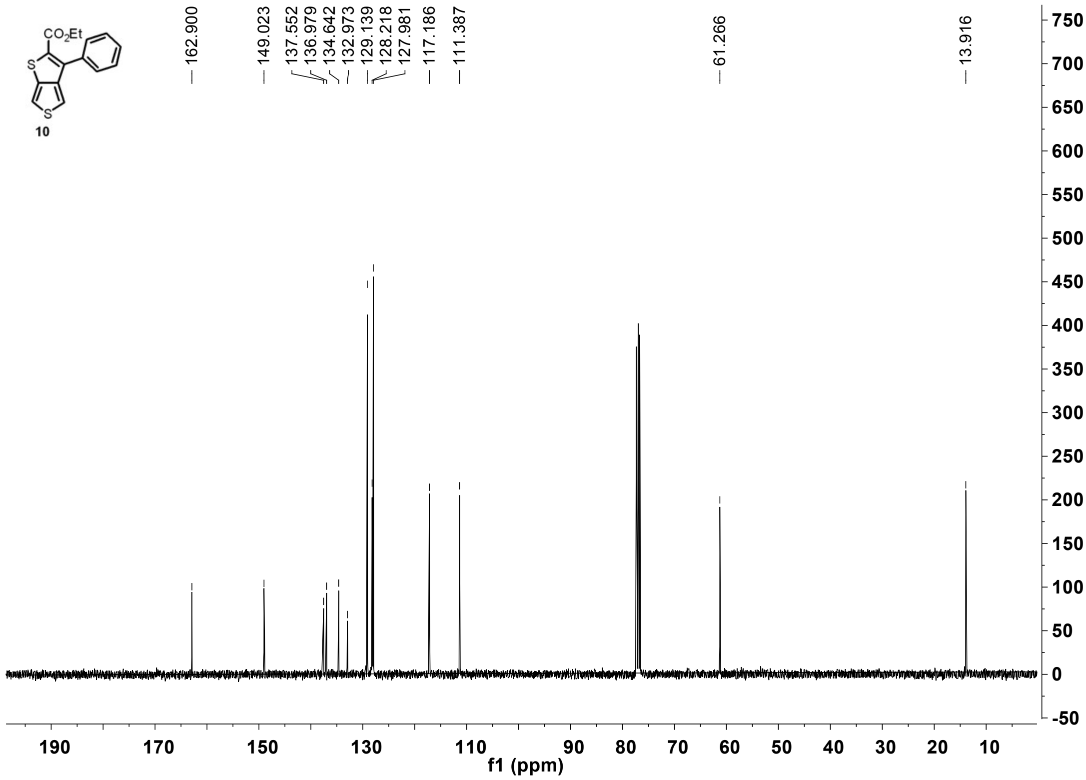


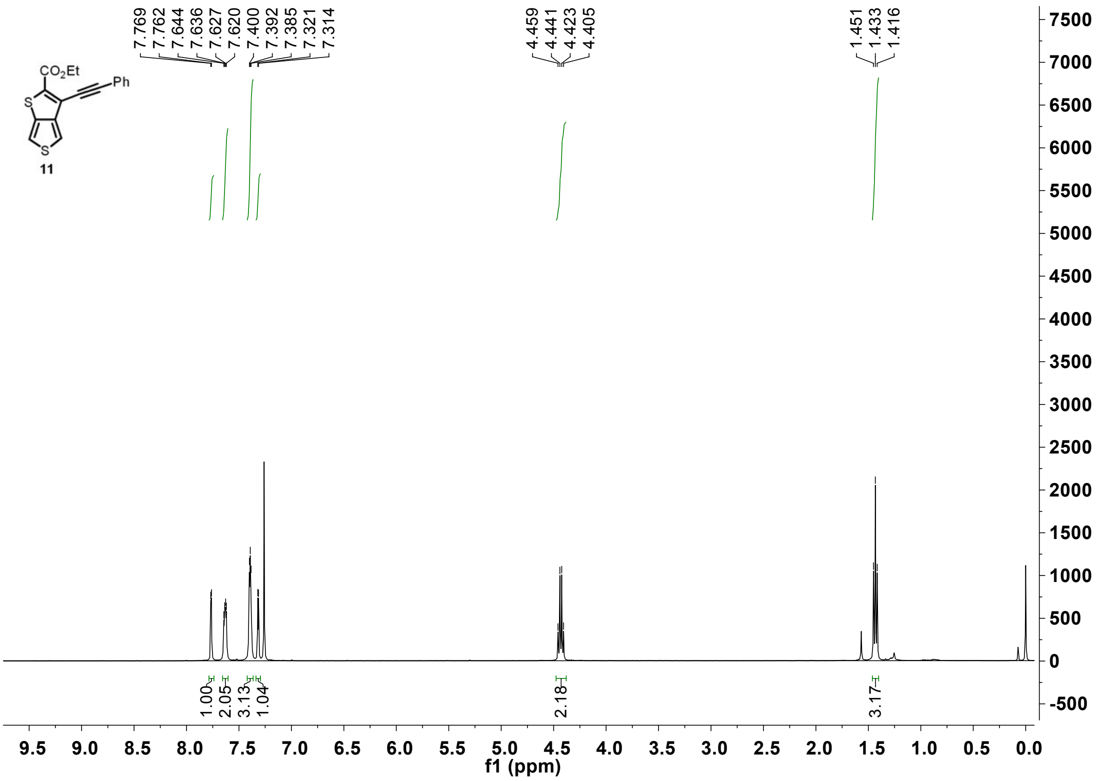
CO2Et
SMe
S
S
162.512
147.422
137.037
132.351
132.154
117.290
111.549
61.515
17.568
14.279
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CO2Et
NH2
S
S
9
7.488
7.157
4.346
4.329
4.311
4.294
1.385
1.367
1.350
1.00
1.05
2.09
2.32
3.42
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

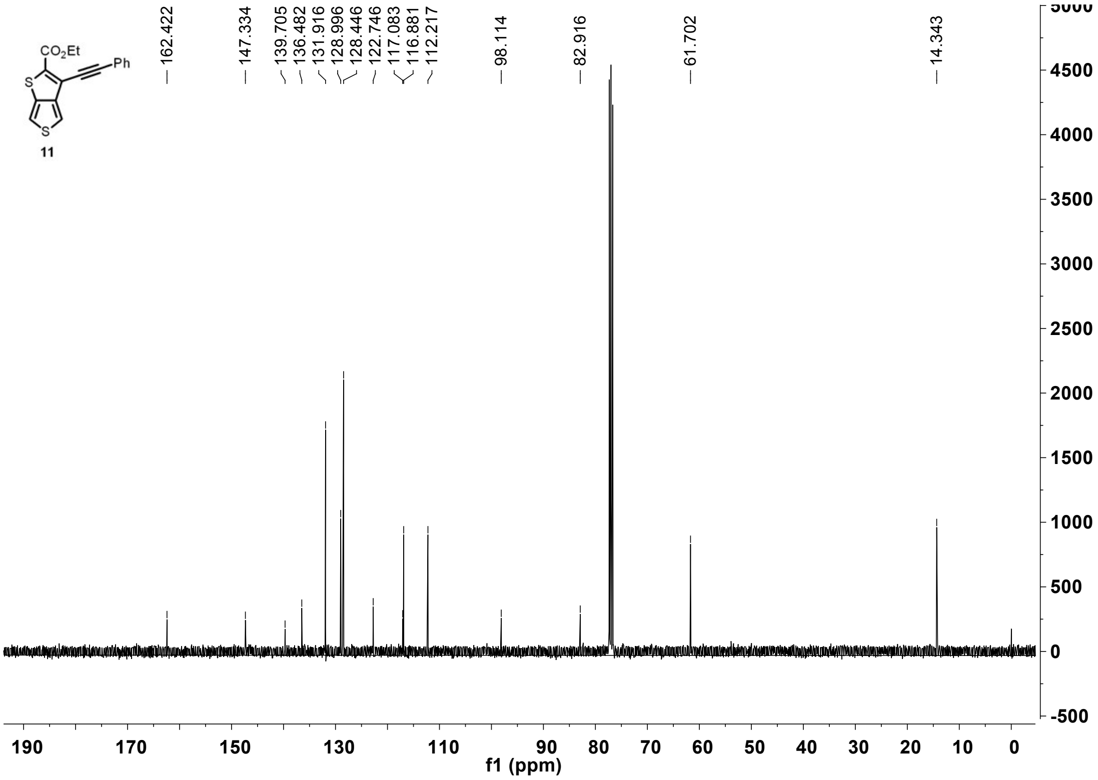

CO2Et
NH2
S
S
9
165.891
143.218
140.949
136.400
115.037
111.882
102.418
60.348
14.463
900
850
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.514
7.509
7.504
7.493
7.490
7.485
7.480
7.475
7.465
7.447
7.442
7.438
7.393
7.386
7.309
7.302
4.257
4.240
4.222
4.204
1.229
1.212
1.194
CO$_2$Et
S
S
5.00
0.93
0.89
2.00
3.17
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

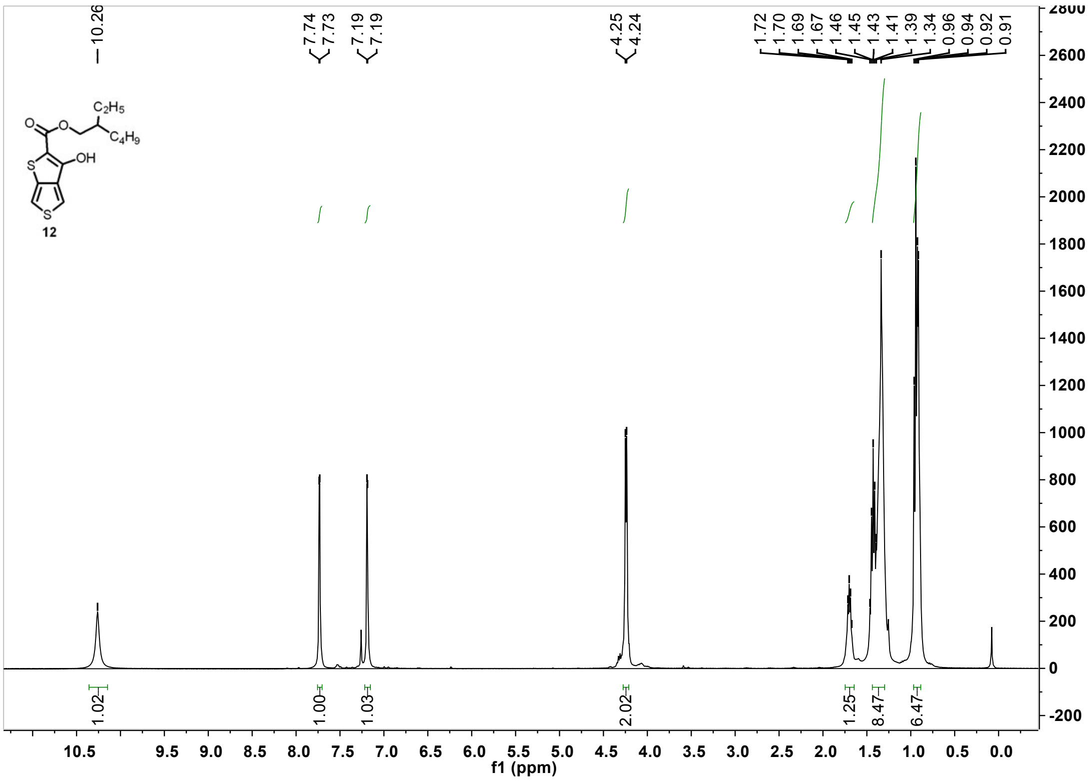

CO$_2$Et
S
S
10
162.900
149.023
137.552
136.979
134.642
132.973
129.139
128.218
127.981
117.186
111.387
61.266
13.916
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190 170 150 130 110 90 80 70 60 50 40 30 20 10
f1 (ppm)

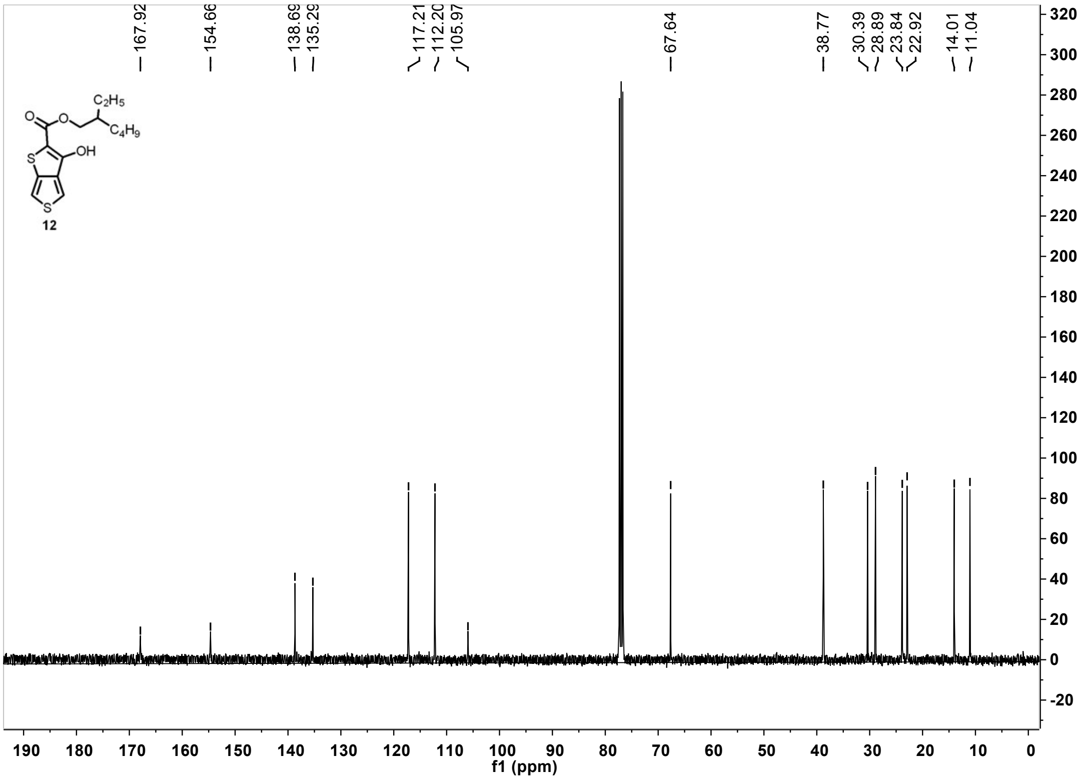


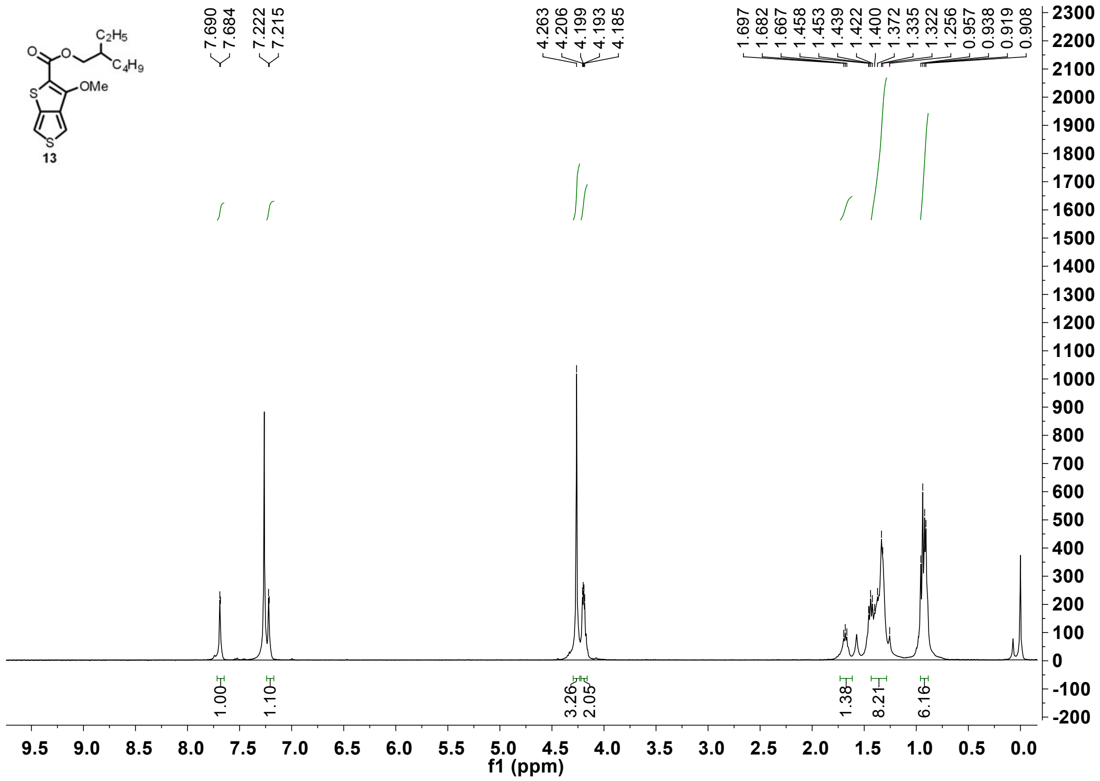
CO2Et
Ph
S
S
11
7.769
7.762
7.644
7.636
7.627
7.620
7.400
7.392
7.385
7.321
7.314
4.459
4.441
4.423
4.405
1.451
1.433
1.416
1.00
2.05
3.13
1.04
2.18
3.17
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

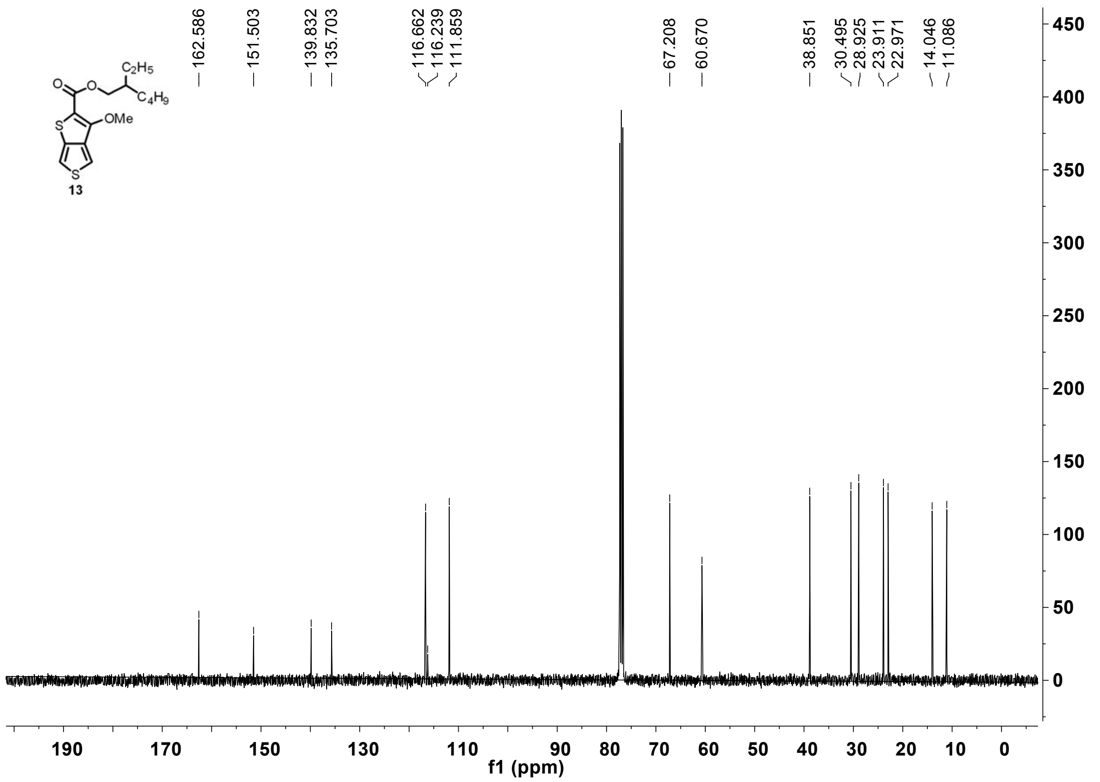


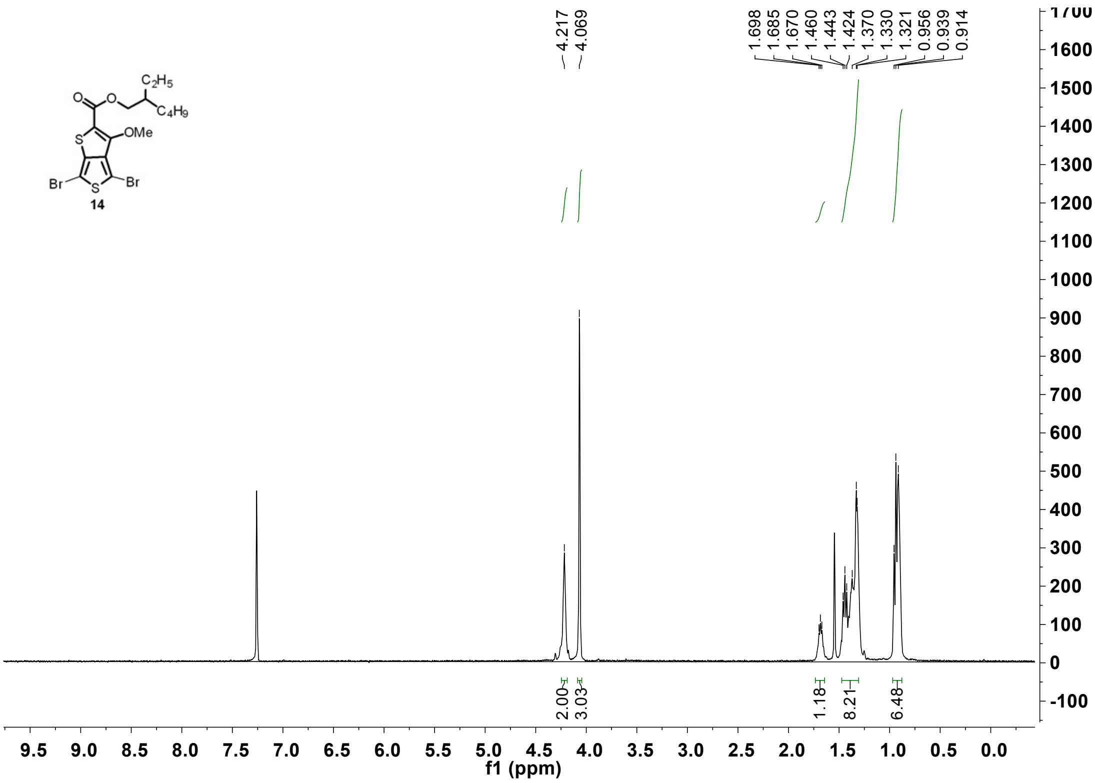
CO2Et
Ph
S
S
11
162.422
147.334
139.705
136.482
131.916
128.996
128.446
122.746
117.083
116.881
112.217
98.114
82.916
61.702
14.343
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.26
7.74
7.73
7.19
7.19
4.25
4.24
1.72
1.70
1.69
1.67
1.46
1.45
1.43
1.41
1.39
1.34
0.96
0.94
0.92
0.91
C_2H_5
C_4H_9
OH
O
S
12
1.02
1.00
1.03
2.02
1.25
8.47
6.47
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

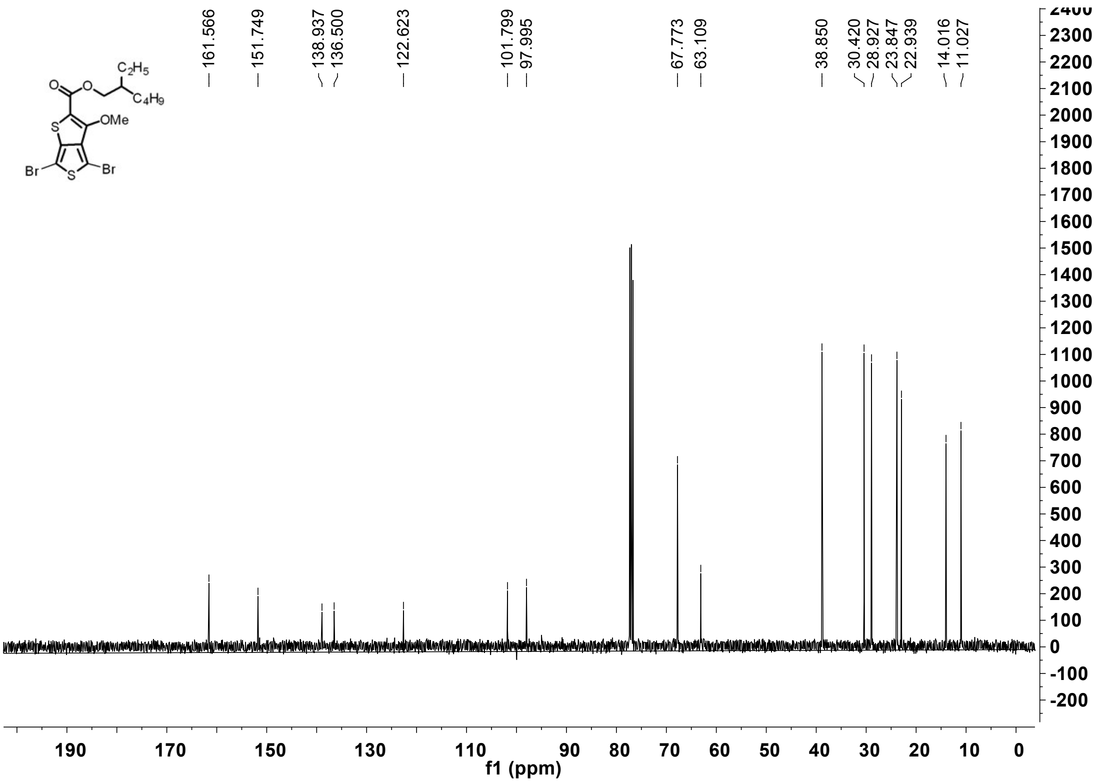

167.92
154.66
138.69
135.29
117.21
112.20
105.97
67.64
38.77
30.39
28.89
23.84
22.92
14.01
11.04
C_2H_5
C_4H_9
OH
O
S
12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20


C2H5
O
O
C4H9
S
OMe
S
13
7.690
7.684
7.222
7.215
4.263
4.206
4.199
4.193
4.185
1.697
1.682
1.667
1.458
1.453
1.439
1.422
1.400
1.372
1.335
1.322
1.256
0.957
0.938
0.919
0.908
1.00
1.10
3.26
2.05
1.38
8.21
6.16
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

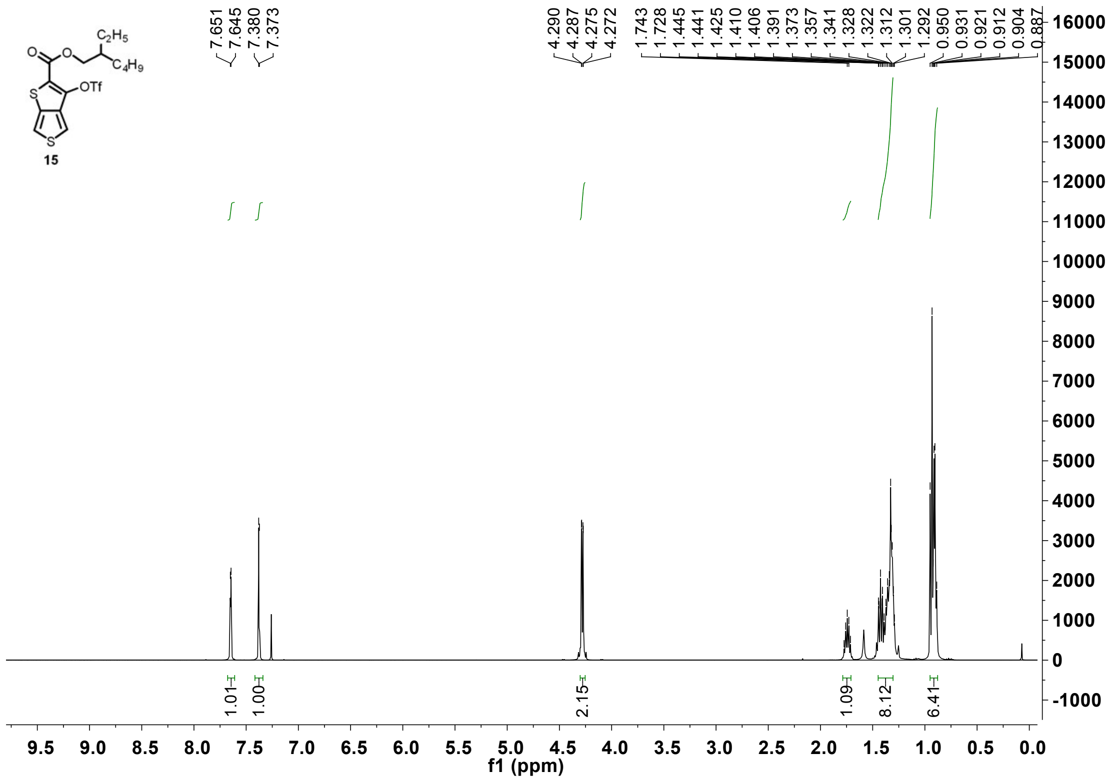

C2H5
O
O
C4H9
S
OMe
S
13
162.586
151.503
139.832
135.703
116.662
116.239
111.859
67.208
60.670
38.851
30.495
28.925
23.911
22.971
14.046
11.086
450
400
350
300
250
200
150
100
50
0
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

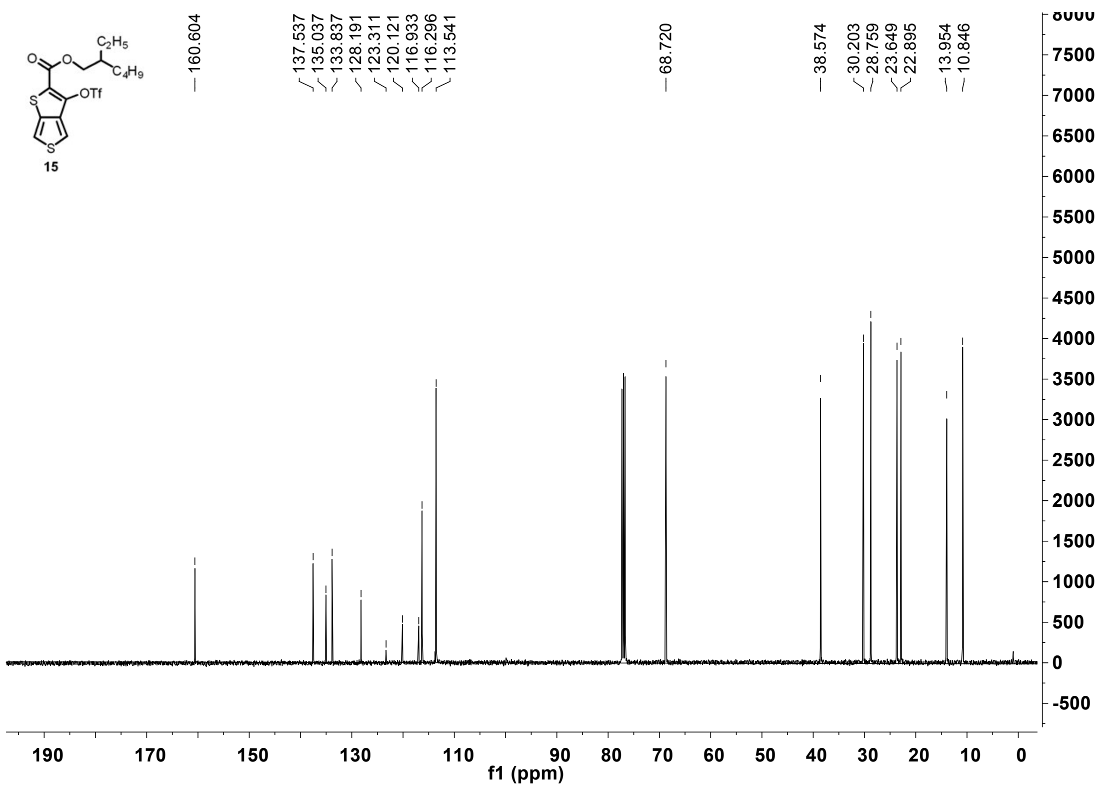

14

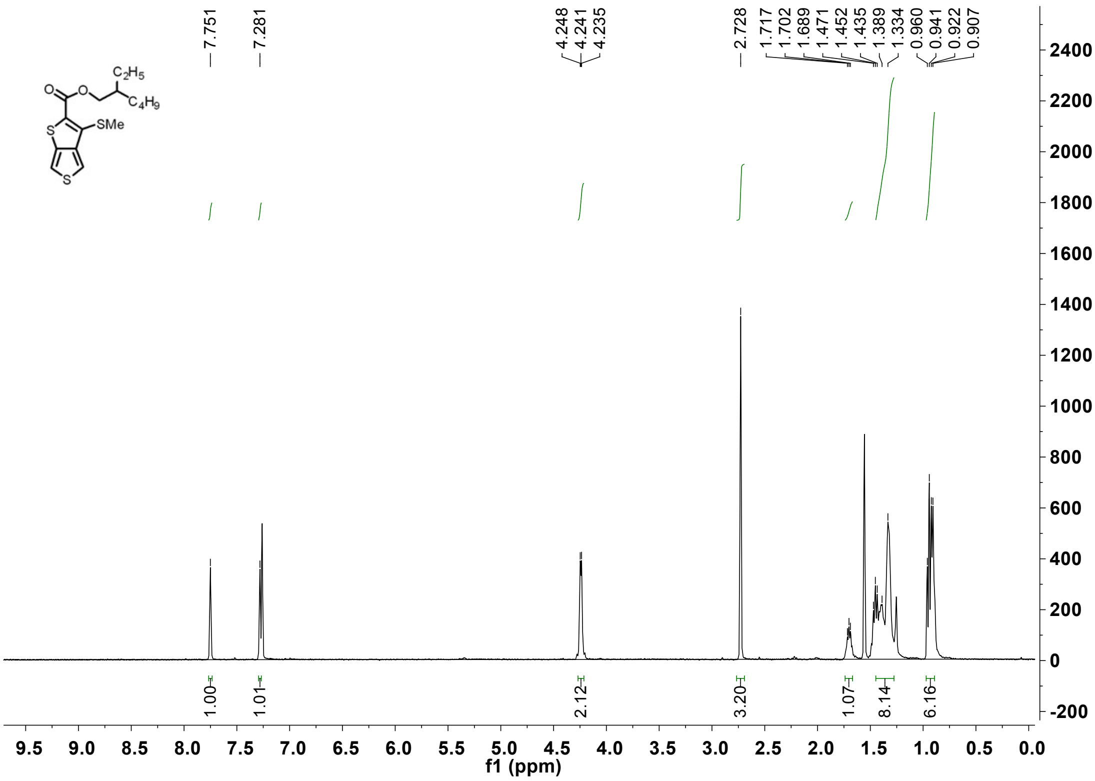
4.217
4.069
1.698
1.685
1.670
1.460
1.443
1.424
1.370
1.330
1.321
0.956
0.939
0.914
2.00
3.03
1.18
8.21
6.48
C2H5
C4H9
OMe
S
Br
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

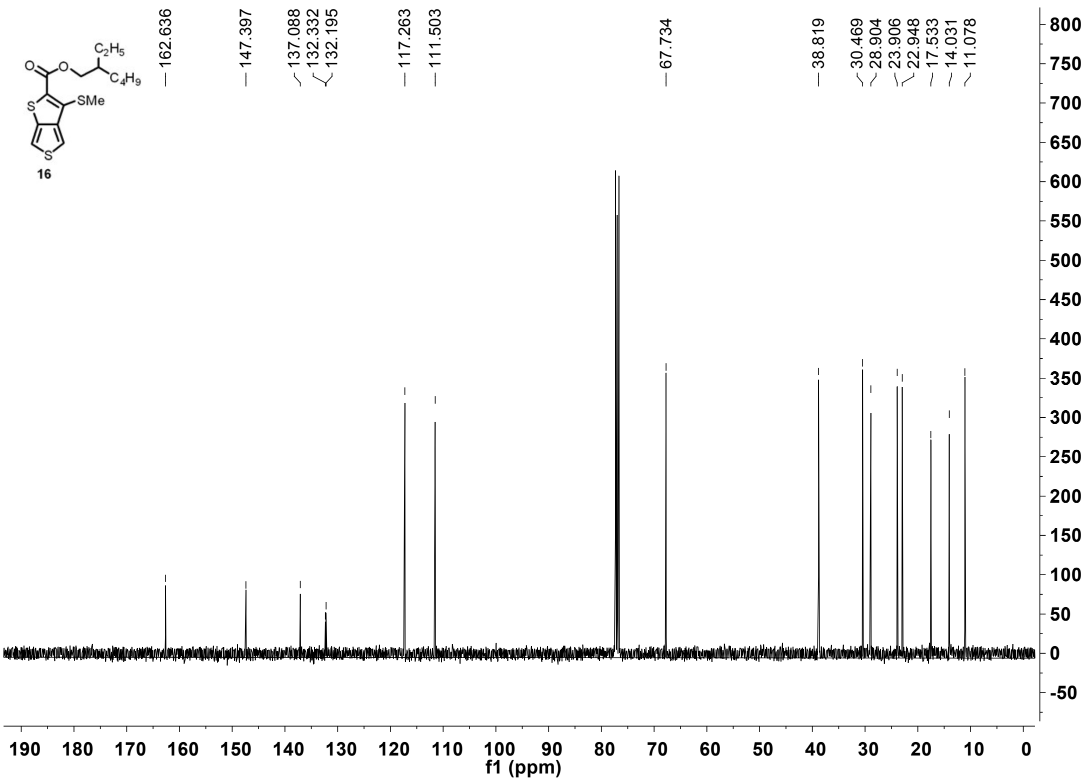


161.566
151.749
138.937
136.500
122.623
101.799
97.995
67.773
63.109
38.850
30.420
28.927
23.847
22.939
14.016
11.027
C2H5
C4H9
OMe
S
Br
f1 (ppm)
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

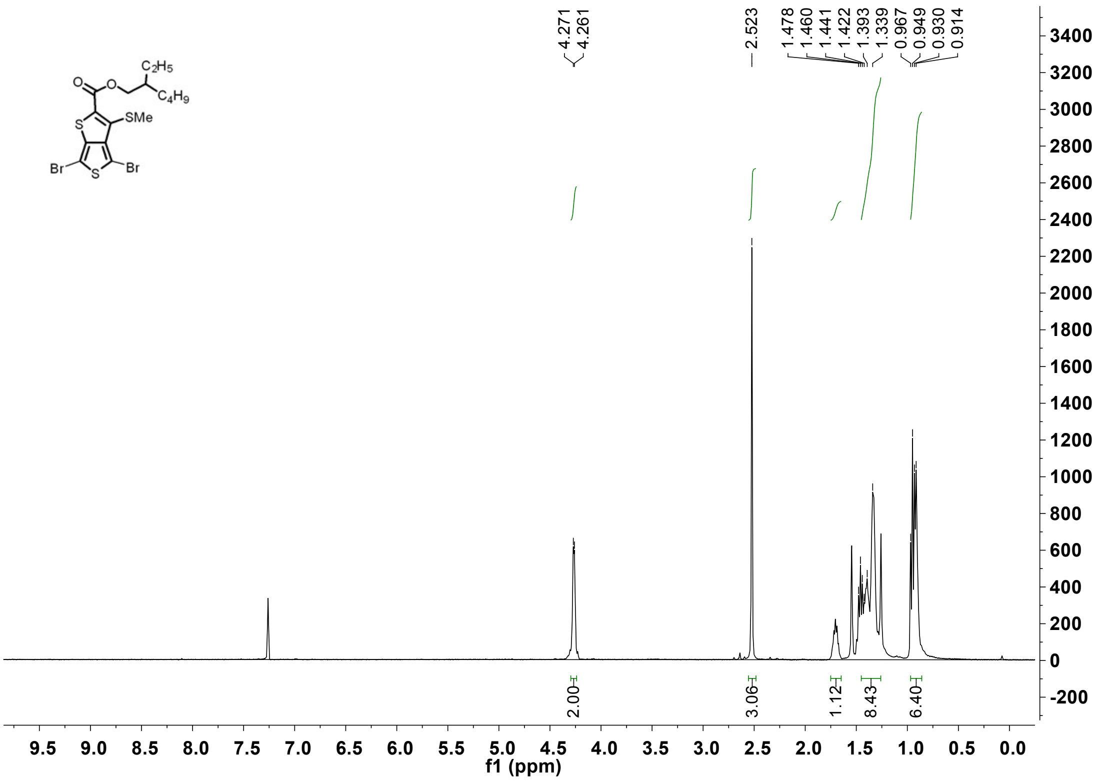

C2H5
C4H9
OTf
15
7.651
7.645
7.380
7.373
4.290
4.287
4.275
4.272
1.743
1.728
1.445
1.441
1.425
1.410
1.406
1.391
1.373
1.357
1.341
1.328
1.322
1.312
1.301
1.292
0.950
0.931
0.921
0.912
0.904
0.887
1.01
1.00
2.15
1.09
8.12
6.41
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

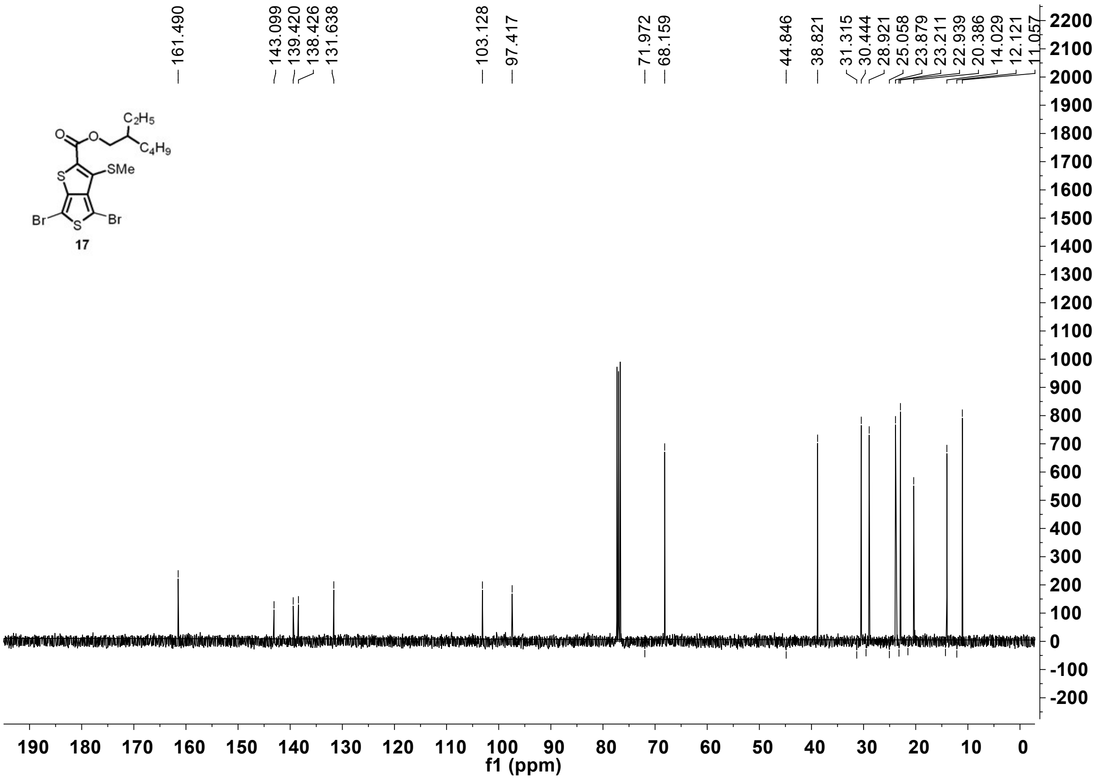

C2H5
C4H9
OTf
15
160.604
137.537
135.037
133.837
128.191
123.311
120.121
116.933
116.296
113.541
68.720
38.574
30.203
28.759
23.649
22.895
13.954
10.846
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

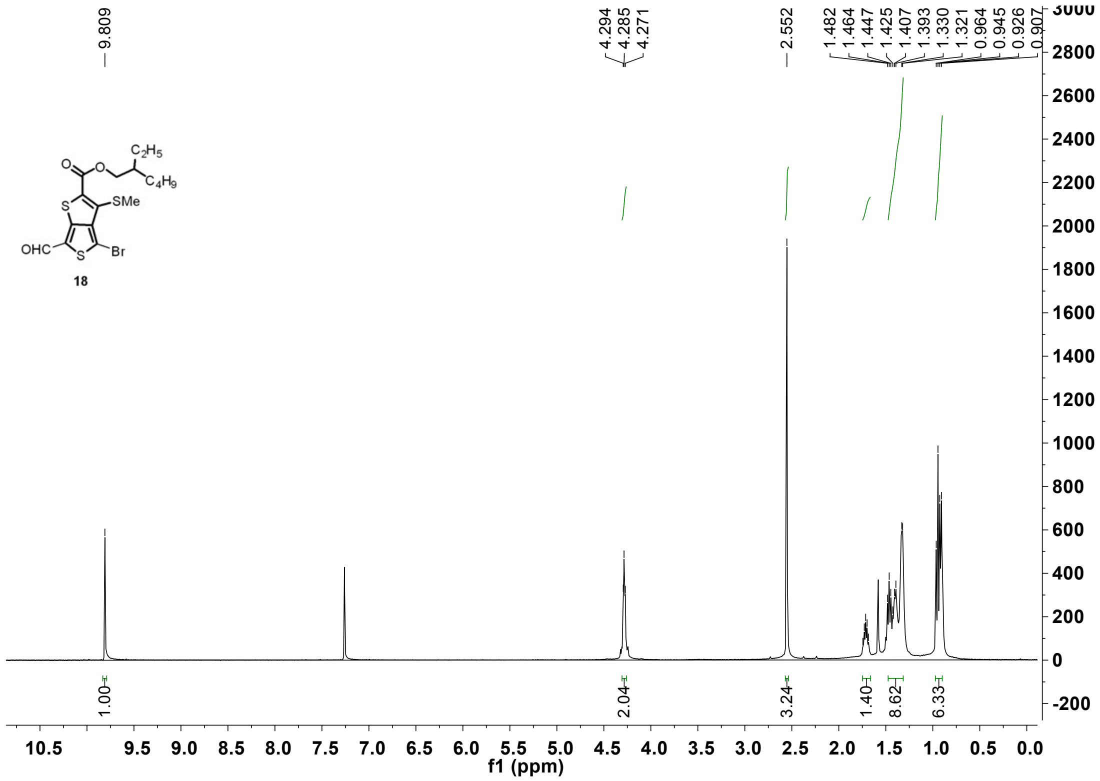

O
O
C2H5
C4H9
S
SMe
S
7.751
7.281
4.248
4.241
4.235
2.728
1.717
1.702
1.689
1.471
1.452
1.435
1.389
1.334
0.960
0.941
0.922
0.907
1.00
1.01
2.12
3.20
1.07
8.14
6.16
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

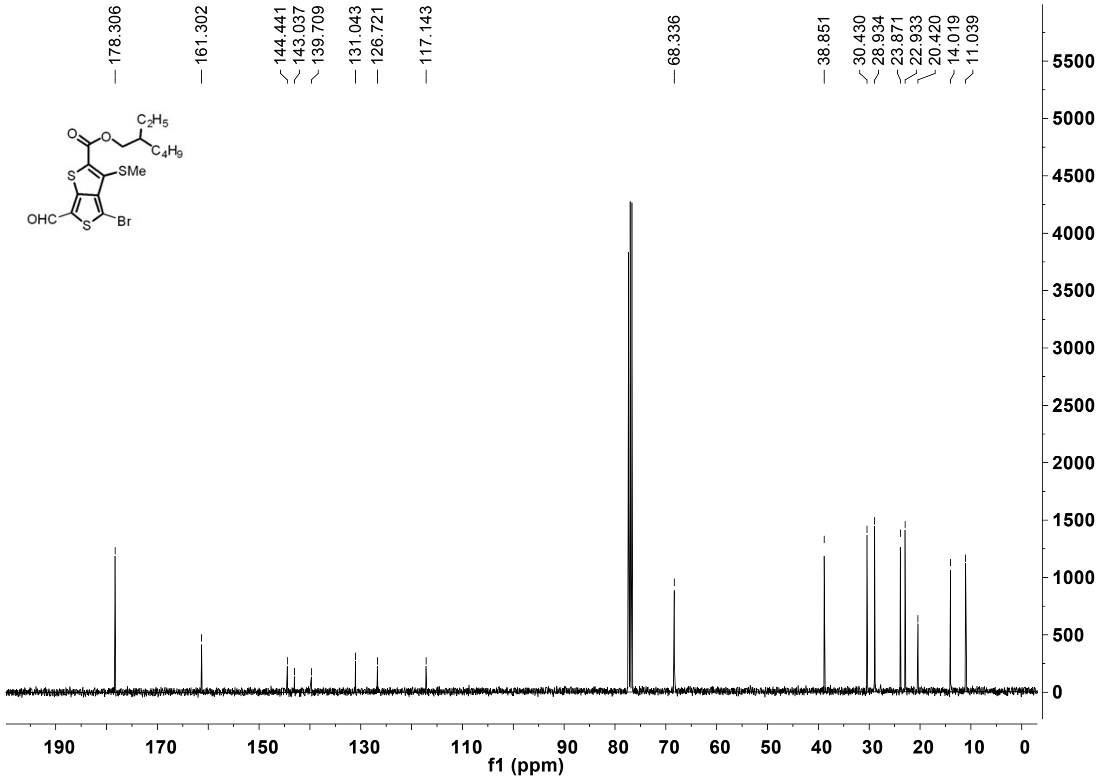

O
O
C2H5
C4H9
S
SMe
S
162.636
147.397
137.088
132.332
132.195
117.263
111.503
67.734
38.819
30.469
28.904
23.906
22.948
17.533
14.031
11.078
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

16


C2H5
O
C4H9
SMe
S
Br
S
Br
4.271
4.261
2.523
1.478
1.460
1.441
1.422
1.393
1.339
0.967
0.949
0.930
0.914
2.00
3.06
1.12
8.43
6.40
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3400 3200 3000 2800 2600 2400 2200 2000 1800 1600 1400 1200 1000 800 600 400 200 0 -200


C2H5
O
C4H9
SMe
S
Br
S
Br
17
161.490
143.099
139.420
138.426
131.638
103.128
97.417
71.972
68.159
44.846
38.821
31.315
30.444
28.921
25.058
23.879
23.211
22.939
20.386
14.029
12.121
11.057
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200


9.809
4.294
4.285
4.271
2.552
1.482
1.464
1.447
1.425
1.407
1.393
1.330
1.321
0.964
0.945
0.926
0.907
C2H5
O
O
C4H9
S
SMe
OHC
S
Br
18
1.00
2.04
3.24
1.40
8.62
6.33
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


178.306
161.302
144.441
143.037
139.709
131.043
126.721
117.143
68.336
38.851
30.430
28.934
23.871
22.933
20.420
14.019
11.039
C2H5
O
O
C4H9
S
SMe
OHC
S
Br
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)