Solution-Phase Parallel Synthesis of a Multi-Substituted Benzo[*b*]thiophene Library

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Supporting Information

Contents

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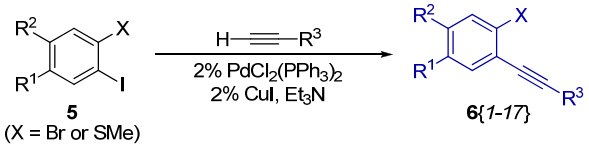
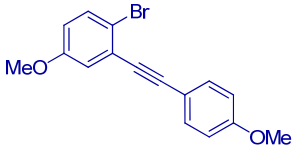
The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ as the solvent using tetramethylsilane (TMS) as an internal standard, unless otherwise stated. Chemical shifts are reported in δ units (ppm) by assigning the TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm and the $CDCl_3$ resonance in the ^{13}C NMR spectrum as 77.23 ppm. All coupling constants, *J*, are reported in Hertz (Hz). Analytical thin layer chromatography (TLC) was performed using commercially prepared 60-mesh silica gel plates, and visualization was effected with short wavelength UV light (254 nm). All melting points are uncorrected. High resolution mass spectra (HRMS) were obtained using a Waters/Micromass LCT Premier TOF instrument. Commercially available reagents were used without further purification unless otherwise stated. The organic solvents (*e.g.* Et_2O, EtOAc, $CHCl_3$, MeOH, EtOH, CH_3CN, DMF, hexane, toluene, etc.) were used as anhydrous solvents. THF and CH_2Cl_2 were distilled from sodium/benzophenone or CaH_2 respectively under an atmosphere of argon prior to use. The palladium catalysts were donated by Johnson Matthey Inc. and Kawaken Fine Chemicals Co. Ltd. The boronic acids were donated by Frontier Scientific and Synthonix Co. Ltd.

◈ **General procedure for the regioselective Sonogashira reaction to form compounds 6**[1]



To a solution of dihalobenzene **5** (10.0 mmol), 2 mol % $PdCl_2(PPh_3)_2$ and 2 mol % CuI in Et_3N (20 mL), the terminal alkyne (10.5 mmol) was added. The reaction mixture was stirred vigorous at 50 °C for *ca*. 5-8 h under an Ar atmosphere. The resulting mixture was diluted with EtOAc (2 × 200 mL). The separated organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexanes as the eluent to afford the corresponding products **6**.

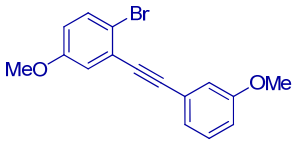
Compound 6{*1*}



The product was obtained as a yellow oil (94% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.80 (s,

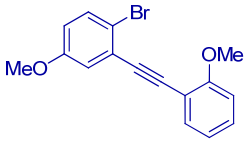
3H), 6.71 (dd, *J* = 3.1, 8.9 Hz, 1H), 6.87 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 3.1 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.51 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.7, 87.1, 94.0, 114.2 (×2), 115.0, 116.2, 116.3, 117.6, 126.3, 133.1, 133.4 (×2), 158.6, 160.1.

Compound 6{*2*}



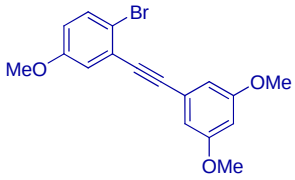
The product was obtained as a yellow oil (91% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.77 (s, 3H), 6.71 (dd, *J* = 3.0, 8.9 Hz, 1H), 6.89 (d, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 3.0 Hz, 1H), 7.10 (s, 1H), 7.15-7.26 (m, 2H), 7.43 (d, *J* = 8.9 Hz, 1H).

Compound 6{*3*}



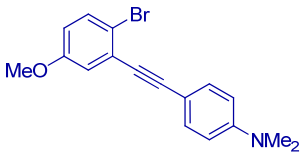
The product was obtained as a yellow oil (87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 3.86 (s, 3H), 6.70 (dd, *J* = 3.0, 8.9 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 3.0 Hz, 1H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 55.9, 90.4, 92.1, 110.8, 112.0, 116.2, 116.4, 117.8, 120.5, 126.2, 130.3, 133.0, 133.7, 158.4, 160.1.

Compound 6{*4*}



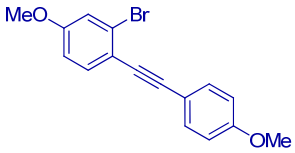
The product was obtained as a yellow oil (83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.80 (s, 6H), 6.48 (t, *J* = 2.2 Hz, 1H), 6.73 (d, *J* = 2.3 Hz, 2H), 6.76 (dd, *J* = 3.0, 8.9 Hz, 1H), 7.08 (d, *J* = 3.0 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6 (×2), 55.7, 87.8, 93.8, 102.3, 109.6 (×2), 116.5, 116.8, 117.9, 124.2, 125.8, 133.2, 158.6, 160.7 (×2).

Compound 6{*5*}



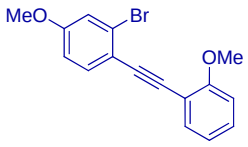
The product was obtained as a white solid (71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.99 (s, 6H), 3.79 (s, 3H), 6.65 (d, *J* = 8.6 Hz, 2H), 6.70 (dd, *J* = 3.0, 8.8 Hz, 1H), 7.05 (d, *J* = 2.9 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.4 (×2), 55.7, 86.5, 95.6, 109.6, 111.9 (×2), 115.9, 116.1, 117.3, 126.9, 133.1 (×2), 133.1, 150.5, 158.6.

Compound 6{*6*}



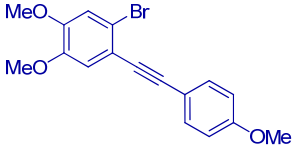
The product was obtained as a yellow solid (73% yield): mp 86-87 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.82 (s, 3H), 6.82 (dd, *J* = 2.2, 8.7 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.8, 86.9, 92.5, 113.7, 114.2 (×2), 115.5, 117.9, 118.1, 126.3, 133.2 (×2), 133.9, 159.7, 159.8.

Compound 6{*7*}



The product was obtained as a pale yellow oil (77% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 3.87 (s, 3H), 6.79 (dd, *J* = 2.6, 8.6 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.91 (td, *J* = 0.9, 7.5 Hz, 1H), 7.13 (d, *J* = 2.6 Hz, 1H), 7.24-7.30 (m, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.52 (dd, *J* = 1.7, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 55.9, 88.9, 92.0, 110.8, 112.5, 113.5, 117.8, 117.9, 120.5, 126.3, 129.9, 133.5, 134.0, 159.7, 159.9.

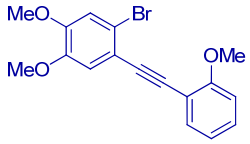
Compound 6{*8*}



The product was obtained as a yellow oil that solidified upon standing to an ivory solid (92% yield): ^{1}H

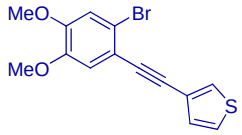
NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 6.86 (d, *J* = 6.8 Hz, 2H), 7.01 (s, 1H), 7.03 (s, 1H), 7.50 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 56.2, 56.3, 87.1, 92.4, 114.1 (×2), 114.9, 115.1, 115.3, 116.7, 117.5, 133.1 (×2), 148.1, 149.6, 159.8.

Compound 6{*9*}



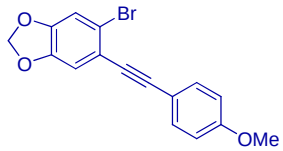
The product was obtained as a yellow oil, which eventually solidified (71% yield): mp = 135-136 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 6.87-6.96 (m, 2H), 7.05 (s, 1H), 7.06 (s, 1H), 7.25-7.28 (m, 1H), 7.53-7.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.9, 56.2, 56.3, 88.9, 92.2, 110.8, 112.3, 115.1, 116.8, 117.5, 120.6, 127.7, 130.0, 133.6, 148.0, 149.7, 159.9.

Compound 6{*10*}



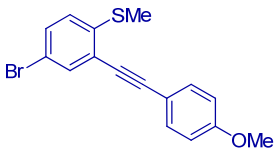
The product was obtained as a dark yellow oil (87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.87 (s, 3H), 7.00 (s, 1H), 7.03 (s, 1H), 7.22 (d, *J* = 5.0 Hz, 1H), 7.27-7.31 (m, 1H), 7.55 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 56.3, 87.5, 87.8, 115.0, 115.1, 116.7, 117.1, 122.2, 125.6, 128.8, 129.9, 148.1, 149.8.

Compound 6{*11*}



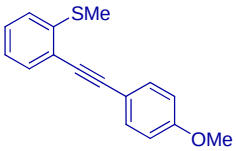
The product was obtained as a yellow solid (84% yield): mp 108-109 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 5.97 (s, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.96 (s, 1H), 7.03 (s, 1H), 7.47 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 87.1, 92.7, 102.2, 112.1, 112.8, 114.2 (×2), 115.3, 117.6, 118.6, 133.2 (×2), 147.1, 148.4, 159.9.

Compound 6{*13*}



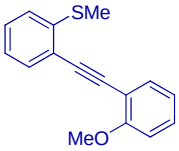
The product was obtained as a dark yellow oil (88% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.78 (s, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 55.4, 84.5, 97.4, 114.1 (×2), 114.8, 117.4, 123.4, 125.4, 131.4, 133.2 (×2), 134.3, 140.8, 160.1.

Compound 6{*15*}



This compound was obtained as a yellow solid in an 88% yield: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.83 (s, 3H), 6.89 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.52 (dd, *J* = 9.2, 2.4 Hz, 2H). The ^{1}H NMR spectral data are in good agreement with the literature data.[2]

Compound 6{*16*}



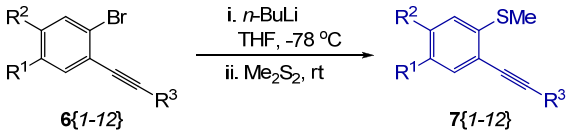
The product was obtained as a pale yellow solid (79% yield): mp 114-115 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.86 (s, 3H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.20-7.29 (m, 2H), 7.49-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 55.9, 90.9, 92.4, 110.8, 112.4, 120.5, 121.7, 124.19, 124.21, 128.6, 130.0, 132.3, 133.6, 141.6, 159.9.

Compound 6{*17*}

The product was obtained as a dark yellow oil (87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 7.08 (dt, *J* = 1.2, 8.7 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.21-7.30 (m, 3H), 7.45 (dd, *J* = 1.1, 7.6 Hz, 1H),

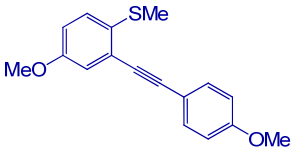
7.55 (dd, *J* = 1.2, 3.0 Hz, 1H); ^{13}C NMR (100 MHz) δ 15.2, 86.5, 91.1, 121.3, 122.3, 124.1, 124.3, 125.5, 128.8, 128.9, 130.0, 132.3, 141.7.

◈ **General procedure for methylthiolation to form compounds 7{*1-12*}**



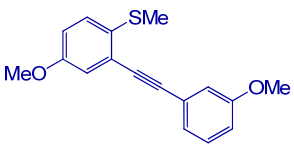
Bromoalkyne **6** (8.0 mmol) was dissolved in dry THF (80 mL) under an argon atmosphere and cooled to -78 °C for 0.5 h. Then, 2.0 equiv of *n*-BuLi (2.0 M solution in cyclohexane, 8.0 mmol) was added dropwise to the stirred solution. After the addition was complete, the reaction solution was stirred for 1 h at -78 °C. Dimethyl disulfide (9.6 mmol) was then added and the reaction mixture was stirred further at this temperature under an Ar atmosphere before being allowed to warm to room temperature for 2 h. The resulting mixture was diluted with EtOAc (2 × 160 mL). The separated organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexanes as the eluent to afford the corresponding products **7**.

Compound 7{*1*}



The product was obtained as a colorless oil (86% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.76 (s, 3H), 3.76 (s, 3H), 6.83 (dd, *J* = 2.8, 8.7 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 2.8 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5, 55.4, 55.5, 86.1, 95.4, 114.1 (×2), 115.2, 115.5, 117.1, 123.9, 127.8, 131.9, 133.2 (×2), 157.3, 159.9; HRMS calcd for $C_{17}H_{16}O_2S$ [M^+], 284.0871, found 284.0873.

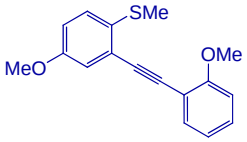
Compound 7{*2*}



The product was obtained as a yellow oil (87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.73 (s,

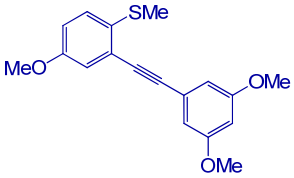
3H), 3.76 (s, 3H), 6.82-6.90 (m, 2H), 7.04-7.15 (m, 3H), 7.16-7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 55.3, 55.4, 87.1, 95.1, 115.0, 115.8, 116.4, 117.2, 123.3, 124.0, 124.2, 127.7, 129.5, 132.2, 157.2, 159.3; HRMS calcd for $C_{17}H_{16}O_2S$ [M^+], 284.0871, found 284.0877.

Compound 7{*3*}



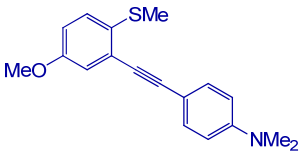
The product was obtained as a yellow oil (93% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (s, 3H), 3.78 (s, 3H), 3.90 (s, 3H), 6.85 (dd, *J* = 2.8, 8.7 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 2.7 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.30 (t, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 55.6, 56.0, 91.4, 91.7, 110.8, 112.4, 115.8, 117.3, 120.6, 124.4, 128.4, 130.1, 132.0, 133.7, 157.5, 160.1; HRMS calcd for $C_{17}H_{16}O_2S$ [M^+], 284.0871, found 284.0877.

Compound 7{*4*}



The product was obtained as a yellow oil (63% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.49 (s, 3H), 3.79 (s, 3H), 3.80 (s, 6H), 6.47 (t, *J* = 2.3 Hz, 1H), 6.74 (d, *J* = 2.3 Hz, 2H), 6.87 (dd, *J* = 2.8, 8.7 Hz, 1H), 7.06 (d, *J* = 2.8 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 55.60 (×2), 55.64, 86.9, 95.3, 102.1, 109.5 (×2), 116.0, 117.3, 123.5, 124.5, 128.0, 132.3, 157.4, 160.6 (×2); HRMS calcd for $C_{18}H_{18}O_3S$ [M^+], 314.0977, found 314.0981.

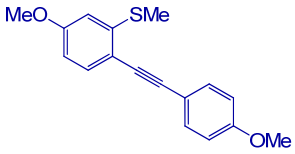
Compound 7{*5*}



The product was obtained as a white solid (79% yield): mp = 109-110 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 2.94 (s, 6H), 3.75 (s, 3H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.80 (dd, *J* = 1.6, 8.7 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 40.2 (×2), 55.5, 85.4, 96.9, 109.7, 111.8 (×2), 115.0, 116.8, 124.6, 127.9, 131.5, 132.8 (×2),

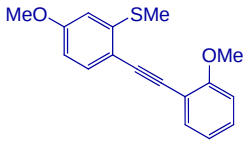
150.3, 157.4; HRMS calcd for $C_{18}H_{19}NOS$ [M^+], 297.1187, found 297.1189.

Compound 7{*6*}



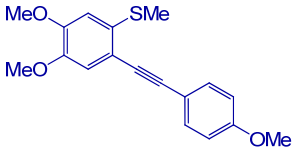
The product was obtained as a yellow solid (89% yield): mp = 86-87 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.81 (s, 3H), 3.82 (s, 3H), 6.63 (dd, *J* = 2.4, 8.5 Hz, 1H), 6.69 (d, *J* = 2.0 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 55.48, 55.54, 85.6, 94.5, 109.4, 110.7, 114.10 (×2), 114.13, 115.8, 133.0 (×2), 133.4, 143.3, 159.6, 160.0; HRMS calcd for $C_{17}H_{16}O_2S$ [M^+], 284.0871, found 284.0875.

Compound 7{*7*}



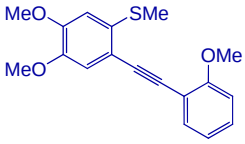
The product was obtained as a pale yellow solid (91% yield): mp = 102-103 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 3.79 (s, 3H), 3.88 (s, 3H), 6.62 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.69 (d, *J* = 2.4 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.91 (td, *J* = 0.9, 8.4 Hz, 1H), 7.26 (td, *J* = 1.7, 9.2 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 1.7, 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 55.4, 55.9, 90.8, 90.9, 109.4, 110.7, 110.8, 112.8, 114.2, 120.5, 129.6, 133.4, 133.6, 143.4, 159.8, 160.0; HRMS calcd for $C_{17}H_{16}O_2S$ [M^+], 284.0871, found 284.0875.

Compound 7{*8*}



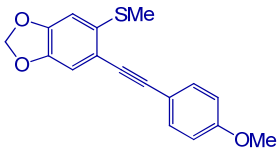
The product was obtained as a yellow oil (83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.82 (s, 3H), 3.88 (s, 3H), 3.91 (s, 3H), 6.80 (s, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.01 (s, 1H), 7.50 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 55.5, 56.18, 56.23, 86.2, 94.1, 110.8, 114.1 (×2), 115.1, 115.6, 115.7, 132.8, 133.0 (×2), 147.1, 149.5, 159.7; HRMS calcd for $C_{18}H_{18}O_3S$ [M^+], 314.0977, found 314.0981.

Compound 7{*9*}



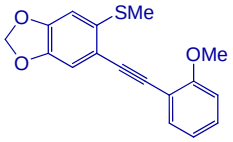
The product was obtained as a yellow oil (81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.54 (s, 3H), 3.86 (s, 3H), 3.90 (s, 6H), 6.81 (s, 1H), 6.86-6.96 (m, 2H), 7.06 (s, 1H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.0, 55.8, 56.0, 56.1, 90.3, 91.5, 110.7, 111.0, 112.6, 115.2, 115.8, 120.5, 129.7, 132.8, 133.4, 146.9, 149.5, 159.8; HRMS calcd for $C_{18}H_{18}O_3S$ [M^+], 314.0977, found 314.0983.

Compound 7{*11*}



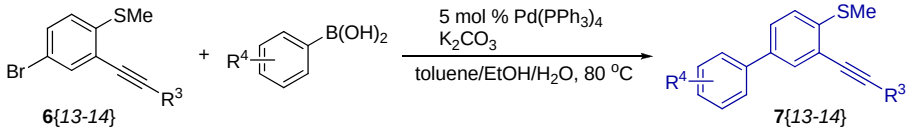
The product was obtained as a yellow oil (63% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.80 (s, 3H), 5.95 (s, 2H), 6.73 (s, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.93 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.4, 55.4, 86.0, 94.5, 101.6, 106.7, 111.9, 114.1 (×2), 115.4, 115.5, 133.0 (×2), 135.1, 145.3, 148.5, 159.7; HRMS calcd for $C_{17}H_{14}O_3S$ [M^+], 298.0664, found 298.0667.

Compound 7{*12*}



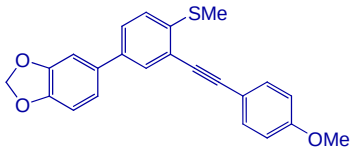
The product was obtained as a pale yellow solid (90% yield): mp 111-112 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.90 (s, 3H), 5.95 (s, 2H), 6.75 (s, 1H), 6.86-6.94 (m, 2H), 6.99 (s, 1H), 7.25-7.31 (m, 1H), 7.51 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 56.0, 90.9, 91.3, 101.7, 107.0, 110.8, 112.2, 112.7, 115.7, 120.6, 129.8, 133.5, 135.3, 145.4, 148.5, 159.9; HRMS calcd for $C_{17}H_{14}O_3S$ [M^+], 298.0664, found 298.0667.

◈ General procedure for the preparation of alkynes 7{*13-14*} by Suzuki-Miyaura coupling[3]



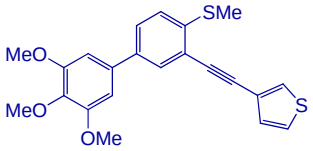
To a solution of bromoalkyne **6**{*13-14*} (3.0 mmol) and 5 mol % $Pd(PPh_3)_4$ in toluene (15 mL) was added K_2CO_3 (9.0 mmol) under an Ar atmosphere. To the resulting mixture was added the arylboronic acid (4.5 mmol) dissolved in ethanol (3 mL). The reaction mixture was heated at 80 °C for 6 h with vigorous stirring. Upon cooling to room temperature, the reaction mixture was extracted with EtOAc (2 × 50 mL). The combined extracts were dried over $MgSO_4$, concentrated, and purified by flash column chromatography using EtOAc/hexane as the eluent to afford the corresponding product **7**{*13-14*}.

Compound 7{*13*}



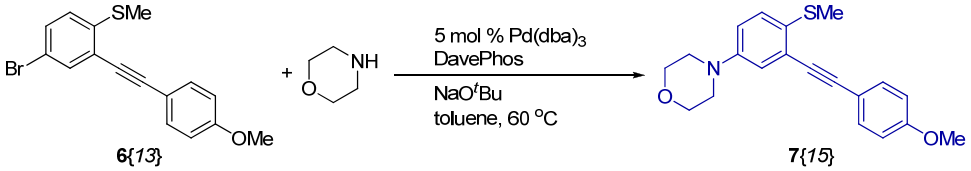
The product was obtained as a yellow solid (72% yield): mp = 141-142 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (s, 3H), 3.81 (s, 3H), 5.98 (s, 2H), 6.83-6.88 (m, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 7.03-7.07 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 1H), 7.41 (dd, *J* = 2.0, 8.3 Hz, 1H), 7.53 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 55.5, 85.8, 96.1, 101.4, 107.4, 108.8, 114.2 (×2), 115.3, 120.4, 122.1, 124.7, 127.0, 130.4, 133.3 (×2), 134.3, 137.2, 140.1, 147.3, 148.3, 159.9; HRMS calcd for $C_{23}H_{18}O_3S$ [M^+], 374.0977, found 374.0986.

Compound 7{*14*}



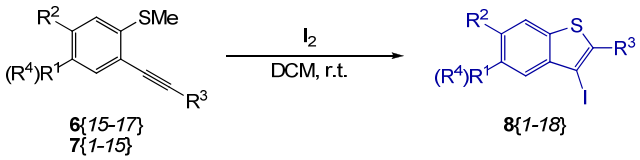
The product was obtained as a yellow oil (68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H), 3.89 (s, 3H), 3.92 (s, 6H), 6.76 (s, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.23-7.27 (m, 1H), 7.29-7.33 (m, 1H), 7.49 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.59 (dd, *J* = 1.0, 2.9 Hz, 1H), 7.67 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 56.4 (×2), 61.1, 86.5, 91.2, 104.1 (×2), 121.7, 122.1, 124.6, 125.6, 127.4, 129.1, 130.0, 130.6, 135.8, 137.6, 137.8, 140.7, 153.6 (×2); HRMS calcd for $C_{22}H_{20}O_3S_2$ [M^+], 396.0854, found 396.0848.

◈ General procedure for the preparation of alkyne 7{*15*} by amination[4]



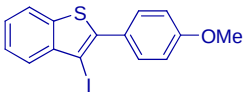
To the bromoalkyne **6**{*13*} (2.0 mmol), 5 mol % $Pd_2(dba)_3$ and NaO*t*Bu (2.8 mmol), DavePhos (0.2 mmol) in toluene (10 mL) was added along with a magnetic stir bar under an Ar atmosphere. To the reagent mixture was added morpholine (3.0 mmol) dissolved in toluene (10 mL) at room temperature. The reaction mixture was heated to 60 °C for 12 h. Upon cooling to room temperature, the reaction mixture was extracted with EtOAc (2 × 40 mL). The combined extracts were dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to obtain the corresponding product **7**{*15*} as a yellow oil (86% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 3H), 3.13 (t, *J* = 4.8 Hz, 4H), 3.81 (s, 3H), 3.84 (t, *J* = 4.8 Hz, 4H), 6.83-6.88 (m, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 2.7 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 49.5 (×2), 55.5, 66.9 (×2), 86.5, 95.0, 114.1 (×2), 115.4, 116.8, 119.5, 124.0, 127.9, 131.0, 133.2 (×2), 149.0, 159.9; HRMS calcd for $C_{20}H_{21}NO_2S$ [M^+], 339.1293, found 339.1299.

General procedure for iodocyclization using I_2 to form compounds 8[5]



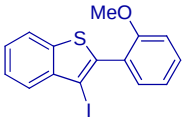
To a solution of 5.0 mmol of the alkyne **6**{*15-17*} or **7**{*1-15*} and CH_2Cl_2 (20 mL) was added gradually 1.2 equiv of I_2 dissolved in CH_2Cl_2 (30 mL). The reaction mixture was allowed to stir at room temperature for up to 10 min. The reaction was monitored by TLC to establish completion. The remaining I_2 was removed by washing with satd aq $Na_2S_2O_3$. The mixture was then extracted by EtOAc (2 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under a vacuum to yield the crude product, which was purified by flash chromatography using EtOAc/hexanes as the eluent to afford the corresponding products **8**.

3-Iodobenzo[*b*]thiophene 8{*1*}



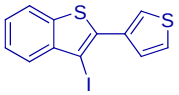
The product was obtained as a white solid (96% yield): mp 84-85 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 79.1, 114.0 (×2), 122.2, 125.4, 125.5, 126.2, 126.9, 131.4 (×2), 138.9, 142.0, 142.2, 160.2; HRMS calcd for $C_{15}H_{11}IOS$ [M^+], 365.9575, found 365.9578.

3-Iodobenzo[*b*]thiophene 8{*2*}



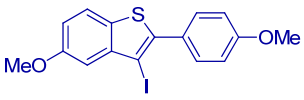
The product was obtained as a pale yellow solid (89% yield): mp 105-106 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (s, 3H), 6.92 (d, *J* = 8.2 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 7.27-7.41 (m, 4H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 82.9, 111.5, 120.5, 122.2, 123.5, 125.2, 125.3, 126.0, 130.8, 132.5, 139.5, 139.7, 141.3, 157.1; HRMS calcd for $C_{15}H_{11}IOS$ [M^+], 365.9575, found 365.9575.

3-Iodobenzo[*b*]thiophene 8{*3*}



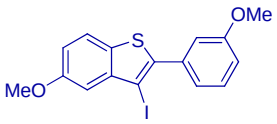
The product was obtained as a pale yellow oil (93% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.26 (m, 2H), 7.29-7.34 (m, 1H), 7.44-7.46 (m, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.69-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 78.8, 122.0, 125.3, 125.49, 125.52, 125.9, 126.1, 128.4, 134.5, 137.1, 138.0, 142.0; HRMS calcd for $C_{12}H_7IS_2$ [M^+], 341.9034, found 341.9037.

3-Iodobenzo[*b*]thiophene 8{*4*}



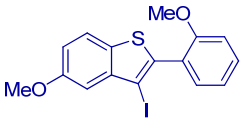
The product was obtained as a pale yellow solid (94% yield): mp 114-115 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 3.90 (s, 3H), 6.95-7.00 (m, 3H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.58-7.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.8, 78.8, 108.4, 114.0 (×2), 115.7, 123.0, 127.1, 131.1 (×2), 131.3, 143.2, 143.5, 158.6, 160.2; HRMS calcd for $C_{16}H_{13}IO_2S$ [M^+], 395.9681, found 395.9684.

3-Iodobenzo[*b*]thiophene 8{*5*}



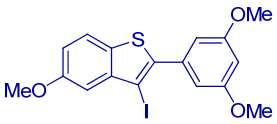
The product was obtained as a yellow oil (89% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.94 (s, 3H), 6.96-7.05 (m, 2H), 7.23-7.29 (m, 3H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 55.9, 79.3, 108.6, 114.9, 115.5, 116.1, 122.6, 123.1, 129.7, 131.2, 136.1, 143.2, 143.4, 158.7, 159.8; HRMS calcd for $C_{16}H_{13}IO_2S$ [M^+], 395.9681, found 395.9686.

3-Iodobenzo[*b*]thiophene 8{*6*}



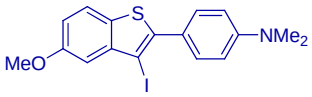
The product was obtained as a yellow oil (94% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.88 (s, 3H), 6.92-7.05 (m, 3H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.34-7.42 (m, 2H), 7.60 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 55.8, 82.6, 108.1, 111.5, 115.7, 120.5, 123.0, 123.7, 130.8, 131.7, 132.5, 141.0, 142.5, 157.1, 158.4; HRMS calcd for $C_{16}H_{13}IO_2S$ [M^+], 395.9681, found 395.9677.

3-Iodobenzo[*b*]thiophene 8{*7*}



The product was obtained as a yellow solid (88% yield): mp 135-136 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 6H), 3.93 (s, 3H), 6.54 (t, *J* = 2.2 Hz, 1H), 6.83 (d, *J* = 2.3 Hz, 2H), 7.02 (dd, *J* = 2.4, 8.7 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.64 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7 (×2), 55.9, 79.2, 101.3, 108.2 (×2), 108.6, 116.1, 123.1, 131.1, 136.5, 143.1, 143.4, 158.7, 160.7 (×2); HRMS calcd for $C_{17}H_{15}IO_3S$ [M^+], 425.9787, found 425.9795.

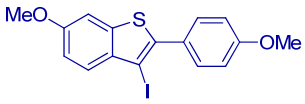
3-Iodobenzo[*b*]thiophene 8{*8*}



The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (s, 6H), 3.91 (s, 3H), 6.75 (d, *J* = 8.7 Hz, 2H), 6.97 (dd, *J* = 2.3, 8.7 Hz, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz,

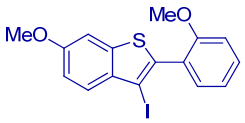
$CDCl_3$) δ 40.5 (×2), 55.8, 77.5, 108.3, 111.8 (×2), 115.2, 122.1, 122.9, 130.88 (×2), 130.93, 143.4, 144.5, 150.7, 158.5; HRMS calcd for $C_{17}H_{16}INO_S$ [M^+], 408.9997, found 408.9995.

3-Iodobenzo[*b*]thiophene 8{*9*}



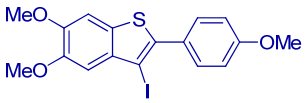
The product was obtained as a yellow solid (95% yield): mp 112-113 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 3.87 (s, 3H), 6.98 (d, *J* = 8.5 Hz, 2H), 7.05 (dd, *J* = 1.9, 8.8 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.9, 78.2, 104.7, 114.1 (×2), 115.3, 126.9, 127.1, 131.4 (×2), 136.2, 139.9, 158.3, 160.0; HRMS calcd for $C_{16}H_{13}IO_2S$ [M^+], 395.9681, found 395.9686.

3-Iodobenzo[*b*]thiophene 8{*10*}



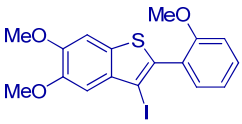
The product was obtained as a colorless oil (93% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.83 (s, 3H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.99-7.06 (m, 2H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.35-7.43 (m, 2H), 7.65 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 55.9, 82.0, 104.6, 111.5, 115.1, 120.5, 123.7, 126.6, 130.7, 132.7, 135.5, 136.9, 140.6, 157.2, 158.2; HRMS calcd for $C_{16}H_{13}IO_2S$ [M^+], 395.9681, found 395.9686.

3-Iodobenzo[*b*]thiophene 8{*11*}



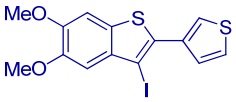
The product was obtained as a pale yellow solid (89% yield): mp 140-142 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.96 (s, 3H), 4.01 (s, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.21 (s, 1H), 7.22 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 56.3, 56.5, 78.2, 103.6, 107.5, 114.0 (×2), 127.2, 130.3, 131.3 (×2), 135.7, 140.2, 149.0, 149.1, 160.0; HRMS calcd for $C_{17}H_{15}IO_3S$ [M^+], 425.9787, found 425.9795.

3-Iodobenzo[*b*]thiophene 8{*12*}



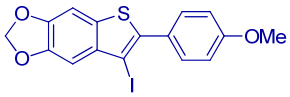
The product was obtained as a yellow solid (83% yield): mp 144-145 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.94 (s, 3H), 4.01 (s, 3H), 6.96-7.07 (m, 2H), 7.21 (s, 1H), 7.23 (s, 1H), 7.35-7.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 56.3, 56.5, 81.9, 103.6, 107.3, 111.5, 120.5, 123.8, 130.7, 131.7, 132.7, 135.1, 137.5, 148.98, 149.02, 157.2; HRMS calcd for $C_{17}H_{15}IO_3S$ [M^+], 425.9787, found 425.9795.

3-Iodobenzo[*b*]thiophene 8{*13*}



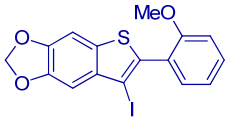
The product was obtained as a yellow oil that solidified upon standing to a yellow solid (84% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.95 (s, 3H), 6.94 (d, *J* = 7.9 Hz, 1H), 7.15-7.24 (m, 3H), 7.39 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.1, 56.2, 71.1, 111.1, 112.9, 121.9, 122.6, 127.3, 127.5, 134.5, 144.3, 148.8, 149.6, 150.6; HRMS calcd for $C_{14}H_{11}IO_2S_2$ [M^+], 401.9245, found 401.9252.

3-Iodobenzo[*b*]thiophene 8{*14*}



The product was obtained as a white solid (94% yield): mp 163-164 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.04 (s, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.14 (s, 1H), 7.23 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 78.3, 101.3, 101.8, 105.4, 114.1 (×2), 127.2, 131.3 (×2), 132.4, 137.1, 140.7, 147.4, 147.7, 160.1; HRMS calcd for $C_{16}H_{11}IO_3S$ [M^+], 409.9474, found 409.9479.

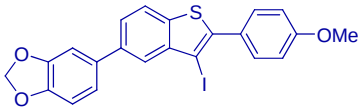
3-Iodobenzo[*b*]thiophene 8{*15*}



The product was obtained as a yellow solid (85% yield): mp 135-136.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 5.97 (s, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 7.11 (s, 1H), 7.21 (s, 1H), 7.33-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.7, 82.0, 101.2, 101.6, 105.1, 111.4, 120.4, 123.7, 130.7, 132.6, 133.0, 136.3, 137.9, 147.3, 147.5, 157.1; HRMS calcd for $C_{16}H_{11}IO_3S$ [M^+],

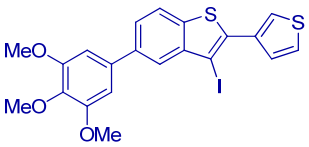
409.9474, found 409.9479.

3-Iodobenzo[*b*]thiophene 8{*16*}



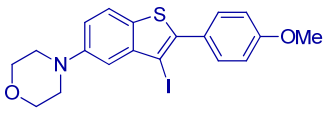
The product was obtained as a yellow solid (83% yield): ^{1}H NMR (400 MHz) δ 3.88 (s, 3H), 6.03 (s, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.14-7.20 (m, 2H), 7.53 (dd, *J* = 1.7, 8.3 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 1H),7.90 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 79.3, 101.4, 108.2, 108.9, 114.1 (×2), 121.2, 122.5, 124.4, 124.9, 127.0, 131.5 (×2), 135.5, 137.6, 138.9, 142.6, 143.0, 147.4, 148.4, 160.3; HRMS calcd for $C_{22}H_{15}IO_3S$ [M^+], 485.9787, found 485.9791.

3-Iodobenzo[*b*]thiophene 8{*17*}



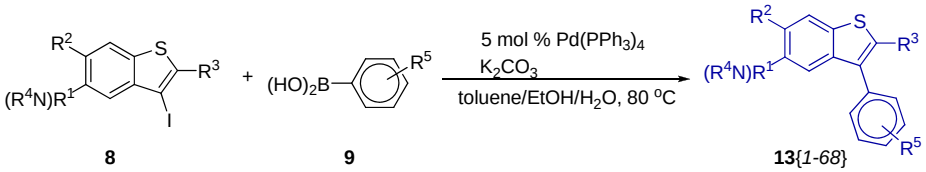
The product was obtained as a yellow oil (88% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.96 (s, 6H), 6.86 (s, 2H), 7.41 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.53-7.57 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.85 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.92 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.5 (×2), 61.2, 78.8, 104.9 (×2), 122.4, 124.5, 125.2, 125.5, 126.1, 128.4, 134.6, 137.1, 137.2, 137.9, 138.1, 139.3, 142.6, 153.6 (×2); HRMS calcd for $C_{21}H_{17}IO_3S_2$ [M^+], 507.9664, found 507.9669.

3-Iodobenzo[*b*]thiophene 8{*18*}



The product was obtained as a yellow solid (89% yield): mp = 147-148 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (t, *J* = 4.7 Hz, 4H), 3.87 (s, 3H), 3.92 (t, *J* = 4.8 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 2.4, 8.8 Hz, 1H), 7.23-7.26 (m, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.60-7.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.5 (×2), 55.6, 67.2 (×2), 79.2, 112.2, 114.1 (×2), 116.8, 122.8, 127.2, 130.9, 131.4 (×2), 143.0, 143.1, 150.3, 160.2; HRMS calcd for $C_{19}H_{18}INO_2S$ [M^+], 451.0103, found 451.0105.

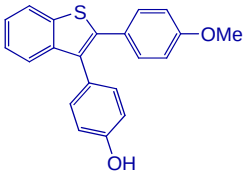
General procedure for the Suzuki-Miyaura coupling to prepare 13{*1-68*}[3]



8 **9** **13**{*1-68*}

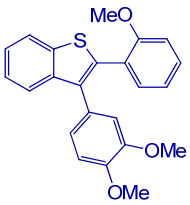
To a 4 dram vial was added the appropriate 3-iodobenzothiophene **8** (0.8-1.2 mmol), boronic acid **9** (1.5 equiv), K_2CO_3 (2.5 equiv) and 5 mol % $Pd(PPh_3)_4$ in 20:5:1 toluene/ethanol/H_2O. The solution was vigorous stirred for 5 min at room temperature, flushed with argon, and then heated to 80 °C until TLC revealed complete conversion of the starting material. Upon cooling to room temperature, the resulting reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, concentrated, and purified by either column chromatography or preparative HPLC to afford the corresponding product.

Benzo[*b*]thiophene 13{*1*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 5.16 (br s, 1H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 7.29-7.34 (m, 2H), 7.54-7.57 (m, 1H), 7.83-7.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 114.0 (×2), 115.9 (×2), 122.2, 123.3, 124.4, 124.5, 127.0, 128.2, 130.9 (×2), 131.9 (×2), 132.1, 138.7, 139.2, 141.3, 155.1, 159.3; HRMS calcd for $C_{22}H_{17}O_4S$ [M+HCOO$^+$], 377.0848, found 377.0848.

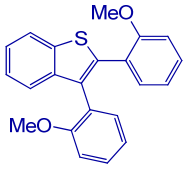
Benzo[*b*]thiophene 13{*6*}



The product was obtained as a colorless oil (85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (s, 3H), 3.65 (s, 3H), 3.88 (s, 3H), 6.78 (d, *J* = 1.6 Hz, 1H), 6.83-6.94 (m, 4H), 7.23-7.31 (m, 2H), 7.32-7.38 (m, 2H), 7.74-7.80 (m, 1H), 7.85-7.89 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 55.9, 56.0, 111.0, 111.3, 113.2,

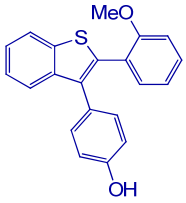
120.6, 122.2, 122.3, 123.3, 123.5, 124.4, 124.4, 128.7, 129.8, 132.8, 134.8, 135.6, 139.8, 139.9, 148.0, 148.6, 157.3; HRMS calcd for $C_{23}H_{20}O_3S$ [M^+], 376.1133, found 376.1133.

Benzo[*b*]thiophene 13{*7*}



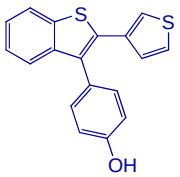
The product was obtained as a pale yellow oil (58% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.57 (s, 6H), 6.60-6.92 (m, 4H), 7.12-7.60 (m, 6H), 7.45-7.50 (m, 1H), 7.65-7.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 55.5, 111.1, 111.2, 120.4, 120.5, 122.1, 123.7, 123.9, 124.0, 124.1, 125.1, 128.9, 129.5, 131.9, 132.0, 132.3, 136.7, 139.7, 140.0, 157.0, 157.5; HRMS calcd for $C_{22}H_{22}NO_2S$ [$M+NH_4^+$], 364.1371, found 364.1371.

Benzo[*b*]thiophene 13{*11*}



The product was obtained as a pale yellow oil (87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (s, 3H), 5.05 (br s, 1H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.82-6.89 (m, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.21-7.29 (m, 2H), 7.31-7.36 (m, 2H), 7.66-7.72 (m, 1H), 7.83-7.87 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 111.4, 115.3 (×2), 120.6, 122.3, 123.3, 123.4, 124.3, 124.4, 128.7, 129.8, 131.2 (×2), 132.8, 134.7, 135.5, 139.9, 140.0, 154.6, 157.2; HRMS calcd for $C_{22}H_{17}O_4S$ [$M+HCOO^+$], 377.0848, found 377.0851.

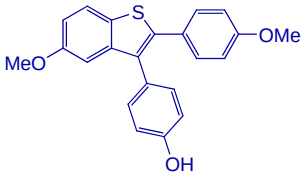
Benzo[*b*]thiophene 13{*17*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (67% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.98 (s, 1H), 6.90-6.93 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.17-7.21 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.28-7.34 (m, 2H), 7.46-7.50 (m, 1H), 7.81-7.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.0 (×2), 122.2, 123.4, 123.6, 124.6, 124.7, 125.6, 128.1, 128.3, 129.9, 131.8 (×2),

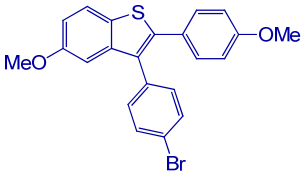
132.6, 135.1, 138.3, 141.5, 155.3; HRMS calcd for $C_{18}H_{12}OS_2$ [M^+], 308.0330, found 308.0325.

Benzo[*b*]thiophene 13{*20*}



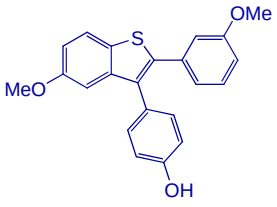
The product was obtained as a pale yellow oil (61% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.78 (s, 3H), 5.12 (br s, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.96-7.03 (m, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.8, 105.8, 114.0 (×2), 114.3, 115.9 (×2), 122.9, 127.1, 128.3, 130.8 (×2), 131.1, 131.85 (×2), 131.89, 140.7, 142.4, 155.0, 157.8, 159.2; HRMS calcd for $C_{22}H_{18}O_3S$ [M^+], 362.0977, found 362.0983.

Benzo[*b*]thiophene 13{*23*}



The product was obtained as a white solid (71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.77 (s, 3H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.94-7.00 (m, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 55.7, 105.3, 114.1 (×2), 114.6, 121.6, 123.0, 126.5, 128.7, 130.9 (×2), 131.1, 132.15 (×2), 132.24 (×2), 134.9, 141.6, 141.7, 158.0, 159.5.

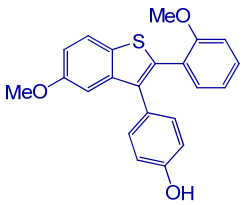
Benzo[*b*]thiophene 13{*25*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (65% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 3H), 3.78 (s, 3H), 5.45 (br s, 1H), 6.77 (dd, *J* = 2.5, 8.2 Hz, 1H), 6.82-6.85 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.98-7.05 (m, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 55.8,

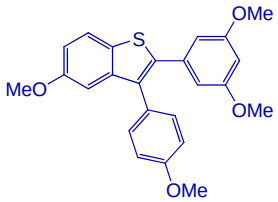
105.9, 114.0, 114.71, 114.74, 115.9 (×2), 122.2, 123.0, 128.1, 129.6, 131.3, 131.8 (×2), 132.9, 135.9, 140.5, 142.2, 155.1, 157.8, 159.3; HRMS calcd for $C_{22}H_{18}O_3S$ [M^+], 362.0977, found 362.0983.

Benzo[*b*]thiophene 13{*31*}



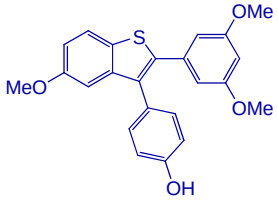
The product was obtained as a pale yellow oil (82% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (s, 3H), 3.79 (s, 3H), 5.74 (br s, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.79-6.89 (m, 2H), 6.99 (dd, *J* = 2.5, 8.7 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.14-7.16 (m, 1H), 7.20-7.27 (m, 2H), 7.71 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.8, 105.8, 111.4, 114.4, 115.4 (×2), 120.5, 123.0, 123.5, 128.6, 129.7, 131.1 (×2), 132.3, 132.7, 134.5, 136.8, 141.0, 154.8, 157.1, 157.6; HRMS calcd for $C_{22}H_{18}O_3S$ [M^+], 362.0977, found 362.0983.

Benzo[*b*]thiophene 13{*36*}



The product was obtained as a yellow solid (68% yield): mp = 172-174 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 6H), 3.78 (s, 3H), 3.85 (s, 3H), 6.34 (t, *J* = 2.2 Hz, 1H), 6.47 (d, *J* = 2.2 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.98-7.04 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4 (×2), 55.5, 55.8, 100.5, 105.8, 107.6 (×2), 114.4 (×2), 114.9, 116.2, 123.0, 131.2, 131.6 (×2), 133.2, 136.4, 140.5, 142.3, 157.9, 159.1, 160.6 (×2); HRMS calcd for $C_{24}H_{21}O_6S$ [M+$HCOO^+$], 437.1059, found 437.1044.

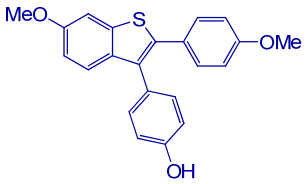
Benzo[*b*]thiophene 13{*37*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (71%

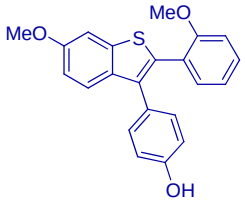
yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 6H), 3.79 (s, 3H), 5.13 (br s, 1H), 6.35 (br s, 1H), 6.48 (d, *J* = 2.2 Hz, 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 6.98-7.04 (m, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4 (×2), 55.8, 100.4, 105.8, 107.7 (×2), 114.8, 115.9 (×2), 123.0, 128.0, 131.2, 131.8 (×2), 133.1, 136.4, 140.5, 142.2, 155.4, 157.8, 160.5 (×2); HRMS calcd for $C_{24}H_{21}O_6S$ [M+HCOO$^+$], 437.1059, found 437.1044.

Benzo[*b*]thiophene 13{*42*}



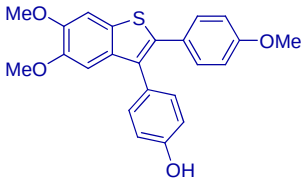
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (64% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.89 (s, 3H), 5.04 (br s, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.94 (dd, *J* = 2.4, 8.9 Hz, 1H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 2H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.44 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.9, 104.8, 114.0 (×2), 114.4, 115.8 (×2), 124.0, 127.2, 128.4, 130.8 (×2), 131.6, 131.9 (×2), 135.4, 136.5, 139.9, 154.9, 157.5, 159.0; HRMS calcd for $C_{22}H_{18}O_3S$ [M$^+$], 362.0977, found 362.0990.

Benzo[*b*]thiophene 13{*47*}



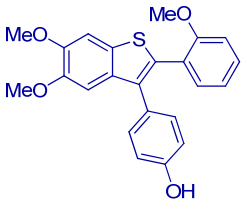
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (58% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.54 (s, 3H), 3.86 (s, 3H), 5.53 (br s, 1H), 6.74 (d, *J* = 8.5 Hz, 2H), 6.80-6.86 (m, 2H), 6.95 (dd, *J* = 2.3, 8.9 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.16-7.24 (m, 2H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.56 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.9, 104.8, 111.4, 114.2, 115.3 (×2), 120.6, 123.5, 124.0, 128.7, 129.5, 131.1 (×2), 132.6, 132.8, 134.18, 134.20, 141.2, 154.7, 157.1, 157.4; HRMS calcd for $C_{22}H_{18}O_3S$ [M$^+$], 362.0977, found 362.0986.

Benzo[*b*]thiophene 13{*49*}



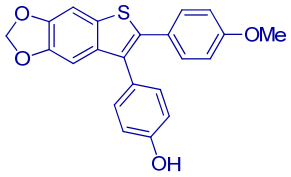
The product was obtained as a yellow solid (61% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.84 (s, 3H), 3.97 (s, 3H), 5.09 (br s, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.97 (s, 1H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 56.3, 56.4, 103.9, 104.7, 114.0 (×2), 116.0 (×2), 127.2, 128.5, 130.7 (×2), 131.2, 131.8 (×2), 134.8, 137.4, 148.4, 148.4, 155.0, 159.0; HRMS calcd for $C_{24}H_{21}O_6S$ [M+HCOO$^+$], 437.1059, found 437.1047.

Benzo[*b*]thiophene 13{*51*}



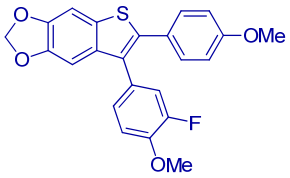
The product was obtained as a yellow oil (53% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56 (s, 3H), 3.84 (s, 3H), 3.95 (s, 3H), 5.50 (br s, 1H), 6.76-6.88 (m, 4H), 7.12 (s, 1H), 7.14-7.28 (m, 4H), 7.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 56.3, 56.4, 103.9, 104.7, 111.4, 115.4 (×2), 120.5, 123.6, 128.9, 129.5, 131.0 (×2), 132.5, 132.8, 133.47, 133.51, 134.3, 148.15, 148.22, 154.8, 157.1; HRMS calcd for $C_{23}H_{20}O_4S$ [M$^+$], 392.1082, found 392.1092.

Benzo[*b*]thiophene 13{*55*}



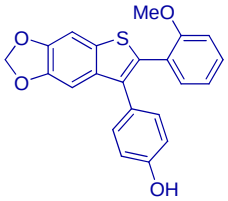
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 4.89 (br s, 1H), 5.99 (s, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.94 (s, 1H), 7.17 (d, *J* = 8.6 Hz, 2H), 7.19 (s, 1H), 7.21 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 101.4, 101.5, 102.3, 114.0 (×2), 115.5, 115.9 (×2), 127.1, 128.4, 130.6 (×2), 131.8 (×2), 132.0, 136.0, 137.6, 146.6, 146.9, 155.0, 159.1; HRMS calcd for $C_{22}H_{16}O_4S$ [M$^+$], 376.0769, found 376.0777.

Benzo[*b*]thiophene 13{*56*}



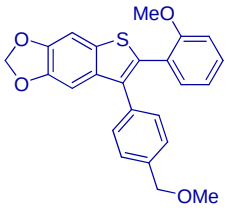
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (64% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.93 (s, 3H), 6.00 (s, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.93 (s, 1H), 6.97-7.07 (m, 3H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.22 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 56.4, 101.5, 101.6, 102.0, 114.1 (×2), 118.1, 118.3, 126.47, 126.50, 126.8, 128.7, 128.8, 130.6 (×2), 132.1, 135.6, 138.2, 146.7, 147.0, 159.2.

Benzo[*b*]thiophene 13{*59*}



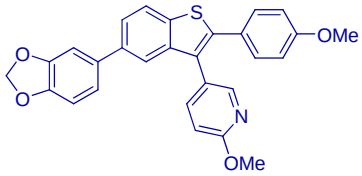
The product was obtained as a pale yellow oil (69% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.55 (s, 3H), 5.48 (br s, 1H), 5.96 (s, 2H), 6.75 (d, *J* = 7.9 Hz, 2H), 6.77-6.87 (m, 2H), 7.08 (s, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.16-7.26 (m, 2H), 7.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 101.4, 101.5, 102.3, 111.4, 115.3 (×2), 120.5, 123.5, 128.7, 129.5, 131.1 (×2), 132.7, 133.3, 133.6, 134.5, 134.6, 146.5, 146.7, 154.7, 157.0; HRMS calcd for $C_{44}H_{36}ONO_8S_2$ [2M+NH_4^+], 770.1882, found 770.1857.

Benzo[*b*]thiophene 13{*60*}



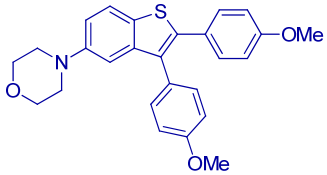
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (77% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 3H), 3.53 (s, 3H), 4.44 (s, 2H), 5.99 (s, 2H), 6.78-6.87 (m, 2H), 7.08 (s, 1H), 7.17-7.29 (m, 6H), 7.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 58.4, 74.8, 101.4, 101.5, 102.3, 111.3, 120.5, 123.3, 127.8 (×2), 129.6, 129.8 (×2), 132.7, 133.4, 134.2, 134.5, 134.6, 135.8, 136.9, 146.6, 146.8, 157.0; HRMS calcd for $C_{24}H_{24}NO_4S$ [M+NH_4^+], 422.1426, found 422.1416.

Benzo[*b*]thiophene 13{*63*}



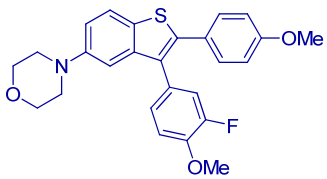
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (81% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 4.00 (s, 3H), 5.99 (s, 2H), 6.78-6.88 (m, 4H), 7.03-7.07 (m, 2H), 7.23-7.26 (m, 2H), 7.50-7.54 (m, 2H), 7.64 (d, *J* = 1.2 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 8.20 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.8, 55.5, 101.4, 108.1, 108.8, 111.2, 114.3 (×2), 120.9, 121.1, 122.6, 124.1, 124.6, 126.4, 128.9, 131.0 (×2), 135.8, 137.2, 137.6, 138.1, 141.0, 141.5, 144.7, 147.2, 148.2, 159.6, 163.5; HRMS calcd for $C_{28}H_{22}NO_4S$ [M+H$^+$], 468.1270, found 468.1270.

Benzo[*b*]thiophene 13{*64*}



The product was obtained as a colorless oil (69% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12 (br s, 4H), 3.78 (s, 3H), 3.86 (br s, 4H), 3.86 (s, 3H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 7.01-7.12 (m, 2H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.8, 55.4, 55.4, 67.1, 109.6, 114.0 (×2), 114.4 (×2), 115.5, 116.0, 122.7, 126.7, 127.1, 127.8, 128.2, 130.8 (×2), 131.7 (×2), 132.0, 142.3, 158.9, 159.2; HRMS calcd for $C_{26}H_{26}NO_3S$ [M+H$^+$], 432.1633, found 432.1633.

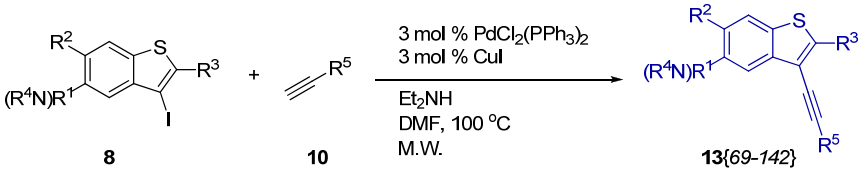
Benzo[*b*]thiophene 13{*66*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (59% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (br s, 4H), 3.79 (s, 3H), 3.88 (br s, 4H), 3.94 (s, 3H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.96-7.12 (m, 5H), 7.22 (d, *J* = 8.9 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.4 (×2), 55.5, 56.4, 67.1 (×2), 113.67, 113.69, 114.1 (×2), 114.5, 116.1, 118.1, 118.3, 122.8,

126.55, 126.58, 126.7, 127.8, 130.8 (×2), 141.9, 147.1, 151.3, 153.8, 159.4; HRMS calcd for $C_{26}H_{25}FNO_3S$ [M+H$^+$], 450.1539, found 450.1552.

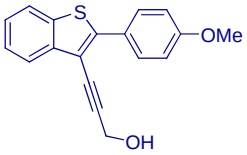
General procedure for the microwave-assisted Sonogashira coupling to prepare 13{*69-142*}[1]



8 **10** **13**{*69-142*}

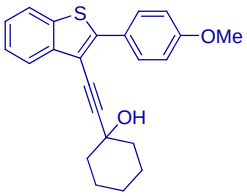
The 3-iodobenzofuran **8** (0.8-1.2 mmol), the alkyne **10** (1.2 equiv), 3 mol % $PdCl_2(PPh_3)_2$, 3 mol % CuI, DMF (1.5 mL) and Et_2NH (1.5 mL) were mixed in a 0.5-2.0 mL Biotage microwave vial equipped with a magnetic stirrer. The vessel was placed in the microwave reactor and irradiated to ramp the temperature from room temperature to 110 ^oC and then held at that temperature for 20 min. The mixture was then cooled down and diluted with EtOAc. The combined organic layers were dried over $MgSO_4$, concentrated, and purified by either column chromatography or preparative HPLC to afford the corresponding products **13**{*69-142*}.

Benzo[*b*]thiophene 13{*69*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (58% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 4.61 (s, 2H), 6.93-7.02 (m, 2H), 7.31-7.43 (m, 2H), 7.75-7.93 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.2, 55.6, 80.6, 92.4, 111.8, 114.3 (×2), 122.2, 123.1, 125.1, 125.2, 126.4, 129.9 (×2), 137.3, 141.4, 147.2, 160.3; HRMS calcd for $C_{18}H_{14}O_2S$ [M$^+$], 294.0715, found 294.0728.

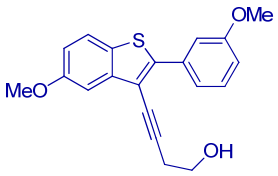
Benzo[*b*]thiophene 13{*71*}



The product was obtained as a pale yellow oil (57% yield): ^1H NMR (400 MHz, $CDCl_3$) δ ^1H NMR (400

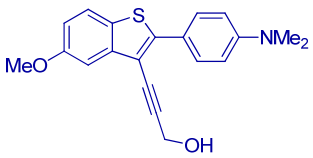
MHz, $CDCl_3$) δ 1.40-1.75 (m, 8H), 2.10-2.32 (m, 2H), 2.50 (s, 1H), 6.92-7.03 (m, 2H), 7.30-7.42 (m, 2H), 7.75-7.92 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7 (×2), 25.5, 40.3 (×2), 55.6, 69.8, 79.1, 95.7, 98.2, 112.1, 114.2 (×2), 122.2, 123.1, 125.1, 126.5, 129.9 (×2), 137.3, 141.4, 146.5, 160.2; HRMS calcd for $C_{46}H_{48}NO_4S_2$ [2M+NH_4^+],742.3025, found 742.3051.

Benzo[*b*]thiophene 13{*90*}



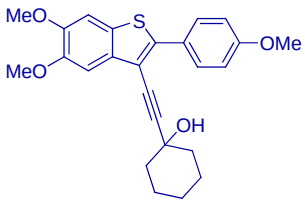
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (66% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (br s, 1H), 2.82 (t, *J* = 6.0 Hz, 2H), 3.87 (t, *J* = 6.0 Hz, 2H), 3.87 (s, 3H), 3.91 (s, 3H), 6.90-7.03 (m, 2H), 7.32-7.39 (m, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.62-7.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 55.6, 55.8, 61.4, 77.1, 92.6, 105.4, 113.8, 114.0, 114.3, 115.6, 120.9, 123.0, 129.9, 130.0, 135.4, 142.5, 146.9, 158.2, 159.7; HRMS calcd for $C_{40}H_{40}NO_6S_2$ [2M+NH_4^+], 694.2297, found 694.2281.

Benzo[*b*]thiophene 13{*102*}



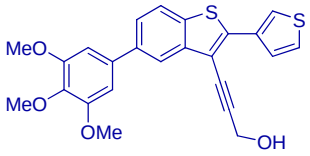
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (58% yield): ^1H NMR (400 MHz, $CDCl_3$) δ 1.87 (br s, 1H), 3.02 (s, 6H), 3.91 (s, 3H), 4.62 (s, 2H), 6.76 (d, *J* = 8.5 Hz, 2H), 6.95 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.30 (d, *J* = 2.5 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.5, 52.3, 55.9, 81.2, 92.2, 105.0, 110.0, 112.1 (×2), 114.7, 121.8, 122.8, 129.2, 129.3 (×2), 142.8, 149.8, 150.8, 158.2; HRMS calcd for $C_{20}H_{20}NO_2S$ [M+H^+], 338.1215, found 338.1208.

Benzo[*b*]thiophene 13{*114*}



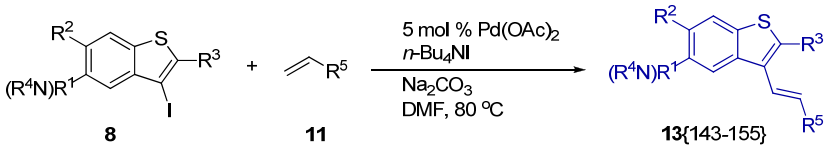
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (74% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50-1.76 (m, 8H), 2.03-2.26 (m, 2H), 3.85 (s, 3H), 3.95 (s, 3H), 3.98 (s, 3H), 6.95 (d, *J* = 8.6 Hz, 2H), 7.20 (s, 1H), 7.29 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.7 (×2), 25.4, 40.3 (×2), 55.6, 56.1, 56.4, 60.6, 79.5, 98.0, 103.8, 104.3, 111.7, 114.1 (×2), 126.8, 129.5 (×2), 129.7, 135.0, 144.5, 148.7, 159.9, 171.4; HRMS calcd for $C_{25}H_{27}O_4S$ [M+H$^+$], 423.1630, found 423.1654.

Benzo[*b*]thiophene 13{*134*}



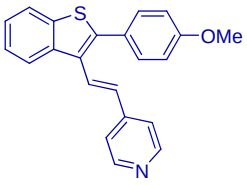
The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (br s, 1H), 3.92 (s, 3H), 3.96 (s, 6H), 4.68 (s, 2H), 6.84 (s, 2H), 7.41-7.44 (m, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 5.0 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.98 (s, 1H), 8.05 (d, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 56.6 (×2), 61.2, 80.6, 93.9, 104.7, 105.1 (×2), 112.2, 121.4, 122.4, 124.2, 125.1, 126.3, 127.3, 134.5, 136.1, 137.4, 139.1, 141.5, 142.7, 153.7 (×2); HRMS calcd for $C_{24}H_{21}O_4S_2$ [M+H$^+$], 437.0881, found 437.0854.

General procedure for the Heck coupling to prepare 13{*143-155*}[6]



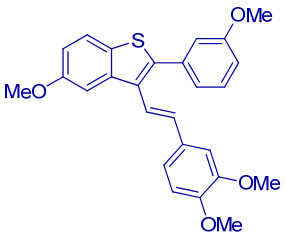
To a 4 dram vial was added the appropriate 3-iodobenzothiophene **8** (1.0 mmol), the styrene **11** (1.2 mmol), 5 mol % $Pd(OAc)_2$, *n*-Bu_4NI (1.0 mmol), Na_2CO_3 (2.5 mmol) and DMF (1.5 mL). The solution was stirred at room temperature and flushed with argon, and then heated to 80 ^{o}C until TLC revealed complete conversion of the starting material. The solution was allowed to cool and diluted with EtOAc. The combined organic layers were dried over $MgSO_4$, concentrated, and purified by either column chromatography or preparative HPLC to afford the corresponding product.

Benzo[*b*]thiophene 13{*146*}



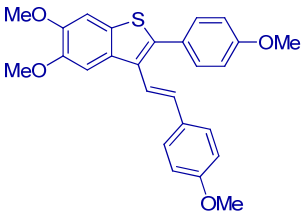
The product was obtained as a pale yellow oil (58% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.00 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 16.8 Hz, 1H), 7.32 (d, *J* = 6.0 Hz, 2H), 7.35-7.52 (m, 3H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 8.57 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 114.4 (×2), 120.8 (×2), 122.6, 123.1, 124.7, 125.1, 126.6, 127.1, 127.8, 128.8, 131.5 (×2), 138.7, 139.2, 143.7, 145.3, 150.4 (×2), 160.2; HRMS calcd for $C_{22}H_{18}NOS$ [M+H$^+$], 344.1109, found 344.1092.

Benzo[*b*]thiophene 13{*151*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (86% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.90 (s, 3H), 3.906 (s, 3H), 3.911 (s, 3H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 2.4, 8.0 Hz, 1H), 7.01-7.05 (m, 3H), 7.06 (s, 1H), 7.08 (s, 1H), 7.12-7.19 (m, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.5, 55.9, 56.1, 56.2, 106.6, 108.8, 111.4, 114.15, 114.18, 115.3, 119.7, 120.9, 122.5, 123.2, 129.5, 129.8, 130.9, 131.8, 132.1, 136.2, 140.4, 141.5, 149.1, 149.3, 157.9, 159.8; HRMS calcd for $C_{26}H_{25}O_4S$ [M+H$^+$],433.1474, found 433.1455.

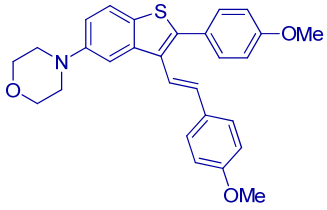
Benzo[*b*]thiophene 13{*154*}



The product was obtained as a pale yellow oil (77% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.811 (s, 3H), 3.813 (s, 3H), 3.97 (s, 3H), 3.98 (s, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.93-7.04 (m, 4H), 7.34 (d, *J* = 8.8 Hz,

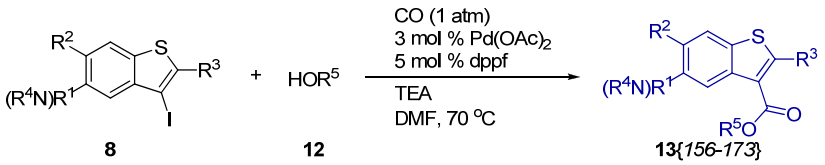
2H), 7.25-7.43 (m, 5H), 7,52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 55.9, 56.36, 56.42, 104.0, 104.9, 111.6, 114.3 (×2), 120.7, 121.1, 127.6 (×2), 129.9, 130.4 (×2), 130.9, 132.1, 132.8, 133.0 (×2), 134.7, 148.2, 148.3, 157.3, 159.3; HRMS calcd for $C_{26}H_{25}O_4S$ [M+H$^+$], 433.1474, found 433.1497.

Benzo[*b*]thiophene 13{*155*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (23% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.22 (br s, 4H), 3.83 (s, 3H), 3.85 (s, 3H), 3.92 (br s, 4H), 6.85-7.12 (m, 7H), 7.43-7.60 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.0 (×2), 55.56, 55.59, 67.1 (×2), 109.7, 114.2 (×2), 114.4 (×2), 116.1, 120.8, 122.9, 127.4, 127.7 (×2), 127.8, 128.9, 130.8, 131.3 (×2), 131.7, 140.4, 141.5, 159.5, 159.7 ; HRMS calcd for $C_{28}H_{27}NO_3S$ [M$^+$], 457.1712, found 457.1719.

General procedure for carboalkoxylation to prepare 13{*156-173*}[7]



8 **12** **13**{*156-173*}

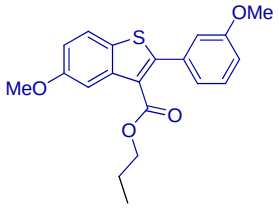
A mixture of 3-iodobenzothiophene **8** (0.1 mmol), 5 mol % dppf, 3 mol % $Pd(OAc)_2$, and TEA (2.0 equiv) in MeOH (1.0 mL) and DMF (1.0 mL) was flushed with an atmosphere of carbon monoxide. The solution was stirred at room temperature and then heated to 70 °C until TLC revealed complete conversion of the starting material. The solution was allowed to cool and diluted with EtOAc. The separated organic layer was washed with water and brine; dried over $MgSO_4$; and concentrated *in vacuo*. The crude product was purified by either column chromatography or preparative HPLC to afford the corresponding product.

Benzo[*b*]thiophene 13{*159*}

The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (86%

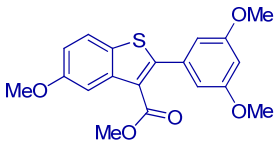
yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.86 (s, 3H), 3.91 (s, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 7.02 (dd, *J* = 2.5, 8.8 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.7, 55.6, 55.8, 106.6, 113.8 (×2), 115.5, 121.9, 122.5, 126.7, 130.9 (×2), 140.1, 153.6, 158.4, 160.3, 164.9; HRMS calcd for $C_{36}H_{32}NaO_8S_2$ [2M+Na^+], 679.1436, found 679.1436.

Benzo[*b*]thiophene 13{*161*}



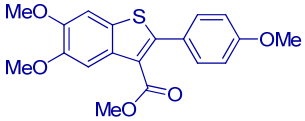
The product was obtained as a pale yellow oil (47% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, *J* = 7.4 Hz, 3H), 1.45-1.55 (m, 2H), 3.84 (s, 3H), 3.91 (s, 3H), 4.13 (t, *J* = 6.6 Hz, 2H), 6.96 (dd, *J* = 2.4, 8.7 Hz, 1H), 7.01-7.70 (m, 3H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 21.9, 55.6, 55.7, 66.6, 106.4, 114.6, 115.2, 115.9, 122.1, 122.5, 123.1, 129.3, 131.1, 135.8, 139.9, 152.9, 158.4, 159.3, 164.4; HRMS calcd for $C_{20}H_{21}O_4S$ [M+H^+], 357.1161, found 357.1158.

Benzo[*b*]thiophene 13{*163*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (70% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.82 (s, 6H), 3.91 (s, 3H), 6.52 (t, *J* = 2.2 Hz, 1H), 6.64 (d, *J* = 2.2 Hz, 2H), 7.04 (dd, *J* = 2.5, 8.8 Hz, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.9, 55.7 (×2), 55.8, 101.2, 106.5, 107.7 (×2), 115.9, 122.6, 122.8, 131.1, 136.1, 139.9, 152.8, 158.5, 160.5, 164.8; HRMS calcd for $C_{38}H_{36}NaO_{10}S_2$ [2M+Na^+], 739.1648, found 739.1670.

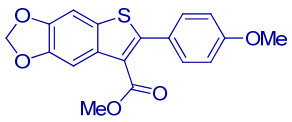
Benzo[*b*]thiophene 13{*166*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (85% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.87 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 6.95 (d, *J* = 8.7 Hz,

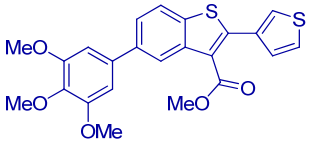
2H), 7.22 (s, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6, 55.5, 56.2, 56.3, 103.1, 105.9, 113.7 (×2), 121.6, 126.8, 130.9 (×2), 131.2, 132.7, 148.6, 148.9, 150.4, 160.1, 164.9; HRMS calcd for $C_{38}H_{36}NaO_{10}S_2$ [2M+Na^+], 739.1648, found 739.1633.

Benzo[*b*]thiophene 13{*168*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (56% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.86 (s, 3H), 6.04 (s, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 7.16 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.7, 55.5, 100.9, 101.7, 103.8, 113.7 (×2), 122.0, 126.6, 130.9 (×2), 132.2, 133.6, 146.9, 147.6, 150.4, 160.2, 164.7; HRMS calcd for $C_{36}H_{32}NO_{10}S_2$ [2M+NH_4^+], 702.1468, found 702.1468.

Benzo[*b*]thiophene 13{*172*}



The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.92 (s, 3H), 3.96 (s, 6H), 6.86 (s, 2H), 7.32 (dd, *J* = 1.3, 5.0 Hz, 1H), 7.40 (dd, *J* = 3.0, 5.0 Hz, 1H), 7.58 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.61 (dd, *J* = 1.3, 3.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 8.46 (d, *J* = 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.0, 56.5 (×2), 61.2, 105.1 (×2), 122.0, 122.7, 123.0, 124.9, 125.7, 125.9, 129.0, 134.0, 137.2, 137.5, 137.9, 139.3, 146.8, 153.7 (×2), 164.6; HRMS calcd for $C_{23}H_{21}O_5S_2$ [M+H^+], 441.0830, found 441.0832.

Benzo[*b*]thiophene 13{*173*}

The product was obtained as a pale yellow oil that solidified upon standing to an ivory solid (68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.24 (t, *J* = 4.8 Hz, 4H), 3.75 (s, 3H), 3.87 (s, 3H), 3.91 (t, *J* = 4.8 Hz, 4H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.09 (dd, *J* = 2.4, 8.8 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.5 (×2), 51.7, 55.6, 67.2 (×2), 110.3, 113.8 (×2),

116.5, 121.9, 122.2, 126.7, 130.80, 130.84 (×2), 140.1, 150.1, 153.2, 160.3, 165.0; HRMS calcd for $C_{21}H_{22}NO_4S$ [M+H$^+$], 384.1270, found 384.1255.

References

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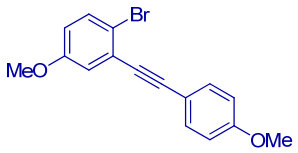
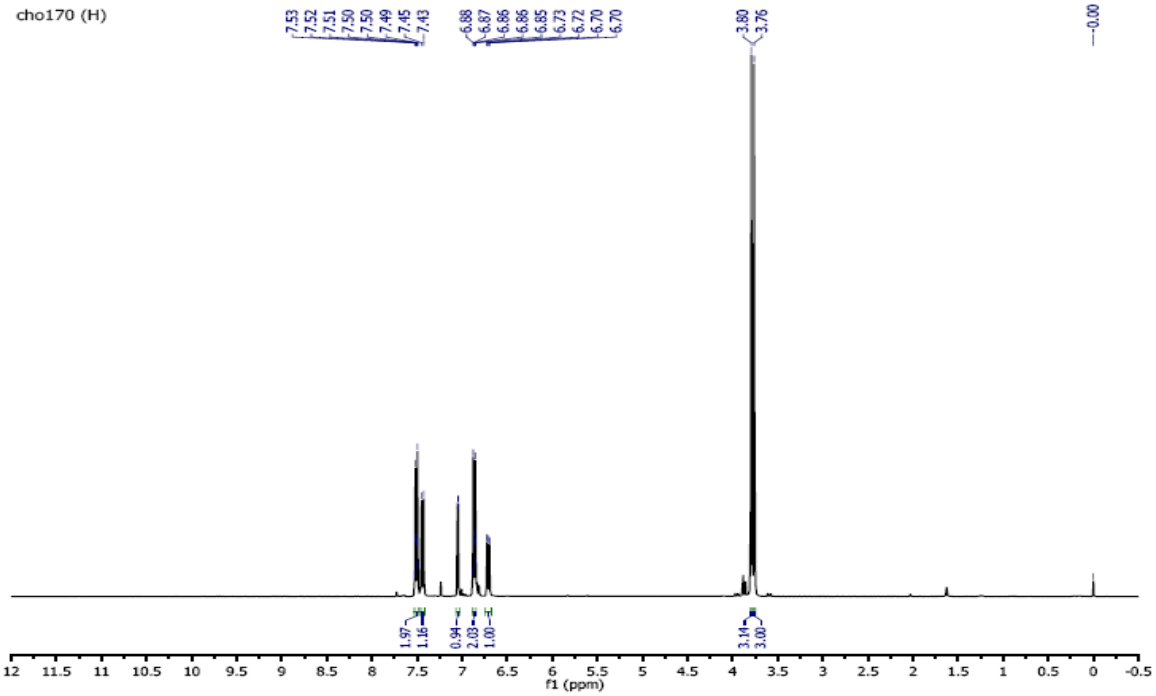
Compound **6**{*1*}


Br
MeO
OMe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7.52
7.51
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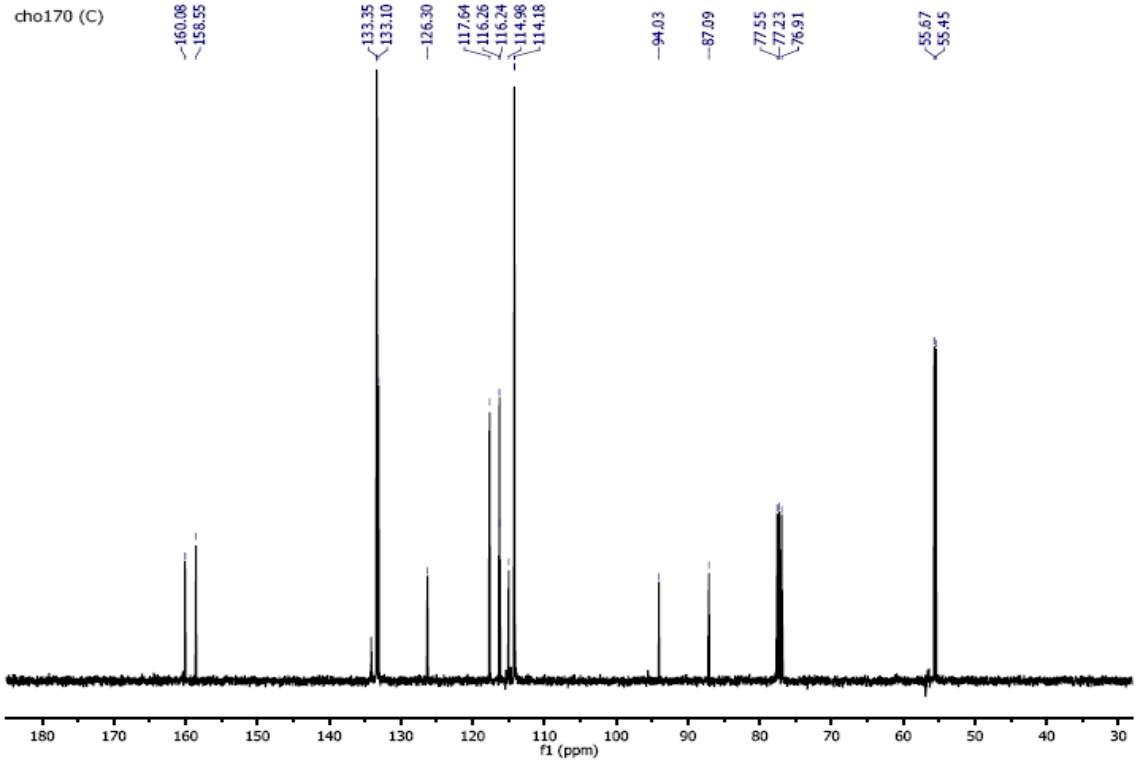
7.50
7.49
7.45
7.43
6.88
6.87
6.86
6.86
6.85
6.73
6.72
6.70
6.70
3.80
3.76
0.00
1.97
1.16
0.94
2.03
1.00
3.14
3.00
f1 (ppm)


cho170 (C)
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158.55
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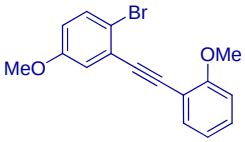
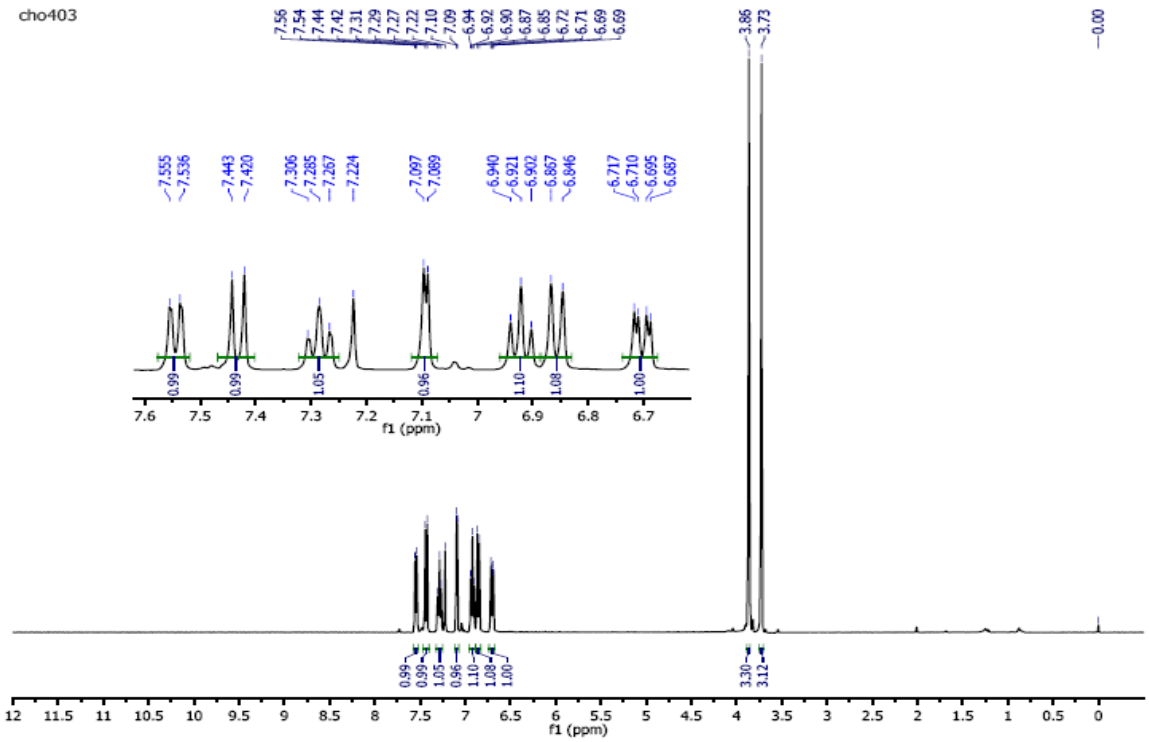
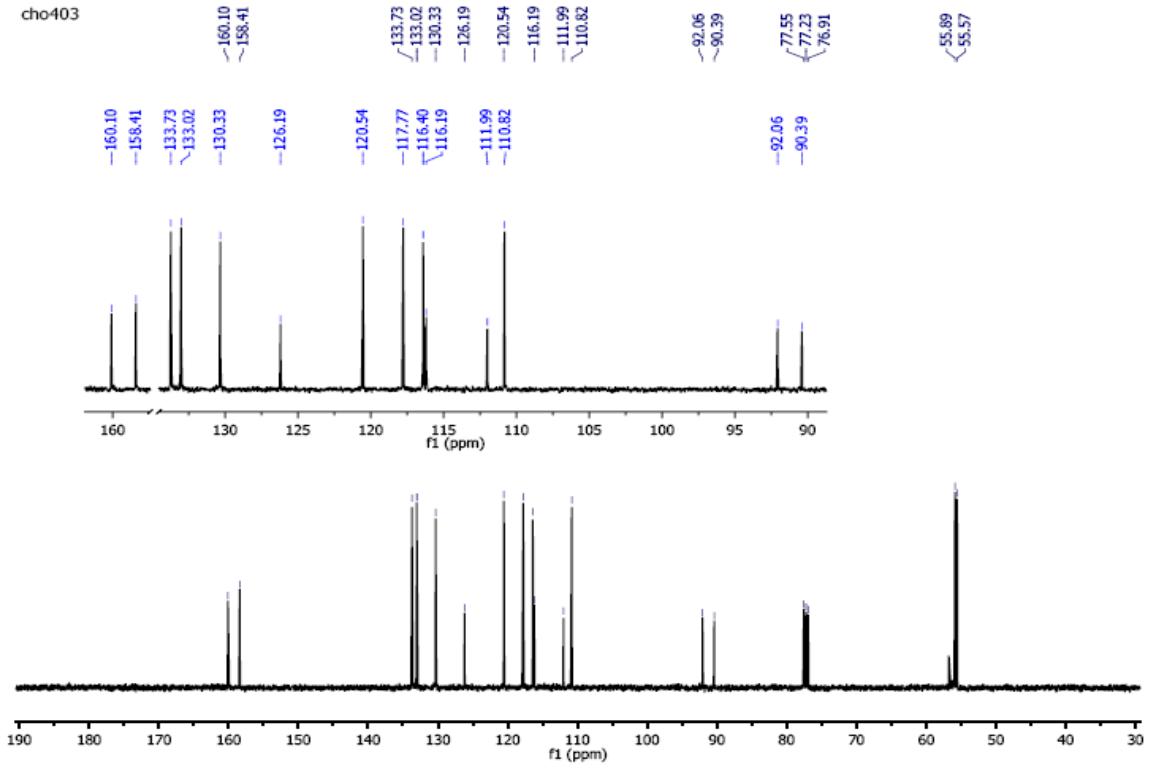
133.10
126.30
117.64
116.26
116.24
114.98
114.18
94.03
87.09
77.55
77.23
76.91
55.67
55.45
f1 (ppm)

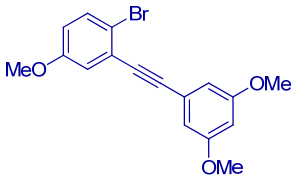
Compound **6**{*3*}

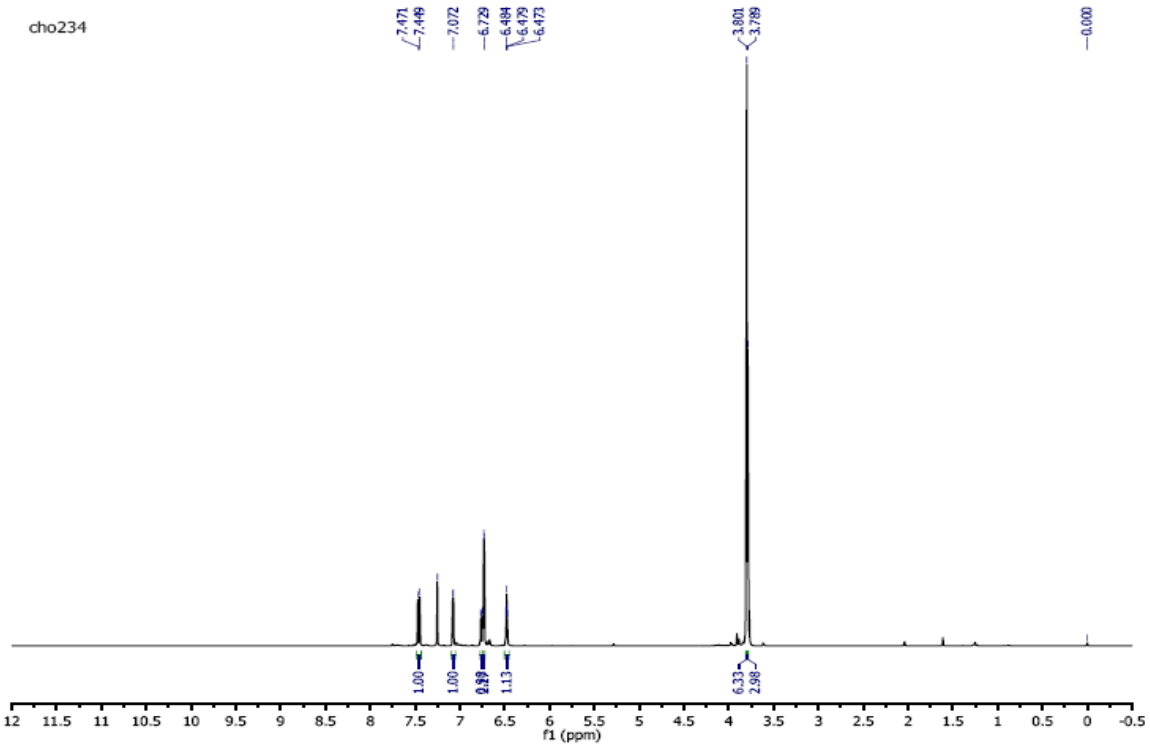


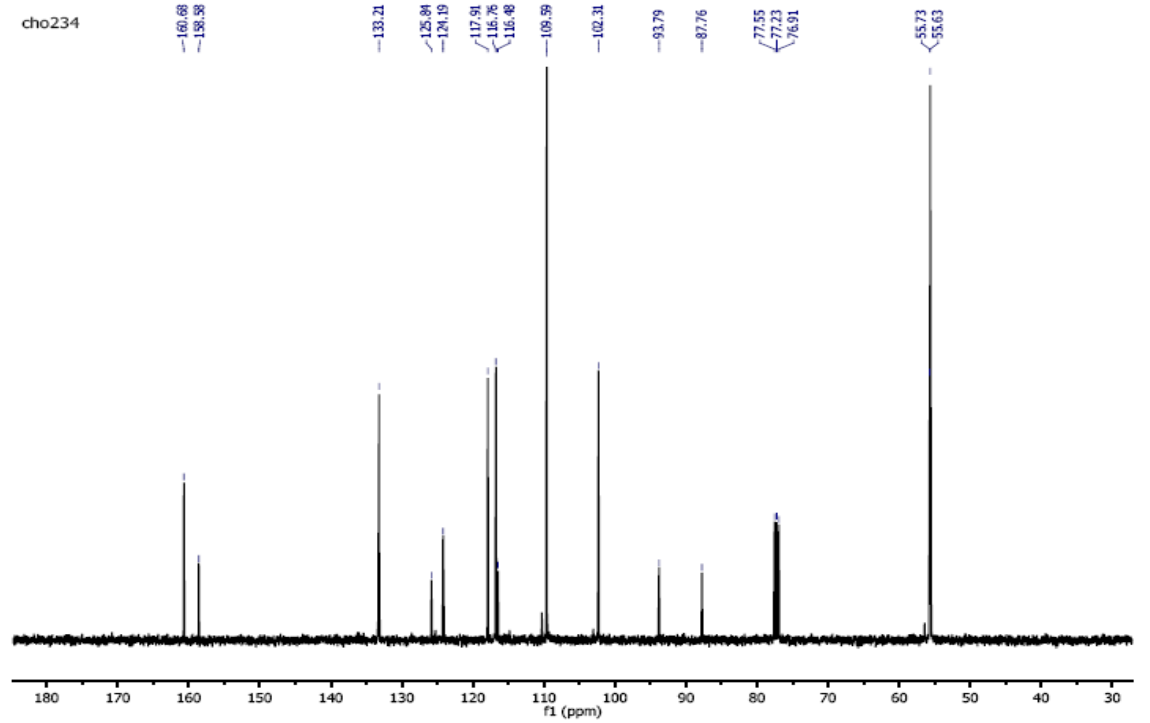




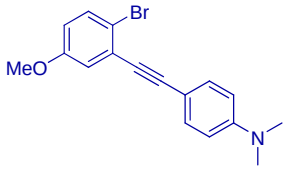
Compound **6**{*4*}

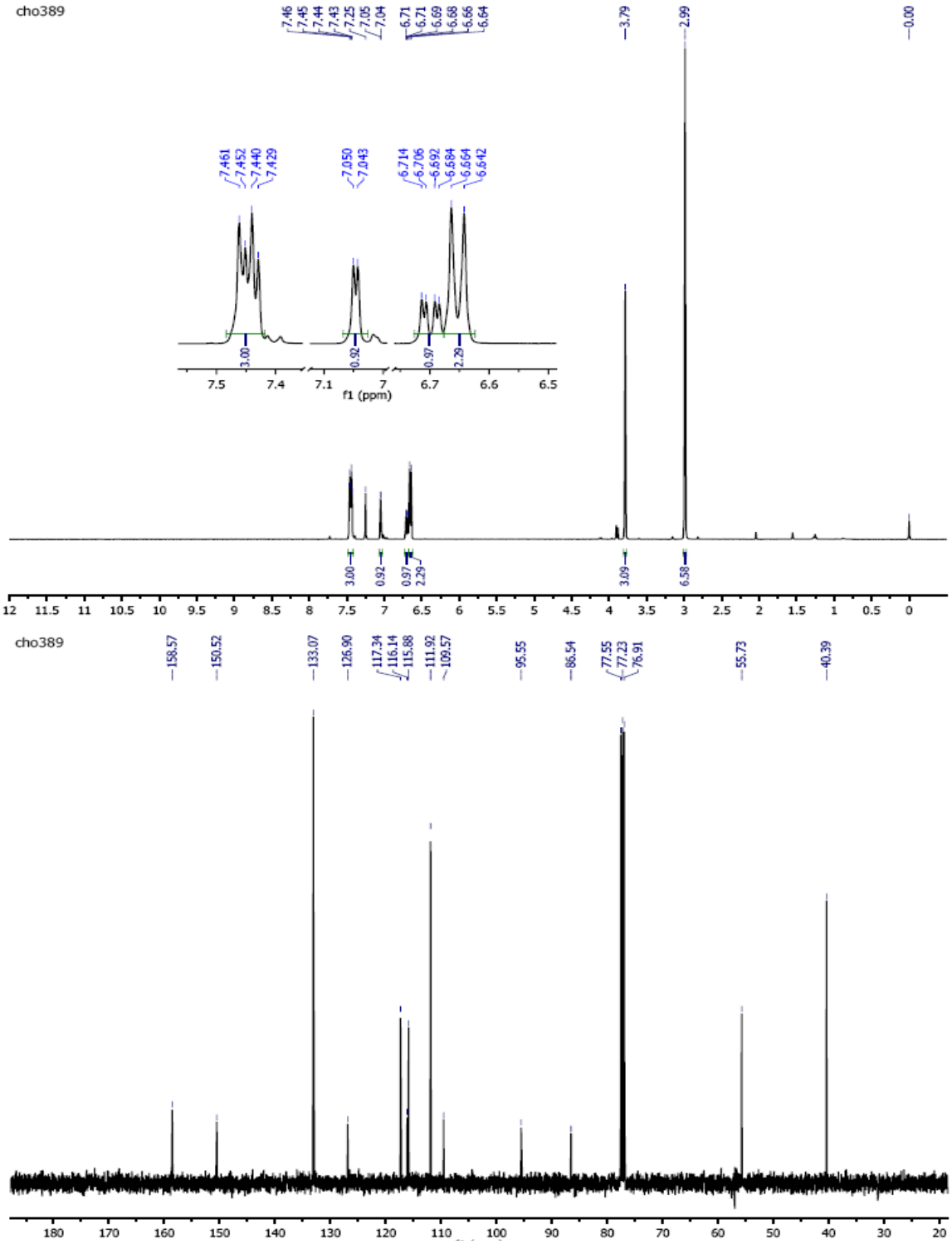

Br
MeO
OMe
OMe


cho234
7.471
7.449
7.072
6.729
6.484
6.479
6.473
3.801
3.789
0.000
1.00
1.00
0.89
1.13
6.33
2.98
f1 (ppm)

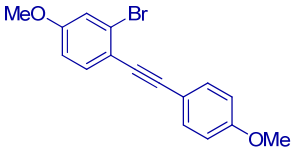

cho234
160.68
158.58
133.21
125.84
124.19
117.91
116.76
116.48
109.59
102.31
93.79
87.76
77.55
77.23
76.91
55.73
55.63
f1 (ppm)

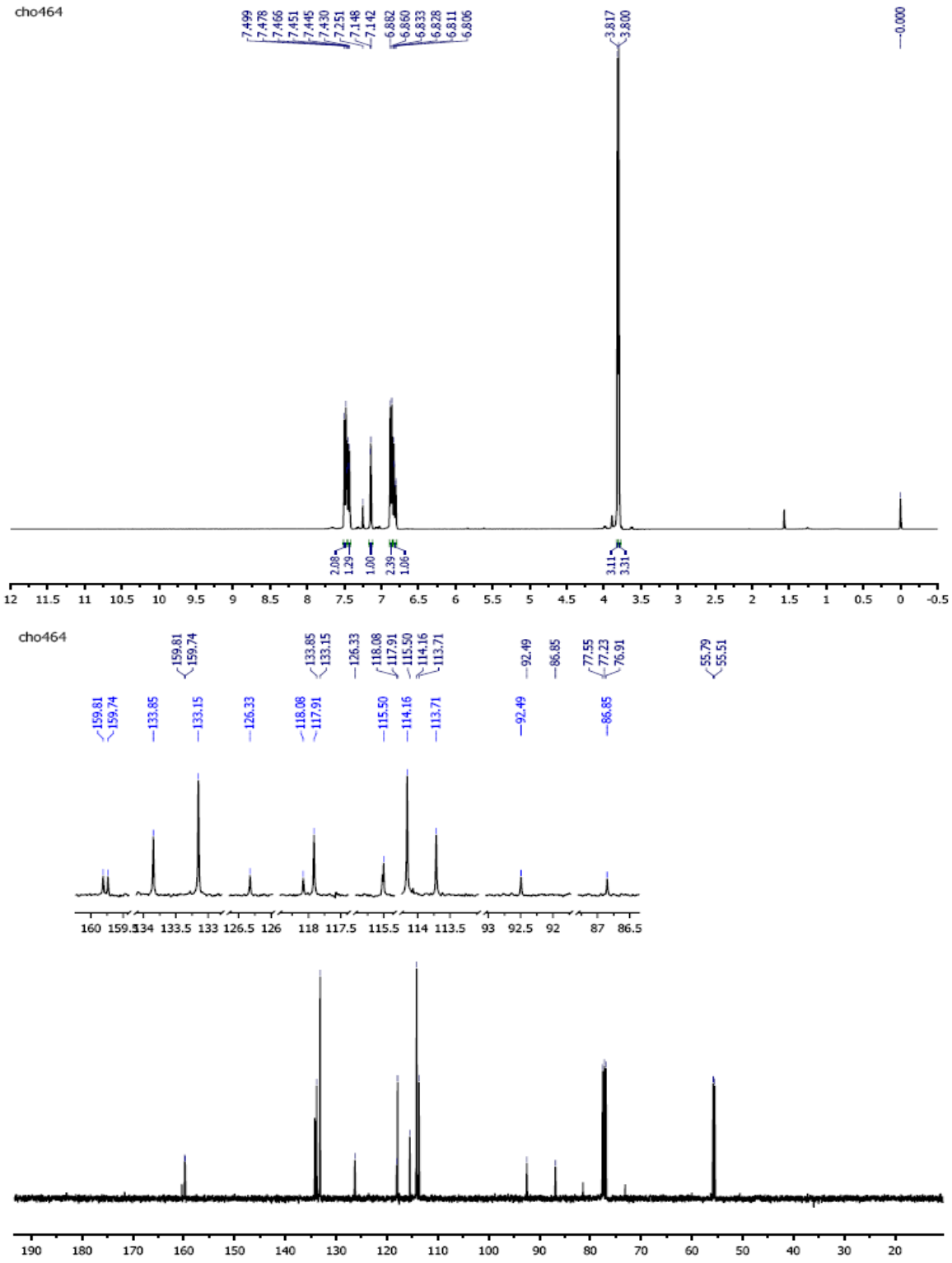
Compound **6**{*5*}


Br
MeO
N

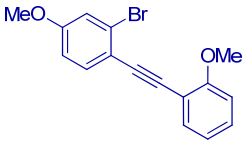

cho389
7.46
7.45
7.44
7.43
7.25
7.05
7.04
6.71
6.71
6.69
6.68
6.66
6.64
3.79
2.99
0.00
7.461
7.452
7.440
7.429
7.050
7.043
6.714
6.706
6.692
6.684
6.664
6.642
3.00
0.92
0.97
2.29
f1 (ppm)
3.09
6.58
cho389
158.57
150.52
133.07
126.90
117.34
116.14
115.88
111.92
109.57
95.55
86.54
77.55
77.23
76.91
55.73
40.39

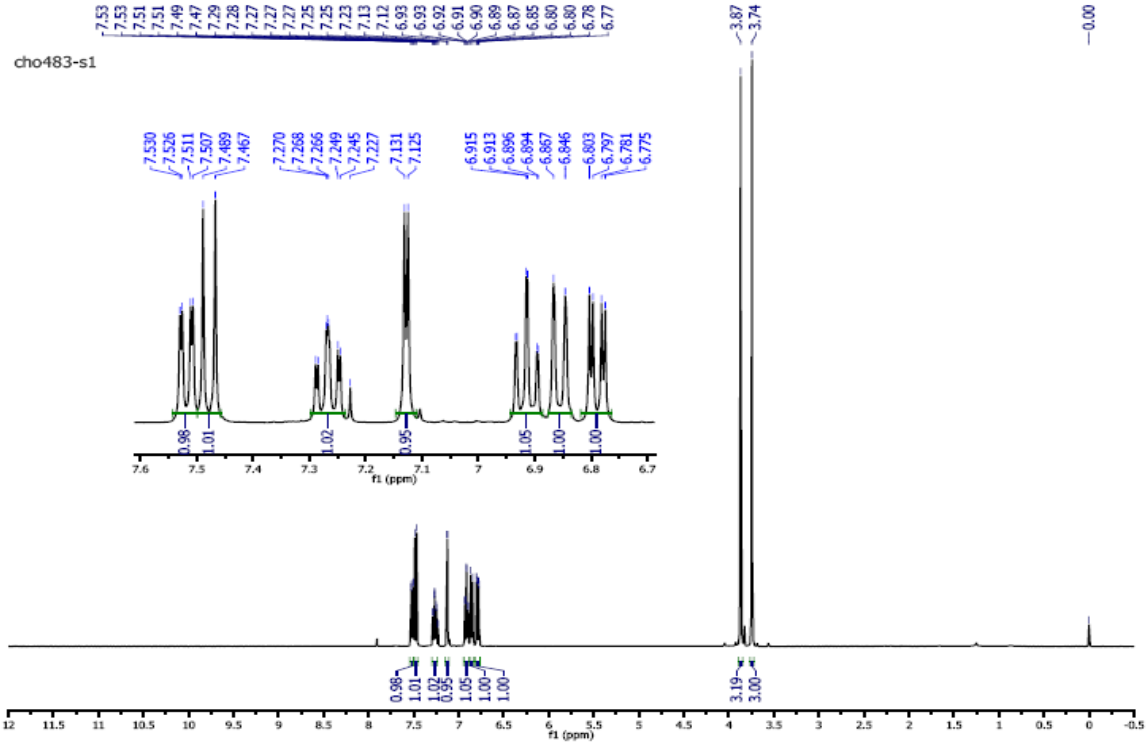
Compound **6**{*6*}

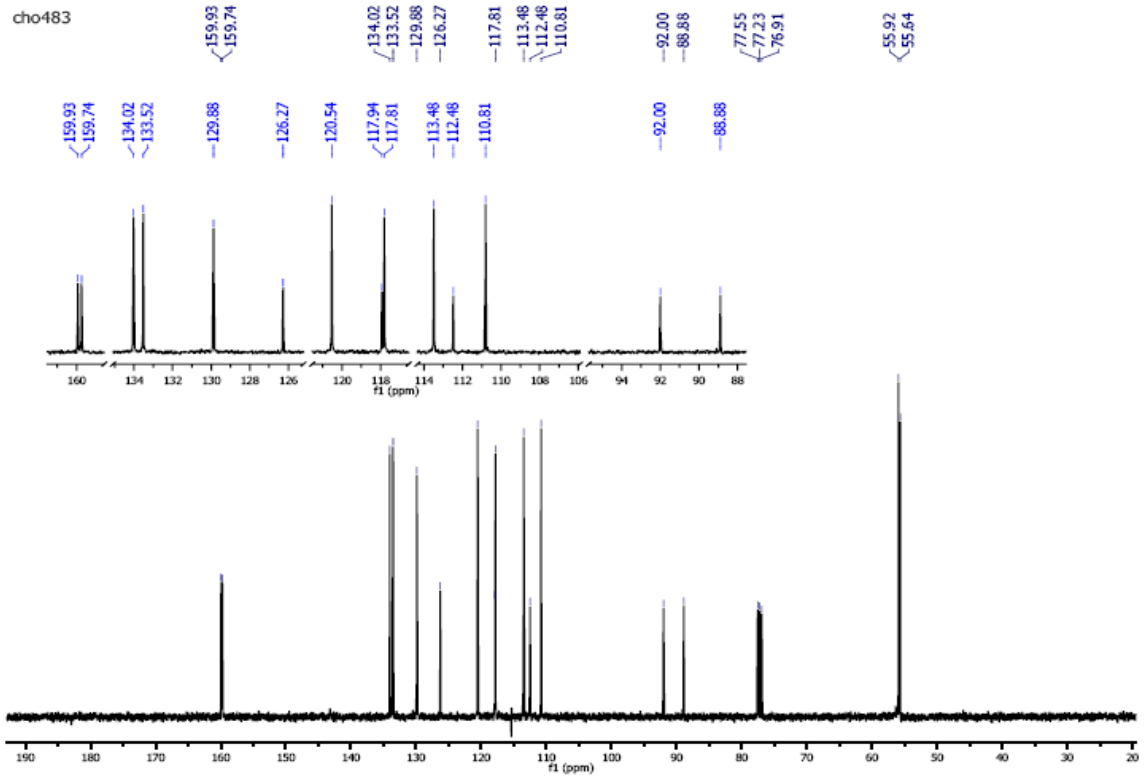

MeO
Br
OMe


cho464
7.499
7.478
7.466
7.451
7.445
7.430
7.251
7.148
7.142
6.882
6.860
6.833
6.828
6.811
6.806
3.817
3.800
0.000
2.08
1.29
1.00
2.39
1.06
3.11
3.31
cho464
159.81
159.74
133.85
133.15
126.33
118.08
117.91
115.50
114.16
113.71
92.49
86.85
77.55
77.23
76.91
55.79
55.51

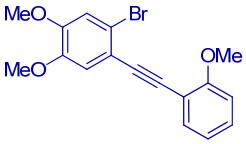
Compound **6**{*7*}

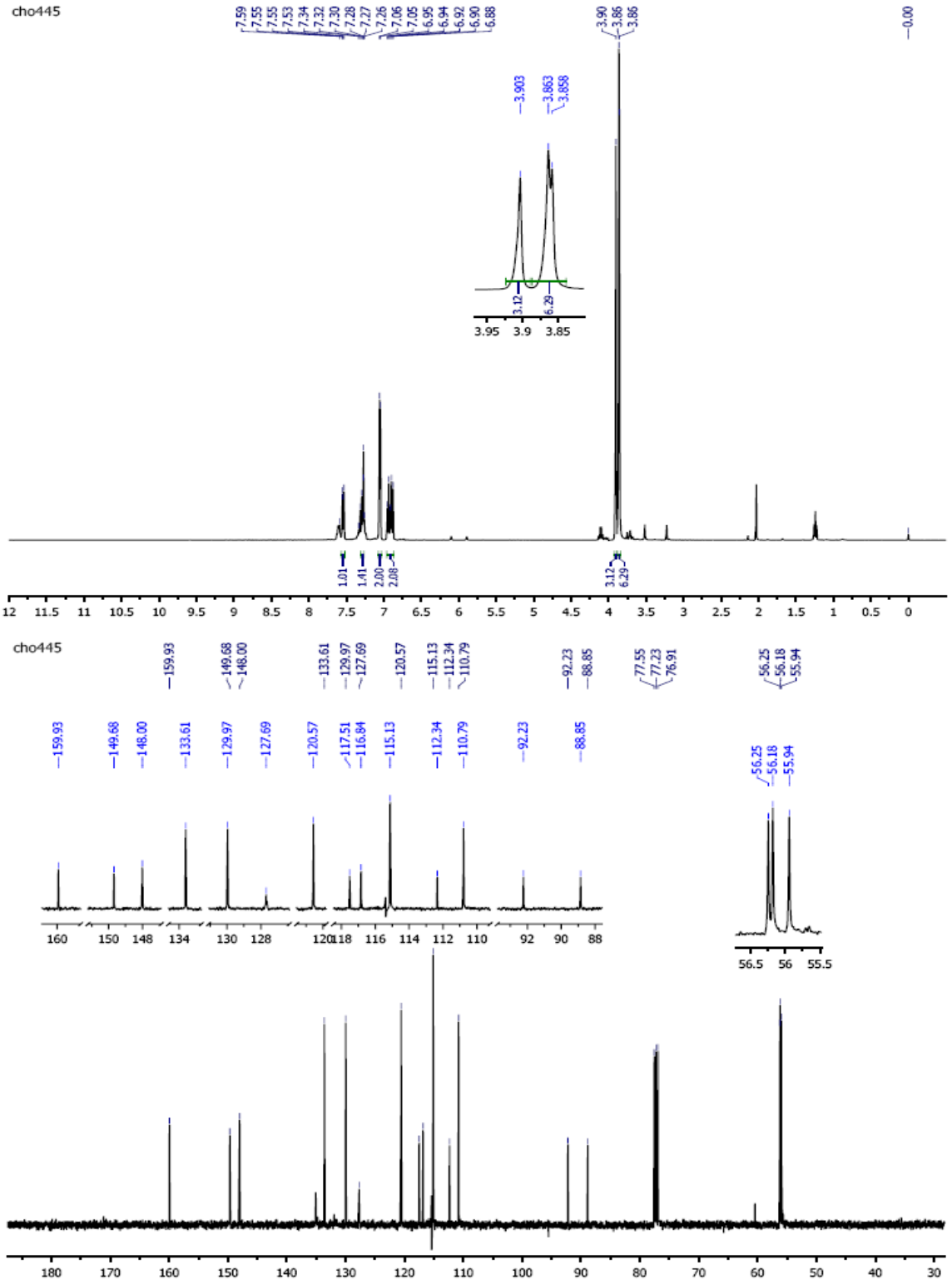




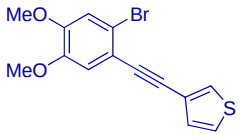


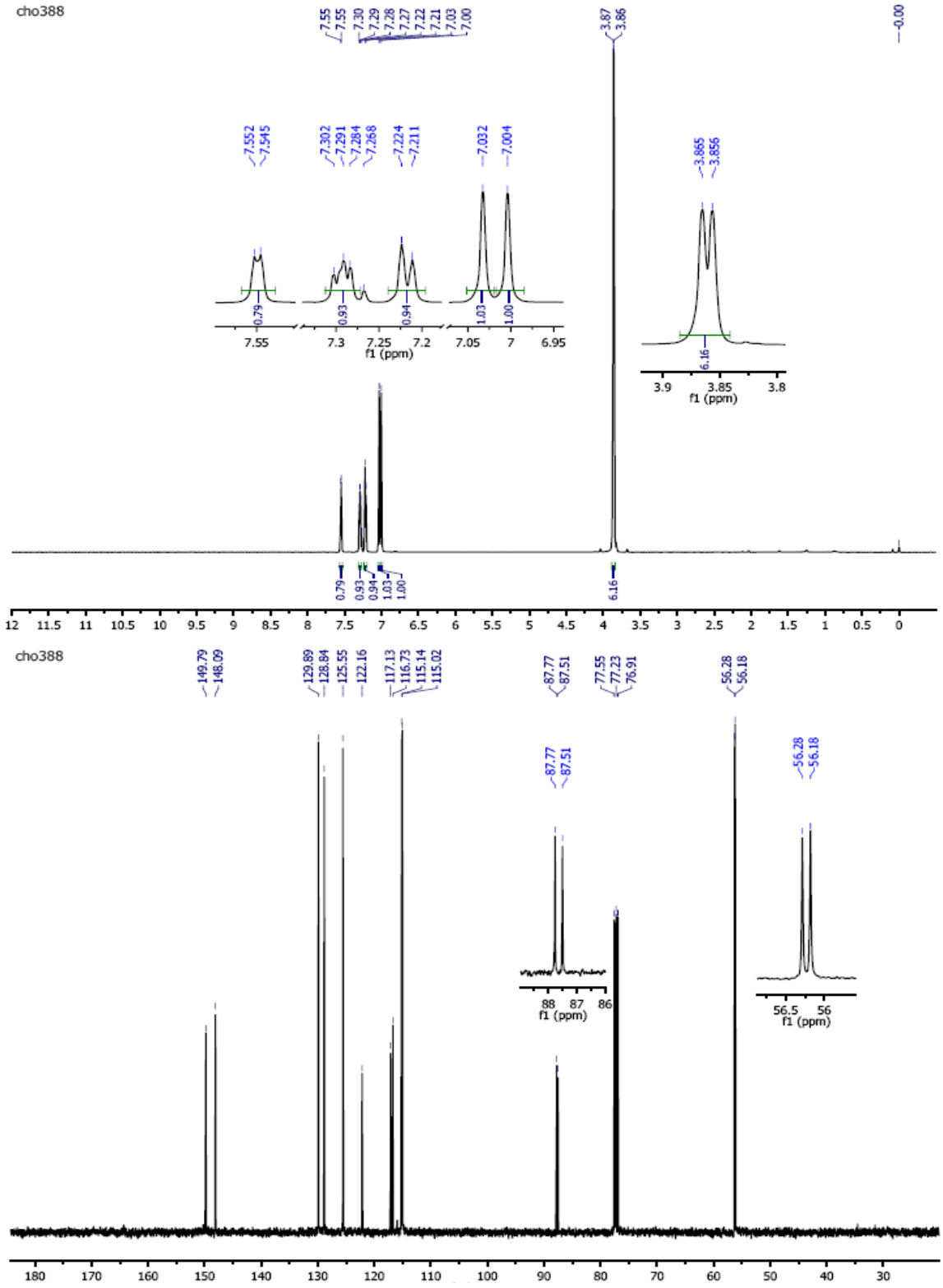
Compound **6**{*9*}


MeO
Br
MeO
OMe

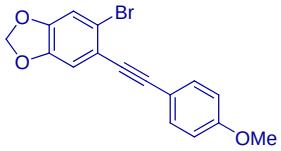

cho445
7.59
7.55
7.55
7.53
7.34
7.32
7.30
7.28
7.27
7.26
7.06
7.05
6.95
6.94
6.92
6.90
6.88
3.90
3.86
3.86
0.00
3.903
3.863
3.858
3.12
6.29
3.95
3.9
3.85
1.01
1.41
2.00
2.08
3.12
6.29
cho445
159.93
149.68
148.00
133.61
129.97
127.69
120.57
115.13
112.34
110.79
92.23
88.85
77.55
77.23
76.91
56.25
56.18
55.94
117.51
116.84
56.5
56
55.5

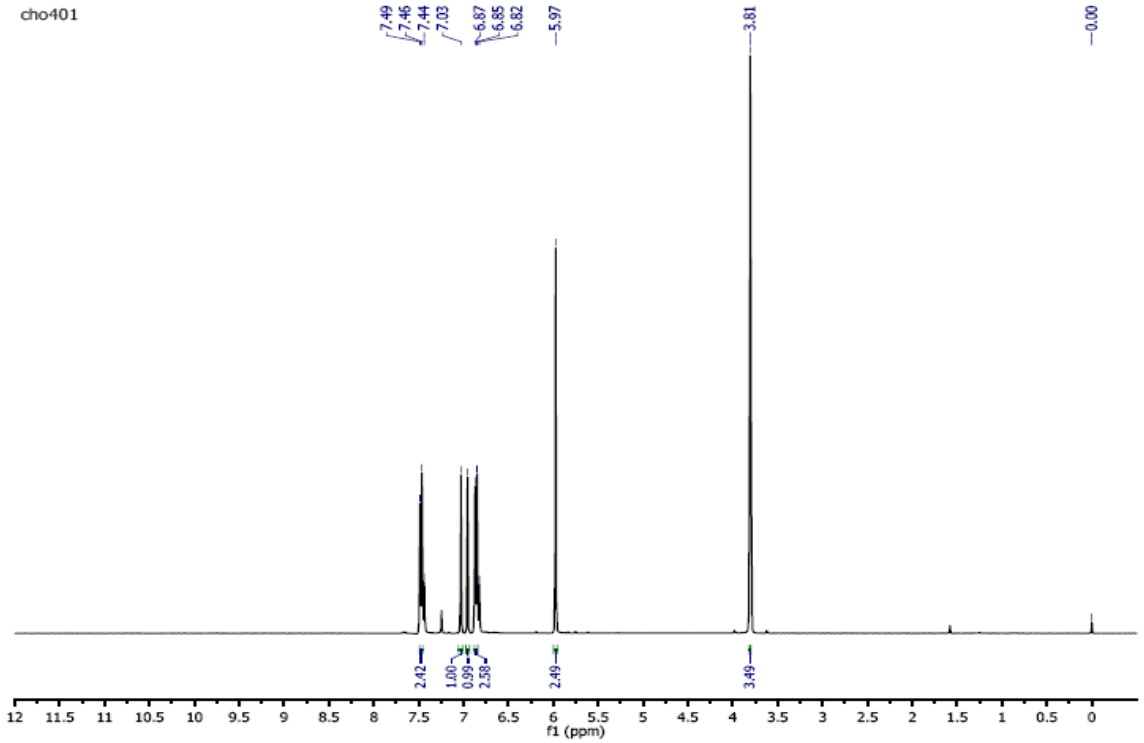
Compound **6**{*10*}

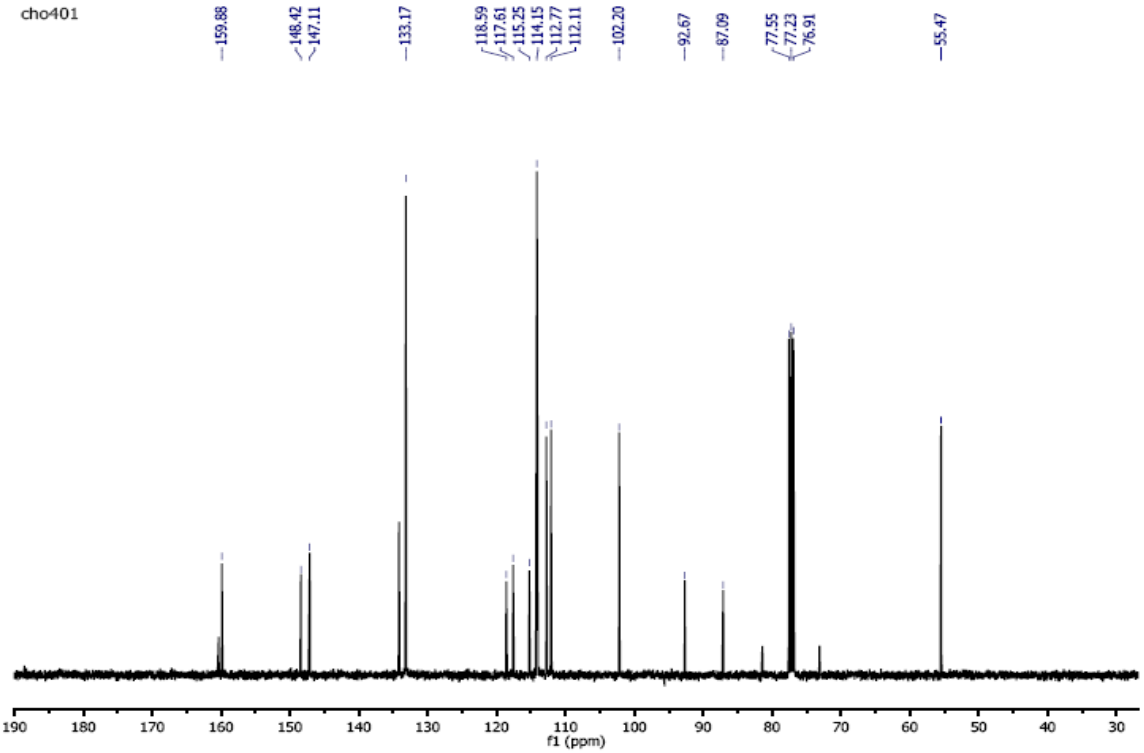




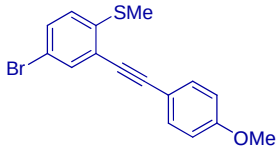
Compound **6**{*11*}

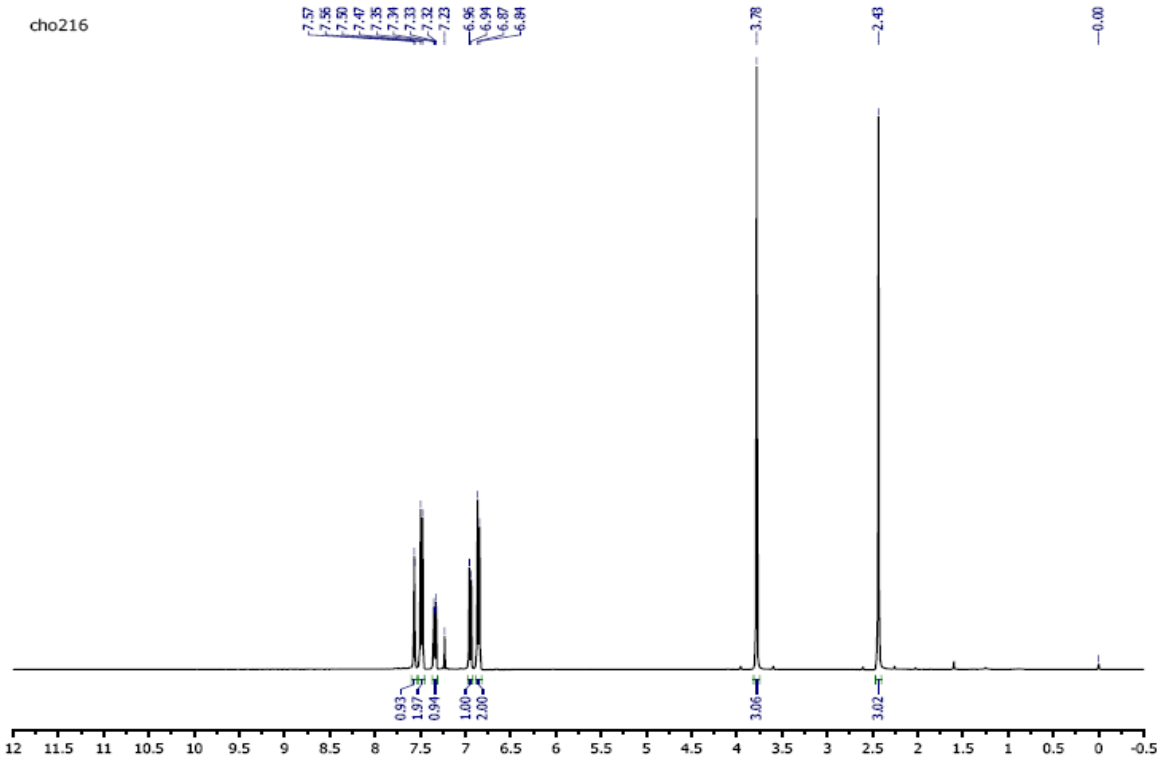


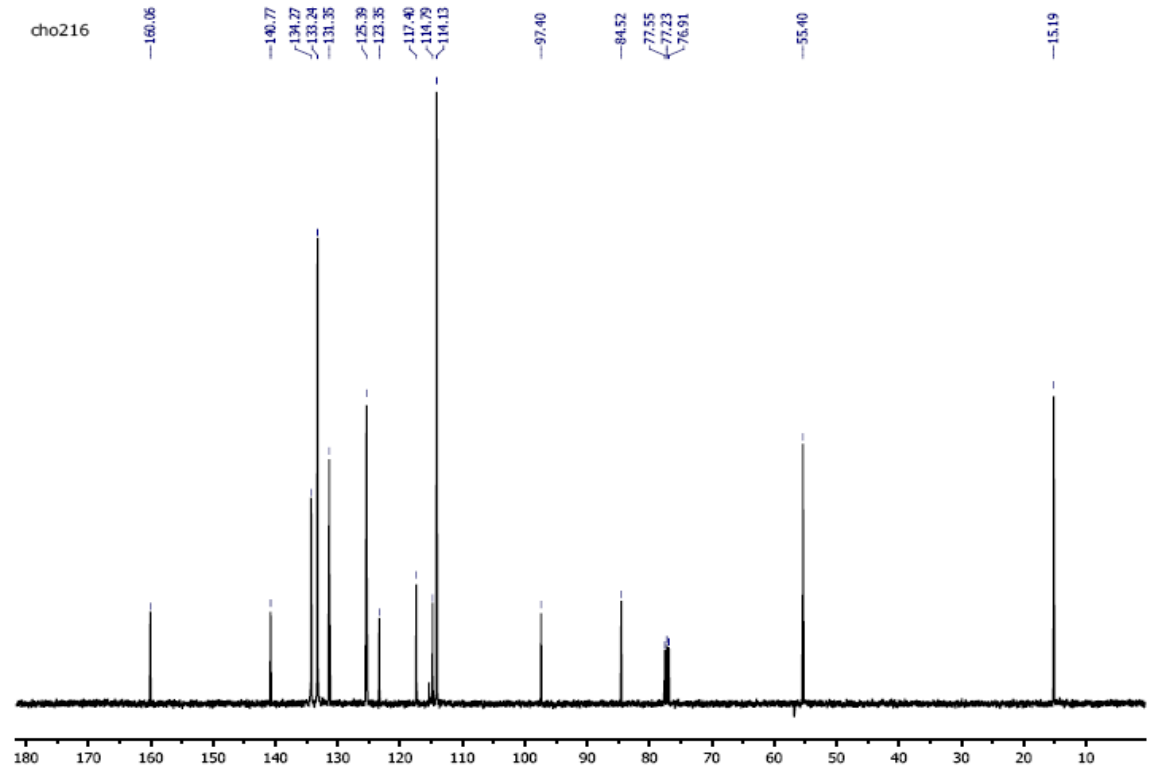




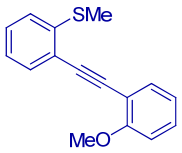
Compound **6**{*13*}

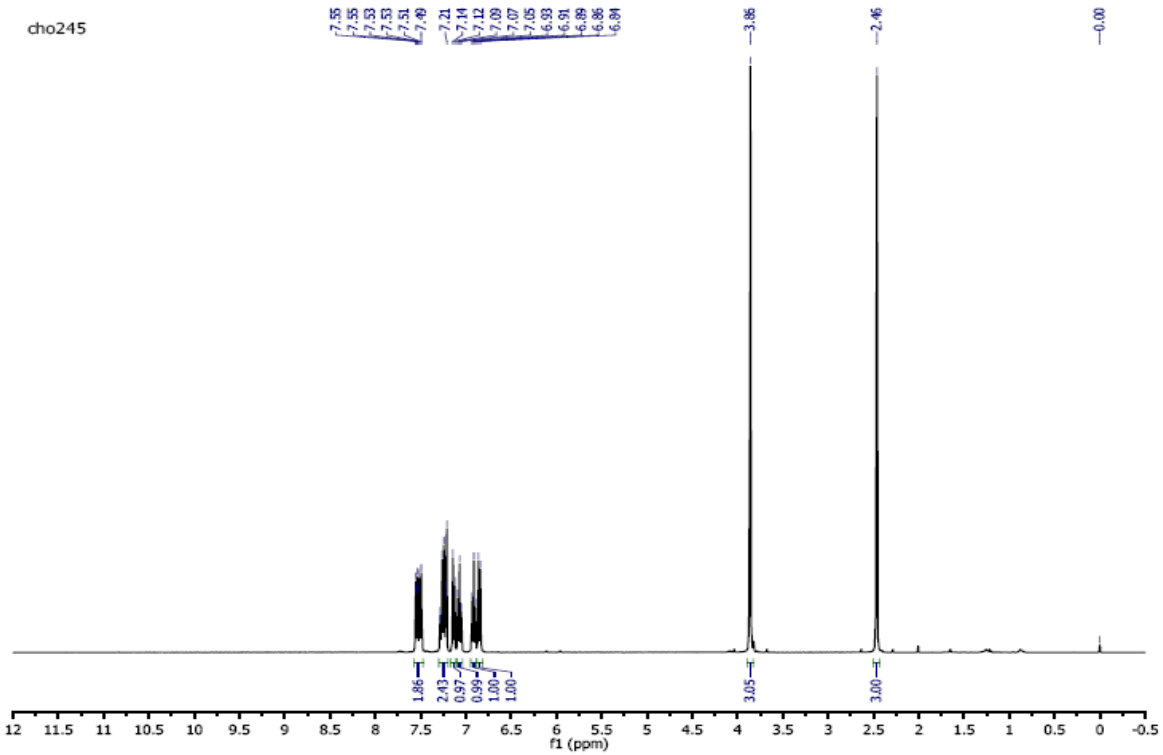


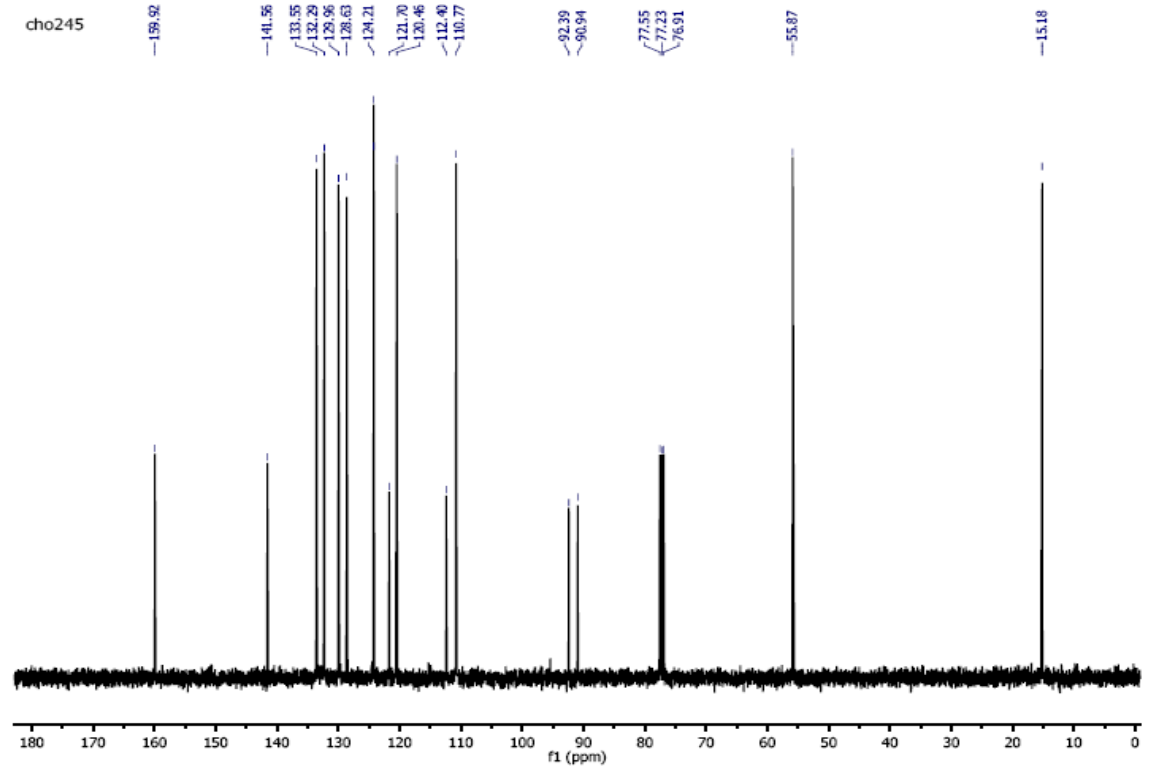




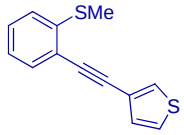
Compound **6**{*16*}

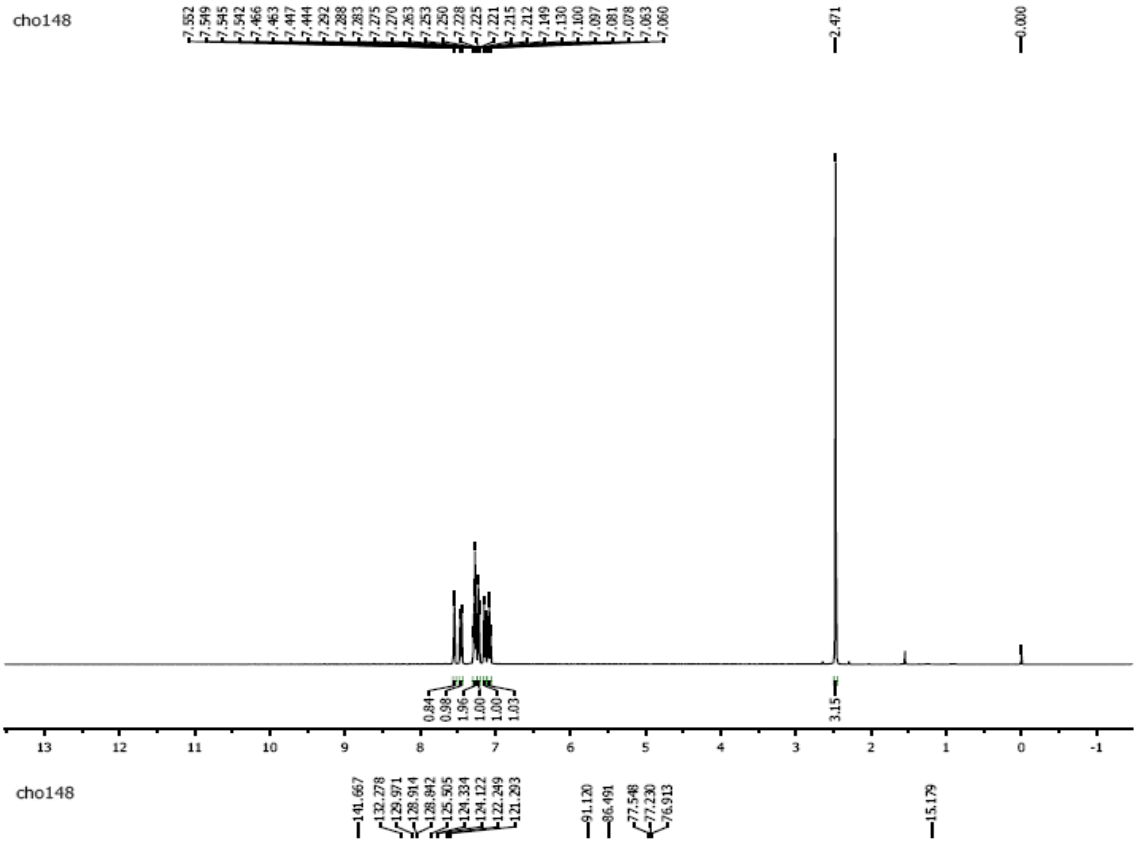


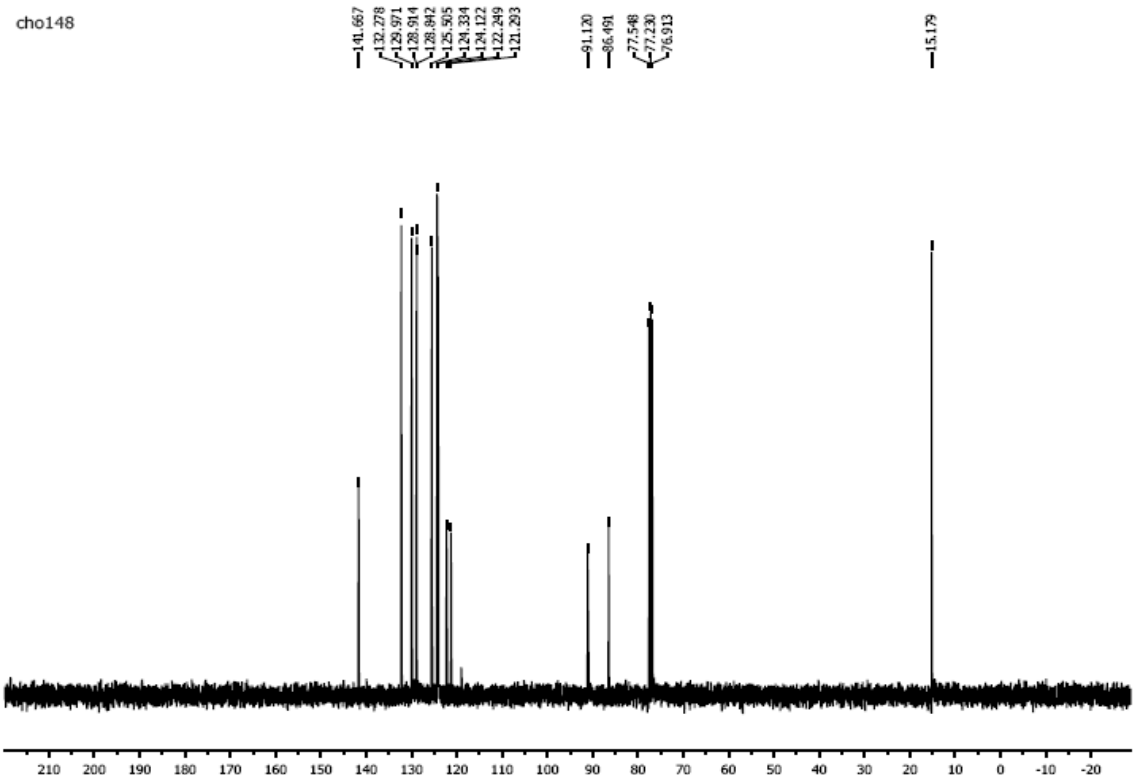




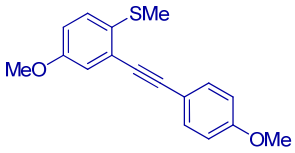
Compound **6**{*17*}

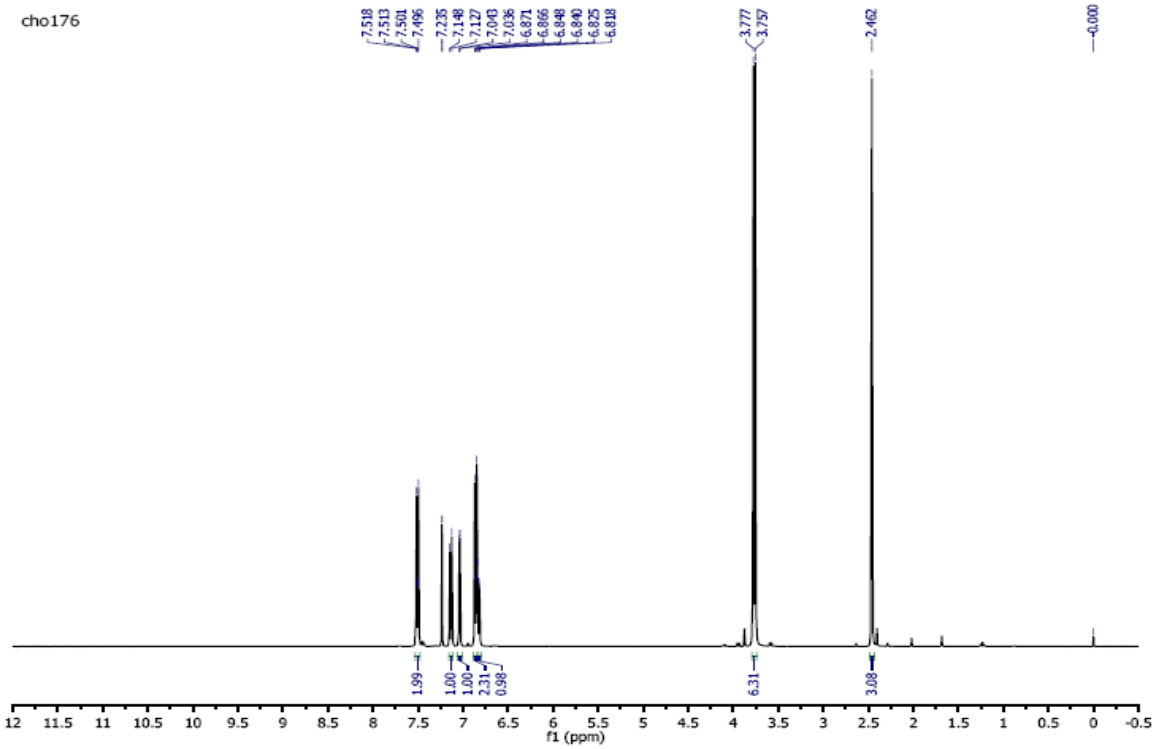


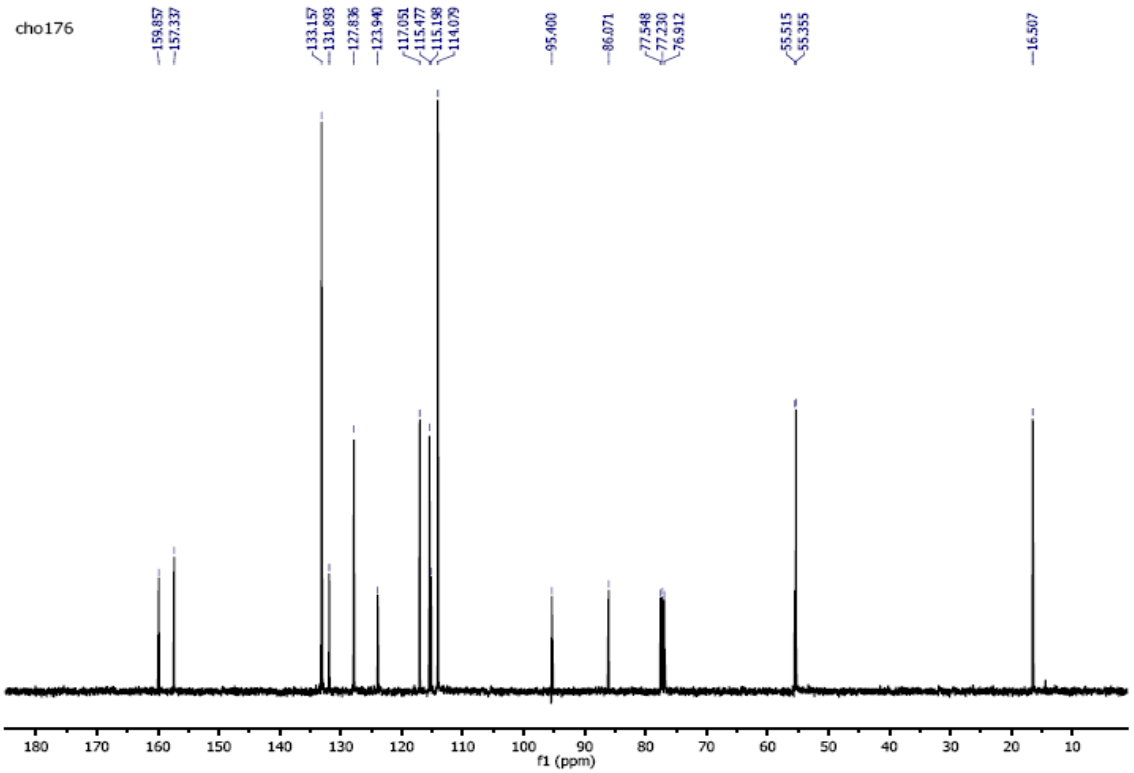




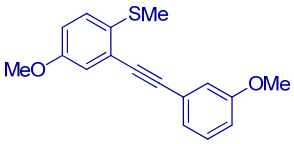
Compound **7**{*1*}

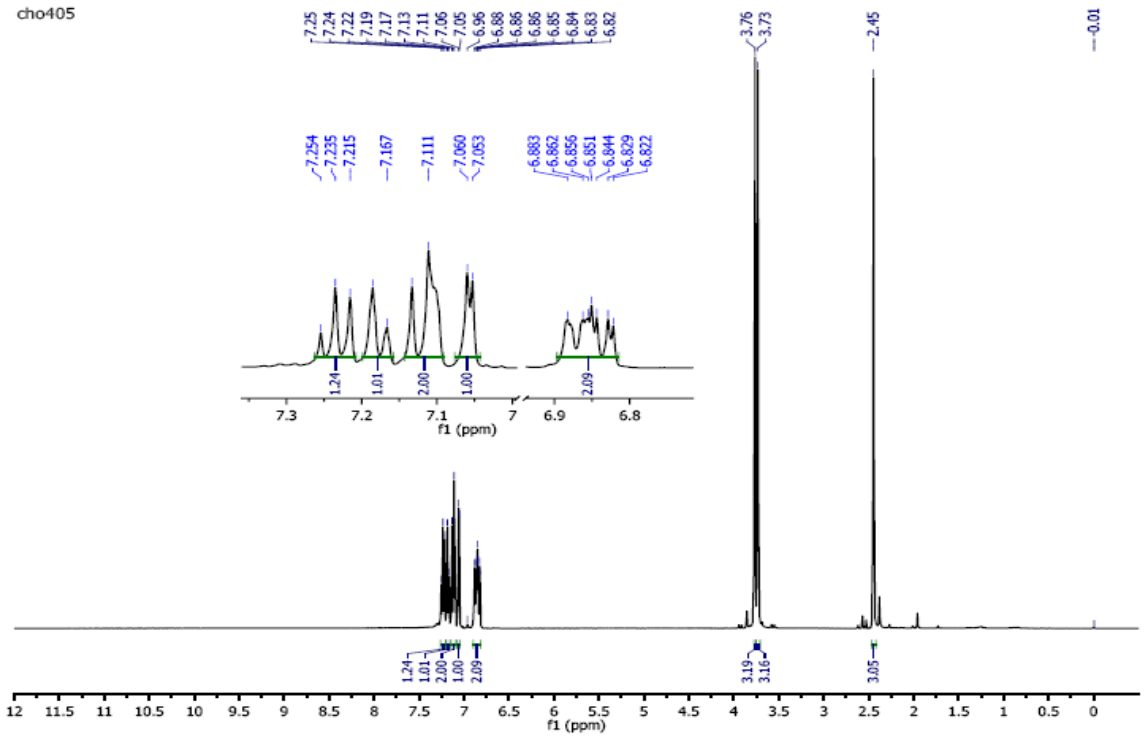

SMe
MeO
OMe

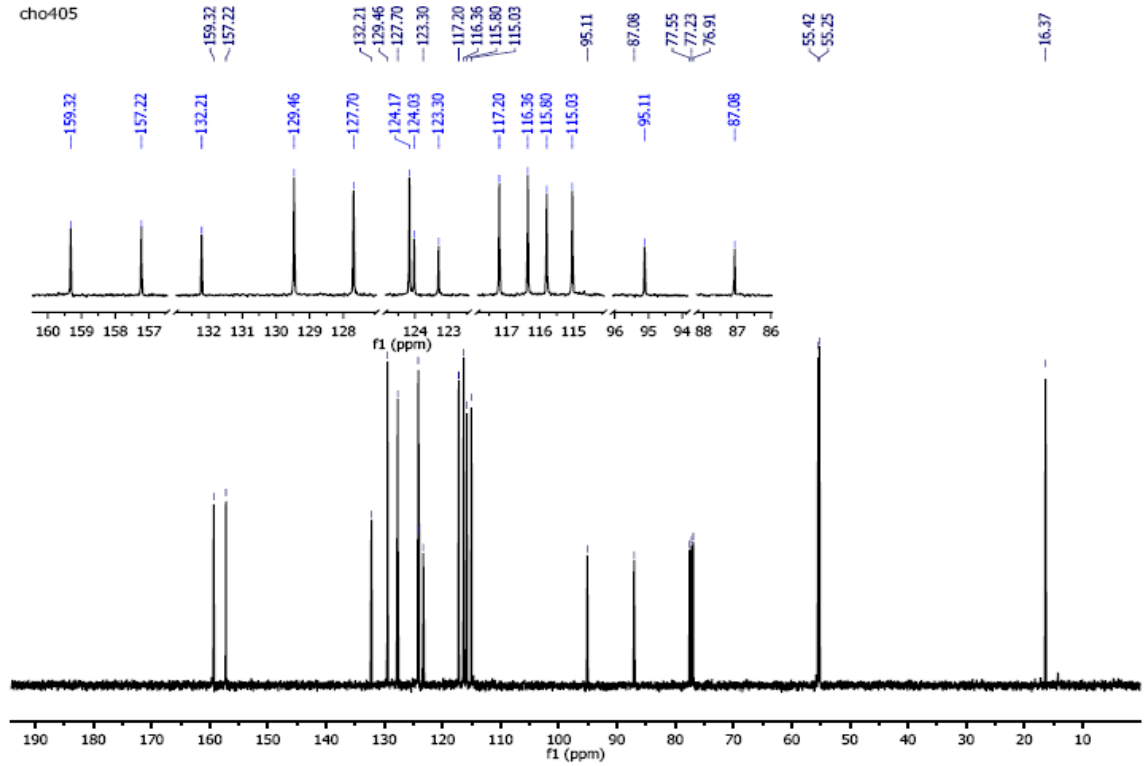

cho176
7.518
7.513
7.501
7.496
7.235
7.148
7.127
7.043
7.036
6.871
6.866
6.848
6.840
6.825
6.818
3.777
3.757
2.462
0.000
1.99
1.00
1.00
2.31
0.98
6.31
3.08
f1 (ppm)


cho176
159.857
157.337
133.157
131.893
127.836
123.940
117.051
115.477
115.198
114.079
95.400
86.071
77.548
77.230
76.912
55.515
55.355
16.507
f1 (ppm)

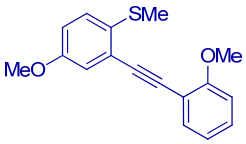
Compound **7**{*2*}

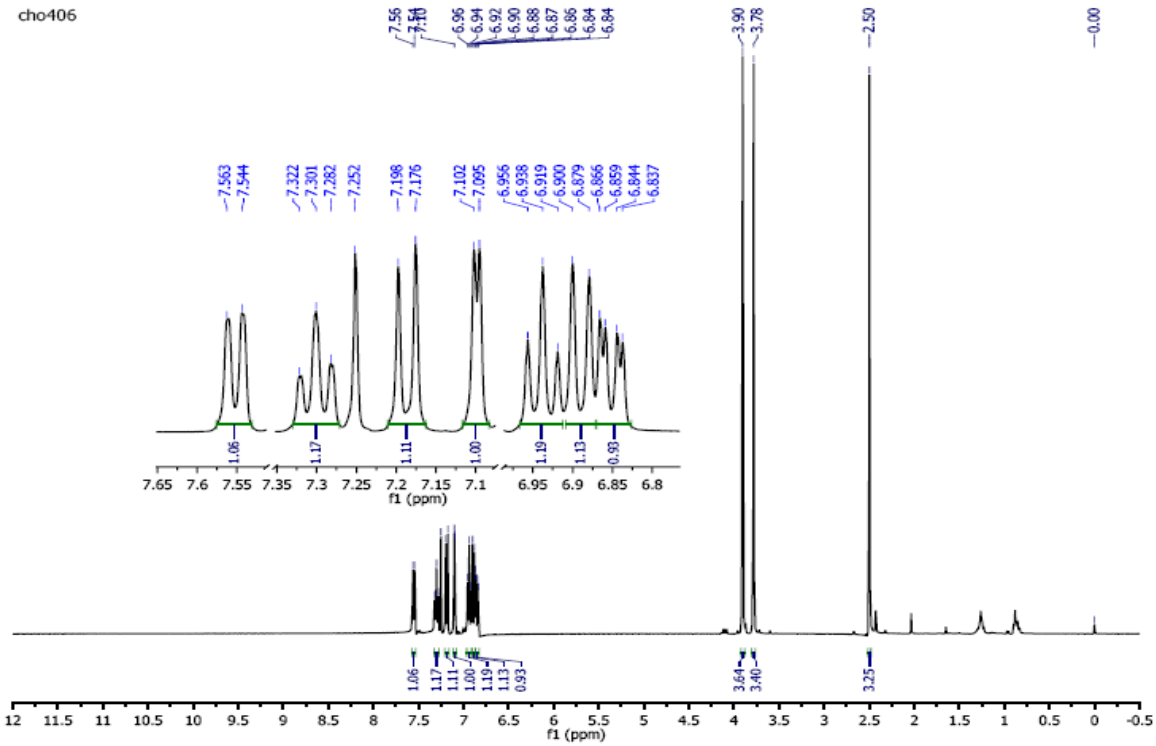

SMe
MeO
OMe

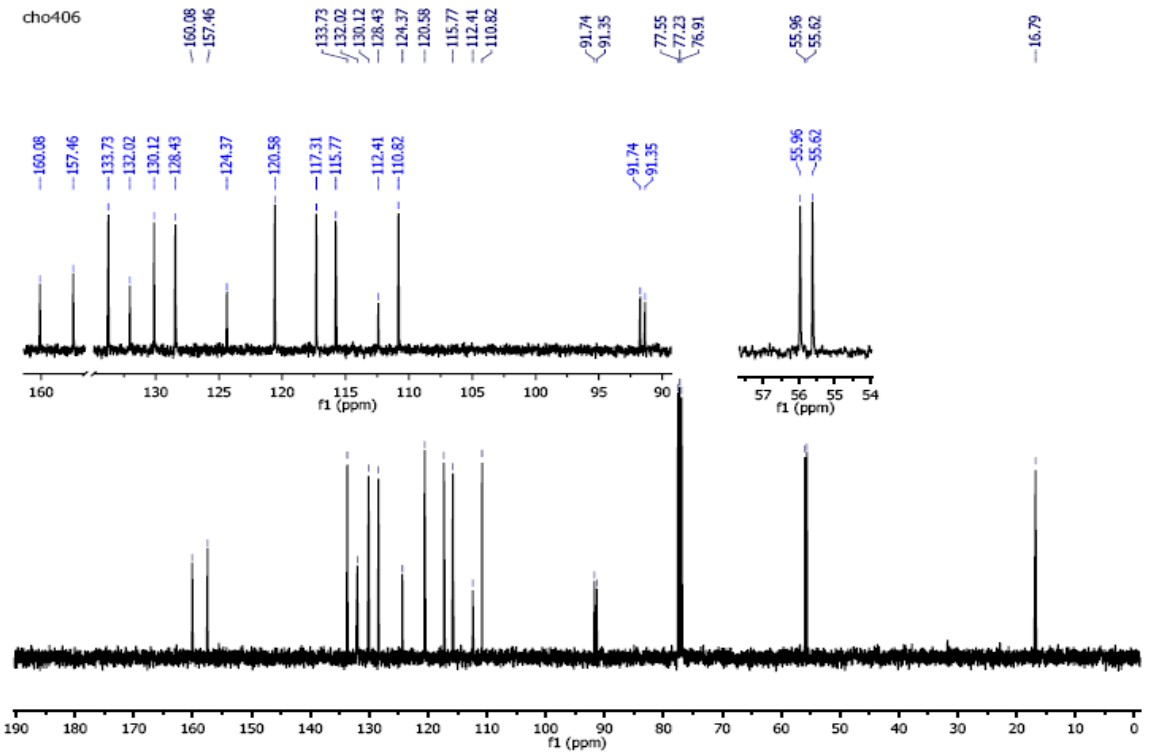

cho405
7.25
7.24
7.22
7.19
7.17
7.13
7.11
7.06
7.05
6.96
6.88
6.86
6.86
6.85
6.84
6.83
6.82
3.76
3.73
2.45
0.01
7.254
7.235
7.215
7.167
7.111
7.060
7.053
6.883
6.862
6.856
6.851
6.844
6.829
6.822
1.24
1.01
2.00
1.00
2.09
f1 (ppm)
3.19
3.16
3.05


cho405
159.32
157.22
132.21
129.46
127.70
123.30
117.20
116.36
115.80
115.03
95.11
87.08
77.55
77.23
76.91
55.42
55.25
16.37
f1 (ppm)

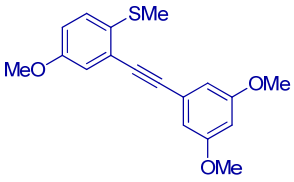
Compound **7**{*3*}

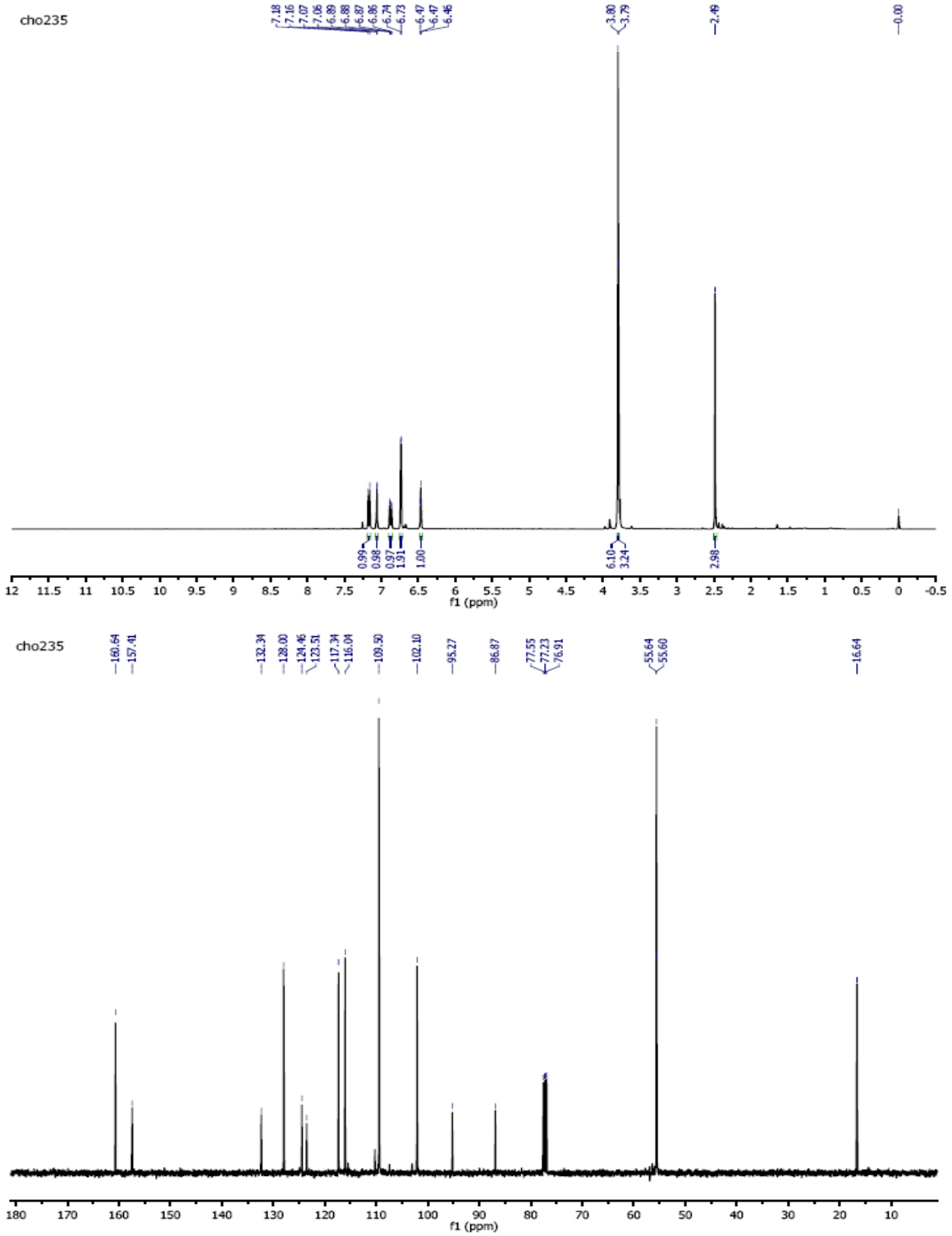

SMe
MeO
OMe


cho406
7.563
7.544
7.322
7.301
7.282
7.252
7.198
7.176
7.102
7.095
6.956
6.938
6.919
6.900
6.879
6.866
6.859
6.844
6.837
6.96
6.94
6.92
6.90
6.88
6.87
6.86
6.84
6.84
3.90
3.78
2.50
0.00
1.06
1.17
1.11
1.00
1.19
1.13
0.93
3.64
3.40
3.25
f1 (ppm)

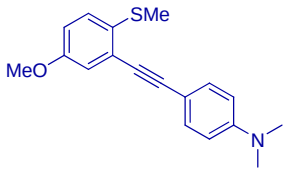

cho406
160.08
157.46
133.73
132.02
130.12
128.43
124.37
120.58
117.31
115.77
112.41
110.82
91.74
91.35
77.55
77.23
76.91
55.96
55.62
16.79
f1 (ppm)

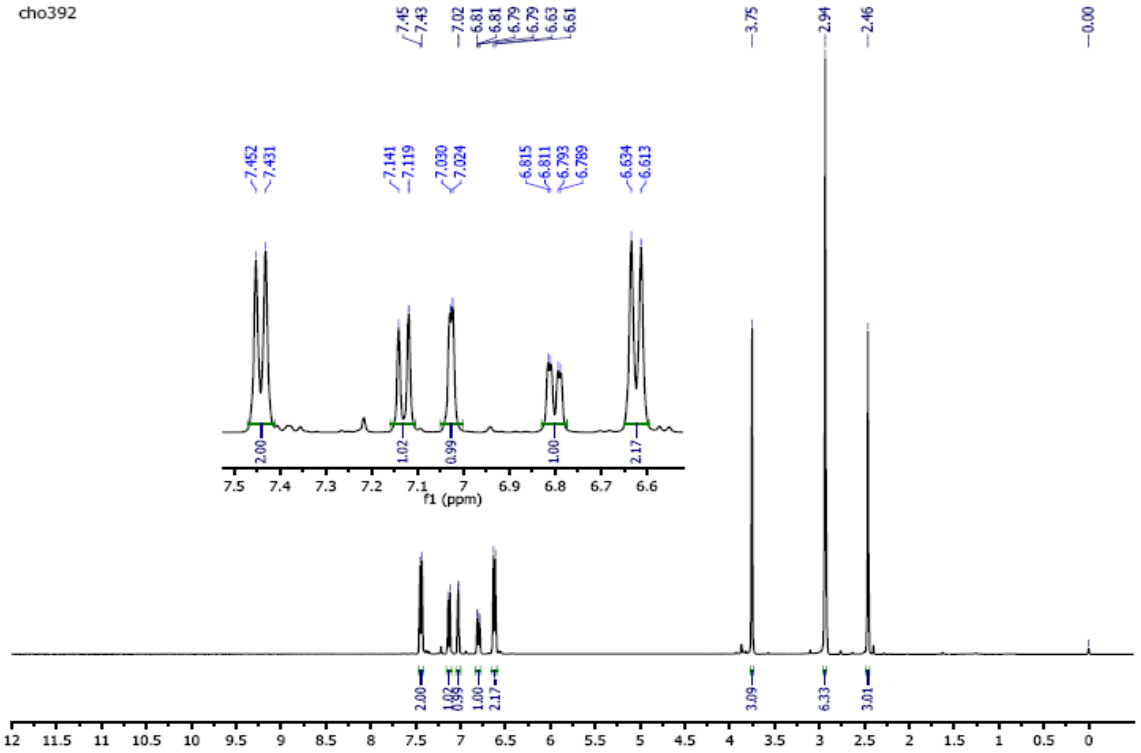
Compound **7**{*4*}

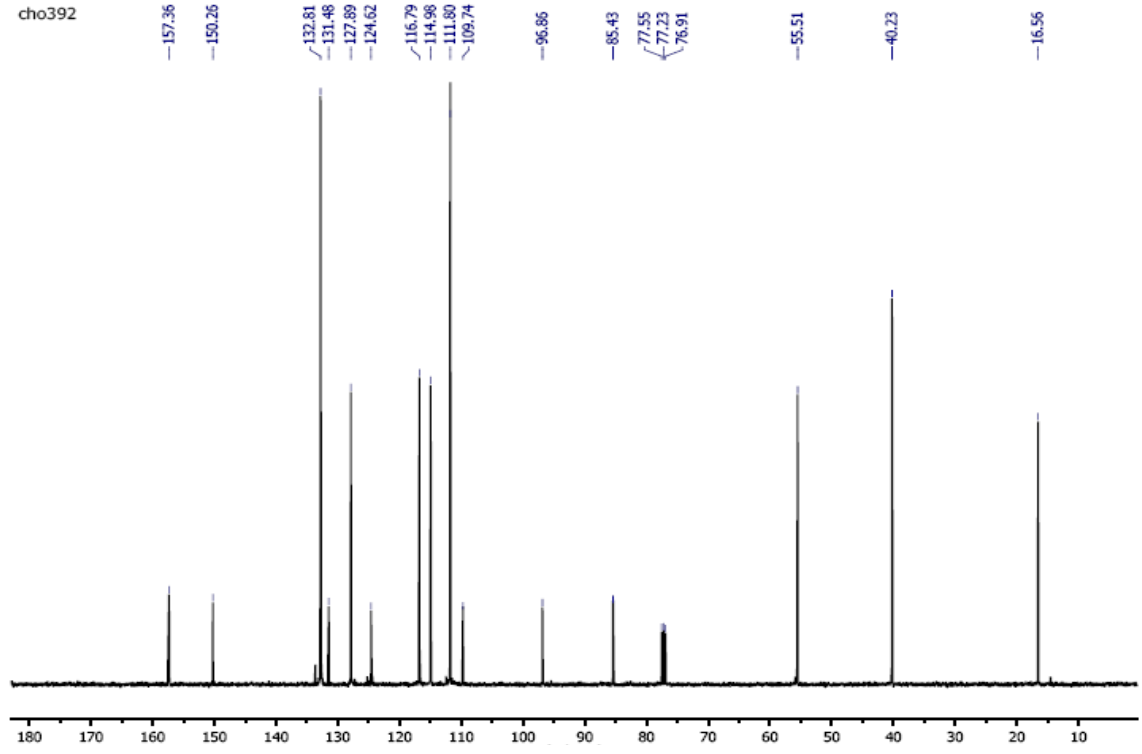

SMe
MeO
OMe
OMe


cho235
7.18
7.16
7.07
7.06
6.89
6.88
6.87
6.86
6.74
6.73
6.47
6.47
6.46
3.80
3.79
2.49
0.00
0.99
0.98
0.97
1.91
1.00
6.10
3.24
2.98
f1 (ppm)
cho235
160.64
157.41
132.34
128.00
124.46
123.51
117.34
116.04
109.30
102.10
95.27
86.87
77.55
77.23
76.91
55.64
55.60
16.64
f1 (ppm)

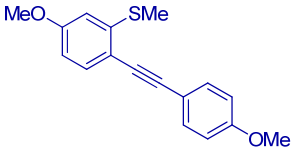
Compound **7**{*5*}

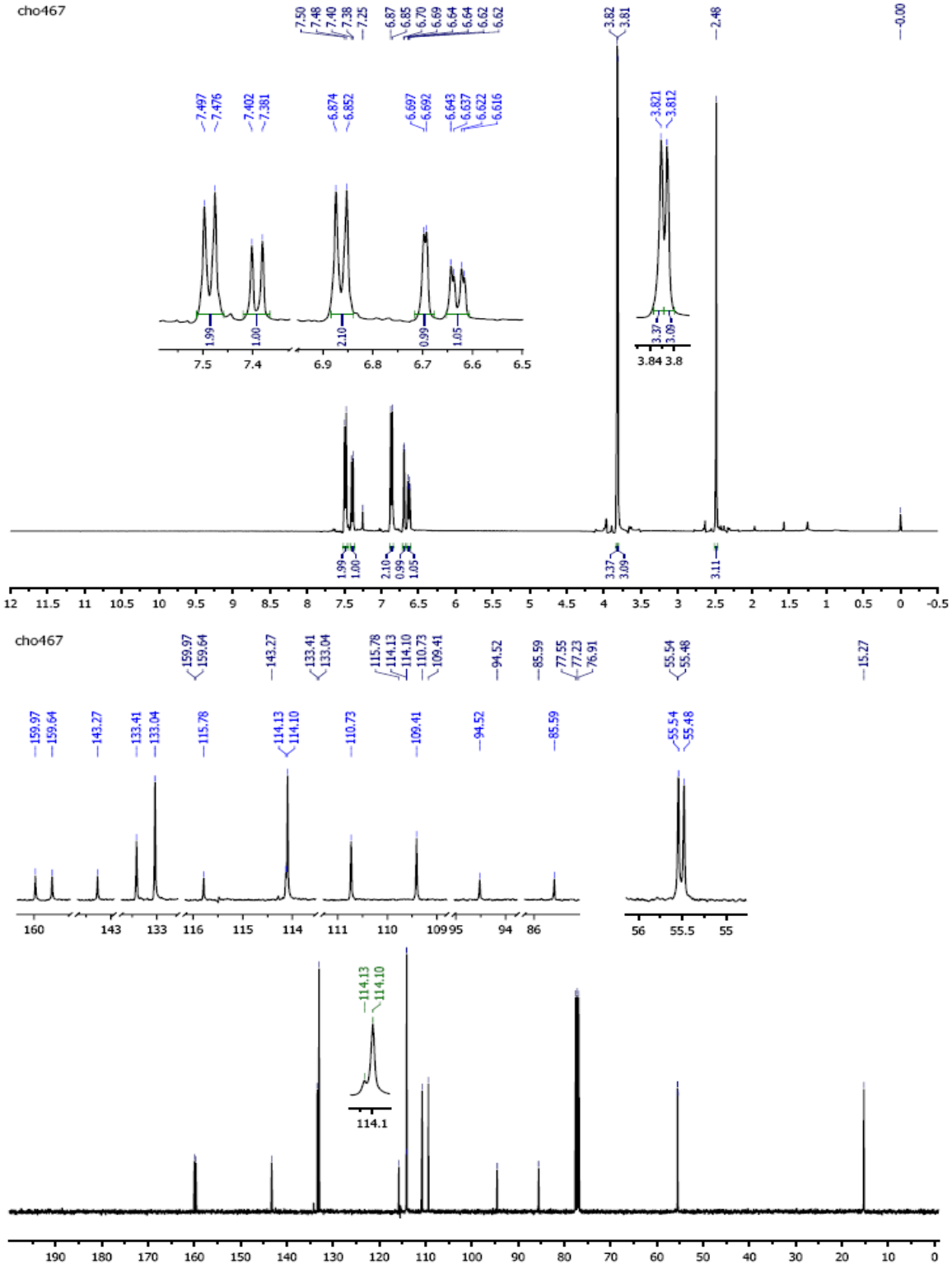

SMe
MeO
N


cho392
7.45
7.43
7.02
6.81
6.81
6.79
6.79
6.63
6.61
3.75
2.94
2.46
0.00
7.452
7.431
7.141
7.119
7.030
7.024
6.815
6.811
6.793
6.789
6.634
6.613
2.00
1.02
0.99
1.00
2.17
f1 (ppm)
3.09
6.33
3.01

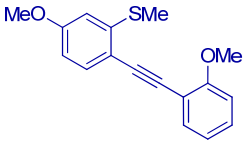

cho392
157.36
150.26
132.81
131.48
127.89
124.62
116.79
114.98
111.80
109.74
96.86
85.43
77.55
77.23
76.91
55.51
40.23
16.56

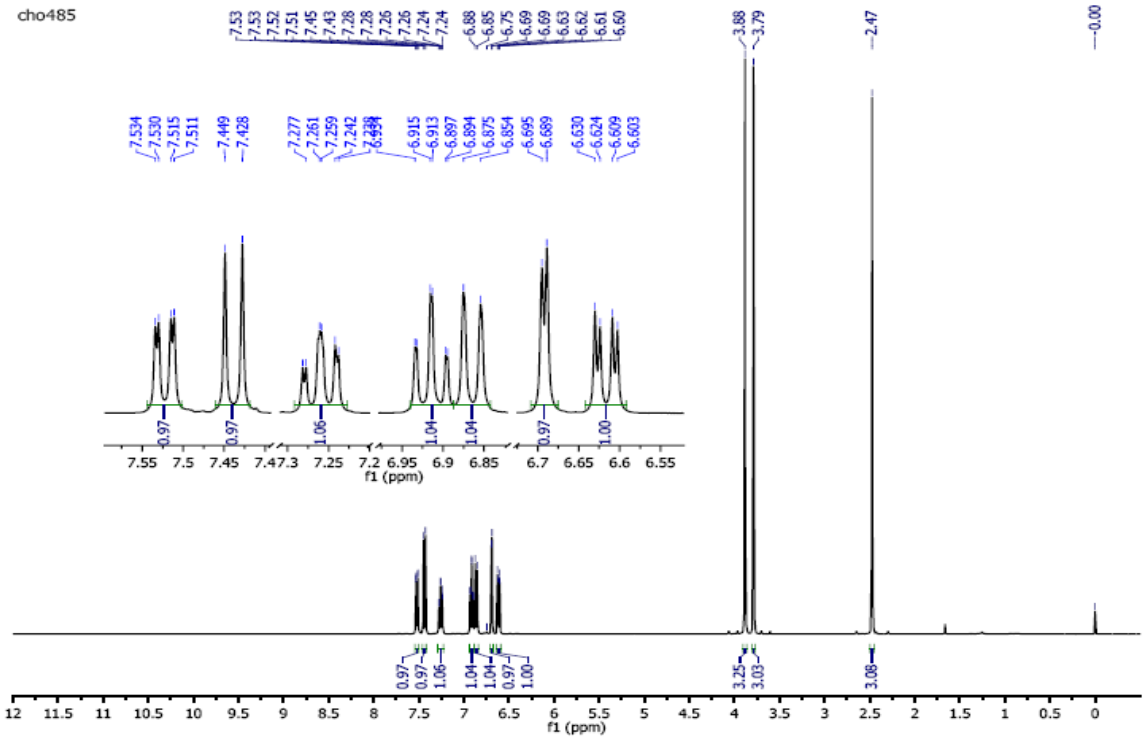
Compound **7**{*6*}

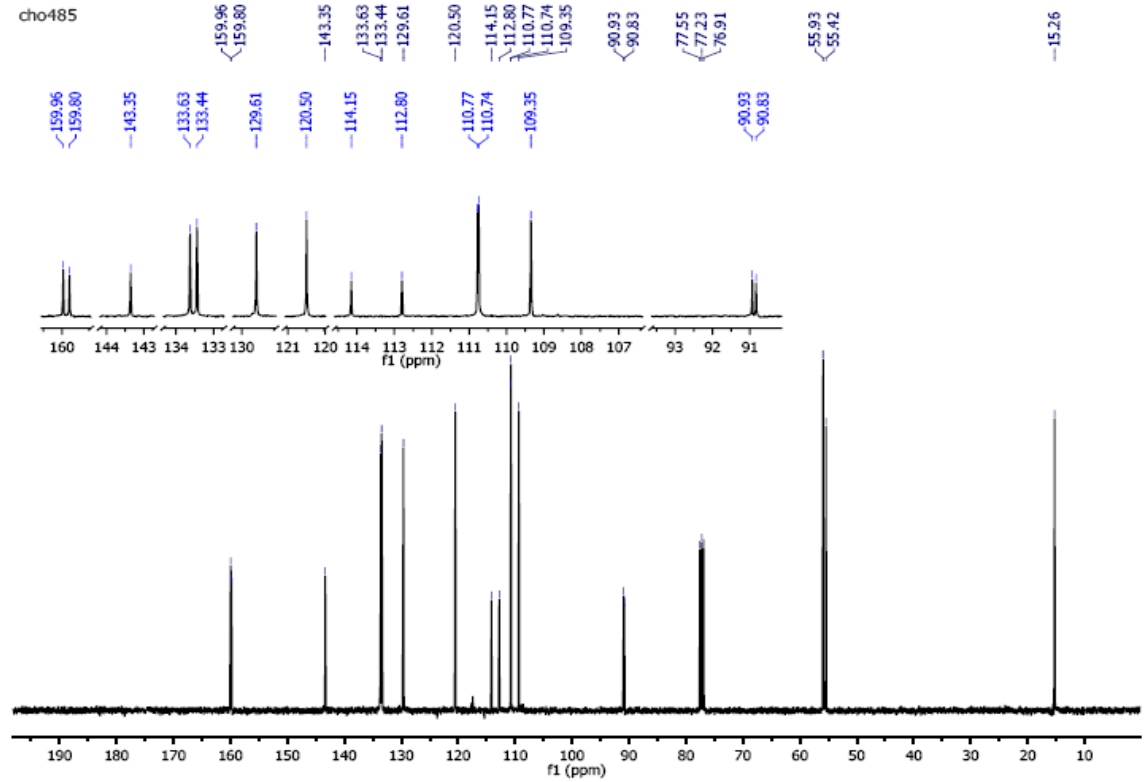

MeO
SMe
OMe


cho467
7.50
7.48
7.40
7.38
7.25
6.87
6.85
6.70
6.69
6.64
6.64
6.62
6.62
3.82
3.81
2.48
0.00
7.497
7.476
7.402
7.381
6.874
6.852
6.697
6.692
6.643
6.637
6.622
6.616
3.821
3.812
1.99
1.00
2.10
0.99
1.05
3.37
3.09
3.84 3.8
3.11
cho467
159.97
159.64
143.27
133.41
133.04
115.78
114.13
114.10
110.73
109.41
94.52
85.59
77.55
77.23
76.91
55.54
55.48
15.27
114.13
114.10
114.1

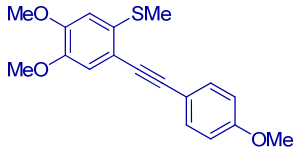
Compound **7**{*7*}

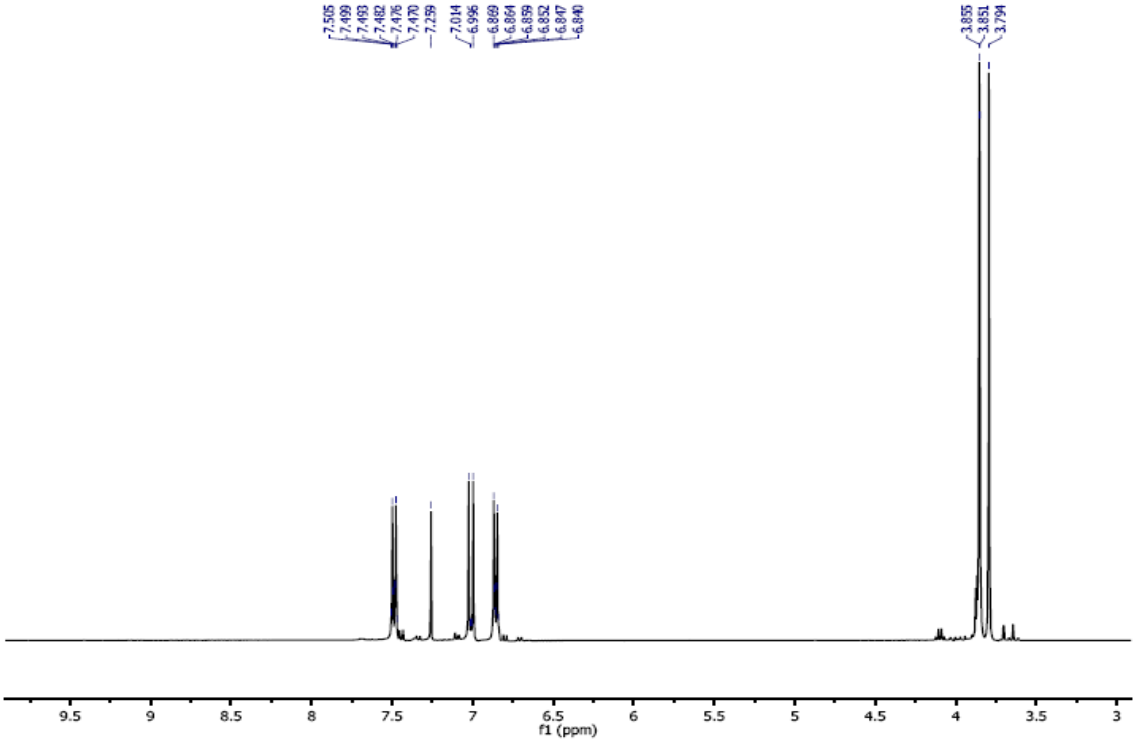


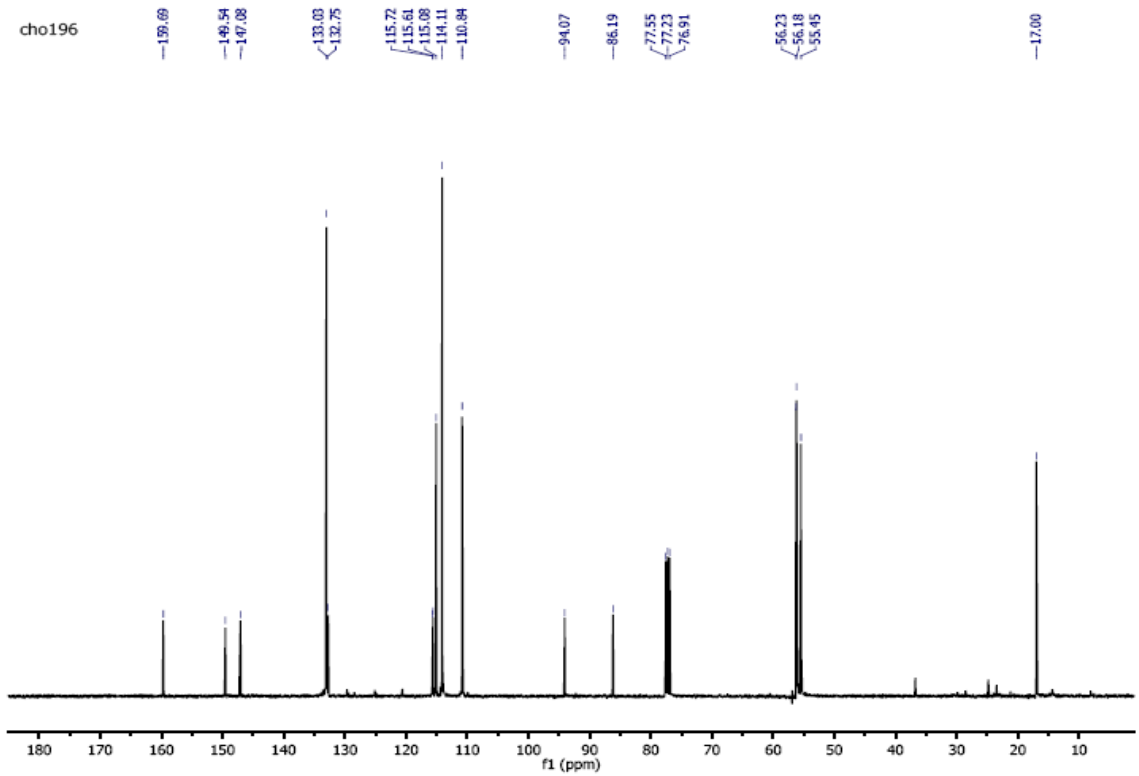




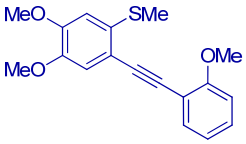
Compound **7**{*8*}

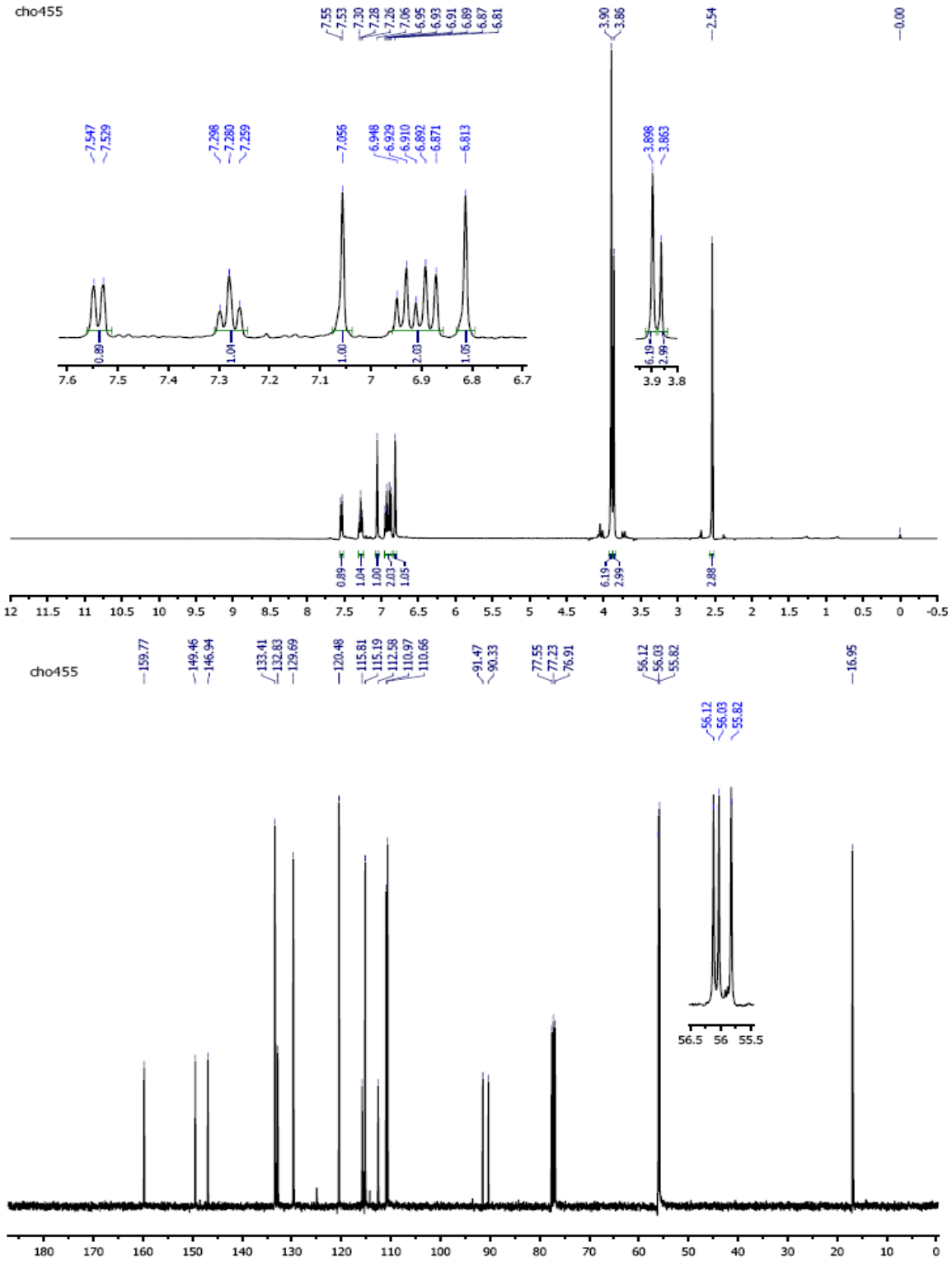

MeO
SMe
MeO
OMe


7.505
7.499
7.493
7.482
7.476
7.470
7.259
7.014
6.996
6.869
6.864
6.859
6.852
6.847
6.840
3.855
3.851
3.794
f1 (ppm)

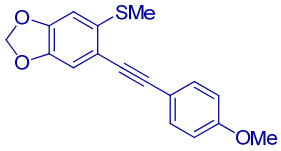

cho196
159.69
149.54
147.08
133.03
132.75
115.72
115.61
115.08
114.11
110.84
94.07
86.19
77.55
77.23
76.91
56.23
56.18
55.45
17.00
f1 (ppm)

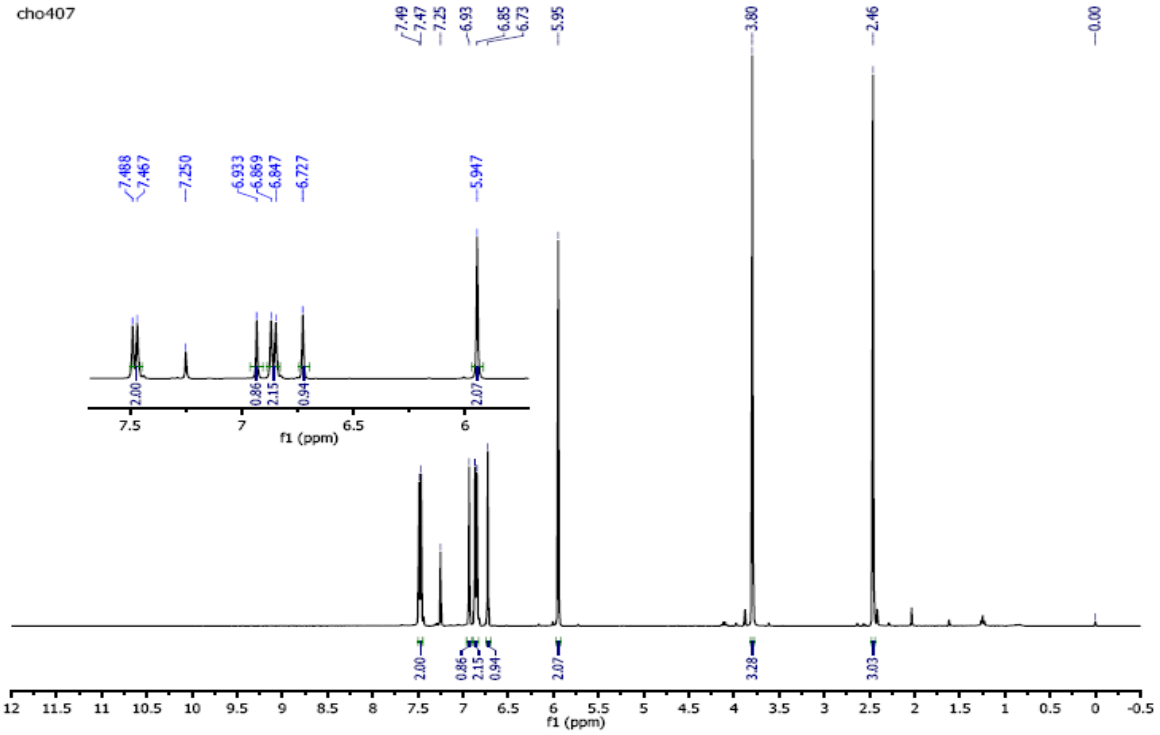
Compound **7**{*9*}

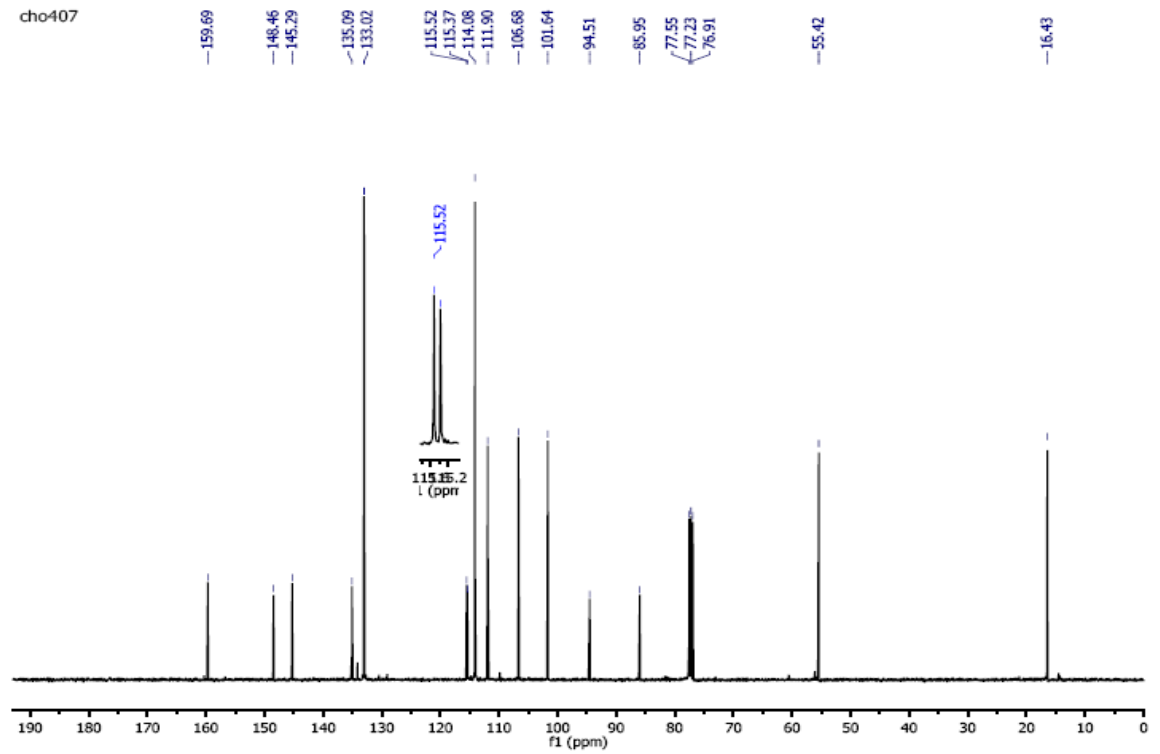




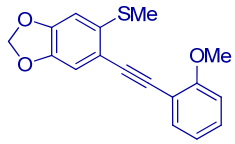
Compound **7**{*11*}

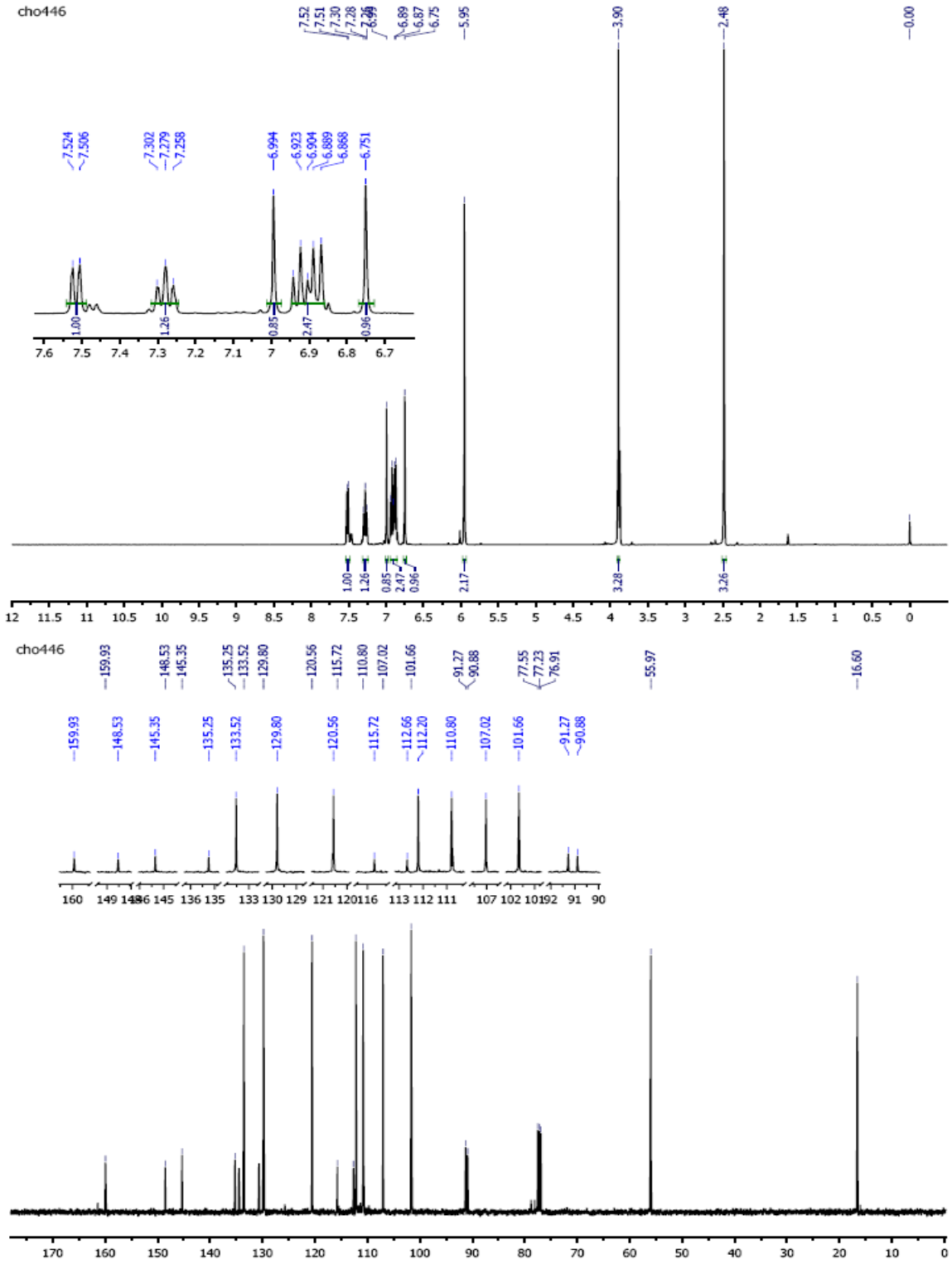




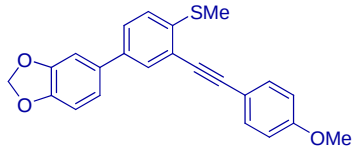


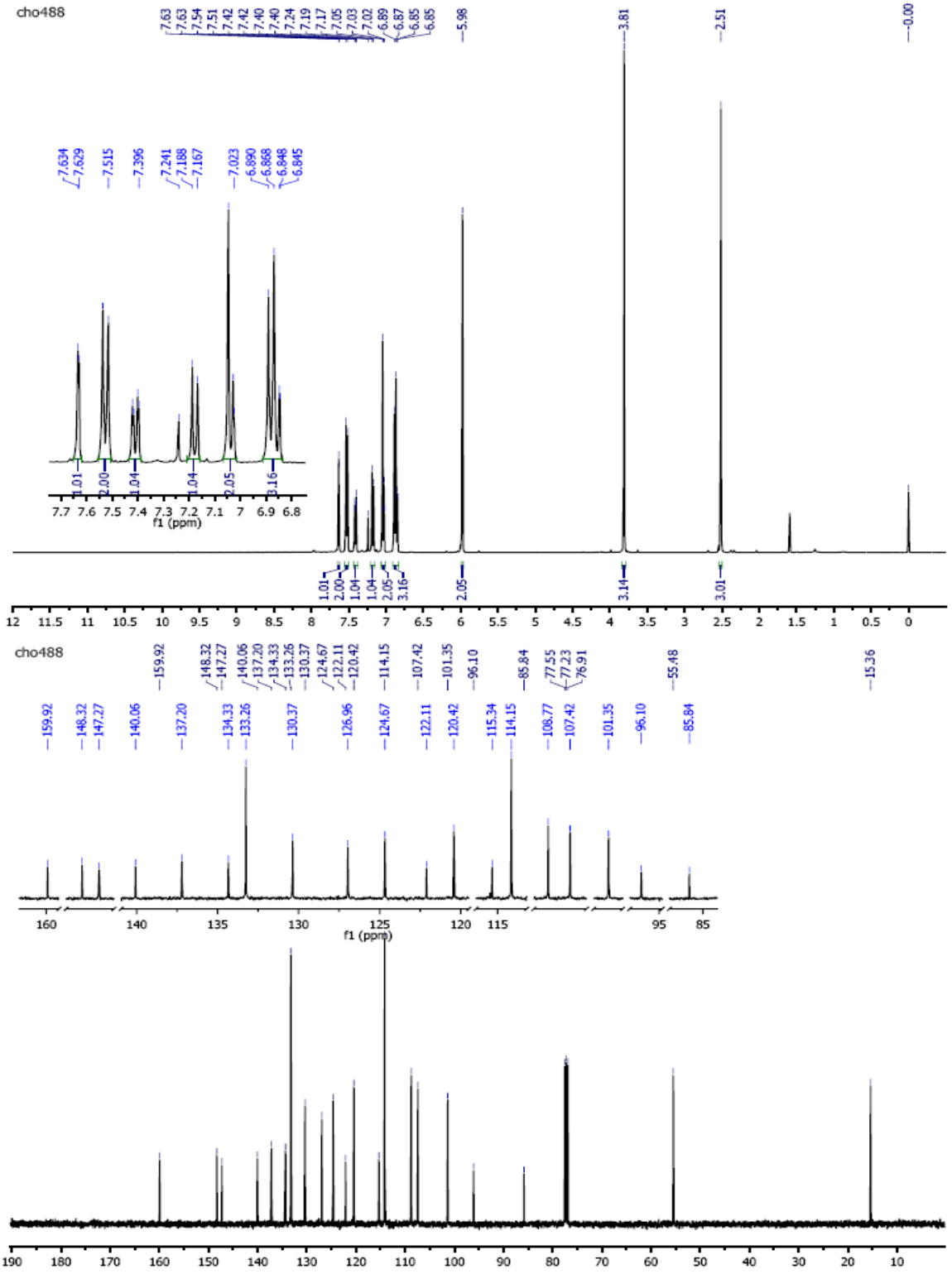
Compound **7**{*12*}



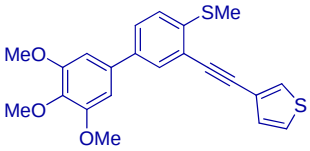


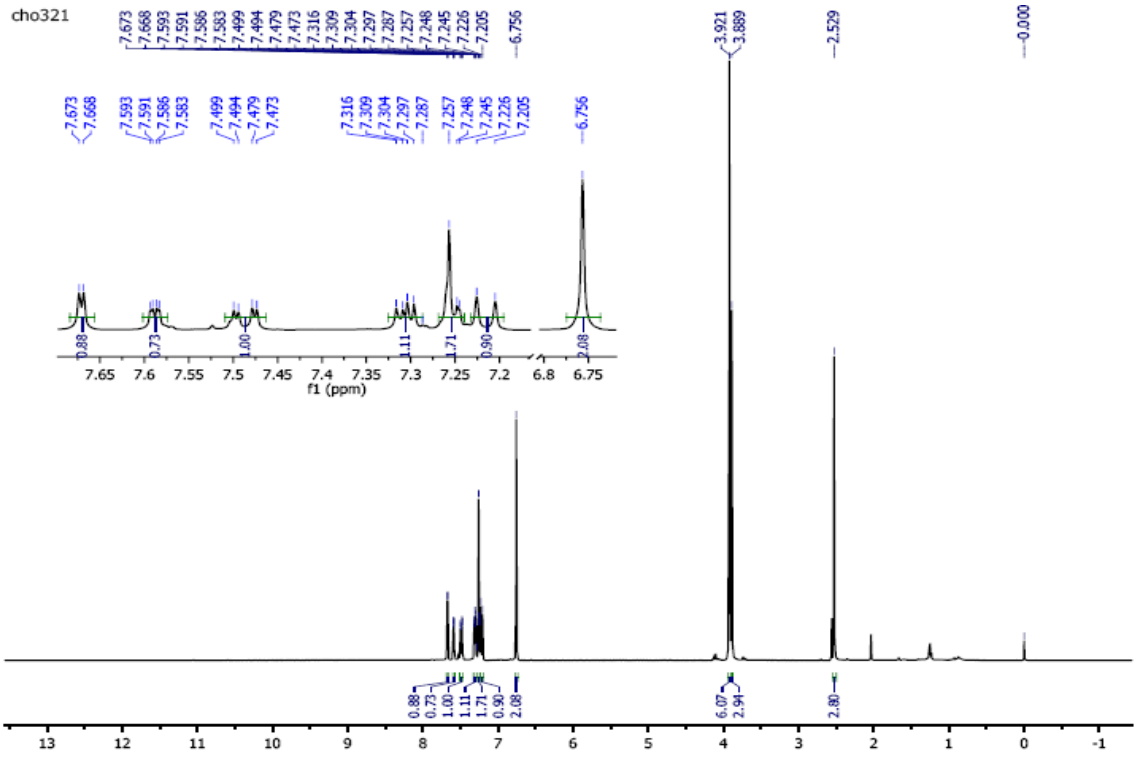
Compound **7**{*13*}

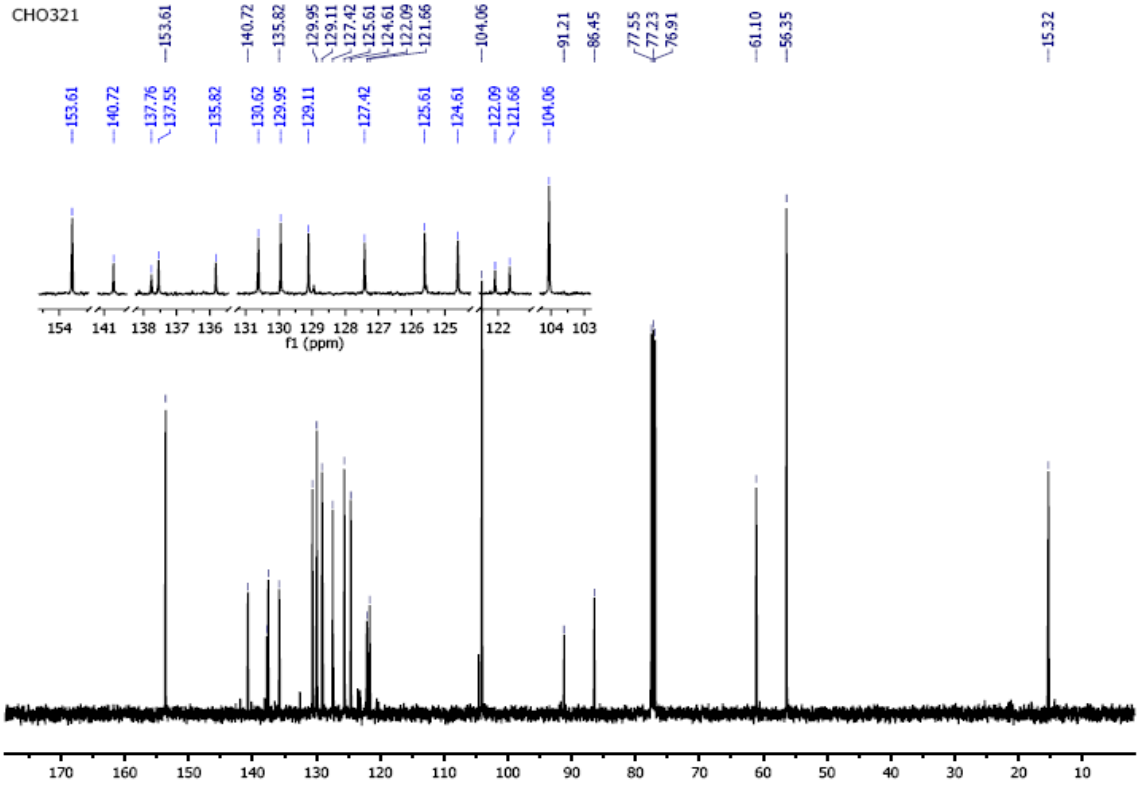




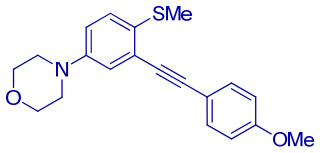
Compound **7**{*14*}

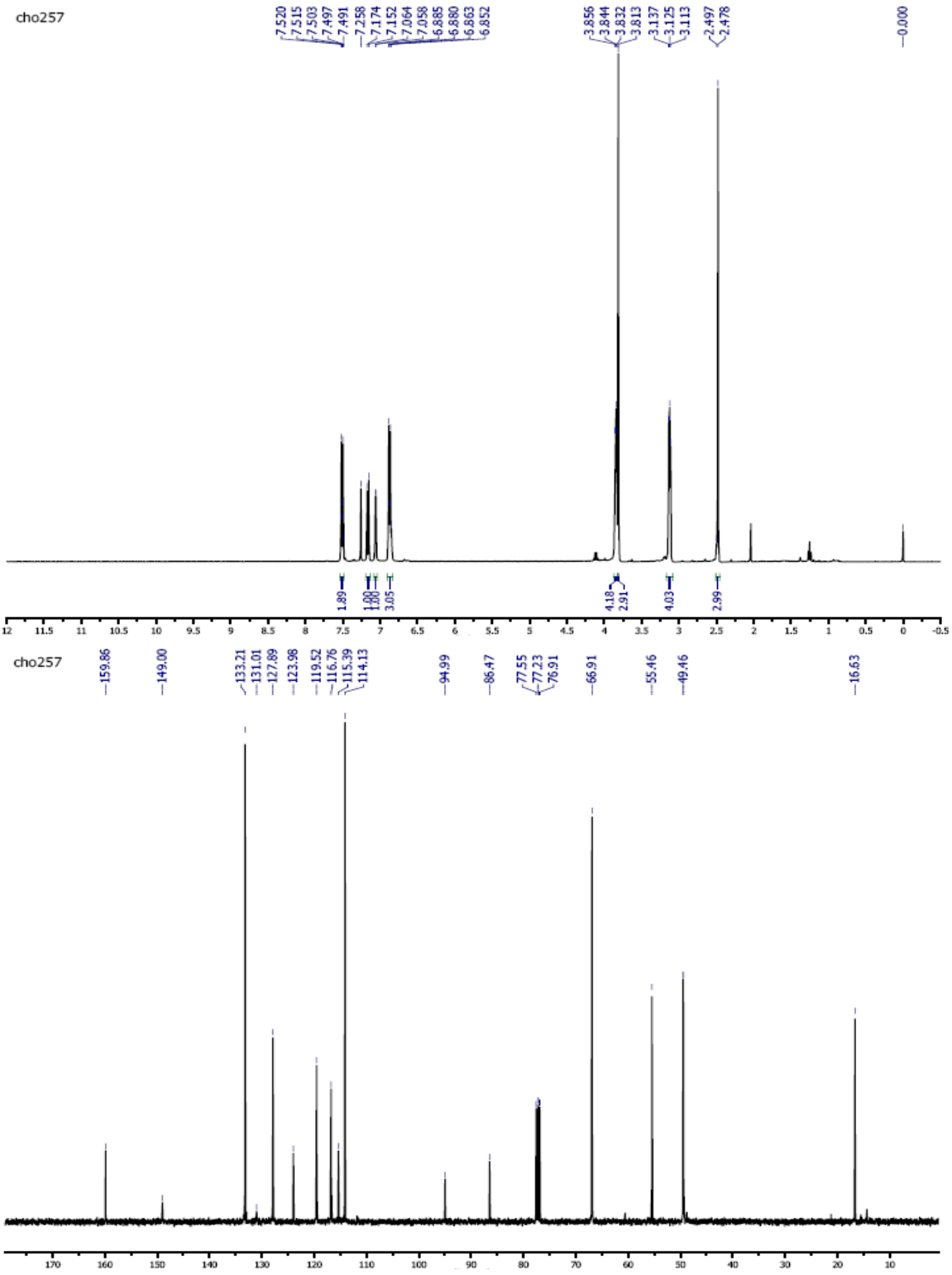




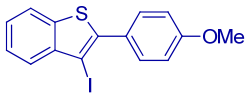


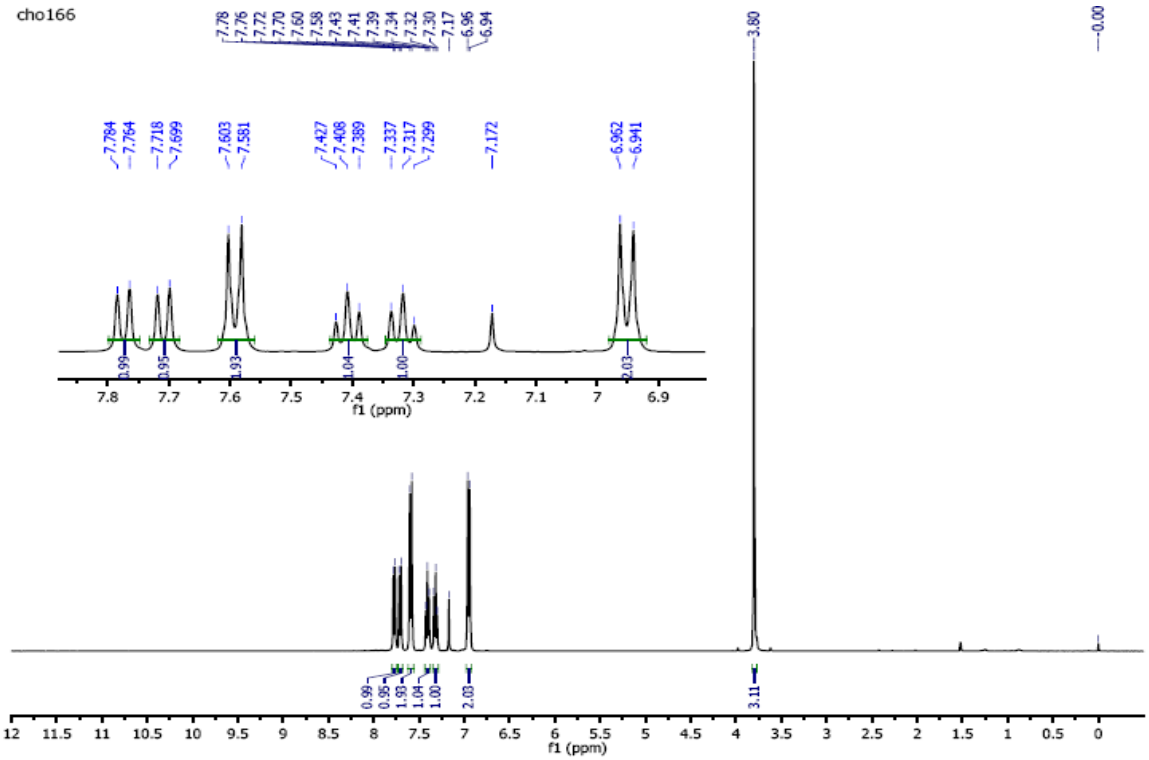
Compound **7**{*15*}

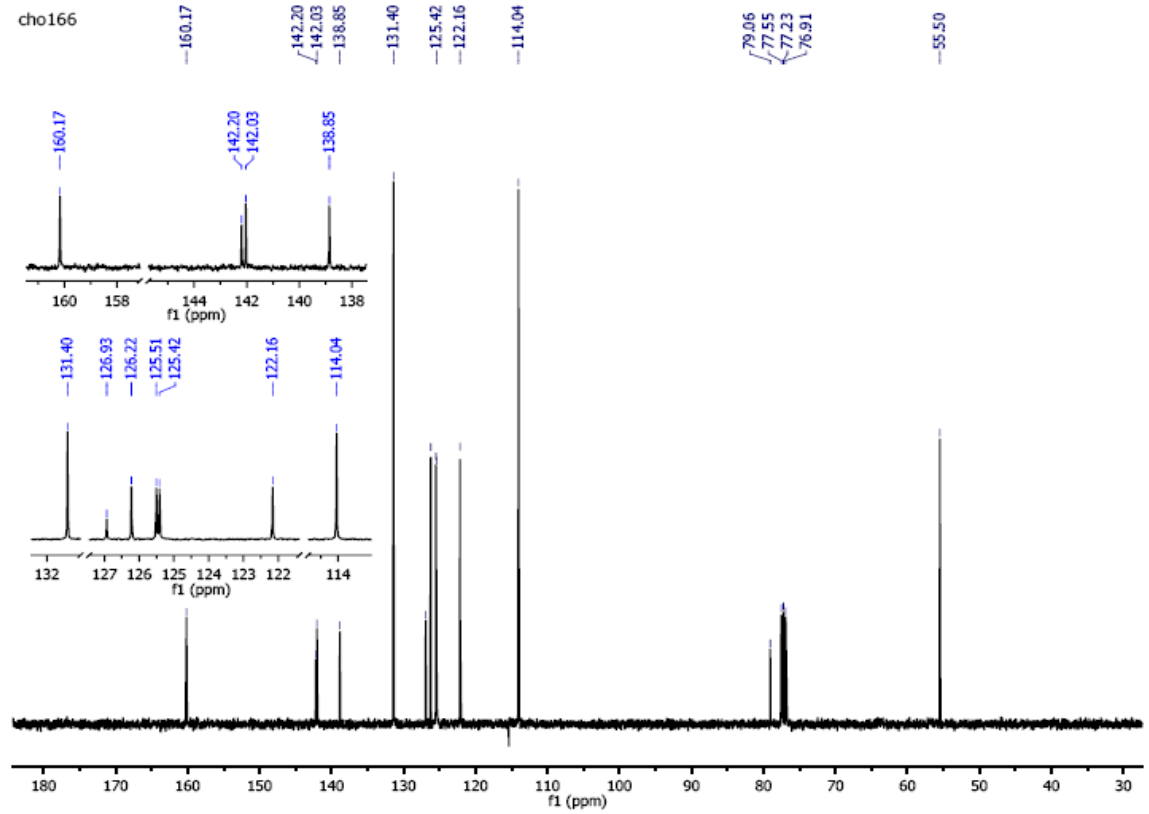




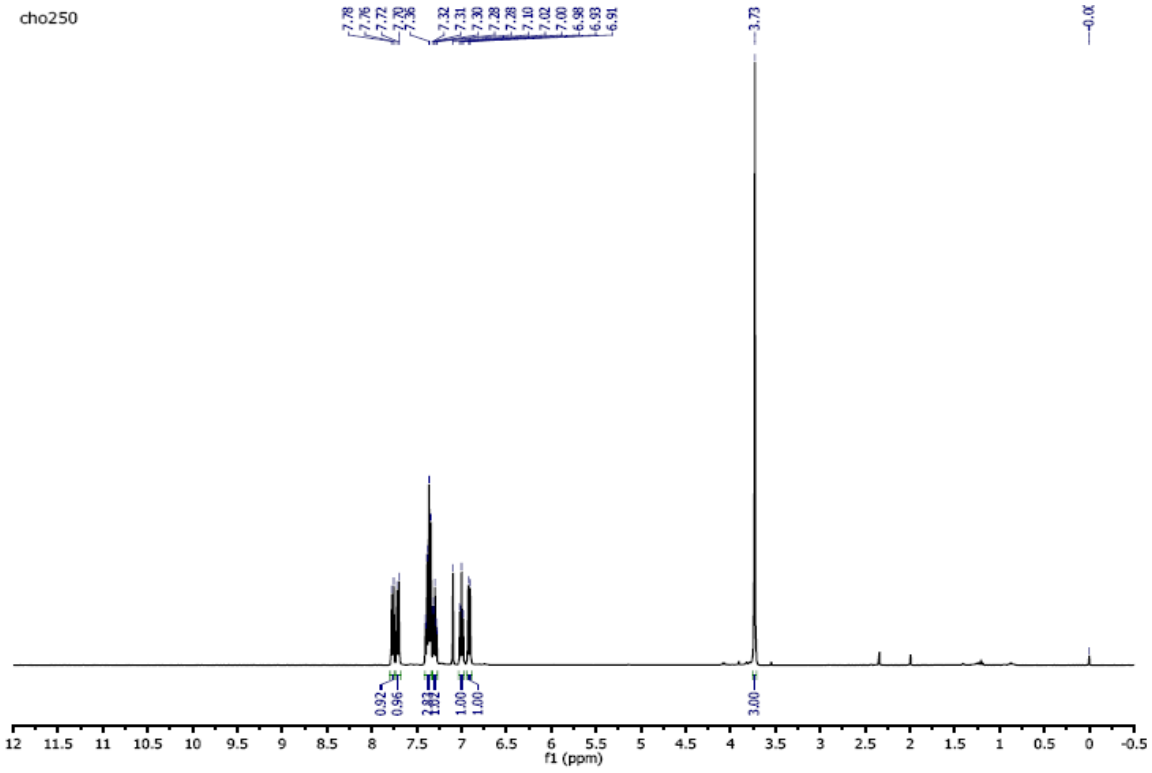
3-Iodobenzo[*b*]thiophene 8{*1*}

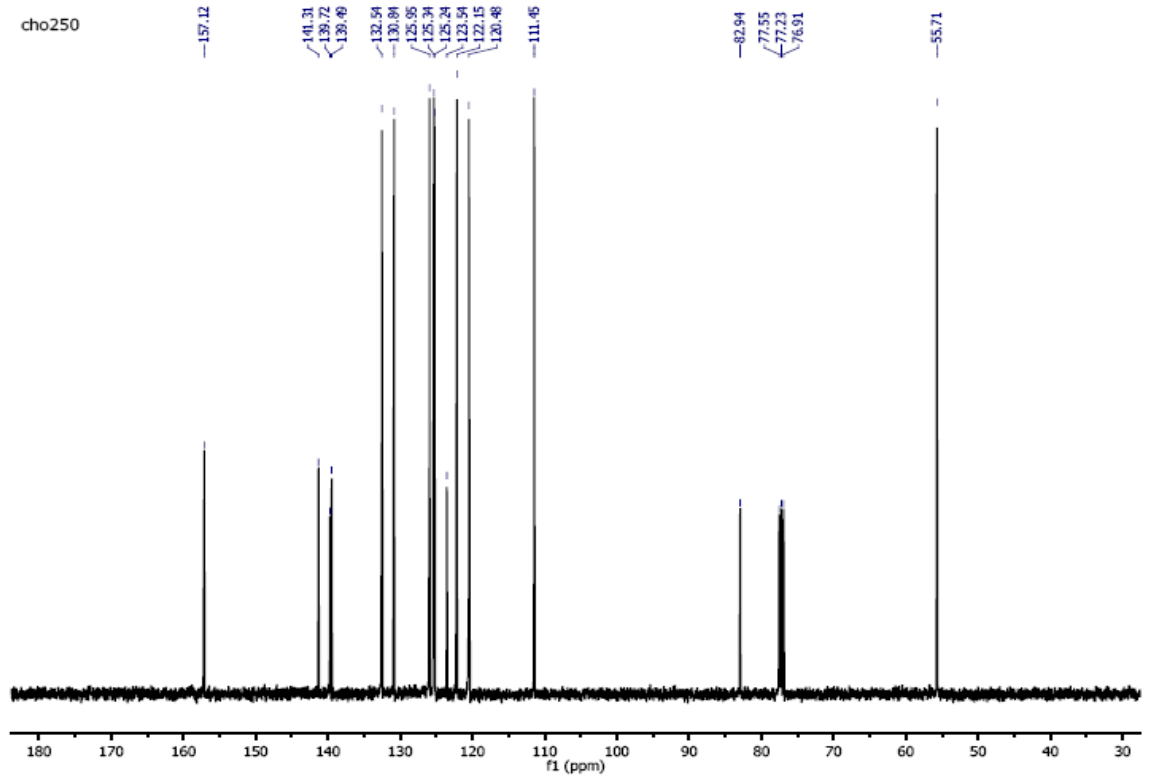




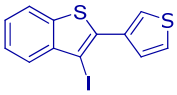


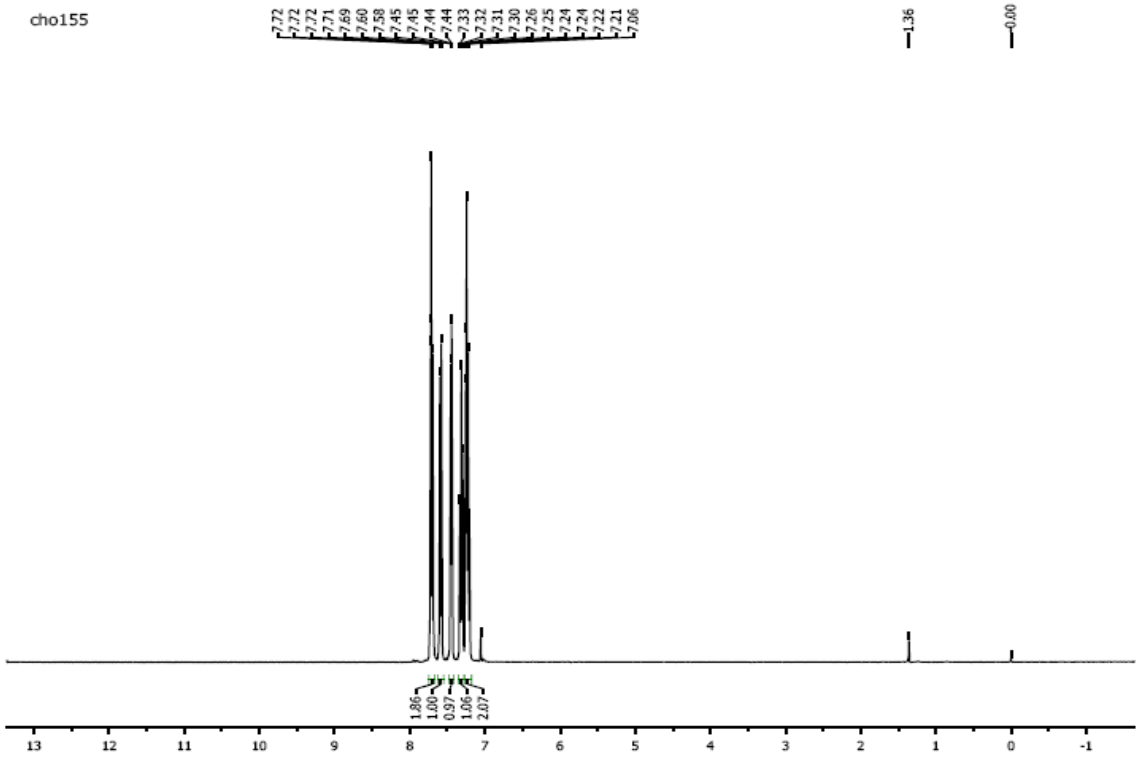
3-Iodobenzo[*b*]thiophene 8{*2*}

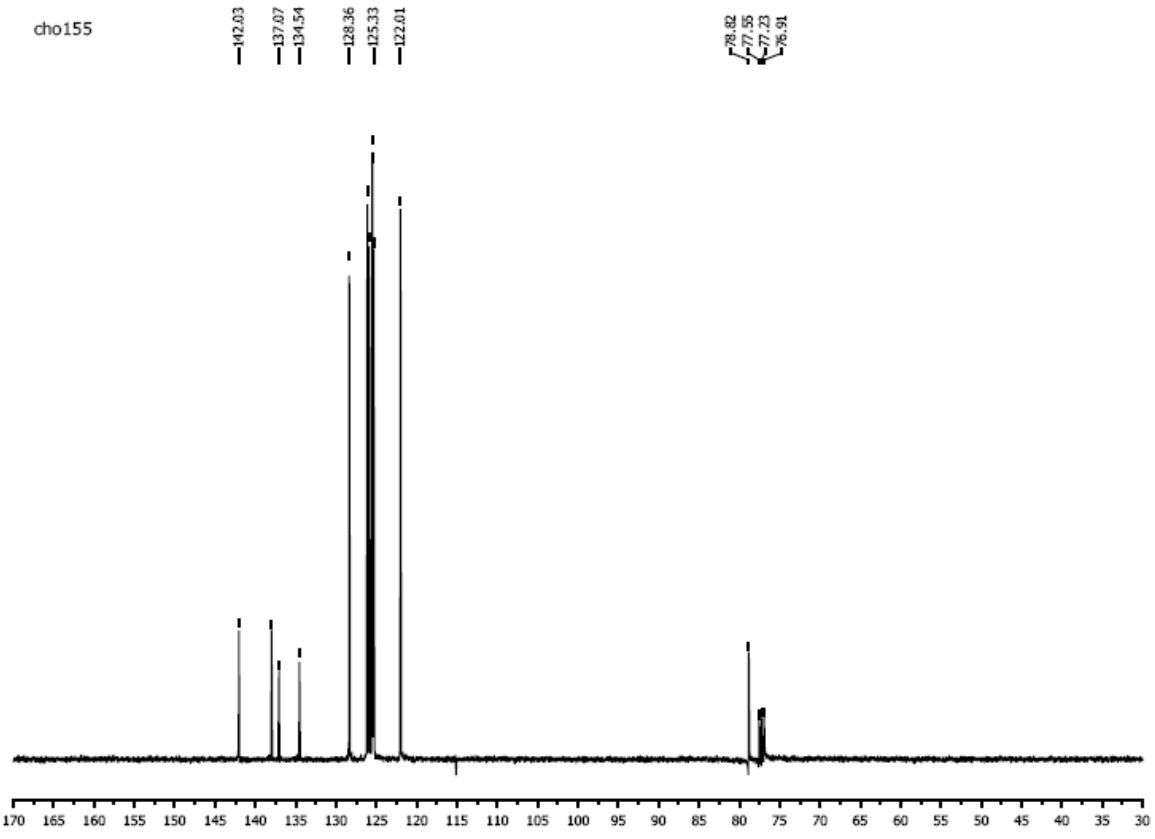




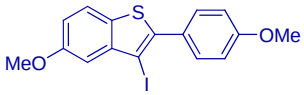
3-Iodobenzo[*b*]thiophene 8{*3*}

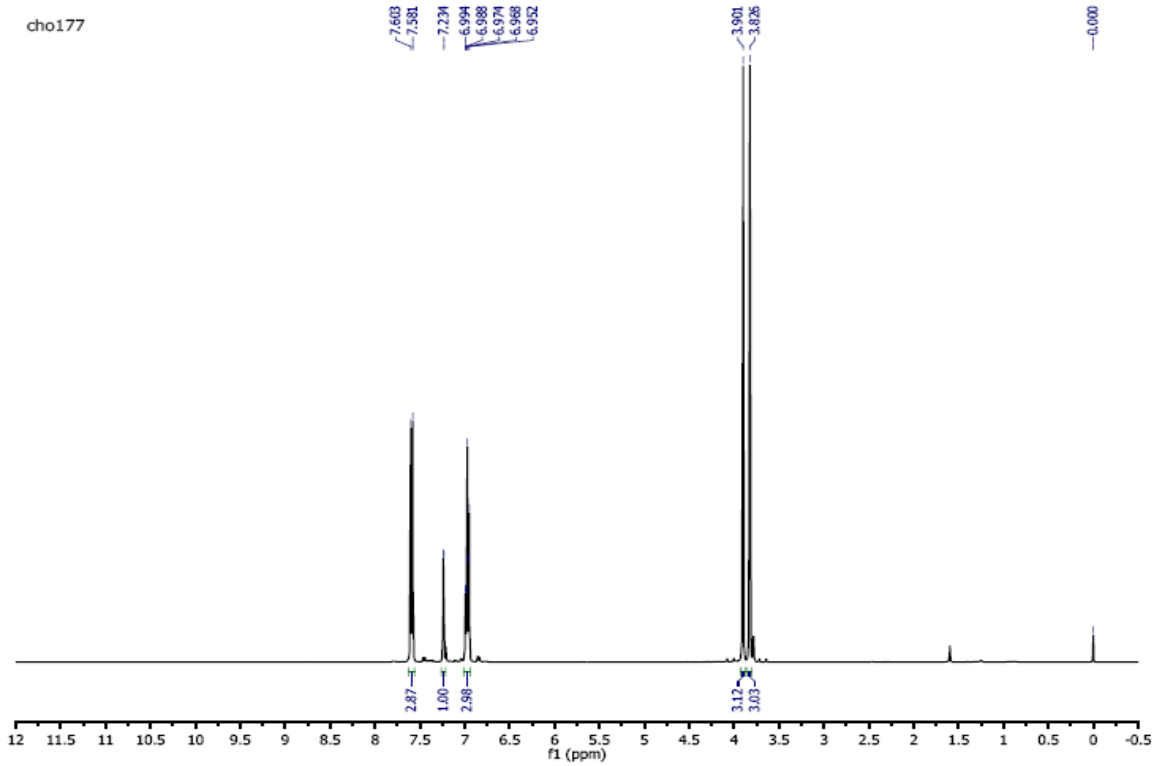


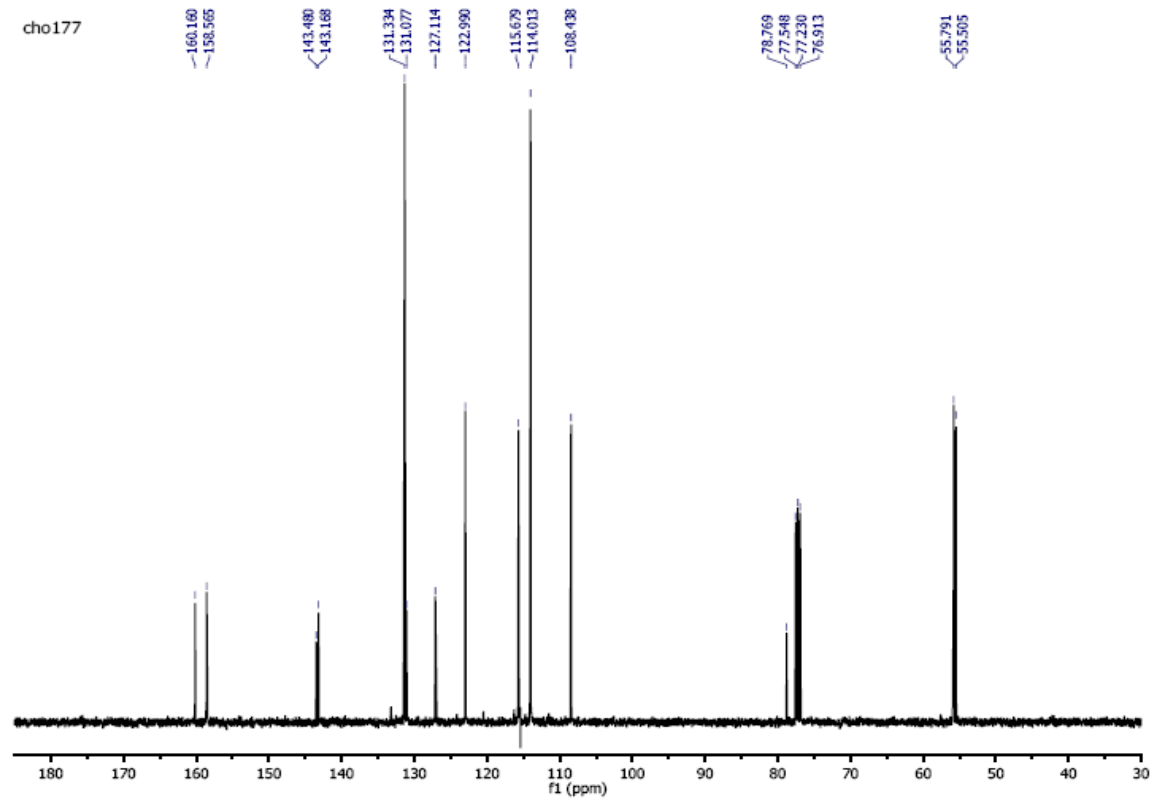




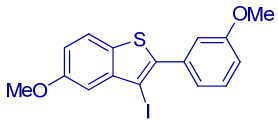
3-Iodobenzo[*b*]thiophene 8{*4*}

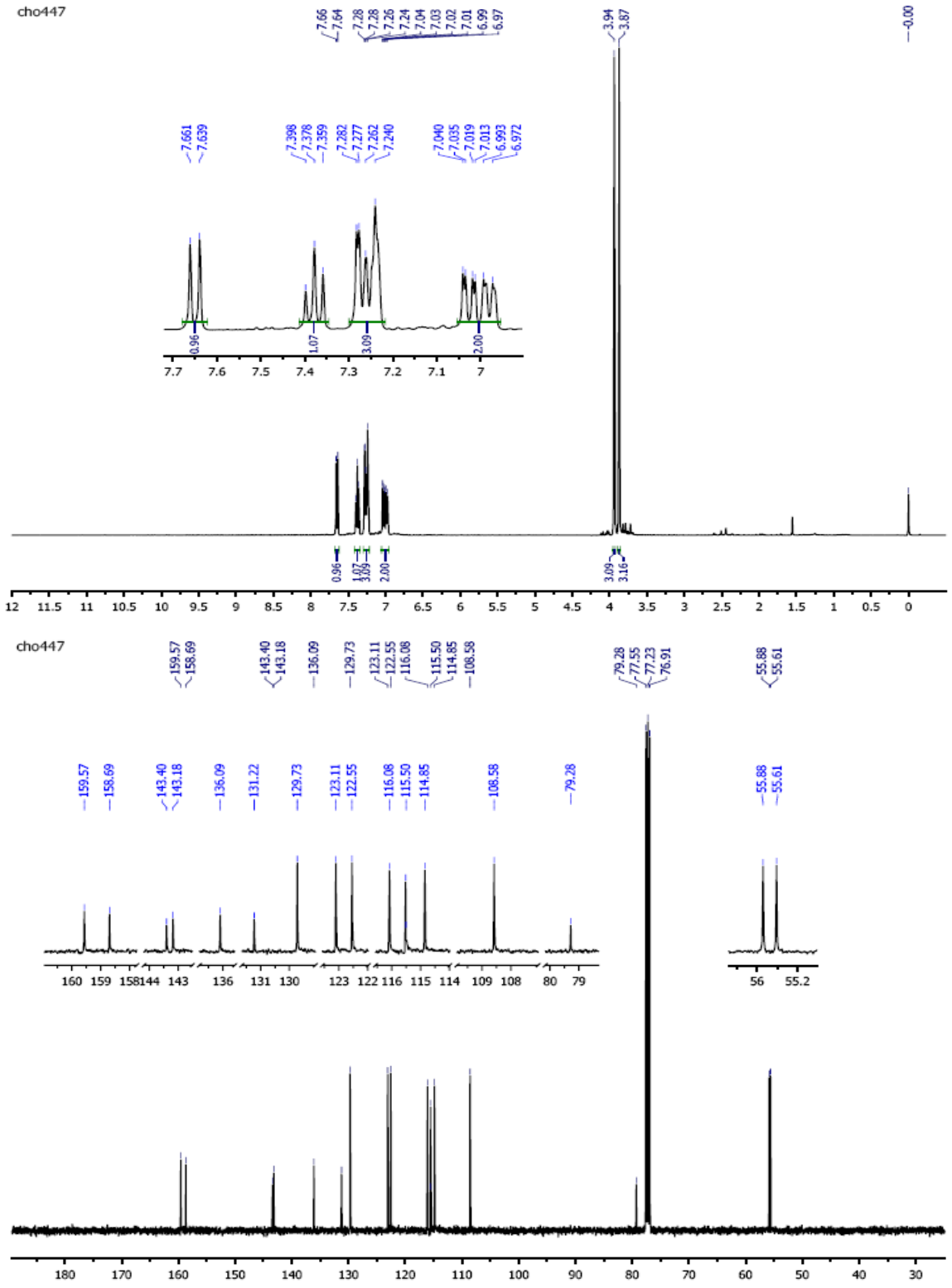




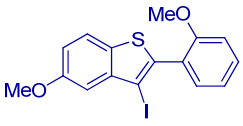


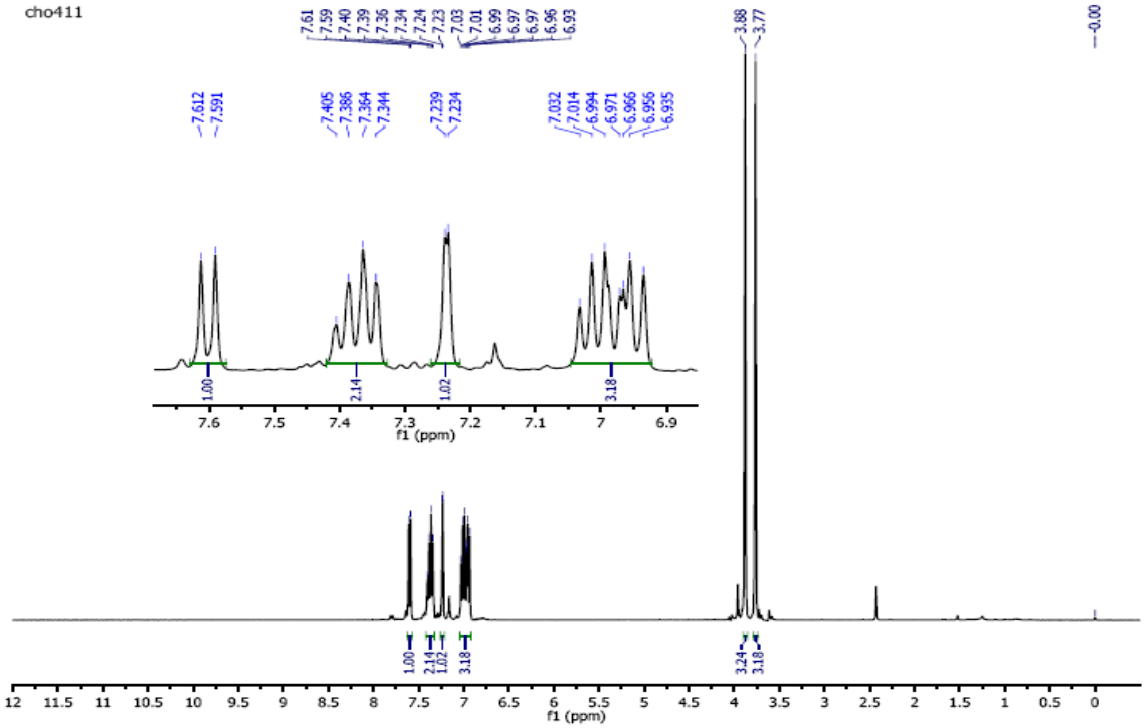
3-Iodobenzo[*b*]thiophene 8{*5*}

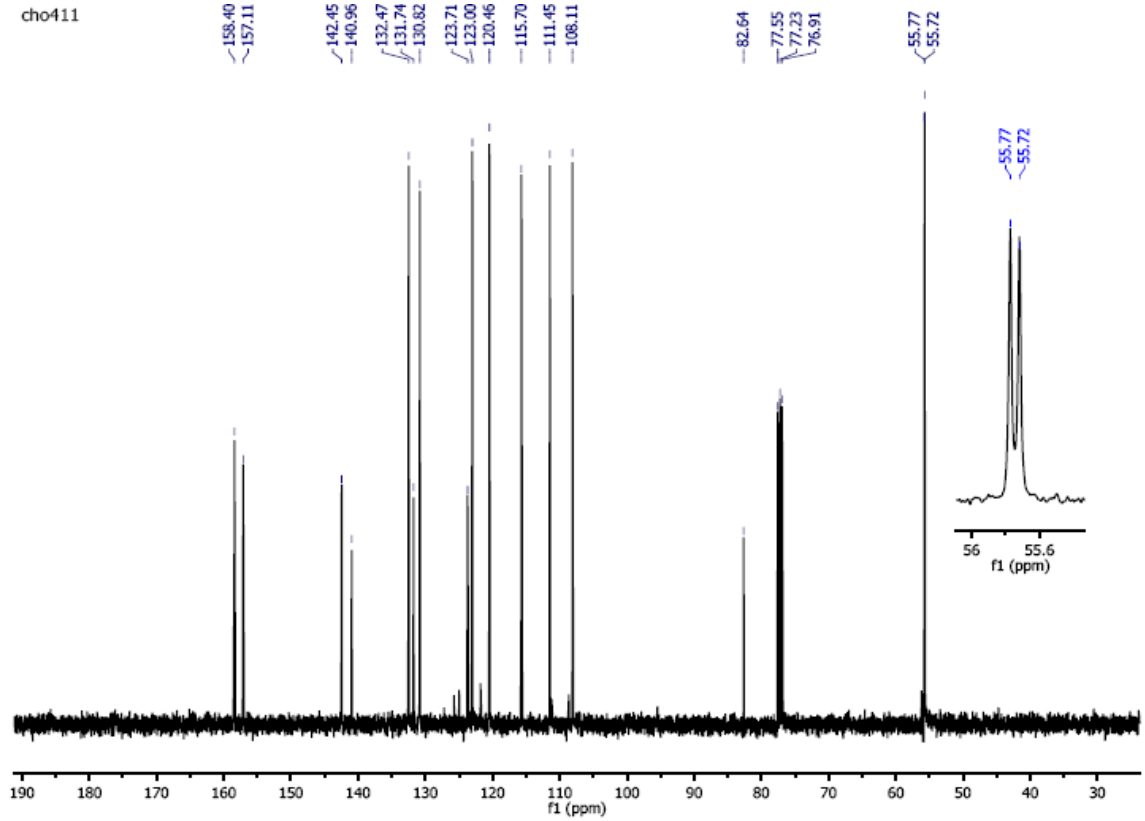




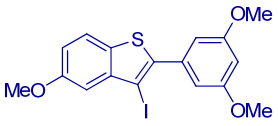
3-Iodobenzo[*b*]thiophene 8{*6*}

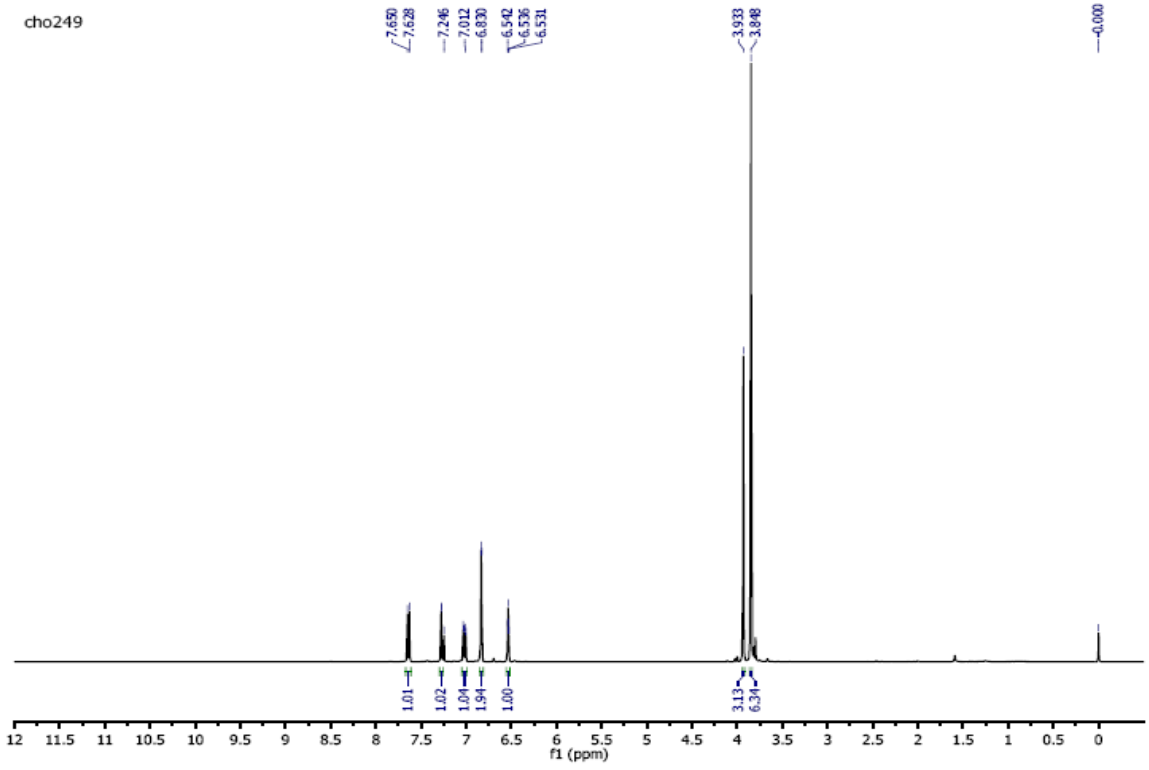


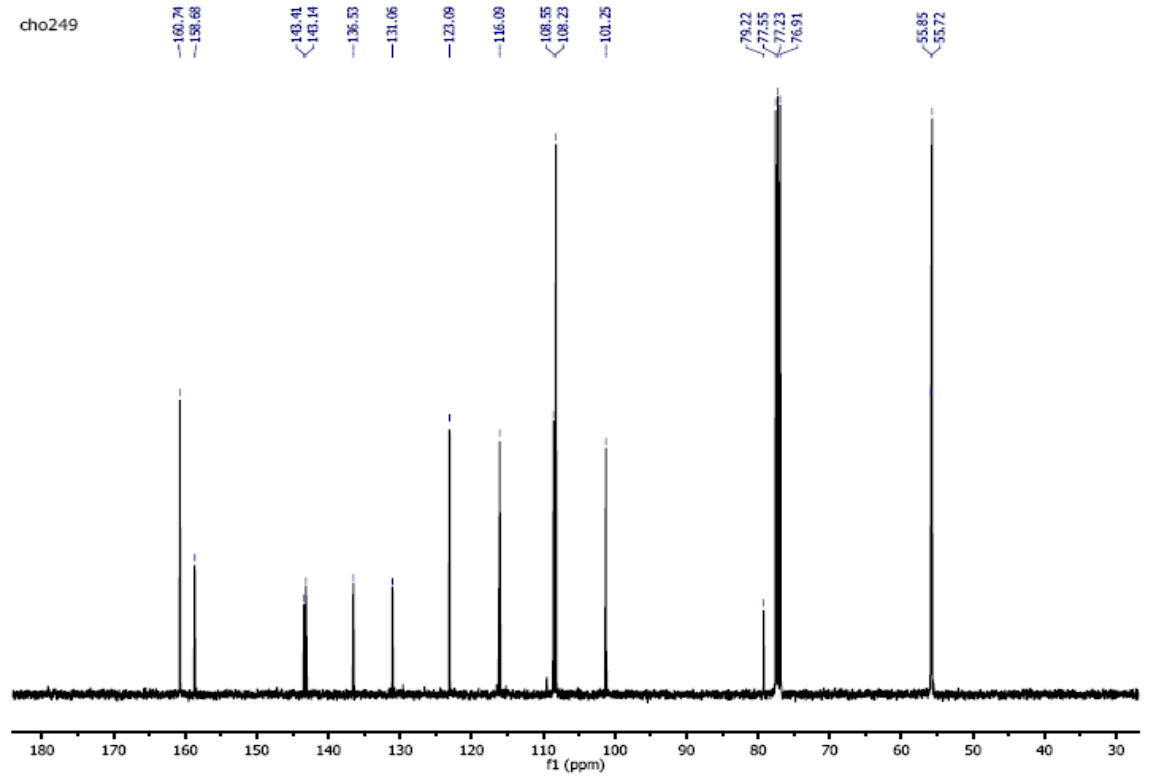




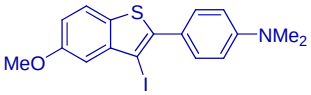
3-Iodobenzo[*b*]thiophene 8{*7*}

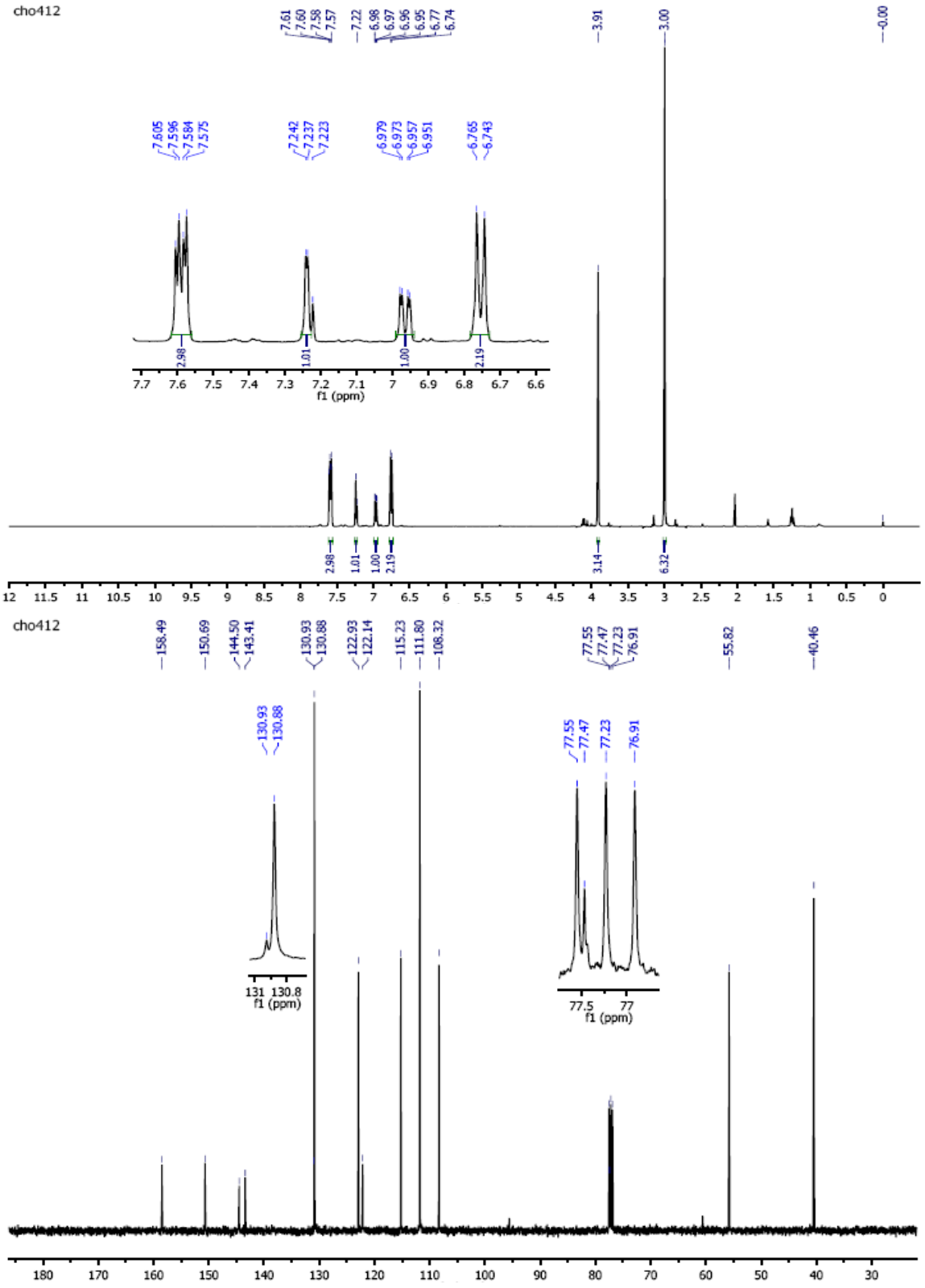




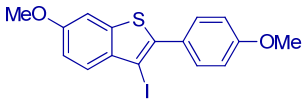


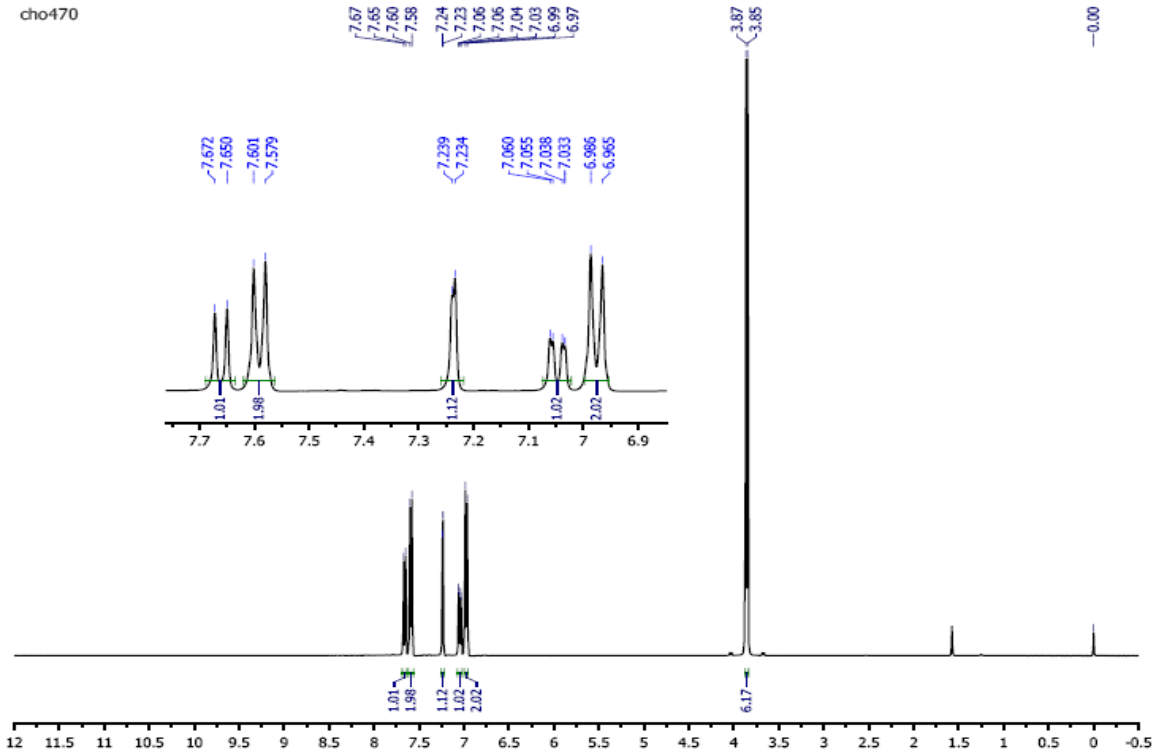
3-Iodobenzo[*b*]thiophene 8{*8*}

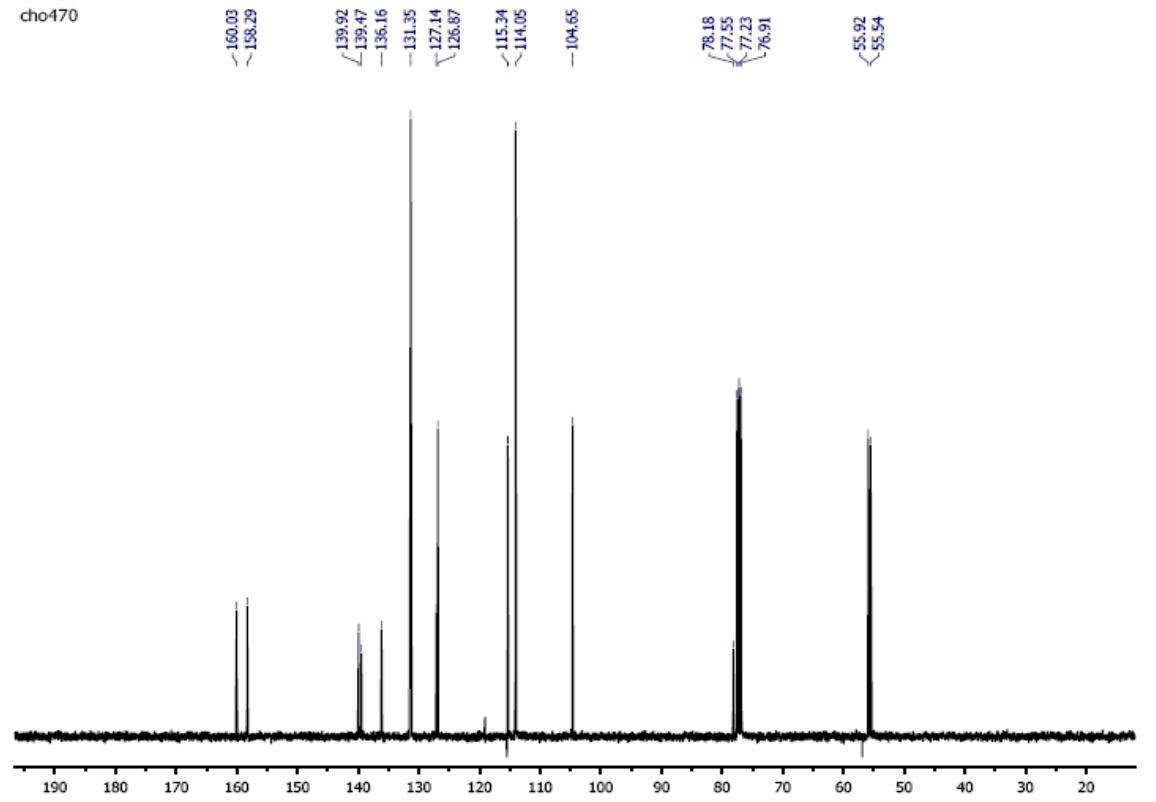




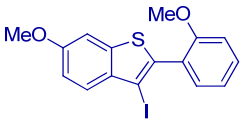
3-Iodobenzo[*b*]thiophene 8{*9*}

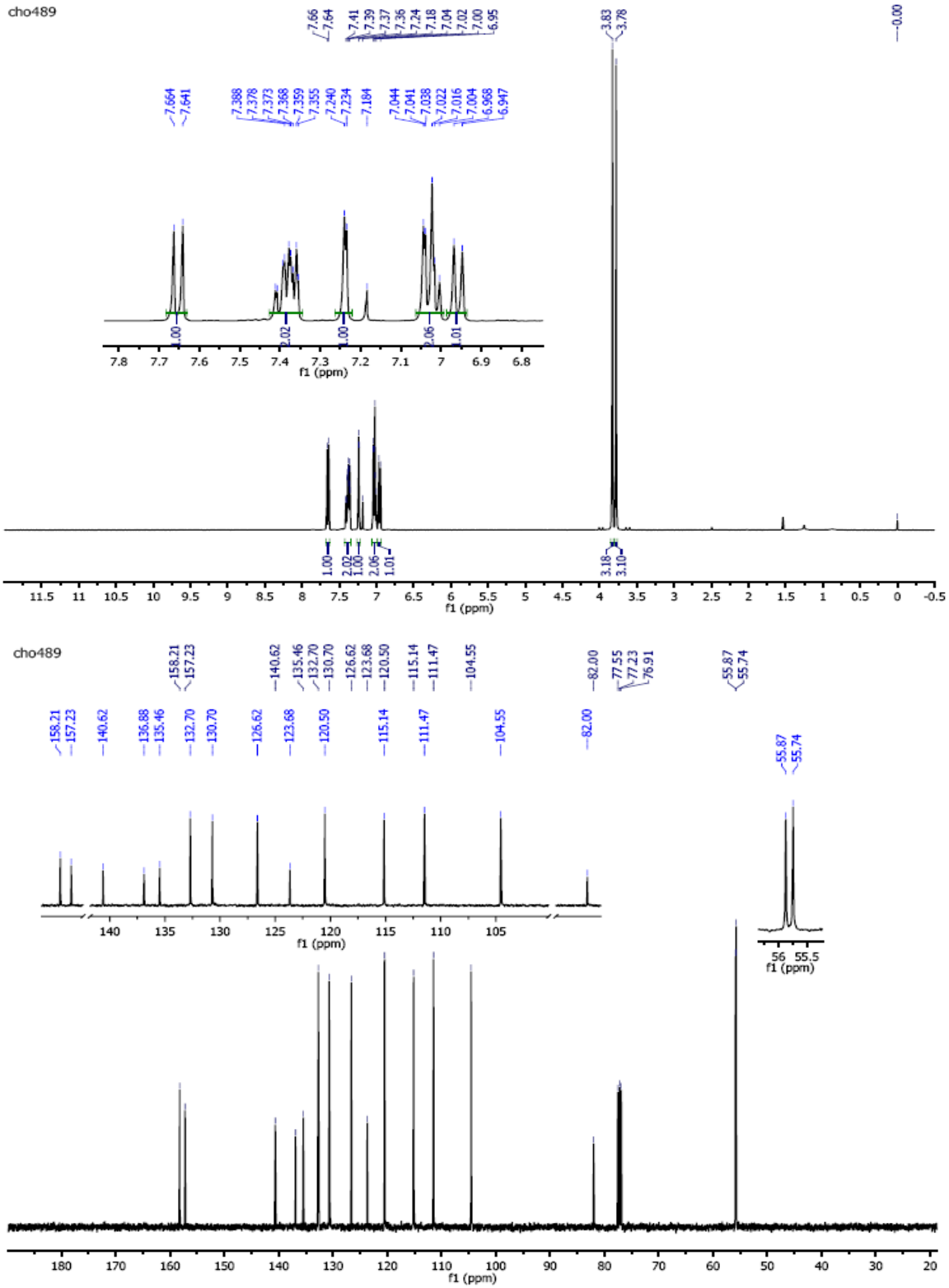




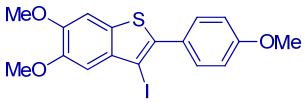


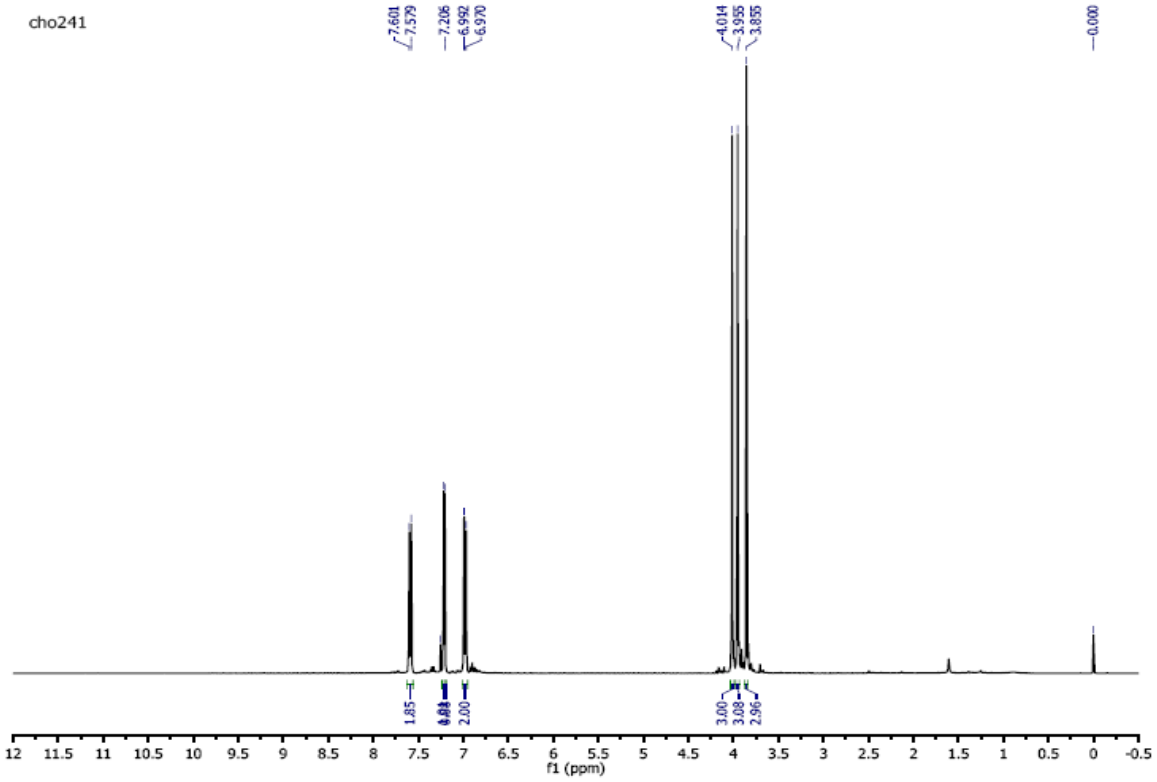
3-Iodobenzo[*b*]thiophene 8{*10*}

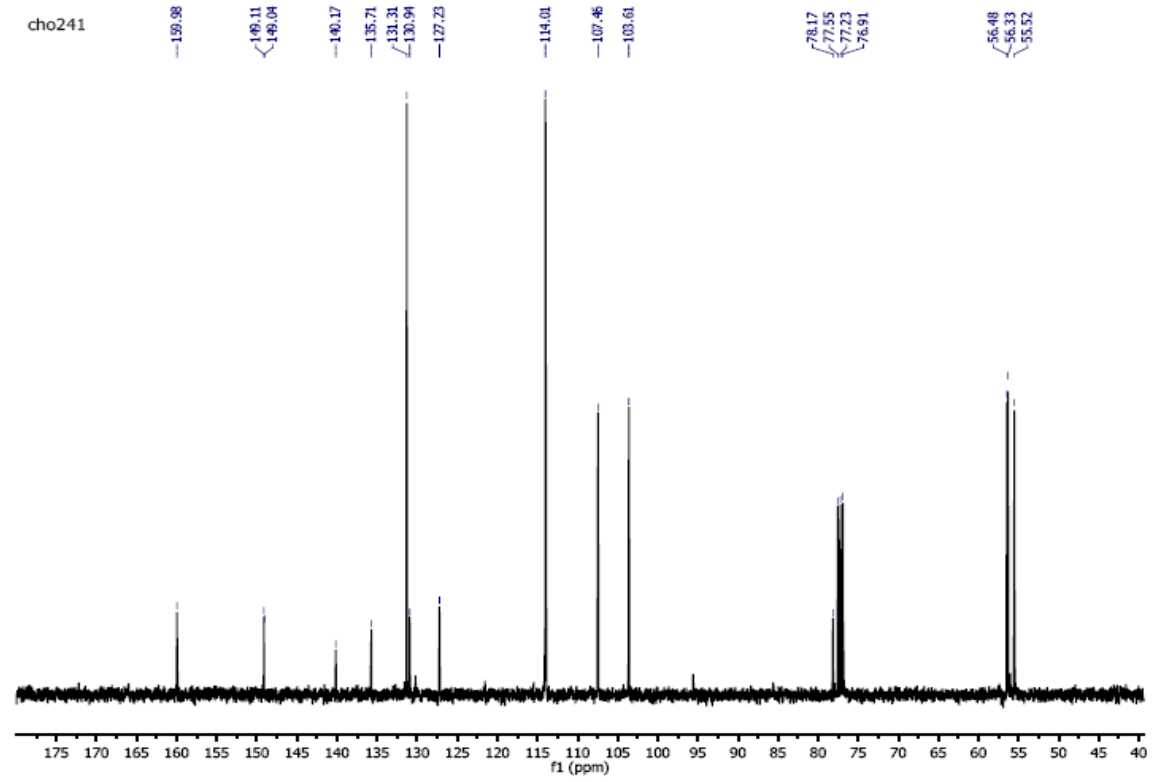




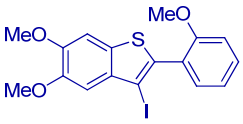
3-Iodobenzo[*b*]thiophene 8{*11*}

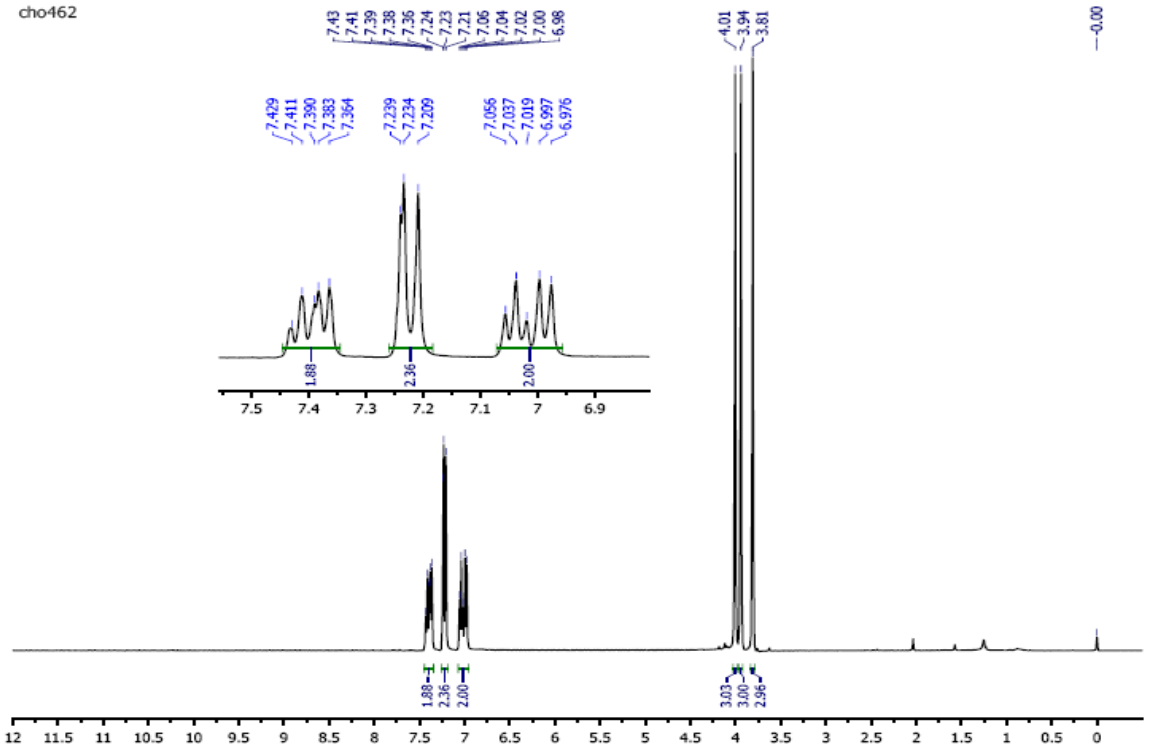


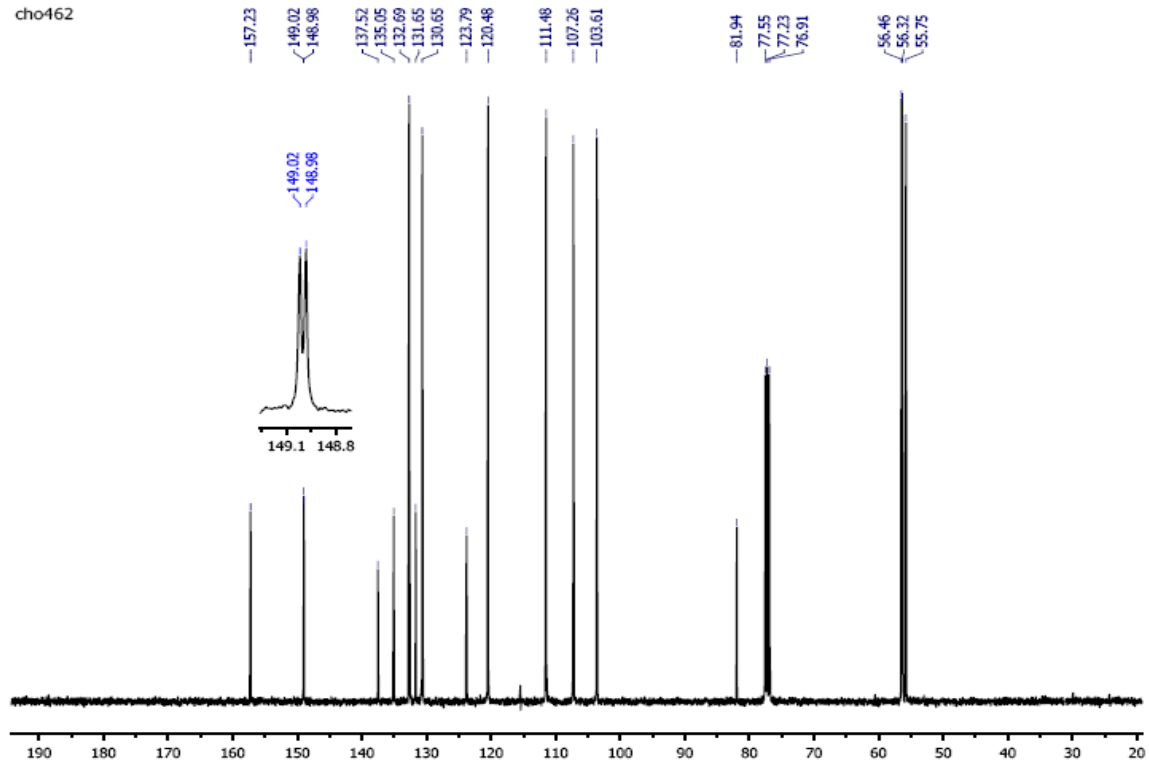




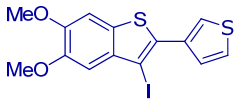
3-Iodobenzo[*b*]thiophene 8{*12*}

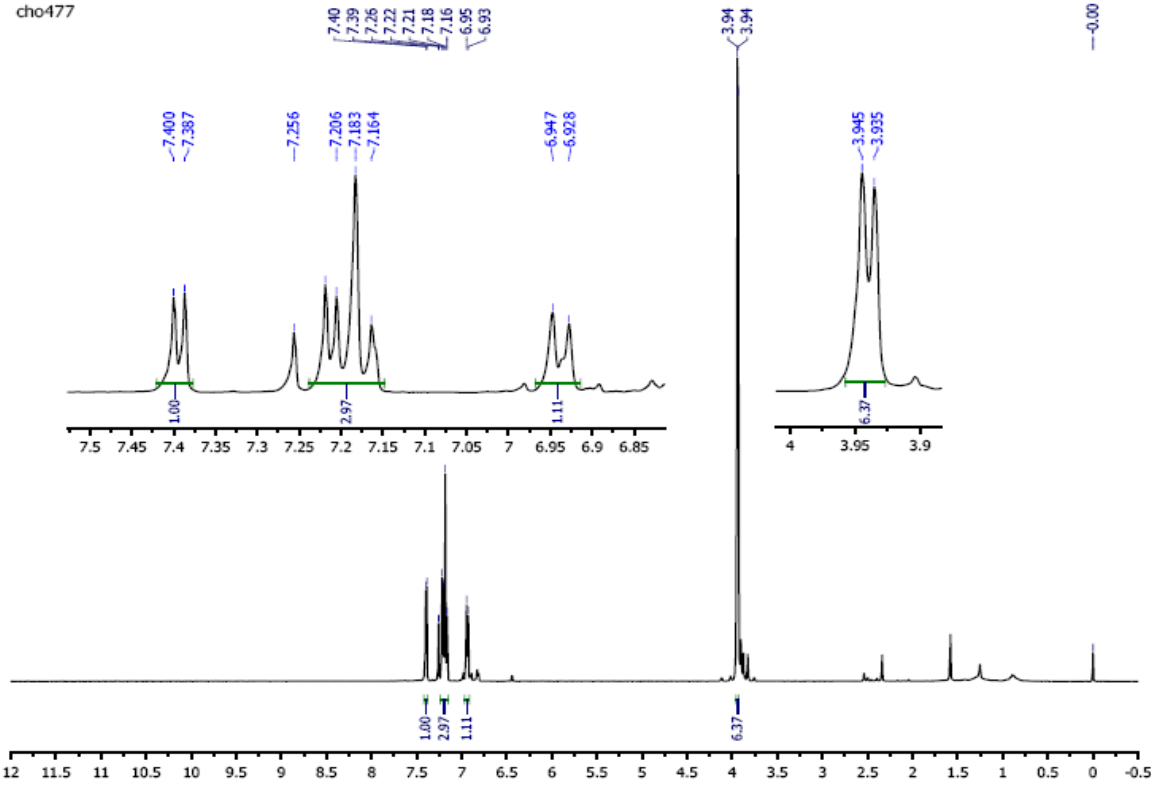


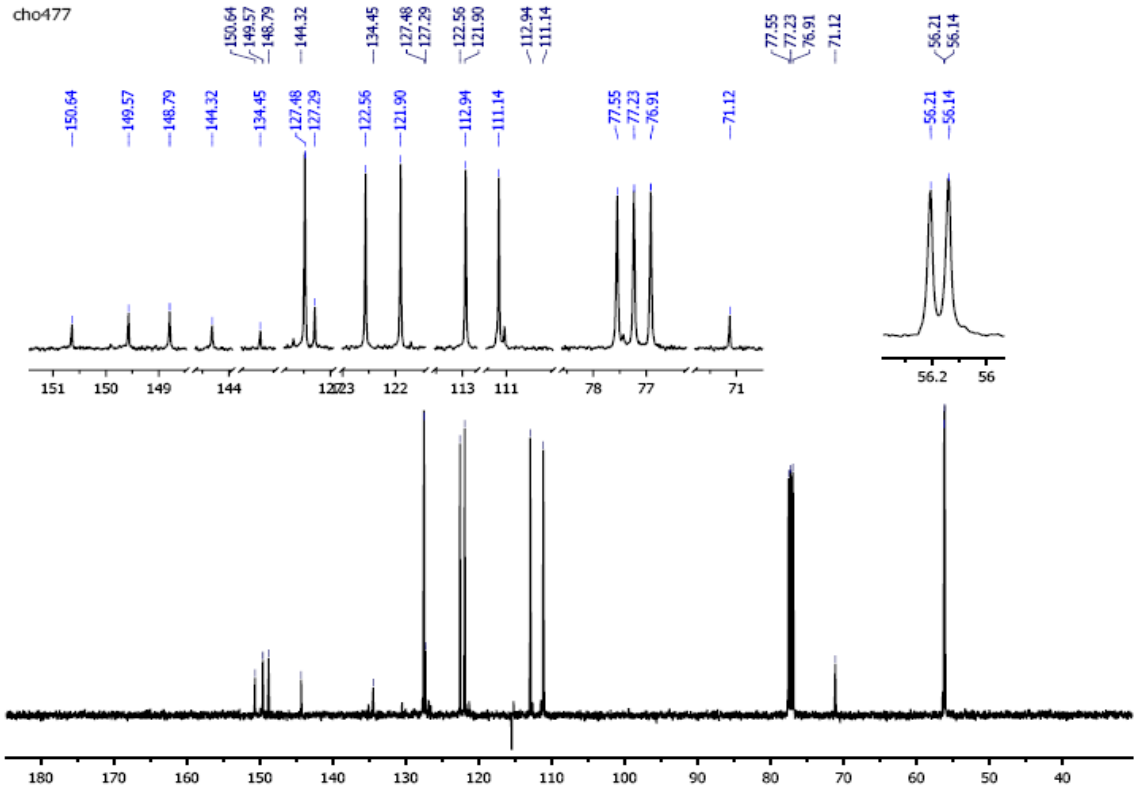




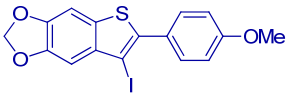
3-Iodobenzo[*b*]thiophene 8{*13*}

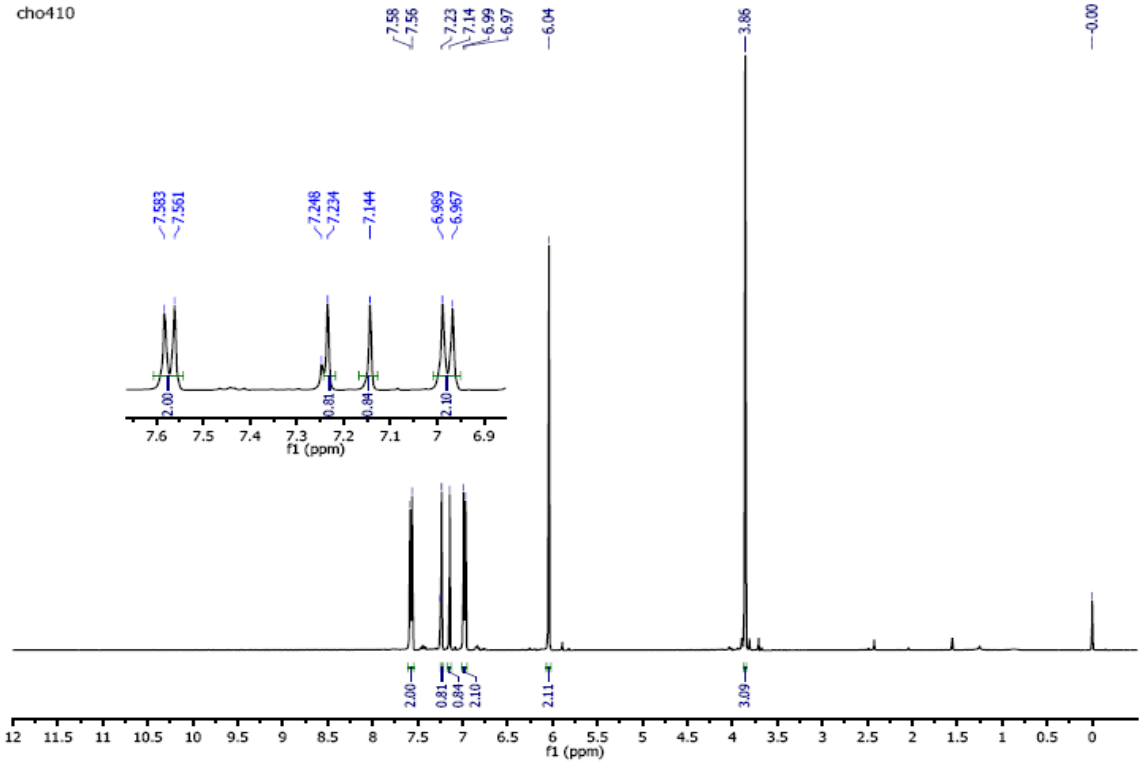


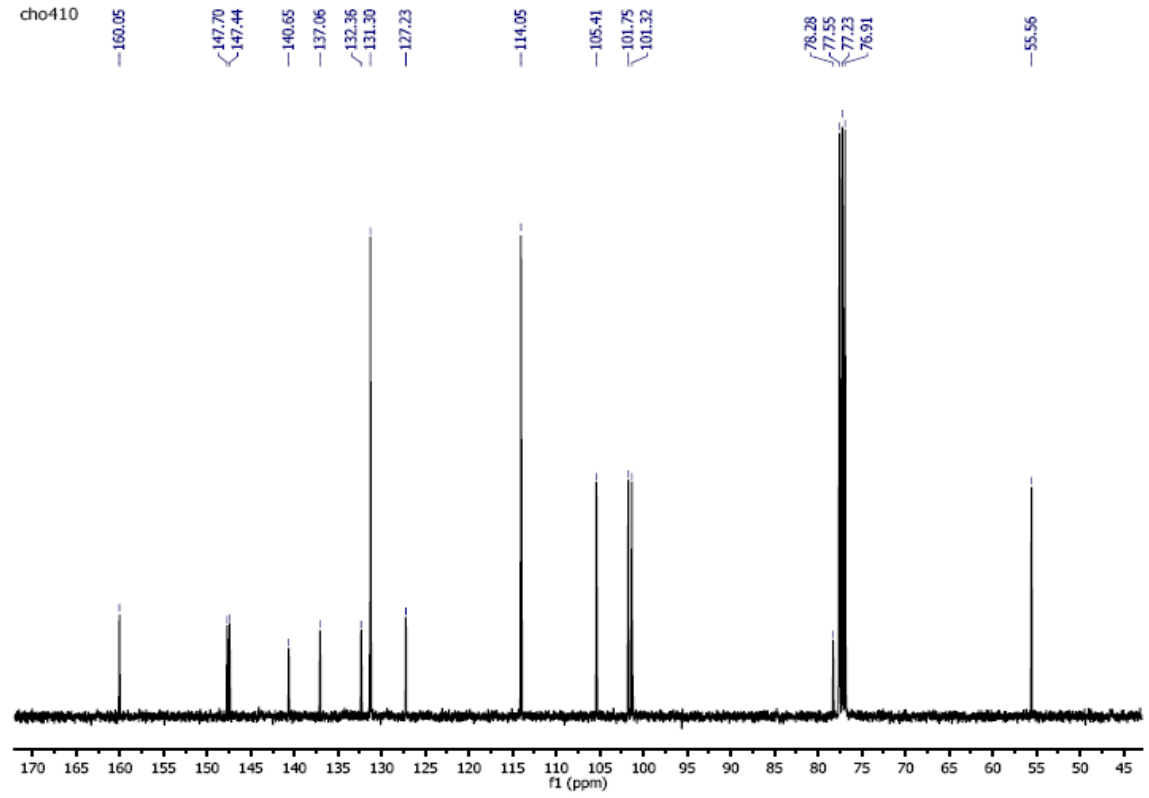




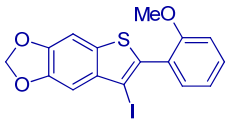
3-Iodobenzo[*b*]thiophene 8{*14*}

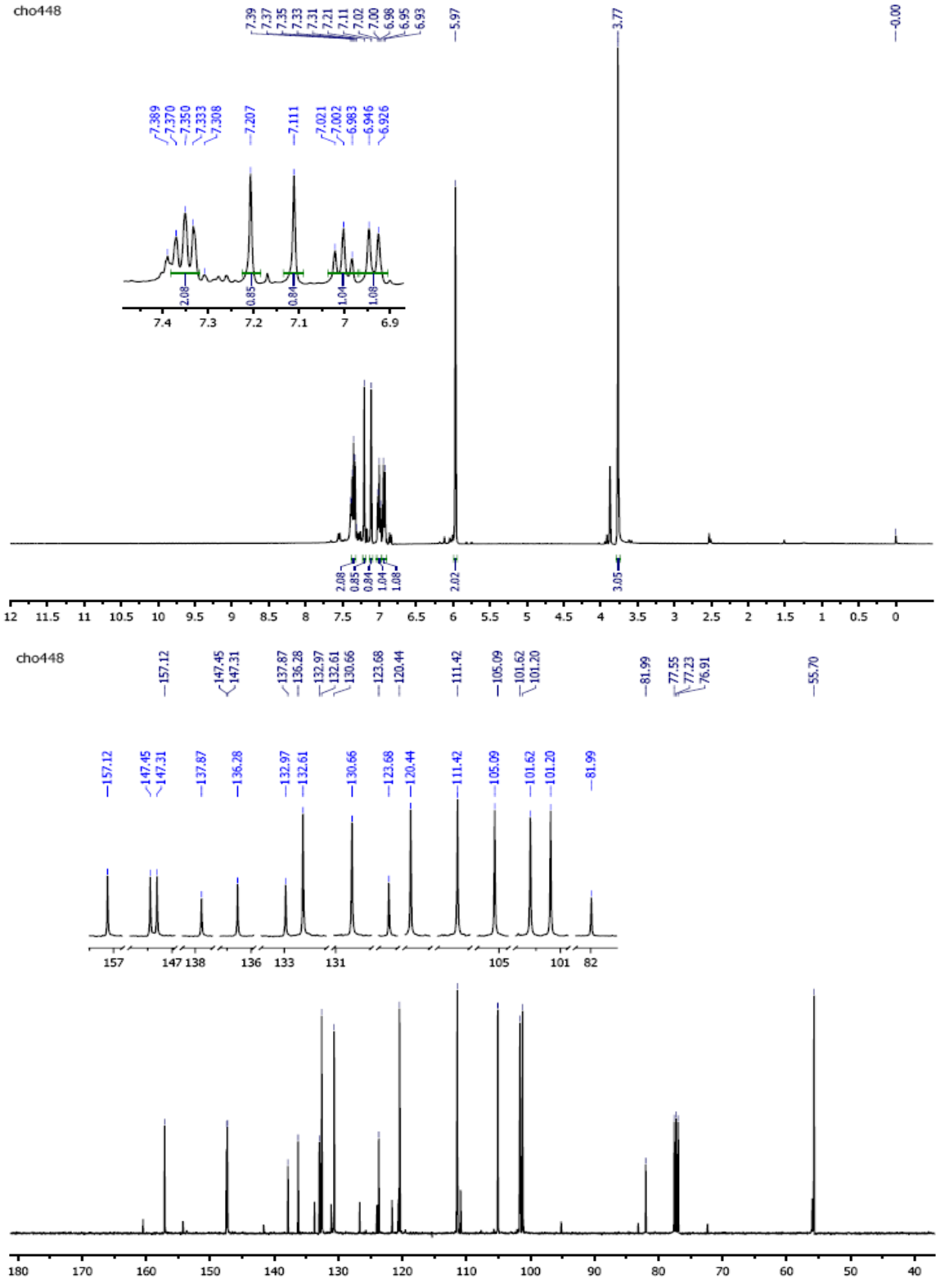




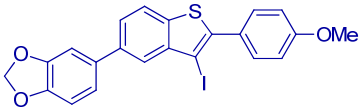


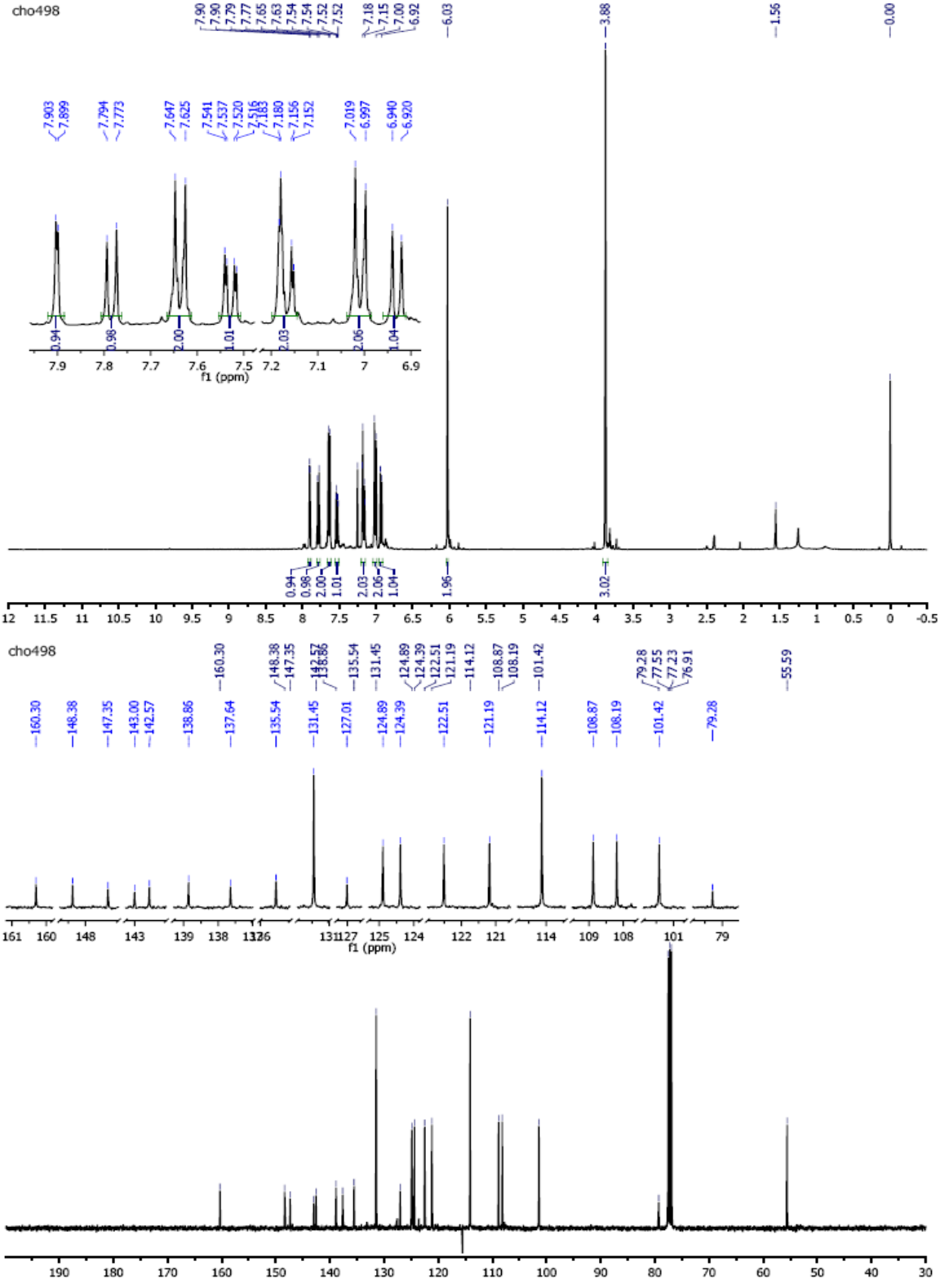
3-Iodobenzo[*b*]thiophene 8{*15*}



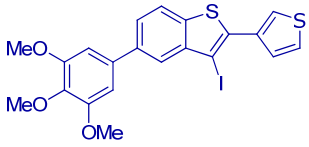


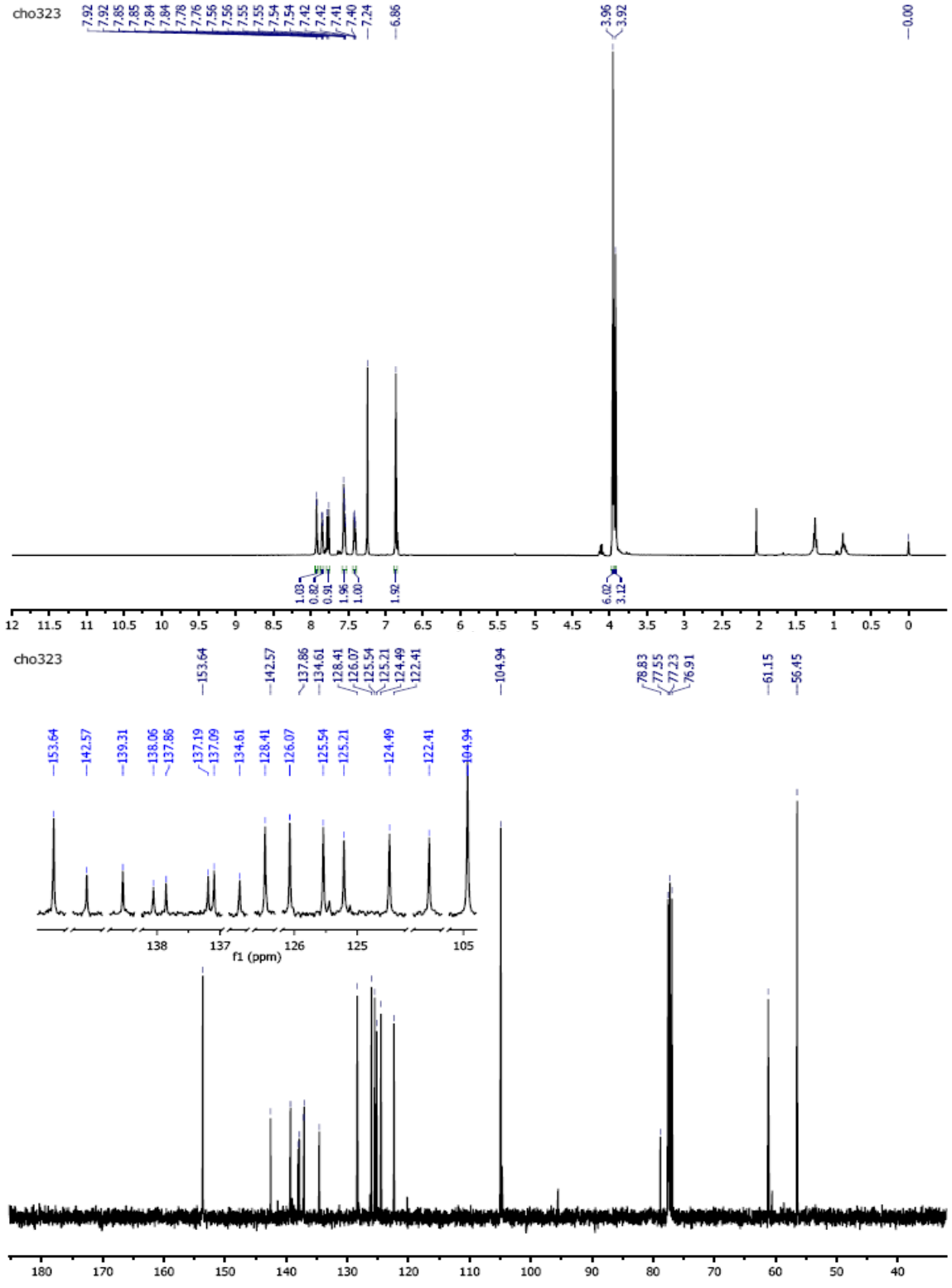
3-Iodobenzo[*b*]thiophene 8{*16*}



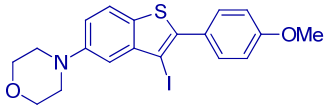


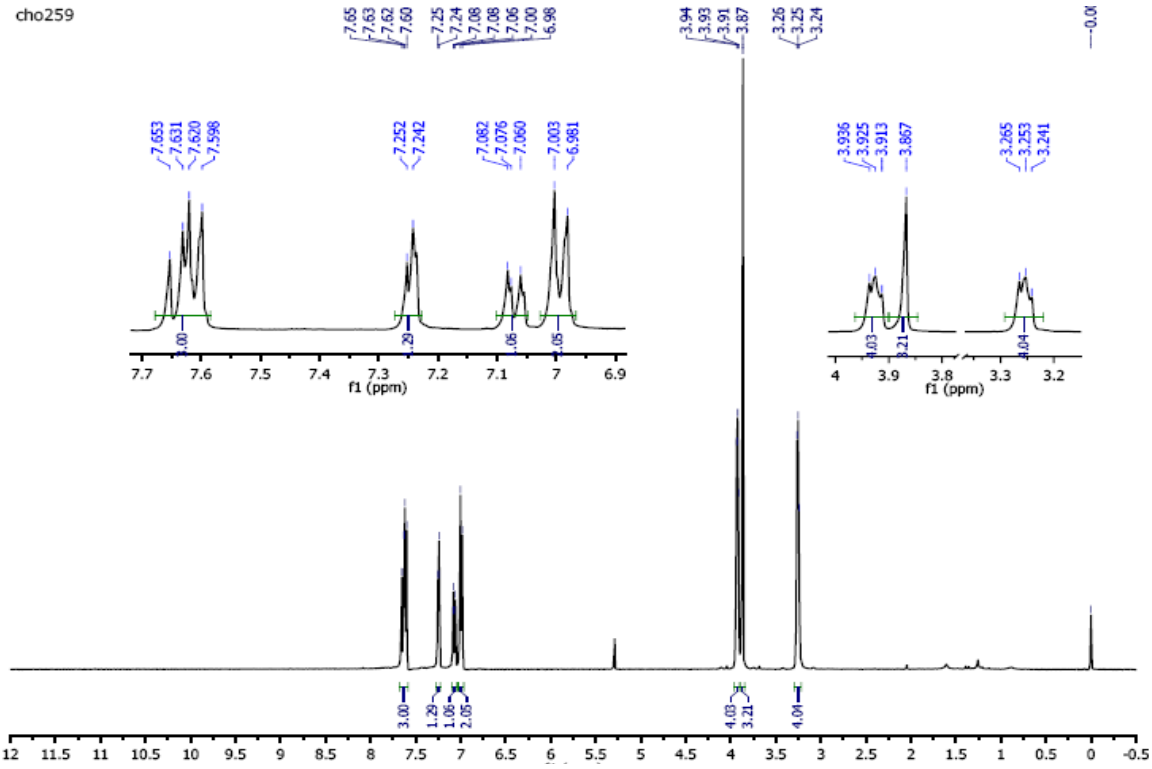
3-Iodobenzo[*b*]thiophene 8{*17*}

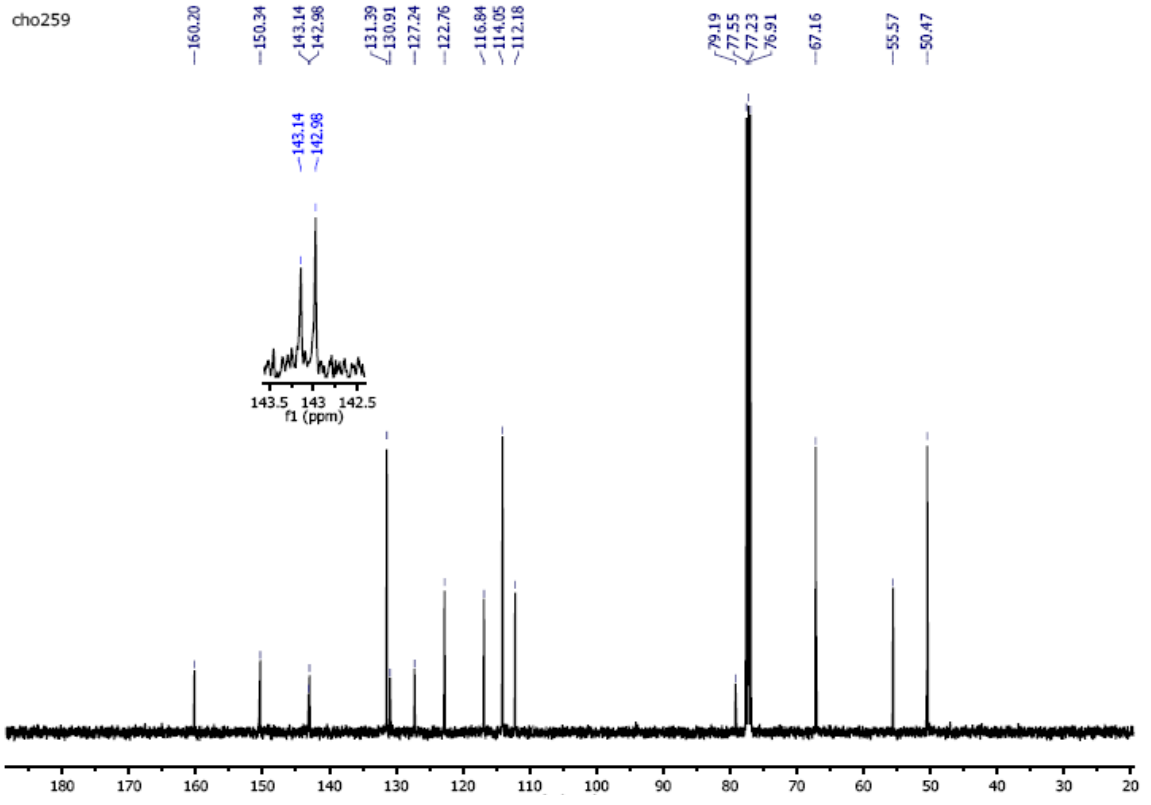




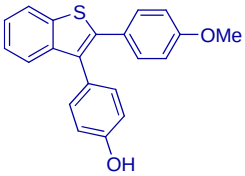
3-Iodobenzo[*b*]thiophene 8{*18*}

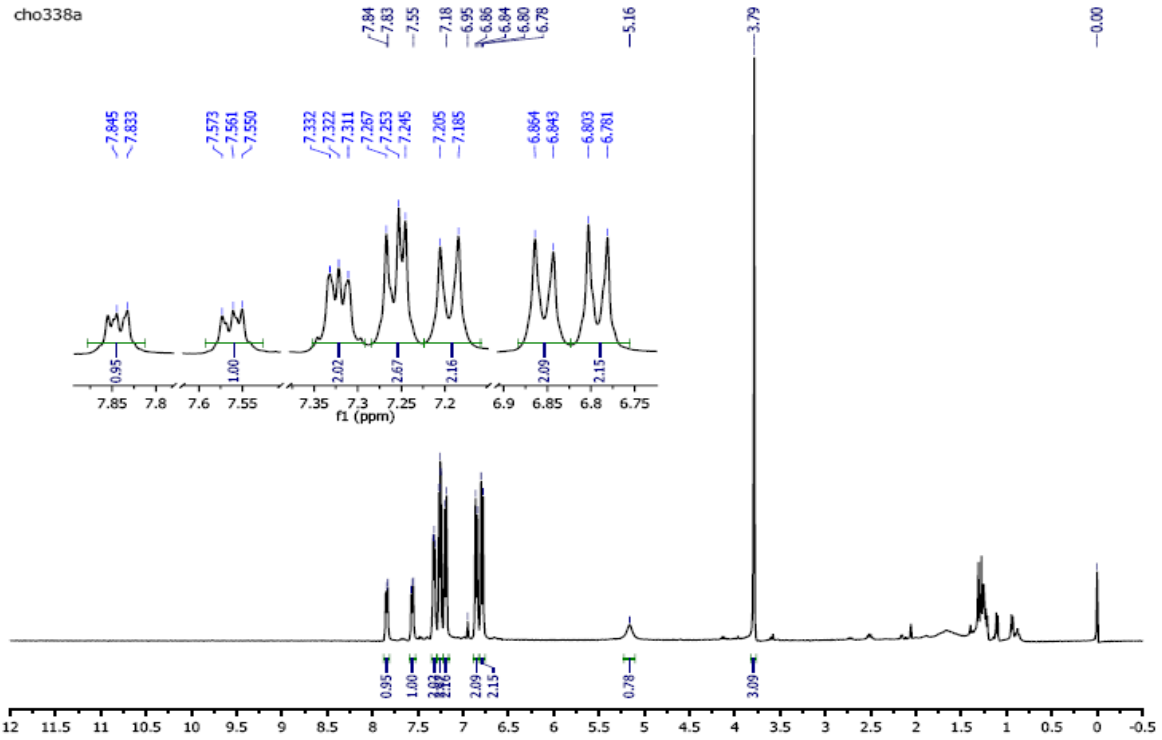


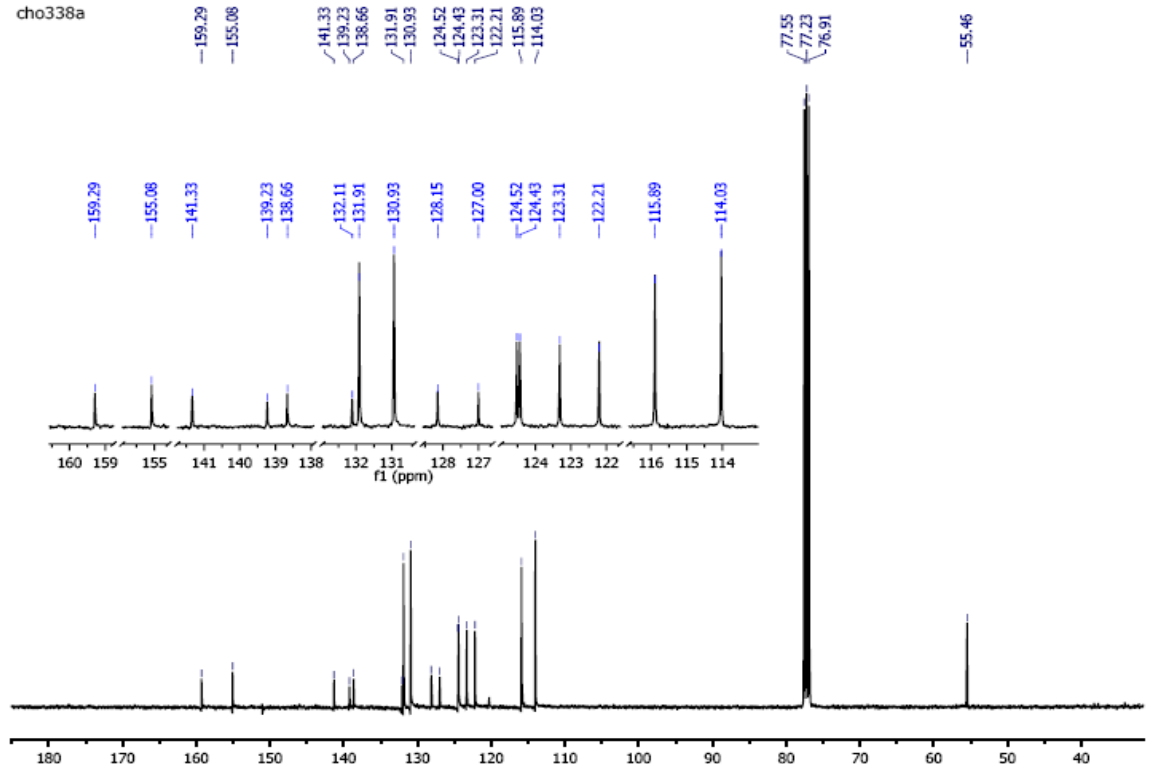




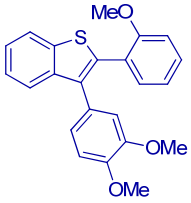
Benzo[*b*]thiophene 13{*1*}

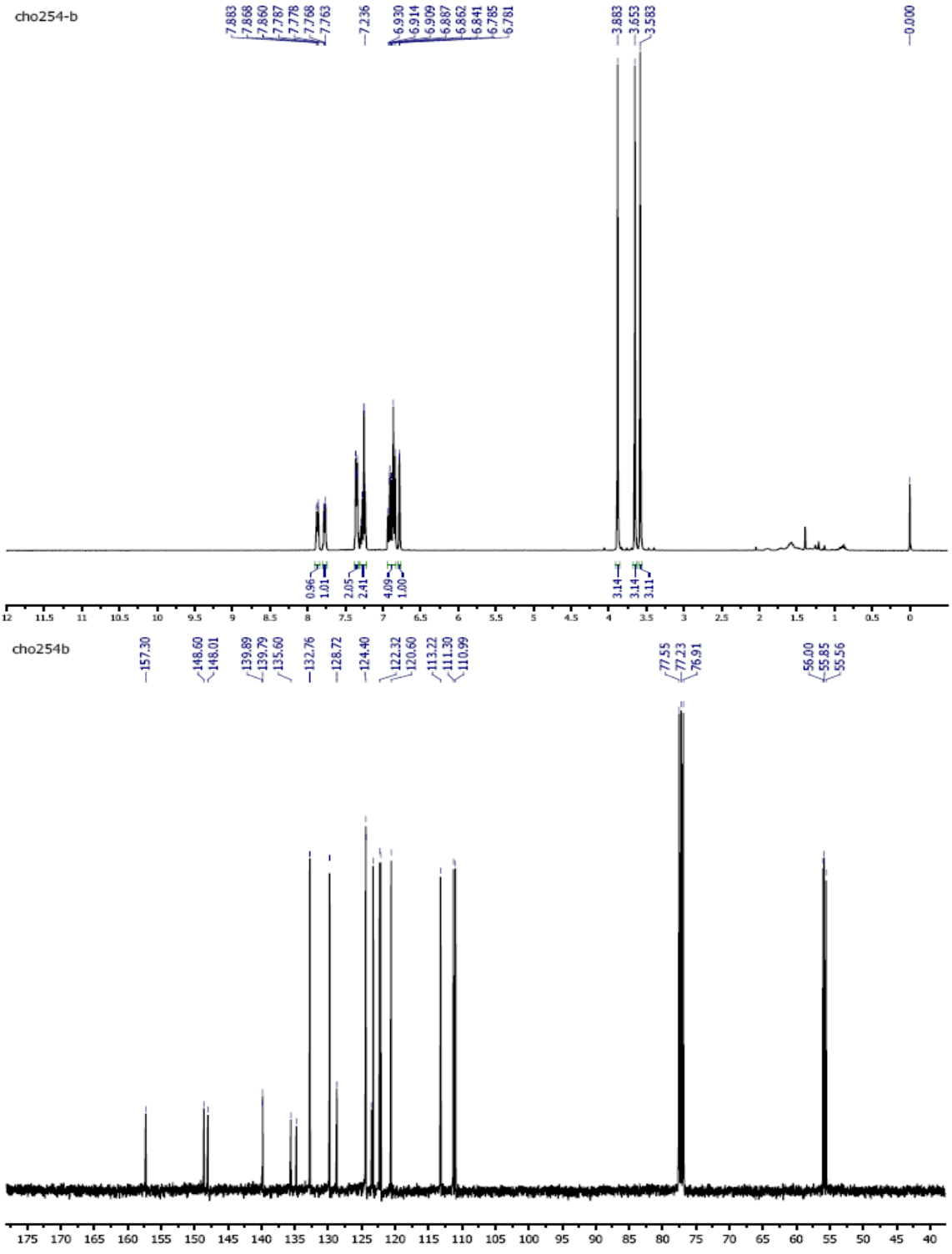




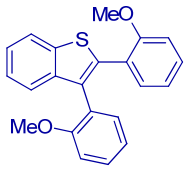


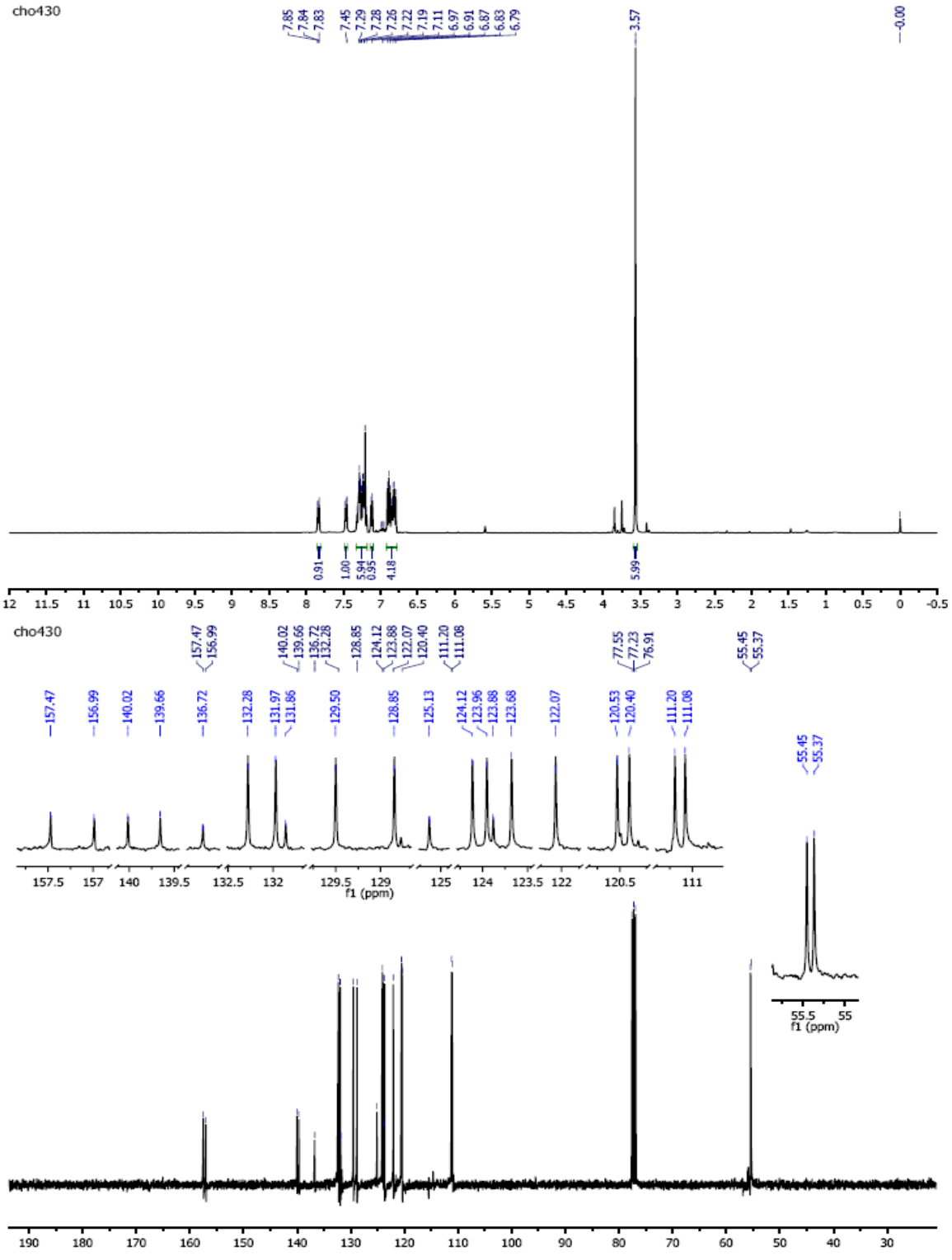
Benzo[*b*]thiophene 13{*6*}



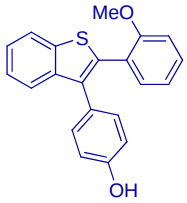


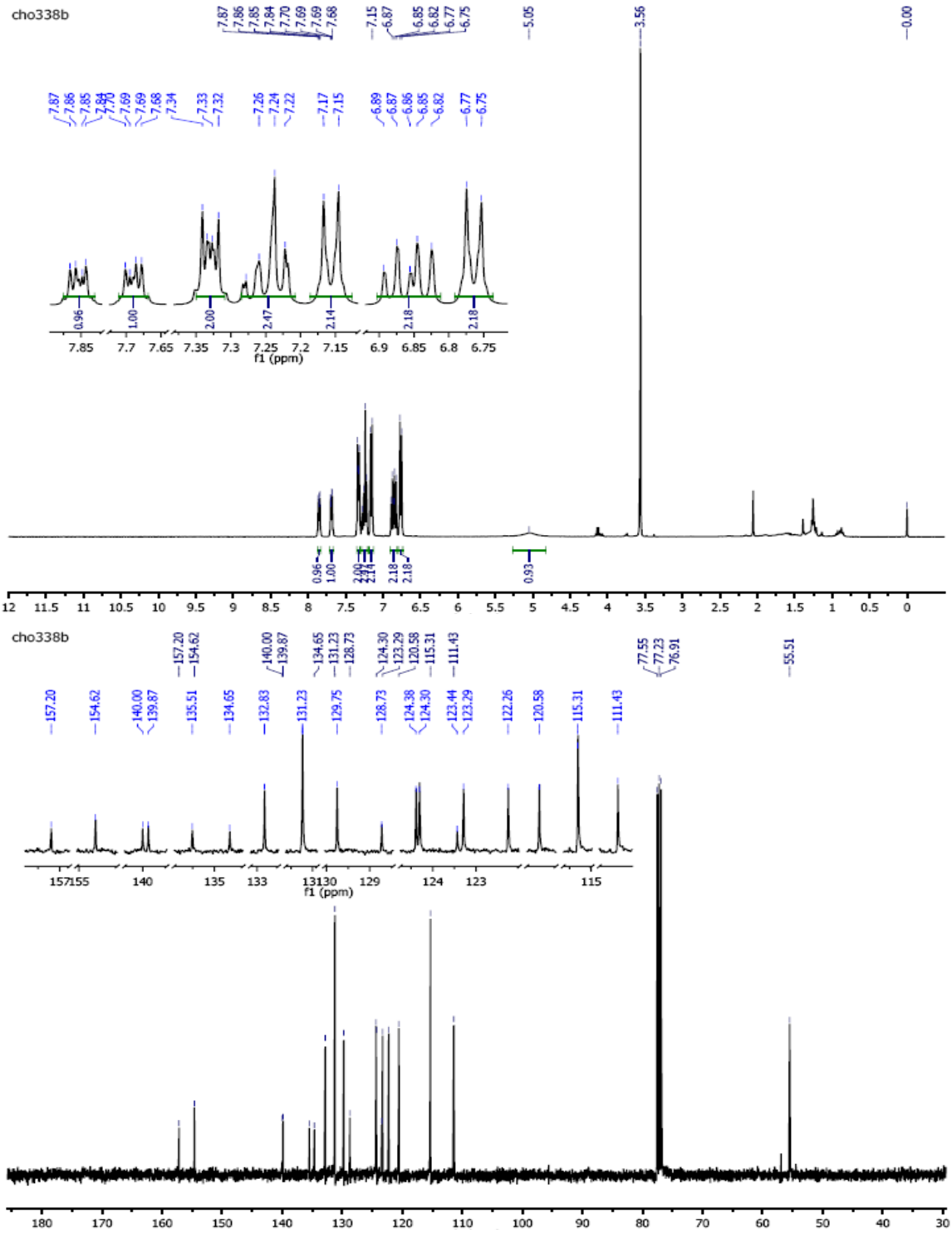
Benzo[*b*]thiophene 13{*7*}



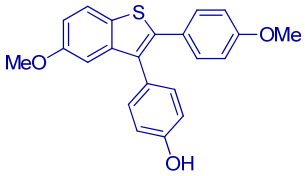


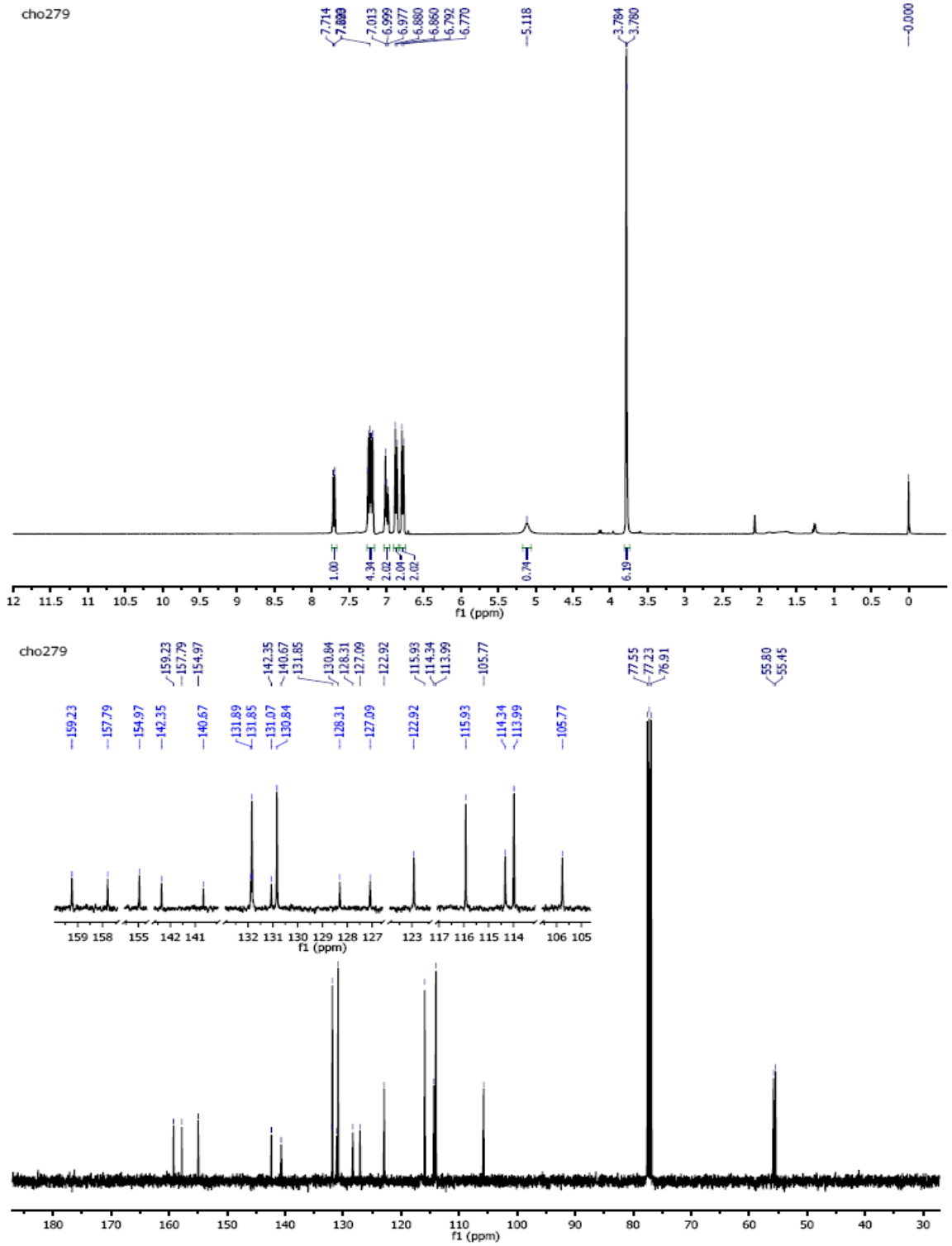
Benzo[*b*]thiophene 13{*11*}



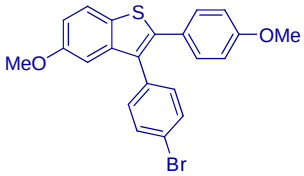


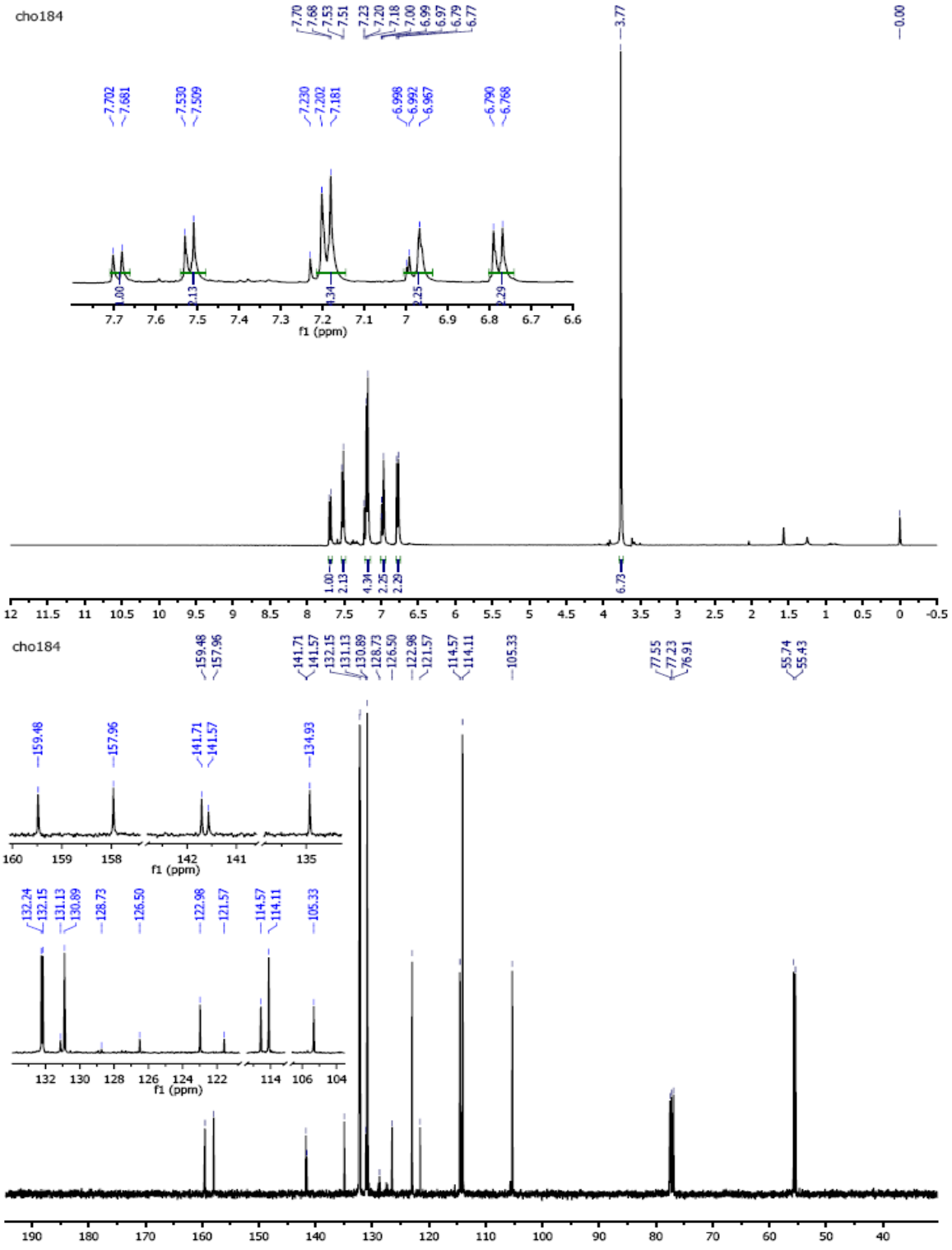
Benzo[*b*]thiophene 13{*20*}



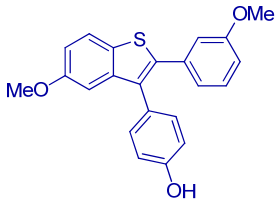


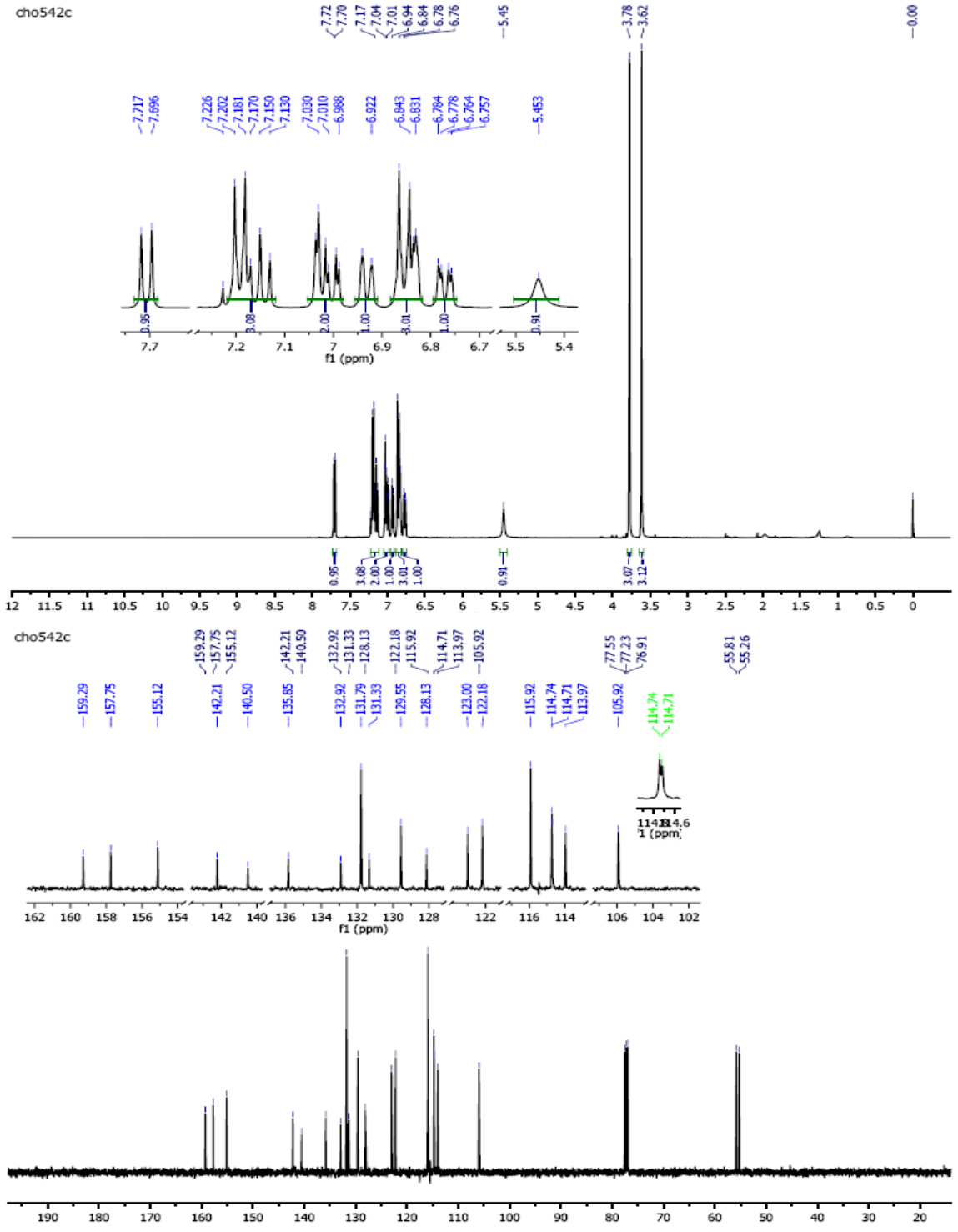
Benzo[*b*]thiophene 13{*23*}



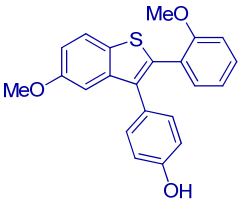


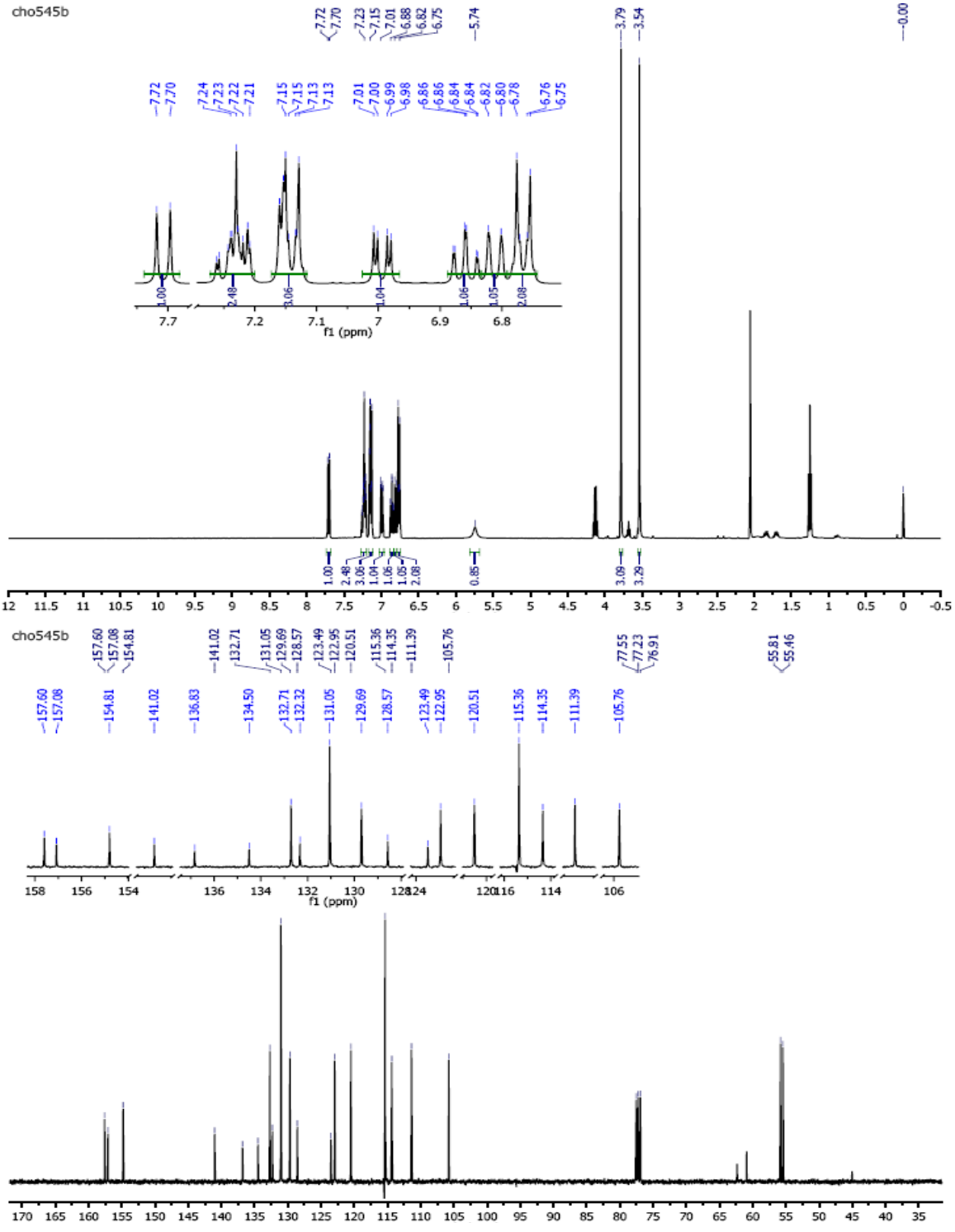
Benzo[*b*]thiophene 13{*25*}



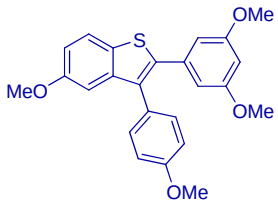


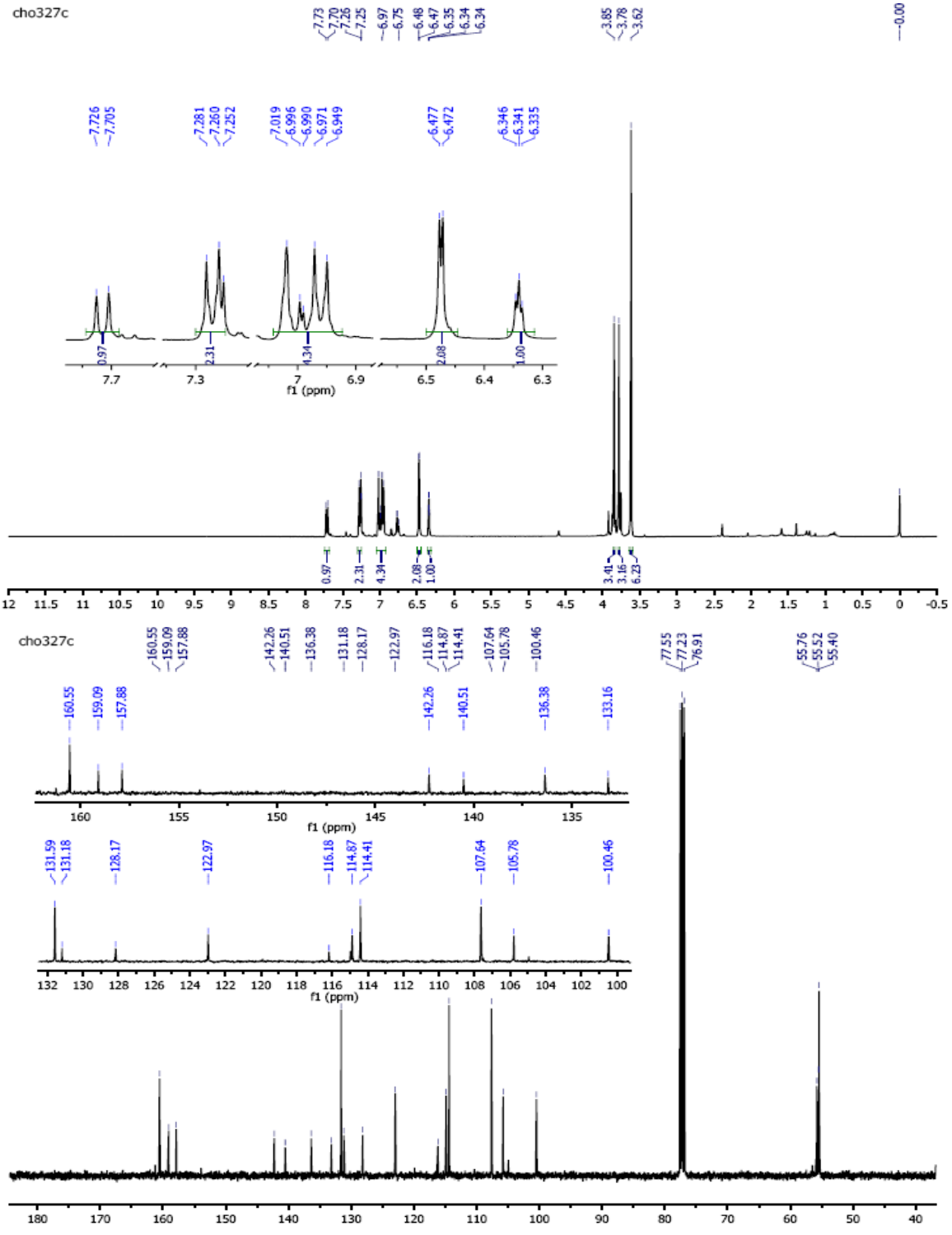
Benzo[*b*]thiophene 13{*31*}



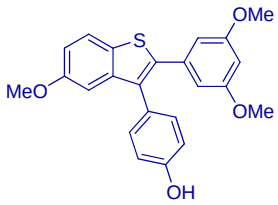


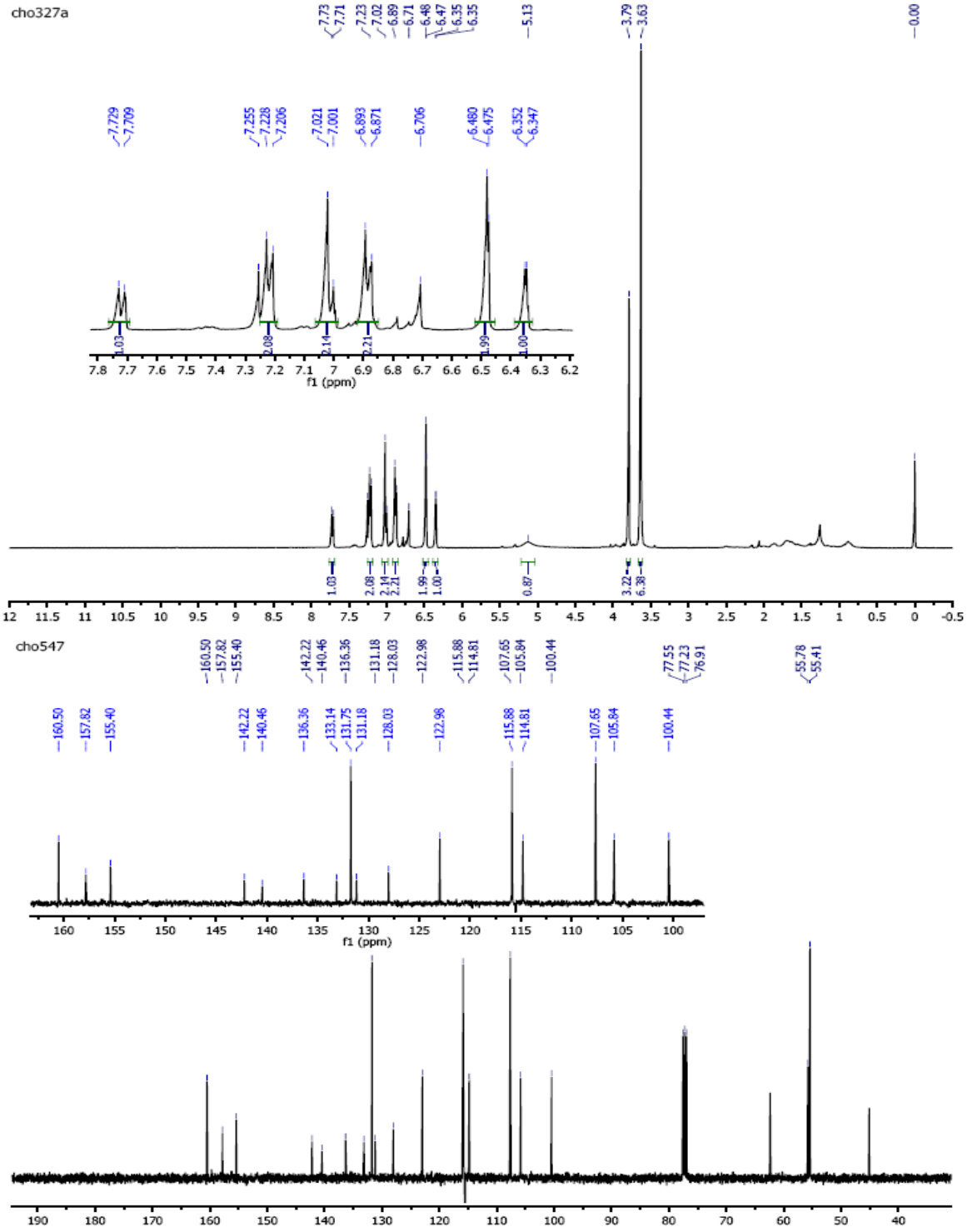
Benzo[*b*]thiophene 13{*36*}



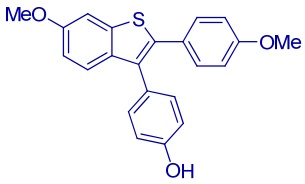


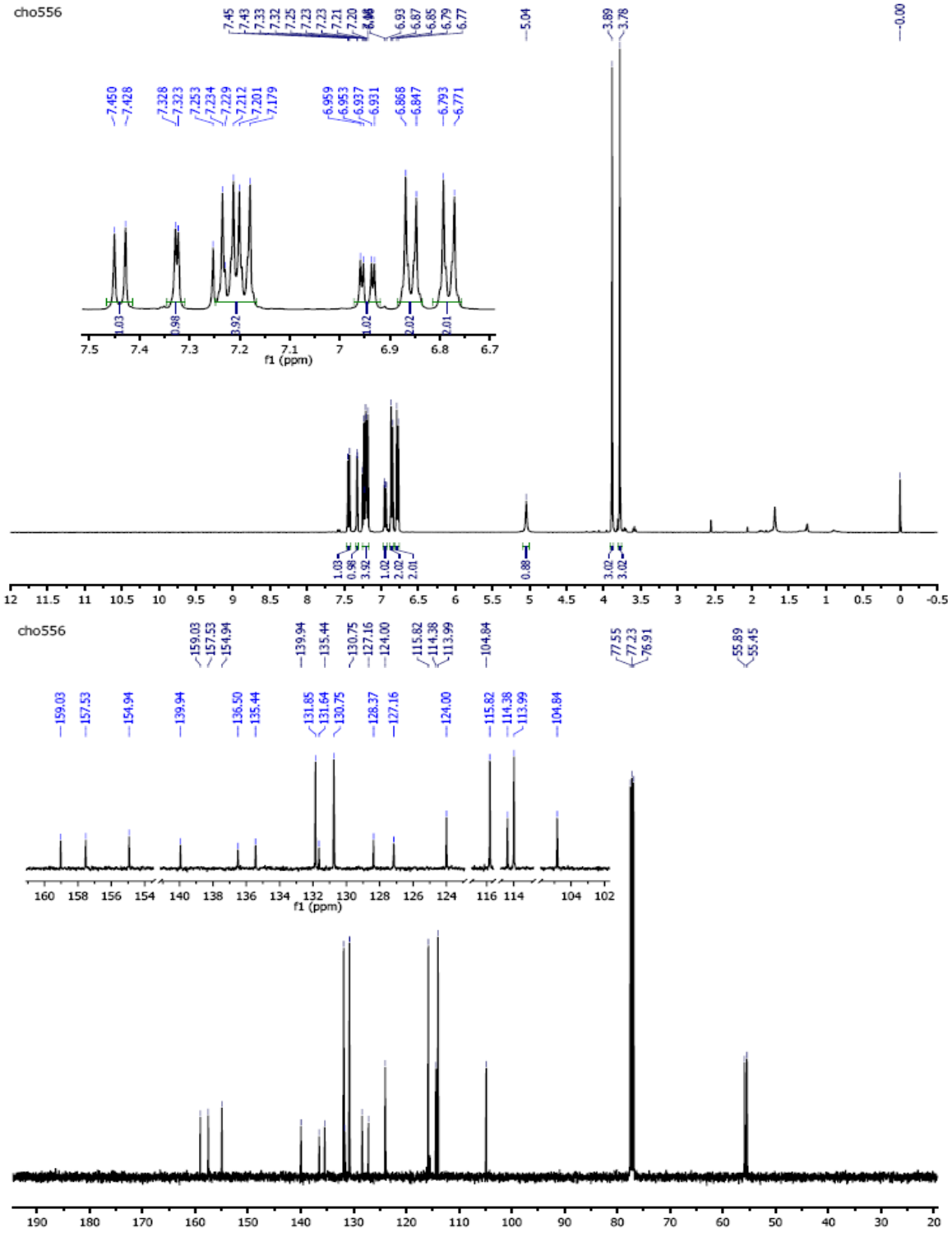
Benzo[*b*]thiophene 13{*37*}



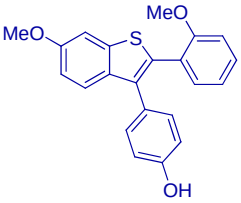


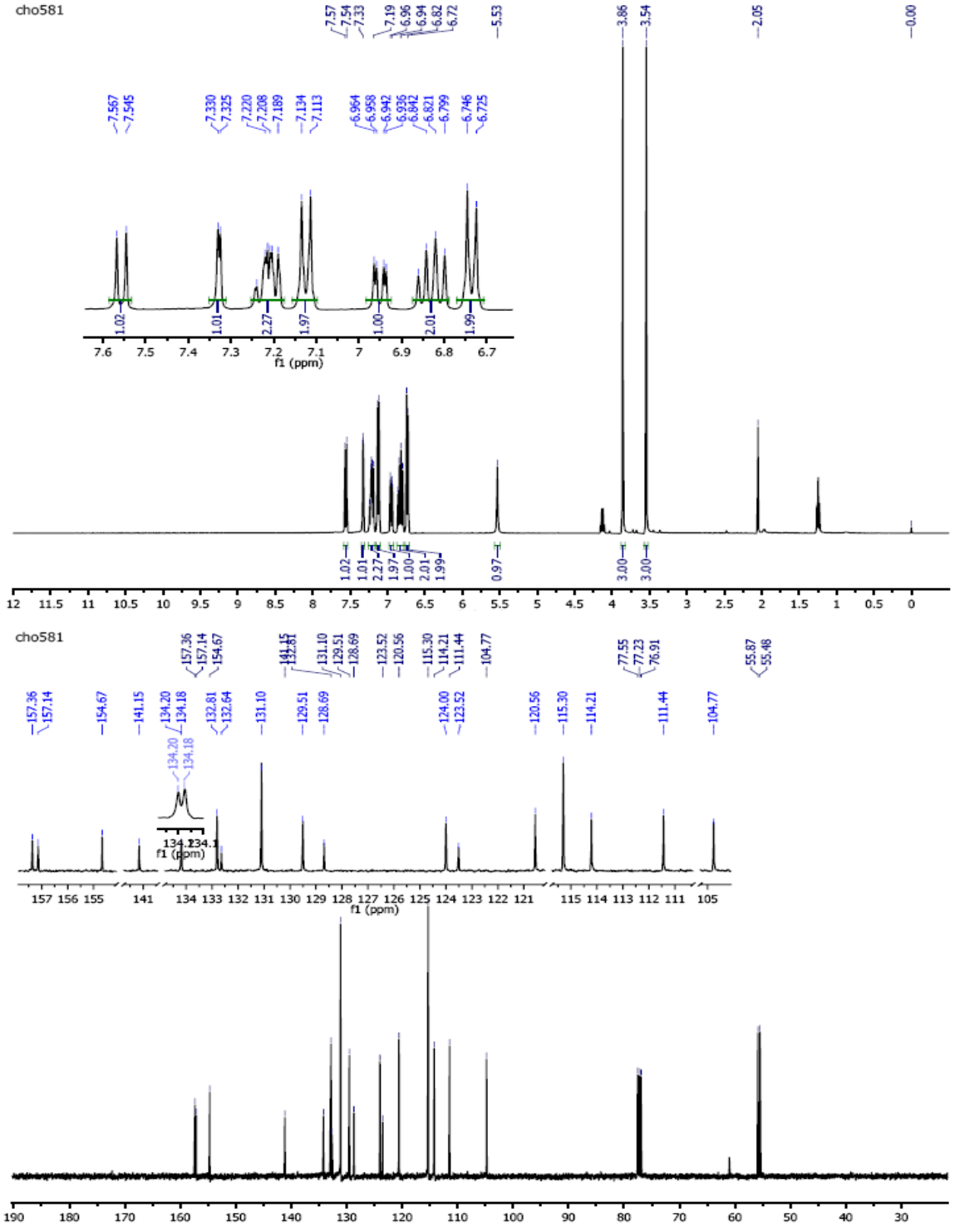
Benzo[*b*]thiophene 13{*42*}



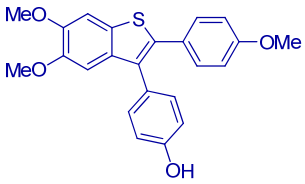


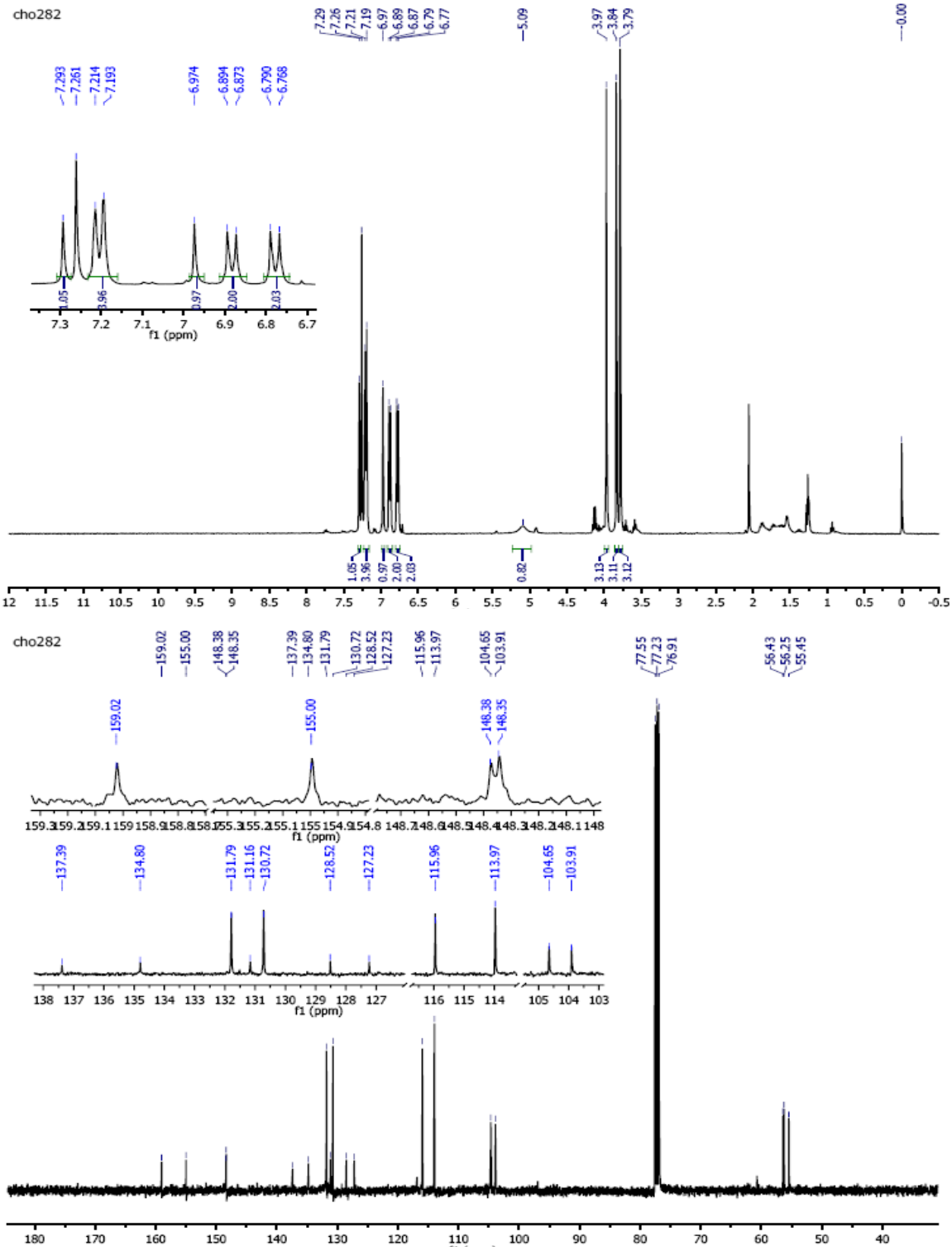
Benzo[*b*]thiophene 13{*47*}



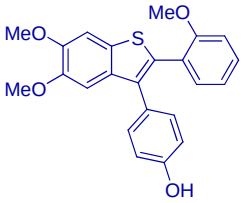


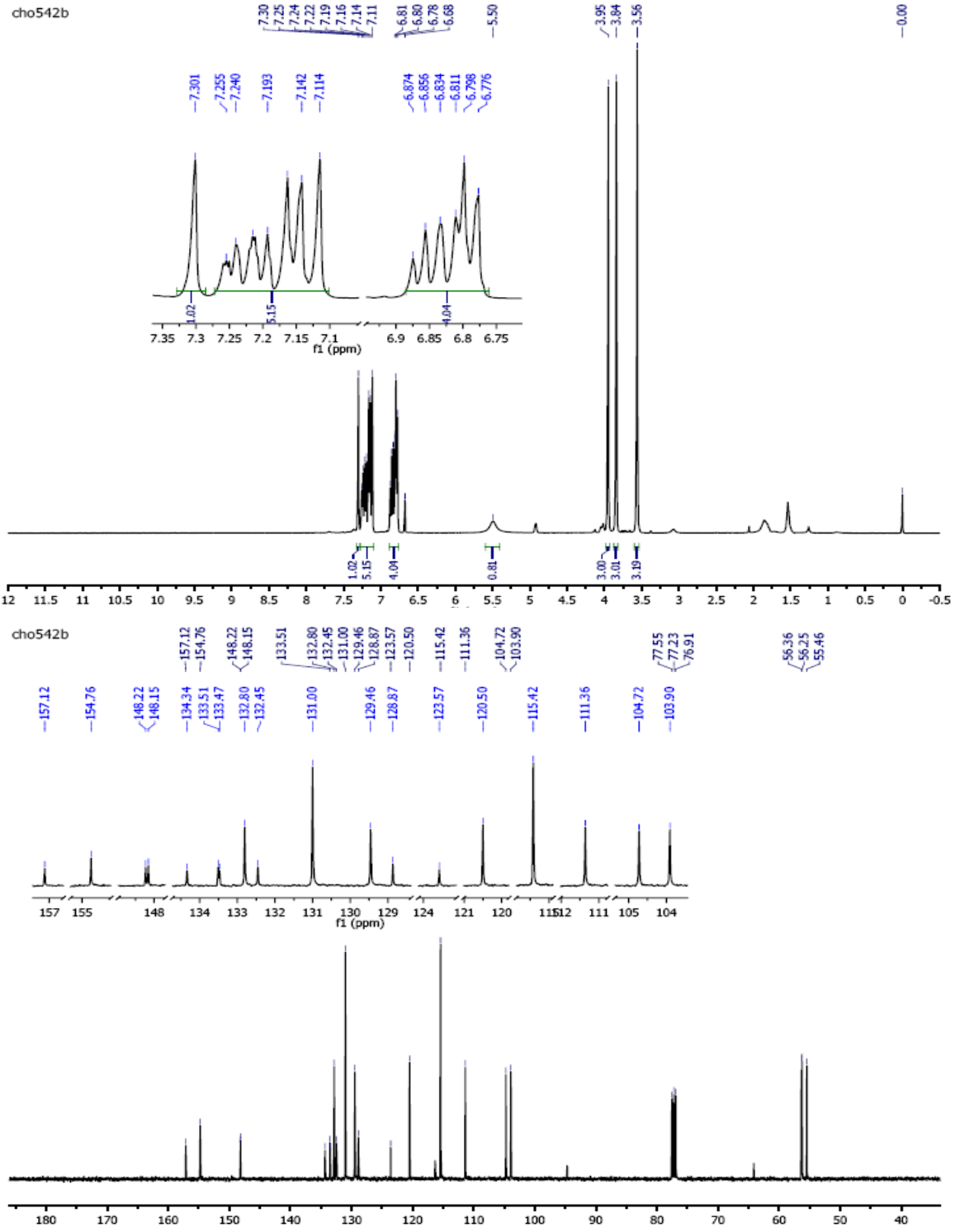
Benzo[*b*]thiophene 13{*49*}



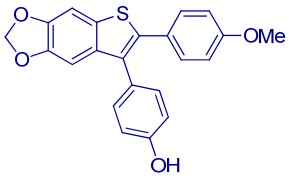


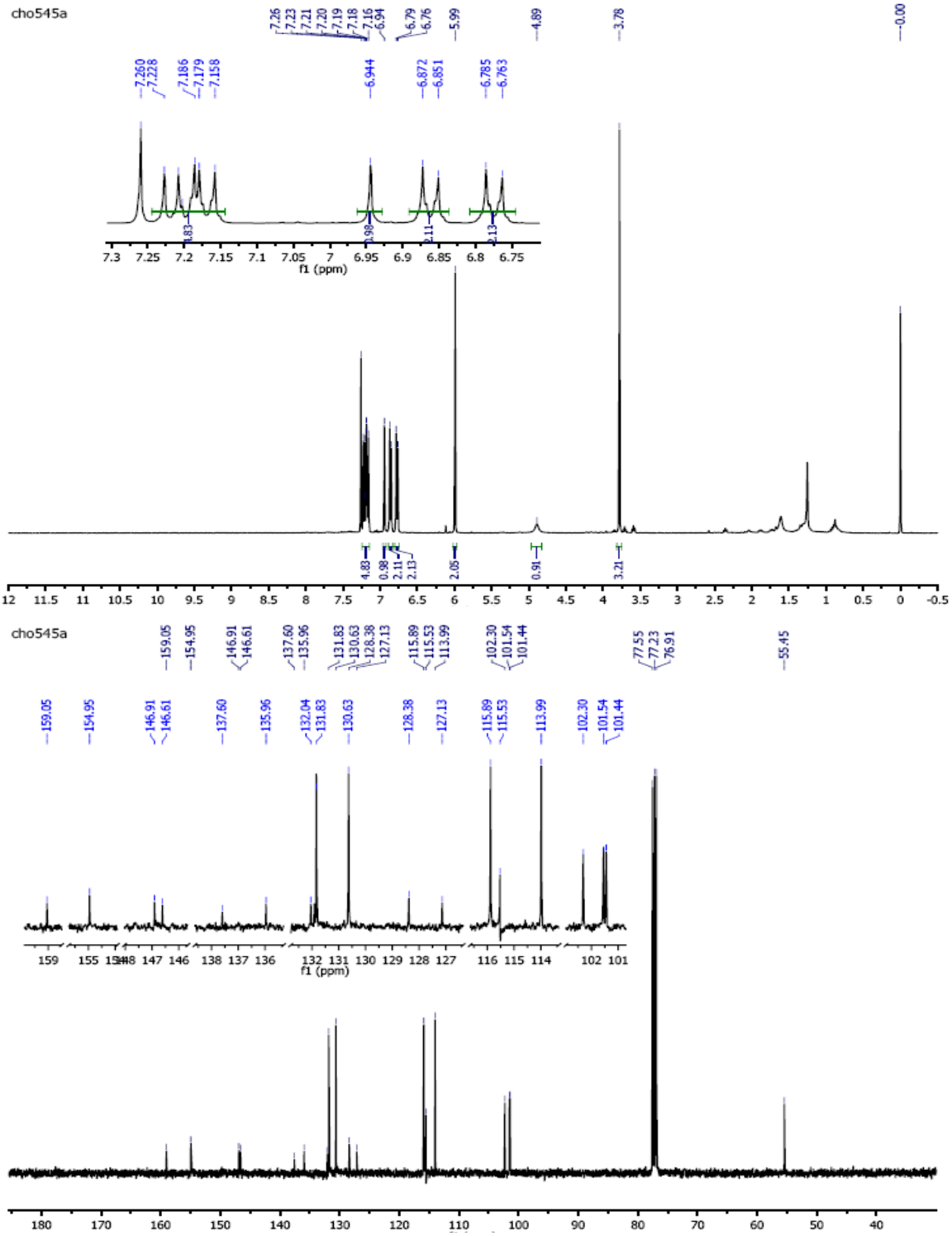
Benzo[*b*]thiophene 13{*51*}



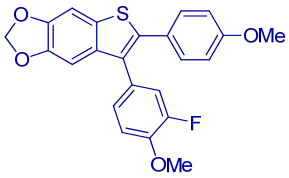


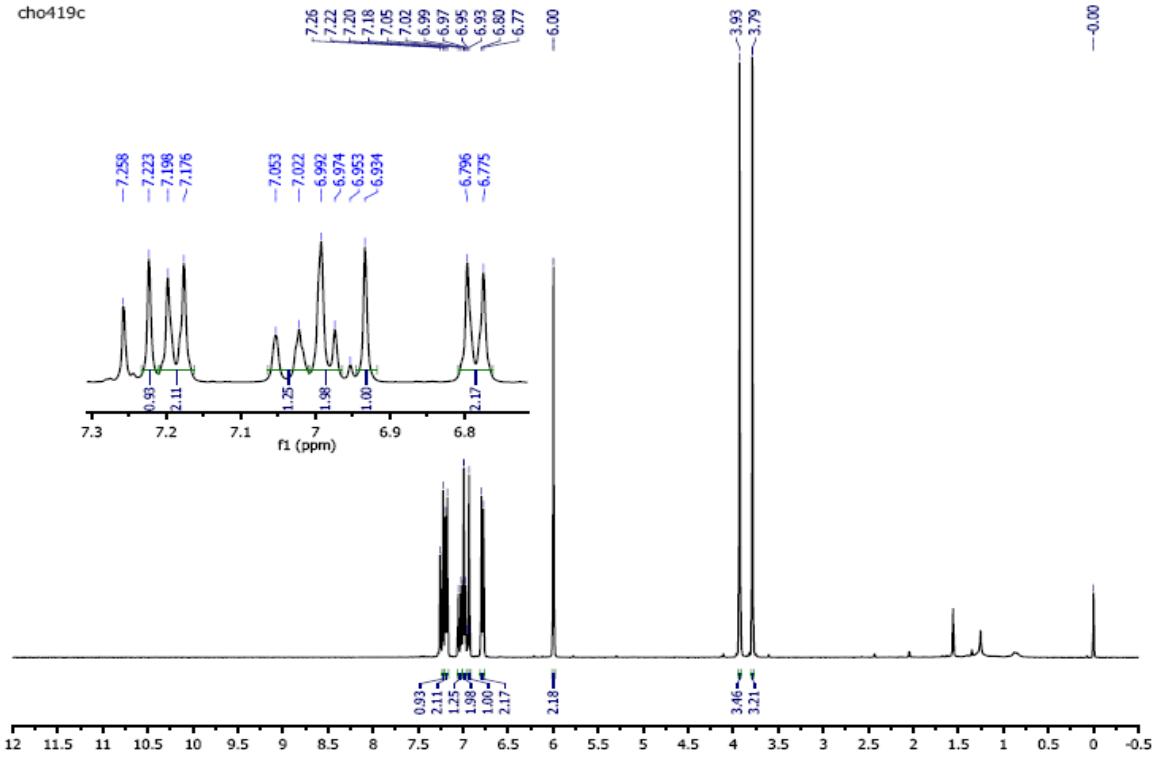
Benzo[*b*]thiophene 13{*55*}

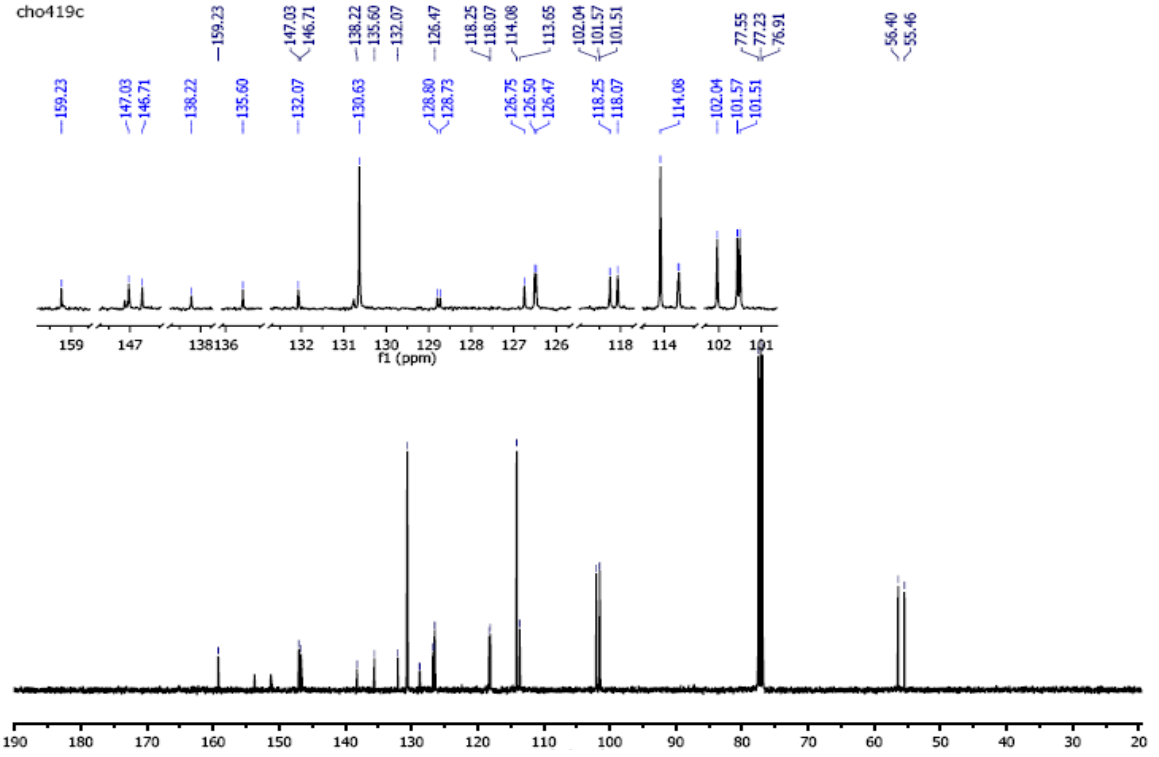




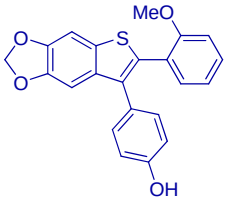
Benzo[*b*]thiophene 13{*56*}

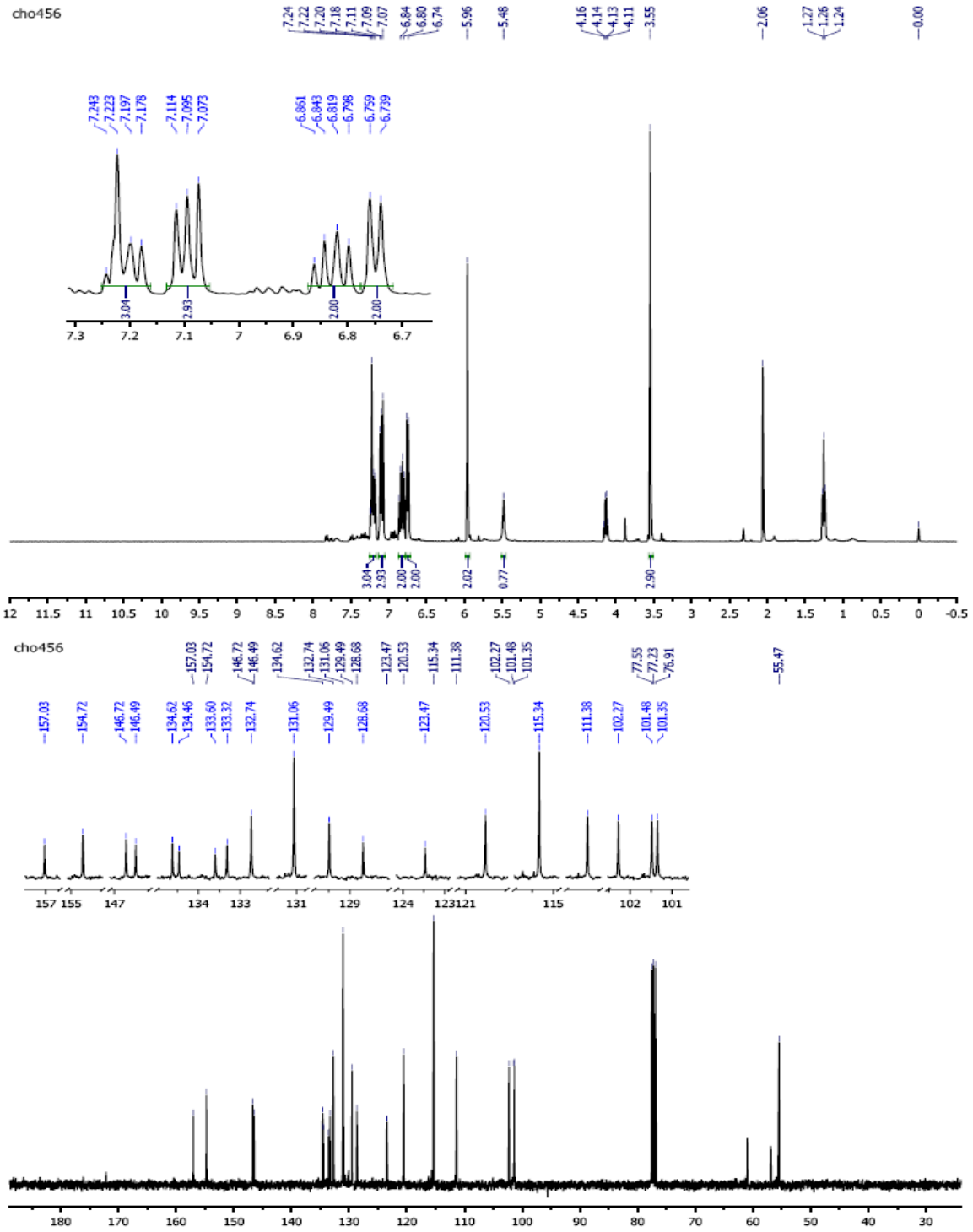




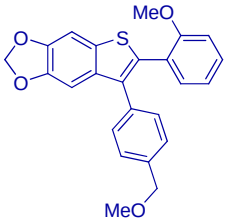


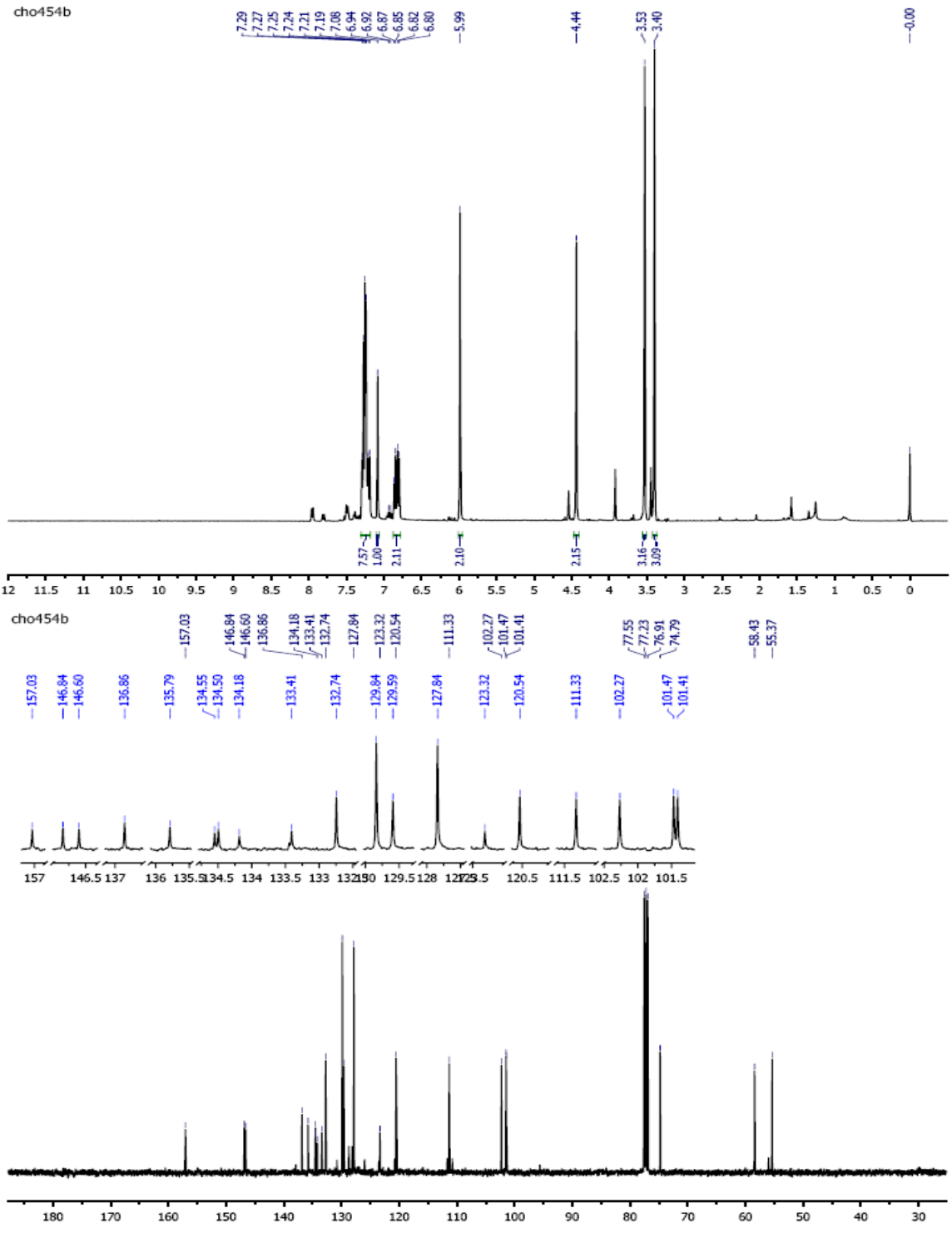
Benzo[*b*]thiophene 13{*59*}



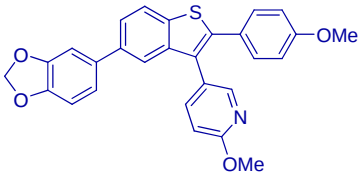


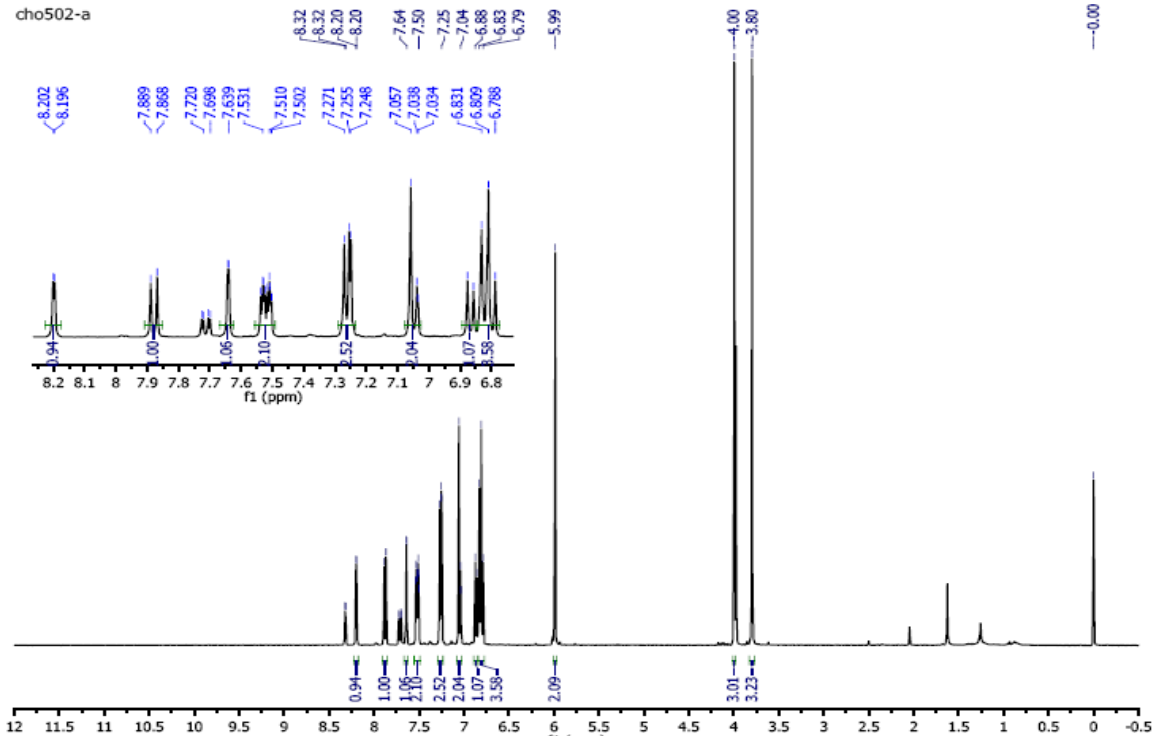
Benzo[*b*]thiophene 13{*60*}

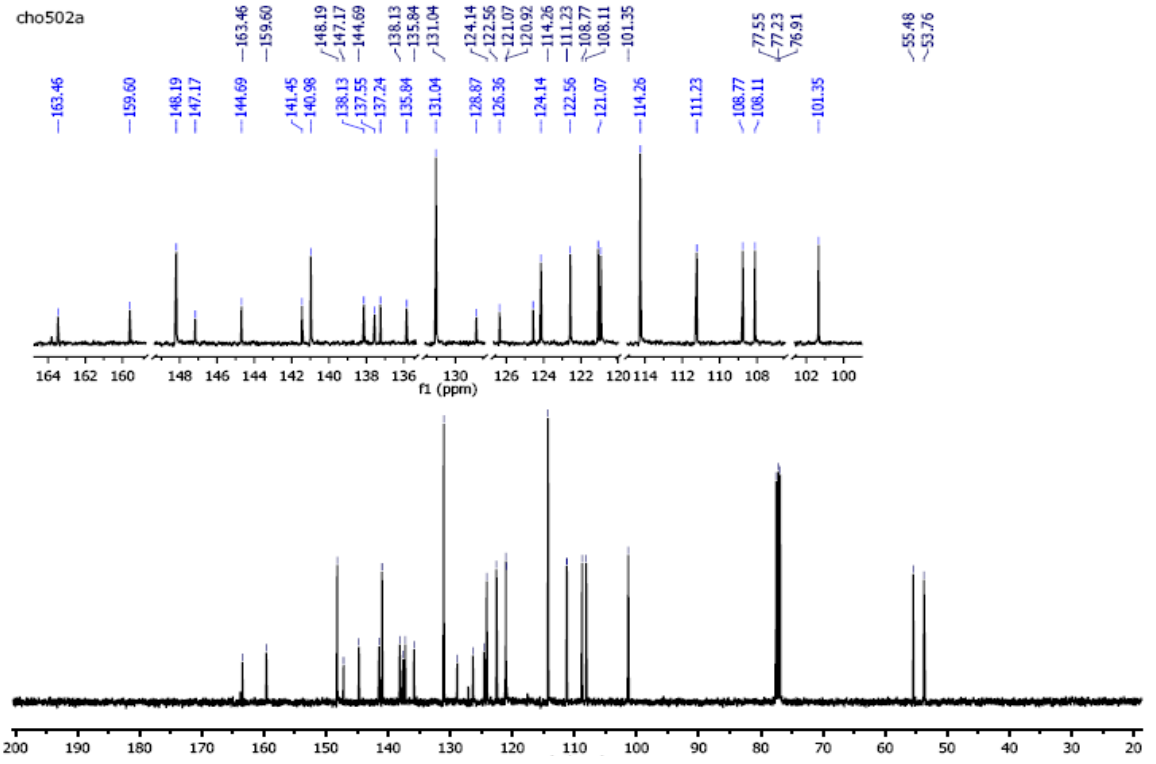




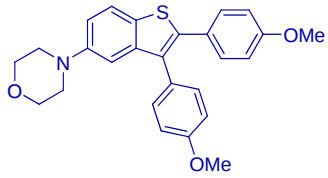
Benzo[*b*]thiophene 13{*63*}

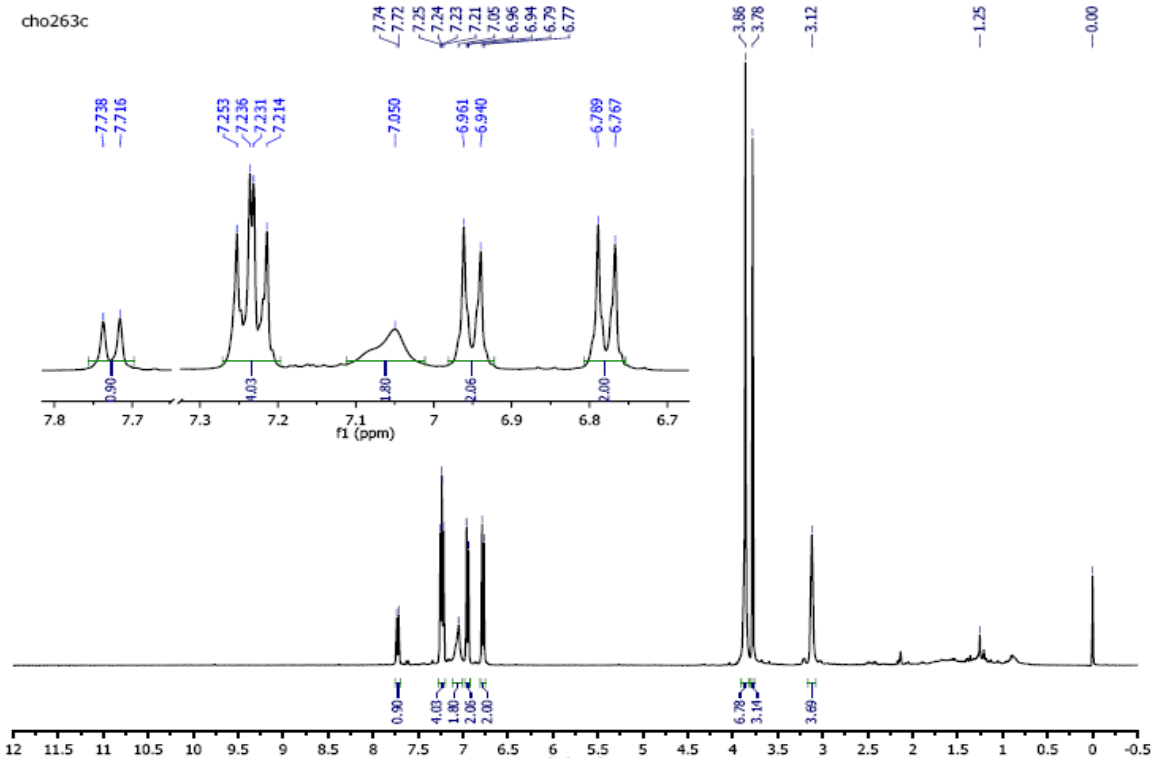


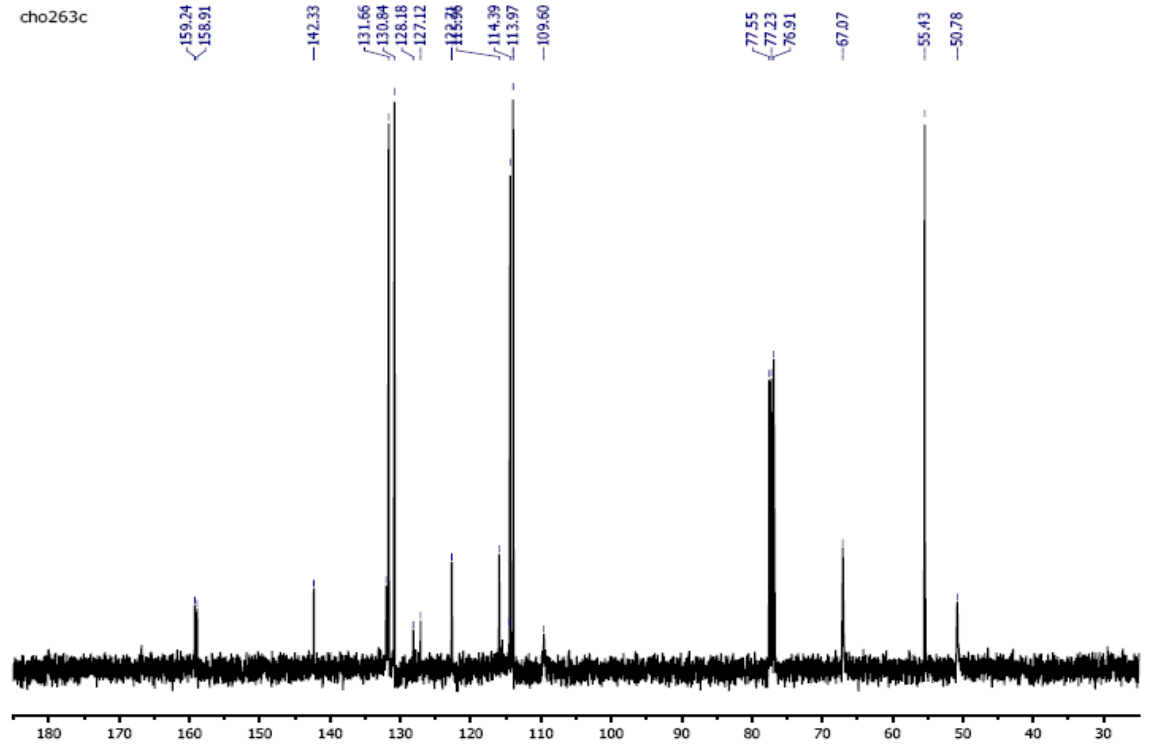




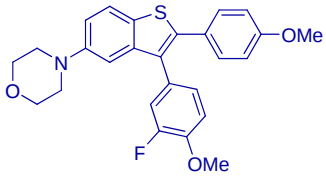
Benzo[*b*]thiophene 13{*64*}

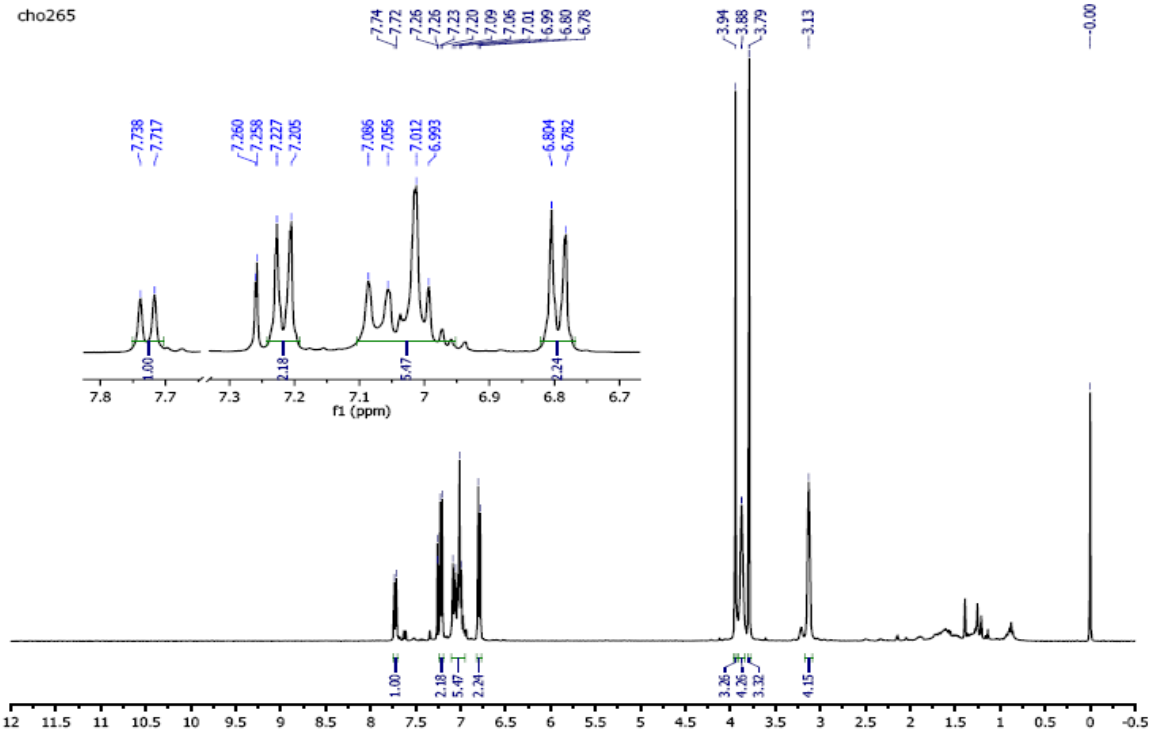


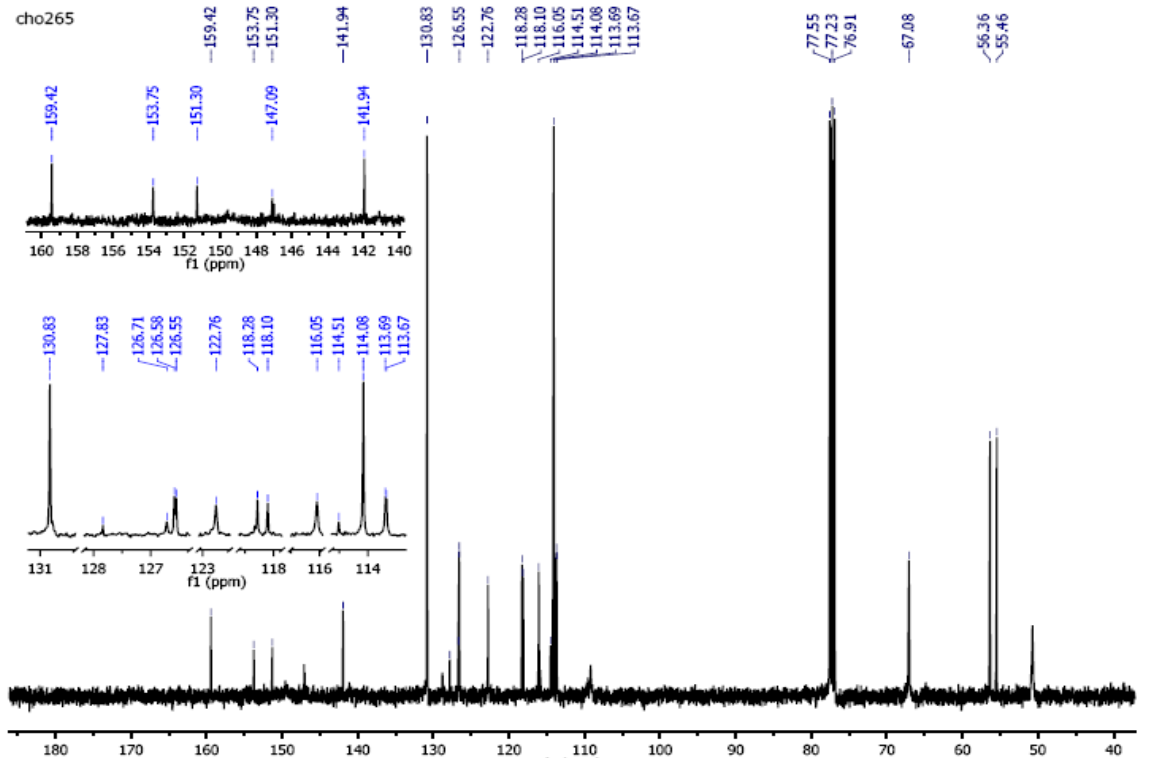




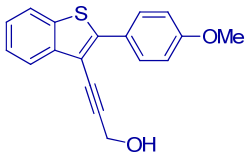
Benzo[*b*]thiophene 13{*66*}

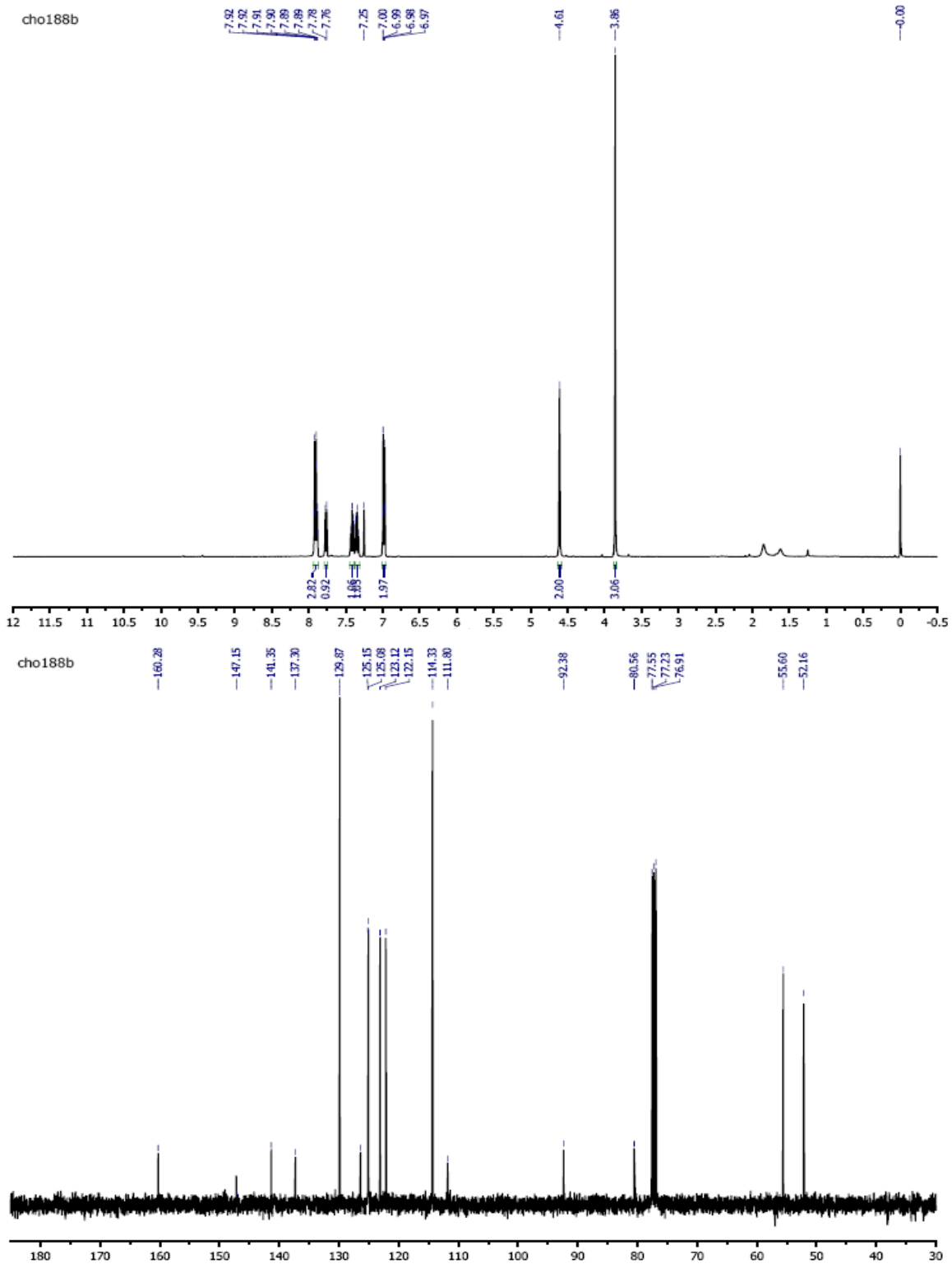




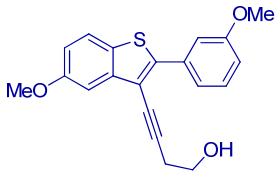


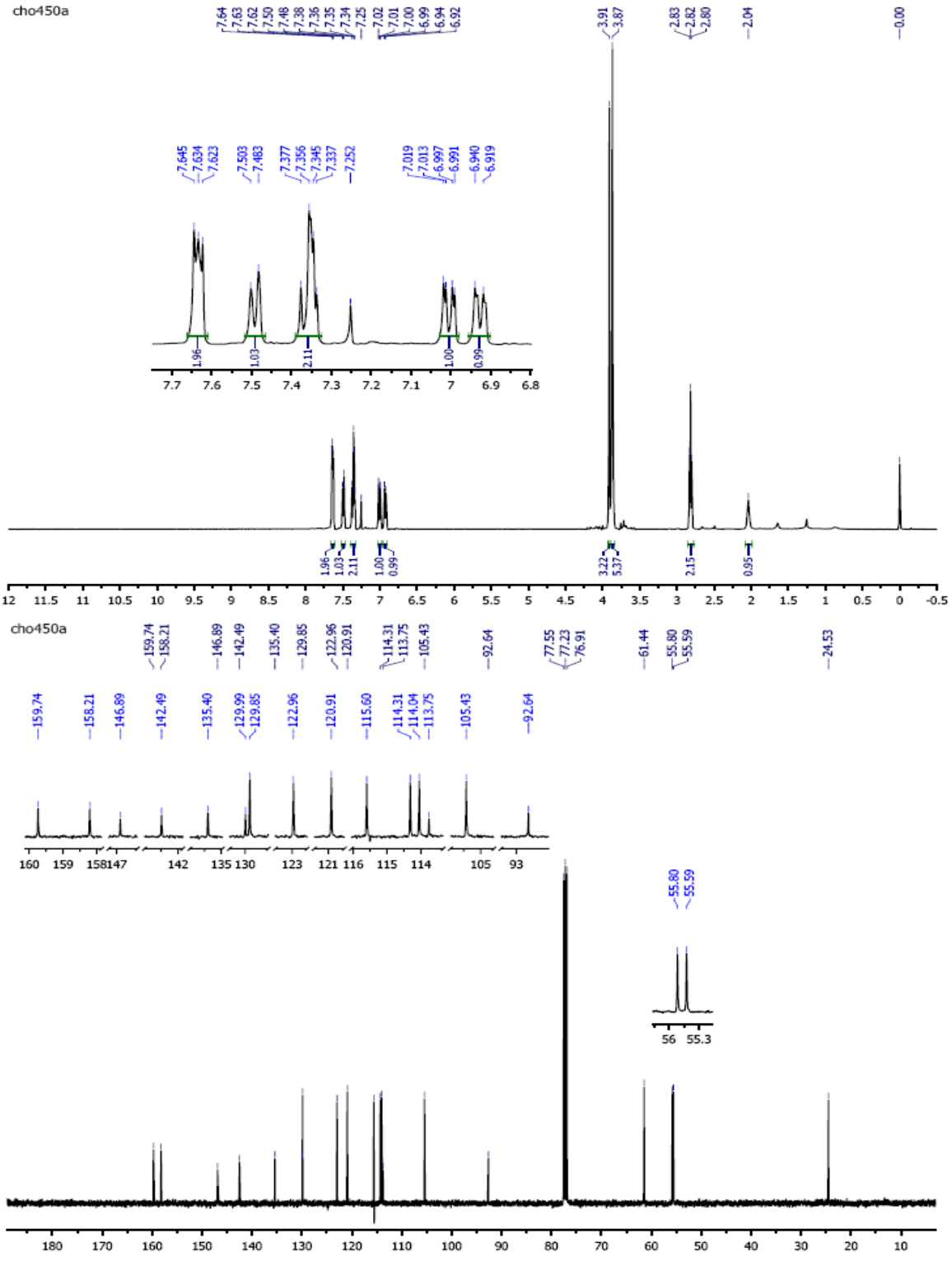
Benzo[*b*]thiophene 13{*69*}



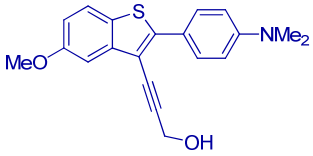


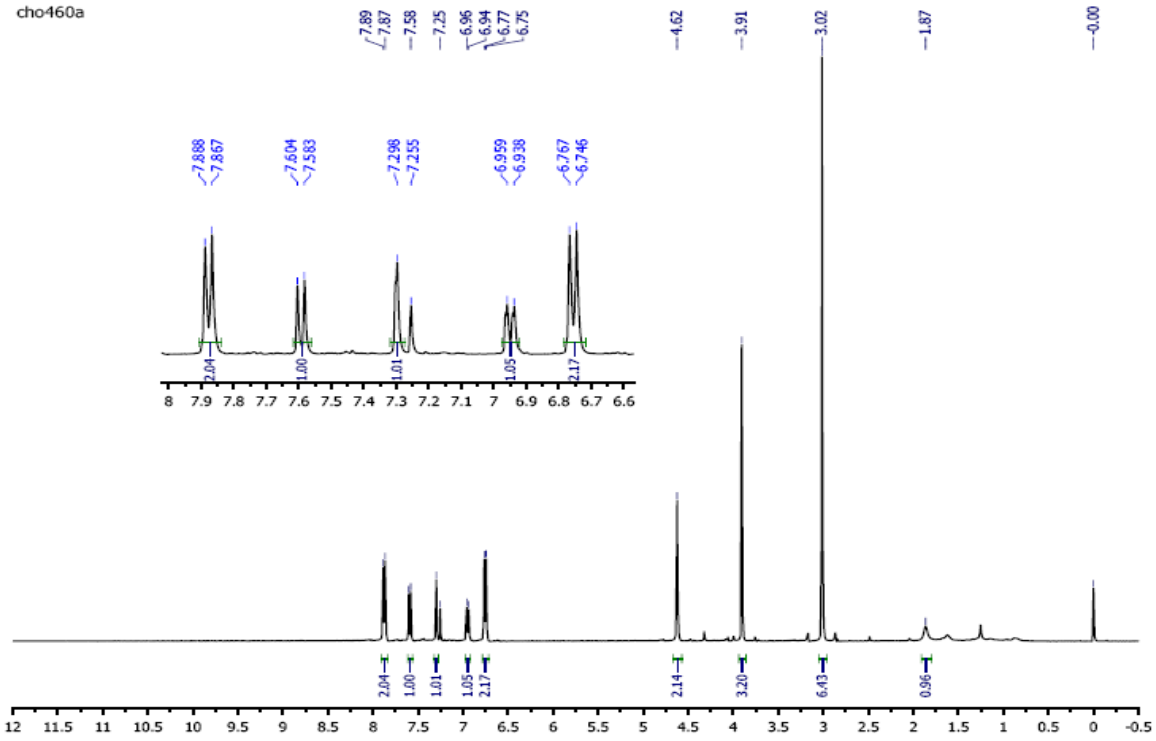
Benzo[*b*]thiophene 13{*90*}

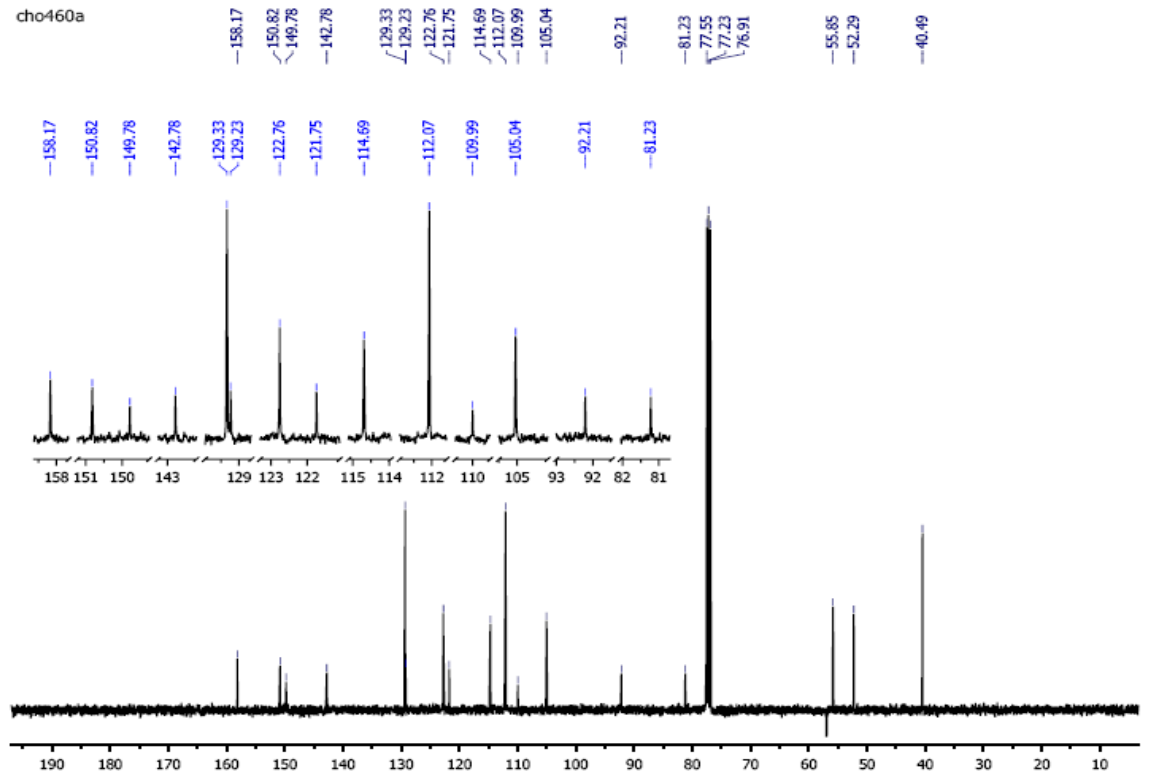




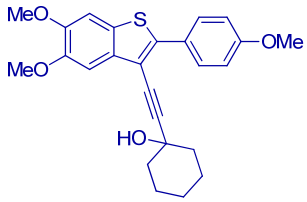
Benzo[*b*]thiophene 13{*102*}

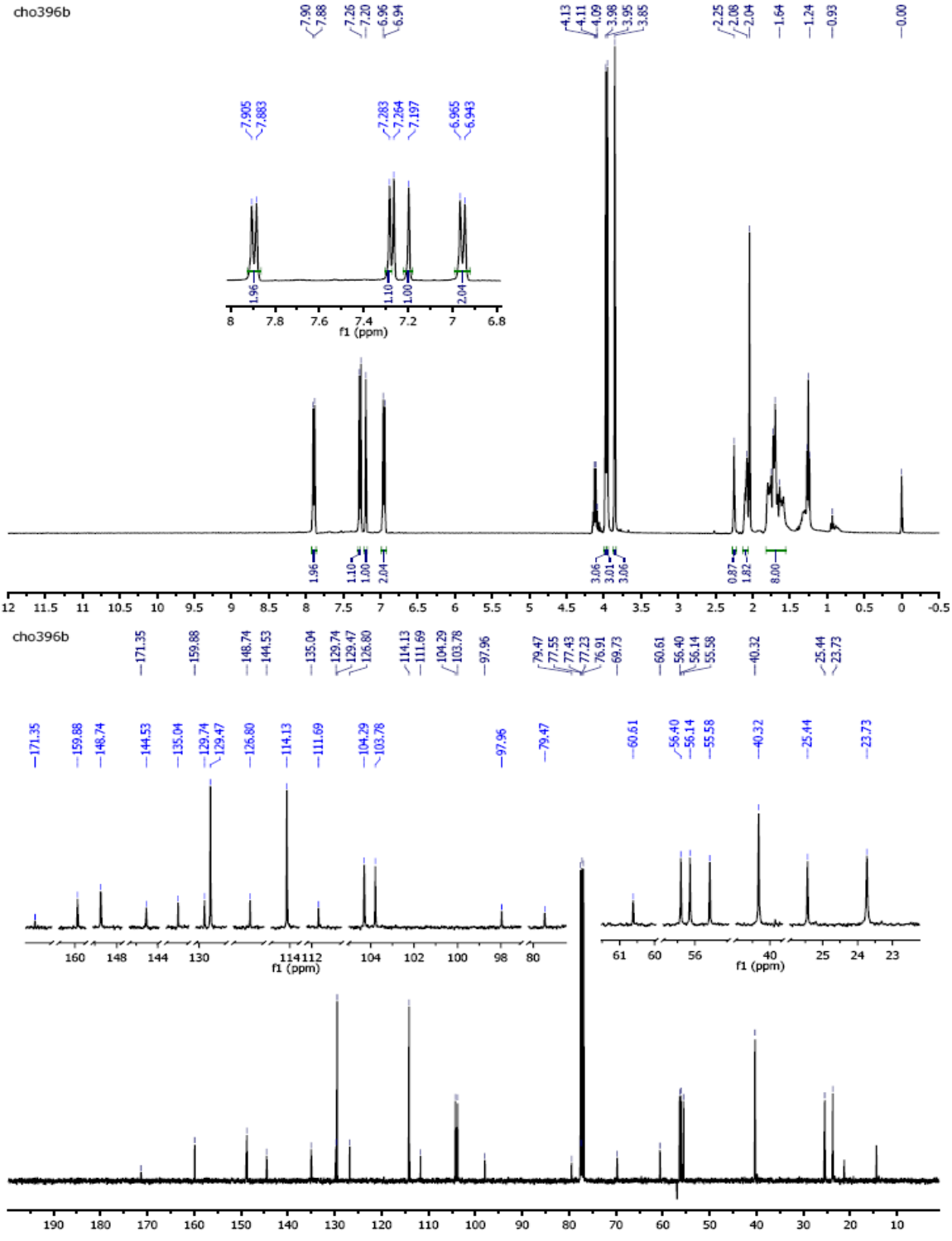




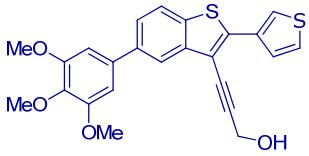


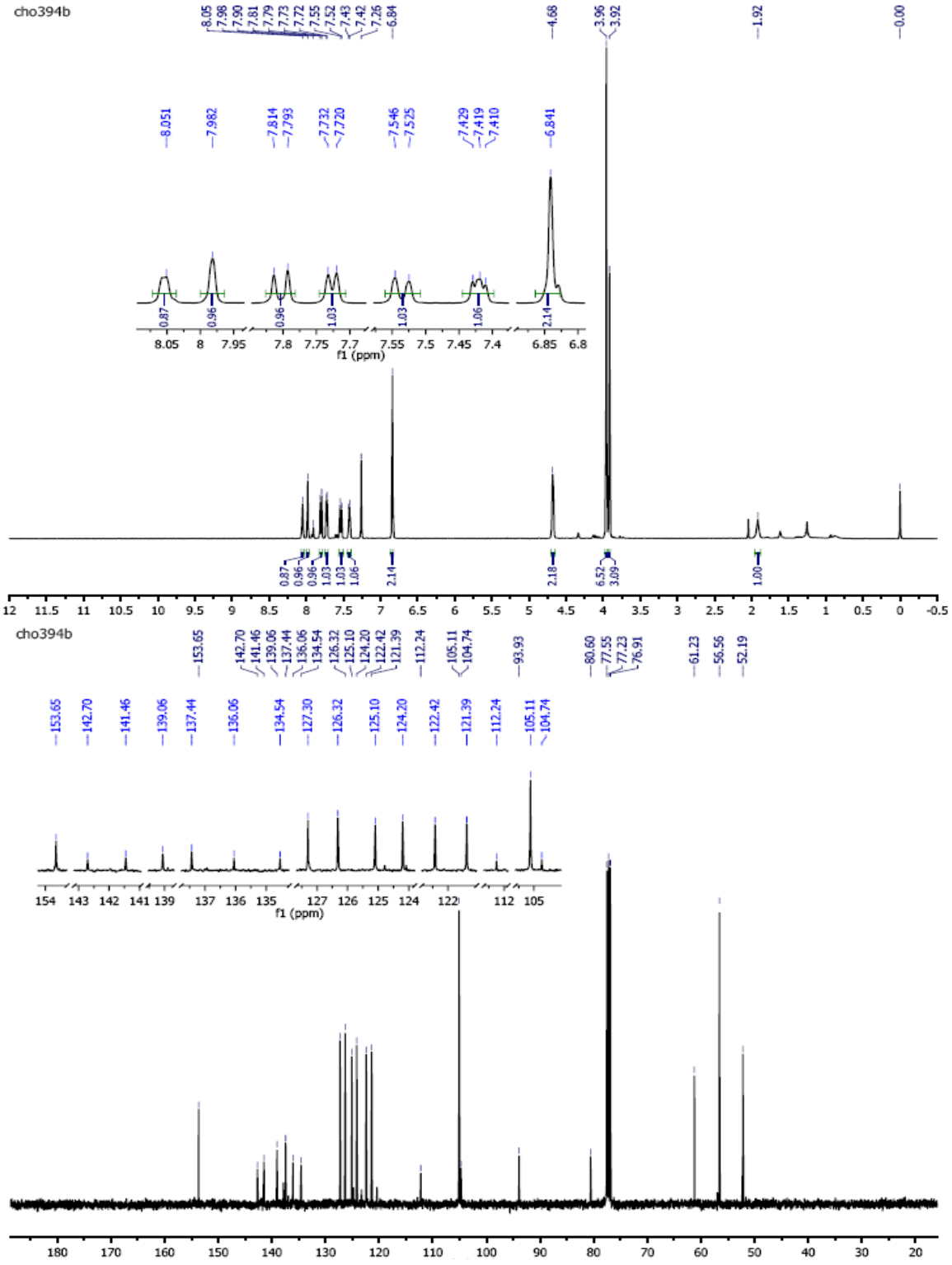
Benzo[*b*]thiophene 13{*114*}



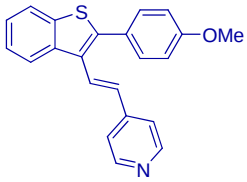


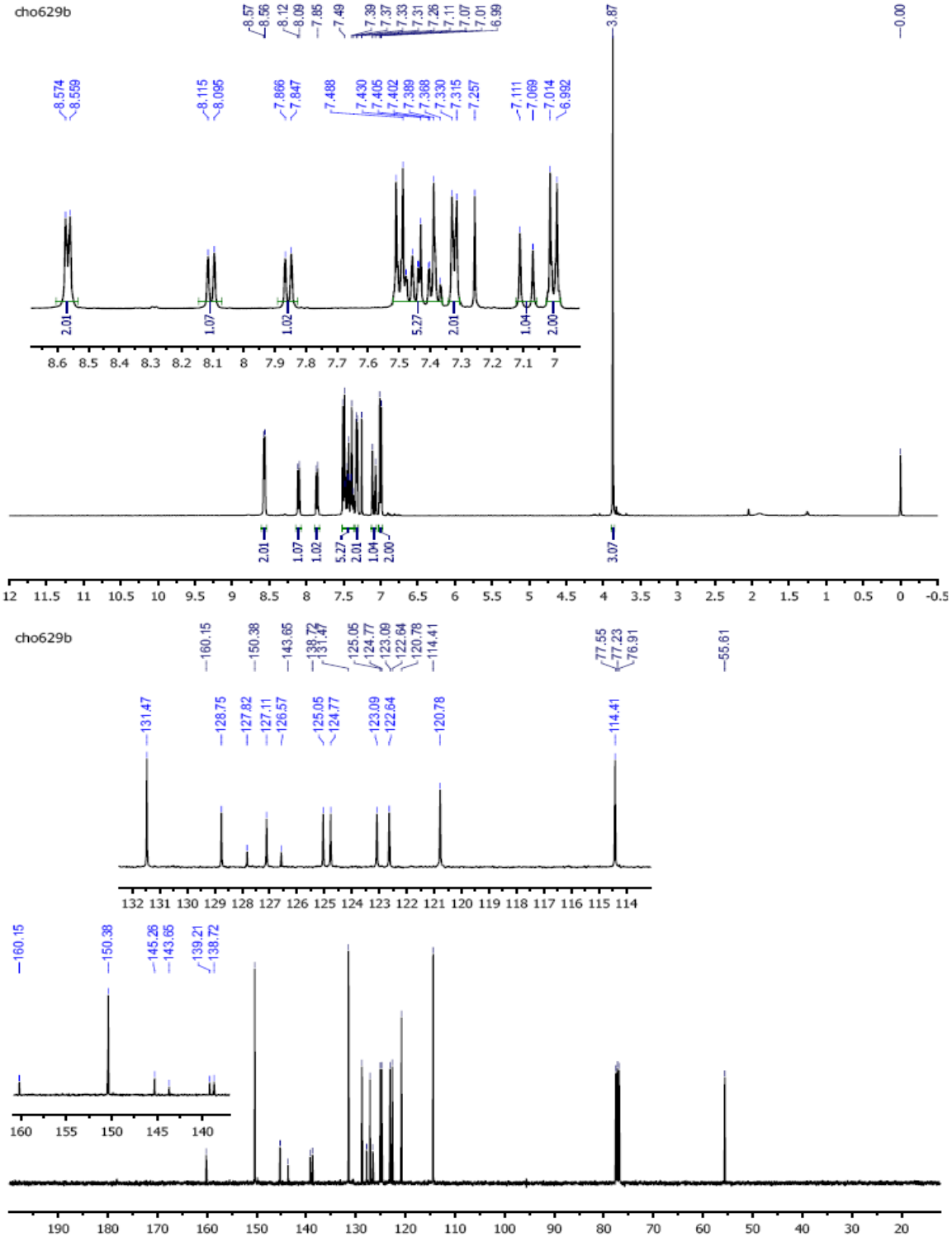
Benzo[*b*]thiophene 13{*134*}



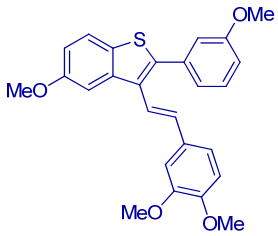


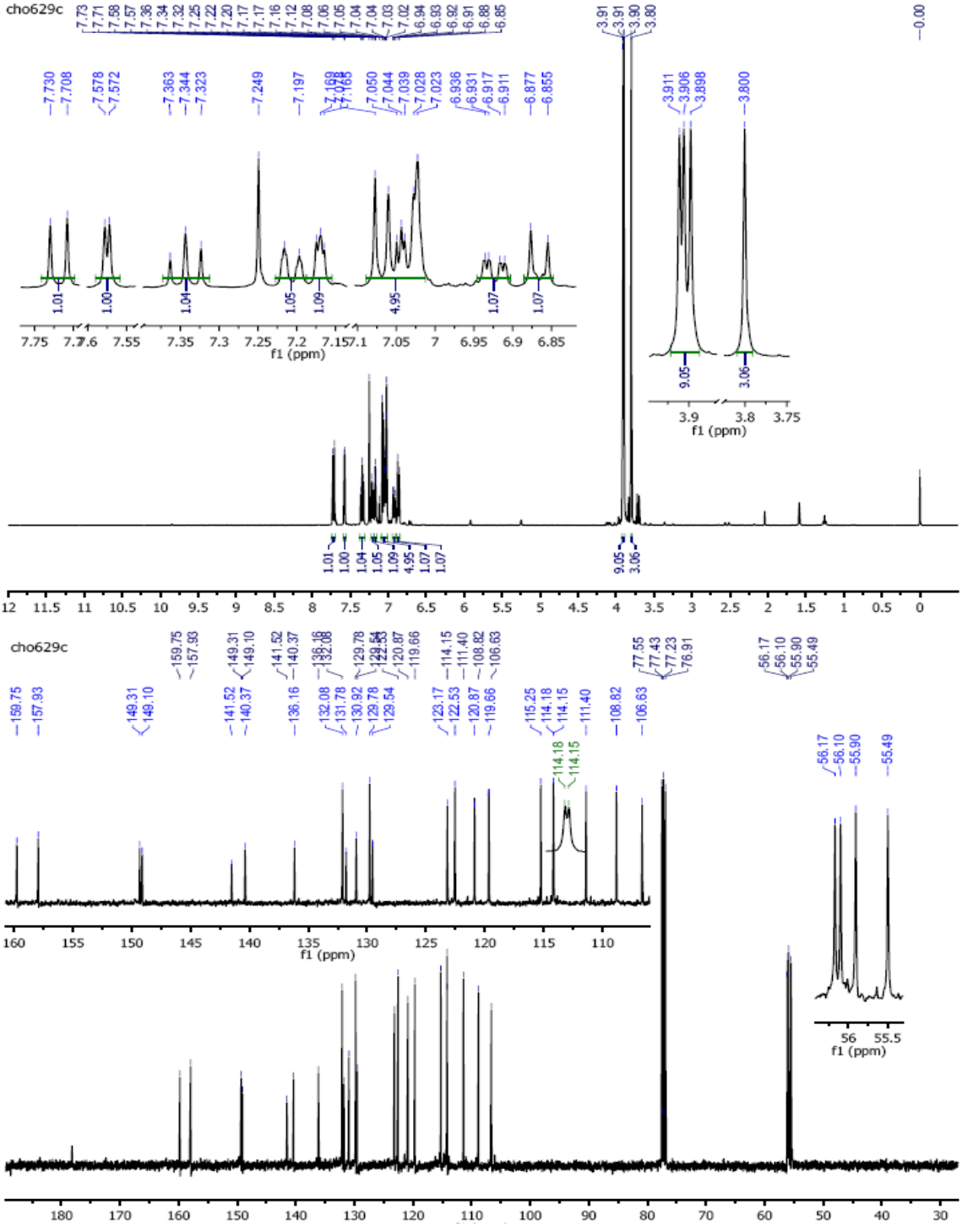
Benzo[*b*]thiophene 13{*146*}



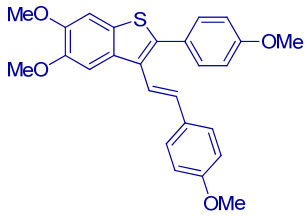


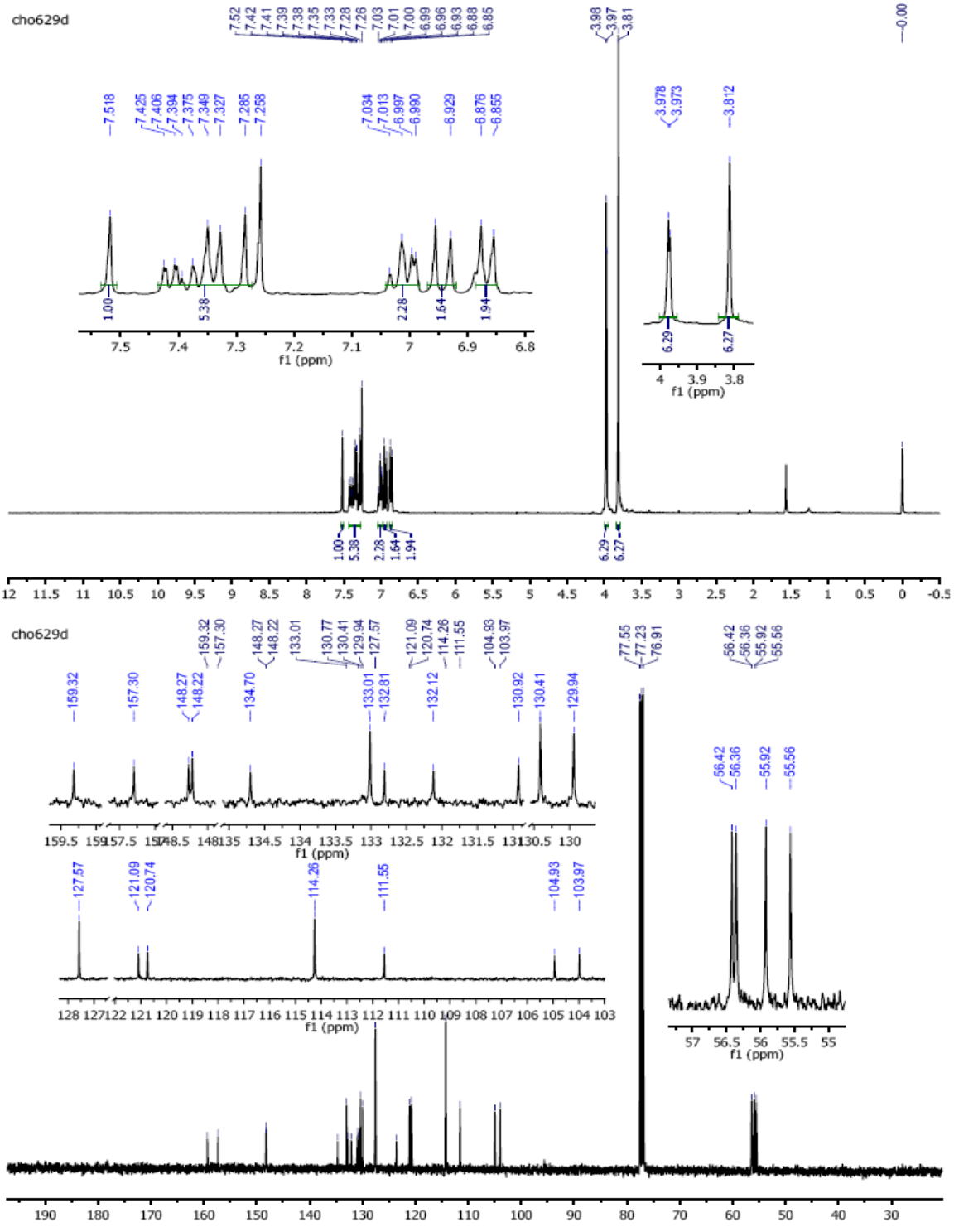
Benzo[*b*]thiophene 13{*151*}



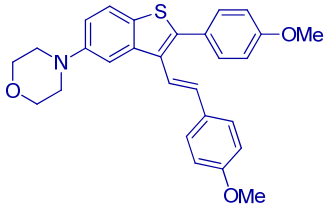


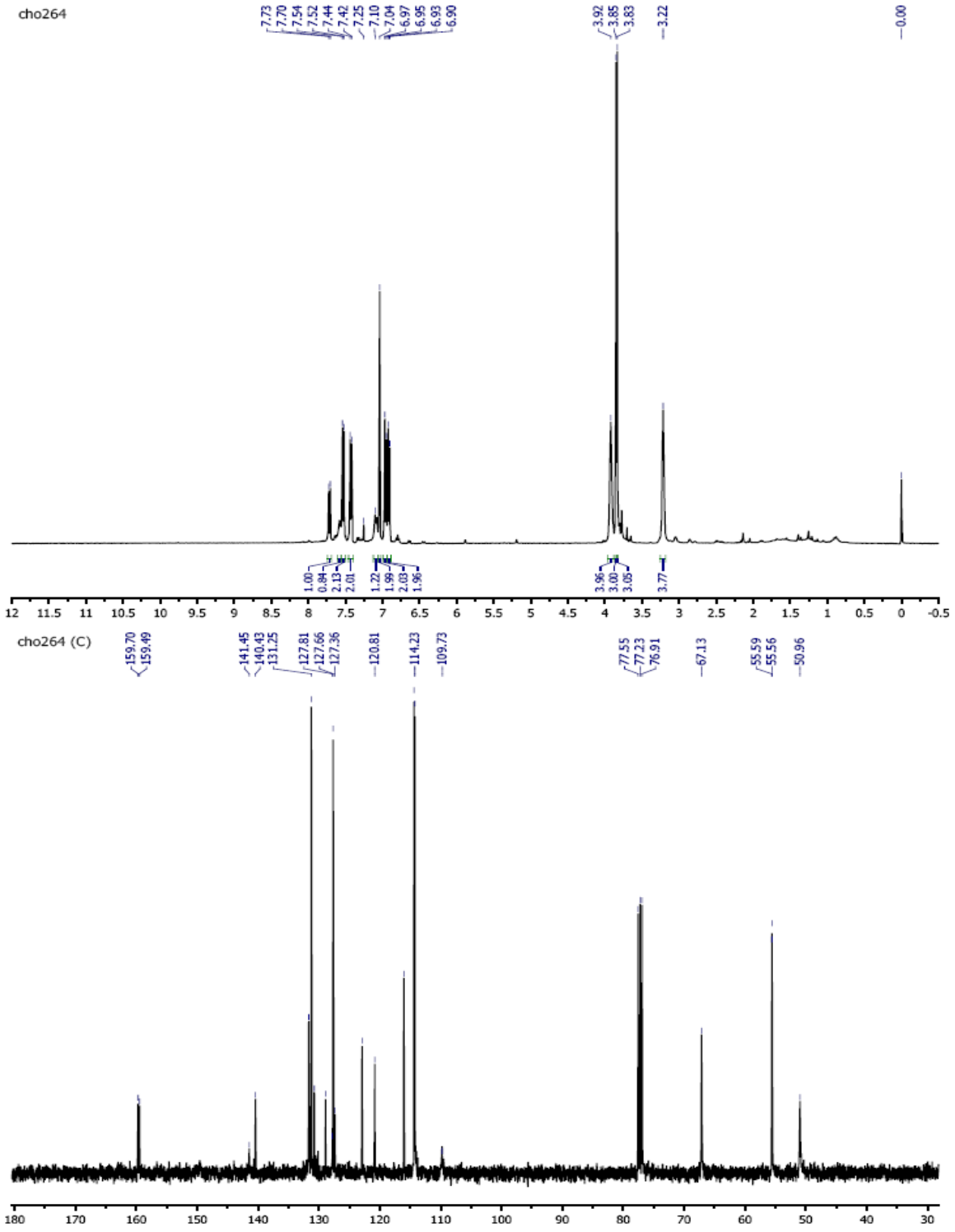
Benzo[*b*]thiophene 13{*154*}



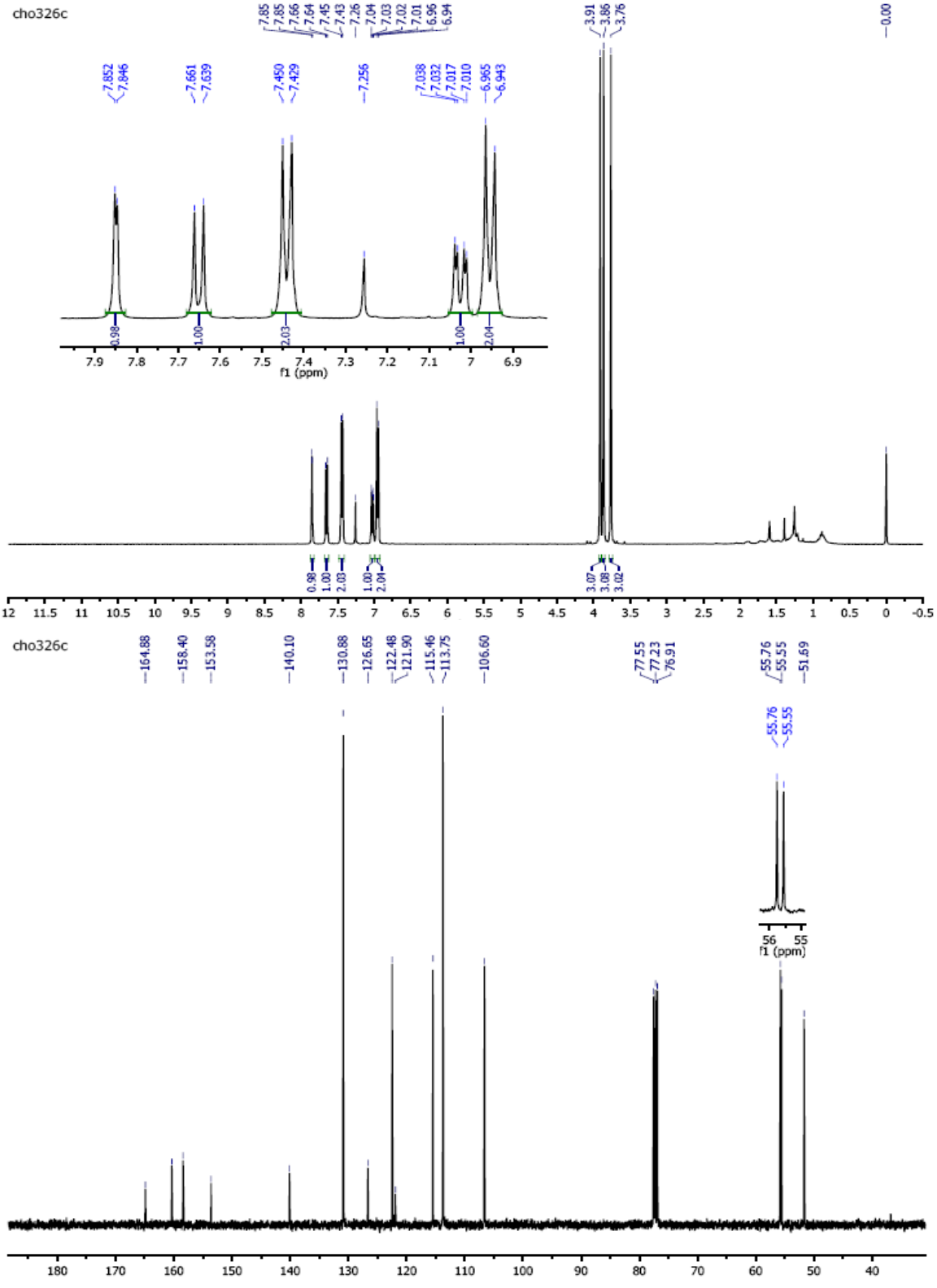


Benzo[*b*]thiophene 13{*155*}

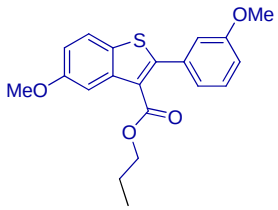


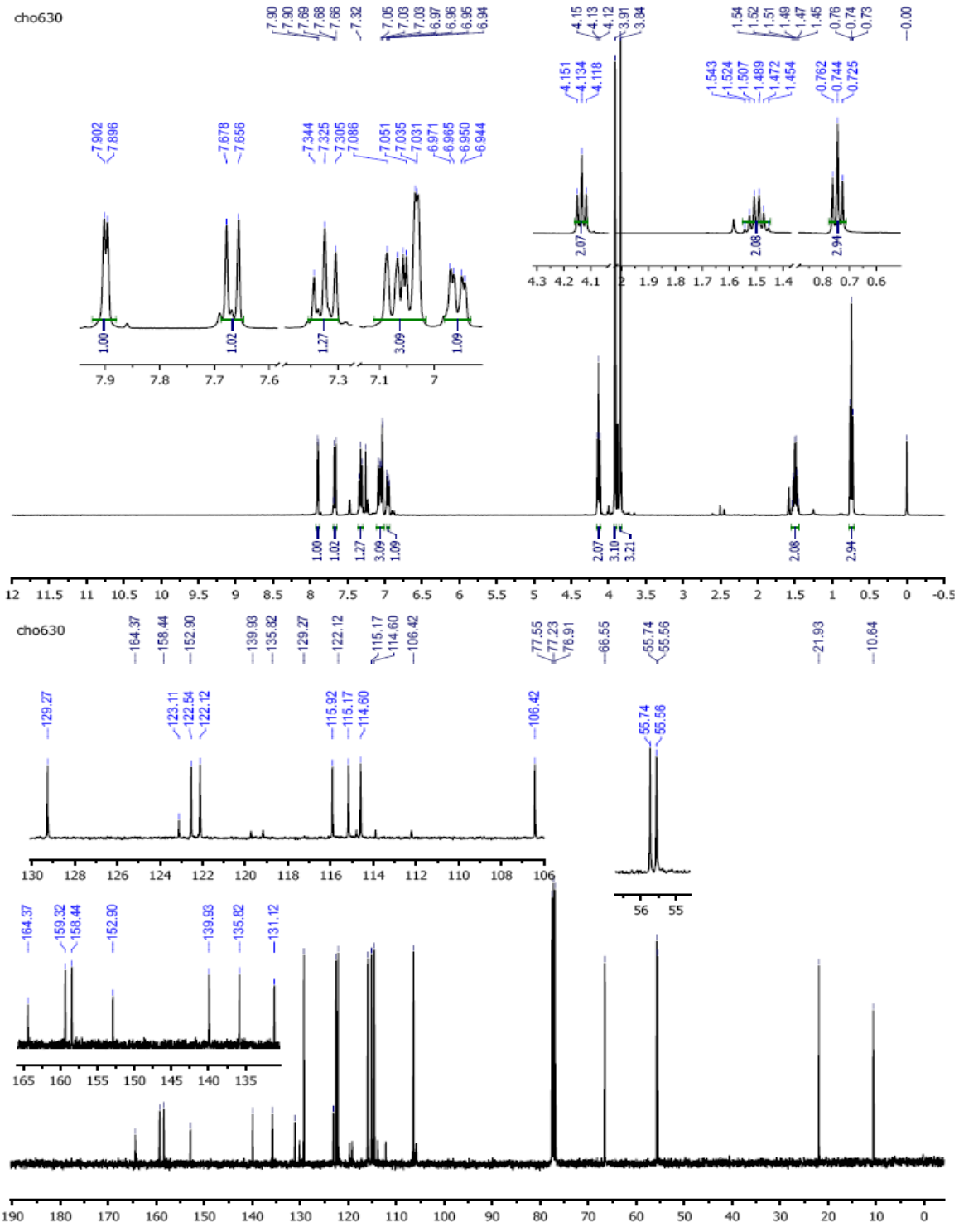


Benzo[*b*]thiophene 13{*159*}

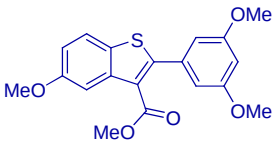


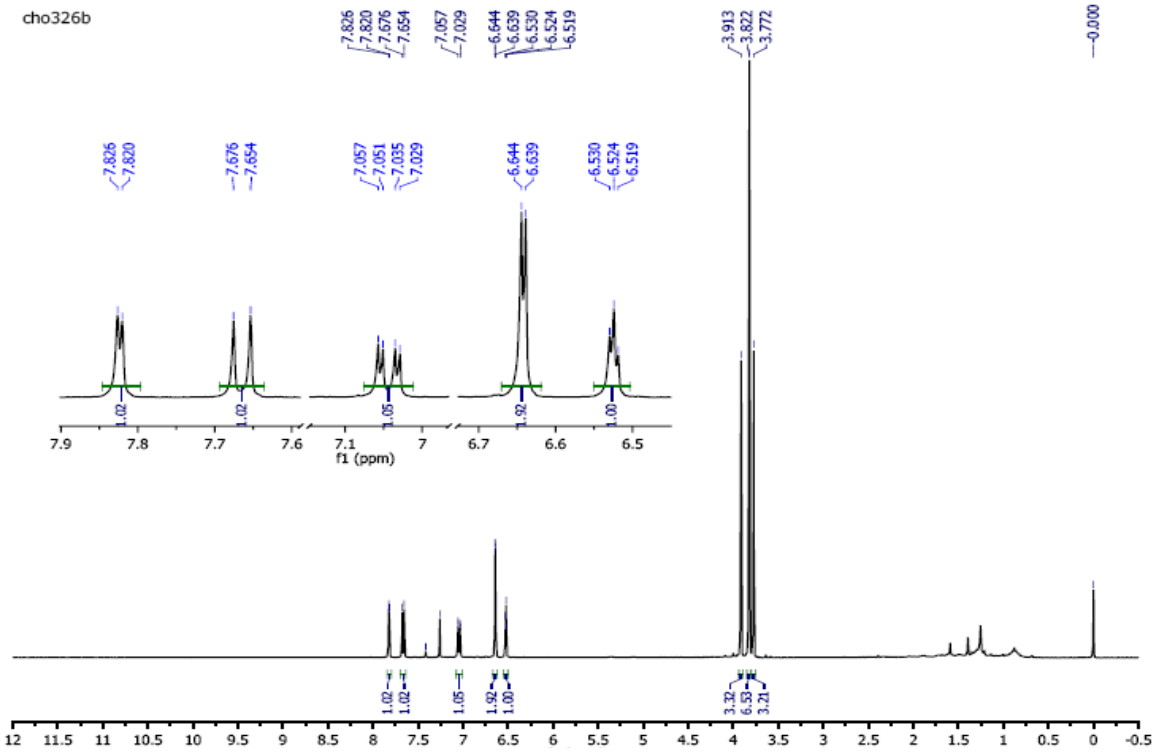
Benzo[*b*]thiophene 13{*161*}

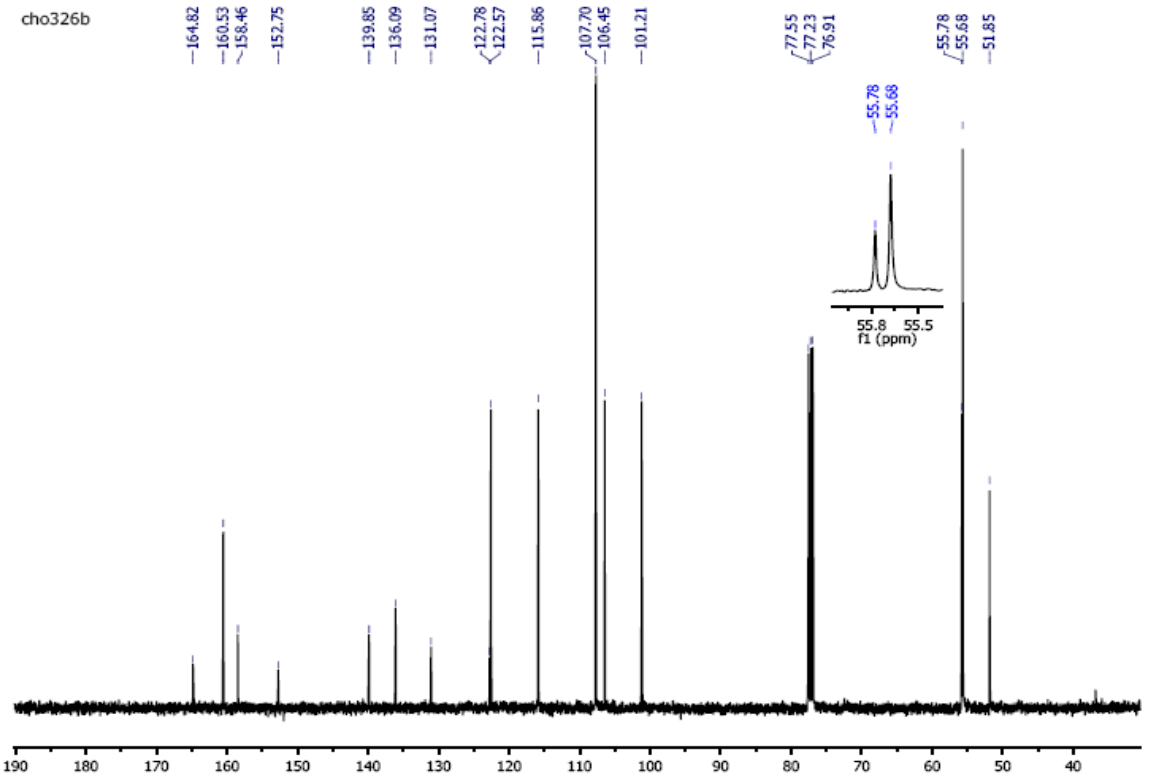




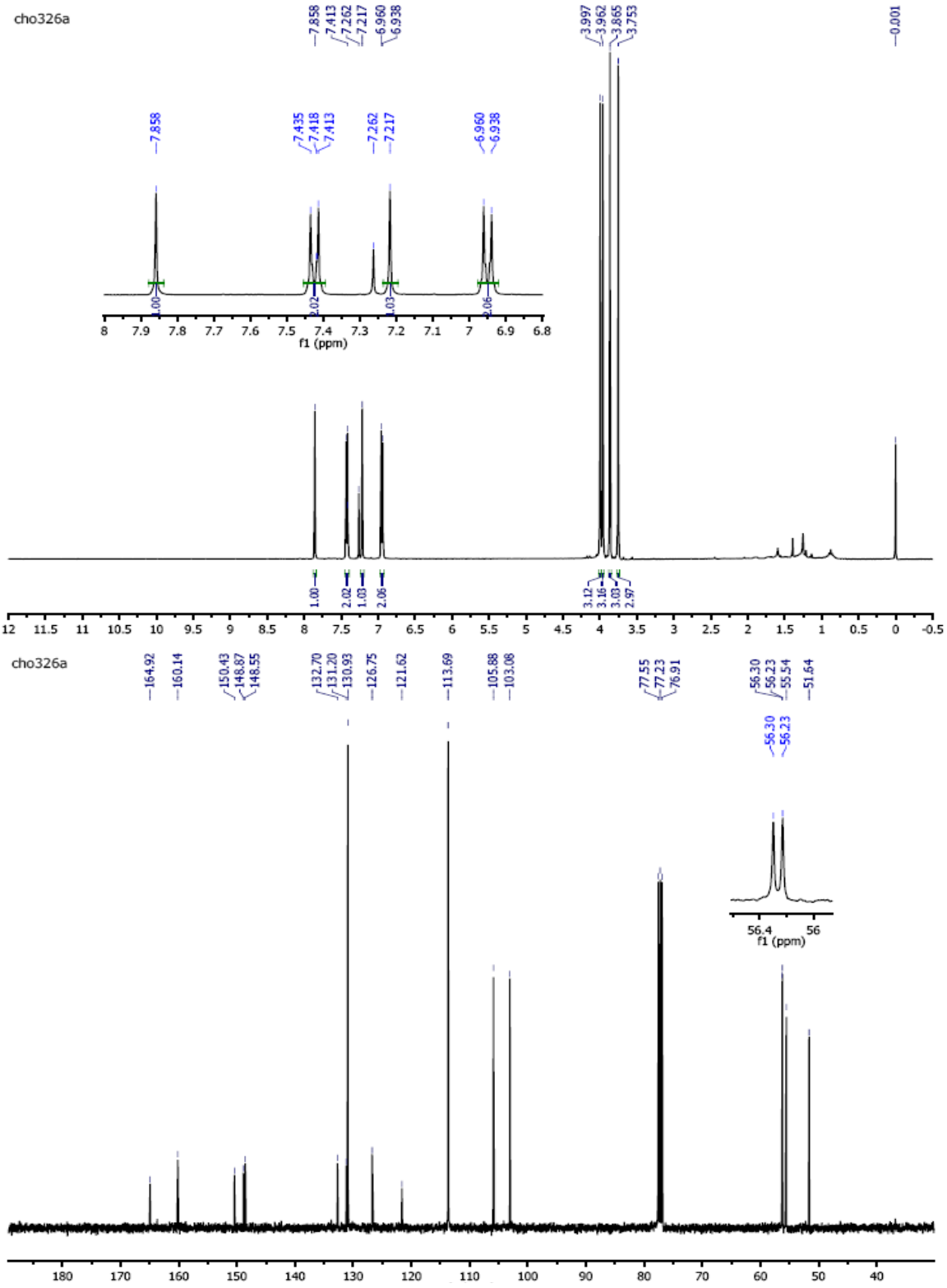
Benzo[*b*]thiophene 13{*163*}



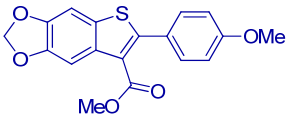


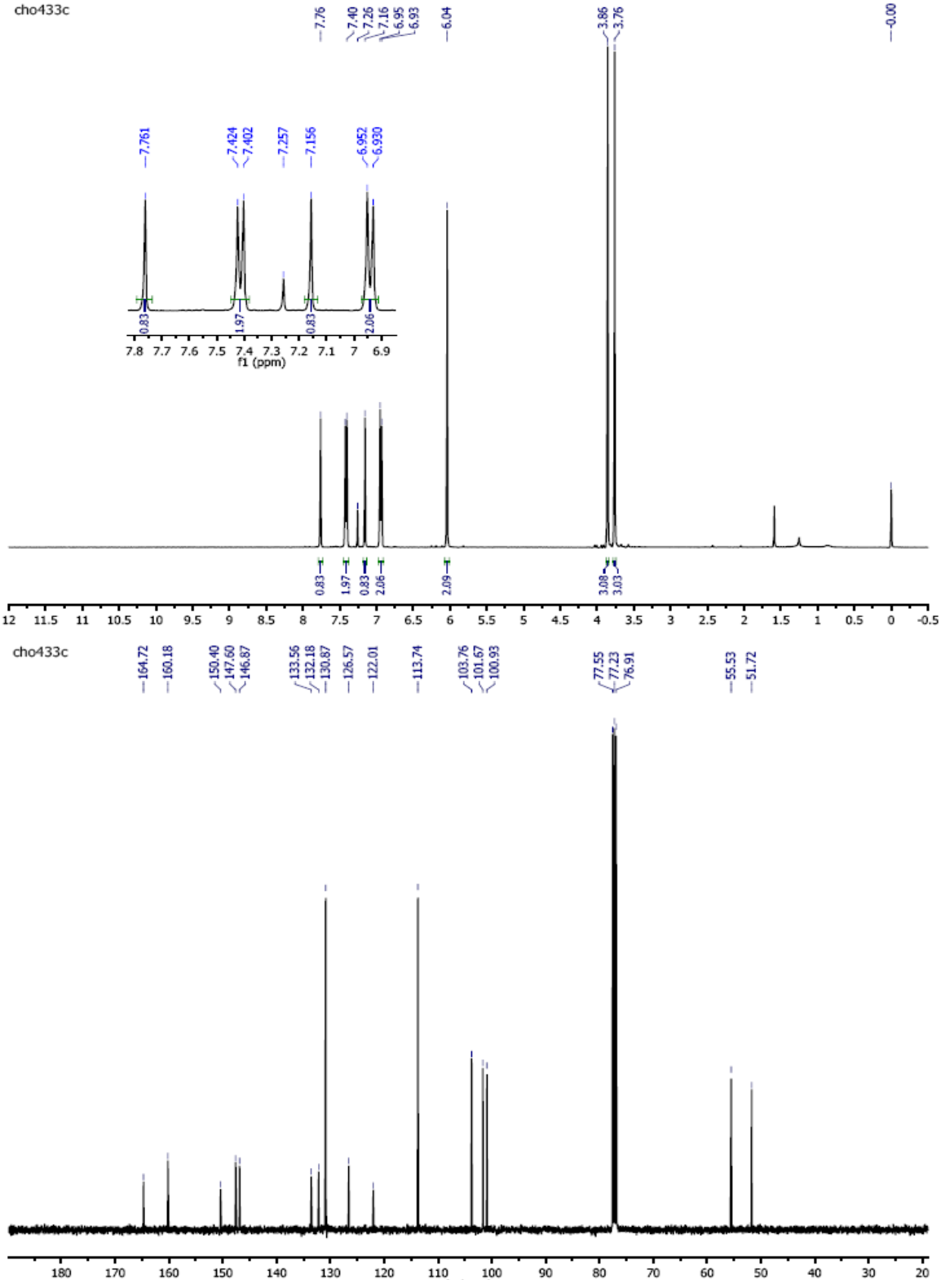


Benzo[*b*]thiophene 13{*166*}

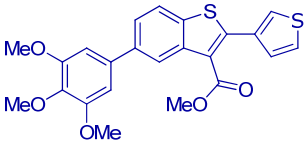


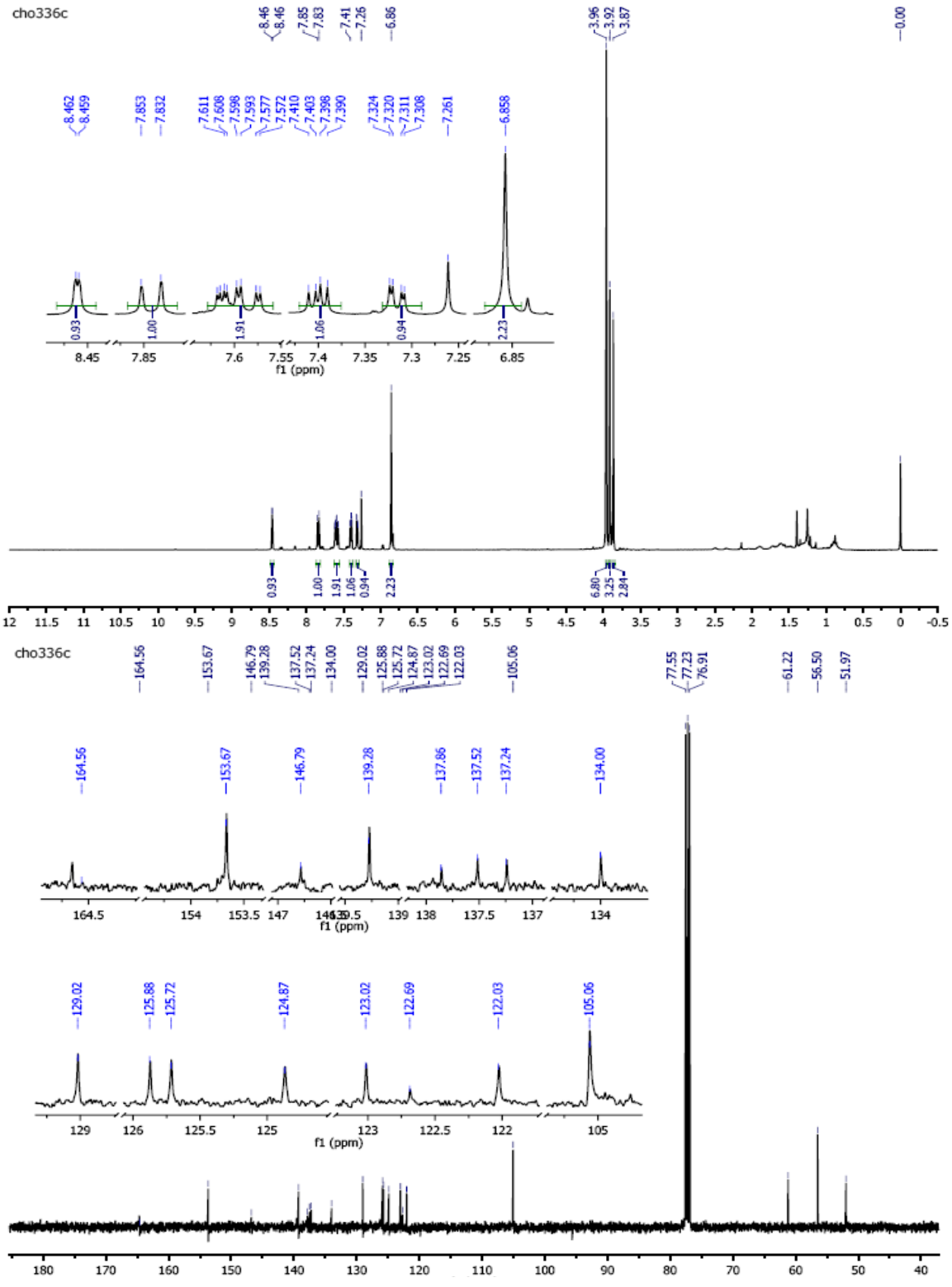
Benzo[*b*]thiophene 13{*168*}





Benzo[*b*]thiophene 13{*172*}





Benzo[*b*]thiophene 13{*173*}