Parallel Synthesis of a Multi-Substituted Benzo[*b*]furan Library

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Supporting Information

Contents

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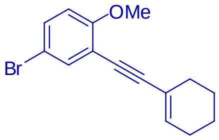
The ^{1}H (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were recorded in $CDCl_3$ as the solvent using tetramethylsilane (TMS) as an internal standard, unless otherwise stated. Chemical shifts are reported in δ units (ppm) by assigning the TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm 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. HPLC analysis was carried out using an Xterra MS C-18 column (5 μM, 4.6 ×150 mm) with gradient elution (10% CH_3CN to 100% CH_3CN) on a Waters Mass Directed Fractionation instrument using a Waters 2767 sample manager and Waters 2525 HPLC pump and a 2487 dual λ absorbance detector, and Water/Micromass ZQ (quadruple) detector. Purification was carried out using an Xterra MS C-18 column (5 μM, 10 × 150 mm), and gradient elution (40% CH_3CN to 100% CH_3CN) with a UV fraction trigger. 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, EtOH, CH_3CN, DMF, hexanes, 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 preparation of bromoalkynes 7{*5-8*}

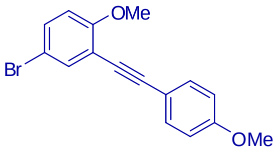
To a solution of 4-bromo-2-iodoanisole [**5**{*3*}, 10.0 mmol], 3 mol % $PdCl_2(PPh_3)_2$ and 3 mol % CuI in Et_3N (20 mL), 10.5 mmol of terminal alkyne **6** was added. The reaction mixture was stirred vigorous between 0 °C and room temperature for *ca*. 1-3 h under an Ar atmosphere. The resulting mixture 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 **7**{*5-8*}.

Bromoalkyne 7{*5*}



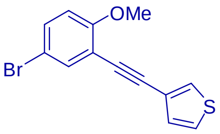
The product was obtained as a yellow oil (84% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.54-1.69 (m, 4H), 2.07-2.16 (m, 2H), 2.18-2.25 (m, 2H), 3.79 (s, 3H), 6.19-6.23 (m, 1H), 6.67 (d, *J* = 8.9 Hz, 1H), 7.28 (dd, *J* = 2.5, 8.9 Hz, 1H), 7.47 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 22.3, 25.8, 29.1, 56.0, 81.6, 96.6, 112.1, 112.1, 115.0, 120.6, 131.7, 135.4, 135.7, 158.8; HRMS calcd for $C_{15}H_{15}BrO$ [M^+], 290.0306, found 290.0309.

Bromoalkyne 7{*6*}



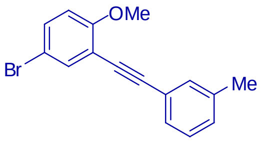
The product was obtained as yellow oil that solidified upon standing to a yellow solid (90% yield): mp 68-70 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.80 (s, 3H), 6.68 (d, *J* = 8.9 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.31 (dd, *J* = 2.5, 8.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 56.0, 83.1, 94.8, 112.3, 114.0 (×2), 114.2, 114.9, 115.1, 132.0, 133.2 (×2), 135.5, 158.9, 159.8; HRMS calcd for $C_{16}H_{13}BrO_2$ [M^+], 316.0099, found 316.0102.

Bromoalkyne 7{*7*}



The product was obtained as a dark yellow oil (94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.74 (d, *J* = 8.8 Hz, 1H), 7.20 (dd, *J* = 1.2, 5.0 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.36 (dd, *J* = 2.5, 8.8 Hz, 1H), 7.54 (dd, *J* = 1.2, 3.0 Hz, 1H), 7.58 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 84.0, 89.9, 112.4, 112.4, 114.6, 122.2, 125.5, 129.2, 130.1, 132.5, 135.8, 159.1; HRMS calcd for $C_{13}H_9BrOS$ [M^+], 291.9557, found 291.9551.

Bromoalkyne 7{*8*}



The product was obtained as a yellow oil (93% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.87 (s, 3H), 6.75 (d, *J* = 8.9 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.36-7.39 (m, 3H), 7.59 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 56.3, 84.1, 95.0, 112.41, 112.44, 114.8, 123.0, 128.4, 128.9, 129.5, 132.42, 132.44, 135.9, 138.1, 159.2; HRMS calcd for $C_{16}H_{13}BrO$ [M^+], 300.0150, found 300.0156.

General procedure for the preparation of alkynes 8{*1-13*} by Suzuki-Miyaura coupling

Method ***A*** (using arylboronic acids **10**)

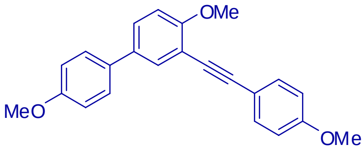
To a solution of bromoalkyne **7**{*5-8*} (2.0 mmol) and 5 mol % $Pd(PPh_3)_4$ in toluene (10 mL) was added K_2CO_3 (6.0 mmol) under an Ar atmosphere. To the resulting mixture was added arylboronic acid **10** (3.0

mmol) dissolved in ethanol (2 mL). The reaction mixture was heated at 80 °C for 8 h with vigorous stirring. 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 flash column chromatography using EtOAc/hexane as the eluent to afford the corresponding product.

*Method **B*** (using heteroarylboronic acids **10**)

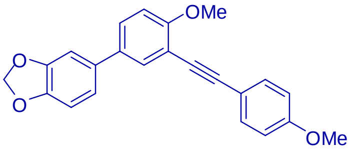
To a solution of bromoalkyne **7**{*5-8*} (2.0 mmol), 5 mol % $Pd(dba)_2$ and 8 mol % PPh_3 in toluene (10 mL) was added KOH (6.0 mmol) under an Ar atmosphere. To the resulting mixture was added heteroarylboronic acid **10** (3.0 mmol) dissolved in ethanol (2 mL). The reaction mixture was heated at 80 °C for 8 h with vigorous stirring. Upon cooling to room temperature, the reaction mixture was extracted with EtOAc.

Alkyne 8{*1*}



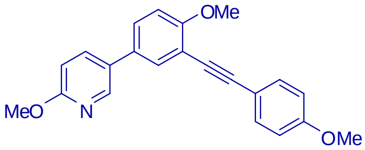
The product was obtained as a pale yellow solid (69% yield): mp 135-137 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.79 (s, 3H), 3.89 (s, 3H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.38, 55.43, 56.1, 84.6, 93.6, 111.1, 113.1, 114.0 (×2), 114.3 (×2), 115.7, 127.7, 127.8 (×2), 131.6, 132.7, 133.3 (×2), 133.4, 158.9, 159.0, 159.6; HRMS calcd for $C_{23}H_{20}O_3$ [M^+], 344.1412, found 344.1412.

Alkyne 8{*2*}



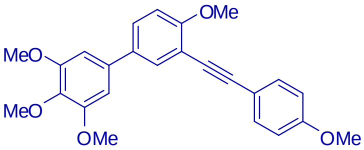
The product was obtained as a white solid (63% yield): mp 132-135 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.87 (s, 3H), 5.93 (s, 2H), 6.81-6.88 (m, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.97-7.01 (m, 2H), 7.35-7.39 (m, 1H), 7.51 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 56.0, 84.5, 93.7, 101.2, 107.3, 108.6, 111.0, 113.1 (×2), 114.0, 115.6, 120.2, 127.8, 131.7, 133.2 (×2), 133.4, 134.5, 146.9, 148.2, 159.0, 159.6; HRMS calcd for $C_{23}H_{18}O_4$ [M^+], 358.1205, found 358.1207.

Alkyne 8{*3*}



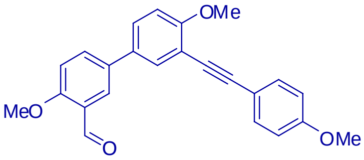
The product was obtained as a yellow oil (57% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.82 (s, 3H), 3.94 (s, 3H), 3.97 (s, 3H), 6.80 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 1H), 7.42 (dd, *J* = 2.4, 8.6 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.75 (dd, *J* = 2.5, 8.6 Hz, 1H), 8.35 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 53.7, 55.5, 56.2, 84.3, 94.0, 110.9, 111.3, 113.5, 114.1 (×2), 115.6, 127.7, 129.2, 130.5, 131.7, 133.3 (×2), 137.3, 144.7, 159.4, 159.8, 163.5; HRMS calcd for $C_{22}H_{19}NO_3$ [M$^+$], 345.1365, found 345.1359.

Alkyne 8{*4*}



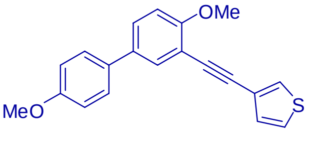
The product was obtained as a yellow oil (63% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.80 (s, 3H), 3.88 (s, 3H), 3.92 (s, 6H), 3.93 (s, 3H), 6.74 (s, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 1H), 7.46 (dd, *J* = 2.2, 8.6 Hz, 1H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.4, 56.1, 56.3 (×2), 61.1, 84.4, 93.8, 104.0 (×2), 111.0, 113.1, 114.0 (×2), 115.5, 128.1, 131.9, 133.2 (×2), 133.8, 136.2, 137.4, 153.5 (×2), 159.3, 159.7; HRMS calcd for $C_{25}H_{24}O_5$ [M$^+$], 404.1624, found 404.1628.

Alkyne 8{*5*}



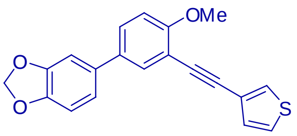
The product was obtained as a yellow oil (72% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.82 (s, 3H), 3.93 (s, 3H), 3.94 (s, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 7.47 (dd, *J* = 2.4, 8.6 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.66-7.76 (m, 2H), 8.03 (d, *J* = 2.1 Hz, 1H), 10.50 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.5, 56.0, 56.2, 84.3, 93.9, 111.2, 112.3, 113.4, 114.1 (×2), 116.2, 125.0, 126.3, 127.7, 131.6, 132.0, 132.8, 133.3 (×2), 134.0, 159.3, 159.7, 161.1, 189.9; HRMS calcd for $C_{24}H_{20}O_4$ [M$^+$], 372.1362, found 372.1353.

Alkyne 8{*6*}



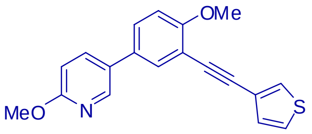
The product was obtained as yellow oil that solidified upon standing to a yellow solid (78% yield): mp 106-108 °C (uncorrected); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.82 (s, 3H), 3.91 (s, 3H), 6.92 (d, *J* = 8.7 Hz, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.21-7.29 (m, 2H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.55 (dd, *J* = 1.2, 2.9 Hz, 1H), 7.68 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.5, 56.2, 85.4, 88.7, 111.1, 112.7, 114.4 (×2), 122.6, 125.4, 127.8 (×2), 128.1, 128.8, 130.2, 131.8, 132.7, 133.5, 159.0; HRMS calcd for $C_{20}H_{16}O_2S$ [M^+], 320.0871, found 320.0862.

Alkyne 8{*7*}



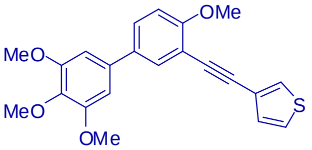
The product was obtained as yellow oil that solidified upon standing to a yellow solid (81% yield): mp 100-101 °C (uncorrected); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (s, 3H), 5.96 (s, 2H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.98-7.03 (m, 2H), 7.21-7.29 (m, 2H), 7.39-7.43 (m, 1H), 7.53-7.57 (m, 1H), 7.63-7.65 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 56.2, 85.3, 88.8, 101.3, 107.4, 108.7, 111.2, 112.8, 120.3, 122.6, 125.4, 128.2, 128.8, 130.2, 132.0, 133.6, 134.5, 147.0, 148.3, 159.2; calcd for $C_{20}H_{14}O_3S$ [M^+], 334.0664, found 334.0668.

Alkyne 8{*8*}



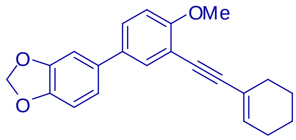
The product was obtained as a dark yellow oil (62% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.97 (s, 3H), 6.80 (d, *J* = 8.6 Hz, 1H), 6.97 (d, *J* = 8.6 Hz, 1H), 7.21-7.31 (m, 2H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.57 (s, 1H), 7.65 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 8.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.8, 56.2, 85.1, 89.0, 111.0, 111.4, 113.1, 122.5, 125.4, 128.0, 129.0, 129.2, 130.2, 130.6, 131.8, 137.3, 144.7, 159.5, 163.6; calcd for $C_{19}H_{15}NO_2S$ [M^+], 321.0823, found 321.0817.

Alkyne 8{*9*}



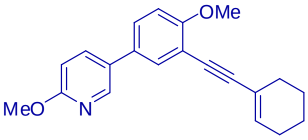
The product was obtained as yellow oil that solidified upon standing to a yellow solid (83% yield): mp 156.5-158 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.92 (s, 6H), 3.94 (s, 3H), 6.74 (s, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 7.21-7.31 (m, 2H), 7.48 (dd, *J* = 2.3, 8.6 Hz, 1H), 7.56 (d, *J* = 2.9 Hz, 1H), 7.68 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 56.4 (×2), 61.1, 85.2, 88.8, 104.1 (×2), 111.1, 112.8, 122.5, 125.4, 128.4, 128.9, 130.1, 132.1, 133.9, 136.1, 137.5, 153.6 (×2), 159.5; HRMS calcd for $C_{22}H_{20}O_4S$ [M^+], 380.1082, found 380.1089.

Alkyne 8{*10*}



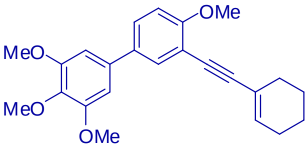
The product was obtained as a pale yellow solid (71% yield): mp 107-108 °C (uncorrected); ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.56-1.70 (m, 4H), 2.10-2.18 (m, 2H), 2.22-2.30 (m, 2H), 3.87 (s, 3H), 5.95 (s, 2H), 6.25 (br s, 1H), 6.84 (t, *J* = 9.1 Hz, 2H), 6.97-7.02 (m, 2H), 7.36 (dd, *J* = 2.4, 8.6 Hz, 1H), 7.55 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.6, 22.4, 25.9, 29.4, 56.0, 83.0, 95.5, 101.2, 107.3, 108.5, 110.9, 113.2, 120.1, 120.9, 127.5, 131.6, 133.3, 134.5, 135.2, 146.8, 148.1, 158.9; HRMS calcd for $C_{22}H_{20}O_3$ [M$^+$], 332.1412, found 332.1409.

Alkyne 8{*11*}



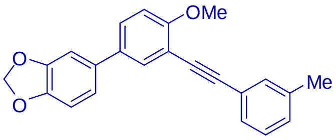
The product was obtained as a pale yellow oil (68% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.61-1.67 (m, 4H), 2.14 (br s, 2H), 2.27 (br s, 2H), 3.90 (s, 3H), 3.96 (s, 3H), 6.26-6.27 (m, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.56 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 8.32 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.7, 22.5, 26.0, 29.4, 53.7, 56.1, 82.8, 95.9, 110.8, 111.2, 113.7, 120.9, 127.5, 129.3, 130.4, 135.6, 137.2, 144.6, 159.3, 163.5; calcd for $C_{21}H_{21}NO_2$ [M$^+$], 319.1572, found 319.1576.

Alkyne 8{*12*}



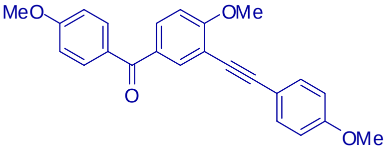
The product was obtained as a pale yellow oil (68% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.59-1.71 (m, 4H), 2.14 (br s, 2H), 2.28 (br s, 2H), 3.88 (s, 3H), 3.89 (s, 3H), 3.91 (s, 6H), 6.26 (br s, 1H), 6.72 (s, 2H), 6.90 (d, *J* = 8.6 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.59 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.6, 22.4, 25.9, 29.3, 56.0, 56.2 (×2), 61.0, 82.9, 95.6, 103.9 (×2), 110.9, 113.2, 120.8, 127.8, 131.8, 133.7, 135.4, 136.1, 137.3, 153.4 (×2), 159.2; calcd for $C_{24}H_{26}O_4$ [M$^+$], 378.1831, found 378.1823.

Alkyne 8{*13*}



The product was obtained as a yellow oil (67% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.33 (s, 3H), 3.88 (s, 3H), 5.94 (s, 2H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.98-7.01 (m, 2H), 7.10-7.12 (m, 1H), 7.20-7.23 (m, 1H), 7.37-7.40 (m, 3H), 7.65 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 56.1, 85.5, 93.9, 101.2, 107.4, 108.7, 111.1, 112.9, 120.2, 123.4, 128.1, 128.3, 128.9, 129.2, 131.9, 132.4, 133.5, 134.5, 138.0, 146.9, 148.2, 159.2; HRMS calcd for $C_{23}H_{18}O_3$ [M^+], 342.1256, found 342.1256.

General procedure for the preparation of alkyne 8{*14*} by carbonylative Suzuki coupling.

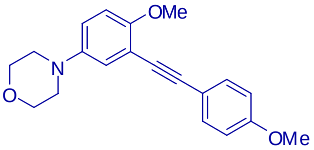


The bromoalkyne **7**{*6*} (2.0 mmol), 4-methoxyphenylboronic acid **10**{*1*} (2.2 mmol), K_2CO_3 (6.0 mmol), NaI (6.0 mmol) and 5 mol % $PdCl_2$(dppf) in toluene (10 mL) were placed in a vial with a magnetic stir bar under an Ar atmosphere. After sealing the vial, the atmosphere was changed to carbon monoxide and the reaction mixture was kept at 80 °C for 24 h with vigorous stirring. Upon cooling to room temperature, the reaction mixture was extracted with EtOAc (2 × 40 mL). The usual work up gave a crude oil, which was purified by chromatography (EtOAc/hexane) to give **8**{*14*} in a 38% yield as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.87 (s, 3H), 3.97 (s, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.76-7.82 (m, 3H), 7.94 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 55.6, 56.3, 83.6, 94.3, 110.2, 112.8, 113.7 (×2), 114.1 (×2), 115.3, 130.5, 130.7, 131.9, 132.4 (×2), 133.3 (×2), 135.6, 159.8, 162.7, 163.1, 193.9; HRMS calcd for $C_{24}H_{20}O_4$ [M^+] 372.1362, found 372.1354.

General procedure for the preparation of alkynes 8{*15-20*} by amination.

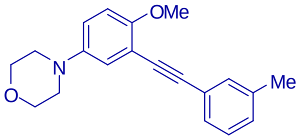
To the bromoalkyne **7**{*5-8*} (2.0 mmol), 5 mol % $Pd_2(dba)_3$ and NaO^{t}Bu (1.4 equiv), DavePhos (0.1 equiv) was added with a magnetic stir bar under an Ar atmosphere. To the reagent mixture was added amine **11** (1.5 equiv) dissolved in toluene (12 mL) at room temperature. The reaction mixture 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/hexanes as the eluent to afford the corresponding product **8**{*15-20*}.

Alkyne 8{*15*}



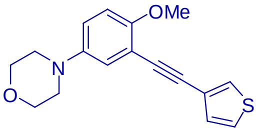
The product was obtained as a dark-brown oil (78% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.05 (t, *J* = 4.8 Hz, 4H), 3.79 (s, 3H), 3.85 (s, 3H), 3.83 (t, *J* = 4.8 Hz, 4H), 6.80-6.88 (m, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 2.8 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.6 (×2), 55.3, 56.4, 67.1 (×2), 84.7, 93.3, 111.9, 113.2, 114.0 (×2), 115.7, 118.0, 121.5, 133.2 (×2), 145.3, 154.4, 159.6; HRMS calcd for $C_{20}H_{21}NO_3$ [M^+] 323.1521, found 323.1519.

Alkyne 8{*16*}



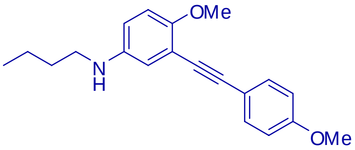
The product was obtained as a dark brown oil (73% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.06 (t, *J* = 4.8 Hz, 4H), 3.84 (t, *J* = 4.8 Hz, 4H), 3.86 (s, 3H), 6.81-6.89 (m, 2H), 7.08 (d, *J* = 2.8 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 50.7 (×2), 56.5, 67.1 (×2), 85.8, 93.5, 112.0, 113.0, 118.3, 121.7, 123.4, 128.3, 128.8, 129.2, 132.4, 138.0, 145.4, 154.5; HRMS calcd for $C_{20}H_{21}NO_2$ [M^+] 307.1572, found 307.1563.

Alkyne 8{*17*}



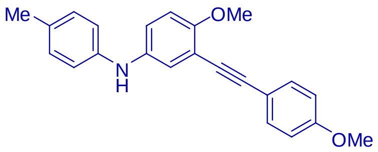
The product was obtained as yellow oil that solidified upon standing to a yellow solid (71% yield): mp 118-119 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.06 (t, *J* = 4.8 Hz, 4H), 3.85 (s, 3H), 3.85 (t, *J* = 4.8 Hz, 4H), 6.82-6.81 (m, 2H), 7.08 (d, *J* = 2.8 Hz, 1H), 7.21-7.30 (m, 2H), 7.53-5.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.7 (×2), 56.4, 67.1 (×2), 85.6, 88.4, 111.9, 112.8, 118.4, 121.7, 122.6, 125.3, 128.8, 130.1, 145.3, 145.4, 154.5; HRMS calcd for $C_{17}H_{17}NO_2S$ [M^+] 299.0980, found 299.0972.

Alkyne 8{*19*}



The product was obtained as a yellow oil (87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.3 Hz, 3H), 1.36-1.47 (m, 2H), 1.53-1.62 (m, 2H), 3.06 (t, *J* = 7.1 Hz, 2H), 3.33 (br s, 1H), 3.81 (s, 3H), 3.84 (s, 3H), 6.57 (dd, *J* = 2.9, 8.8 Hz, 1H), 6.76 (d, *J* = 11.7 Hz, 1H), 6.77 (s, 1H), 6.85 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 20.5, 31.9, 44.8, 55.4, 56.8, 85.0, 93.0, 112.8, 113.4, 114.0 (×2), 114.6, 115.9, 117.6, 133.3 (×2), 142.6, 152.6, 159.6; HRMS calcd for $C_{20}H_{23}NO_2$ [M^+] 309.1729, found 309.1717.

Alkyne 8{*20*}

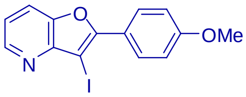


The product was obtained as a yellow oil (93% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.80 (s, 3H), 3.87 (s, 3H), 5.44 (br s, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.84-6.89 (m, 4H), 6.98 (dd, *J* = 2.8, 8.8 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 2.8 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 55.4, 56.5, 84.5, 93.6, 112.1, 113.6, 114.0 (×2), 115.7, 117.3 (×2), 120.8, 124.4, 129.9, 130.0 (×2), 133.3 (×2), 136.8, 141.9, 155.1, 159.7; HRMS calcd for $C_{23}H_{21}NO_2$ [M^+] 343.1572, found 343.1562.

General procedure for the iodocyclization of compounds 9{*1-24*}

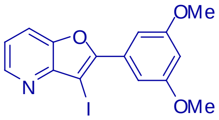
To a solution of 1.6 mmol of the alkyne **7** and/or **8** and 15 mL of CH_2Cl_2 was added gradually 1.5 equiv of ICl dissolved in 10 mL of CH_2Cl_2. The reaction mixture was allowed to stir at room temperature for 1-2 h. The reaction was monitored by TLC to establish completion. The excess ICl was removed by washing with satd aq $Na_2S_2O_3$. The mixture was then extracted by EtOAc (2 × 30 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 on silica gel using EtOAc/hexanes as the eluent.

3-Iodobenzofuran 9{*3*}



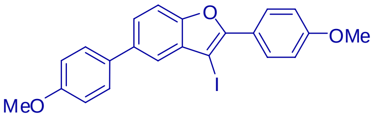
The product was obtained as yellow oil that solidified upon standing to a dark brown solid (76% yield): mp 108 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.24 (dd, *J* = 8.2, 4.8 Hz, 1H), 7.69 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.18 (d, *J* = 9.0 Hz, 2H), 8.59 (dd, *J* = 4.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 62.4, 114.2 (×2), 118.0, 120.0, 122.1, 129.4 (×2), 146.6, 146.9, 149.8, 156.6, 161.0; HRMS calcd for $C_{14}H_{10}INO_2$ [M^+] 350.9756, found 350.9744.

3-Iodobenzofuran 9{*4*}



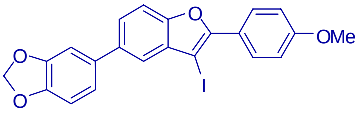
The product was obtained as dark yellow semi-solid (58% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 6H), 6.59 (t, *J* = 2.2 Hz, 1H), 7.32 (dd, *J* = 8.3, 4.8 Hz, 1H), 7.42 (d, *J* = 2.2 Hz, 2H), 7.77 (dd, *J* = 1.2, 8.3 Hz, 1H), 8.64 (dd, *J* = 1.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.8, 64.8, 102.9, 105.9 (×2), 118.5, 120.6, 131.2, 146.9, 147.1, 149.6, 156.2, 161.0 (×2); HRMS calcd for $C_{15}H_{12}INO_3$ [M^+] 380.9862, found 380.9861.

3-Iodobenzofuran 9{*5*}



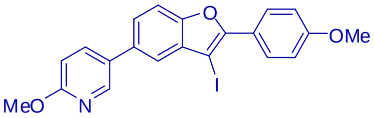
The product was obtained as a pale yellow solid (93% yield): mp 165-168 °C (uncorrected); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.86 (s, 3H), 3.87 (s, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.47-7.53 (m, 3H), 7.58 (d, *J* = 8.7 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.6, 55.6, 59.8, 111.3, 114.1 (×2), 114.4 (×2), 119.6, 122.8, 124.7, 126.6, 128.6 (×2), 129.2 (×2), 133.2, 134.0, 137.0, 153.2, 159.2, 160.5; HRMS calcd for $C_{22}H_{17}IO_3$ [M$^+$] 456.0222, found 456.0231.

3-Iodobenzofuran 9{*6*}



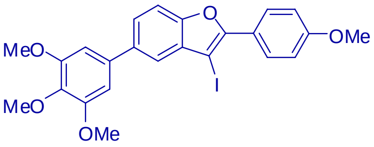
The product was obtained as an ivory solid (89% yield): mp 148-150 °C (uncorrected); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.86 (s, 3H), 6.00 (s, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.07-7.12 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.45 (s, 2H), 7.49 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.6, 59.8, 101.4, 108.2, 108.8, 111.3, 114.1 (×2), 114.3, 119.8, 121.1, 124.8, 128.0 (×2), 133.2, 135.8, 137.1, 147.1, 148.3, 153.3, 154.0, 160.5; HRMS calcd for $C_{22}H_{15}IO_4$ [M$^+$] 470.0015, found 470.0023.

3-Iodobenzofuran 9{*7*}



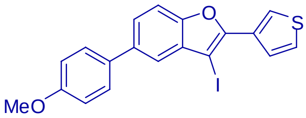
The product was obtained as a pale yellow solid (87% yield): mp 167-169 °C (uncorrected); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.86 (s, 3H), 3.99 (s, 3H), 6.82 (d, *J* = 8.6 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.42-7.49 (m, 3H), 7.82 (dd, *J* = 2.6, 8.6 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 2H), 8.43 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 53.8, 55.6, 59.6, 110.9, 111.6, 114.1 (×2), 119.7, 122.6, 124.4, 129.2 (×2), 130.4, 133.4, 133.9, 137.9, 145.3, 153.4, 154.1, 160.6, 163.6; HRMS calcd for $C_{21}H_{16}INO_3$ [M$^+$] 457.0175, found 457.0183.

3-Iodobenzofuran 9{*8*}



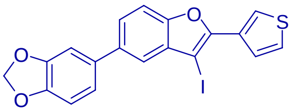
The product was obtained as a pale yellow solid (90% yield): mp 130-131 °C (uncorrected); ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.88 (s, 3H), 3.91 (s, 3H), 3.96 (s, 6H), 6.83 (s, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 7.50-7.53 (m, 3H), 8.14 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.6, 56.5 (×2), 59.7, 61.2, 105.0, 111.3, 114.2 (×2), 115.5, 117.0, 120.0, 122.6, 125.0, 128.0, 129.2 (×2), 133.2, 137.6, 153.6, 154.2, 160.6; HRMS calcd for $C_{24}H_{21}IO_5$ [M^+] 516.0434, found 516.0437.

3-Iodobenzofuran 9{*10*}



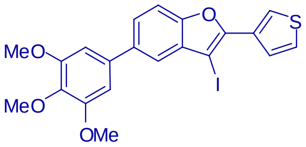
The product was obtained as a yellow solid (91% yield): mp 128-131 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.98 (d, *J* = 8.7 Hz, 2H), 7.39-7.44 (m, 1H), 7.45-7.52 (m, 3H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.90 (dd, *J* = 5.1, 1.2 Hz, 1H), 8.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 60.8, 111.3, 114.4 (×2), 119.5, 124.8, 125.0, 126.1, 126.5, 128.6 (×2), 131.3, 132.8, 133.9, 137.1, 151.4, 152.9, 159.2; HRMS calcd for $C_{19}H_{13}IO_2S$ [M^+] 431.9681, found 431.9688.

3-Iodobenzofuran 9{*11*}



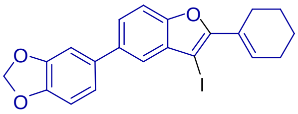
The product was obtained as a yellow oil (83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (s, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.06-7.12 (m, 2H), 7.41-7.54 (m, 4H), 7.91 (dd, *J* = 5.2, 1.1 Hz, 1H), 8.18 (dd, *J* = 2.9, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 60.8, 101.4, 108.2, 108.8, 111.3, 119.8, 121.1, 124.9, 125.1, 126.2, 126.5, 131.3, 132.8, 135.7, 137.2, 147.1, 148.3, 151.5, 153.0; calcd for $C_{19}H_{11}IO_3S$ [M^+] 445.9474, found 445.9479.

3-Iodobenzofuran 9{*13*}



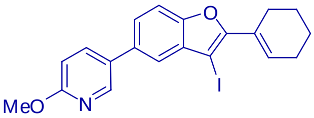
The product was obtained as a pale yellow solid (88% yield): mp 113-115 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.95 (s, 6H), 6.81 (s, 2H), 7.41-7.43 (m, 1H), 7.47-7.52 (m, 3H), 7.90-7.92 (m, 1H), 8.18-8.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.4 (×2), 60.6, 61.1, 104.9 (×2), 111.3, 119.9, 124.9, 125.3, 126.2, 126.4, 131.1, 132.7, 137.4, 137.6, 151.6, 153.1, 153.5 (×2); HRMS calcd for $C_{21}H_{17}IO_4S$ [M^+] 491.9892, found 491.9902.

3-Iodobenzofuran 9{*14*}



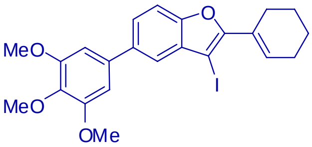
The product was obtained as a colorless oil that solidified upon standing to a dark black semi-solid (91% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67-1.72 (m, 2H), 1.76-1.81 (m, 2H), 2.27-2.30 (m, 2H), 2.61-2.64 (m, 2H), 6.00 (s, 2H), 6.79-6.84 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.08-7.11 (m, 1H), 7.36-7.47 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.9, 22.7, 25.9, 26.9, 59.2, 101.3, 108.2, 108.7, 111.1, 111.4, 119.8, 121.1, 124.6, 128.1, 132.1, 135.9, 136.9, 147.0, 148.2, 152.8, 155.9; HRMS calcd for $C_{21}H_{17}IO_3$ [M$^+$] 444.0222, found 444.0232.

3-Iodobenzofuran 9{*15*}



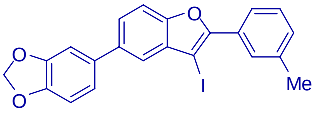
The product was obtained as a pale yellow semi-solid (88% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.58-1.84 (m, 2H), 2.01-2.15 (m, 2H), 2.21-2.36 (m, 2H), 2.45-2.60 (m, 2H), 4.00 (s, 3H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.89 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.47-7.56 (m, 3H), 7.84 (dd, *J* = 8.6, 2.5 Hz, 1H), 8.42 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 16.4, 25.9, 32.0, 53.8, 54.1, 61.9, 111.0, 111.8, 120.0, 124.9, 129.2, 130.4, 132.9, 134.0, 136.4, 138.0, 145.3, 153.2, 153.5, 163.7; calcd for $C_{20}H_{18}INO_2$ [M$^+$] 431.0382, found 431.0393.

3-Iodobenzofuran 9{*16*}



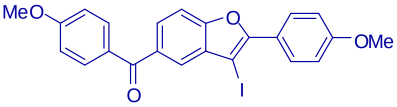
The product was obtained as a pale yellow semi-solid (92% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.67-1.72 (m, 2H), 1.76-1.81 (m, 2H), 2.27-2.30 (m, 2H), 2.61-2.64 (m, 2H), 3.91 (s, 3H), 3.95 (s, 6H), 6.78-6.84 (m, 1H), 6.81 (s, 2H), 7.40-7.48 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.9, 22.7, 25.9, 26.9, 56.5, 59.1 (×2), 61.2, 105.0 (×2), 111.1, 120.0, 124.8, 128.1, 132.3, 132.9, 137.3, 137.6, 137.7, 153.0, 153.6 (×2), 156.0; HRMS calcd for $C_{23}H_{23}IO_4$ [M$^+$] 490.0641, found 490.0657.

3-Iodobenzofuran 9{*17*}



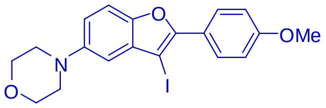
The product was obtained as a pale yellow solid (87% yield): mp 123-124 °C (uncorrected); ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.41 (s, 3H), 5.94 (s, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.04-7.08 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.41 (s, 2H), 7.47 (s, 1H), 7.93 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.7, 61.3, 101.3, 108.1, 108.7, 111.3, 120.0, 121.0, 124.8, 125.1, 128.1, 128.5, 129.9, 130.2, 133.0, 135.7, 137.0, 138.3, 147.0, 148.2, 153.3, 153.8; HRMS calcd for $C_{22}H_{15}IO_3$ [M$^+$] 454.0066, found 454.0073.

3-Iodobenzofuran 9{*18*}



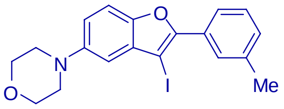
The product was obtained as an ivory solid (82% yield): mp 136-137 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.90 (s, 3H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.78 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.82-7.87 (m, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 55.7, 59.7, 111.0, 113.7 (×2), 114.2 (×2), 122.2, 124.1, 127.6, 129.3 (×2), 130.7, 132.7 (×2), 134.2, 154.8, 156.0, 160.8, 163.3, 195.2; HRMS calcd for $C_{23}H_{17}IO_4$ $[M^+]$ 484.0172, found 484.0180.

3-Iodobenzofuran 9{*19*}



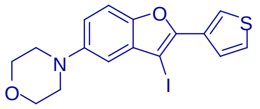
The product was obtained as a yellow solid (84% yield): mp 147-149 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 (t, *J* = 4.7 Hz, 4H), 3.83 (s, 3H), 3.89 (t, *J* = 4.7 Hz, 4H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.96-6.99 (m, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.9 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3 (×2), 55.5, 59.9, 67.2 (×2), 108.1, 111.5, 114.0 (×2), 116.4, 122.8, 129.0 (×2), 133.1, 148.8, 149.0, 153.8, 160.3; HRMS calcd for $C_{19}H_{18}INO_3$ $[M^+]$ 435.0331, found 435.0339.

3-Iodobenzofuran 9{*20*}



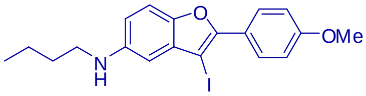
The product was obtained as a yellow solid (82% yield): mp 112-113.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.18 (t, *J* = 4.7 Hz, 4H), 3.90 (t, *J* = 4.7 Hz, 4H), 6.88 (d, *J* = 2.2 Hz, 1H), 7.00 (dd, *J* = 2.3, 8.9 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.36 (m, 2H), 7.96 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 51.3 (×2), 61.2, 67.2 (×2), 108.3, 111.7, 116.9, 124.8, 128.1, 128.5, 130.1, 130.2, 133.1, 138.3, 148.9, 149.2, 153.9; HRMS calcd for $C_{19}H_{18}INO_2$ $[M^+]$ 419.0382, found 419.0390.

3-Iodobenzofuran 9{*21*}



The product was obtained as a yellow solid (81% yield): mp 141-142 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 (t, *J* = 4.7 Hz, 4H), 3.88 (t, *J* = 4.7 Hz, 4H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.96 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.36-7.40 (m, 1H), 7.87-7.89 (m, 1H), 8.13-8.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.2 (×2), 60.9, 67.2 (×2), 108.0, 111.6, 116.6, 124.5, 126.0, 126.4, 131.4, 132.8, 148.7, 148.8, 151.4; HRMS calcd for $C_{16}H_{14}INO_2S$ $[M^+]$ 410.979022, found 410.9796.

3-Iodobenzofuran 9{*23*}

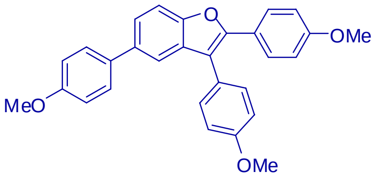


The product was obtained as a pale yellow semi-solid (51% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.6 Hz, 3H), 1.42-1.50 (m, 2H), 1.61-1.69 (m, 2H), 3.17 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 6.55 (d, *J* = 2.0 Hz, 1H), 6.63 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 20.6, 31.9, 45.0, 55.6, 59.7, 103.1, 111.6, 113.4, 114.0 (×2), 123.1, 129.0 (×2), 133.5, 145.5, 147.7, 153.5, 160.3; HRMS calcd for $C_{19}H_{20}INO_2$ [M^+] 421.0539, found 421.0549.

General procedure for Suzuki-Miyaura coupling to prepare 14{*1-31*}

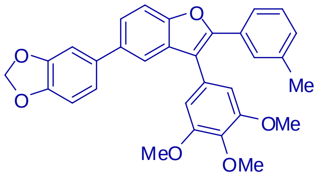
To a 4 dram vial was added the appropriate 3-iodobenzofuran **9** (0.8-1.5 mmol), boronic acid **10** (1.5 equiv), KOH (3.0 equiv) and 5 mol % $Pd(PPh_3)_4$ in 20:5:1 toluene/ethanol/H_2O. The solution was vigorous stirred for 5 min at room temperature, flushed with argon, and then heated to 80 °C until 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.

2,3,5-Trisubstituted benzo[*b*]furan 14{*6*}



The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (88% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.83 (s, 3H), 3.88 (s, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.47 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.52-7.55 (m, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.57 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.48, 55.50, 55.56, 111.2, 114.1 (×2), 114.3 (×2), 114.7 (×2), 115.5, 116.0, 117.9, 123.7, 125.3, 128.5 (×2), 128.6 (×2), 131.1 (×2), 131.3, 134.5, 136.3, 151.2, 153.3, 159.0, 159.2, 159.8; HRMS calcd for $C_{29}H_{25}O_4$ [$M+H^+$] 437.1753, found 437.1744.

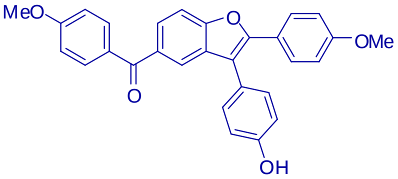
2,3,5-Trisubstituted benzo[*b*]furan 14{*22*}



The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (73% yield):

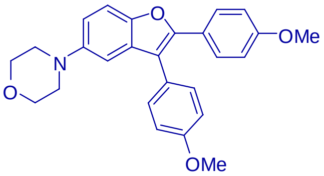
^{1}H NMR (400 MHz, CDCl$_3$) δ 2.35 (s, 3H), 3.81 (s, 6H), 3.96 (s, 3H), 5.99 (s, 2H), 2.03 (s, 2H), 6,88 (d, J = 7.9 Hz, 1H), 7.03-7.08 (m, 2H), 7.11-7.15 (m, 1H), 7.18-7.23 (m, 1H), 7.43-7.50 (m, 2H), 7.56-7.63 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.8, 56.5 (×2), 61.3, 101.4, 107.0 (×2), 108.2, 108.8, 111.4, 117.7, 118.3, 121.0, 124.4, 127.6, 127.9, 128.5, 129.5, 130.5, 130.8, 131.0, 136.3, 136.7, 137.8, 138.3, 147.0, 148.3, 151.5, 153.5, 153.9 (×2); HRMS calcd for $C_{31}H_{27}O_6$ [M+H$^+$] 495.1808, found 495.1802.

2,3,5-Trisubstituted benzo[*b*]furan 14{*24*}



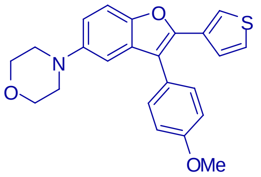
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (69% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.81 (s, 3H), 3.87 (s, 3H), 6.86 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 8.5 Hz, 4H), 7.33 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.9 Hz, 2H), 7.71 (dd, J = 1.7, 8.5 Hz, 1H), 7.84 (d, J = 8.8 Hz, 2H), 7.97 (d, J = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 55.5, 55.7, 110.6, 113.8 (×2), 114.2 (×2), 116.2, 116.4 (×2), 122.5, 123.1, 124.0, 127.0, 128.7 (×2), 130.7, 131.0, 131.1 (×2), 132.9 (×2), 133.4, 152.1, 156.1, 156.2, 160.0, 163.4, 196.6; HRMS calcd for $C_{29}H_{23}O_5$ [M+H$^+$] 451.1545, found 451.1548.

2,3,5-Trisubstituted benzo[*b*]furan 14{*25*}



The product was obtained as a yellow oil that solidified upon standing to a yellow solid (85% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.11 (t, J = 4.7 Hz, 4H), 3.80 (s, 3H), 3.87 (t, J = 4.7 Hz, 4H), 3.88 (s, 3H), 6.84 (d, J = 8.9 Hz, 2H), 6.91-7.10 (m, 2H), 7.01 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.7 Hz, 2H), 7.40-7.43 (m, 1H), 7.56 (d, J = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 51.74 (×2), 55.46, 55.48, 67.2 (×2), 106.8, 111.4, 114.0 (×2), 114.7 (×2), 115.6, 115.9, 123.7, 125.4, 126.5, 128.4 (×2), 131.1 (×2), 131.4, 149.4, 151.4, 159.1, 159.7; HRMS calcd for $C_{26}H_{26}NO_4$ [M+H$^+$] 416.1862, found 416.1851.

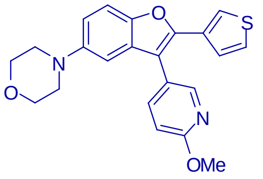
2,3,5-Trisubstituted benzo[*b*]furan 14{*27*}



The product was obtained as a yellow oil that solidified upon standing to a yellow solid (83% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.10 (t, J = 4.7 Hz, 4H), 3.86 (t, J = 4.7 Hz, 4H), 3.89 (s, 3H), 6.91 (d, J = 2.3

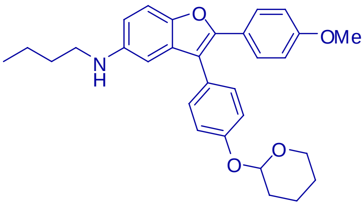
Hz, 1H), 6.98 (dd, *J* = 2.4, 8.9 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 1.2, 5.1 Hz, 1H), 7.23-7.25 (m, 1H), 7.40-7.43 (m, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.55 (dd, *J* = 3.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6 (×2), 55.5, 67.2 (×2), 106.8, 114.4, 114.6 (×2), 115.0, 115.8, 116.5, 122.7, 124.9, 125.8, 126.1, 131.1, 131.2 (×2), 132.2, 148.5, 149.3, 159.4; HRMS calcd for $C_{23}H_{22}NO_3S$ [M+H$^+$] 392.1320, found 392.1312.

2,3,5-Trisubstituted benzo[*b*]furan 14{*28*}



The product was obtained as a yellow oil that solidified upon standing to a yellow solid (71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12 (t, *J* = 4.7 Hz, 4H), 3.88 (t, *J* = 4.7 Hz, 4H), 4.03 (s, 3H), 6.86-6.92 (m, 2H), 7.02 (d, *J* = 8.9 Hz, 1H), 7.16-7.30 (m, 1H), 7.44 (d, *J* = 8.9 Hz, 1H), 7.55-7.59 (m, 1H), 7.69 (dd, *J* = 2.3, 8.5 Hz, 1H), 8.33 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.6 (×2), 53.9, 67.2 (×2), 101.3, 106.4, 111.5, 111.6, 113.2, 116.1, 121.7, 123.2, 125.9, 126.3, 126.7, 130.8, 131.8, 140.5, 147.7, 149.1, 163.9; HRMS calcd for $C_{22}H_{21}N_2O_3S$ [M+H$^+$] 393.1273, found 393.1270.

2,3,5-Trisubstituted benzo[*b*]furan 14{*31*}

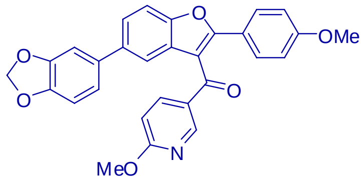


The product was obtained as a yellow oil that solidified upon standing to a dark yellow solid (68% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3H), 1.37-1.48 (m, 2H), 1.57-1.75 (m, 6H), 1.87-1.94 (m, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 3.64-4.05 (m, 2H), 3.81 (s, 3H), 5.49 (t, *J* = 3.3 Hz, 1H), 6.63-6.69 (m, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 9.3 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 19.3, 25.5, 30.7, 31.8, 45.6, 55.5, 62.7, 96.8, 111.4, 112.7, 114.0 (×2), 115.7, 116.1, 117.0 (×2), 118.1, 123.9, 126.7, 128.4 (×2), 131.0, 131.5, 148.2, 151.0, 156.6, 159.6; HRMS calcd for $C_{30}H_{34}NO_4$ [M+H$^+$] 472.2488, found 472.2456.

General procedure for carbonylative Suzuki coupling to prepare 14{*32-45*}

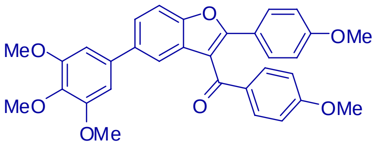
A mixture of 3-iodobenzofuran **9** (0.1 mmol), boronic acid **10** (1.1 equiv), K_2CO_3 (3.0 equiv), NaI (3.0 equiv) and 3 mol % $PdCl_2(PPh_3)_2$ in anisole (2.0 mL) were added to a vial with a magnetic stir bar under an Ar atmosphere. After sealing the vial, the atmosphere was changed to carbon monoxide and the reaction mixture was kept at 80 °C for 12 h with vigorous stirring. Upon cooling to room temperature, the reaction mixture was diluted with EtOAc. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexanes as the eluent to afford both the corresponding carbonyl-containing product **14**{*32,34,36,38,40,42,44*} and the direct coupling product **14**{*33,35,37,39,41,43,45*}.

2,3,5-Trisubstituted benzo[*b*]furan 14{*34*}



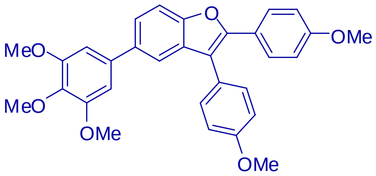
The product was obtained as a pale yellow oil (44% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.94 (s, 3H), 5.99 (s, 2H), 6.70 (d, *J* = 8.7 Hz, 1H), 6.85-6.89 (m, 1H), 6.86 (d, *J* = 9.0 Hz, 2H), 7.00-7.07 (m, 2H), 7.49 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 0.8 Hz, 1H), 8.07 (dd, *J* = 2.4, 8.7 Hz, 1H), 8.62 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.3, 55.6, 101.3, 108.2, 108.7, 111.1, 111.4, 114.3 (×2), 115.5, 119.3, 121.1, 121.9, 124.8, 127.5, 129.1, 130.3 (×2), 135.8, 137.5, 139.7, 147.1, 148.2, 151.3, 153.3, 158.3, 158.6, 161.1, 166.9, 189.9; HRMS calcd for $C_{29}H_{22}NO_6$ [M+H^{+}] 480.1447, found 480.1456.

2,3,5-Trisubstituted benzo[*b*]furan 14{*38*}



The product was obtained as a pale yellow oil (41% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.83 (s, 3H), 3.88 (s, 3H), 3.91 (s, 6H), 6.73 (s, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 7.47-7.53 (m, 1H), 7.58-7.65 (m, 2H), 7.69 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.56, 55.69, 56.4 (×2), 61.2, 104.8 (×2), 111.3, 113.9 (×2), 114.2 (×2), 115.2, 119.7, 122.2, 124.6, 129.6, 130.0 (×2), 130.8, 132.5 (×2), 132.55, 137.55, 137.61, 143.7, 153.5 (×2), 160.9, 163.88, 163.93; HRMS calcd for $C_{32}H_{29}O_7$ [M+H^{+}] 525.1913, found 525.1918.

2,3,5-Trisubstituted benzo[*b*]furan 14{*39*}

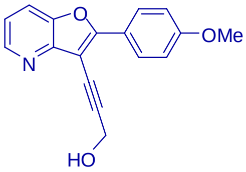


The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (31% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.89 (s, 6H), 3.91 (s, 6H), 6.76 (s, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 7.45-7.48 (m, 1H), 7.49-7.58 (m, 2H), 7.61 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.49, 55.51, 56.5 (×2), 61.2, 105.0 (×2), 111.2, 114.1 (×2), 114.7 (×2), 115.9, 118.2, 123.5, 124.1, 125.2, 128.6 (×2), 131.1 (×2), 131.2, 137.0, 137.4, 138.2, 151.5, 153.5 (×2), 153.6, 159.2, 159.9; HRMS calcd for $C_{31}H_{29}O_6$ [M+H^{+}] 497.1964, found 497.1967.

General procedure for Sonogashira coupling to prepare 14{*46-77*}

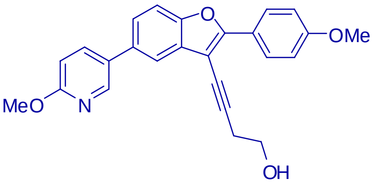
To a 4 dram vial was added the appropriate 3-iodobenzofuran **9** (0.8-1.5 mmol), the alkyne **6** (1.2 equiv), 3 mol % $PdCl_2(PPh_3)_2$, 3 mol % CuI, DMF (1.5 mL) and Et_2NH (1.5 mL). The solution was stirred at room temperature and flushed with argon, and then heated to 50 °C until TLC revealed complete 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.

2,3-Disubstituted furo[*b*]pyridine 14{*49*}



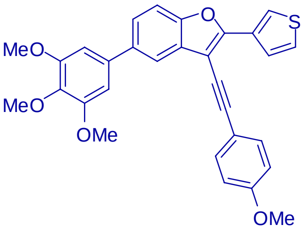
The product was obtained as a yellow oil that solidified upon standing to a dark yellow solid (77% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51 (br s, 1H), 3.85 (s, 3H), 4.70 (s, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 7.19 (dd, *J* = 8.3, 4.8 Hz, 1H), 7.70 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.22 (d, *J* = 9.0 Hz, 2H), 8.56 (dd, *J* = 4.8, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 55.6, 75.9, 97.2, 98.0, 114.4 (×2), 118.2, 119.3, 122.1, 128.1 (×2), 146.2, 146.8, 149.0, 159.8, 161.2; HRMS calcd for $C_{17}H_{14}NO_3$ [$M+H^+$] 280.0974, found 280.0987.

2,3,5-Trisubstituted benzo[*b*]furan 14{*62*}



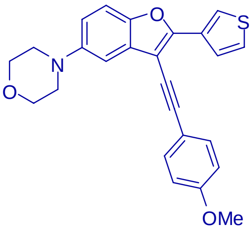
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (79% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (br s, 1H), 2.88 (t, *J* = 6.3 Hz, 2H), 3.87 (s, 3H), 3.93 (br s, 2H), 3.99 (s, 3H), 6.82 (d, *J* = 8.5 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.40 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.49 (dd, *J* = 1.9, 8.5 Hz, 1H), 7.68 (d, *J* = 1.3 Hz, 1H), 7.83 (dd, *J* = 2.5, 8.5 Hz, 1H), 8.21 (d, *J* = 8.9 Hz, 2H), 8.43 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 53.8, 55.6, 61.5, 74.2, 94.2, 97.6, 110.9, 111.5, 114.3 (×2), 118.1, 123.0, 124.0, 127.7 (×2), 130.6, 131.2, 133.6, 138.0, 145.3, 152.9, 157.3, 160.5, 163.6; HRMS calcd for $C_{25}H_{22}NO_4$ [$M+H^+$] 400.1549, found 400.1552.

2,3,5-Trisubstituted benzo[*b*]furan 14{*67*}



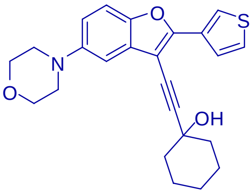
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (82% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.91 (s, 3H), 3.96 (s, 6H), 6.83 (s, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.44 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.48-7.53 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 1.0 Hz, 1H), 7.98 (dd, *J* = 5.1, 0.8 Hz, 1H), 8.16 (dd, *J* = 3.0, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 56.5 (×2), 61.2, 79.6, 96.9, 105.0 (×2), 111.4, 114.4 (×2), 115.5, 118.8, 123.9, 124.9, 125.8, 126.4, 130.2, 131.8, 133.2 (×2), 134.2, 135.4, 137.6, 137.8, 153.1, 153.6 (×2), 154.5, 160.1; HRMS calcd for $C_{30}H_{25}O_5S$ [M+H$^+$] 497.1423, found 497.1421.

2,3,5-Trisubstituted benzo[*b*]furan 14{*75*}



The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (83% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (t, *J* = 4.7 Hz, 4H), 3.85 (s, 3H), 3.90 (t, *J* = 4.7 Hz, 4H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.99 (dd, *J* = 2.3, 8.9 Hz, 1H), 7.17 (d, *J* = 2.2 Hz, 1H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.38-7.43 (m, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.93 (d, *J* = 5.1 Hz, 1H), 7.98-8.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4 (×2), 55.6, 67.3 (×2), 79.9, 96.7, 98.7, 107.0, 111.6, 114.3 (×2), 115.6, 116.3, 123.5, 125.7, 126.3, 130.4, 132.0, 133.2 (×2), 148.6, 148.8, 154.4, 160.0; HRMS calcd for $C_{25}H_{22}NO_3S$ [M+H$^+$] 416.1320, found 416.1317.

2,3,5-Trisubstituted benzo[*b*]furan 14{*77*}

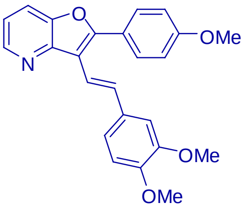


The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (86% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30-1.62 (m, 8H), 2.12-2.30 (m, 2H), 2.51 (s, 1H), 3.16 (t, *J* = 4.7 Hz, 4H), 3.91 (t, *J* = 4.7 Hz, 4H), 6.95 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 7.40 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.87 (dd, *J* = 5.1, 1.2 Hz, 1H), 8.05 (dd, *J* = 3.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 (×2), 25.4, 40.3 (×2), 51.4 (×2), 67.2 (×2), 69.6, 76.0, 98.1, 100.7, 106.8, 111.6, 116.3, 123.6, 125.6, 126.3, 130.4, 131.8, 148.6, 148.7, 154.5; HRMS calcd for $C_{24}H_{26}NO_3S$ [M+H$^+$] 408.1633, found 408.1628.

General procedure for Heck coupling to prepare 14{*78-98*}

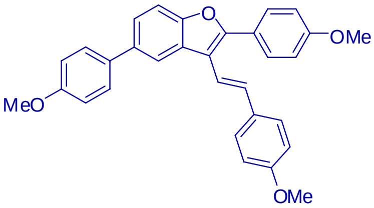
To a 4 dram vial was added the appropriate 3-iodobenzofuran **9** (0.8-1.5 mmol), the styrene **12** (1.2 equiv), 5 mol % $Pd(OAc)_2$, *n*-Bu_4NI (1.0 equiv), Na_2CO_3 (2.5 equiv) and DMF (1.5 mL). The solution was stirred at room temperature and flushed with argon, and then heated to 80 °C until TLC 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.

2,3-Disubstituted furo[*b*]pyridine 14{*81*}



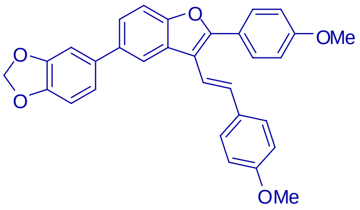
The product was obtained as a yellow oil that solidified upon standing to a dark yellow solid (72% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 3H), 3.91 (s, 3H), 3.94 (s, 3H), 6.88 (d, J = 8.3 Hz, 1H), 7.07 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 1.9 Hz, 1H), 7.17-7.25 (m, 3H), 7.74 (dd, J = 1.3, 8.2 Hz, 1H), 7.81 (d, J = 8.9 Hz, 2H), 8.22 (d, J = 16.1 Hz, 1H), 8.63 (dd, J = 1.3, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.6, 56.1, 56.1, 109.8, 111.4, 113.9, 114.6 (×2), 116.1, 117.7, 119.0, 119.3, 123.3, 129.7 (×2), 131.5, 132.7, 145.7, 147.5, 148.1, 148.9, 149.1, 156.1, 160.7; HRMS calcd for $C_{24}H_{22}NO_4$ [M+H$^+$] 388.1549, found 388.1548.

2,3,5-Trisubstituted benzo[*b*]furan 14{*83*}



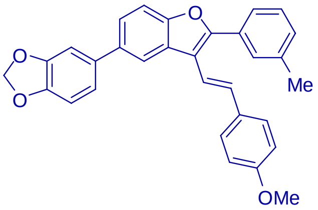
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (69% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.87 (s, 3H), 3.88 (s, 3H), 6.93 (d, J = 8.8 Hz, 2H), 6.97-7.05 (m, 4H), 7.16-7.31 (m, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.45-7.56 (m, 2H), 7.59 (d, J = 8.9 Hz, 2H), 7.77 (d, J = 8.9 Hz, 2H), 8.02 (d, J = 1.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.59, 55.61, 55.61, 111.4, 113.8, 114.38 (×2), 114.40 (×2), 114.45 (×2), 118.2, 119.1, 123.8, 124.0, 127.6 (×2), 128.8 (×2), 129.5 (×2), 130.5, 130.8, 130.9, 134.7, 136.6, 153.76, 153.78, 159.1, 159.4, 160.2; HRMS calcd for $C_{31}H_{27}O_4$ [M+H$^+$] 463.1909, found 463.1921.

2,3,5-Trisubstituted benzo[*b*]furan 14{*85*}



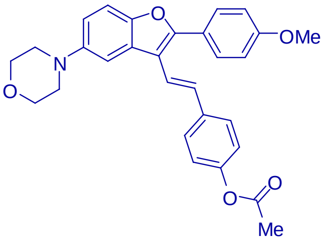
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (76% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.88 (s, 3H), 6.01 (s, 2H), 6.89-6.95 (m, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 7.07-7.15 (m, 2H), 7.21 (s, 1H), 7.25 (d, *J* = 1.5 Hz, 1H), 7.44-7.55 (m, 4H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.98 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.59, 55.62, 101.3, 108.4, 108.8, 111.4, 113.8, 114.4 (×2), 114.5 (×2), 118.2, 119.2, 121.2, 123.7, 124.1, 127.6 (×2), 128.8, 129.5 (×2), 130.5, 130.8, 136.5, 136.7, 147.0, 148.2, 153.8, 153.9, 159.4, 160.2; HRMS calcd for $C_{31}H_{25}O_5$ [M+H$^+$] 477.1702, found 477.1708.

2,3,5-Trisubstituted benzo[*b*]furan 14{*92*}



The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (76% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.84 (s, 3H), 6.01 (s, 2H), 6.88-6.95 (m, 3H), 7.07-7.13 (m, 2H), 7.19-7.32 (m, 3H), 7.36-7.42 (t, *J* = 7.6 Hz, 1H), 7.44-7.57 (m, 4H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.66 (s, 1H), 8.00 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 55.6, 101.4, 108.4, 108.8, 111.5, 114.4 (×2), 114.9, 118.0, 119.4, 121.2, 124.4, 125.4, 127.7 (×2), 128.5, 128.6, 128.8, 129.7, 130.8, 130.9, 131.0, 136.5, 136.7, 138.7, 147.0, 148.2, 153.8, 154.0, 159.5; HRMS calcd for $C_{31}H_{25}O_4$ [M+H$^+$] 461.1753, found 461.1759.

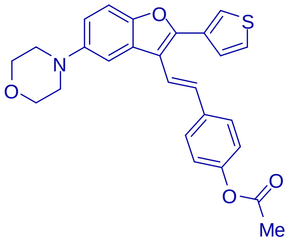
2,3,5-Trisubstituted benzo[*b*]furan 14{*95*}



The product was obtained as a yellow oil that solidified upon standing to a yellow solid (64% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.19 (t, *J* = 4.7 Hz, 4H), 3.93 (t, *J* = 4.7 Hz, 4H), 2.88 (s, 3H), 6.98-7.04 (m, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 7.10 (s, 1H), 7.12 (s, 1H), 7.38 (d, *J*

= 2.3 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 51.8 (×2), 55.6, 67.3 (×2), 108.1, 111.6, 113.4, 114.5 (×2), 115.7, 120.9, 122.1 (×2), 123.6, 127.3 (×2), 128.7, 129.5 (×2), 129.6, 136.0, 148.6, 149.9, 150.1, 154.5, 160.2, 169.8; HRMS calcd for $C_{29}H_{28}NO_5$ [M+H$^+$] 470.1967, found 470.1978.

2,3,5-Trisubstituted benzo[*b*]furan 14{*97*}

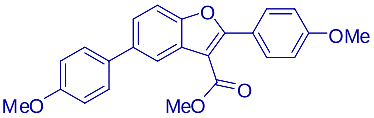


The product was obtained as a yellow oil that solidified upon standing to a yellow solid (64% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 3H), 3.19 (t, *J* = 4.7 Hz, 4H), 3.93 (t, *J* = 4.7 Hz, 4H), 7.03 (dd, *J* = 2.3, 8.9 Hz, 1H), 7.13 (d, *J* = 8.5 Hz, 2H), 7.16-7.34 (m, 2H), 7.37 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 7.44-7.47 (m, 1H), 7.54-7.58 (m, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 51.8 (×2), 67.3 (×2), 108.1, 111.7, 114.1, 115.5, 116.1, 120.2, 122.2 (×2), 124.2, 126.6, 126.7, 127.4 (×2), 128.4, 130.2, 132.1, 135.8, 148.7, 149.8, 150.2, 169.8; HRMS calcd for $C_{26}H_{24}NO_4S$ [M+H$^+$] 446.1426, found 446.1435.

General procedure for carboalkoxylation to prepare 14{*99-121*}

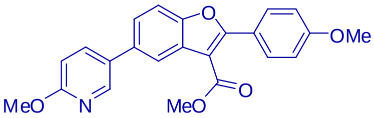
A mixture of 3-iodobenzofuran **9** (0.1 mmol), 5 mol % dppf, 3 mol % $Pd(OAc)_2$, and TEA (2.0 equiv) in MeOH (1.0 mL) and DMF (1.0 mL) was flushed with an atmosphere of carbon monoxide. The solution was stirred at room temperature and then heated to 70 °C until TLC revealed complete conversion of the 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.

2,3,5-Trisubstituted benzo[*b*]furan 14{*106*}



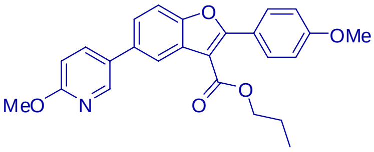
The product was obtained as a colorless oil that solidified upon standing to a white solid (71% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.89 (s, 3H), 3.96 (s, 3H), 7.01 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.49-7.56 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 8.05 (d, *J* = 9.0 Hz, 2H), 8.17 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 55.60, 55.62, 107.8, 111.2, 113.8 (×2), 114.4 (×2), 120.7, 122.2, 124.5, 127.9, 128.8 (×2), 131.3 (×2), 134.4, 137.5, 153.0, 159.2, 161.4, 161.9, 164.9; HRMS calcd for $C_{24}H_{21}O_5$ [M+H$^+$] 389.1389, found 389.1397.

2,3,5-Trisubstituted benzo[*b*]furan 14{*109*}



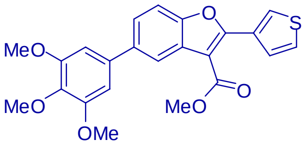
The product was obtained as a colorless oil that solidified upon standing to a white solid (76% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.89 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 6.85 (d, *J* = 8.6 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 7.46 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 8.6, 2.6 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 1.4 Hz, 1H), 8.45 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 51.9, 53.8, 55.6, 107.7, 111.0, 111.5, 113.8 (×2), 120.8, 122.0, 124.2, 128.1, 130.7, 131.4 (×2), 134.4, 138.0, 145.4, 153.2, 161.5, 162.1, 163.6, 164.7; HRMS calcd for $C_{23}H_{20}NO_5$ [M+H$^+$] 390.1341, found 390.1346.

2,3,5-Trisubstituted benzo[*b*]furan 14{*110*}



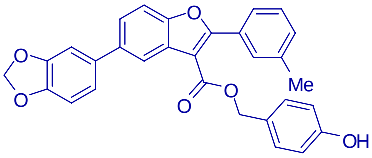
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (69% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.04 (t, *J* = 7.4 Hz, 3H), 1.57-1.58 (m, 2H), 3.89 (s, 3H), 4.01 (s, 3H), 4.34 (t, *J* = 6.7 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 7.48 (dd, *J* = 1.9, 8.5 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 2.6, 8.6 Hz, 1H), 8.06 (d, *J* = 9.0 Hz, 2H), 8.19 (d, *J* = 1.4 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 10.9, 22.4, 53.8, 55.6, 66.6, 108.0, 111.0, 111.6, 113.8 (×2), 115.5, 120.8, 122.1, 124.2, 128.3, 130.7, 131.4 (×2), 134.3, 138.0, 145.3, 153.3, 161.5, 163.6, 164.4; HRMS calcd for $C_{25}H_{24}NO_5$ [M+H$^+$] 418.1654, found 418.1659.

2,3,5-Trisubstituted benzo[*b*]furan 14{*115*}



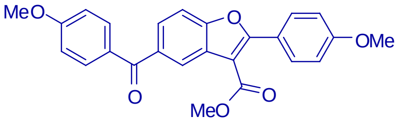
The product was obtained as a pale yellow oil that solidified upon standing to a yellow solid (80% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.92 (s, 3H), 3.96 (s, 6H), 4.01 (s, 3H), 6.83 (s, 2H), 7.42 (dd, *J* = 5.1, 3.1 Hz, 1H), 7.51-7.57 (m, 2H), 7.92 (dd, *J* = 1.2, 5.1 Hz, 1H), 8.16 (d, *J* = 1.2 Hz, 1H), 8.62 (dd, *J* = 1.2, 3.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 52.0, 56.5 (×2), 61.2, 105.7 (×2), 107.8, 111.2, 115.5, 121.3, 125.1, 125.5, 127.5, 128.1, 129.6, 130.6, 137.9, 138.2, 152.9, 153.6 (×2), 157.5, 164.7; HRMS calcd for $C_{46}H_{44}O_{12}NS_2$ [2M+NH$_4^+$] 866.2305, found 866.2322.

2,3,5-Trisubstituted benzo[*b*]furan 14{*118*}



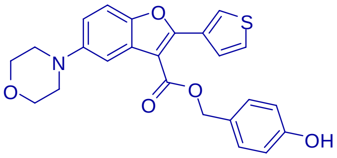
The product was obtained as a colorless oil that solidified upon standing to a white solid (71% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.43 (s, 3H), 4.72 (s, 2H), 6.00 (s, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 7.07-7.14 (m, 2H), 7.22-7.26 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.52-7.62 (m, 2H), 7.88-7.93 (m, 2H), 8.26 (d, *J* = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 21.7, 65.0, 101.4, 108.3, 108.8, 111.6, 121.0, 121.2, 122.1 (×2), 125.1, 127.1, 127.6, 128.3, 128.4 (×2), 129.4, 130.3, 131.7, 135.9, 137.9, 138.1, 138.9, 147.2, 148.3, 150.0, 153.4, 162.7, 163.2; HRMS calcd for $C_{30}H_{23}O_6$ [M+H$^+$] 479.1495, found 479.1502.

2,3,5-Trisubstituted benzo[*b*]furan 14{*119*}



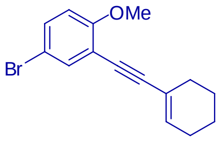
The product was obtained as a colorless oil that solidified upon standing to a pale yellow solid (74% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.89 (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 8.45 (d, *J* = 1.4 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 52.0, 55.6, 55.7, 108.0, 111.0, 113.7 (×2), 113.9 (×2), 121.6, 125.2, 127.26, 127.31, 130.7 (×2), 131.4 (×2), 132.8, 134.7, 155.5, 161.7, 162.5, 163.3, 164.5, 195.5; HRMS calcd for $C_{25}H_{21}O_6$ [M+H$^+$] 417.1338, found 417.1347.

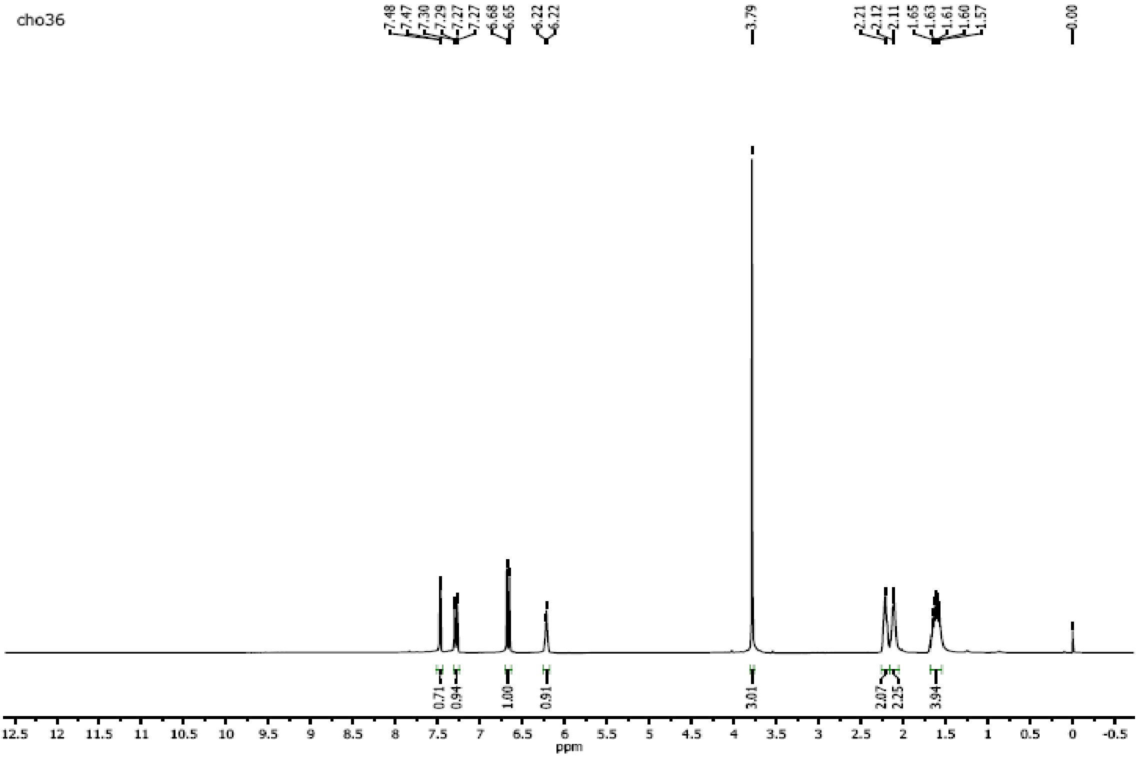
2,3,5-Trisubstituted benzo[*b*]furan 14{*121*}

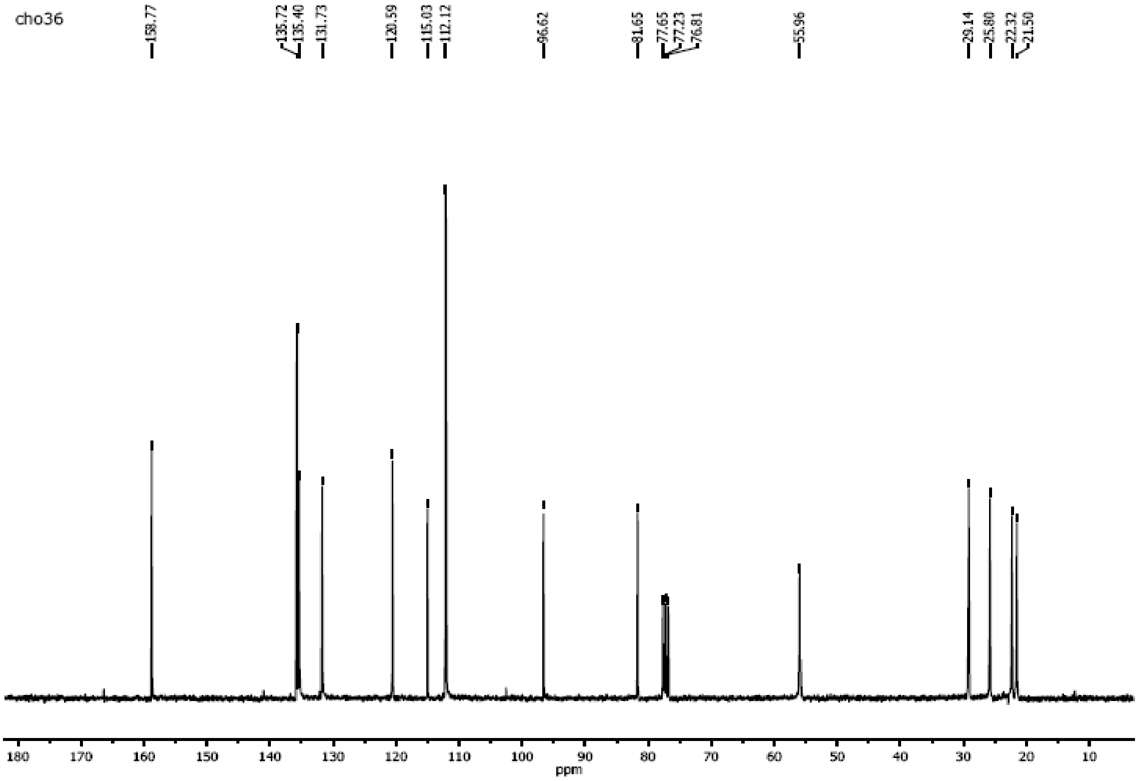


The product was obtained as a yellow oil that solidified upon standing to a yellow solid (54% yield): ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.18 (t, *J* = 4.7 Hz, 4H), 3.88 (t, *J* = 4.7 Hz, 4H), 4.74 (s, 2H), 7.05 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.34-7.40 (m, 1H), 7.43-7.50 (m, 3H), 7.65 (d, *J* = 2.3 Hz, 1H), 7.91 (dd, *J* = 5.2, 1.2 Hz, 1H), 8.63 (dd, *J* = 3.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 51.2 (×2), 64.9, 67.2 (×2), 107.0, 109.4, 111.6, 116.5, 122.3 (×2), 125.5, 127.5, 128.2, 128.4 (×2), 130.0, 130.5, 139.1, 148.7, 149.3, 150.0, 158.7, 163.1; HRMS calcd for $C_{48}H_{46}N_2O_{10}S_2$ [2M+NH$_4^+$] 874.2594, found 874.2607.

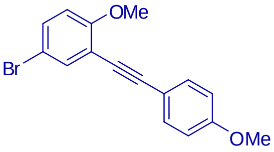
Bromoalkyne 7{*5*}

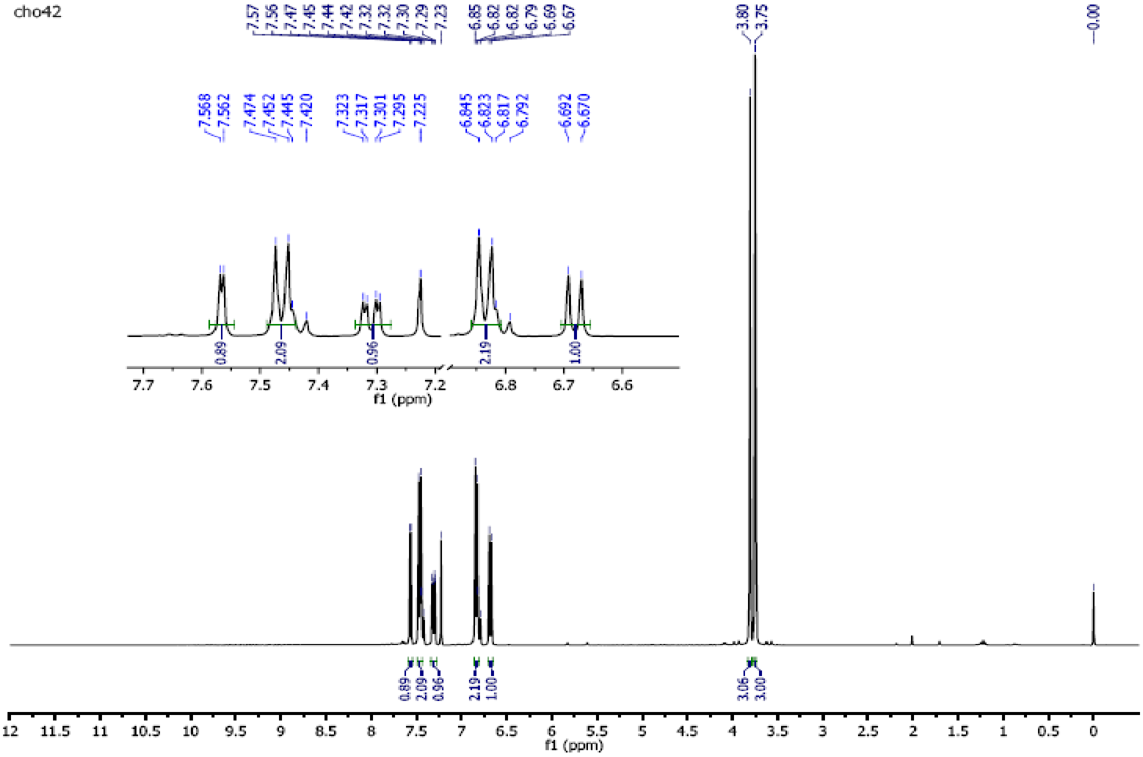


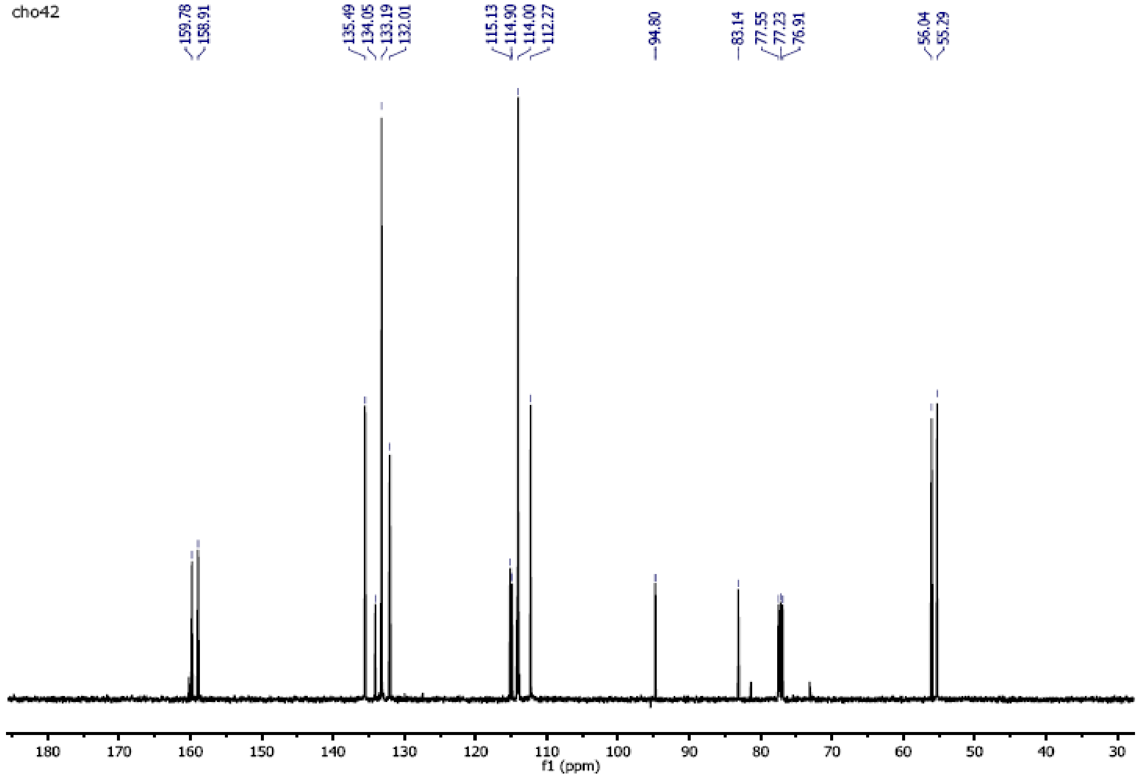




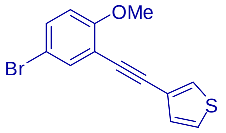
Bromoalkyne 7{*6*}

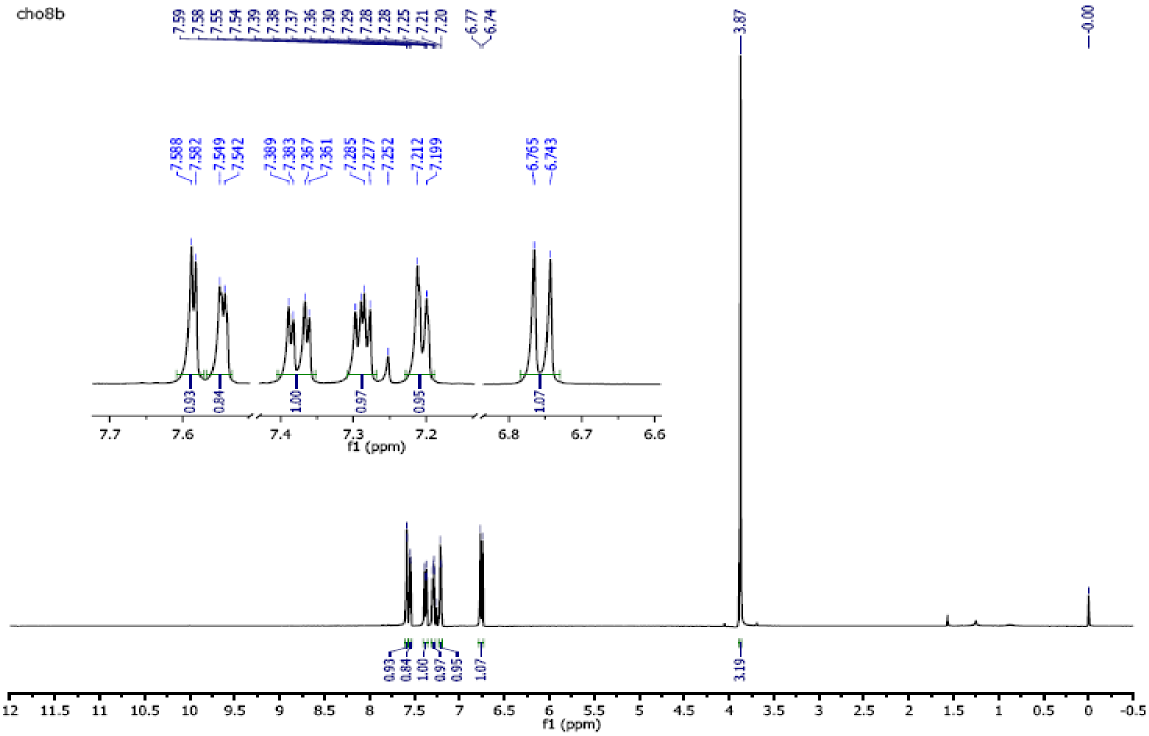


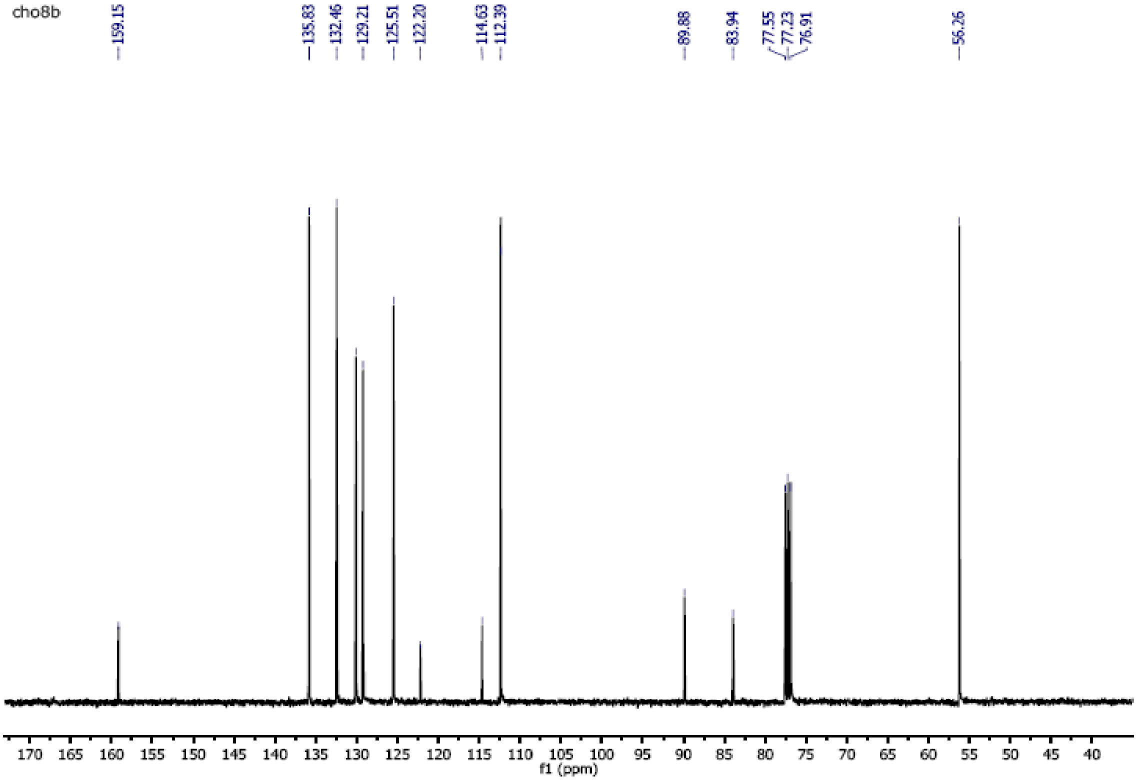




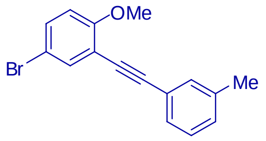
Bromoalkyne 7{*7*}

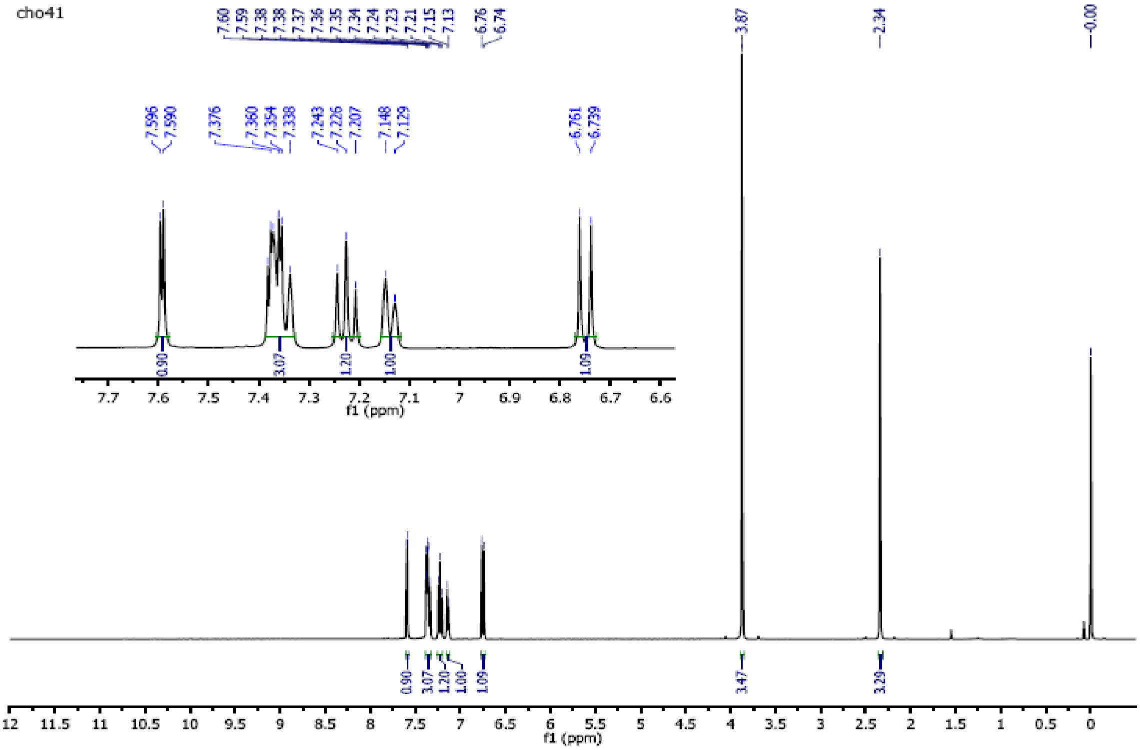


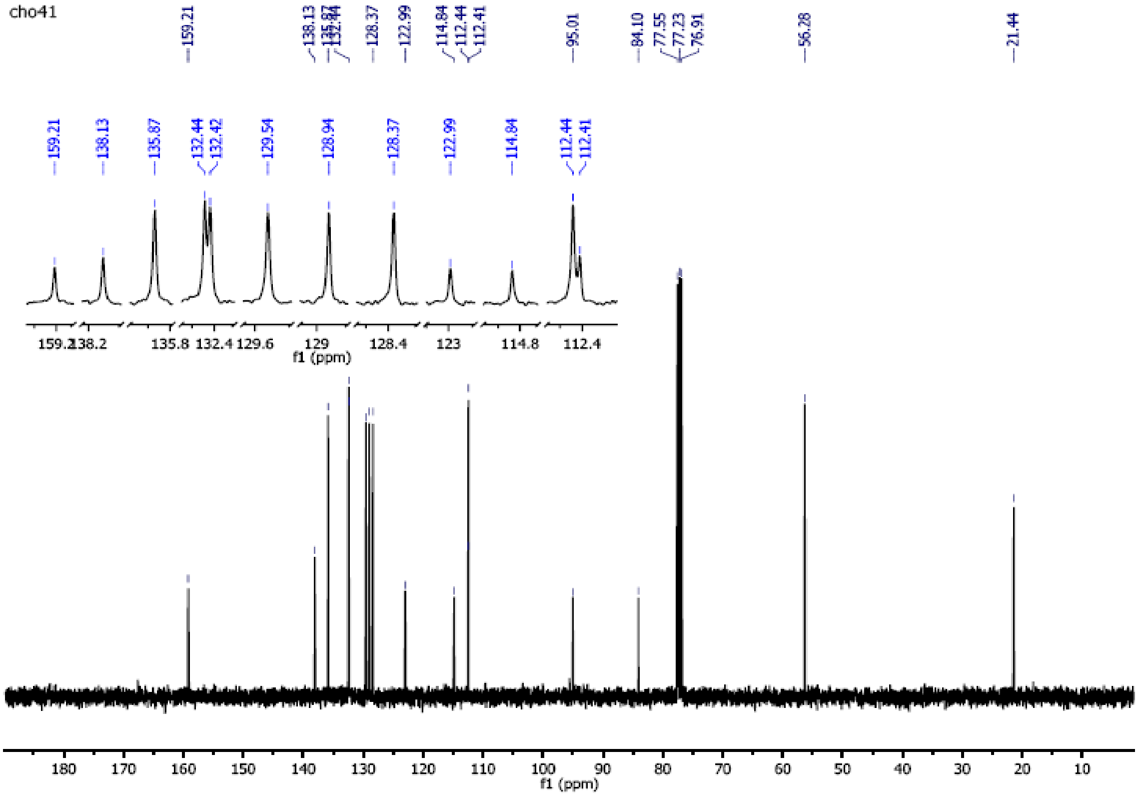




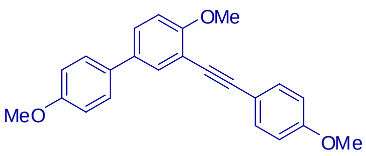
Bromoalkyne 7{*8*}



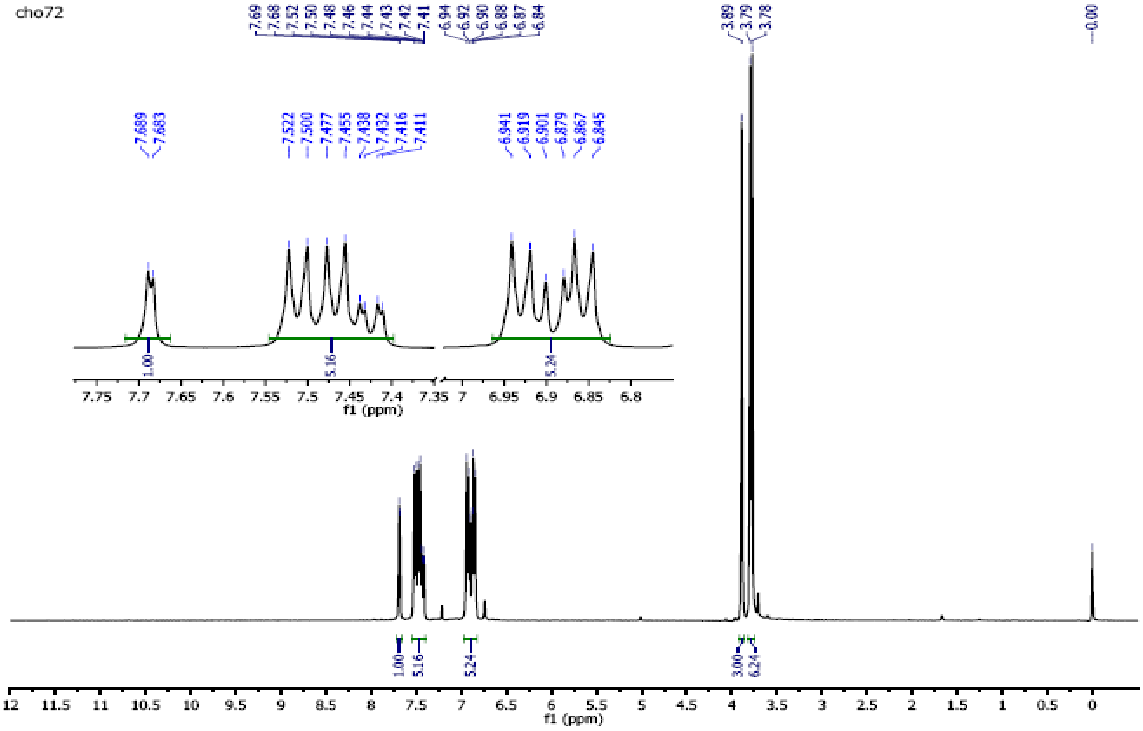




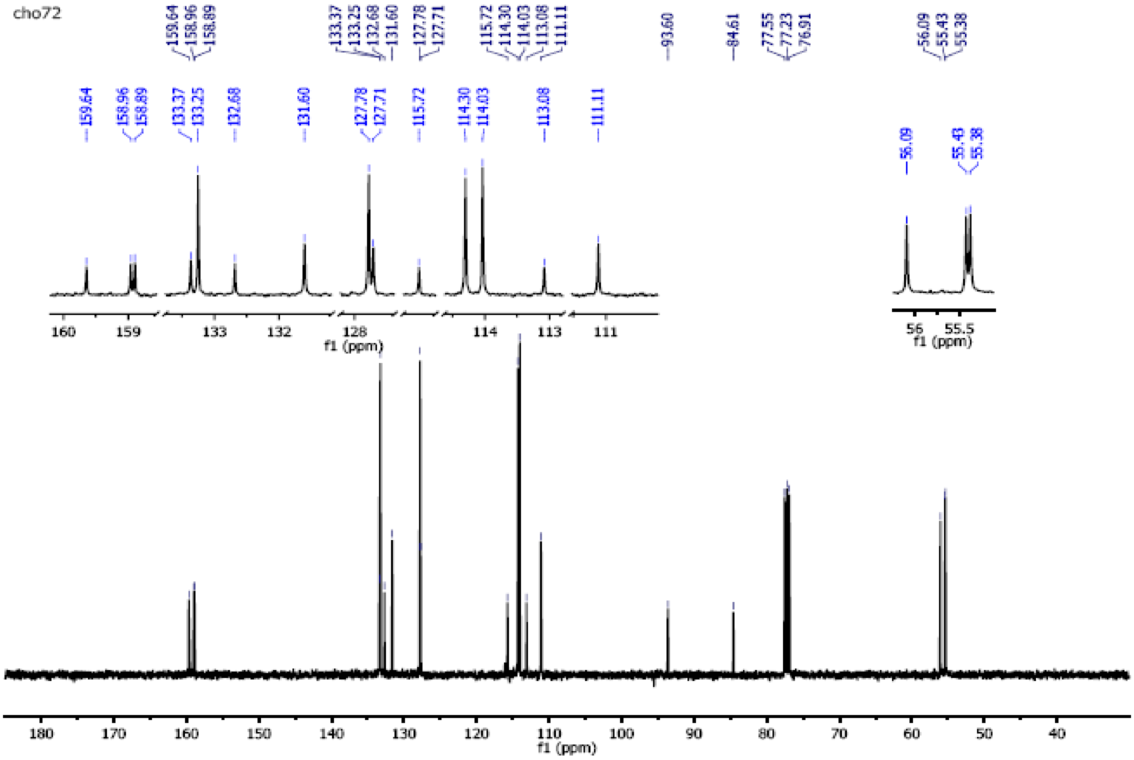
Alkyne 8{*1*}



OMe
MeO
OMe

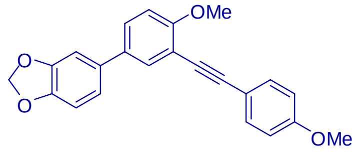


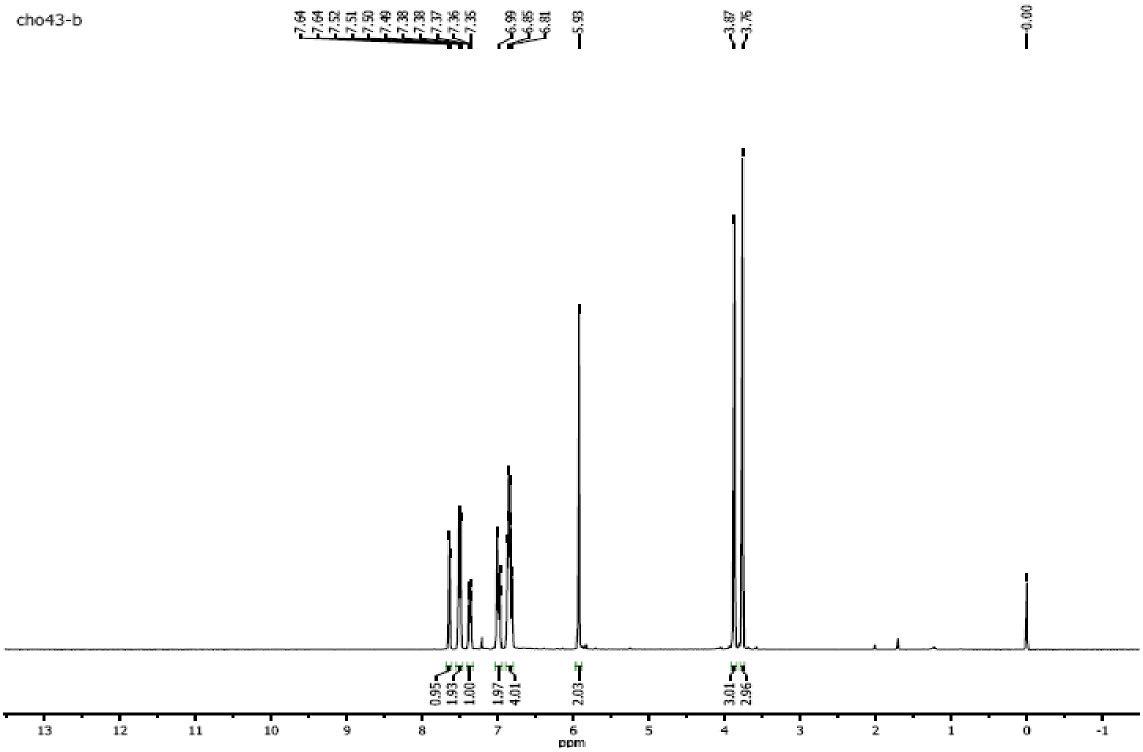
cho72
7.69
7.68
7.52
7.50
7.48
7.46
7.44
7.43
7.42
7.41
6.94
6.92
6.90
6.88
6.87
6.84
3.89
3.79
3.78
0.00
7.689
7.683
7.522
7.500
7.477
7.455
7.438
7.432
7.416
7.411
6.941
6.919
6.901
6.879
6.867
6.845
1.00
5.16
5.24
3.00
6.24
f1 (ppm)

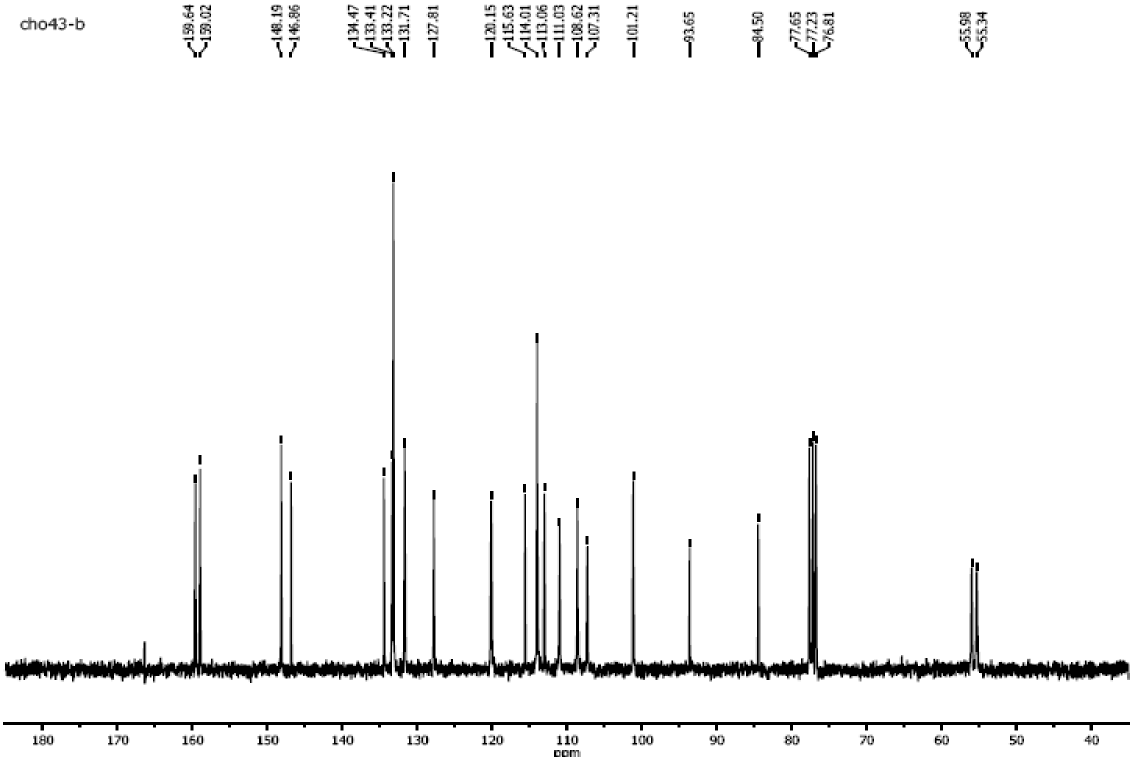


cho72
159.64
158.96
158.89
133.37
133.25
132.68
131.60
127.78
127.71
115.72
114.30
114.03
113.08
111.11
93.60
84.61
77.55
77.23
76.91
56.09
55.43
55.38
f1 (ppm)

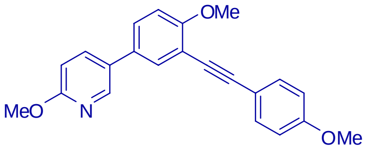
Alkyne 8{*2*}


OMe
O
O
OMe

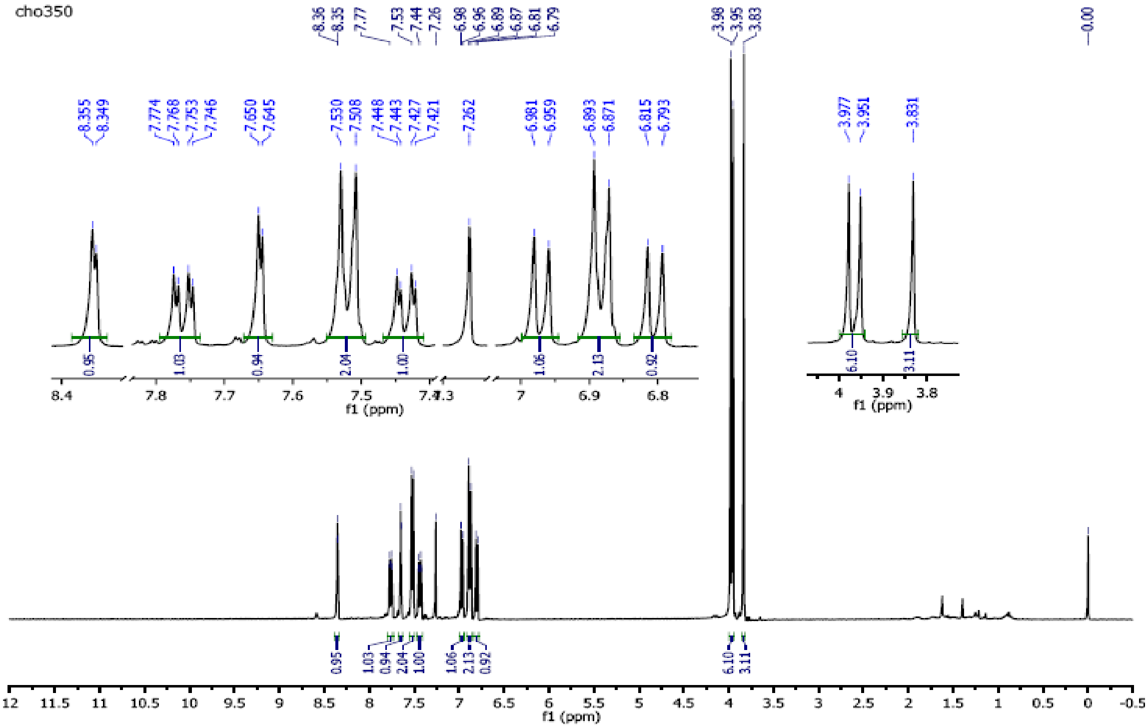

cho43-b
7.64
7.64
7.52
7.51
7.50
7.49
7.38
7.38
7.37
7.36
7.35
6.99
6.85
6.81
5.93
3.87
3.76
0.00
0.95
1.93
1.00
1.97
4.01
2.03
3.01
2.96
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


cho43-b
159.64
159.02
148.19
146.86
134.47
133.41
133.22
131.71
127.81
120.15
115.63
114.01
113.06
111.03
108.62
107.31
101.21
93.65
84.50
77.65
77.23
76.81
55.98
55.34
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

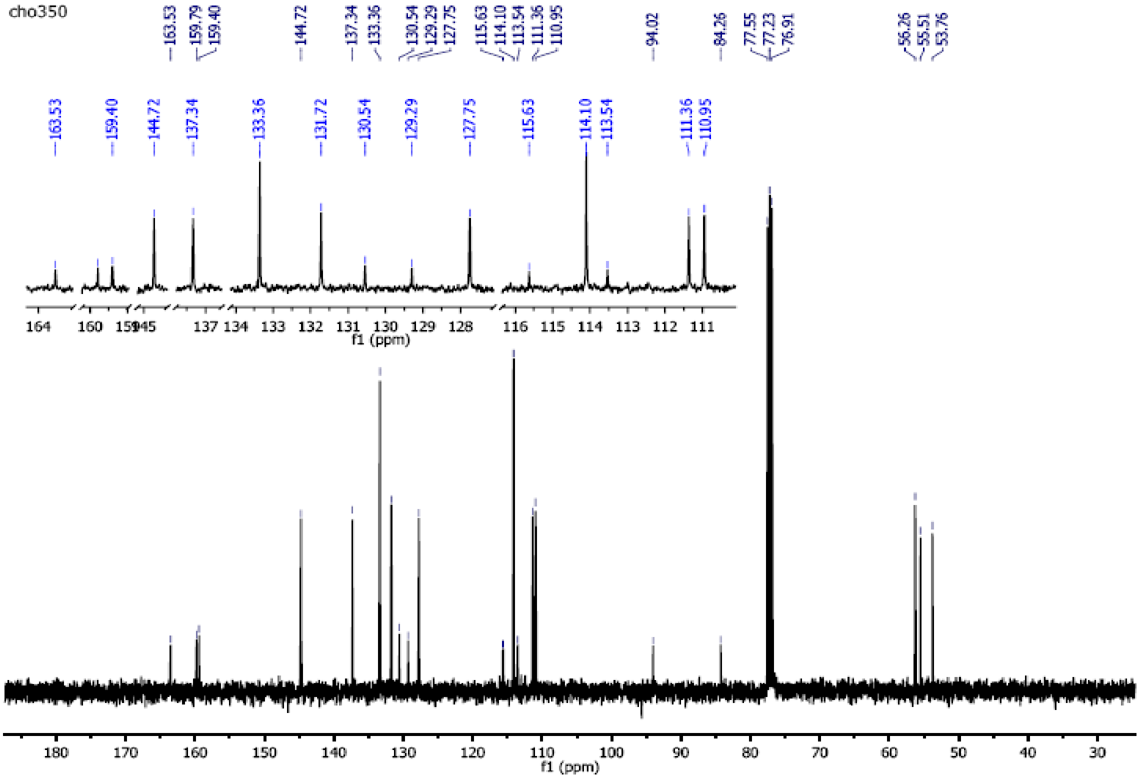
Alkyne 8{*3*}



OMe
MeO
N
OMe

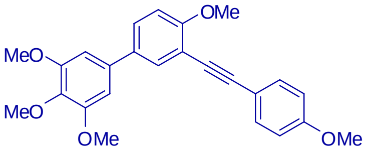


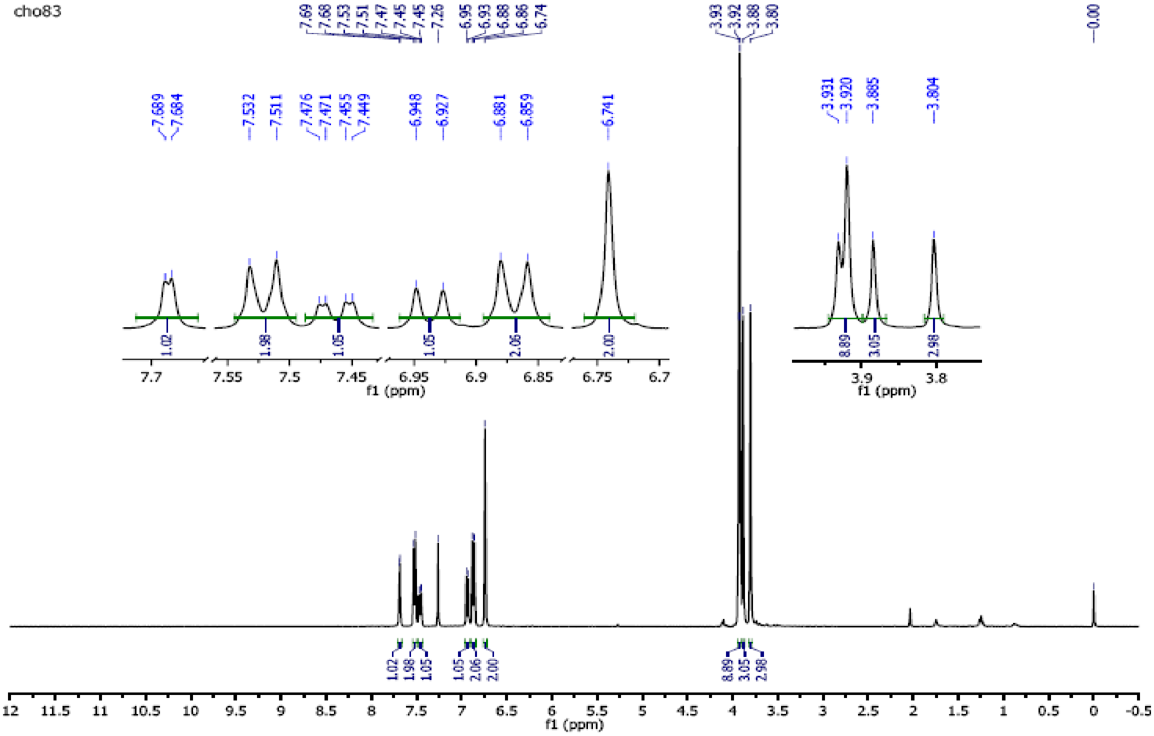
cho350
8.36
8.35
7.77
7.53
7.44
7.26
6.98
6.96
6.89
6.87
6.81
6.79
3.98
3.95
3.83
0.00
8.355
8.349
7.774
7.768
7.753
7.746
7.650
7.645
7.530
7.508
7.448
7.443
7.427
7.421
7.262
6.981
6.959
6.893
6.871
6.815
6.793
3.977
3.951
3.831
0.95
1.03
0.94
2.04
1.00
1.06
2.13
0.92
6.10
3.11
f1 (ppm)

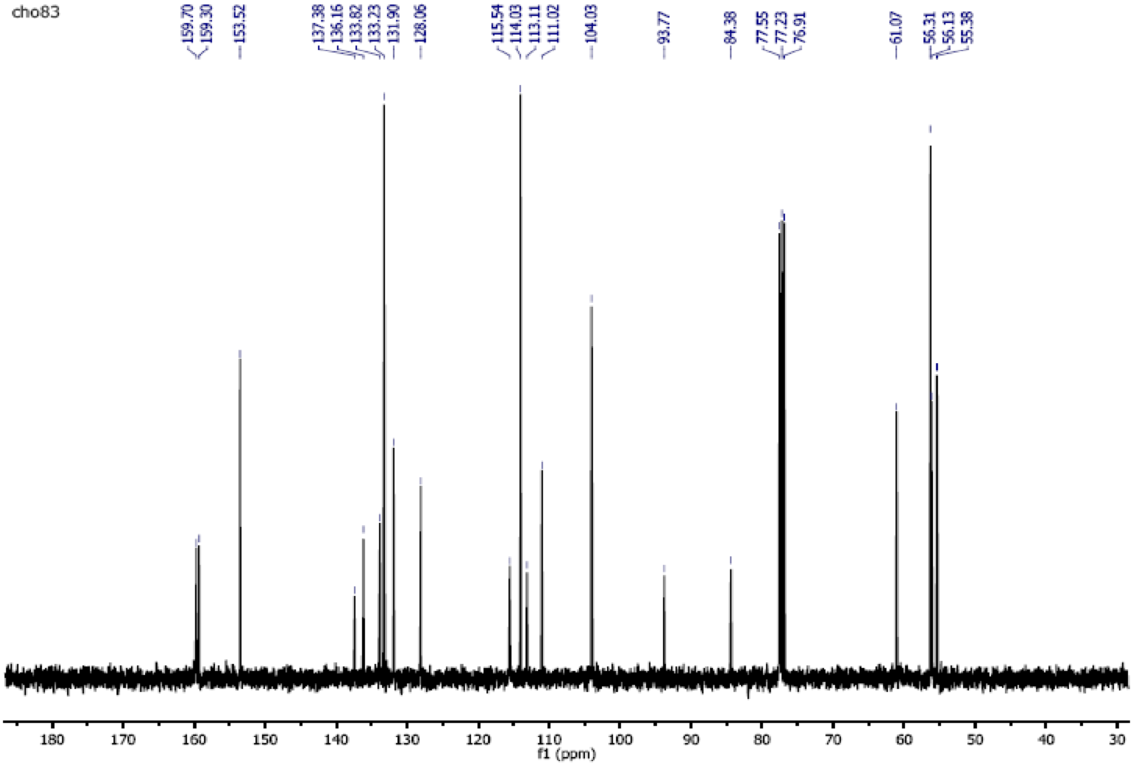


cho350
163.53
159.79
159.40
144.72
137.34
133.36
130.54
129.29
127.75
115.63
114.10
113.54
111.36
110.95
94.02
84.26
77.55
77.23
76.91
56.26
55.51
53.76
131.72
f1 (ppm)

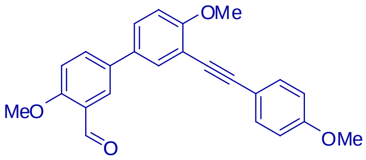
Alkyne 8{*4*}

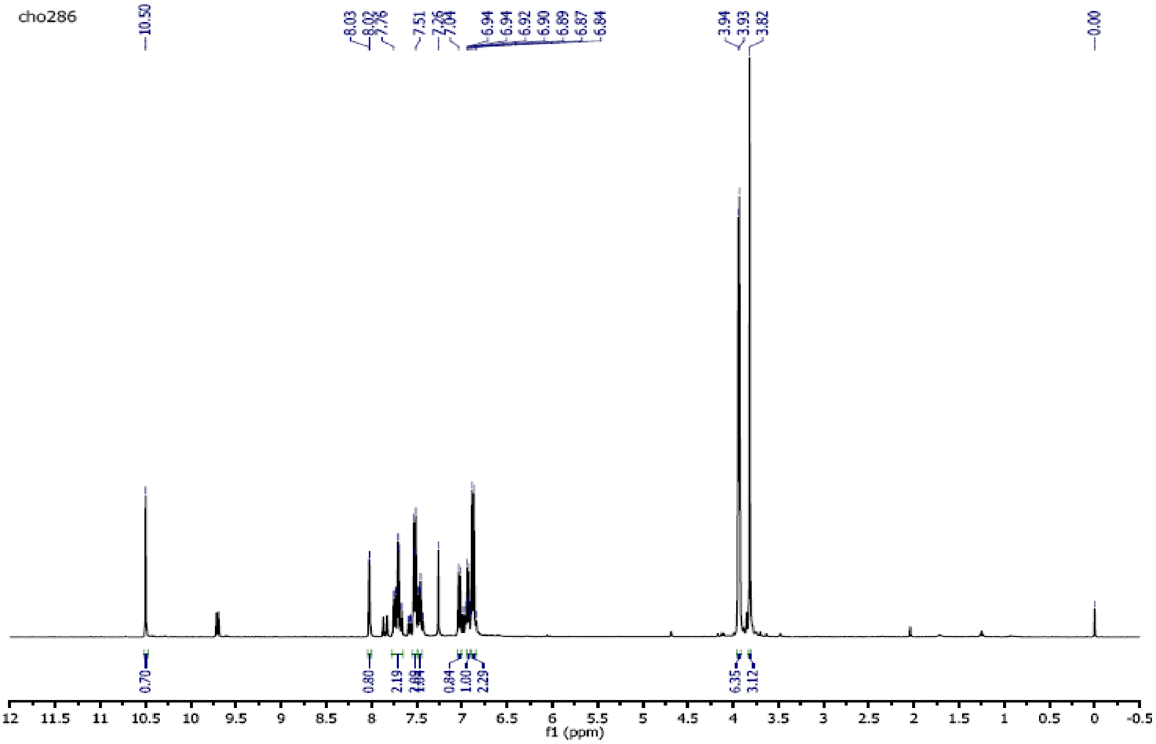

OMe
MeO
MeO
OMe
OMe

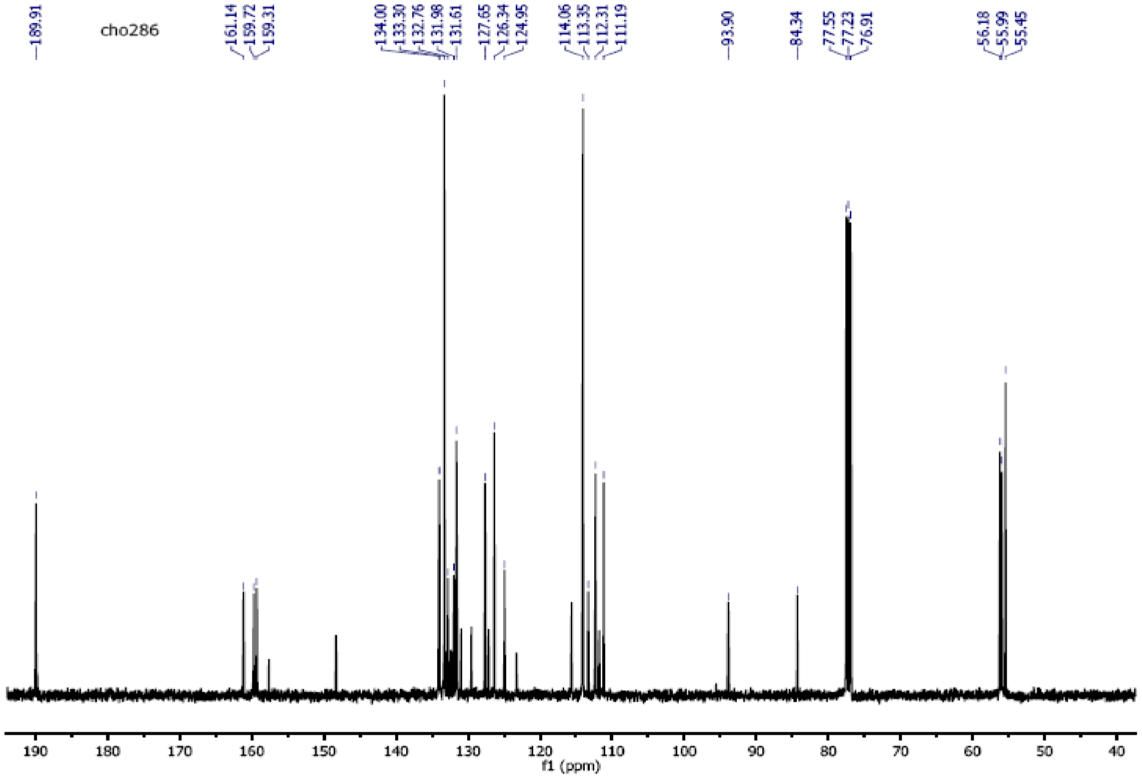

cho83
7.69
7.68
7.53
7.51
7.47
7.45
7.45
7.26
6.95
6.93
6.88
6.86
6.74
3.93
3.92
3.88
3.80
0.00
7.689
7.684
7.532
7.511
7.476
7.471
7.455
7.449
6.948
6.927
6.881
6.859
6.741
3.931
3.920
3.885
3.804
1.02
1.98
1.05
1.05
2.06
2.00
8.89
3.05
2.98
f1 (ppm)


cho83
159.70
159.30
153.52
137.38
136.16
133.82
133.23
131.90
128.06
115.54
114.03
113.11
111.02
104.03
93.77
84.38
77.55
77.23
76.91
61.07
56.31
56.13
55.38
f1 (ppm)

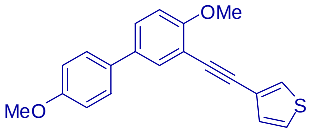
Alkyne 8{*5*}


OMe
MeO
O
OMe

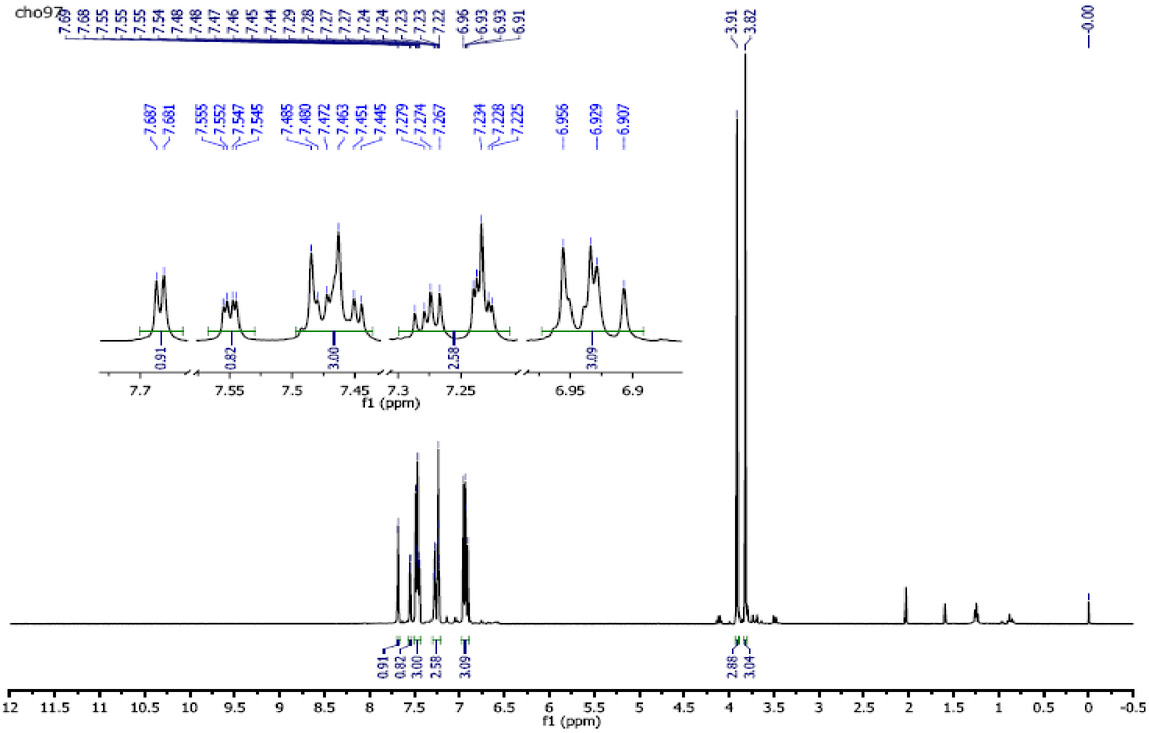

cho286
10.50
8.03
8.02
7.76
7.51
7.26
7.04
6.94
6.94
6.92
6.90
6.89
6.87
6.84
3.94
3.93
3.82
0.00
0.70
0.80
2.19
0.84
1.00
2.29
6.35
3.12
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
f1 (ppm)


cho286
189.91
161.14
159.72
159.31
134.00
133.30
132.76
131.98
131.61
127.65
126.34
124.95
114.06
113.35
112.31
111.19
93.90
84.34
77.55
77.23
76.91
56.18
55.99
55.45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

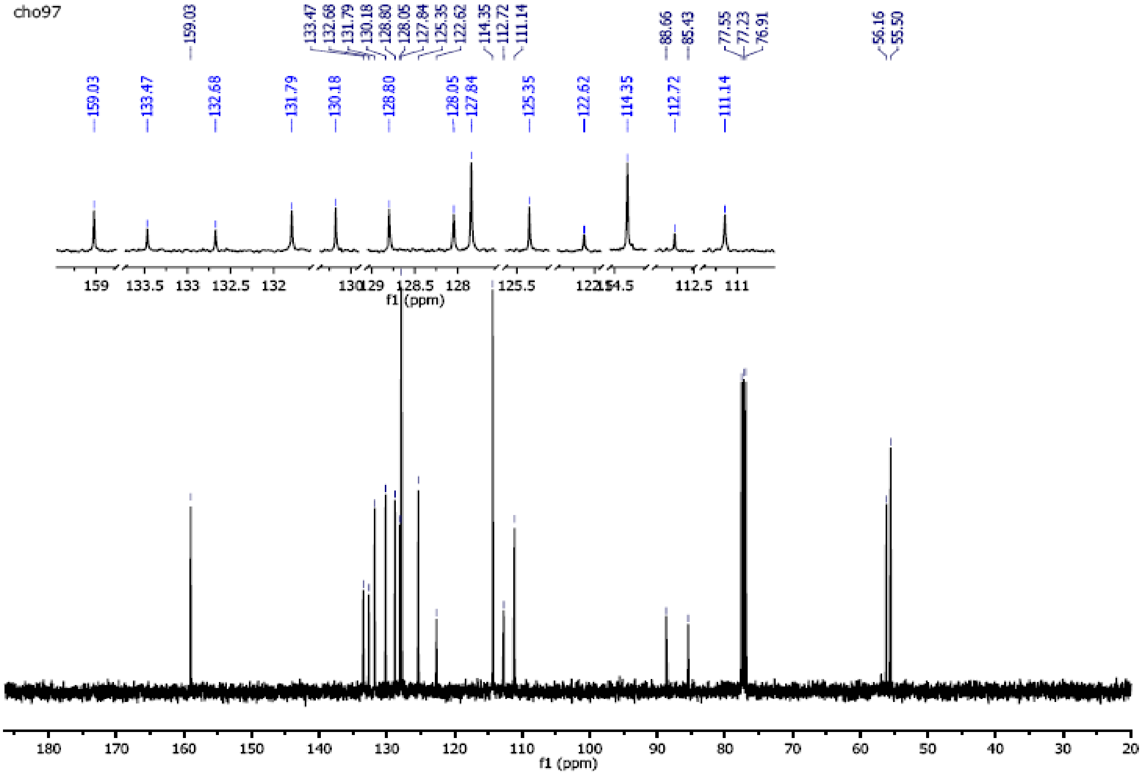
Alkyne 8{*6*}



OMe
MeO
S

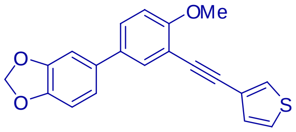


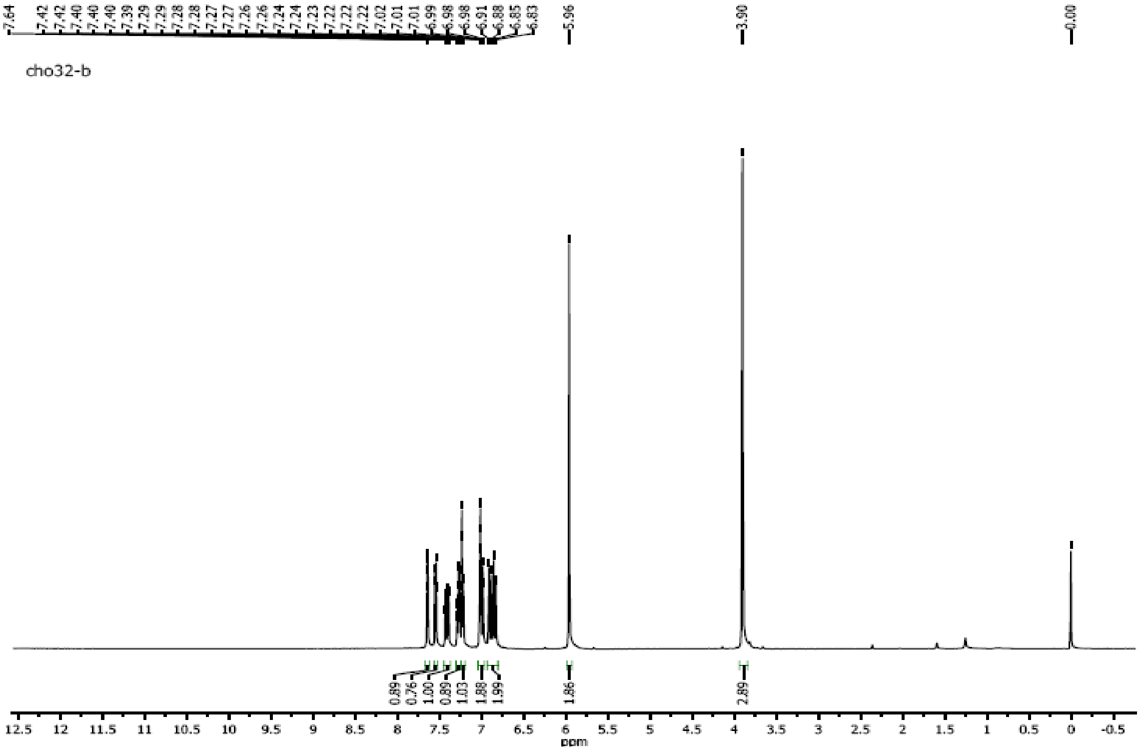
cho97
7.69
7.68
7.55
7.55
7.55
7.54
7.48
7.48
7.47
7.46
7.45
7.44
7.29
7.28
7.27
7.27
7.24
7.24
7.23
7.23
7.22
6.96
6.93
6.93
6.91
3.91
3.82
0.00
7.687
7.681
7.555
7.552
7.547
7.545
7.485
7.480
7.472
7.463
7.451
7.445
7.279
7.274
7.267
7.234
7.228
7.225
6.956
6.929
6.907
0.91
0.82
3.00
2.58
3.09
7.7
7.55
7.5
7.45
7.3
7.25
6.95
6.9
f1 (ppm)
0.91
0.82
3.00
2.58
3.09
2.88
3.04
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
f1 (ppm)

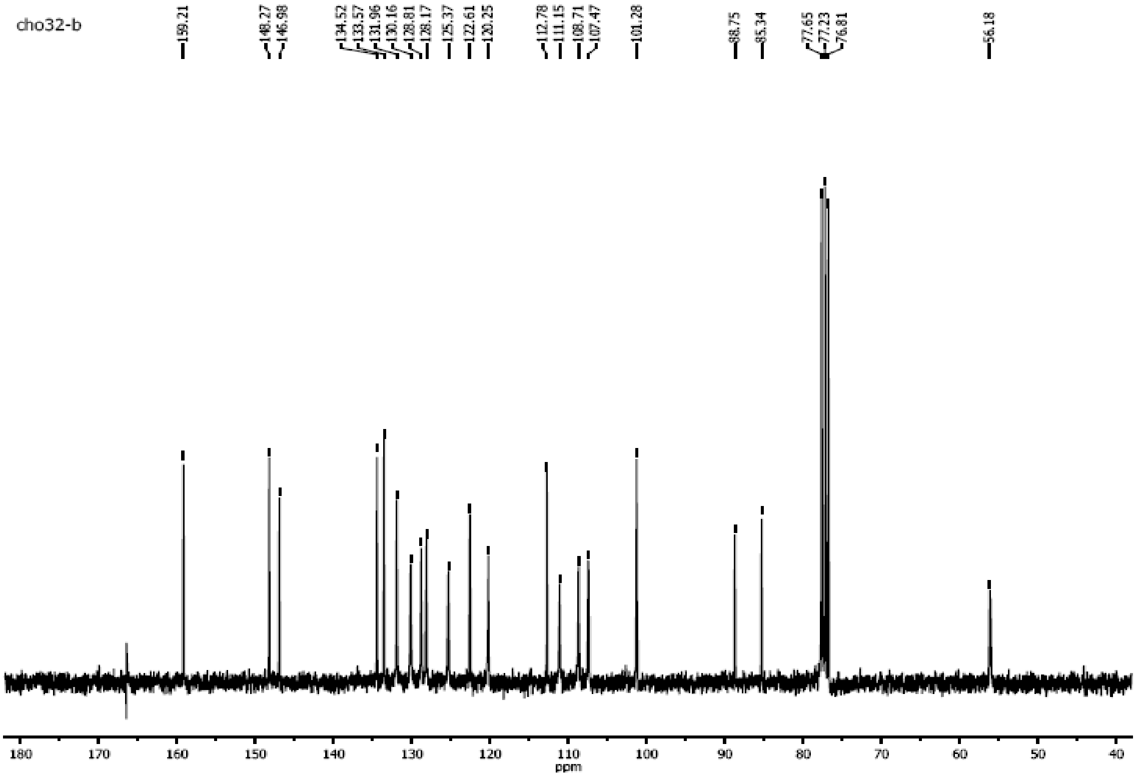


cho97
159.03
133.47
132.68
131.79
130.18
128.80
128.05
127.84
125.35
122.62
114.35
112.72
111.14
88.66
85.43
77.55
77.23
76.91
56.16
55.50
159
133.5
133
132.5
132
130
129
128.5
128
125.5
122.5
114.5
112.5
111
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

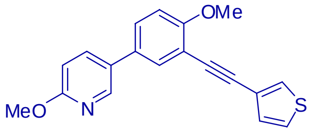
Alkyne 8{*7*}

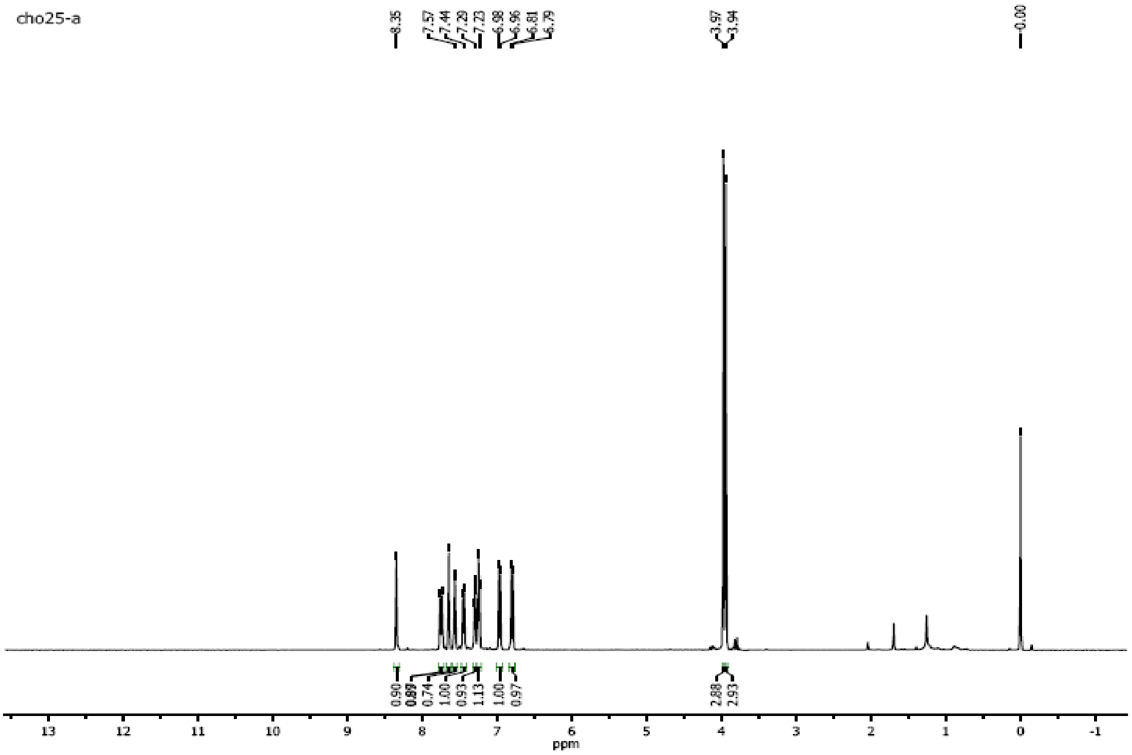

OMe
O
O
S

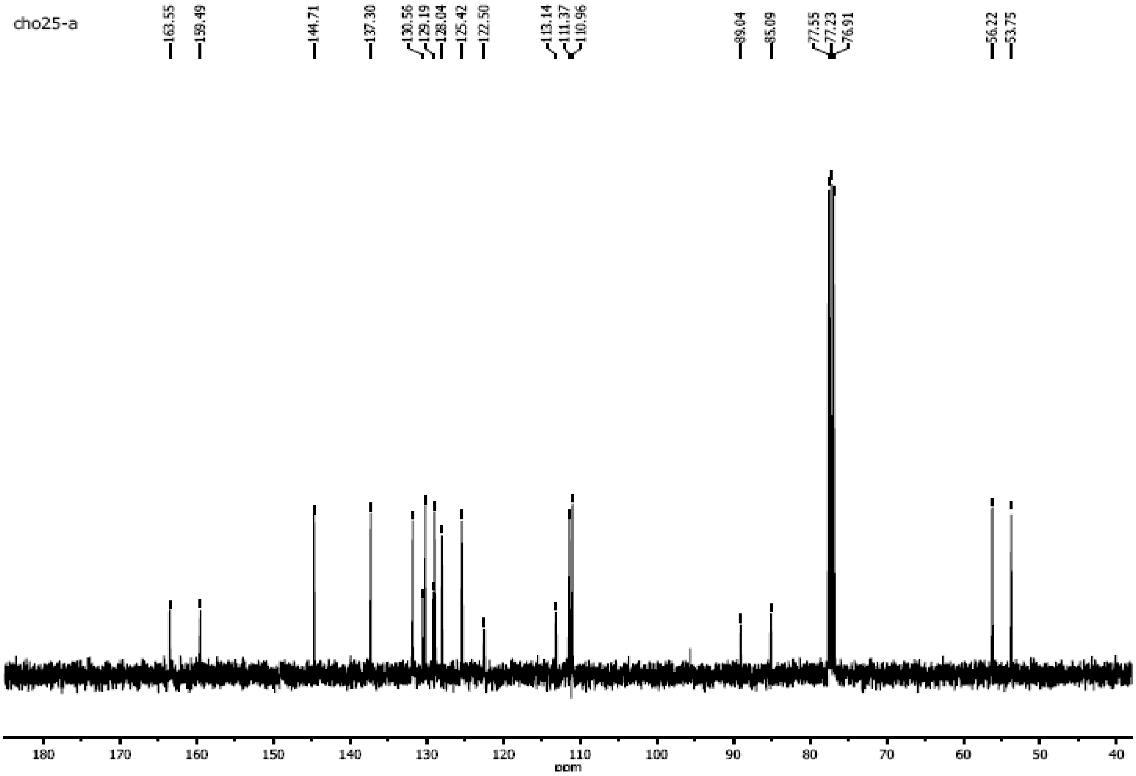

7.64
7.42
7.42
7.40
7.40
7.40
7.39
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.24
7.24
7.23
7.22
7.22
7.22
7.02
7.01
7.01
6.99
6.98
6.98
6.91
6.88
6.85
6.83
5.96
3.90
0.00
cho32-b
0.89
0.76
1.00
0.89
1.03
1.88
1.99
1.86
2.89
12.5
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
ppm


cho32-b
159.21
148.27
146.98
134.52
133.57
131.96
130.16
128.81
128.17
125.37
122.61
120.25
112.78
111.15
108.71
107.47
101.28
88.75
85.34
77.65
77.23
76.81
56.18
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

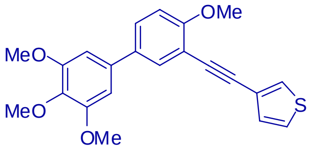
Alkyne 8{*8*}


OMe
MeO
N
S

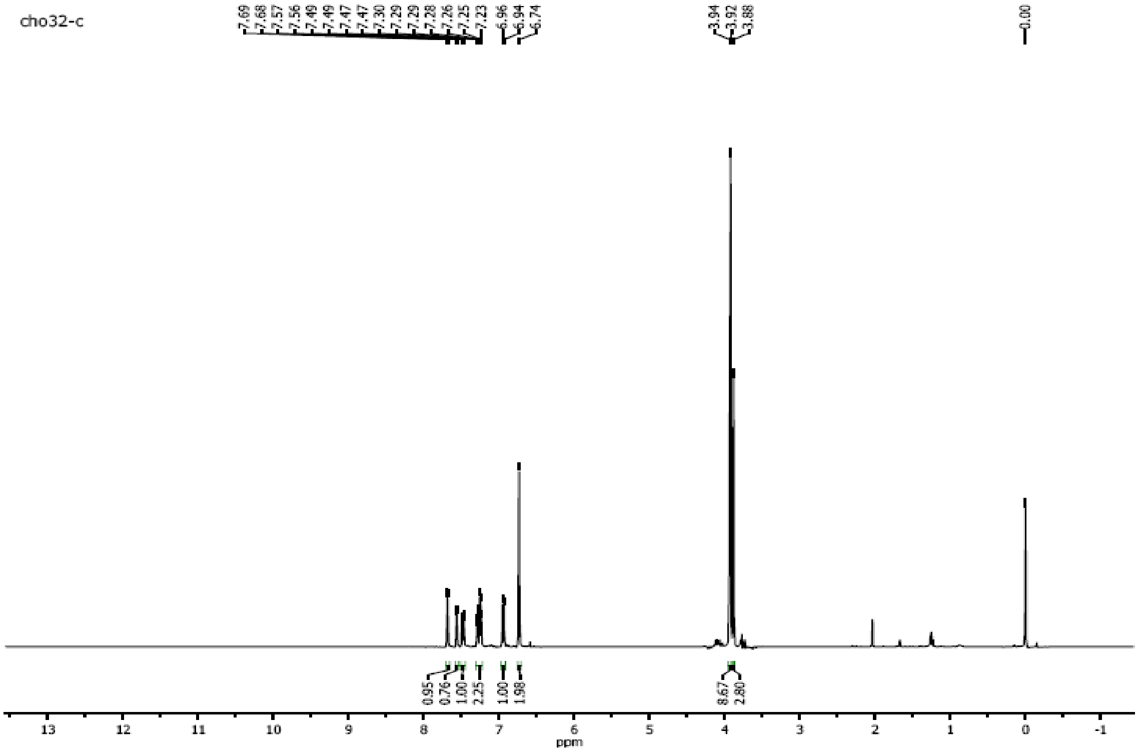

cho25-a
8.35
7.57
7.44
7.29
7.23
6.98
6.96
6.81
6.79
3.97
3.94
0.00
0.90
0.89
0.74
1.00
0.93
1.13
1.00
0.97
2.88
2.93
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


cho25-a
163.55
159.49
144.71
137.30
130.56
129.19
128.04
125.42
122.50
113.14
111.37
110.96
89.04
85.09
77.55
77.23
76.91
56.22
53.75
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

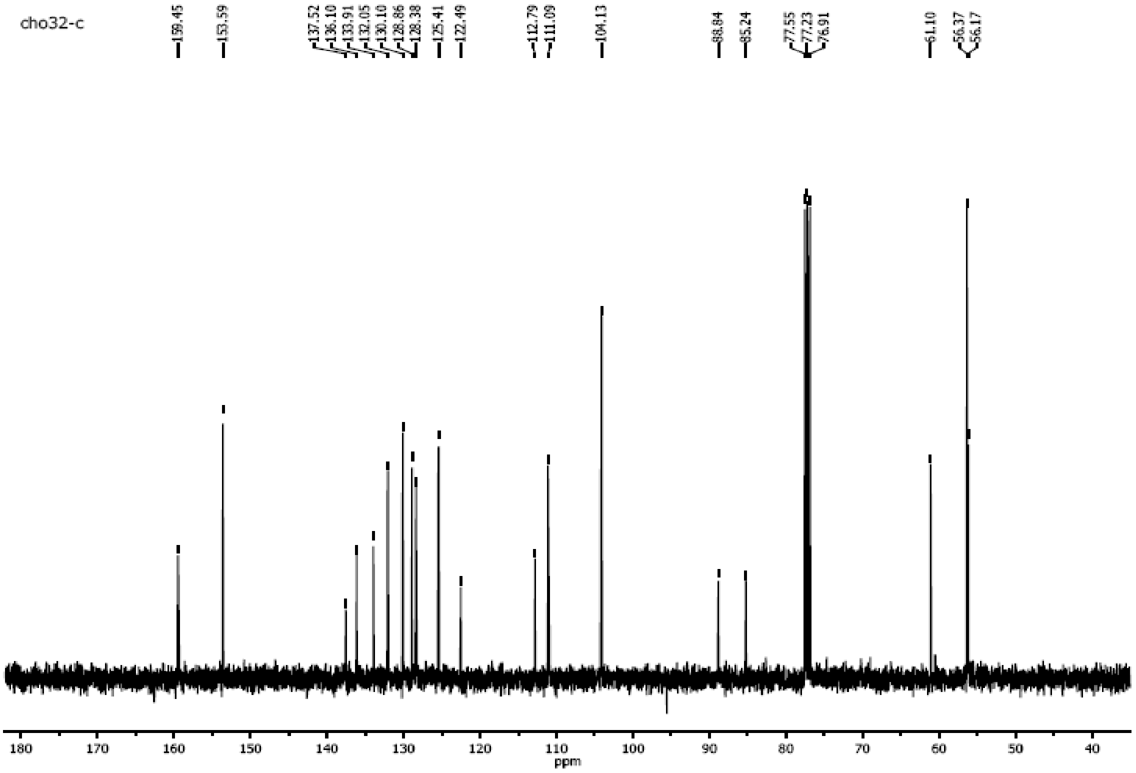
Alkyne 8{*9*}



OMe
MeO
MeO
OMe
S

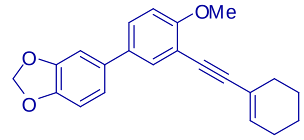


cho32-c
7.69
7.68
7.57
7.56
7.49
7.49
7.47
7.47
7.30
7.29
7.29
7.28
7.26
7.25
7.23
6.96
6.94
6.74
3.94
3.92
3.88
0.00
0.95
0.76
1.00
2.25
1.00
1.98
8.67
2.80
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

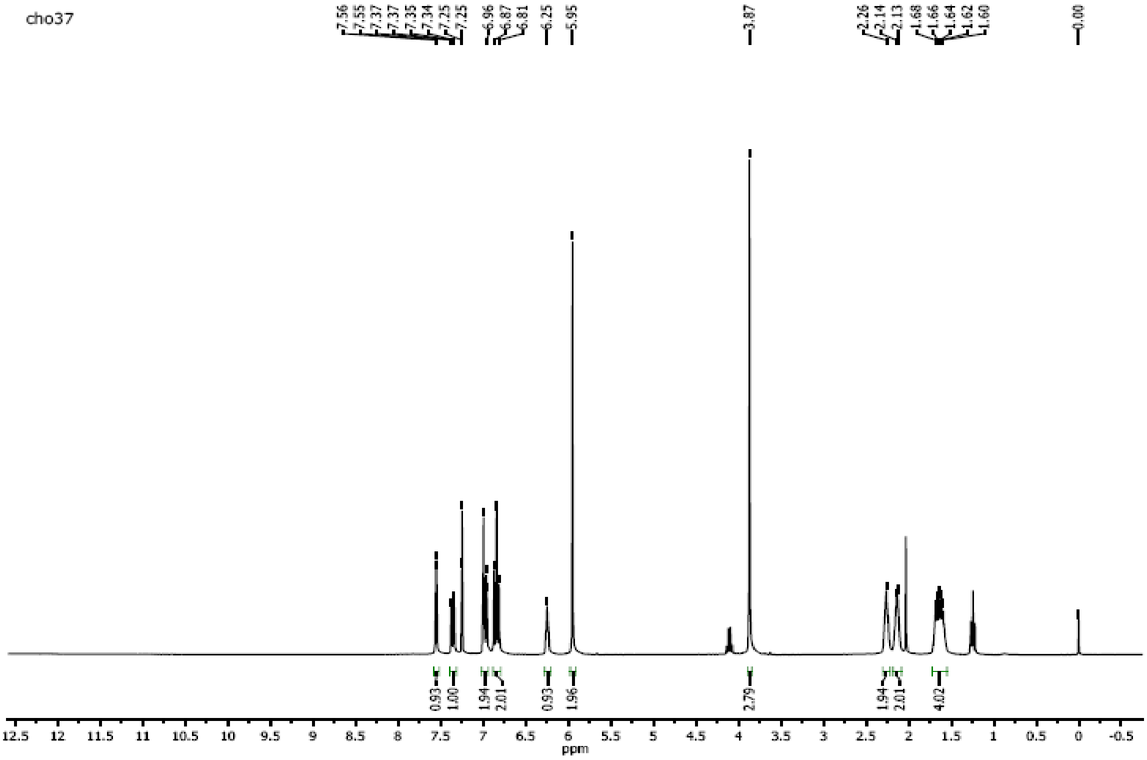


cho32-c
159.45
153.59
137.52
136.10
133.91
132.05
130.10
128.86
128.38
125.41
122.49
112.79
111.09
104.13
88.84
85.24
77.55
77.23
76.91
61.10
56.37
56.17
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

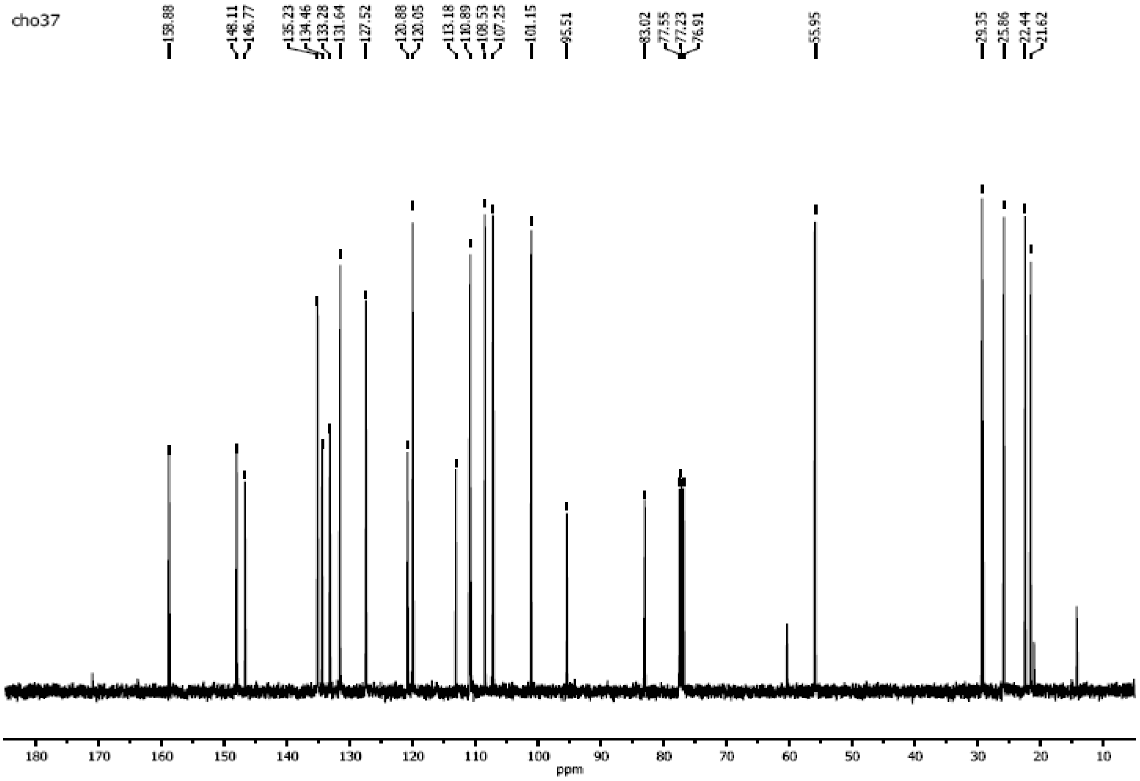
Alkyne 8{*10*}



OMe
O
O

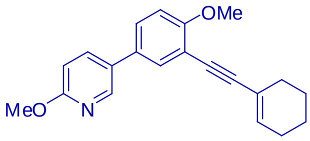


cho37
7.56
7.55
7.37
7.37
7.35
7.34
7.25
7.25
6.96
6.87
6.81
6.25
5.95
3.87
2.26
2.14
2.13
1.68
1.66
1.64
1.62
1.60
0.00
0.93
1.00
1.94
2.01
0.93
1.96
2.79
1.94
2.01
4.02
12.5
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
ppm

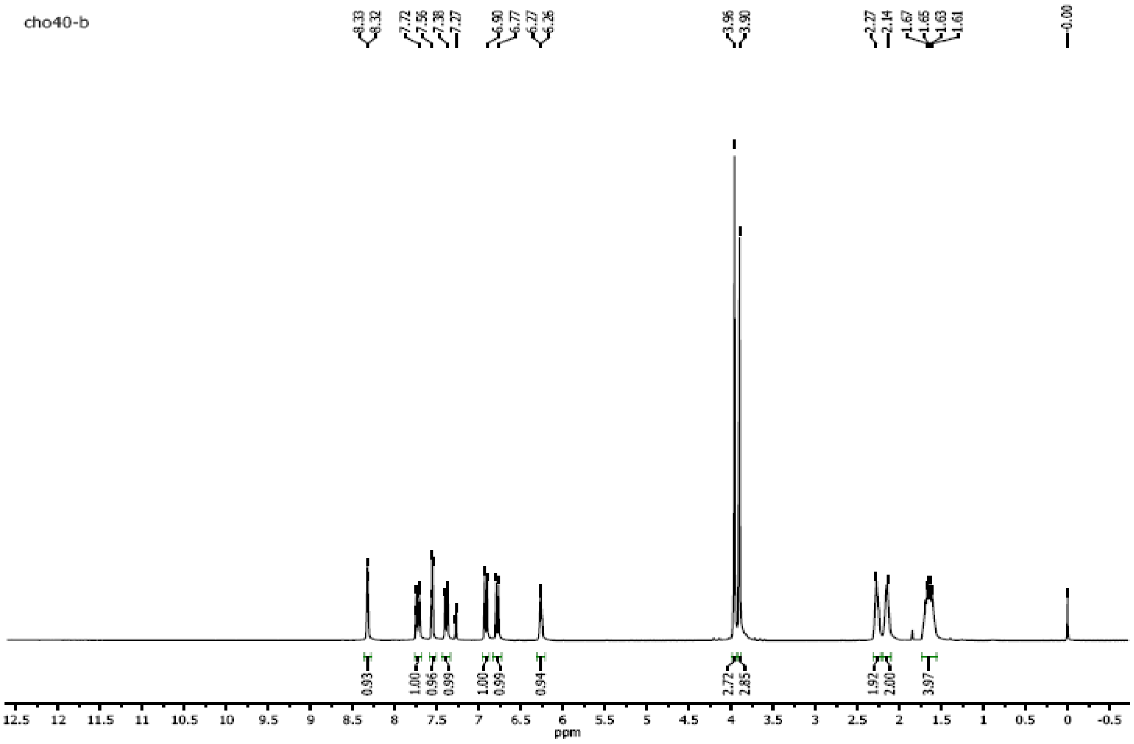


cho37
158.88
148.11
146.77
135.23
134.46
133.28
131.64
127.52
120.88
120.05
113.18
110.89
108.53
107.25
101.15
95.51
83.02
77.55
77.23
76.91
55.95
29.35
25.86
22.44
21.62
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

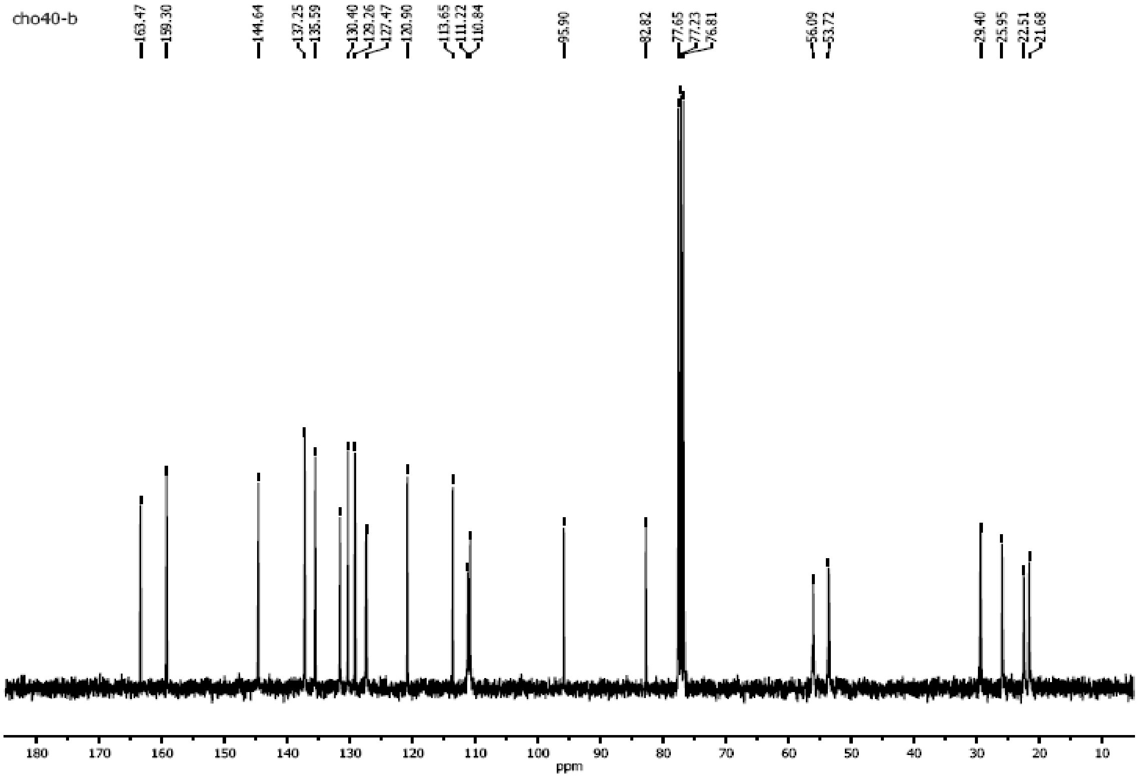
Alkyne 8{*11*}



OMe
MeO
N

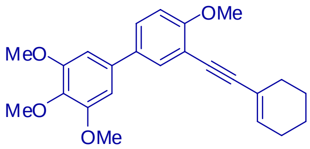


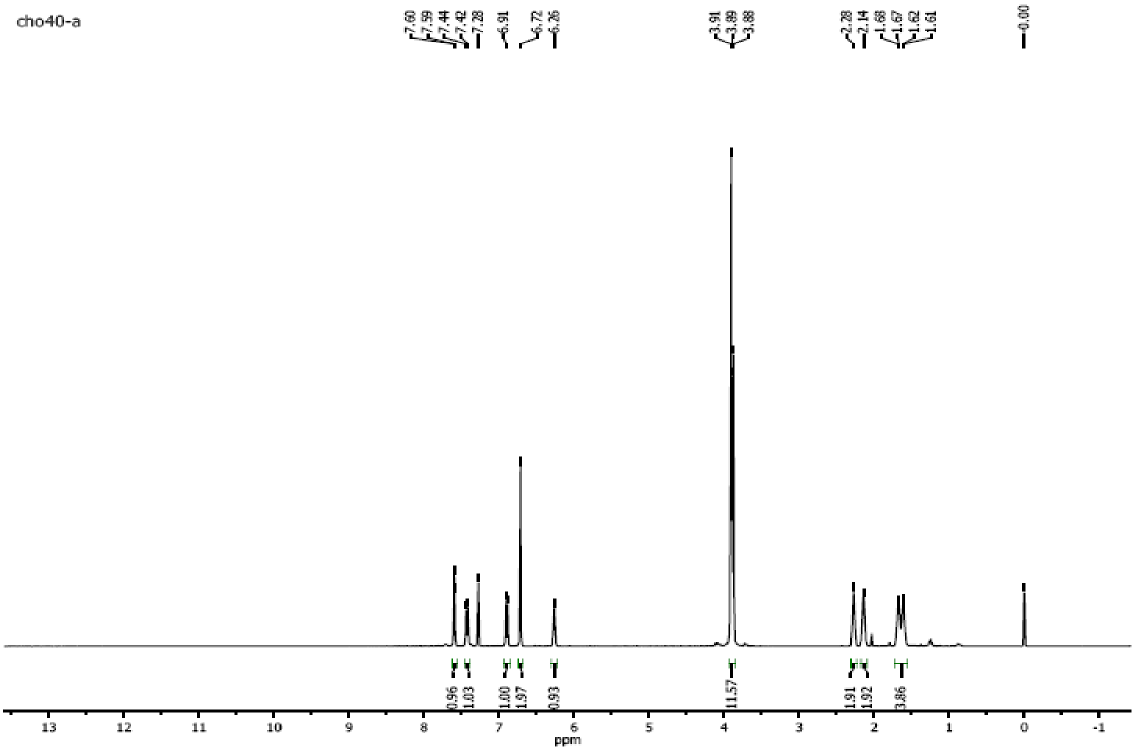
cho40-b
8.33
8.32
7.72
7.56
7.38
7.27
6.90
6.77
6.27
6.26
3.96
3.90
2.27
2.14
1.67
1.65
1.63
1.61
0.00
0.93
1.00
0.96
0.99
1.00
0.99
0.94
2.72
2.85
1.92
2.00
3.97
12.5
12
11.5
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
ppm

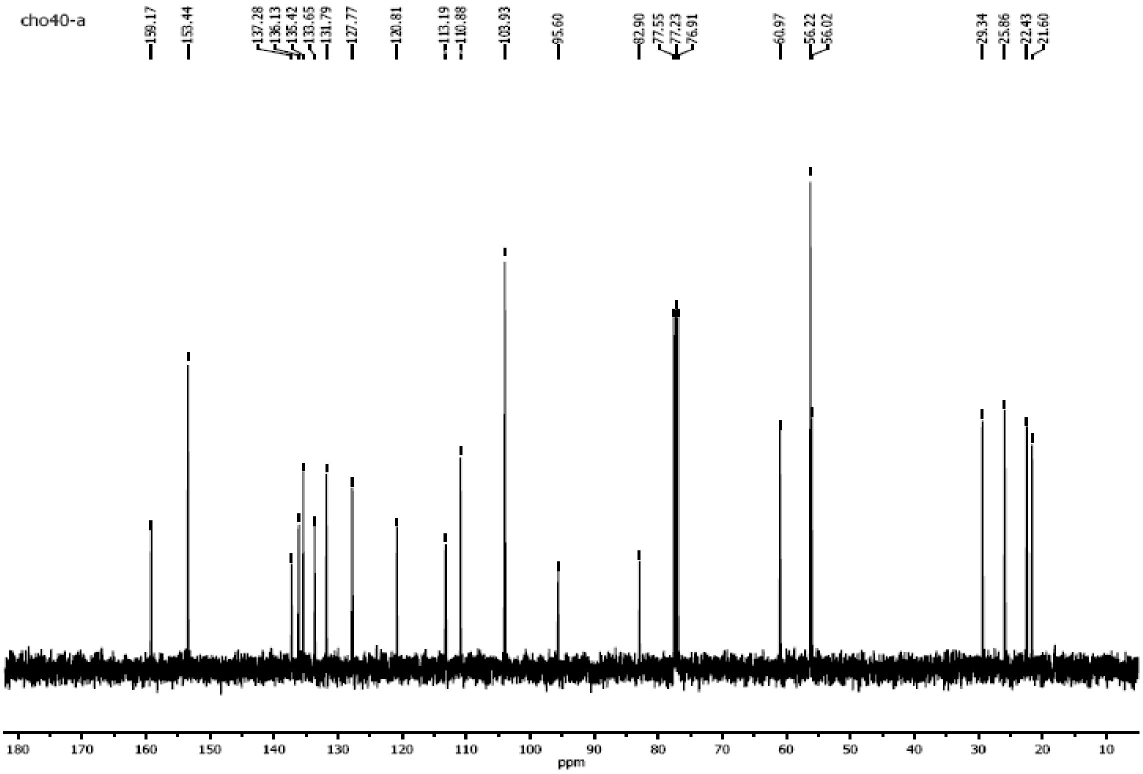


cho40-b
163.47
159.30
144.64
137.25
135.59
130.40
129.26
127.47
120.90
113.65
111.22
110.84
95.90
82.82
77.65
77.23
76.81
56.09
53.72
29.40
25.95
22.51
21.68
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

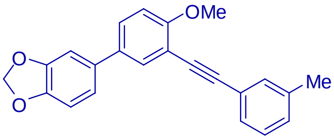
Alkyne 8{*12*}

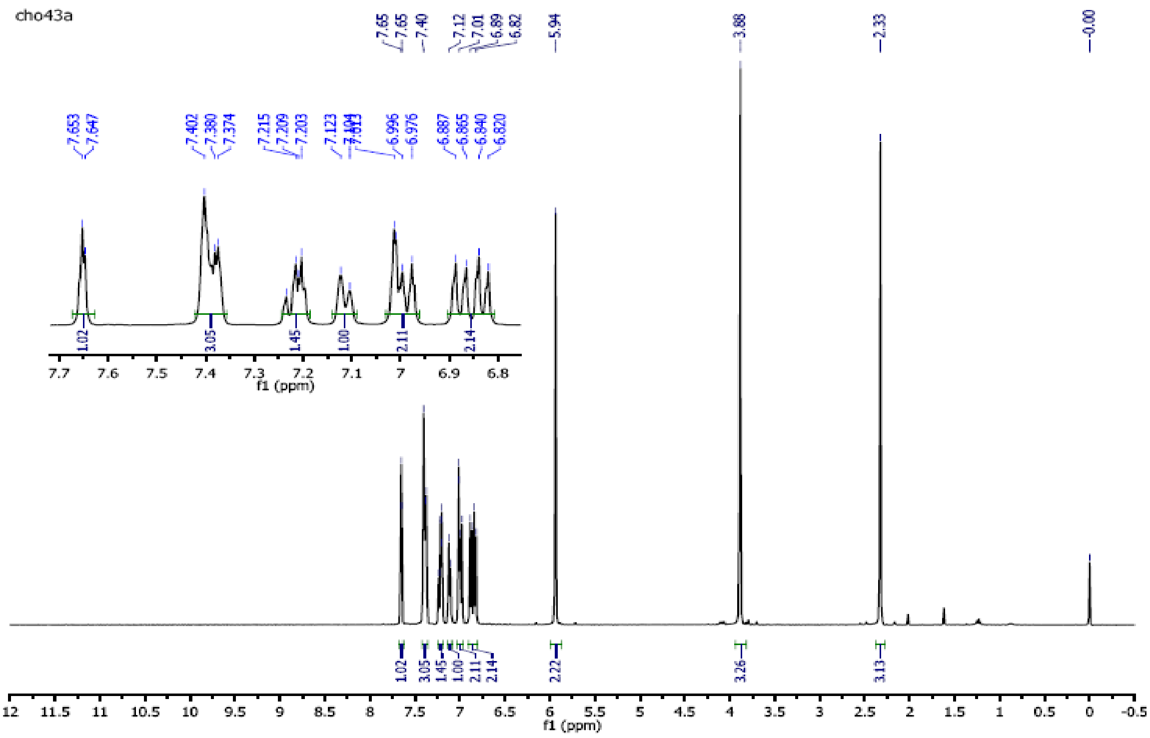

OMe
MeO
MeO
OMe

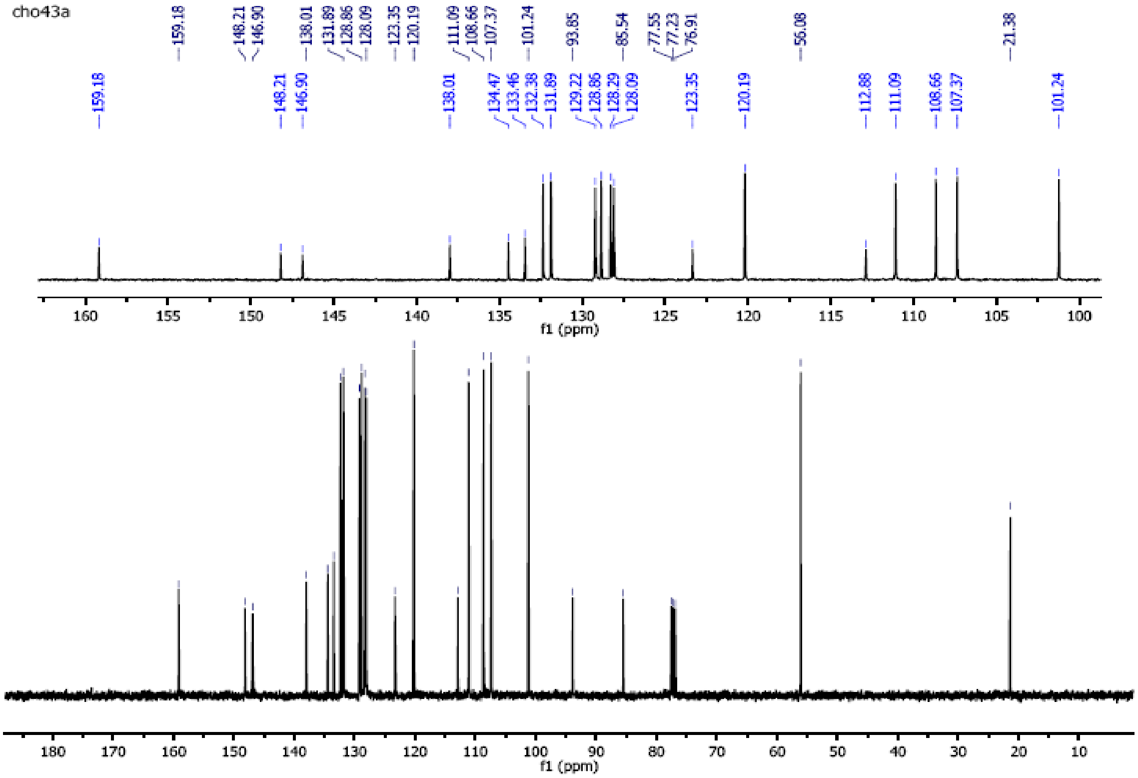

cho40-a
7.60
7.59
7.44
7.42
7.28
6.91
6.72
6.26
3.91
3.89
3.88
2.28
2.14
1.68
1.67
1.62
1.61
0.00
0.96
1.03
1.00
1.97
0.93
11.57
1.91
1.92
3.86
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


cho40-a
159.17
153.44
137.28
136.13
135.42
133.65
131.79
127.77
120.81
113.19
110.88
103.93
95.60
82.90
77.55
77.23
76.91
60.97
56.22
56.02
29.34
25.86
22.43
21.60
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

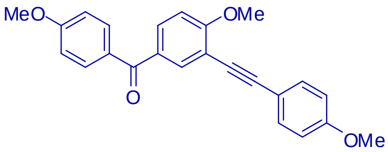
Alkyne 8{*13*}

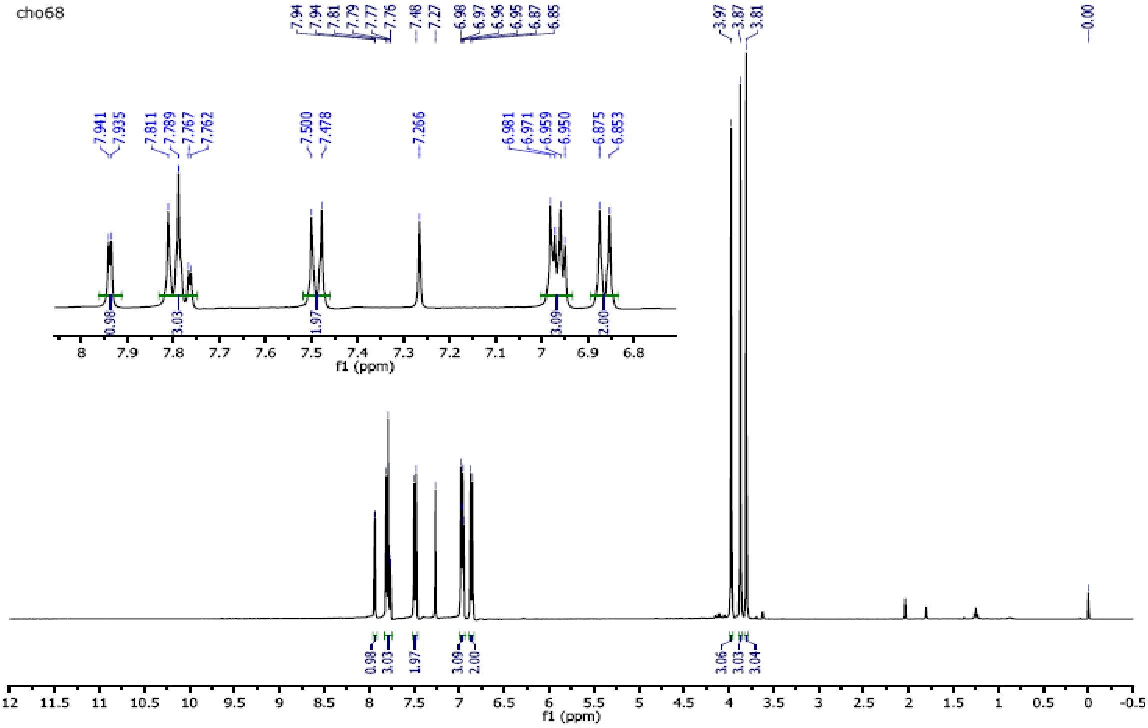

OMe
O
O
Me

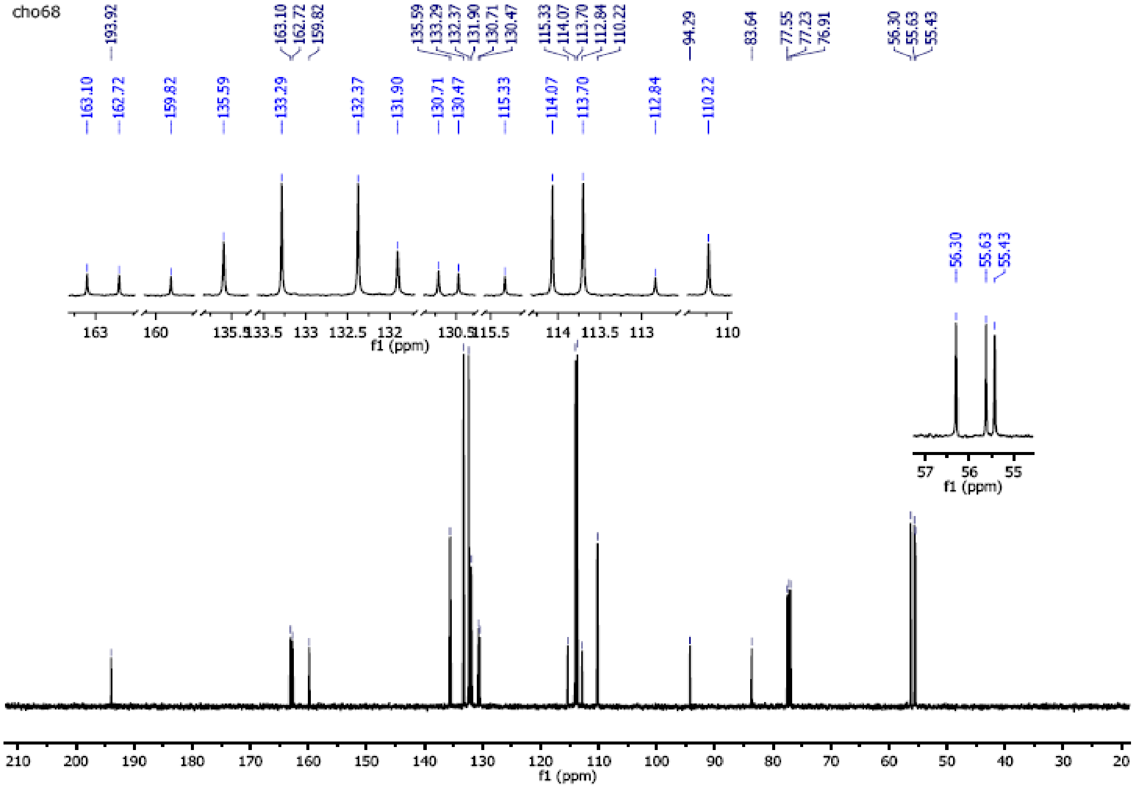

cho43a
7.65
7.65
7.40
7.12
7.01
6.89
6.82
5.94
3.88
2.33
-0.00
7.653
7.647
7.402
7.380
7.374
7.215
7.209
7.203
7.123
7.104
7.013
6.996
6.976
6.887
6.865
6.840
6.820
1.02
3.05
1.45
1.00
2.11
2.14
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7 6.9 6.8
f1 (ppm)
1.02
3.05
1.45
1.00
2.11
2.14
2.22
3.26
3.13
12 11.5 11 10.5 10 9.5 9 8.5 8 7.5 7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0 -0.5
f1 (ppm)


cho43a
159.18
148.21
146.90
138.01
131.89
128.86
128.09
123.35
120.19
111.09
108.66
107.37
101.24
93.85
85.54
77.55
77.23
76.91
56.08
21.38
159.18
148.21
146.90
138.01
134.47
133.46
132.38
131.89
129.22
128.86
128.29
128.09
123.35
120.19
112.88
111.09
108.66
107.37
101.24
160 155 150 145 140 135 130 125 120 115 110 105 100
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

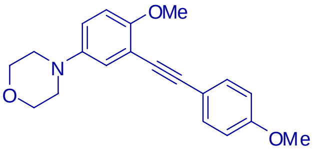
Alkyne 8{*14*}

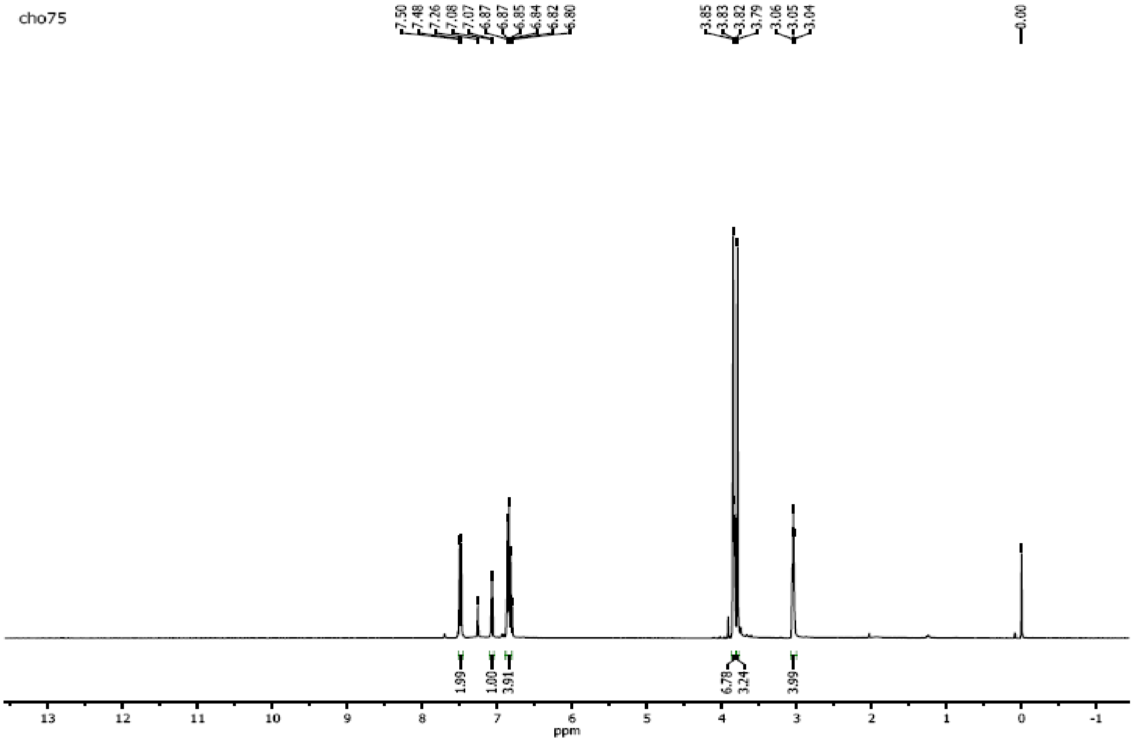

MeO
OMe
O
OMe

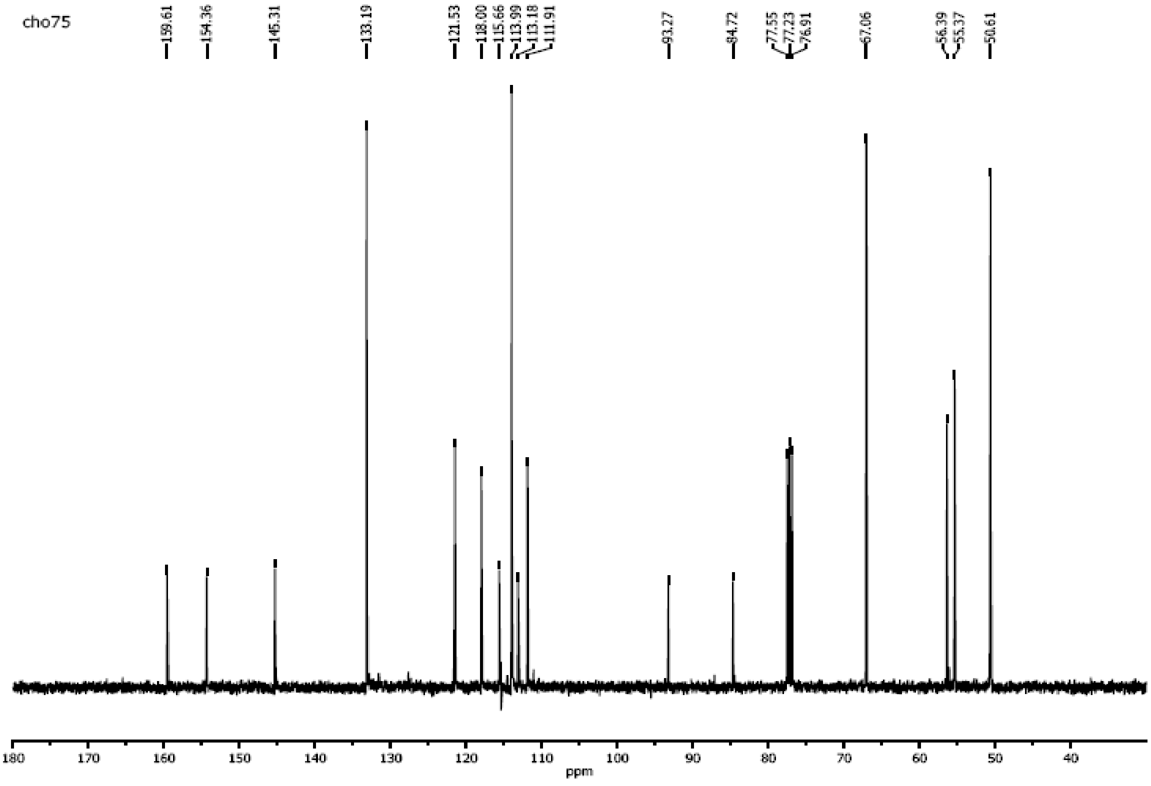

cho68
7.94
7.94
7.81
7.79
7.77
7.76
7.48
7.27
6.98
6.97
6.96
6.95
6.87
6.85
3.97
3.87
3.81
0.00
7.941
7.935
7.811
7.789
7.767
7.762
7.500
7.478
7.266
6.981
6.971
6.959
6.950
6.875
6.853
0.98
3.03
1.97
3.09
2.00
8 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7 6.9 6.8
f1 (ppm)
0.98
3.03
1.97
3.09
2.00
3.06
3.03
3.04
12 11.5 11 10.5 10 9.5 9 8.5 8 7.5 7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0 -0.5
f1 (ppm)


cho68
193.92
163.10
162.72
159.82
135.59
133.29
132.37
131.90
130.71
130.47
115.33
114.07
113.70
112.84
110.22
94.29
83.64
77.55
77.23
76.91
56.30
55.63
55.43
163.10
162.72
159.82
135.59
133.29
132.37
131.90
130.71
130.47
115.33
114.07
113.70
112.84
110.22
163 160 135.5 133.5 133 132.5 132 130.5 115.5 114 113.5 113 110
f1 (ppm)
56.30
55.63
55.43
57 56 55
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

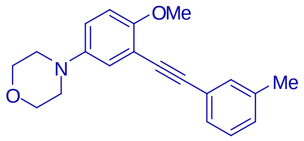
Alkyne 8{*15*}

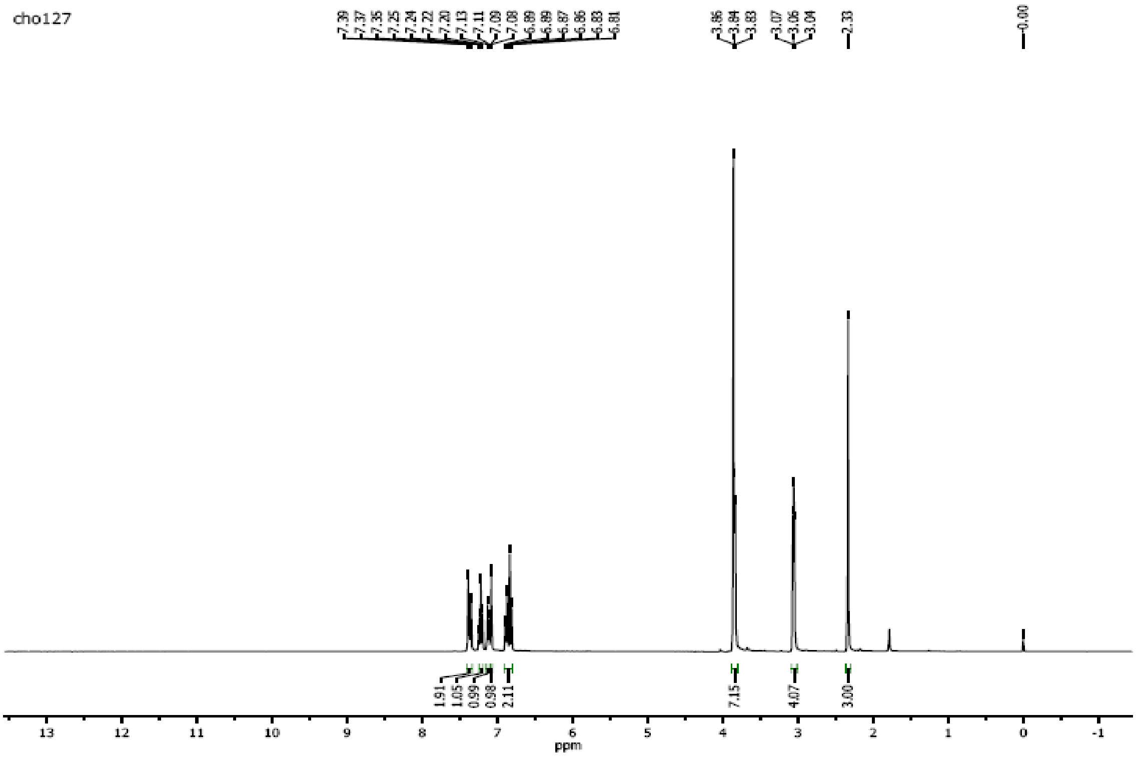

OMe
N
O
OMe

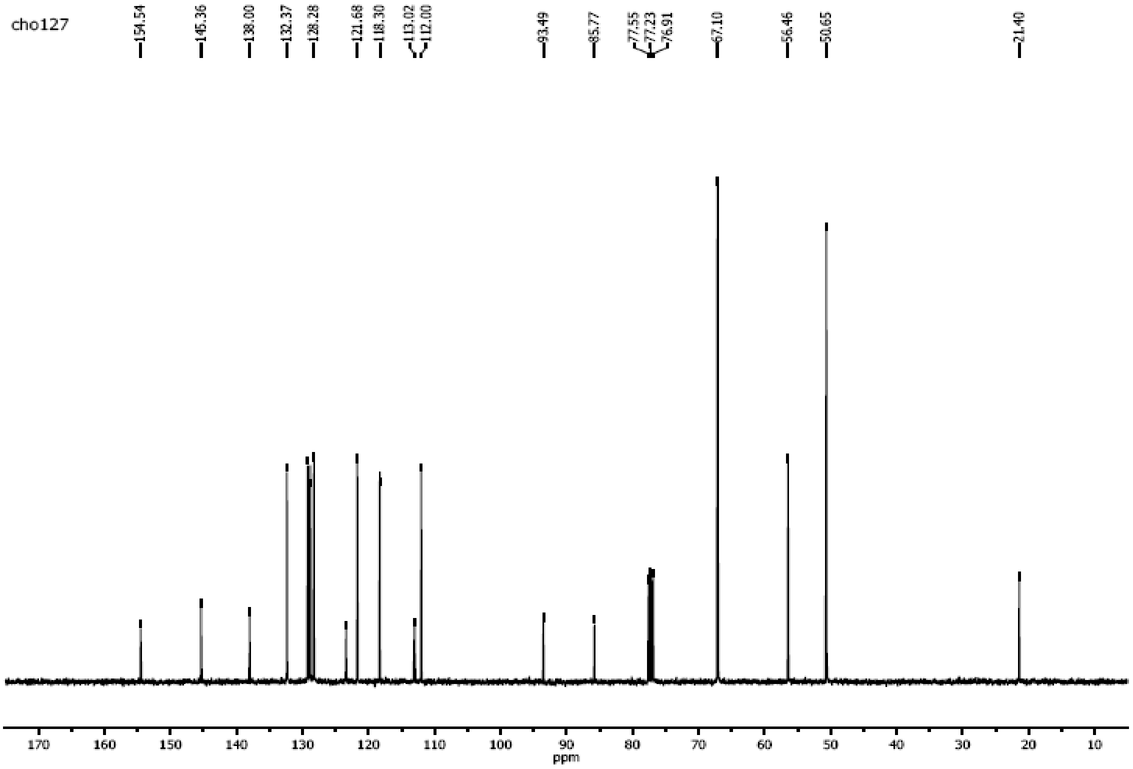

cho75
7.50
7.48
7.26
7.08
7.07
6.87
6.87
6.85
6.84
6.82
6.80
3.85
3.83
3.82
3.79
3.06
3.05
3.04
0.00
1.99
1.00
3.91
6.78
3.24
3.99
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


cho75
159.61
154.36
145.31
133.19
121.53
118.00
115.66
113.99
113.18
111.91
93.27
84.72
77.55
77.23
76.91
67.06
56.39
55.37
50.61
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
ppm

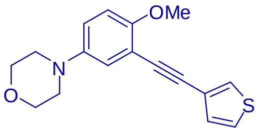
Alkyne 8{*16*}

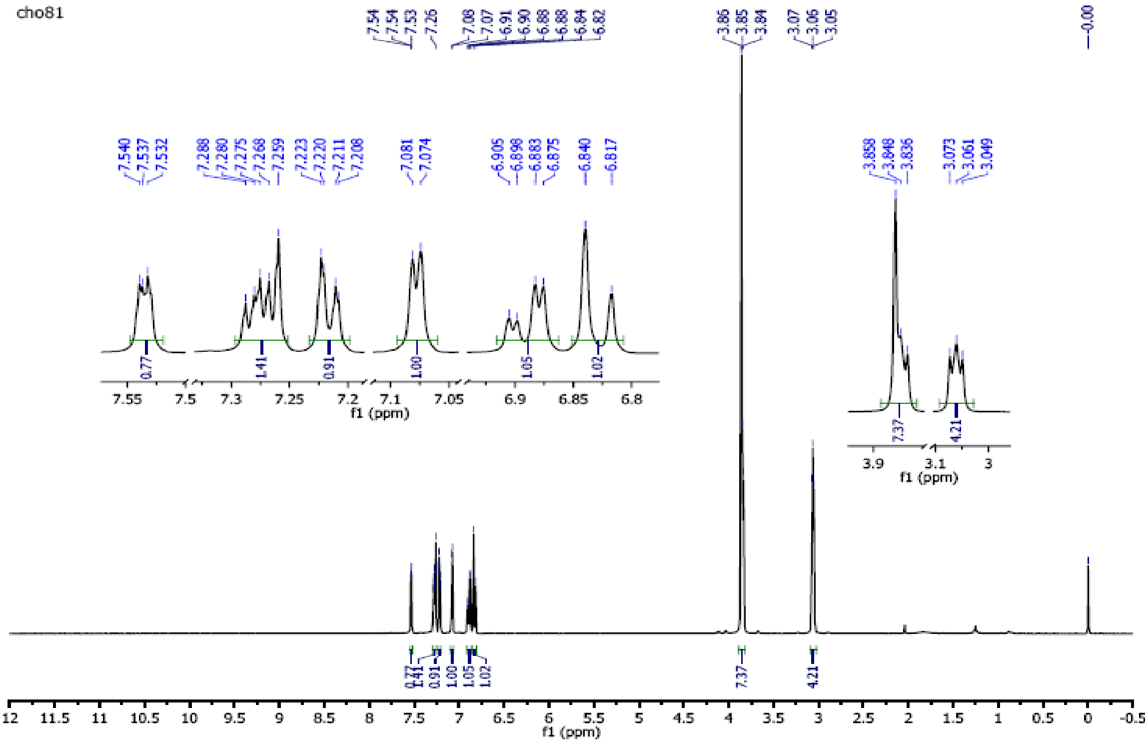

OMe
N
O
Me

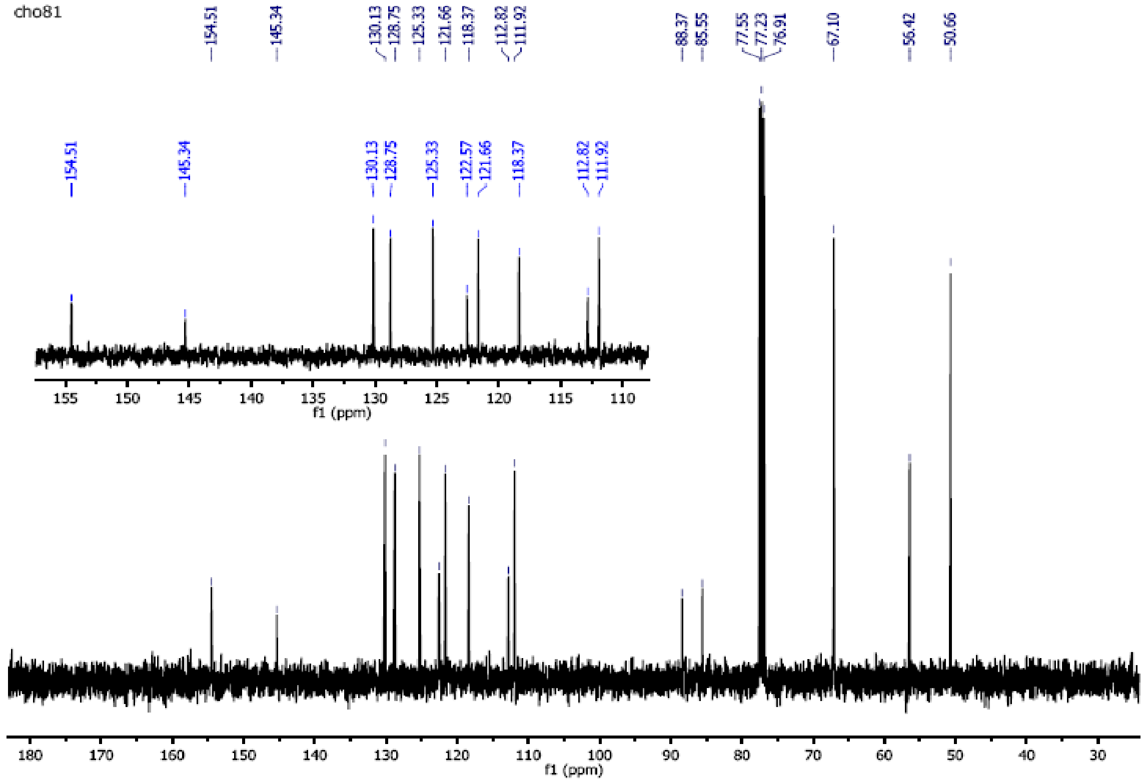

cho127
7.39
7.37
7.35
7.25
7.24
7.22
7.20
7.13
7.11
7.09
7.08
6.89
6.89
6.87
6.86
6.83
6.81
3.86
3.84
3.83
3.07
3.06
3.04
2.33
-0.00
1.91
1.05
0.99
0.98
2.11
7.15
4.07
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


cho127
154.54
145.36
138.00
132.37
128.28
121.68
118.30
113.02
112.00
93.49
85.77
77.55
77.23
76.91
67.10
56.46
50.65
21.40
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

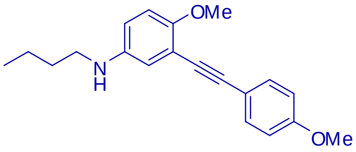
Alkyne **8**{*17*}

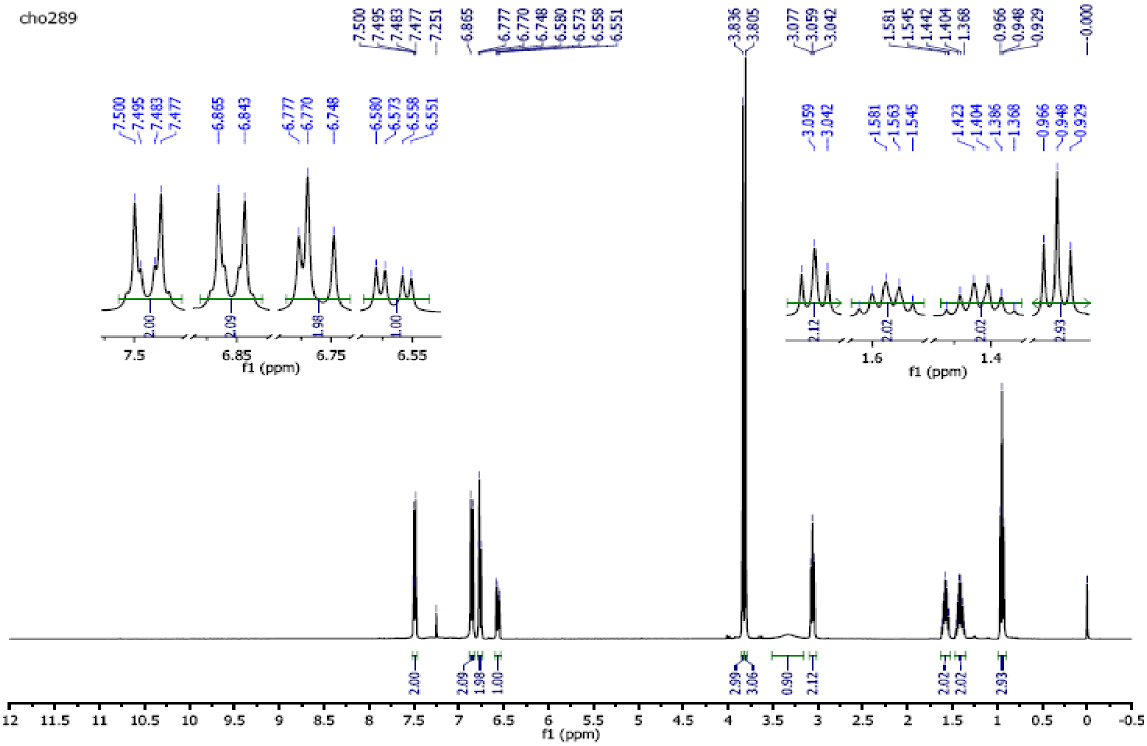

OMe
N
O
S

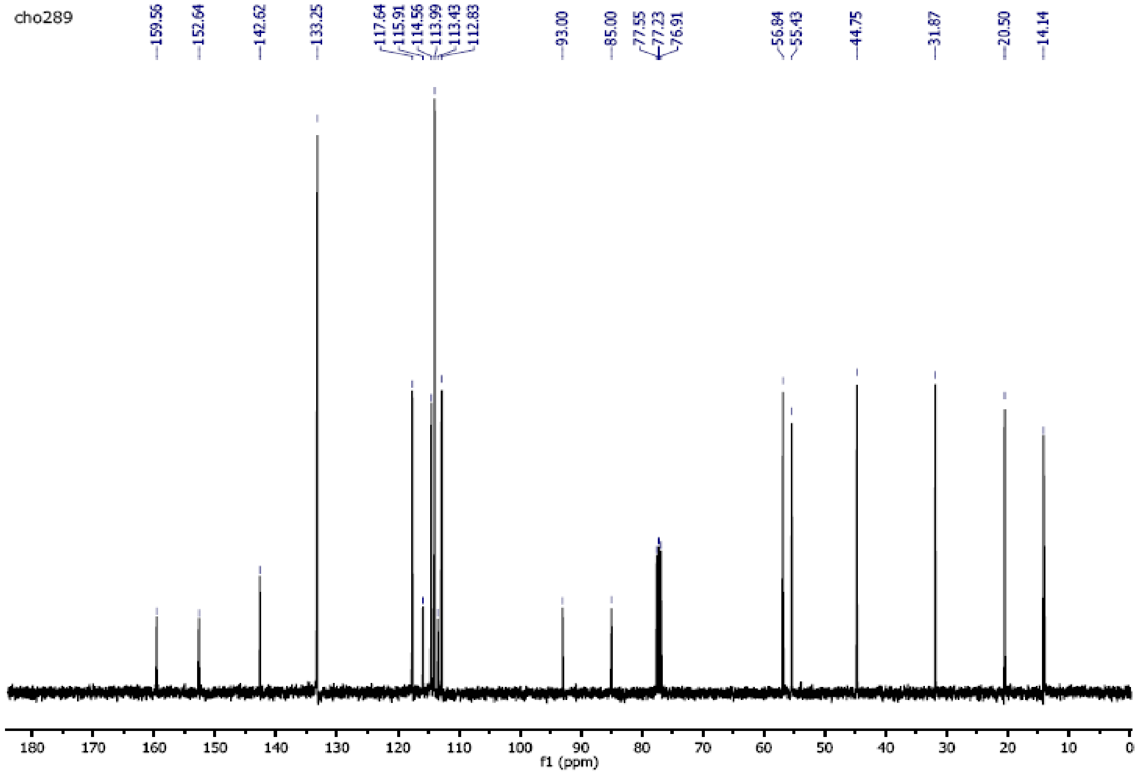

cho81
7.54
7.54
7.53
7.26
7.08
7.07
6.91
6.90
6.88
6.88
6.84
6.82
3.86
3.85
3.84
3.07
3.06
3.05
0.00
7.540
7.537
7.532
7.288
7.280
7.275
7.268
7.259
7.223
7.220
7.211
7.208
7.081
7.074
6.905
6.898
6.883
6.875
6.840
6.817
3.858
3.848
3.836
3.073
3.061
3.049
0.77
1.41
0.91
1.00
1.05
1.02
7.37
4.21
f1 (ppm)


cho81
154.51
145.34
130.13
128.75
125.33
121.66
118.37
112.82
111.92
88.37
85.55
77.55
77.23
76.91
67.10
56.42
50.66
122.57
f1 (ppm)

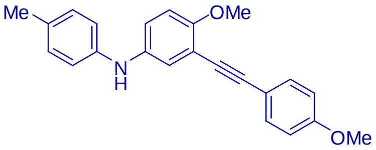
Alkyne 8{*19*}

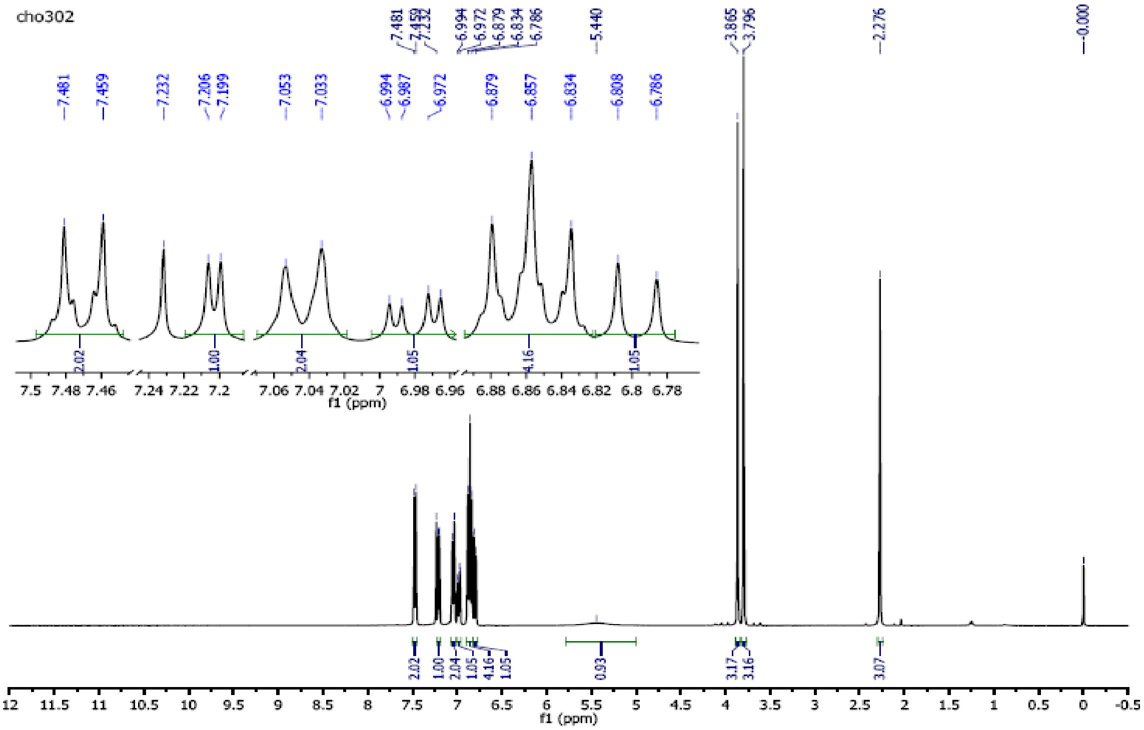

OMe
N
H
OMe

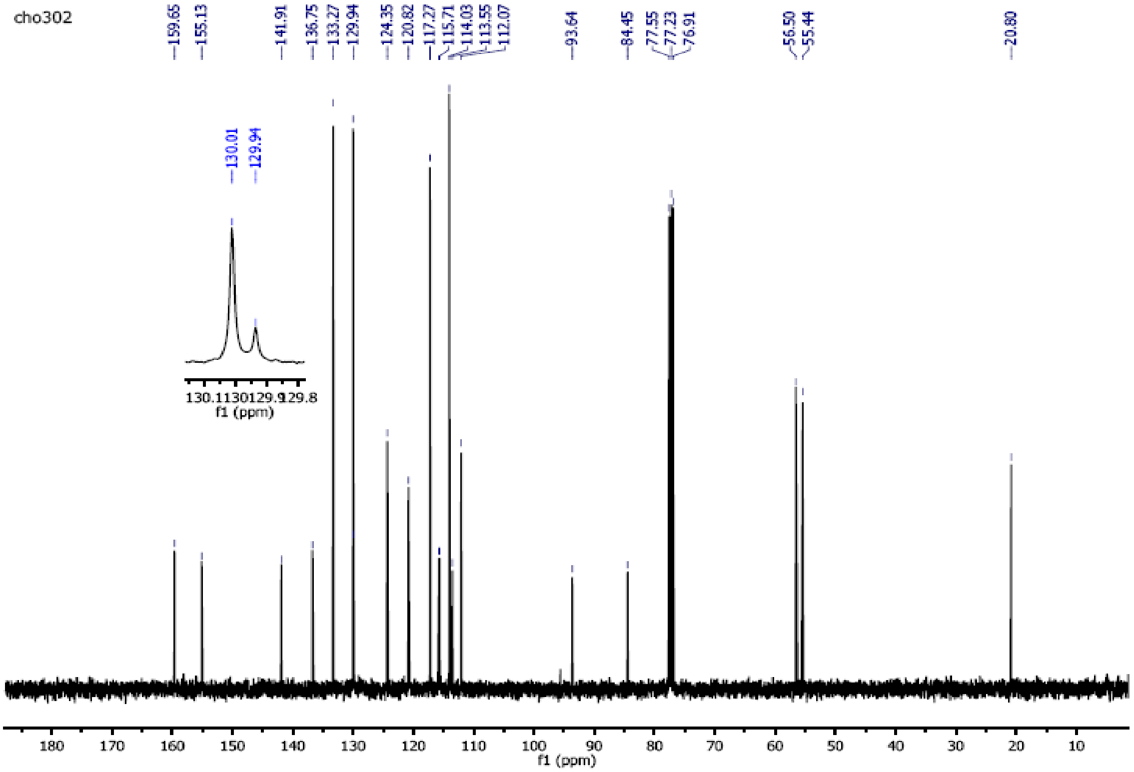

cho289
7.500
7.495
7.483
7.477
7.251
6.865
6.777
6.770
6.748
6.580
6.573
6.558
6.551
3.836
3.805
3.077
3.059
3.042
1.581
1.545
1.442
1.404
1.368
0.966
0.948
0.929
-0.000
6.843
1.563
1.423
1.386
2.00
2.09
1.98
1.00
2.99
3.06
0.90
2.12
2.02
2.02
2.93
f1 (ppm)


cho289
159.56
152.64
142.62
133.25
117.64
115.91
114.56
113.99
113.43
112.83
93.00
85.00
77.55
77.23
76.91
56.84
55.43
44.75
31.87
20.50
14.14
f1 (ppm)

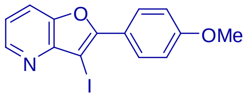
Alkyne 8{*20*}

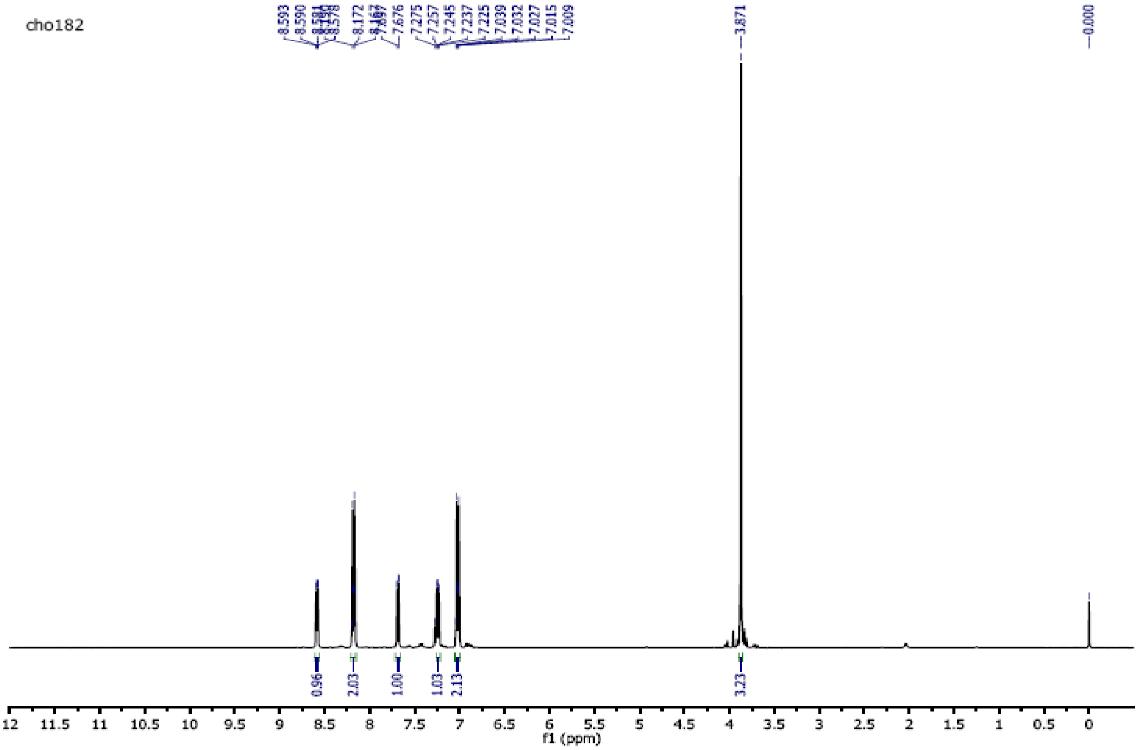

Me
OMe
N
H
OMe

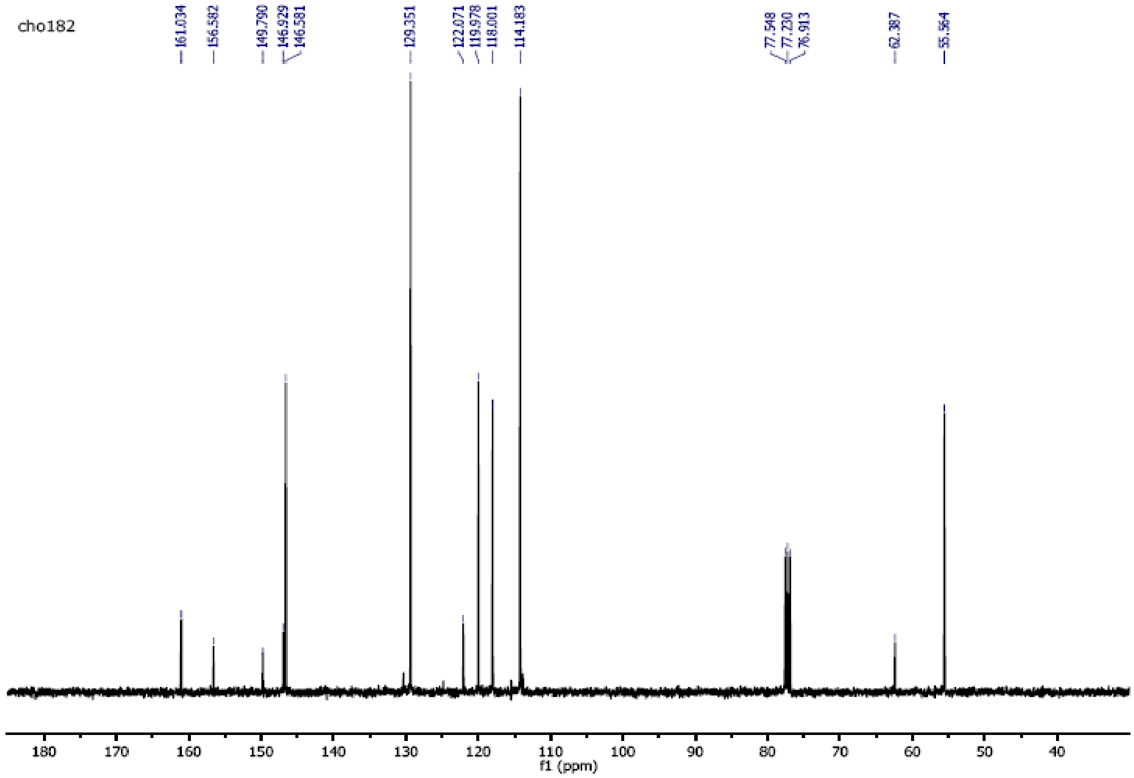

cho302
7.481
7.459
7.232
7.206
7.199
7.053
7.033
6.994
6.987
6.972
6.879
6.857
6.834
6.808
6.786
5.440
3.865
3.796
2.276
-0.000
2.02
1.00
2.04
1.05
4.16
1.05
0.93
3.17
3.16
3.07
7.5 7.48 7.46 7.24 7.22 7.2 7.06 7.04 7.02 7 6.98 6.96 6.88 6.86 6.84 6.82 6.8 6.78
f1 (ppm)
12 11.5 11 10.5 10 9.5 9 8.5 8 7.5 7 6.5 6 5.5 5 4.5 4 3.5 3 2.5 2 1.5 1 0.5 0 -0.5
f1 (ppm)


cho302
159.65
155.13
141.91
136.75
133.27
129.94
124.35
120.82
117.27
115.71
114.03
113.55
112.07
93.64
84.45
77.55
77.23
76.91
56.50
55.44
20.80
130.01
129.94
130.1130129.9129.8
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

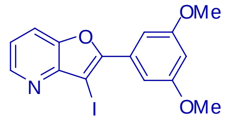
3-Iodobenzofuran 9{*3*}

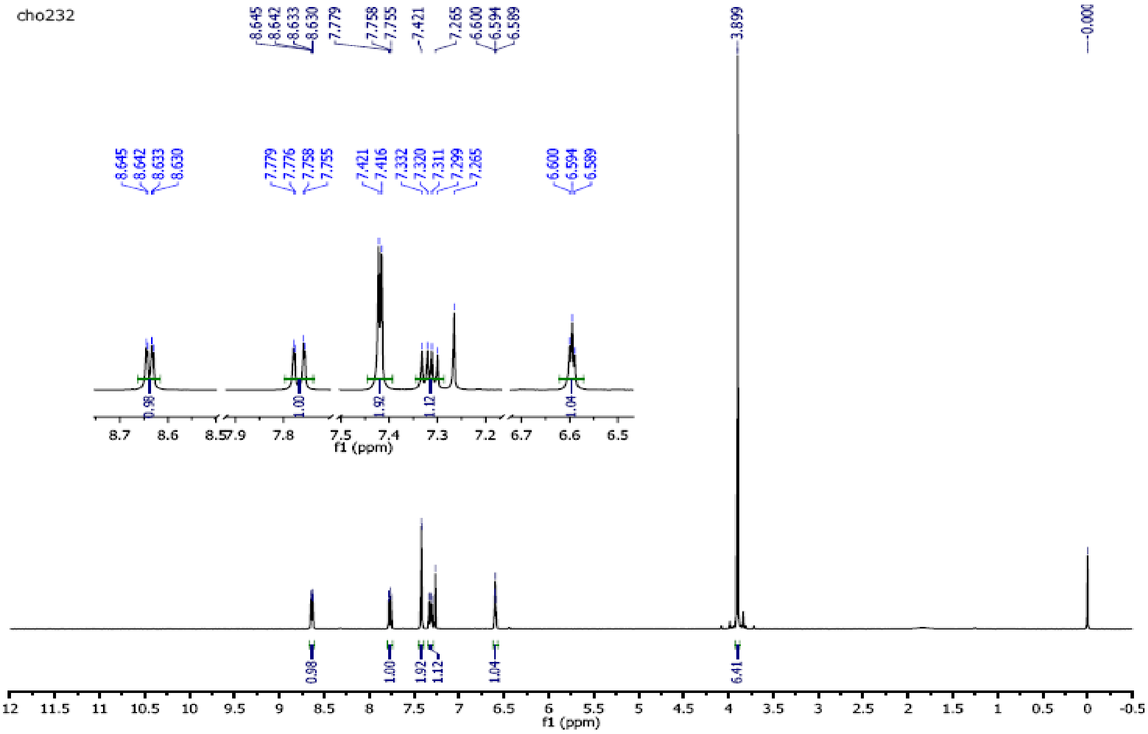


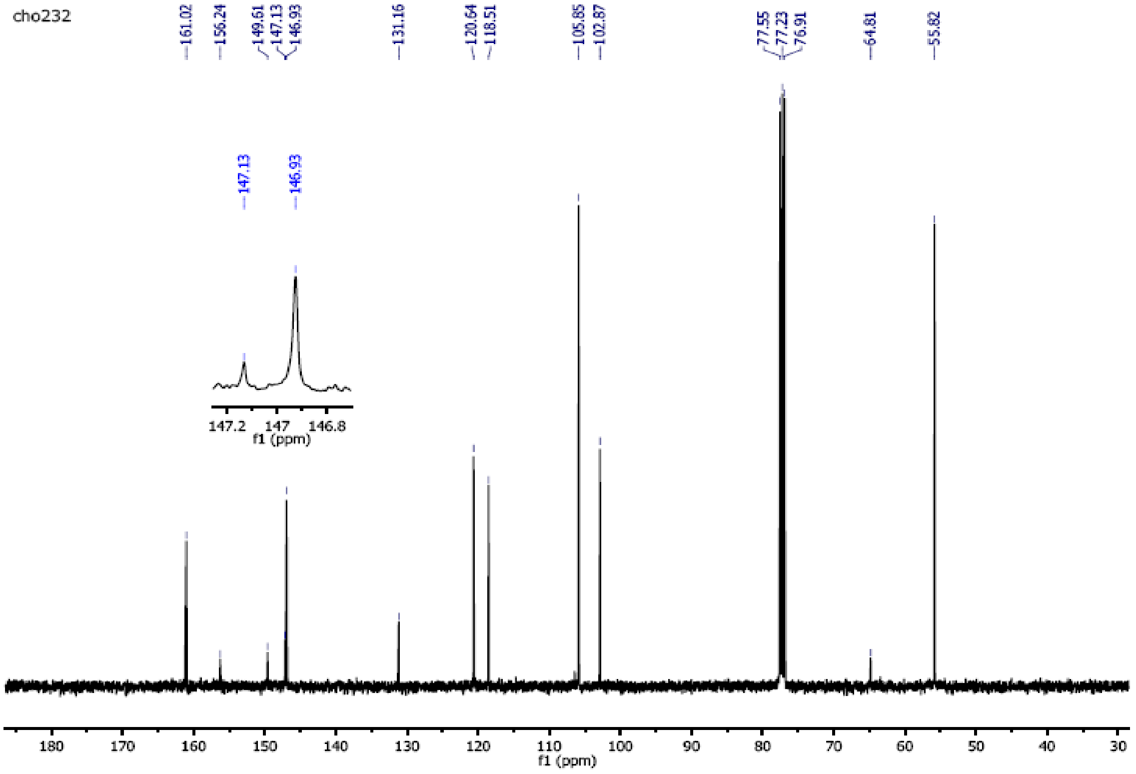




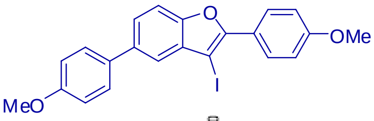
3-Iodobenzofuran 9{*4*}

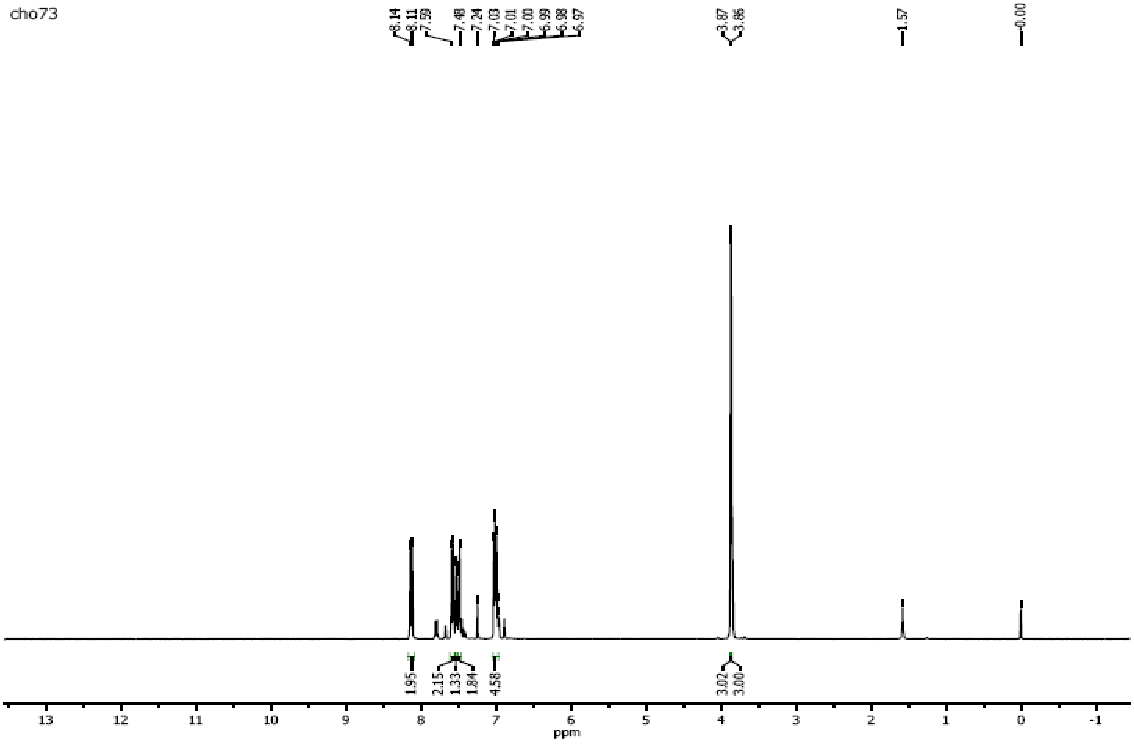


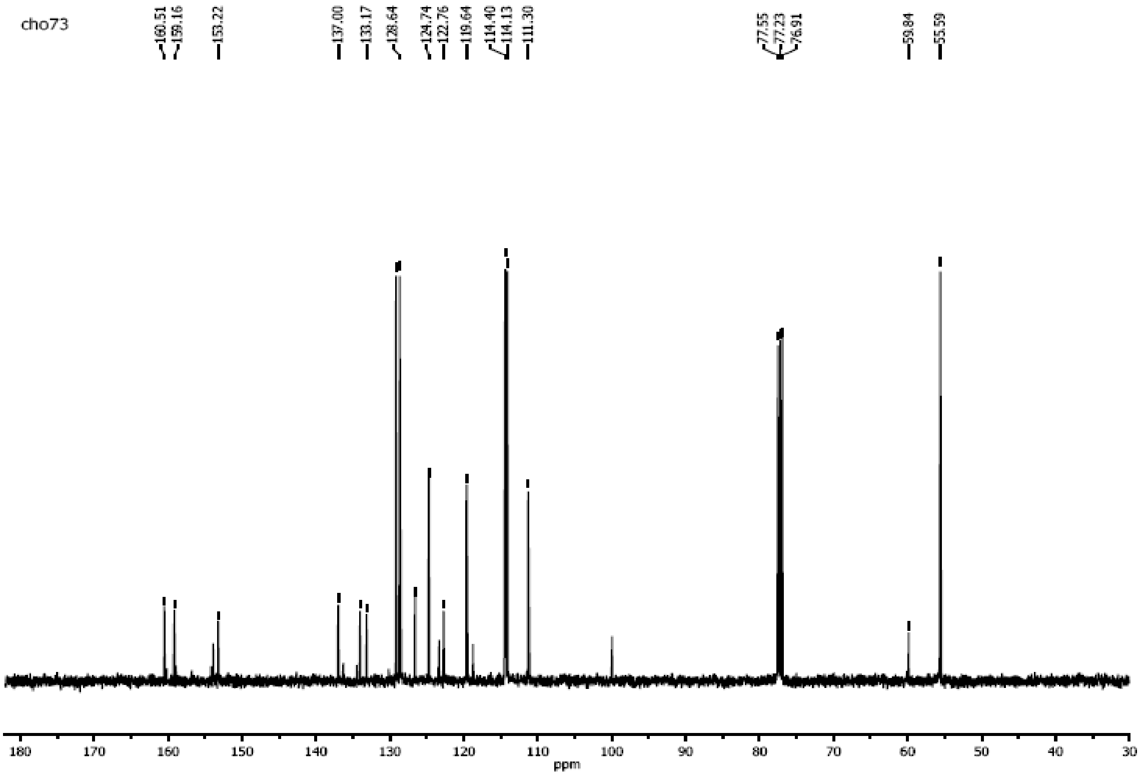




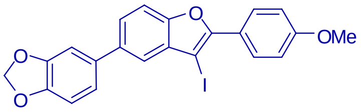
3-Iodobenzofuran 9{*5*}

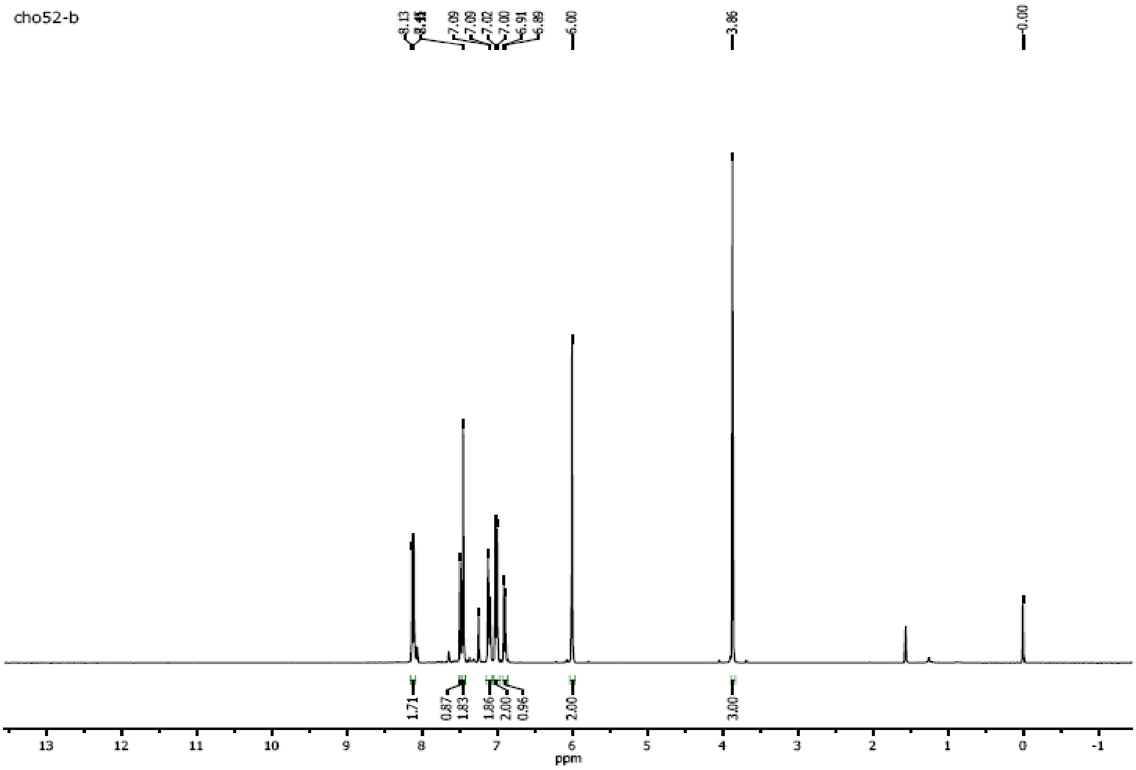


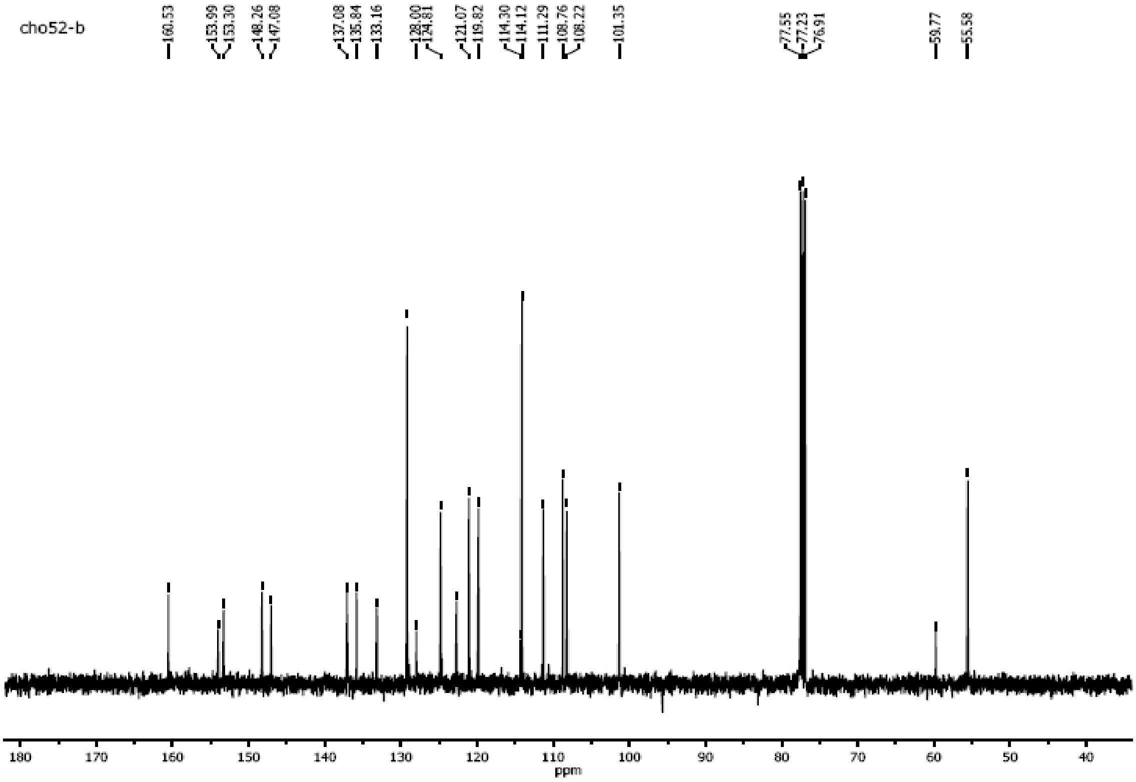




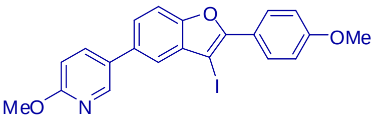
3-Iodobenzofuran 9{*6*}

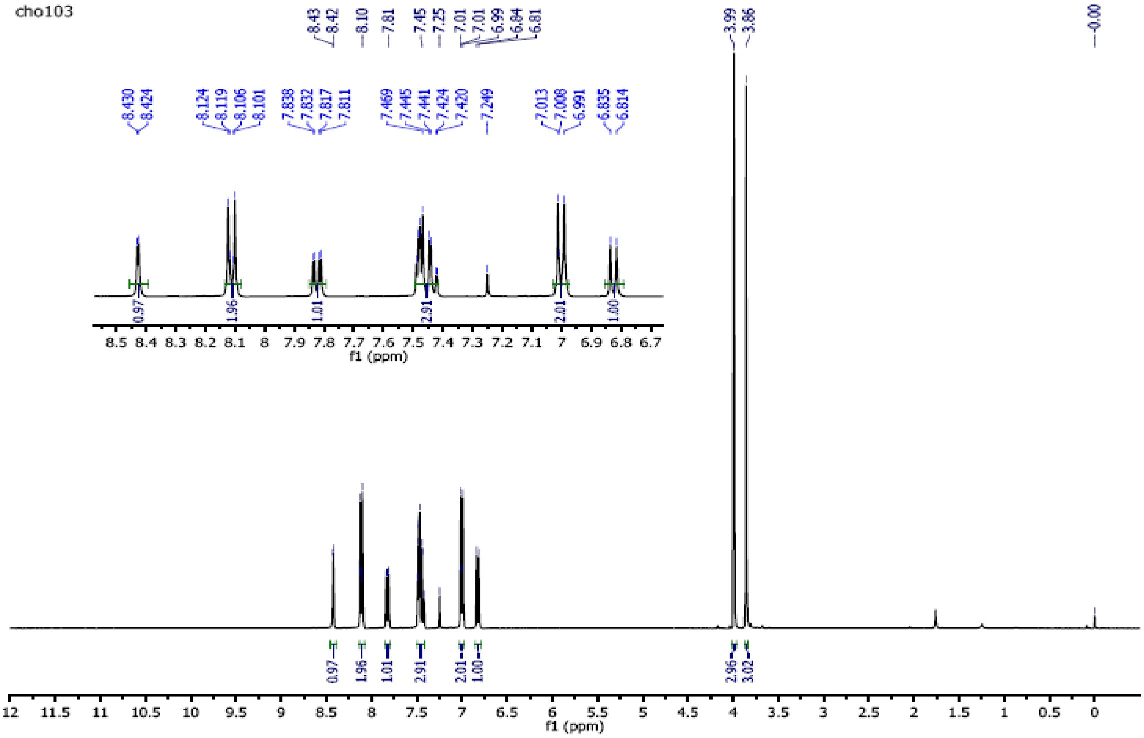


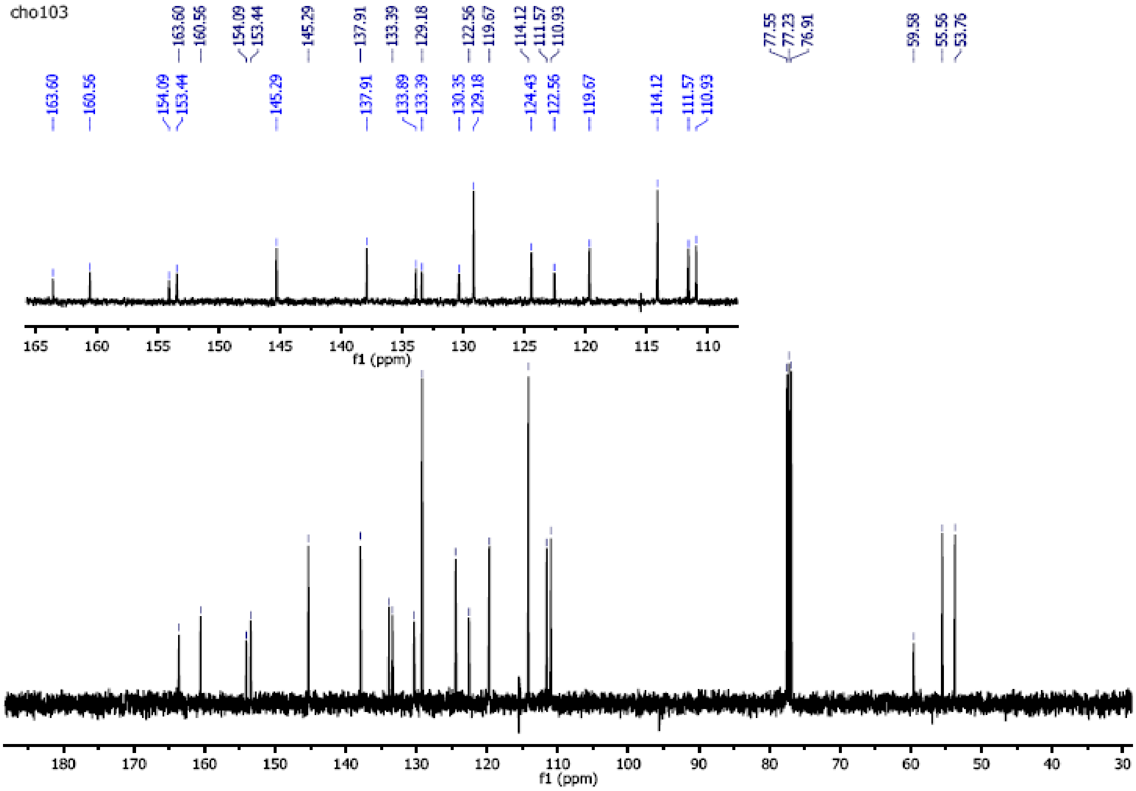




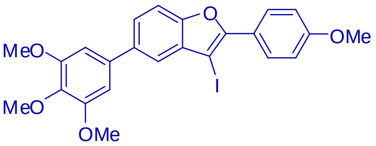
3-Iodobenzofuran 9{*7*}

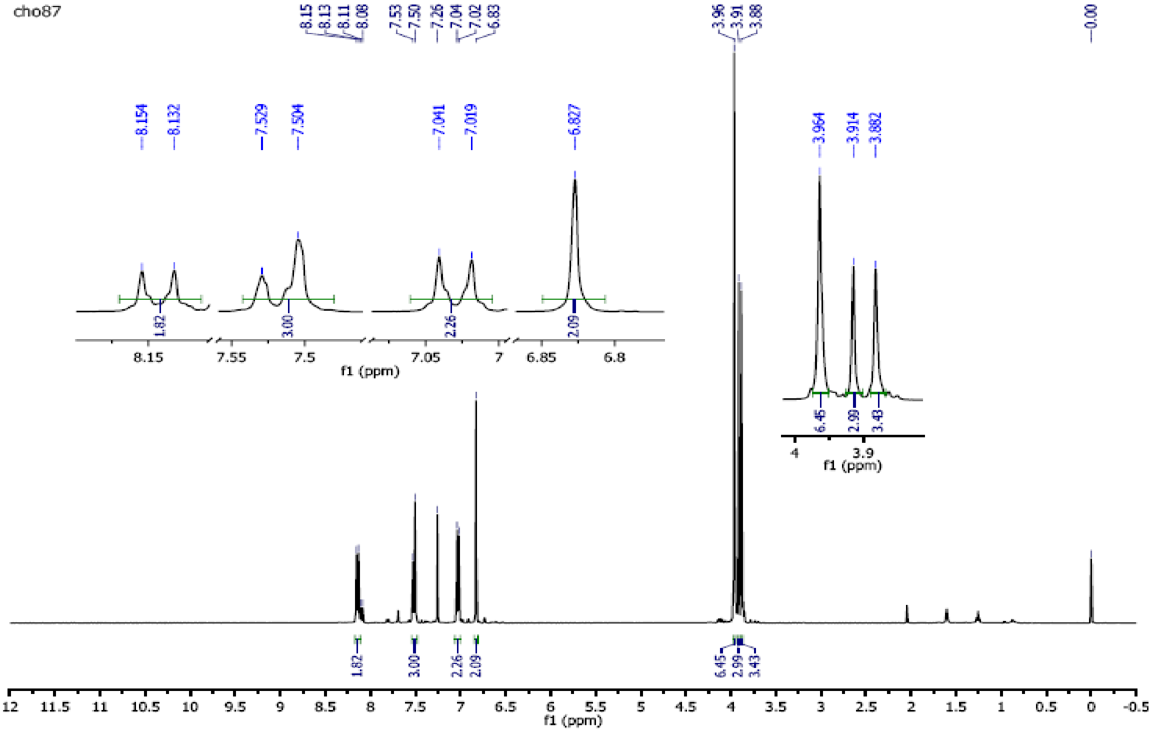


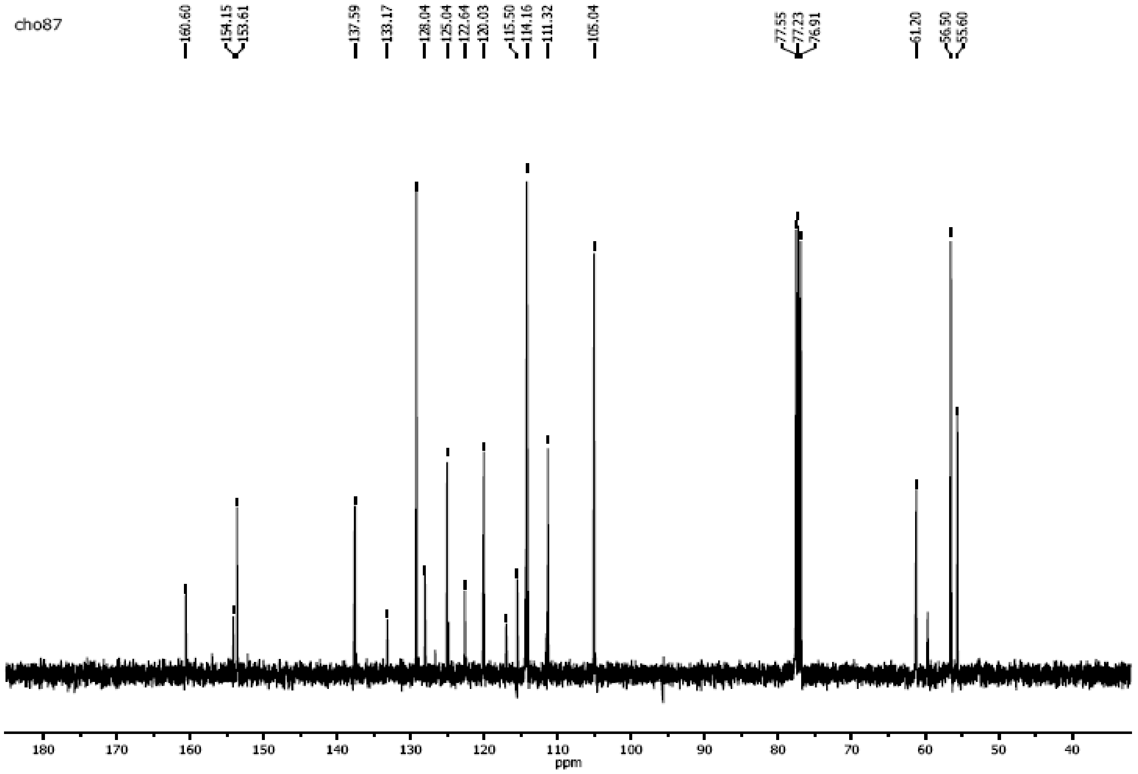




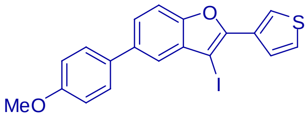
3-Iodobenzofuran 9{*8*}

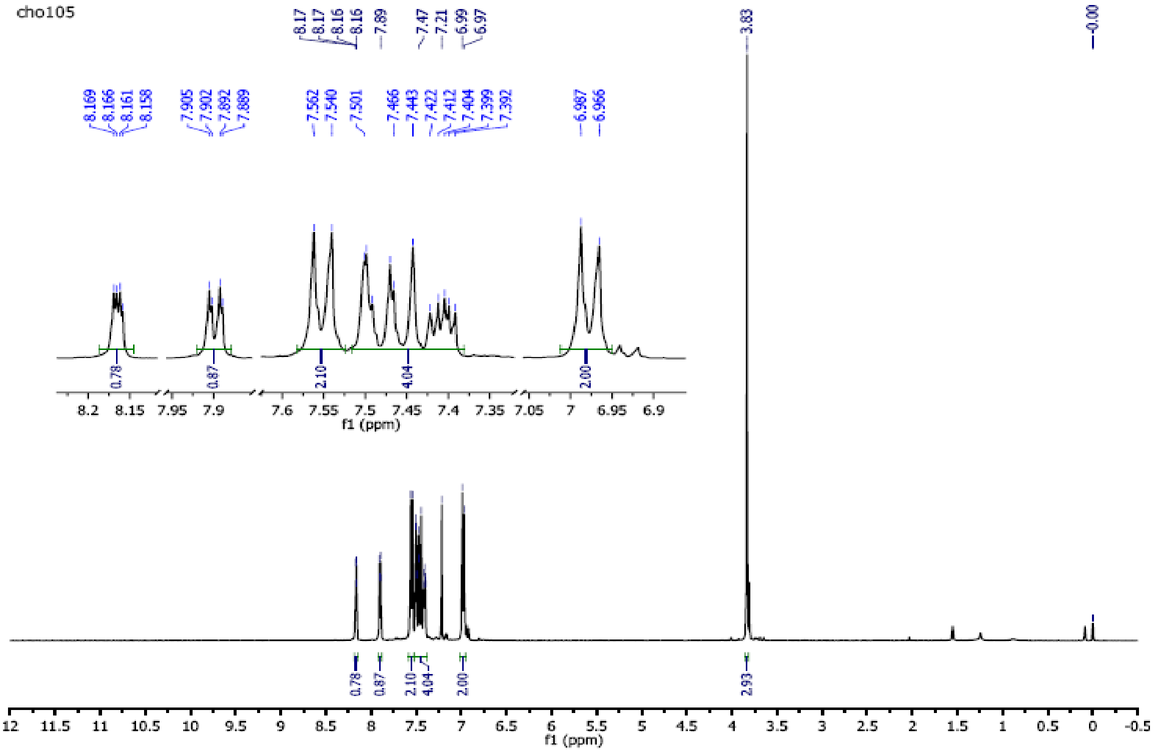


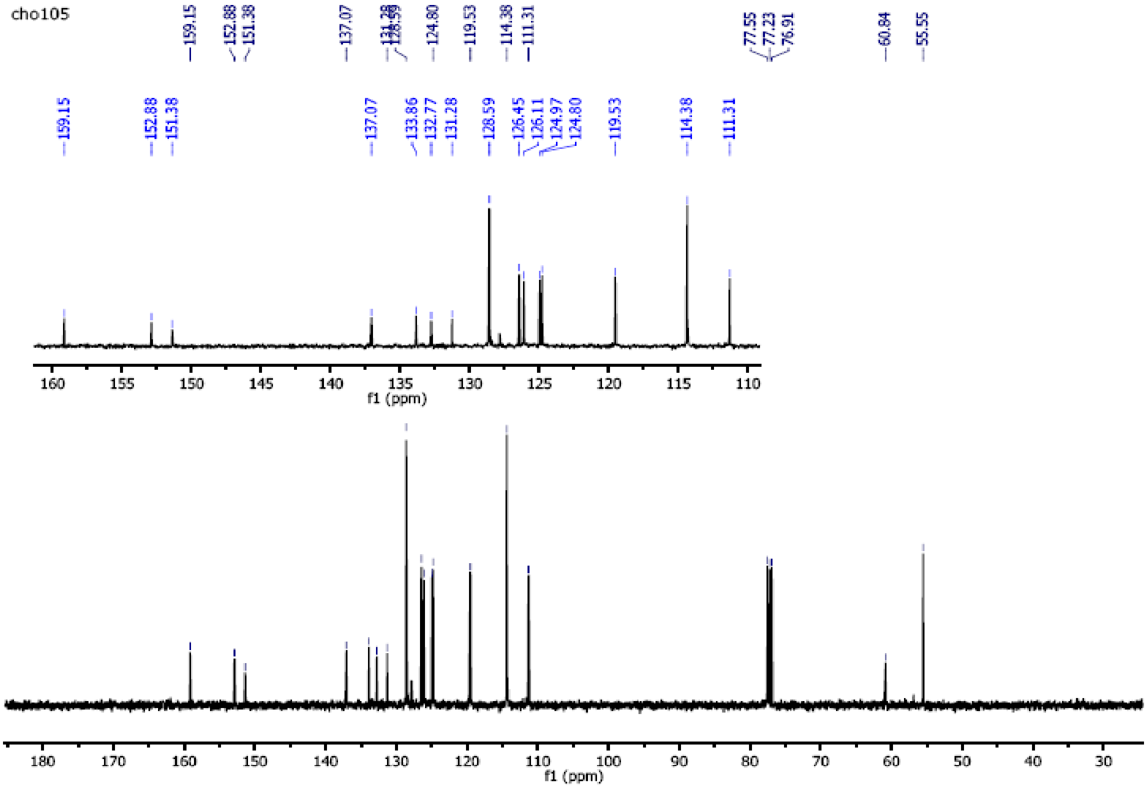




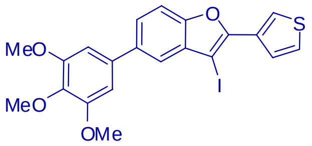
3-Iodobenzofuran 9{*10*}

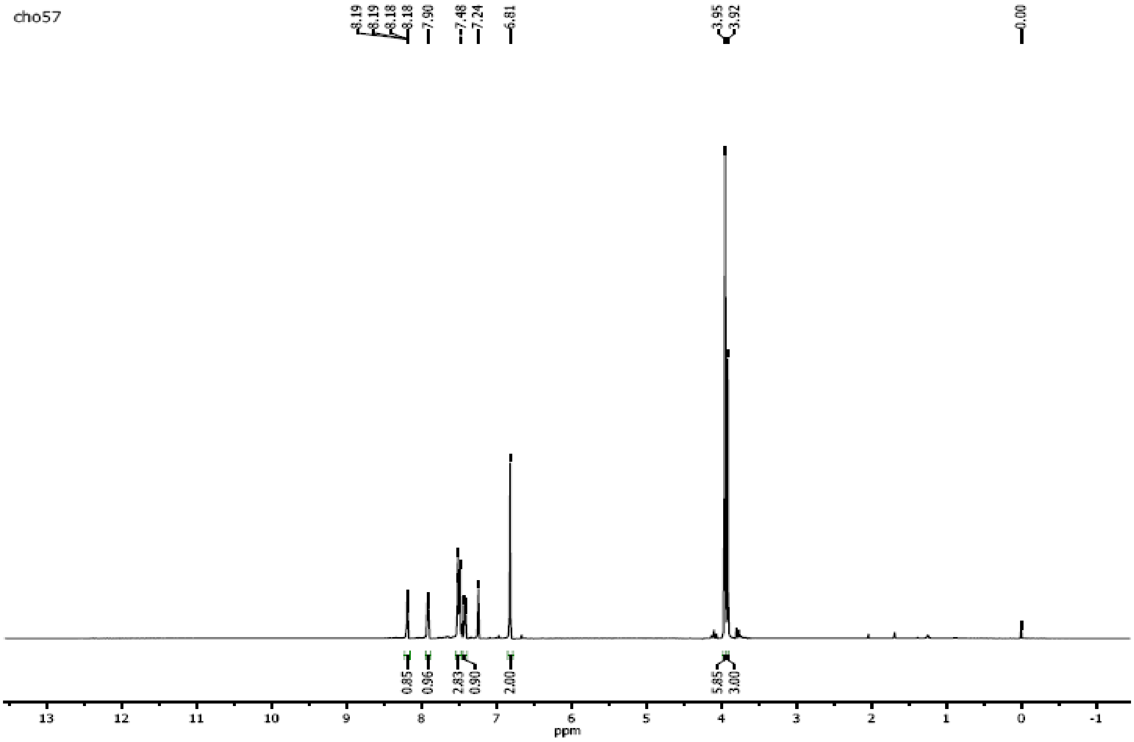


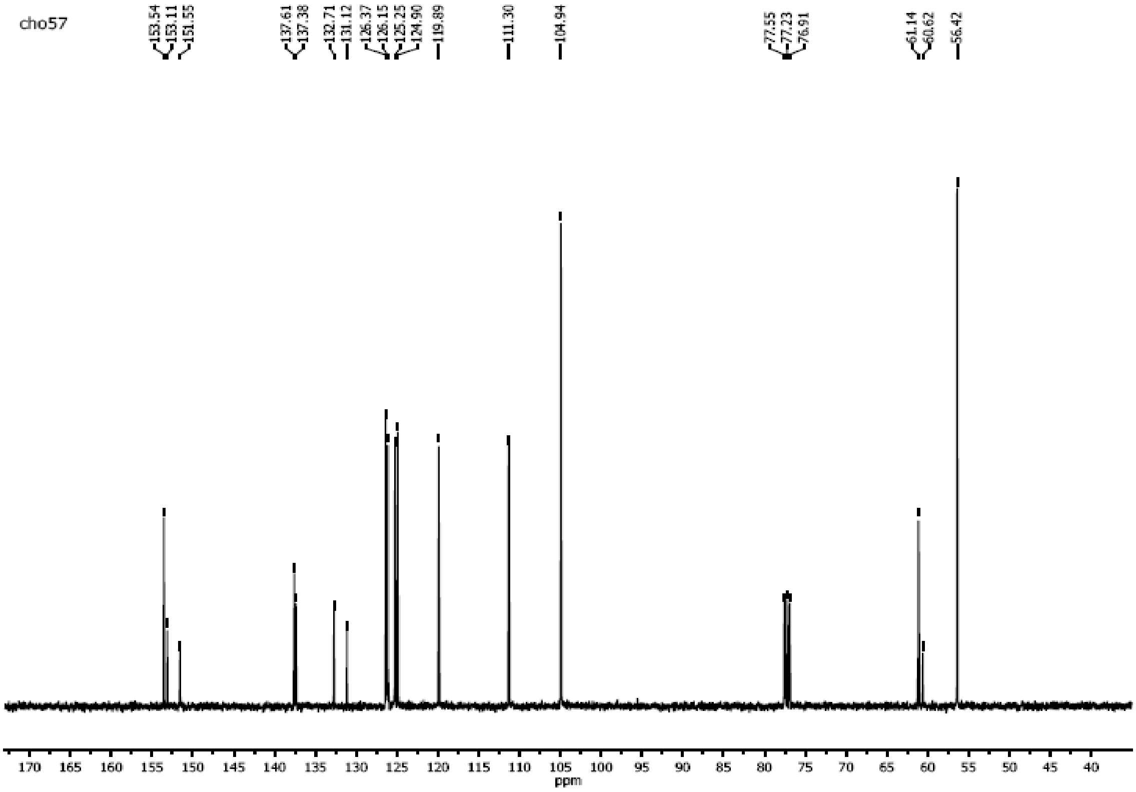




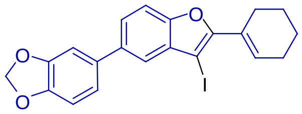
3-Iodobenzofuran **9**{*13*}

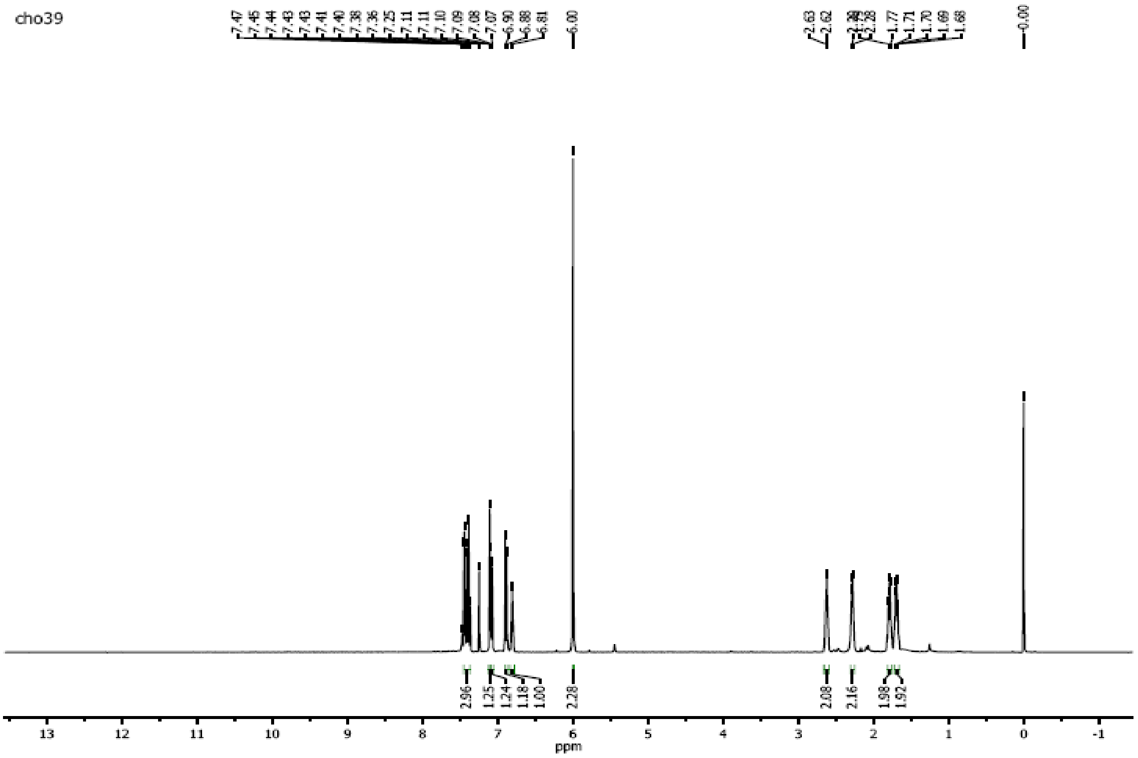


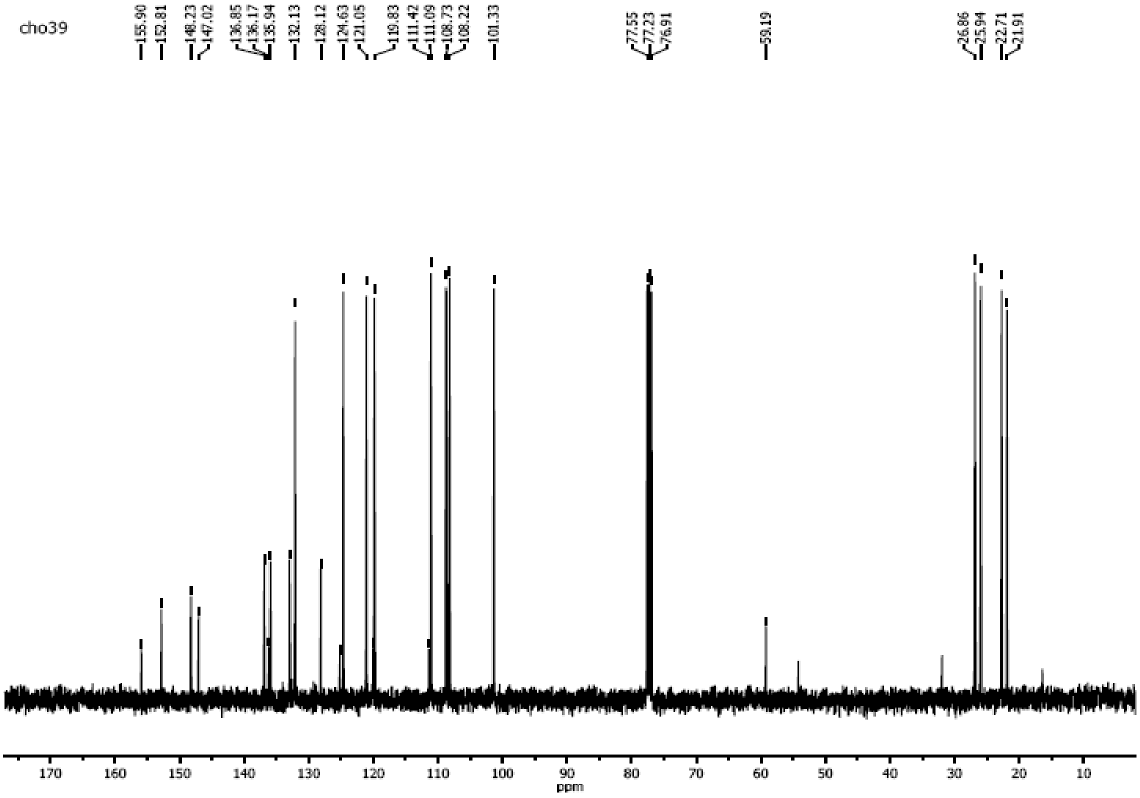




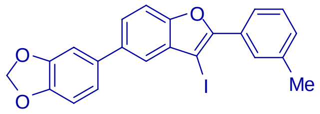
3-Iodobenzofuran 9{*14*}

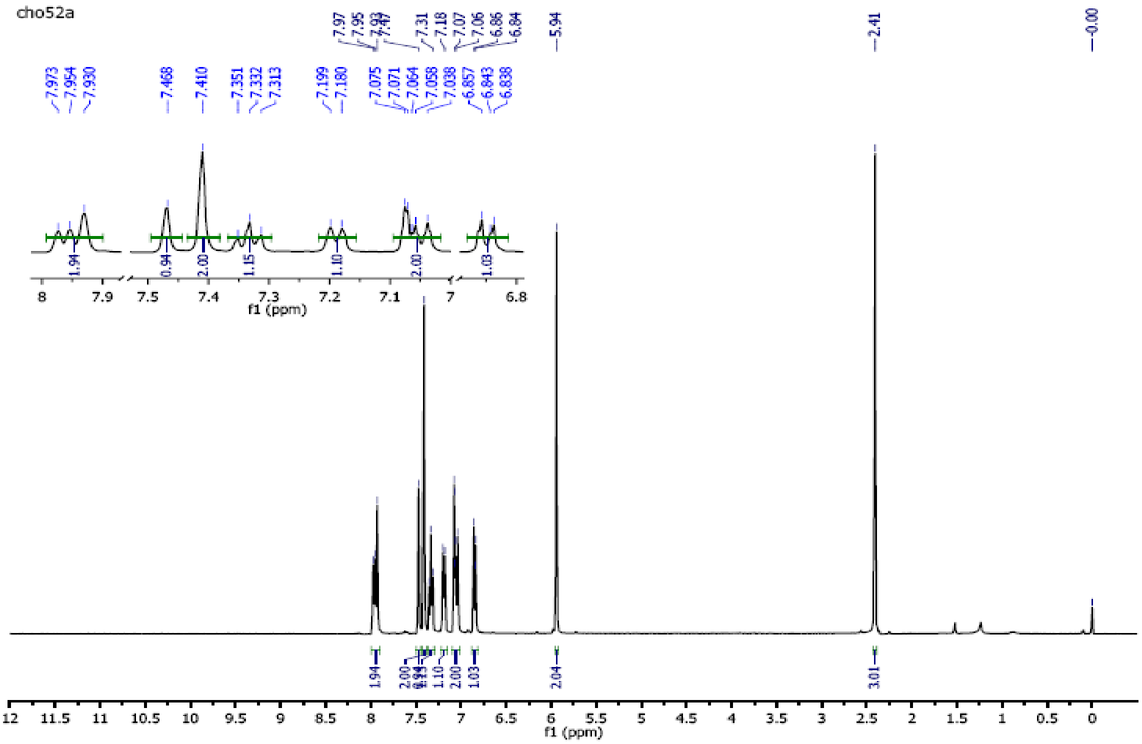


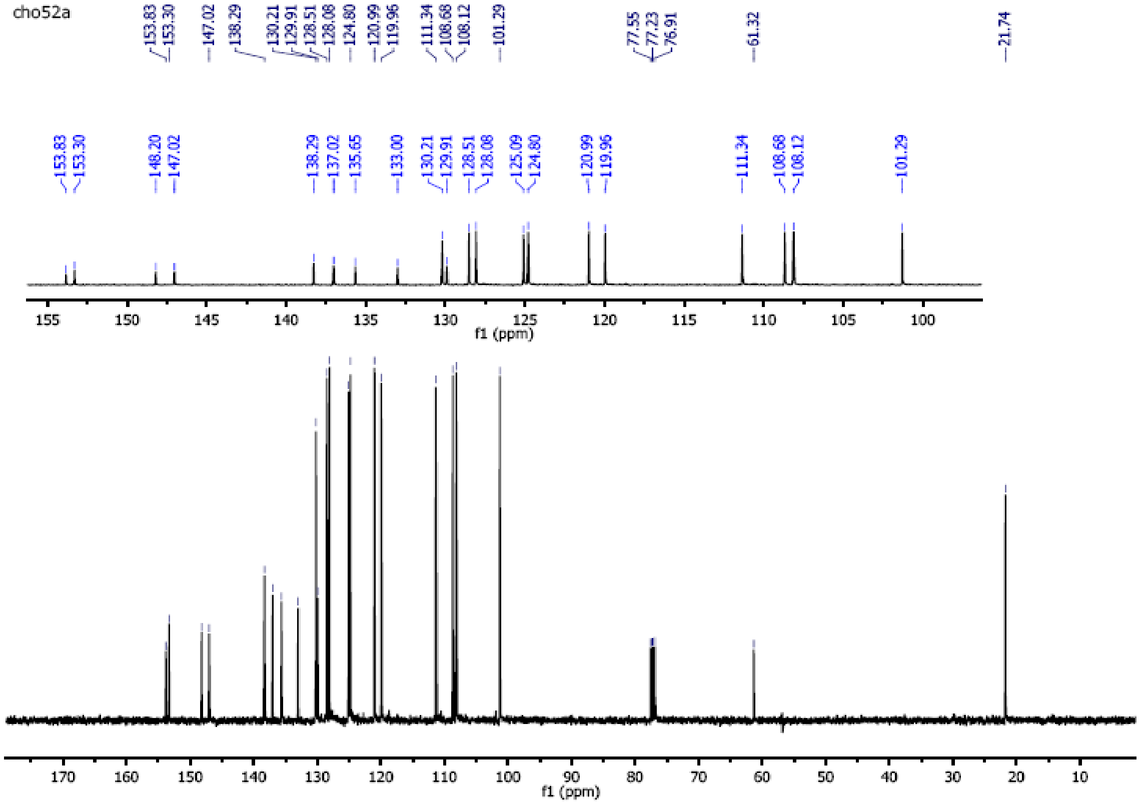




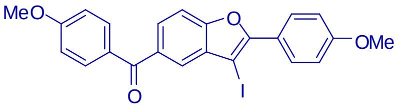
3-Iodobenzofuran 9{*17*}

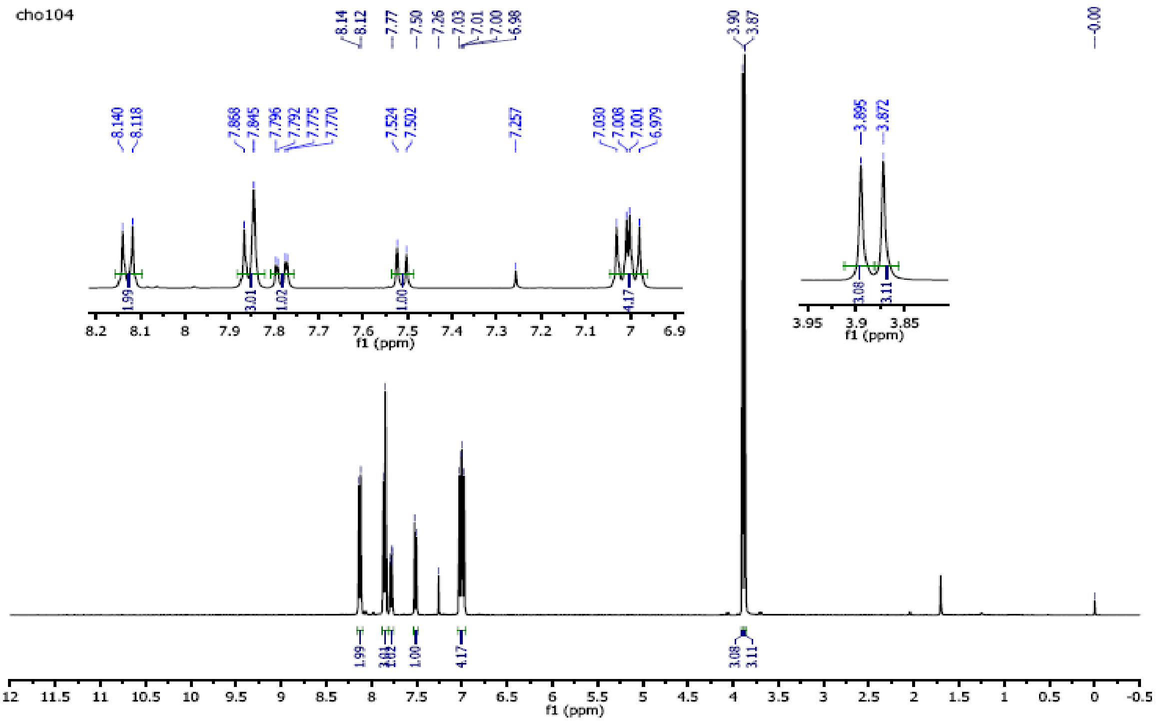


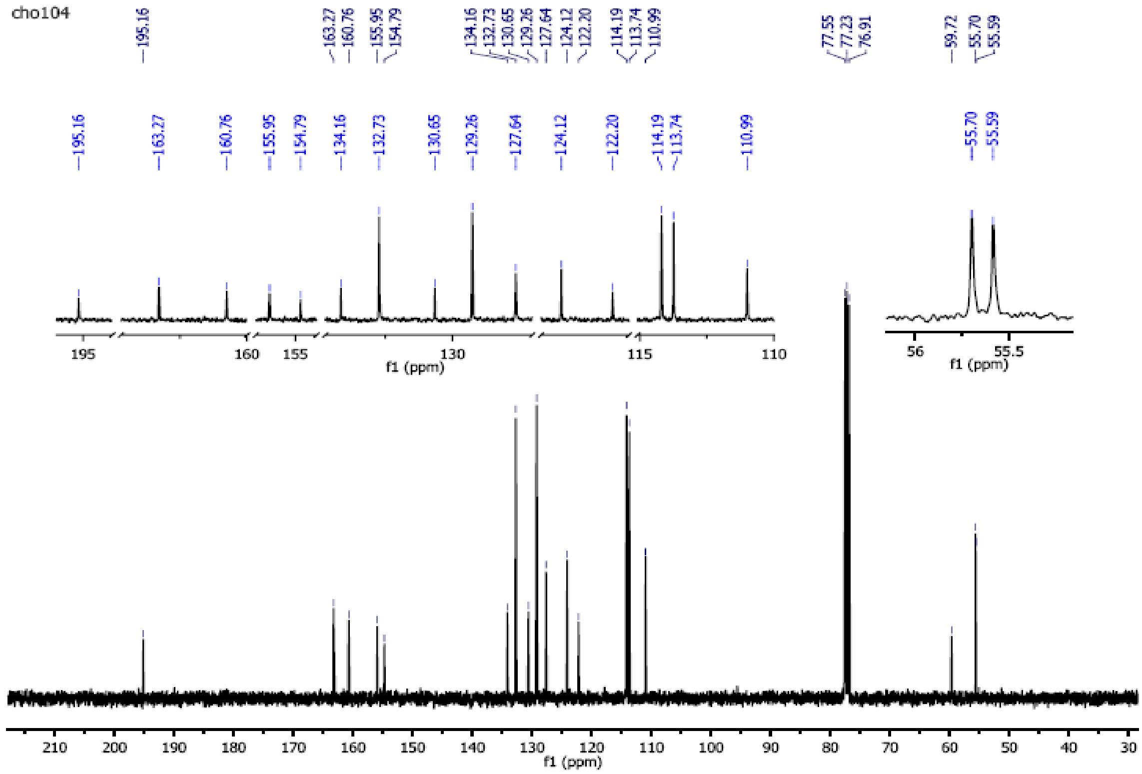




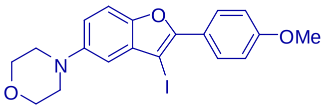
3-Iodobenzofuran 9{*18*}

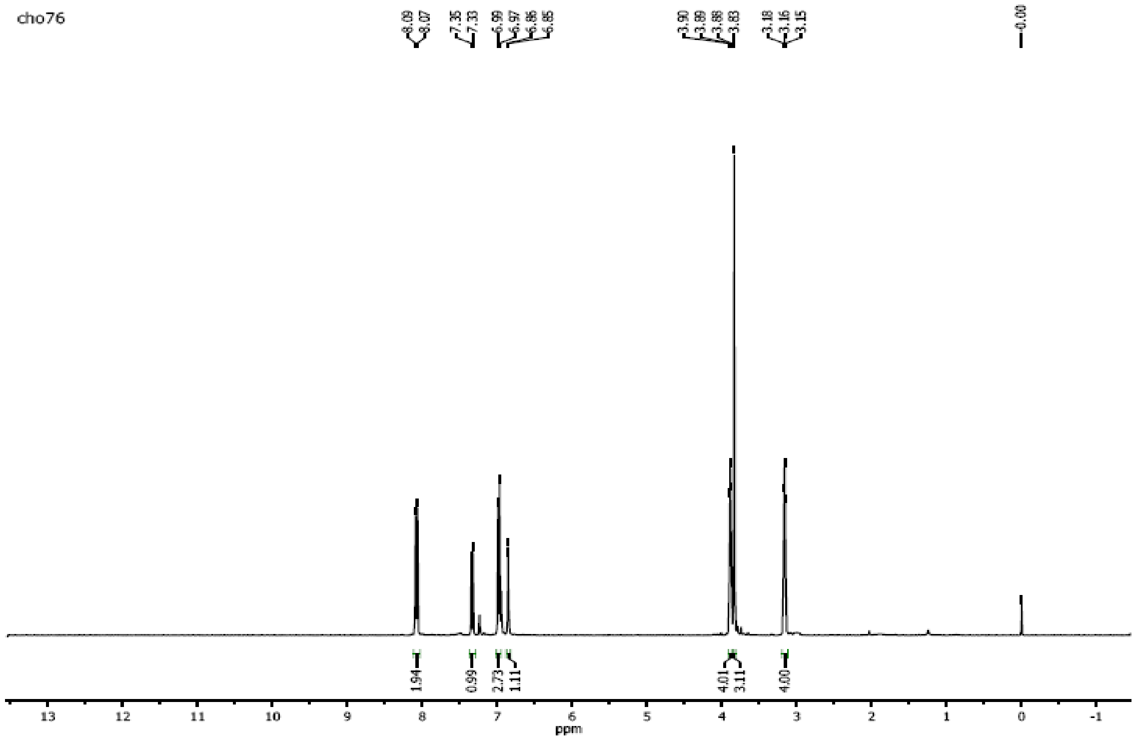


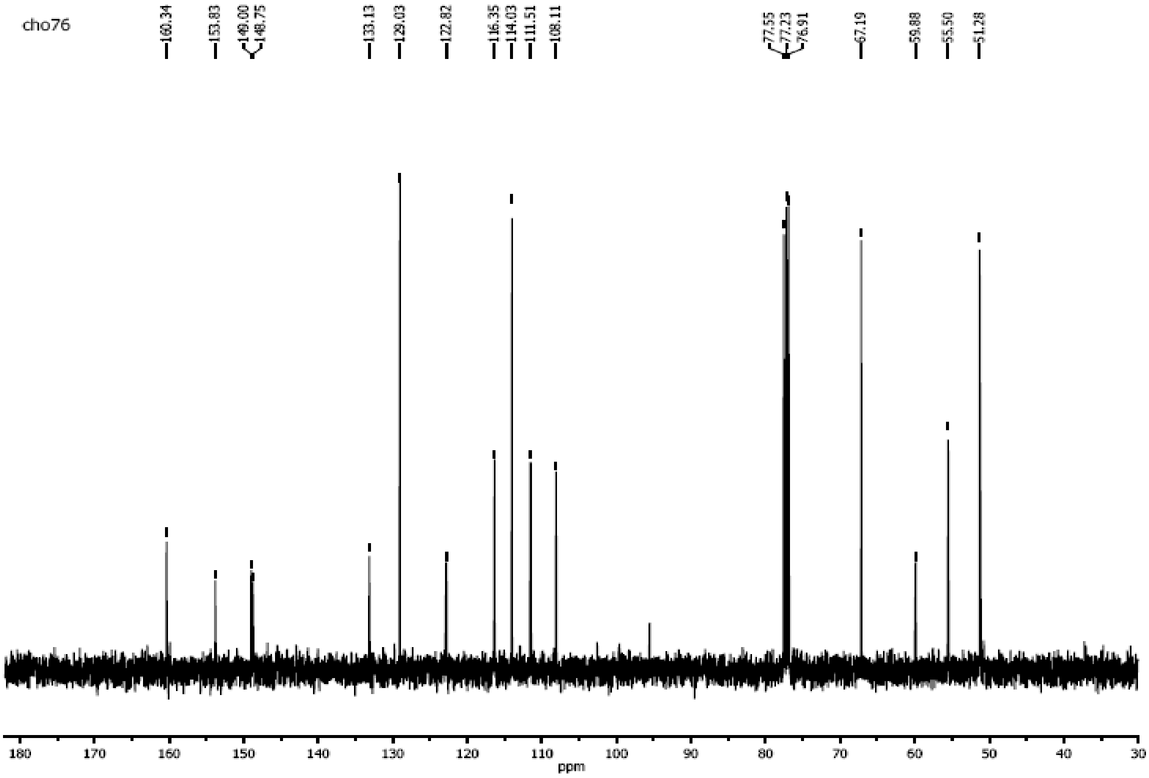




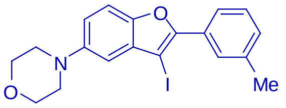
3-Iodobenzofuran 9{*19*}

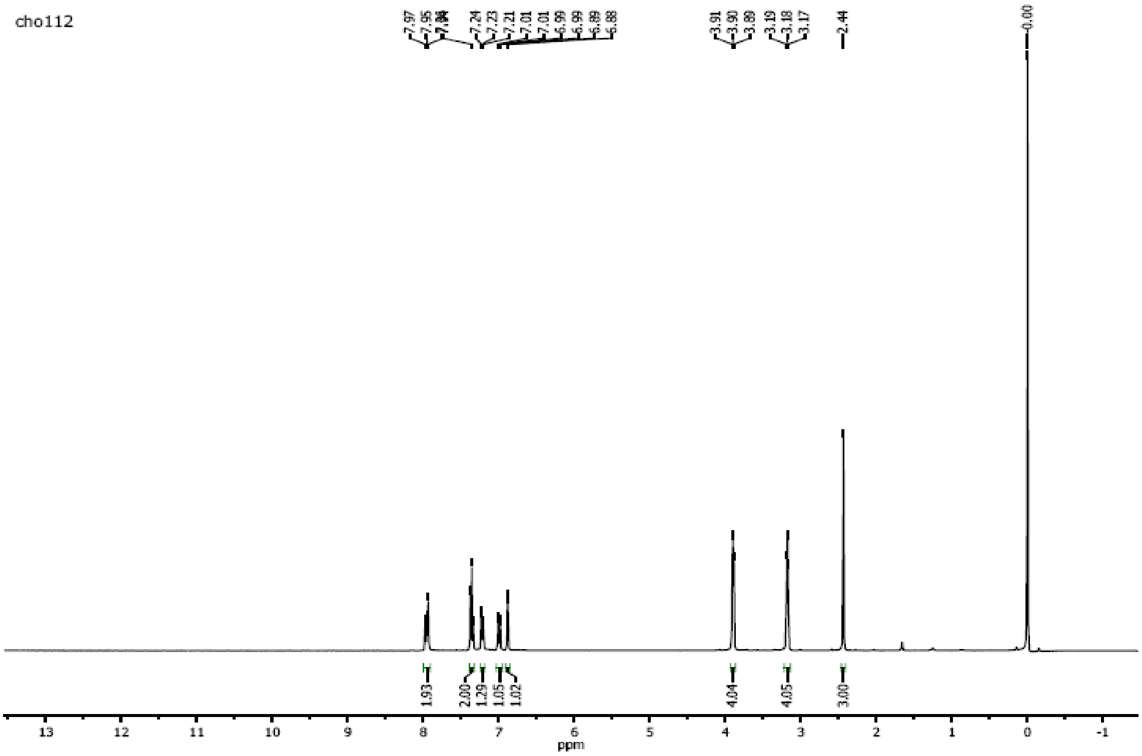


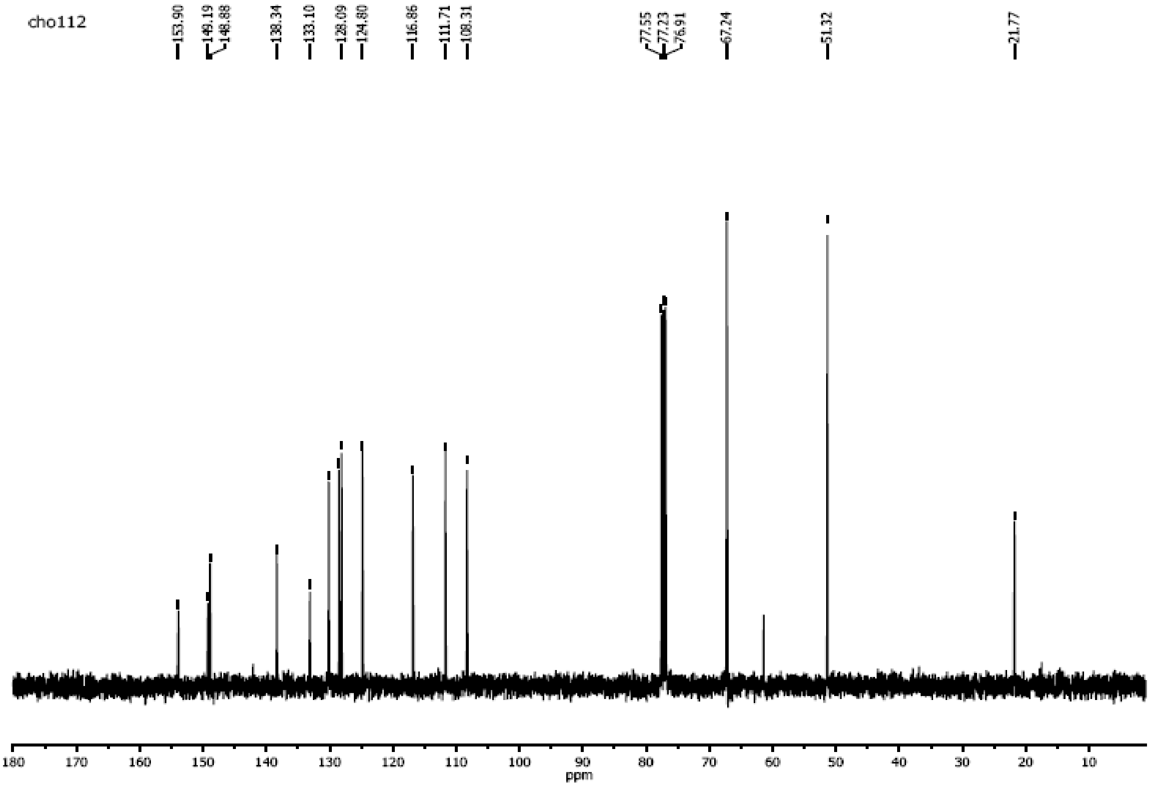




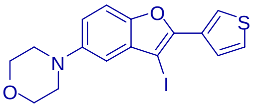
3-Iodobenzofuran 9{*20*}

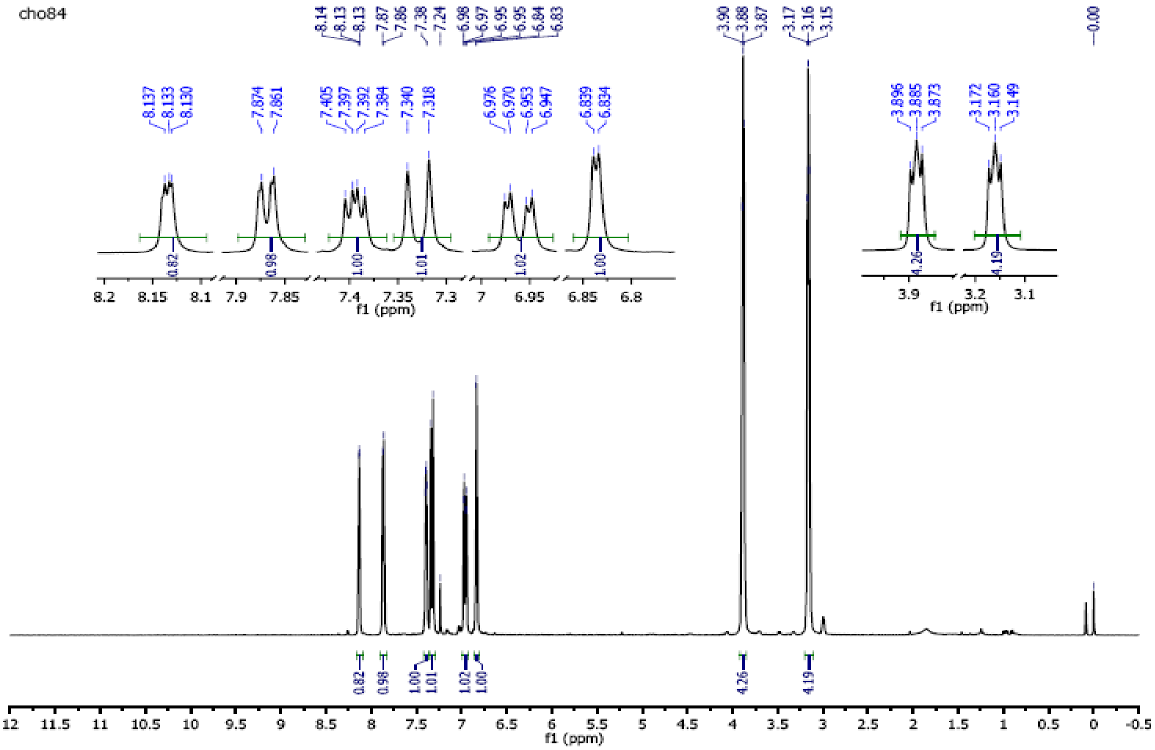


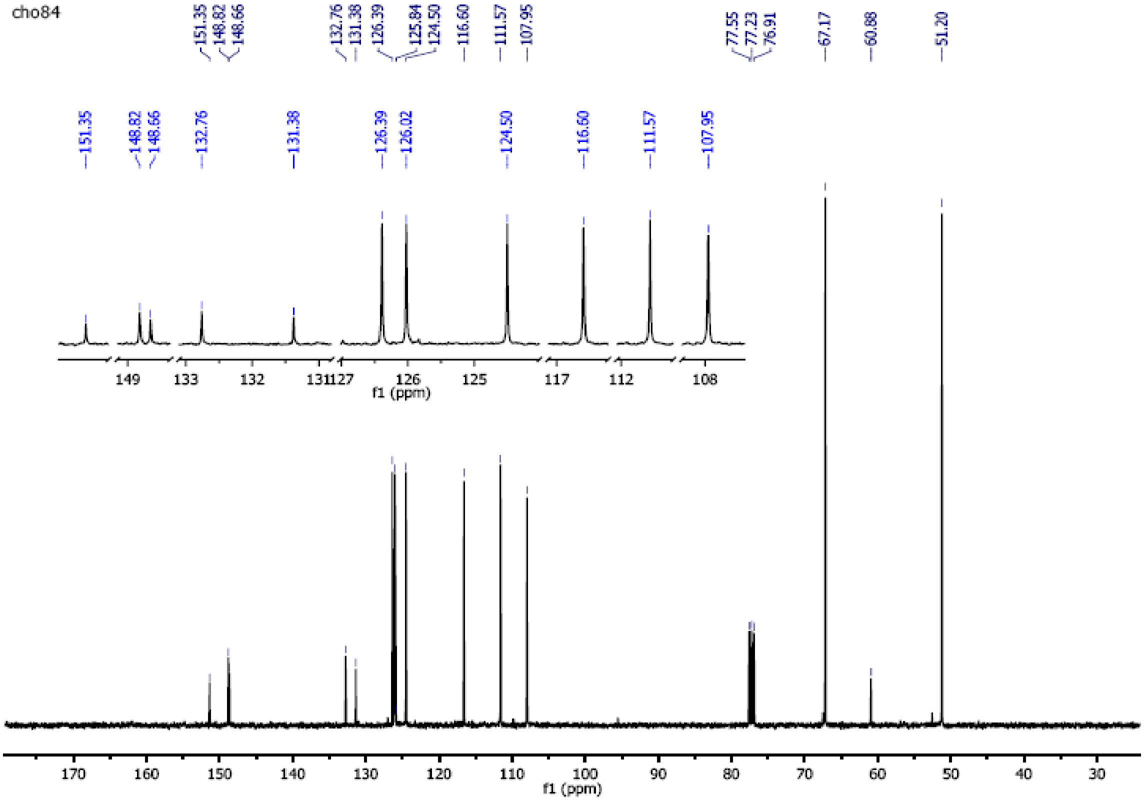




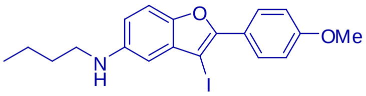
3-Iodobenzofuran 9{*21*}

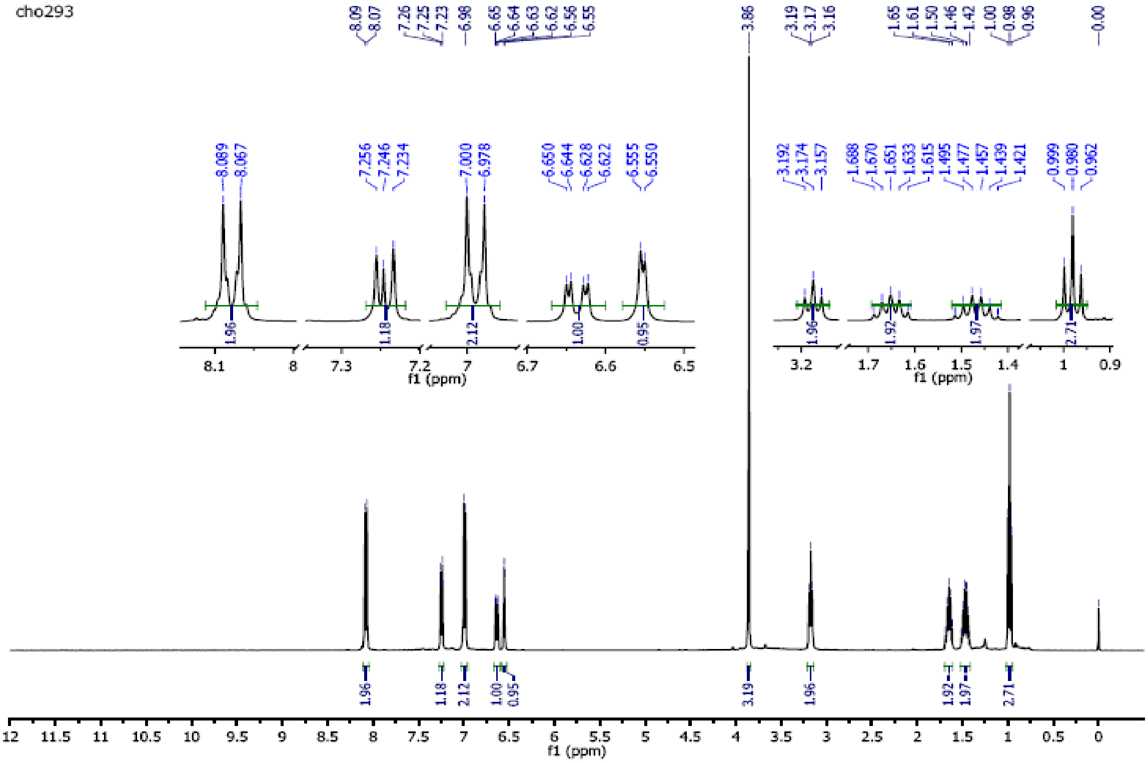


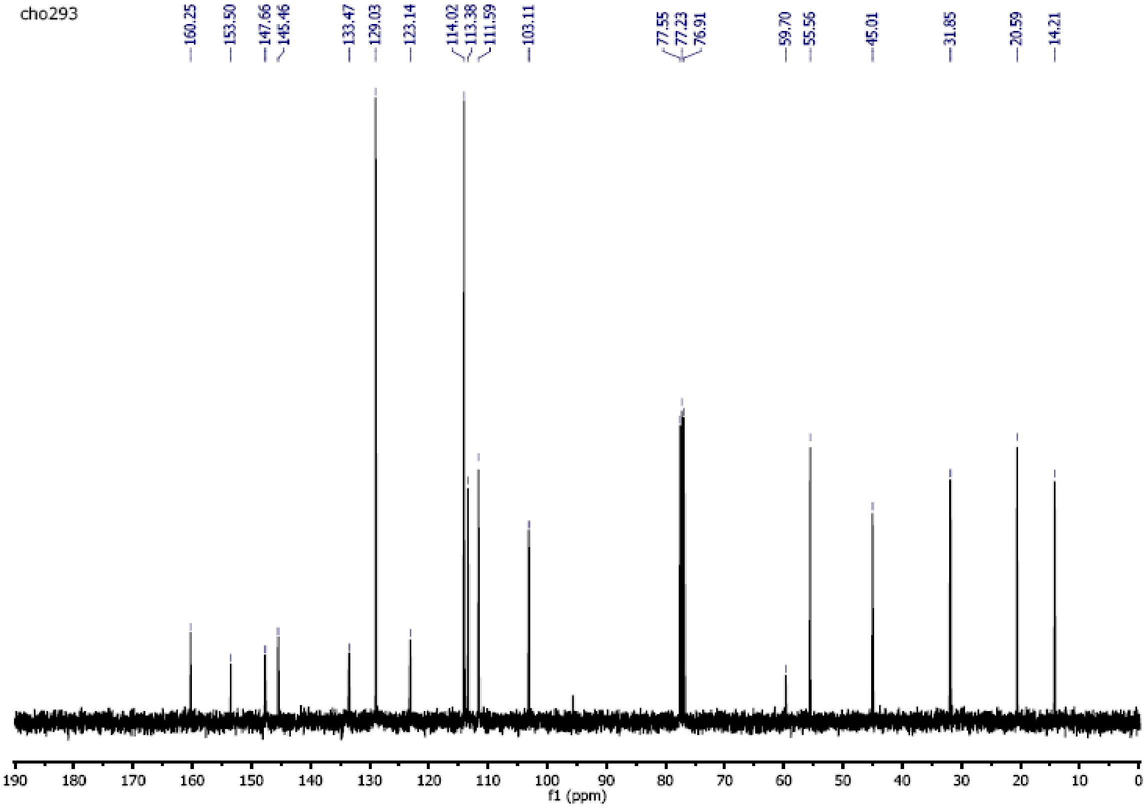




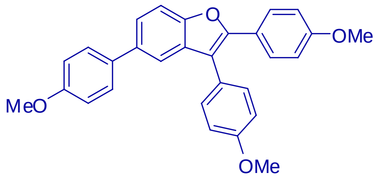
3-Iodobenzofuran 9{*23*}

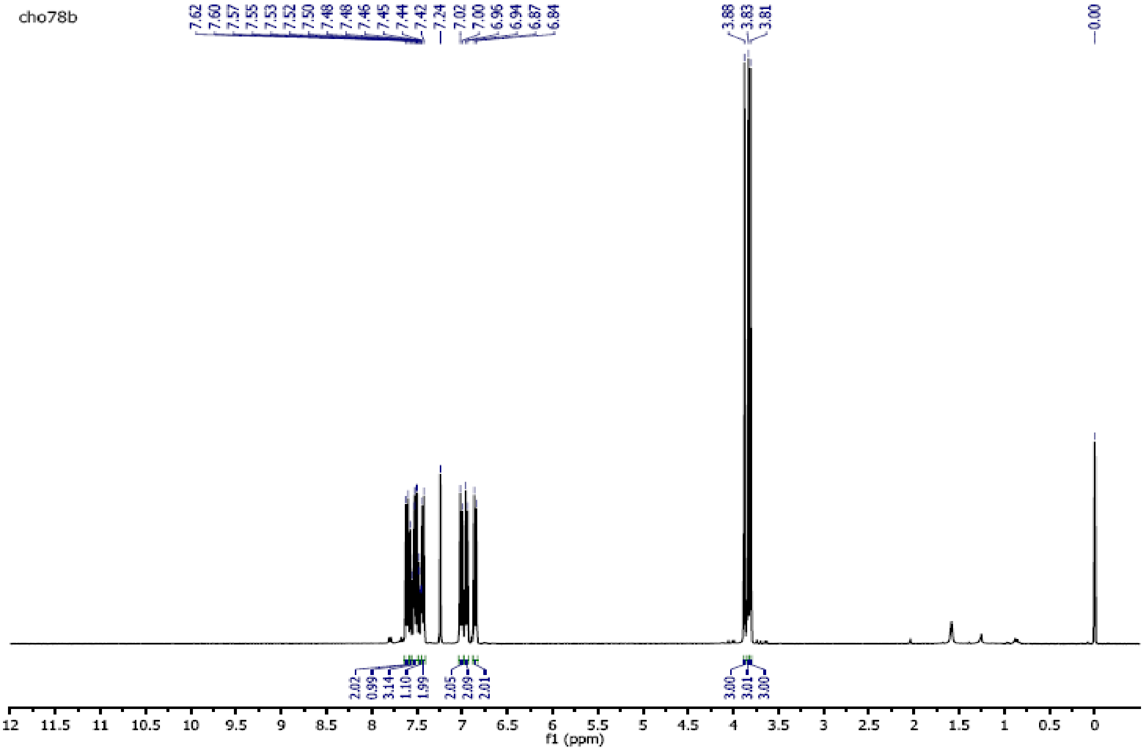


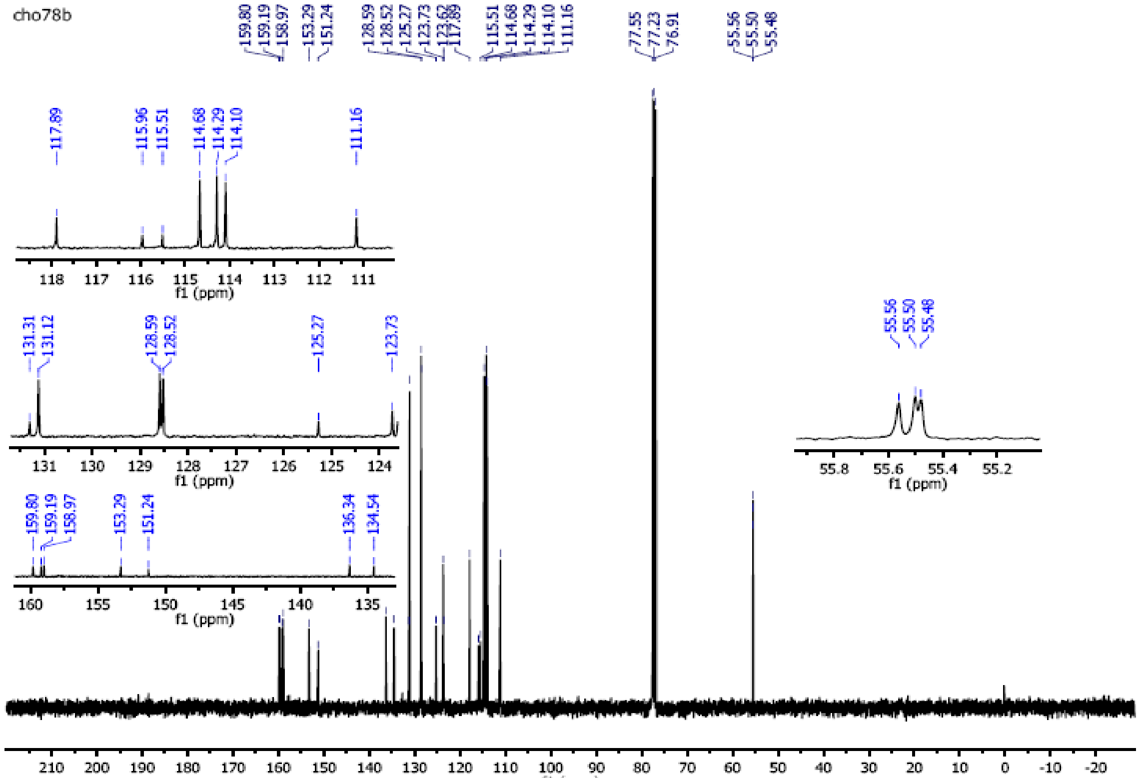




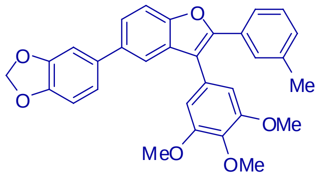
2,3,5-Trisubstituted benzo[*b*]furan 14{*6*}

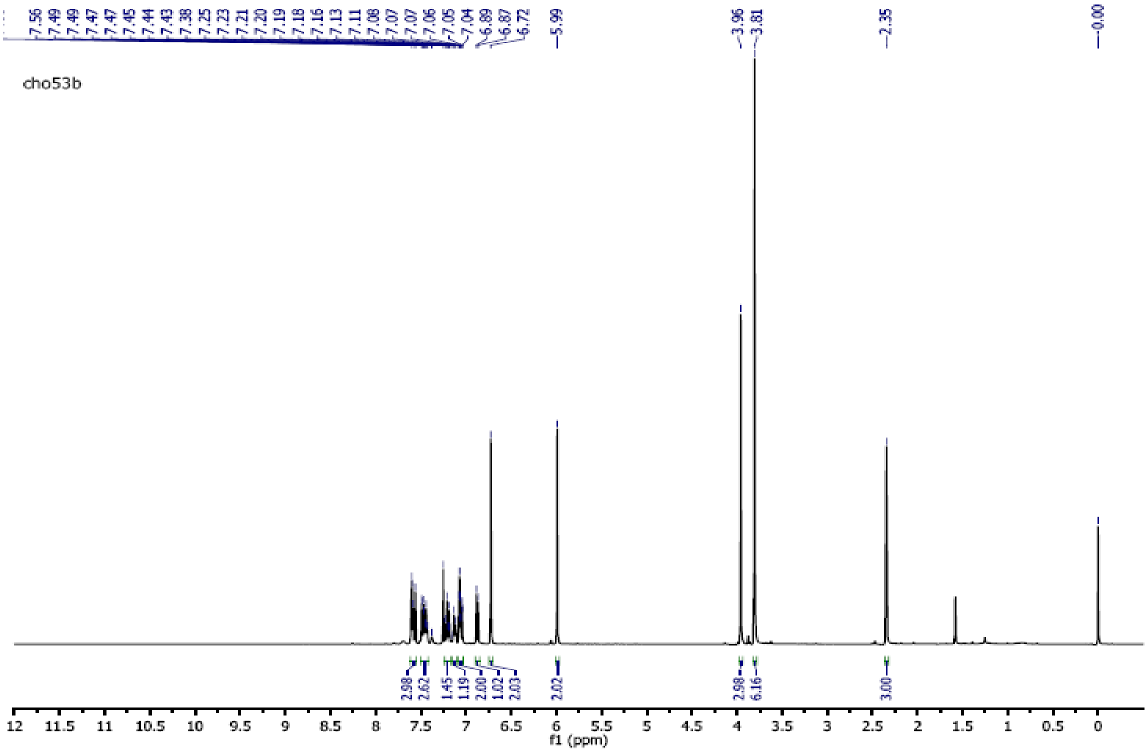


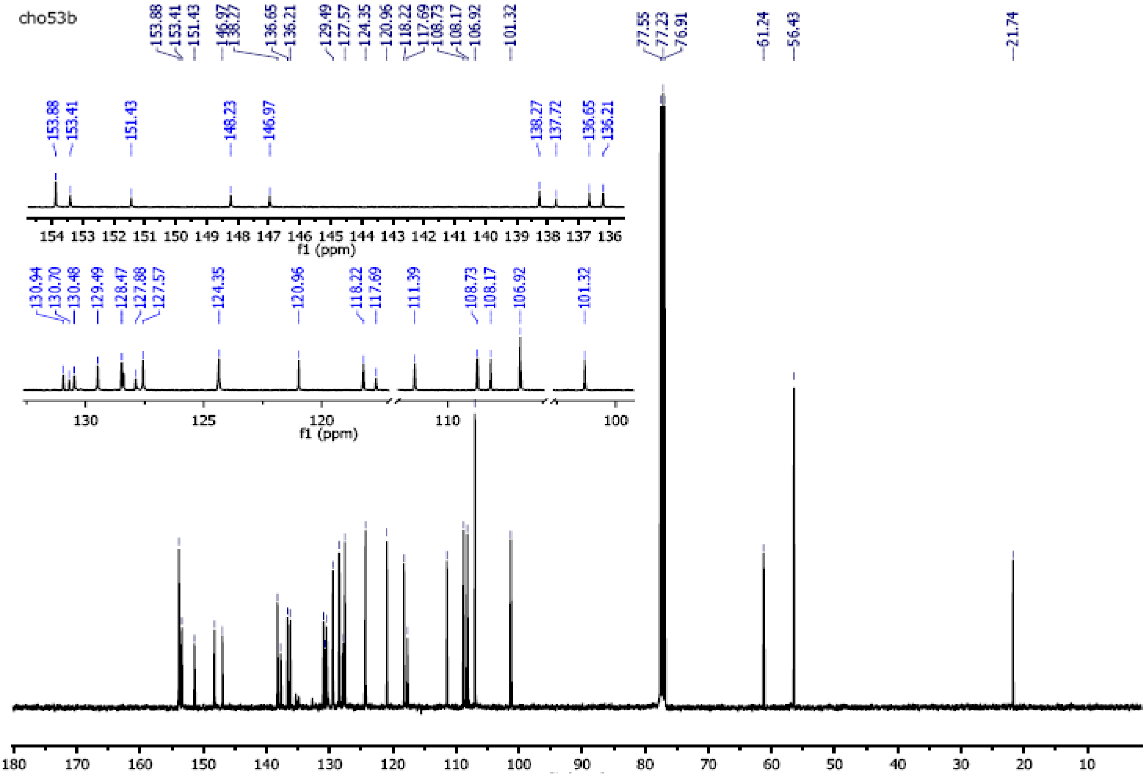




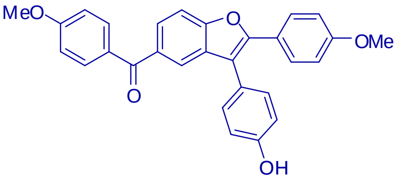
2,3,5-Trisubstituted benzo[*b*]furan 14{*22*}

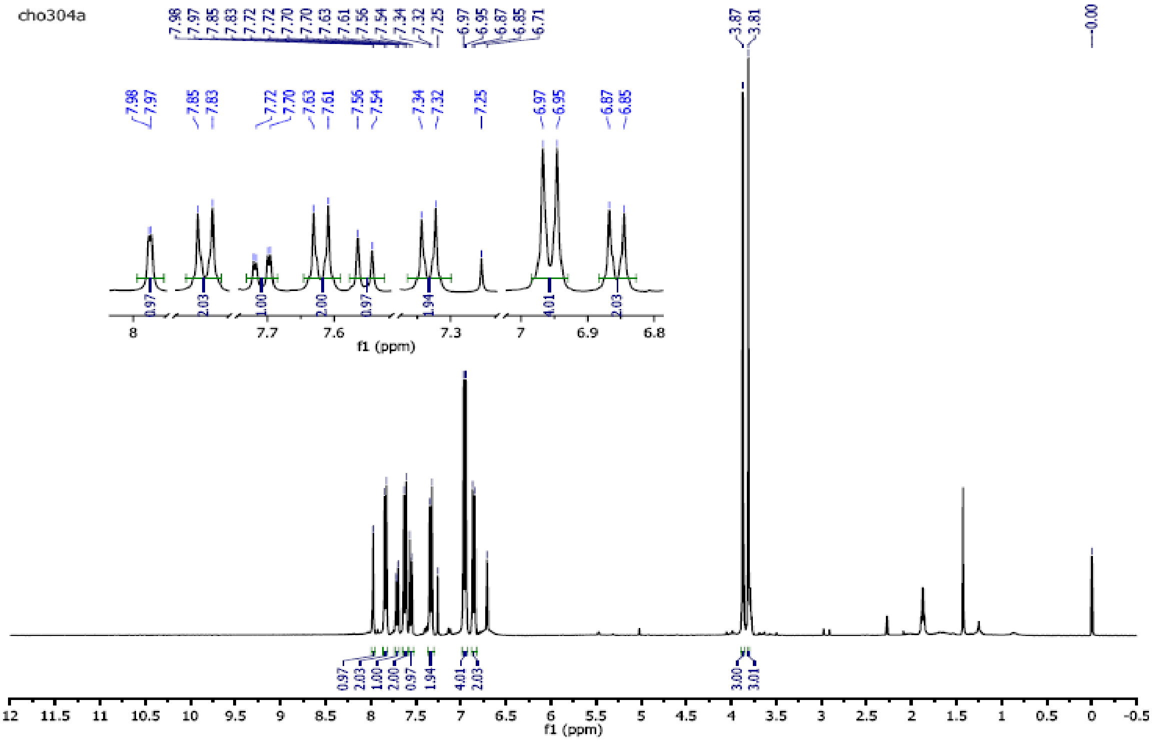


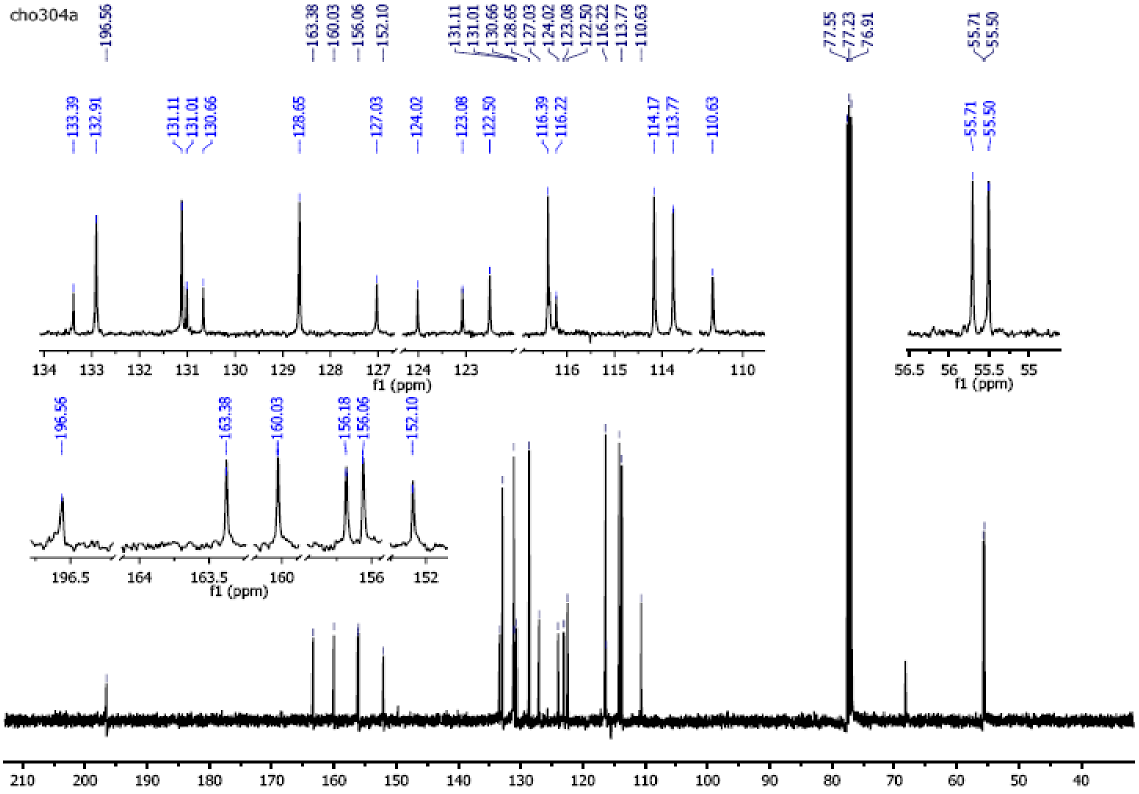




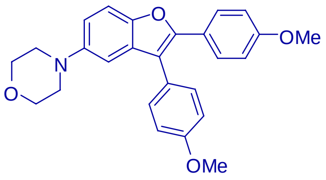
2,3,5-Trisubstituted benzo[*b*]furan 14{*24*}

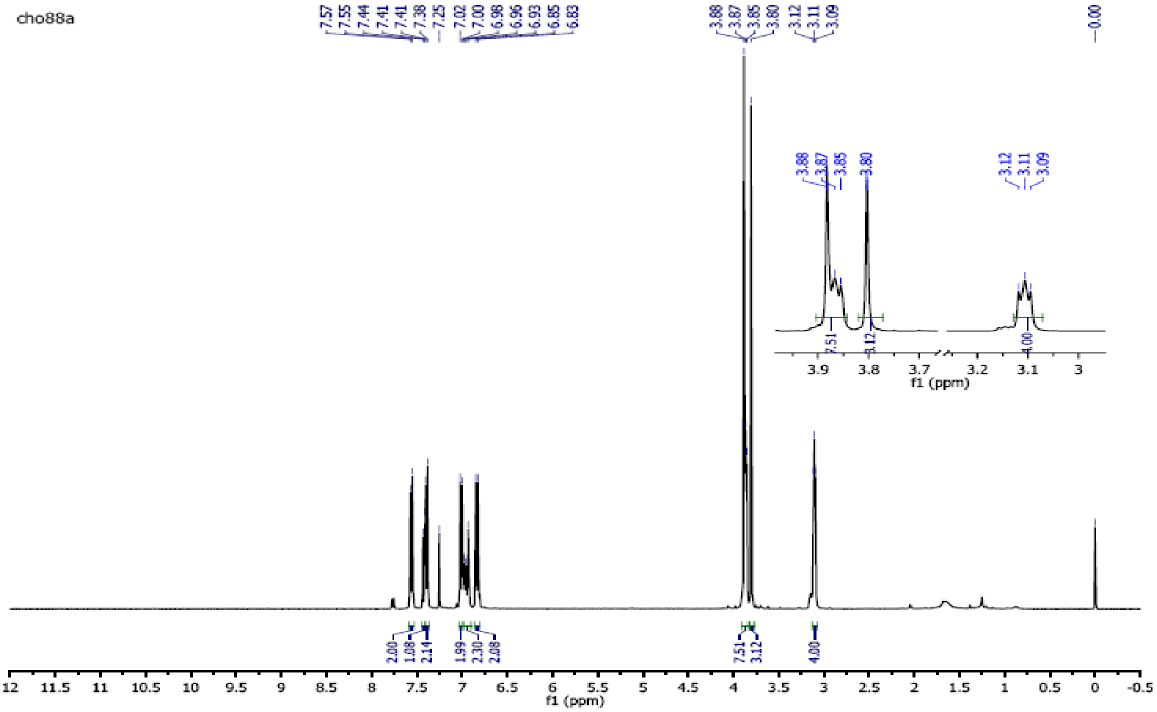


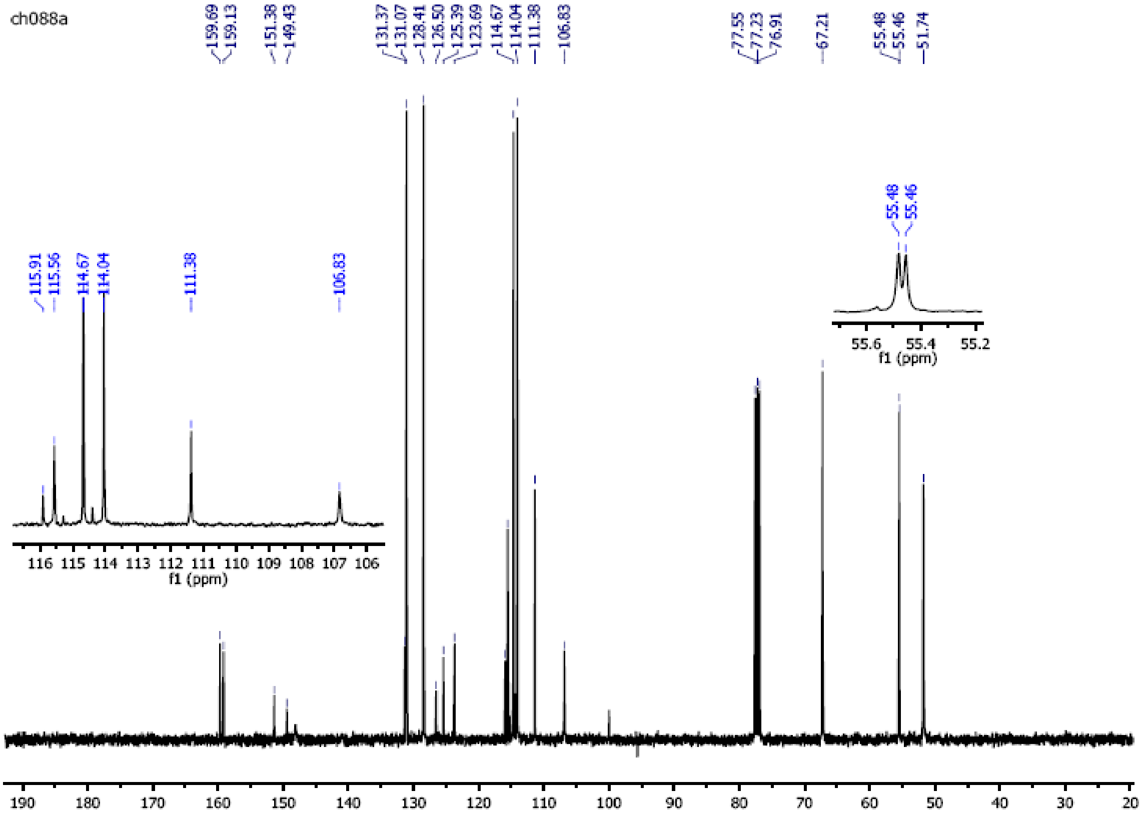




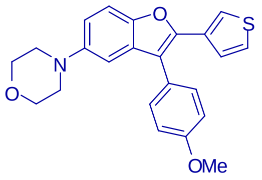
2,3,5-Trisubstituted benzo[*b*]furan 14{*25*}

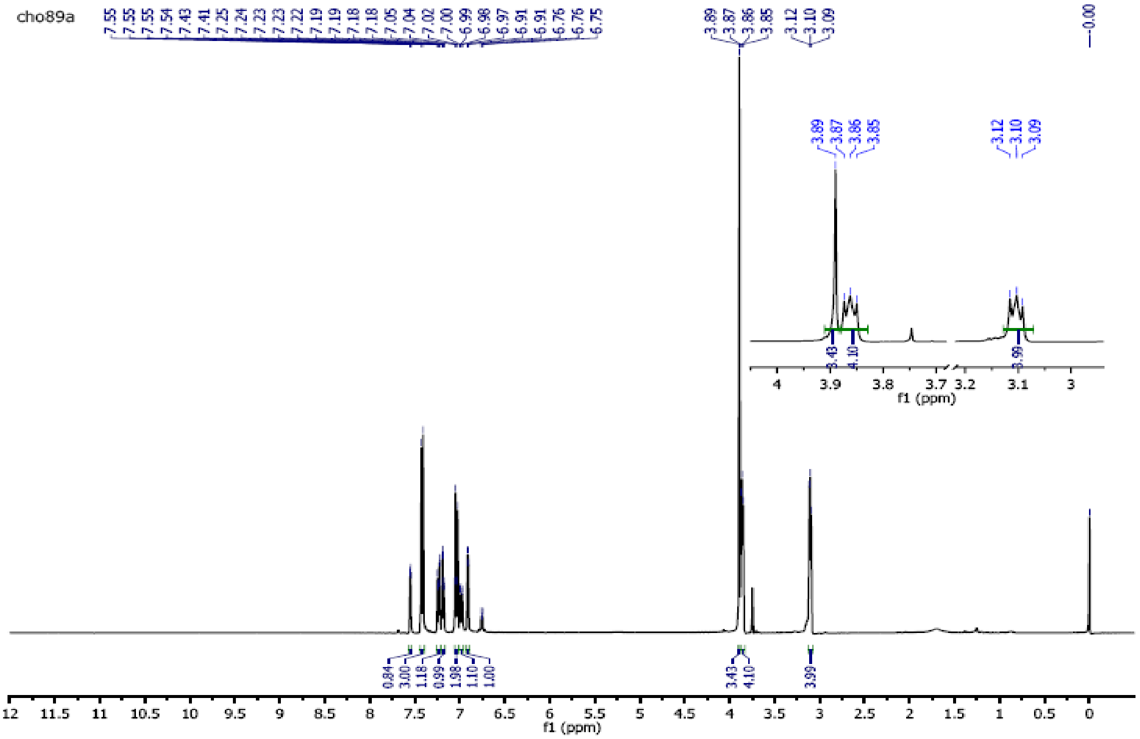


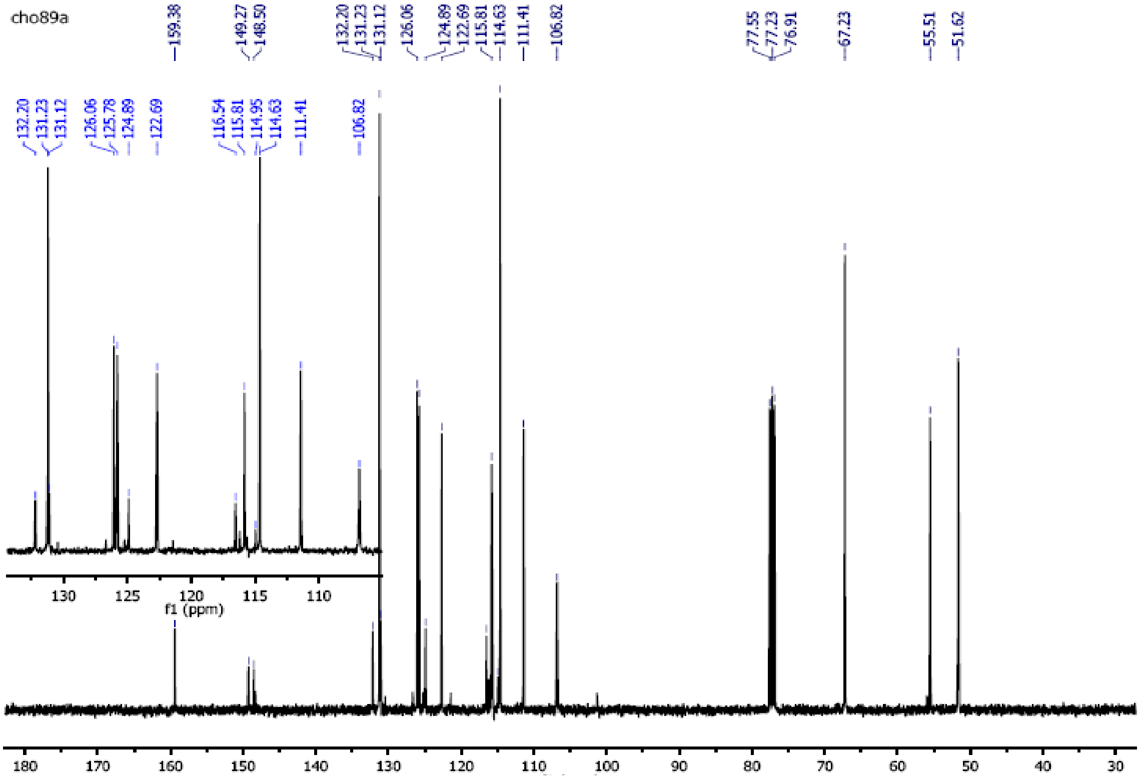




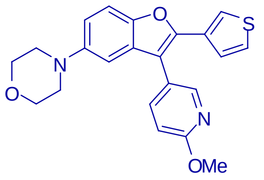
2,3,5-Trisubstituted benzo[*b*]furan 14{*27*}

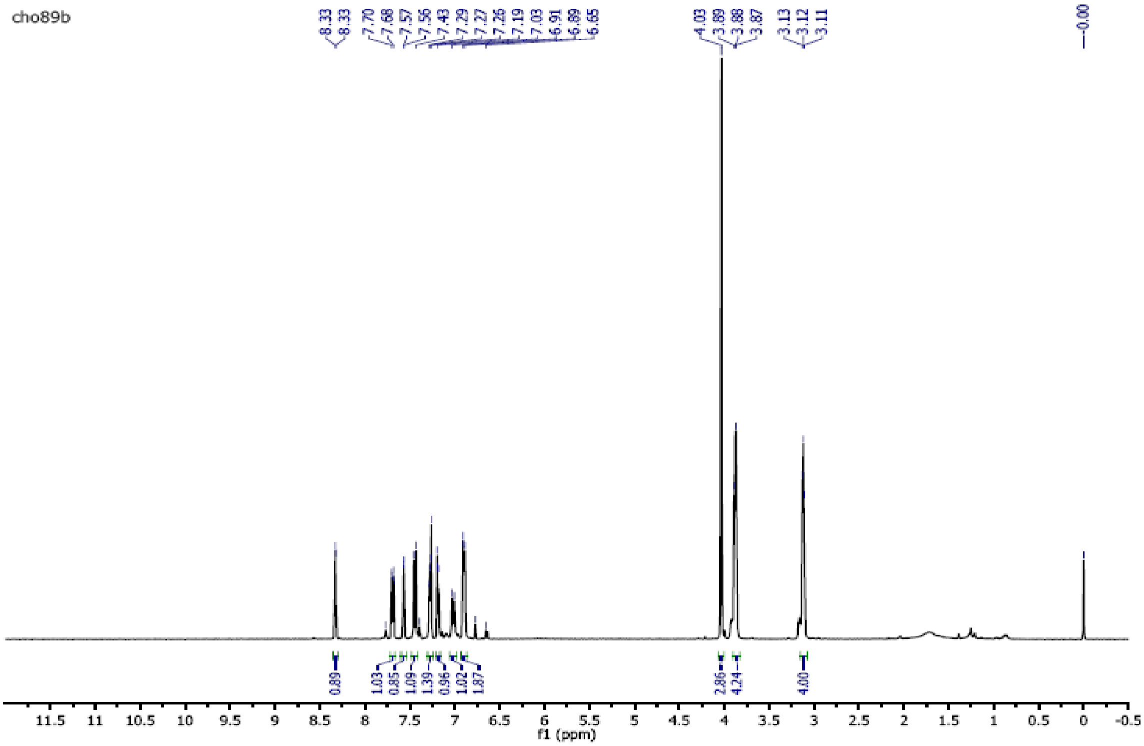


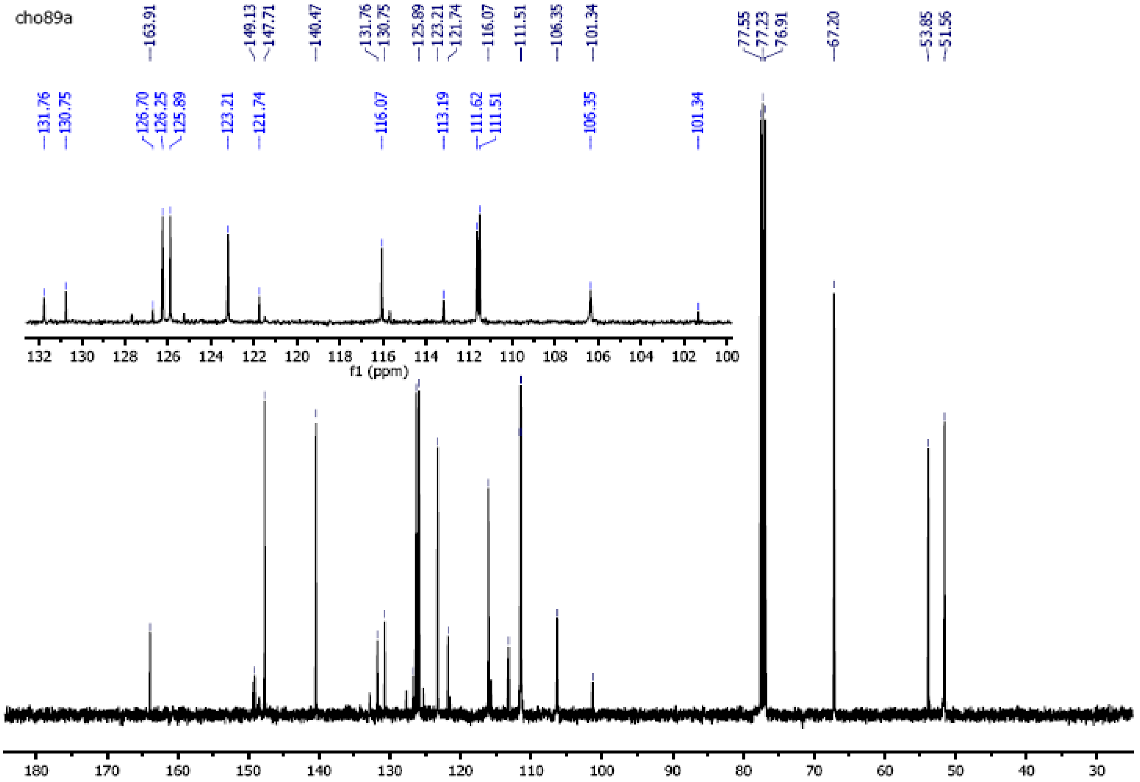




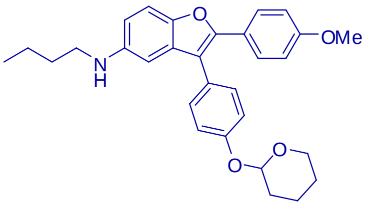
2,3,5-Trisubstituted benzo[*b*]furan 14{*28*}

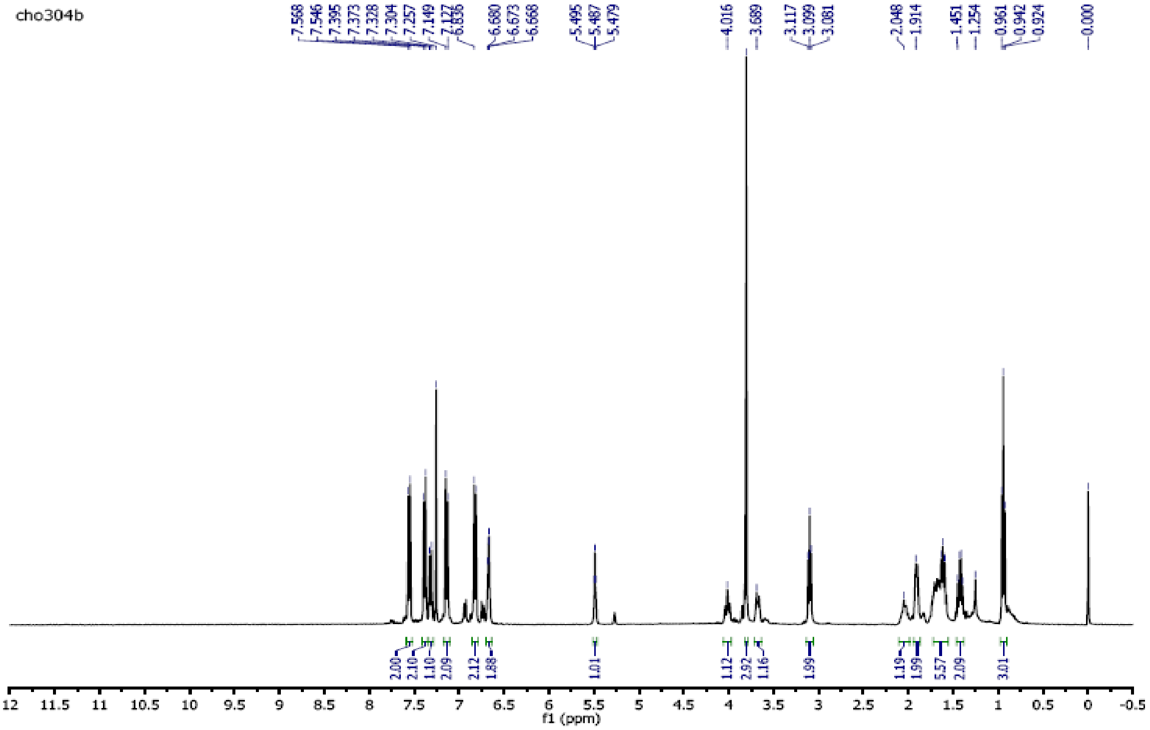


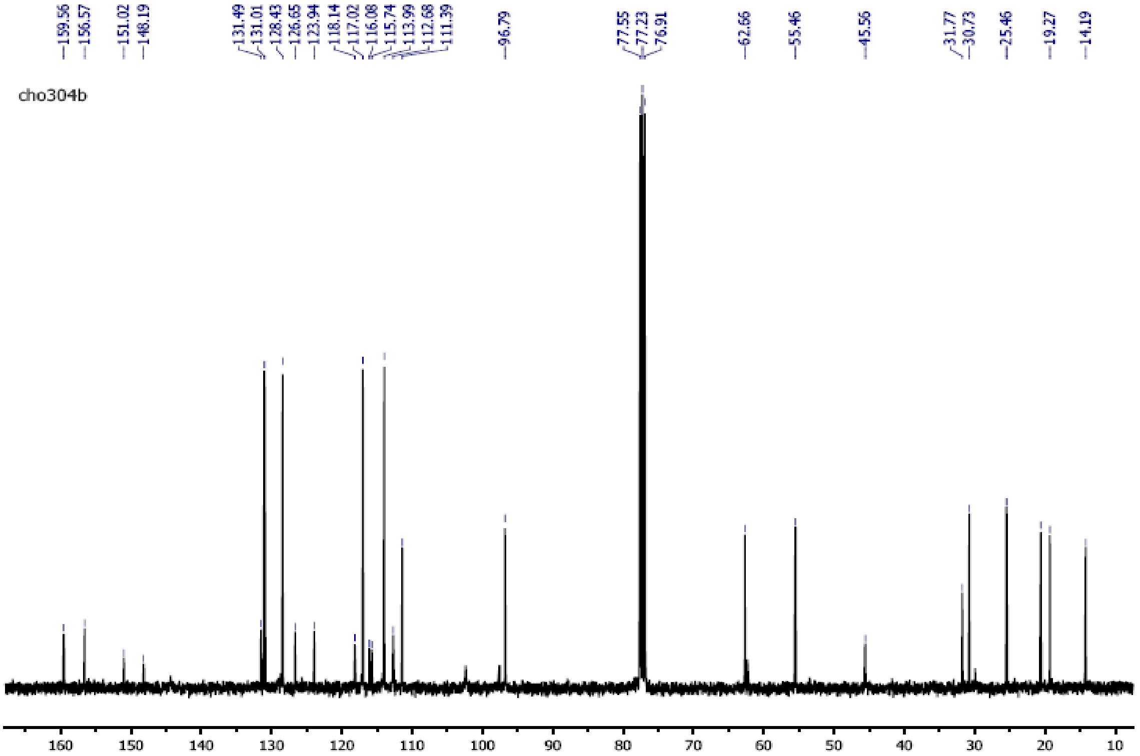




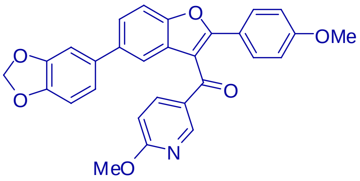
2,3,5-Trisubstituted benzo[*b*]furan 14{*31*}

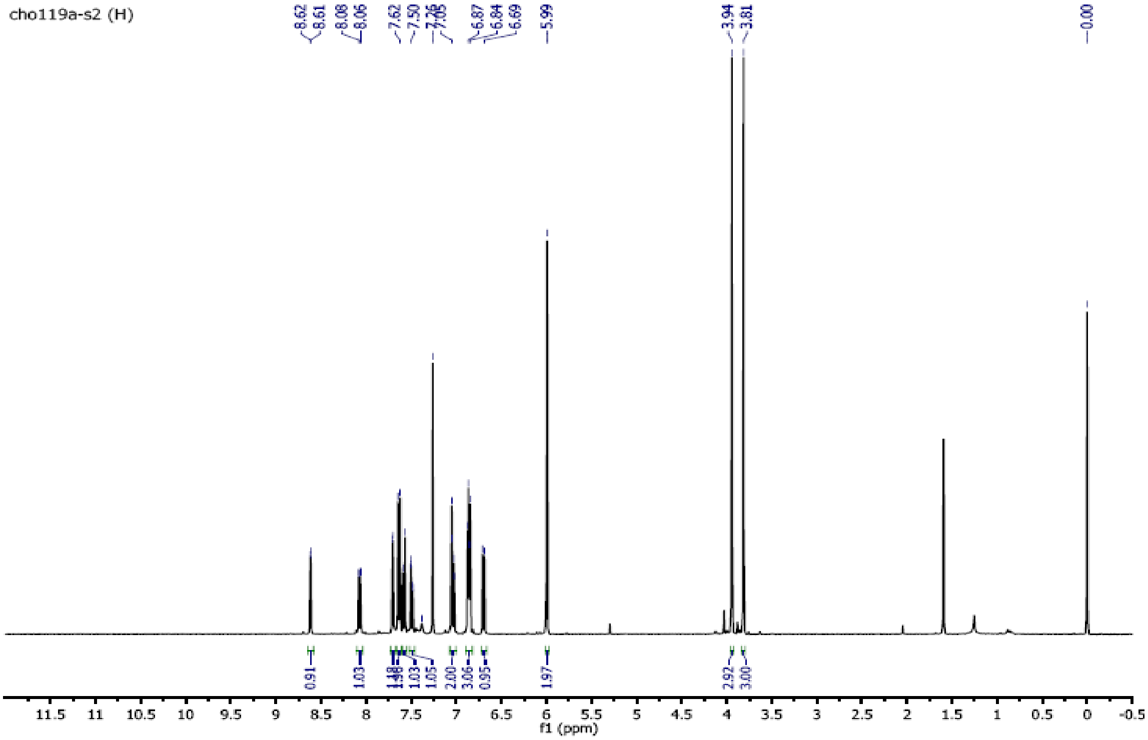


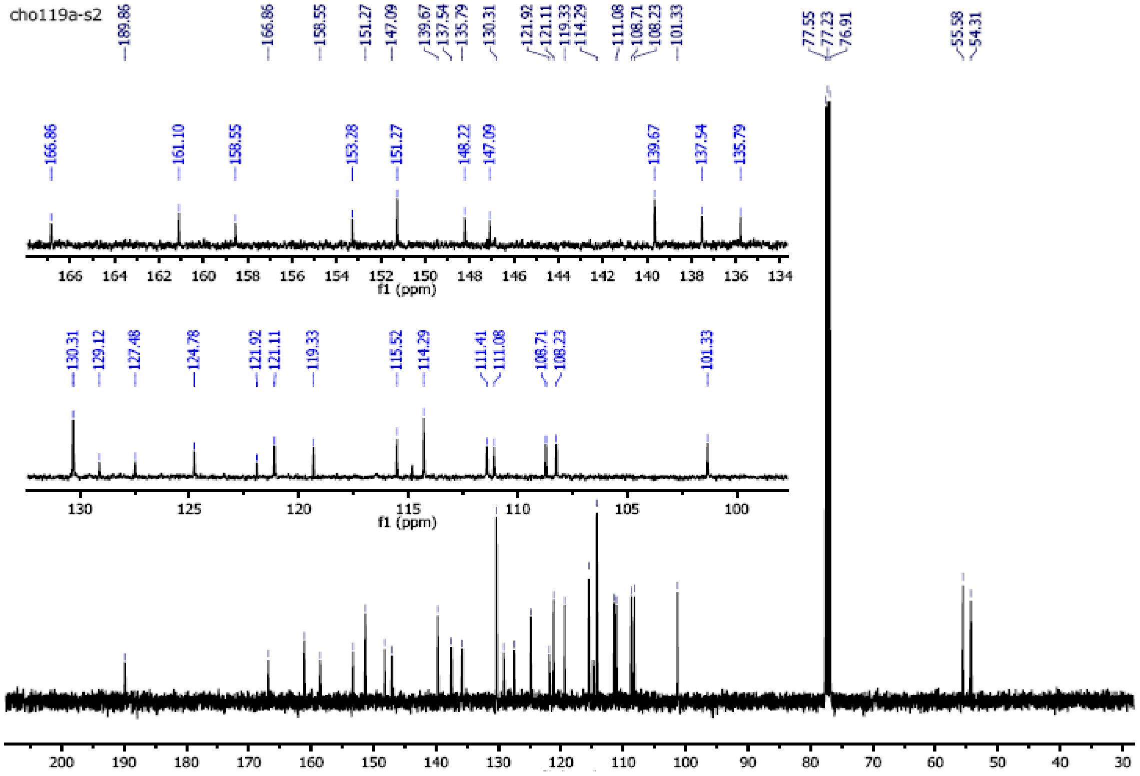




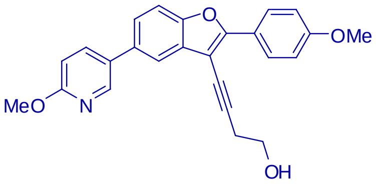
2,3,5-Trisubstituted benzo[*b*]furan 14{*34*}

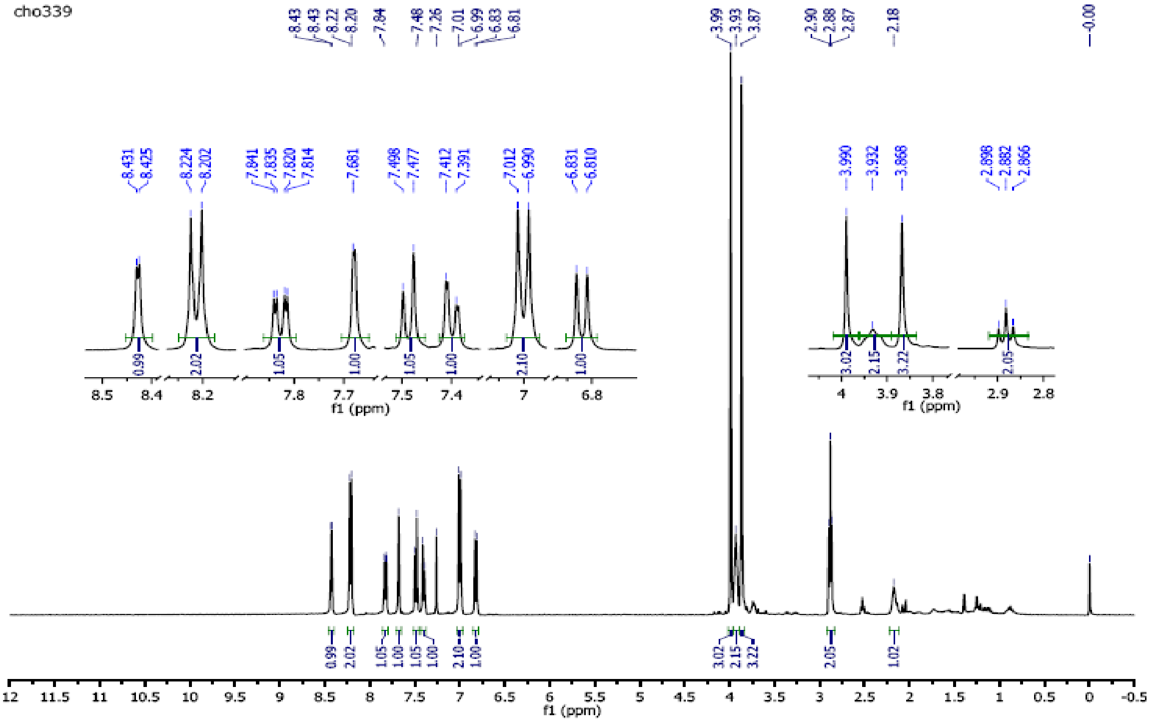


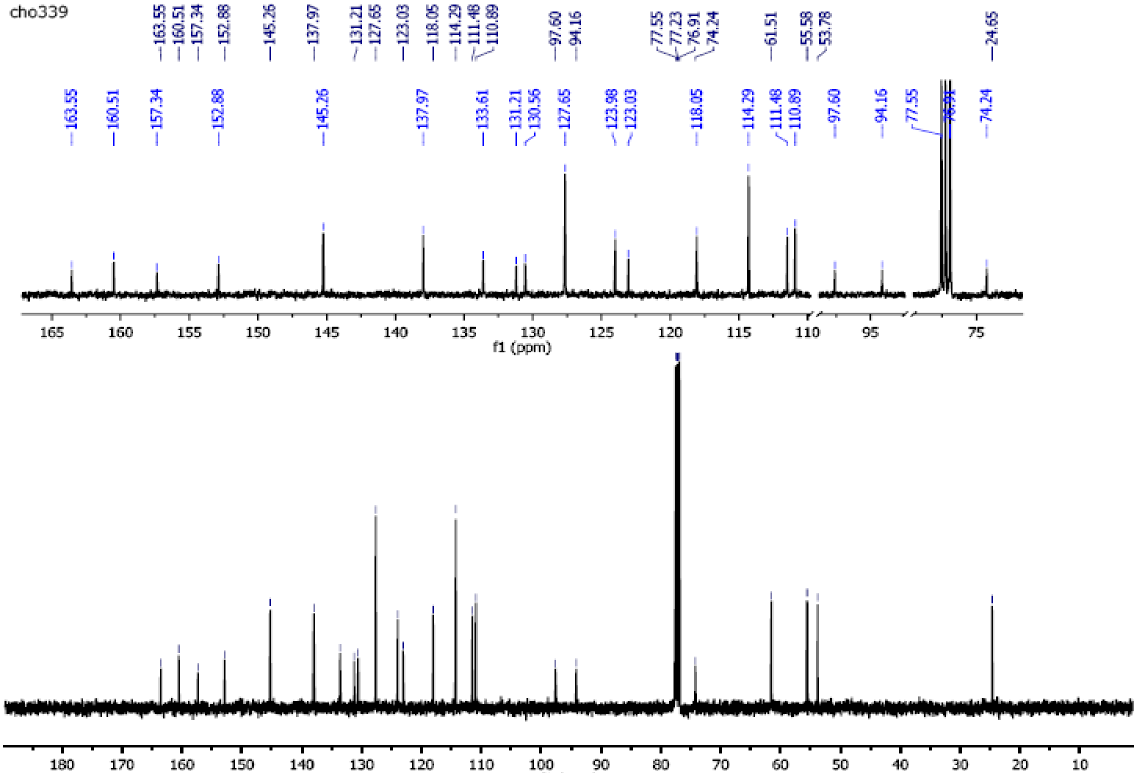




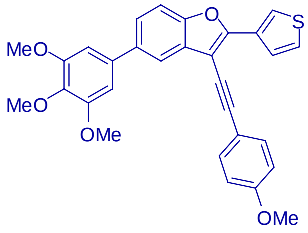
2,3,5-Trisubstituted benzo[*b*]furan 14{*62*}

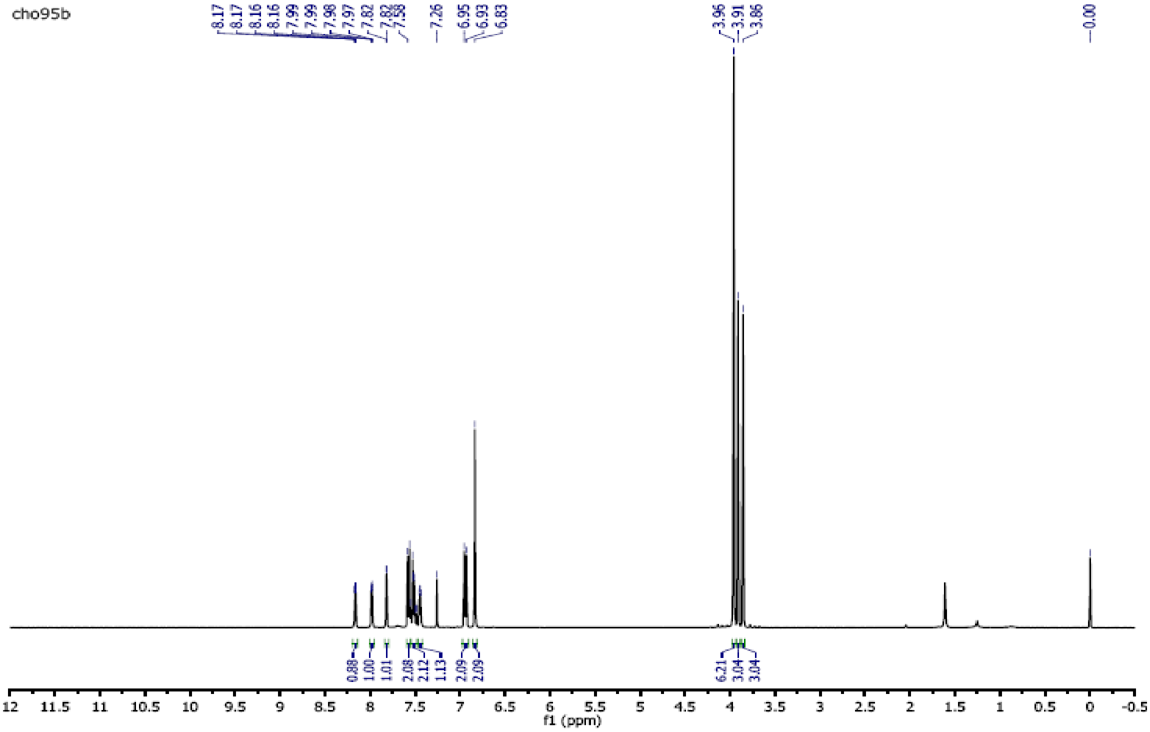


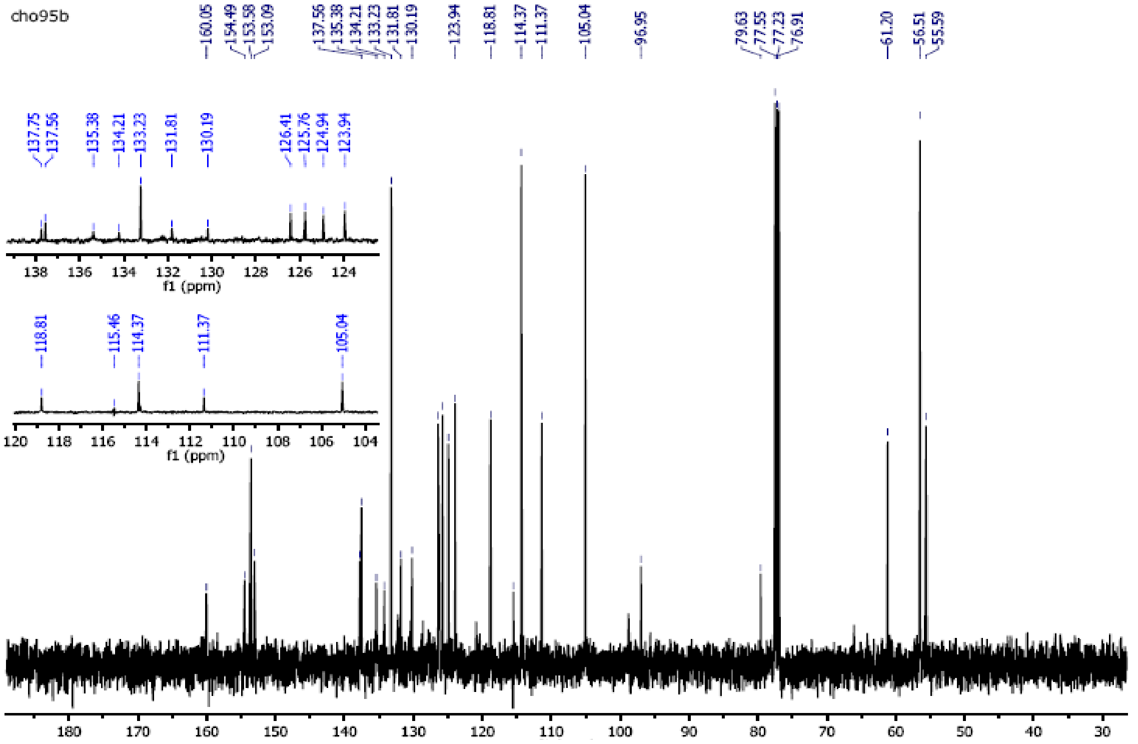




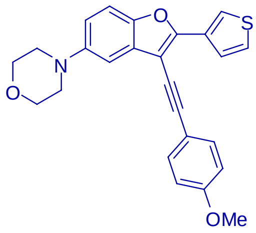
2,3,5-Trisubstituted benzo[*b*]furan 14{*67*}

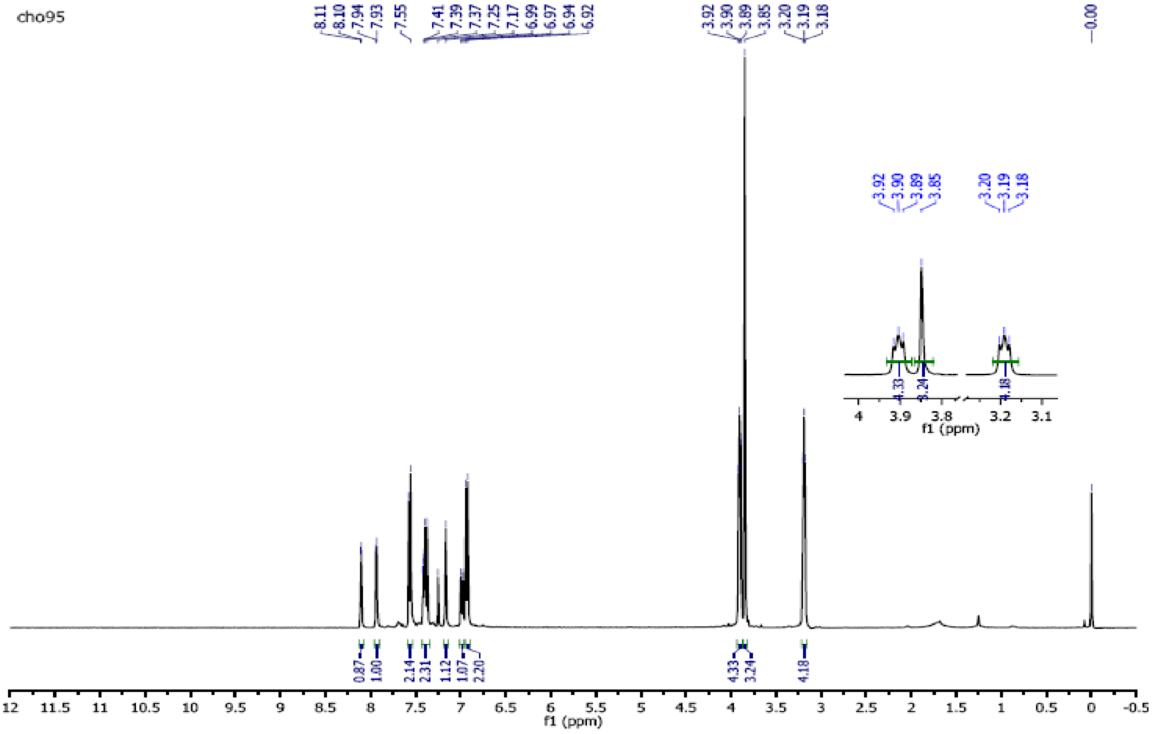


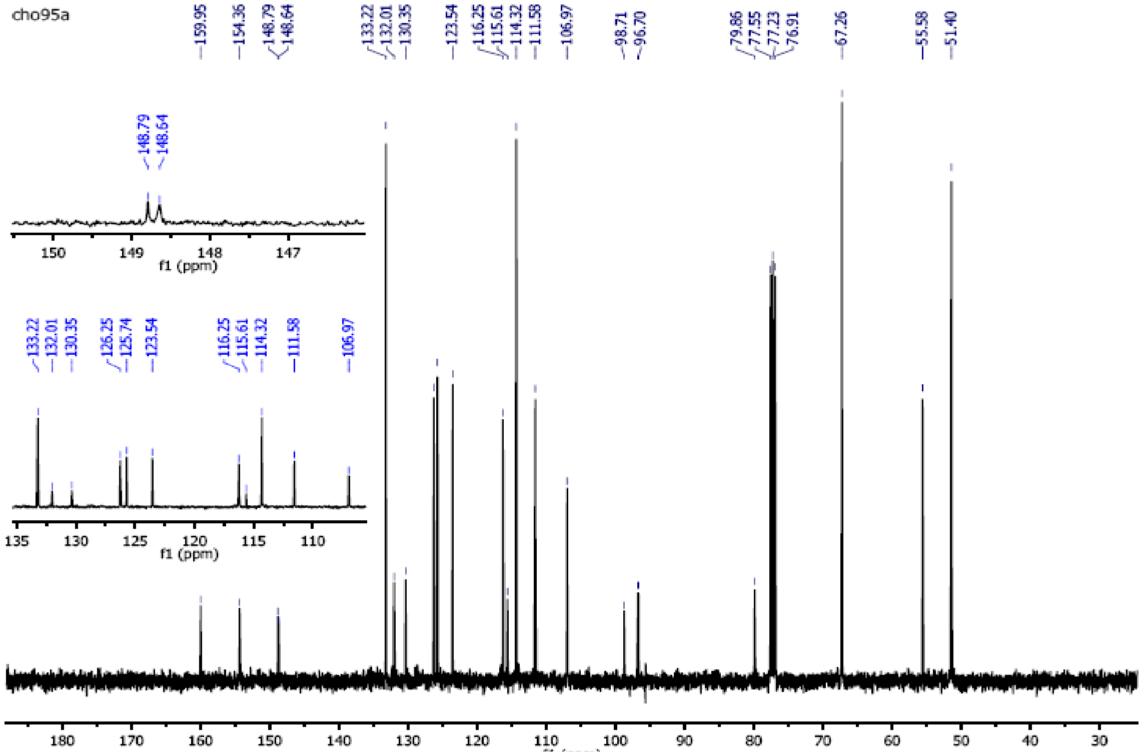




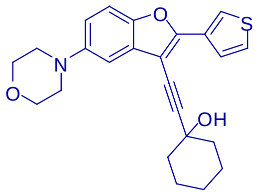
2,3,5-Trisubstituted benzo[*b*]furan 14{*75*}

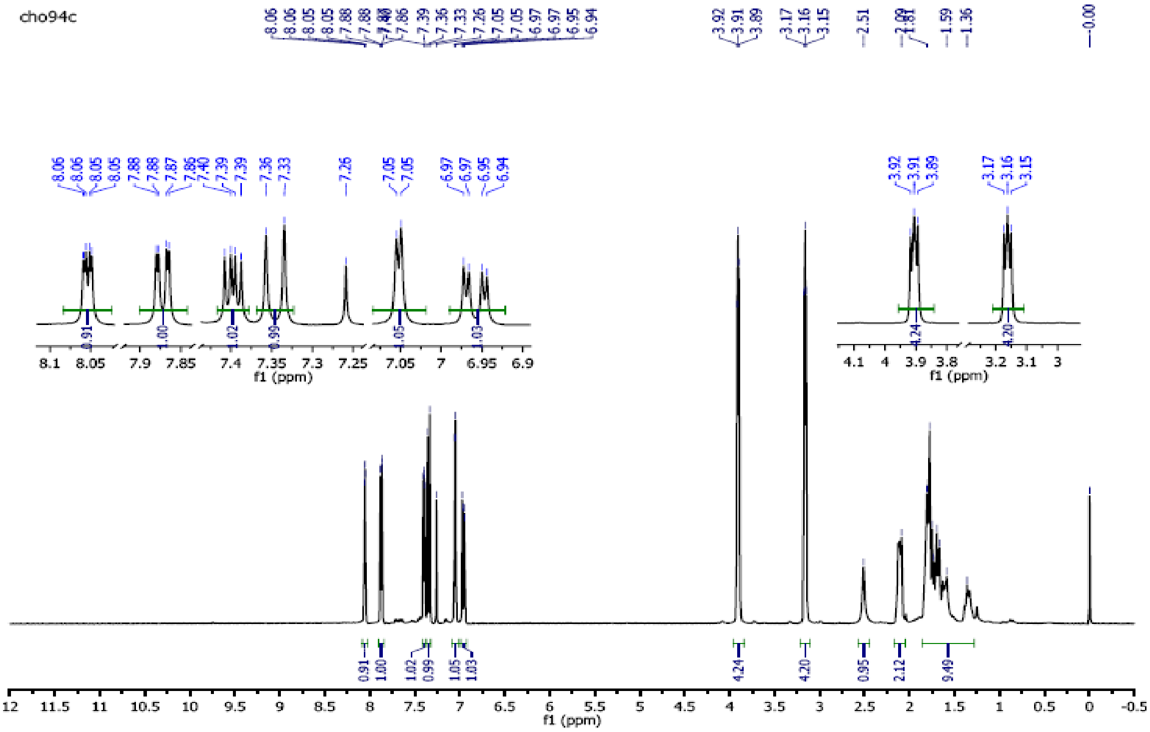


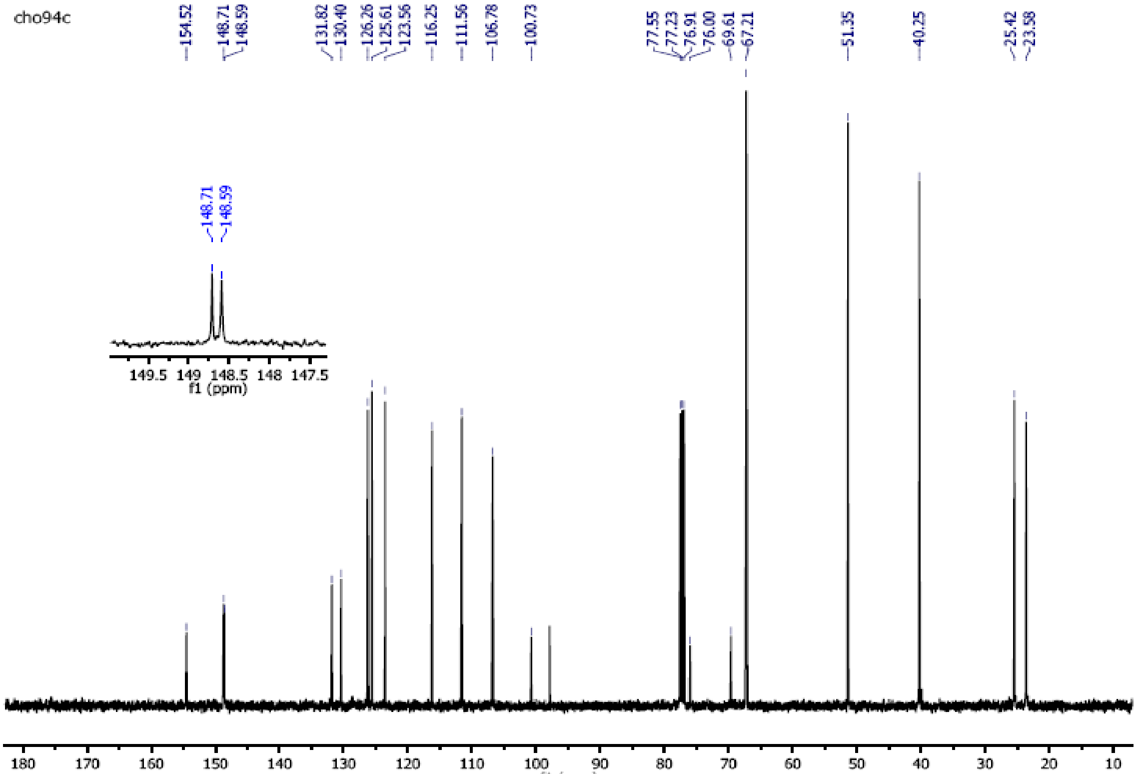




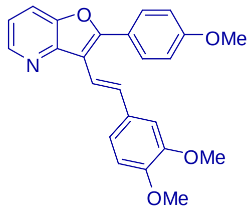
2,3,5-Trisubstituted benzo[*b*]furan 14{*77*}

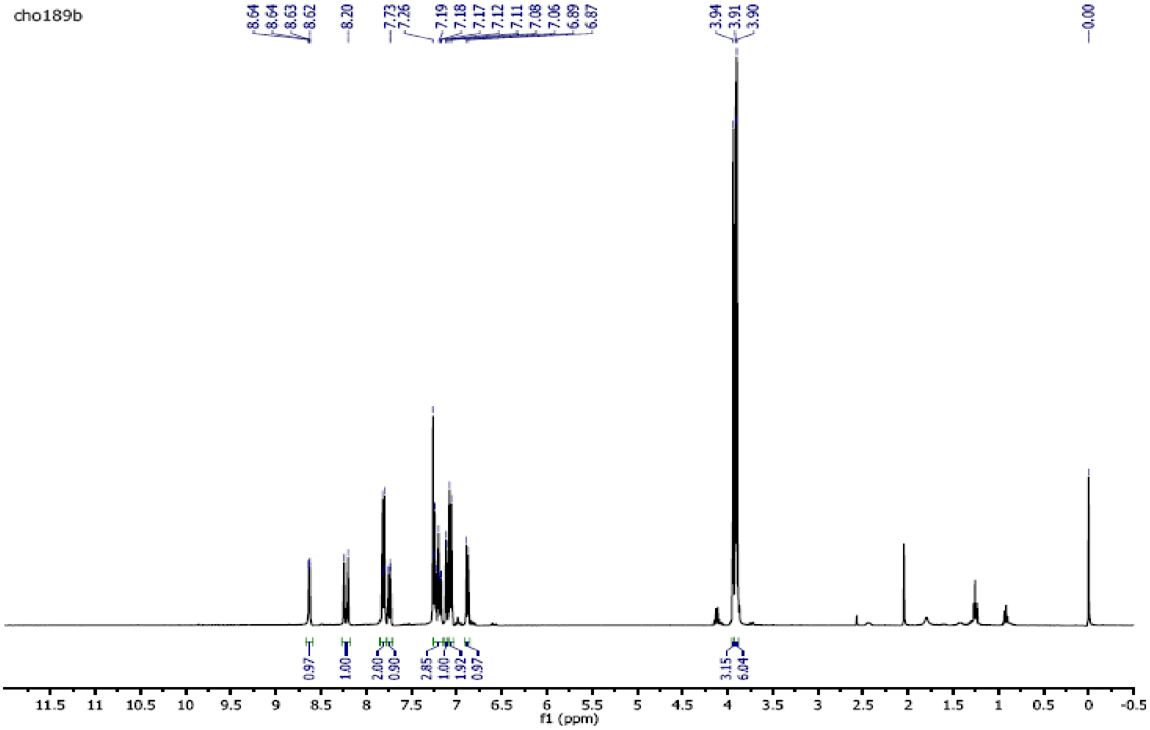


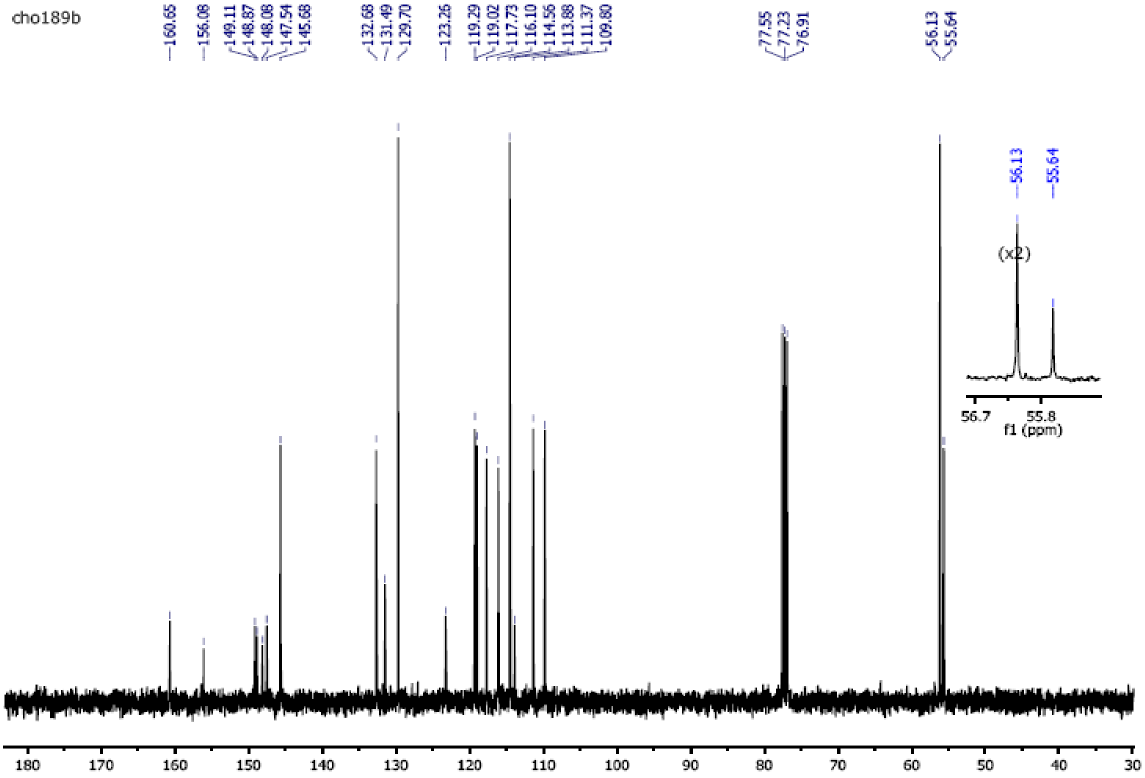




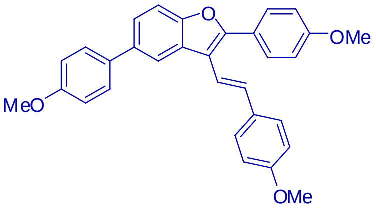
2,3-Disubstituted furo[*b*]pyridine 14{*81*}

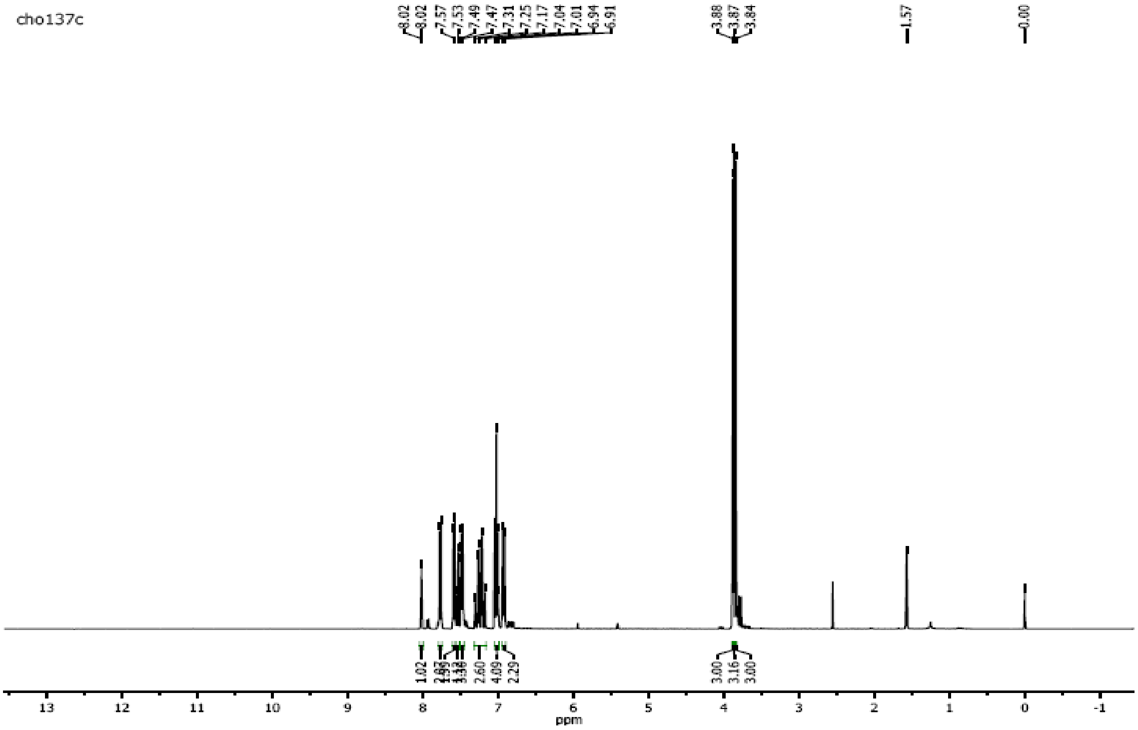


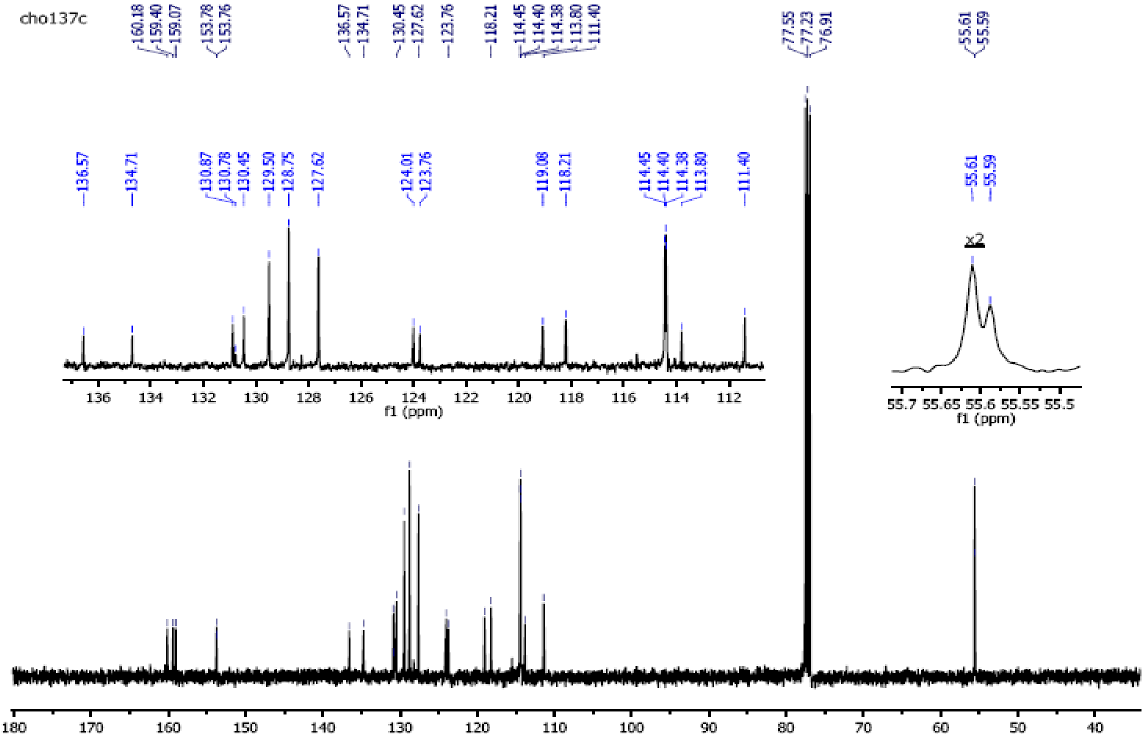




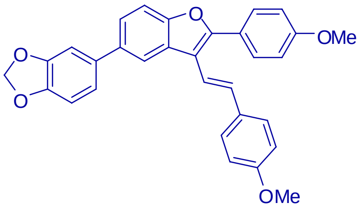
2,3,5-Trisubstituted benzo[*b*]furan 14{*83*}

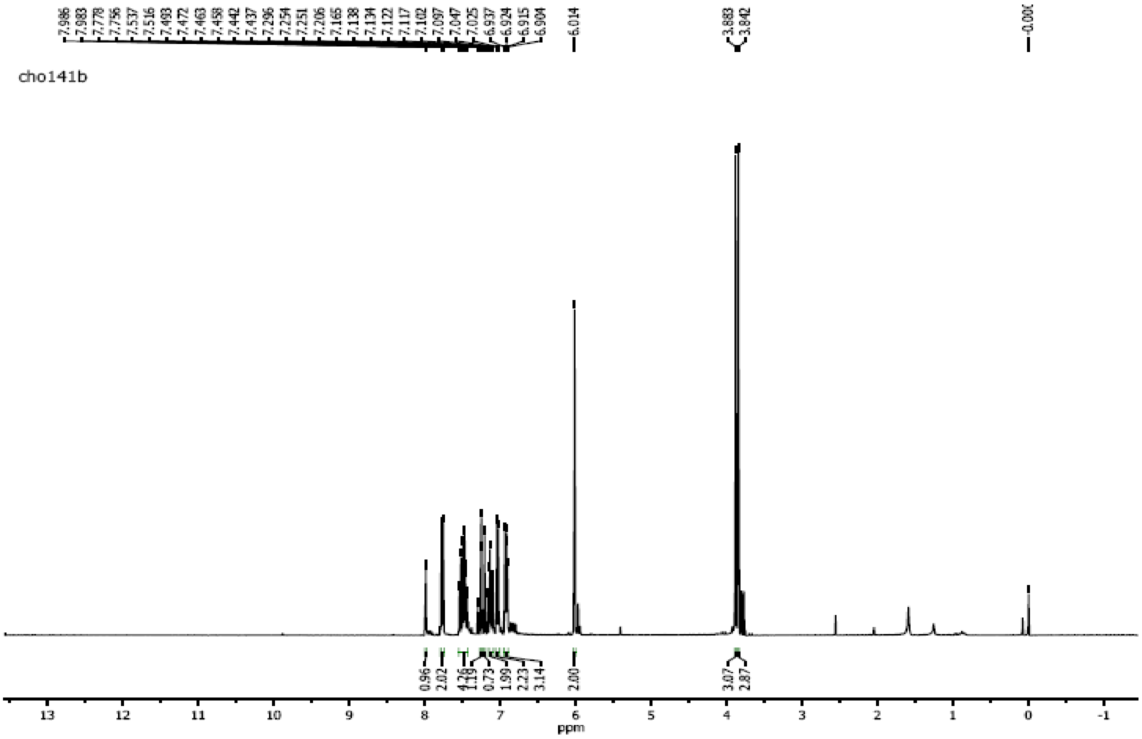


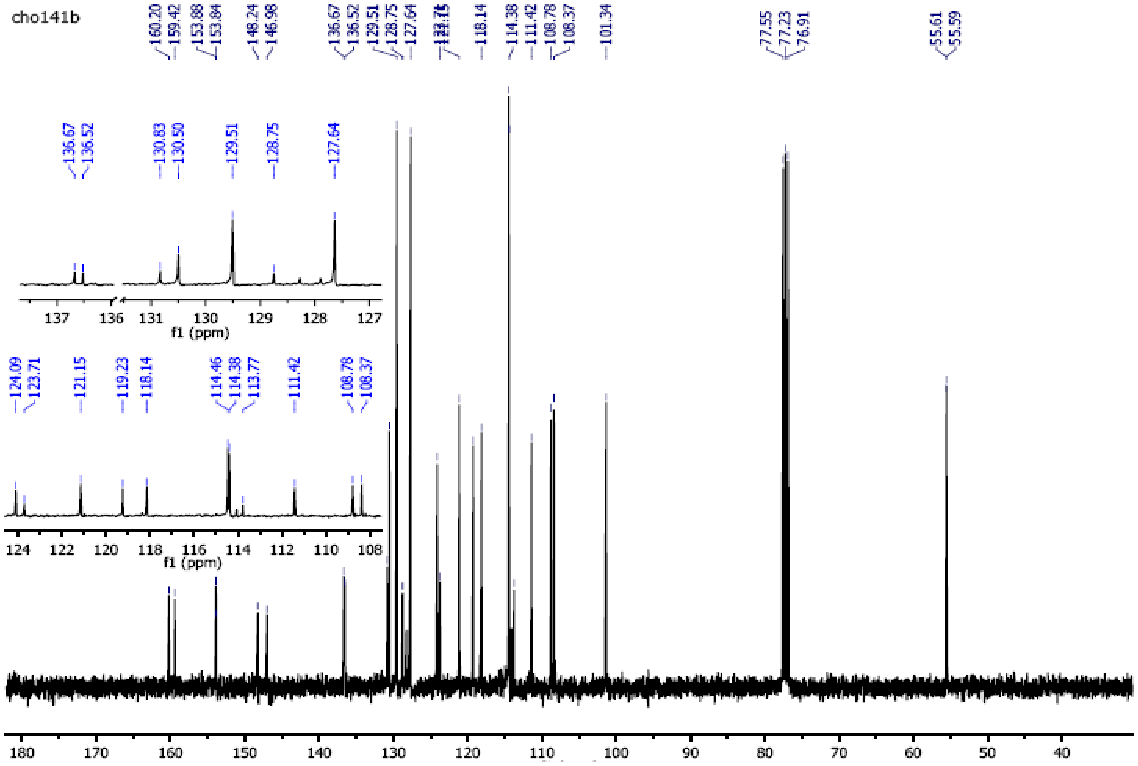




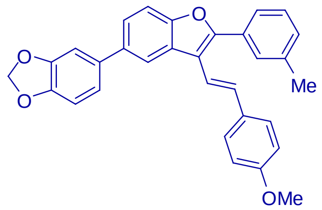
2,3,5-Trisubstituted benzo[*b*]furan 14{*85*}

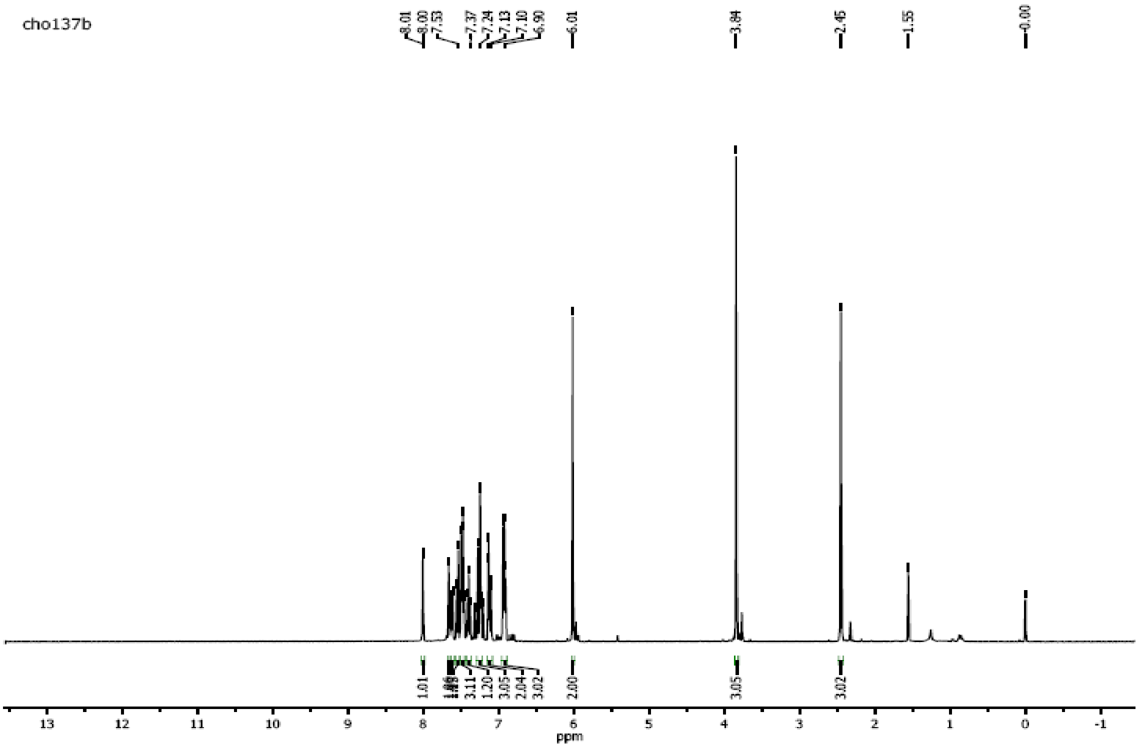


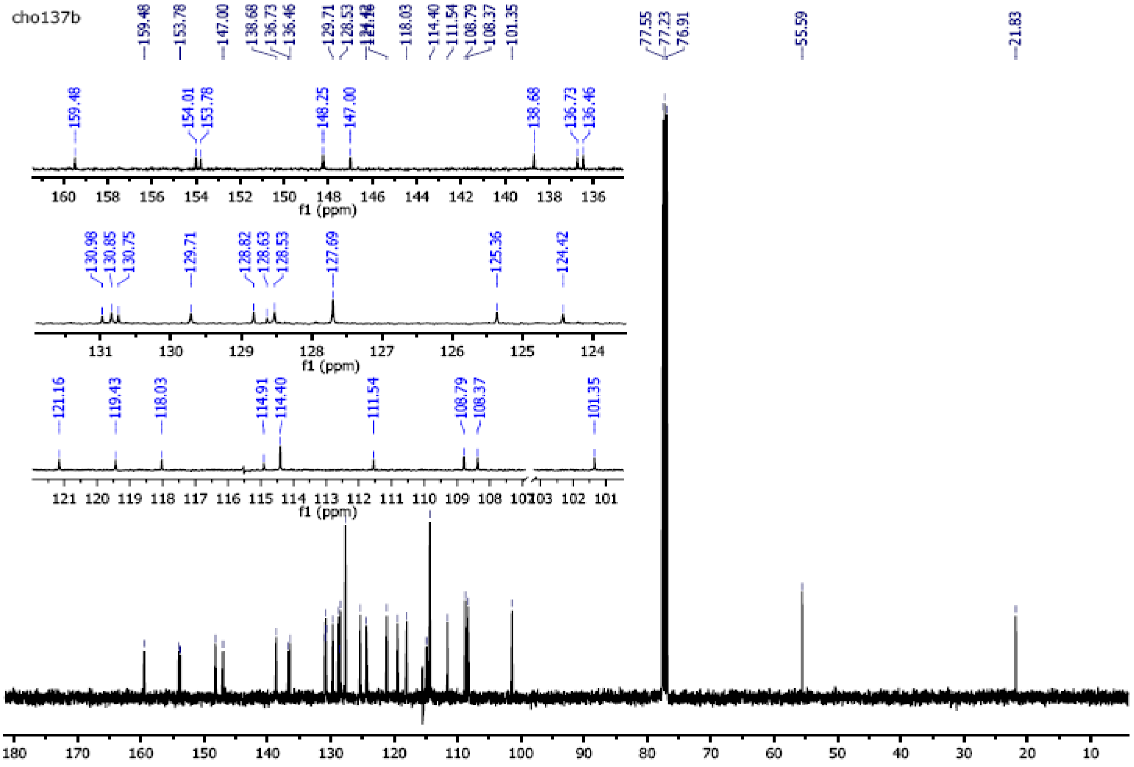




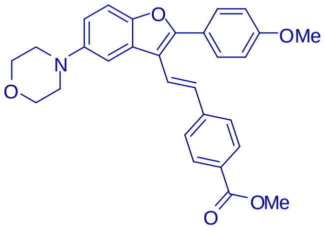
2,3,5-Trisubstituted benzo[*b*]furan 14{*92*}

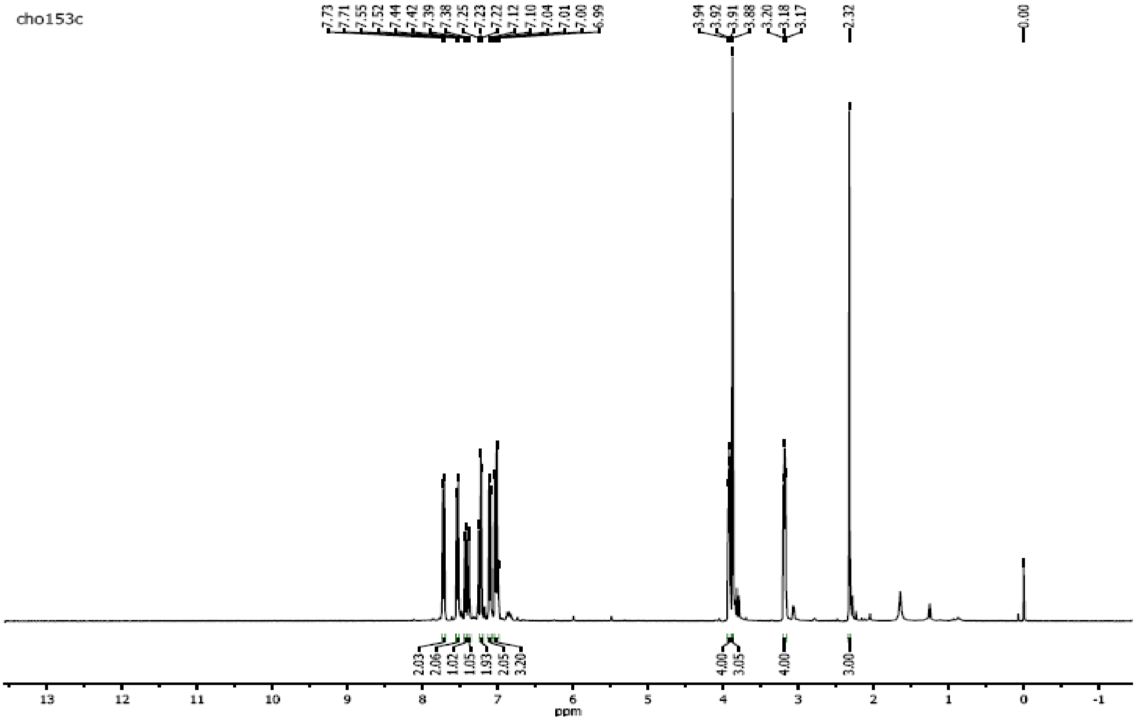


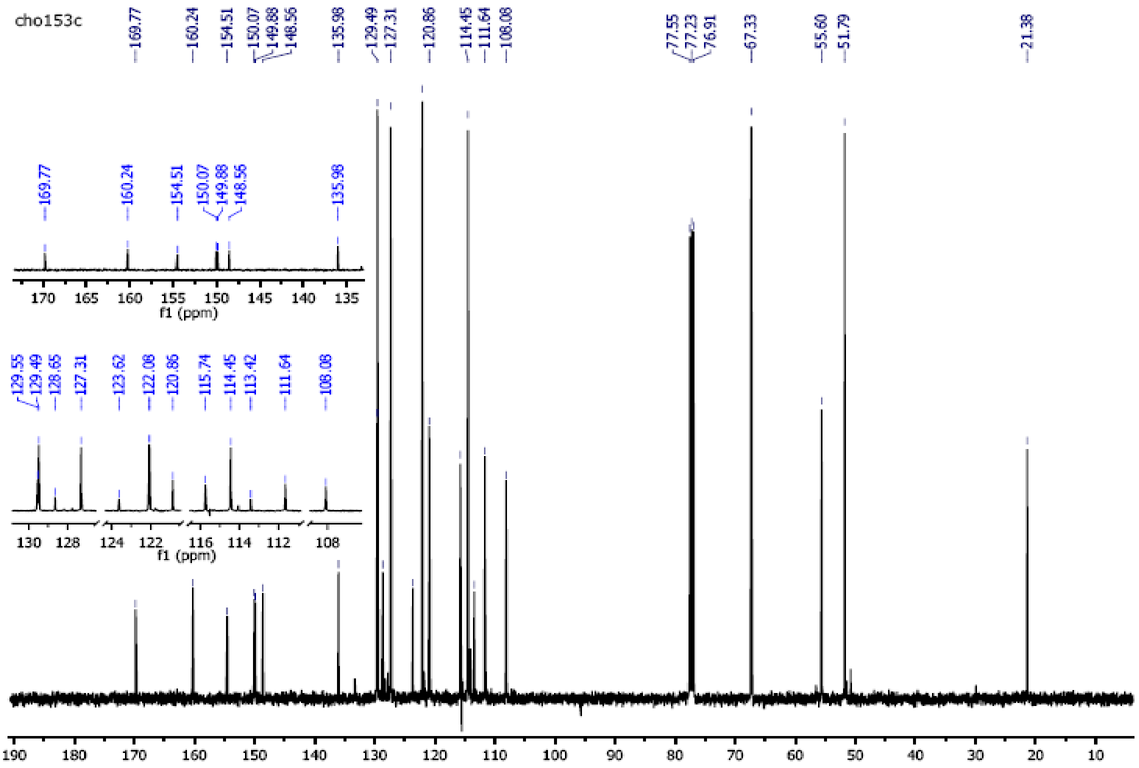




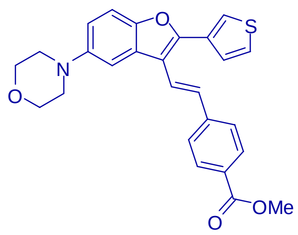
2,3,5-Trisubstituted benzo[*b*]furan 14{*95*}

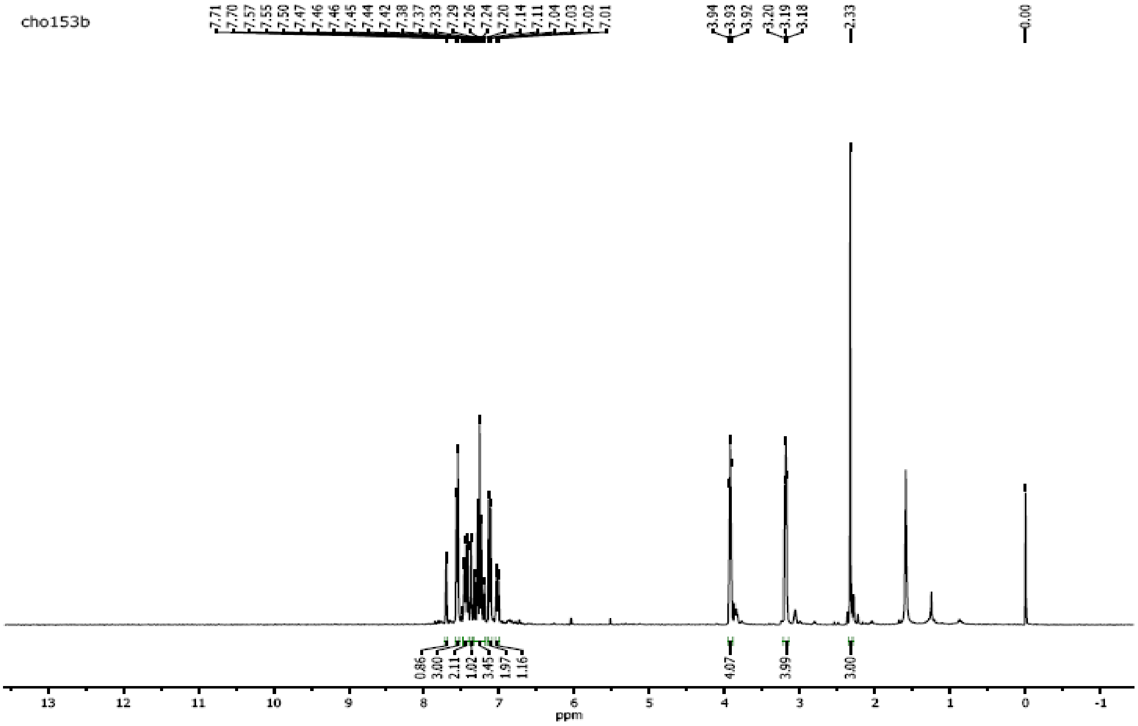


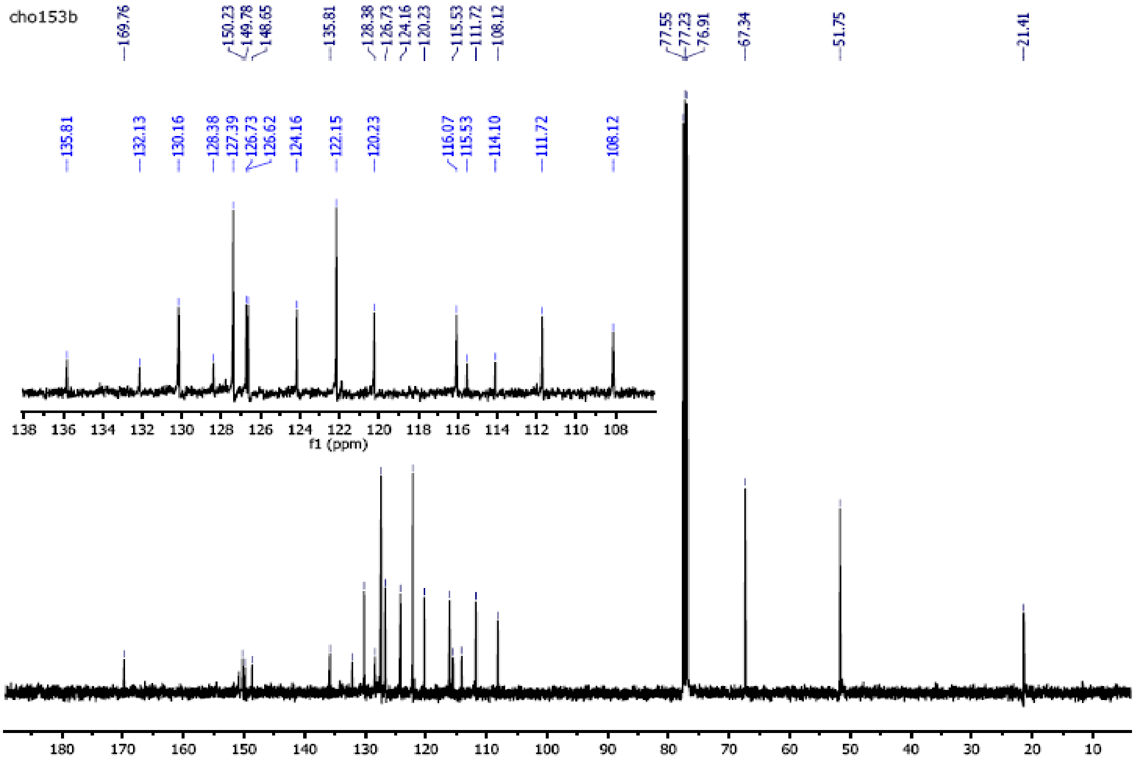




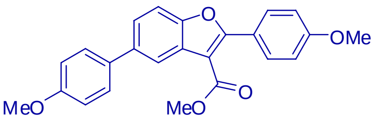
2,3,5-Trisubstituted benzo[*b*]furan 14{*97*}

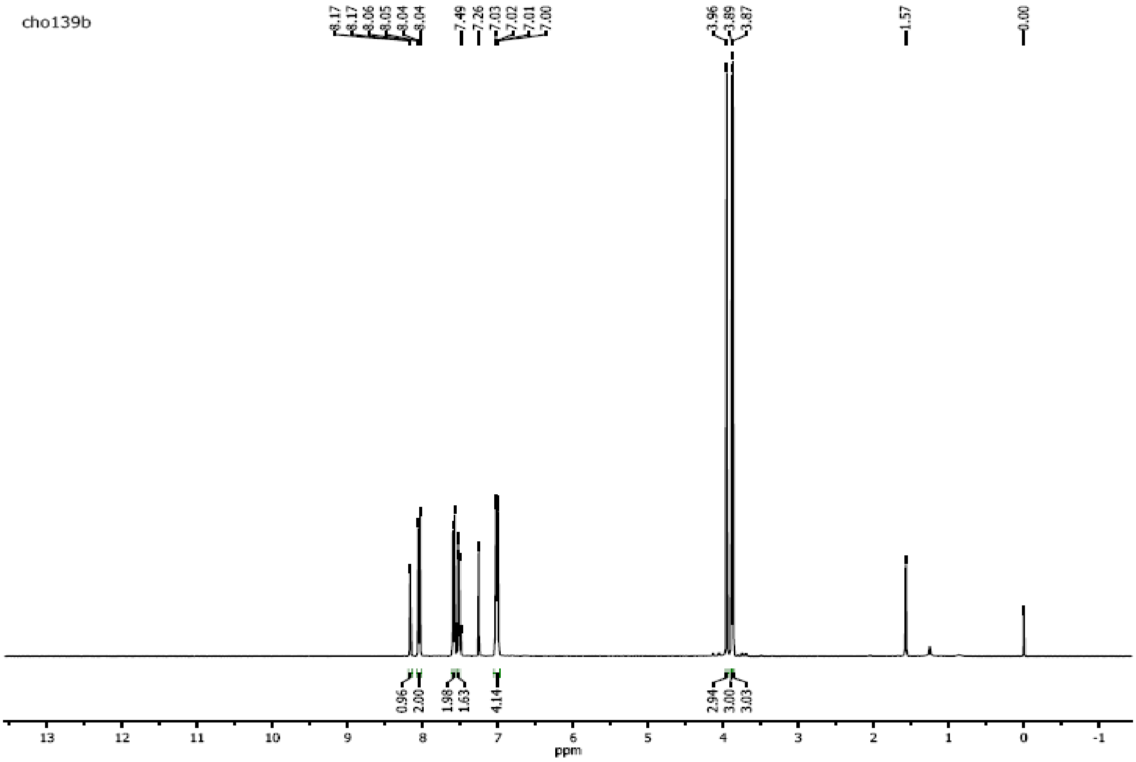


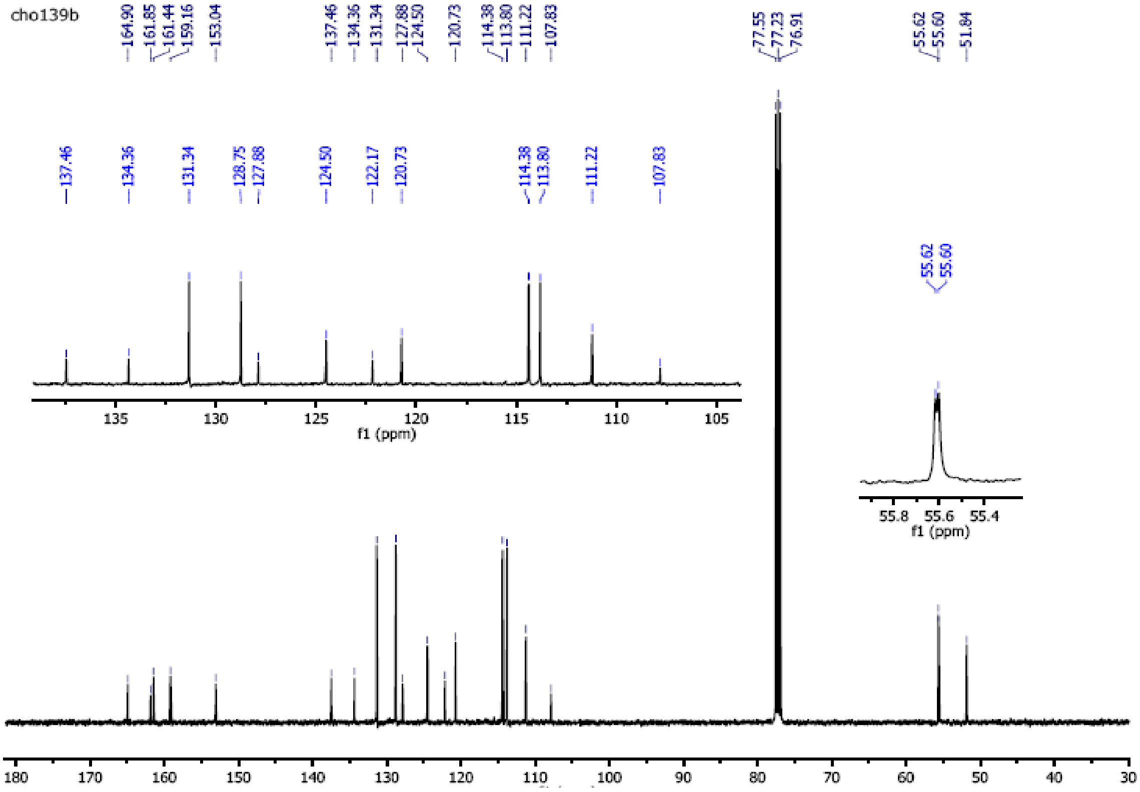




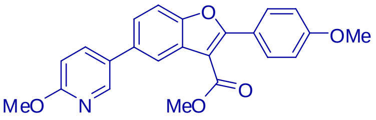
2,3,5-Trisubstituted benzo[*b*]furan 14{*106*}

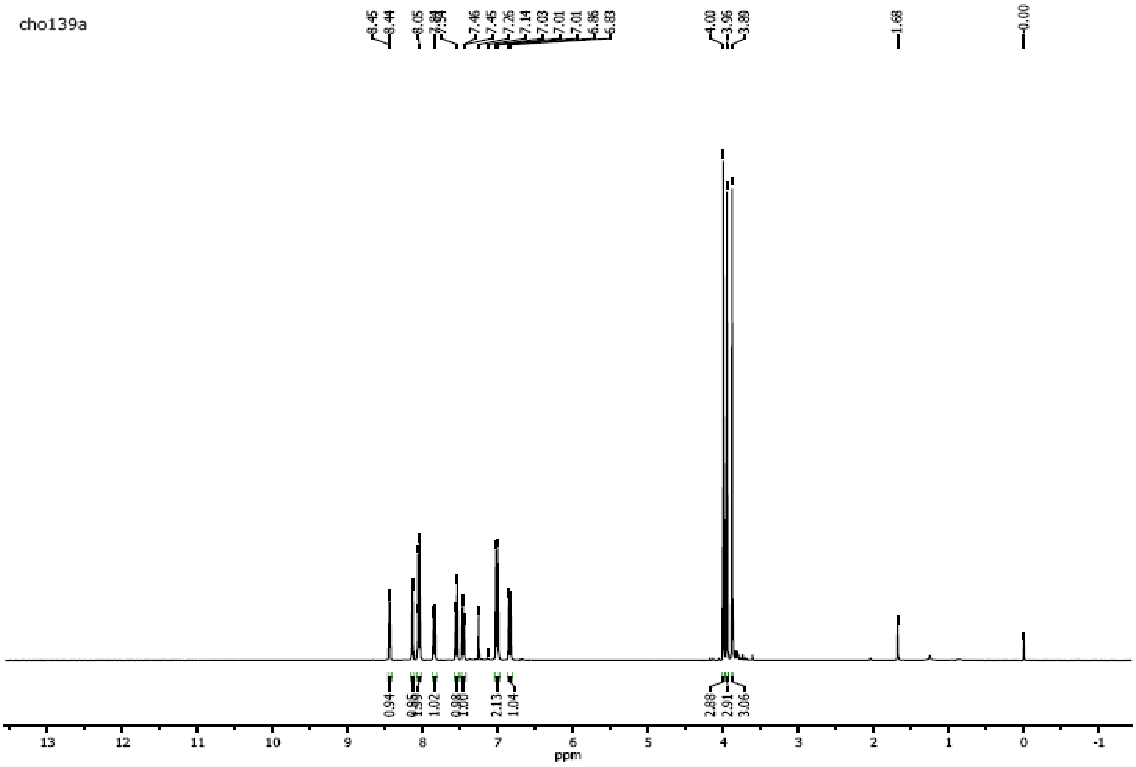


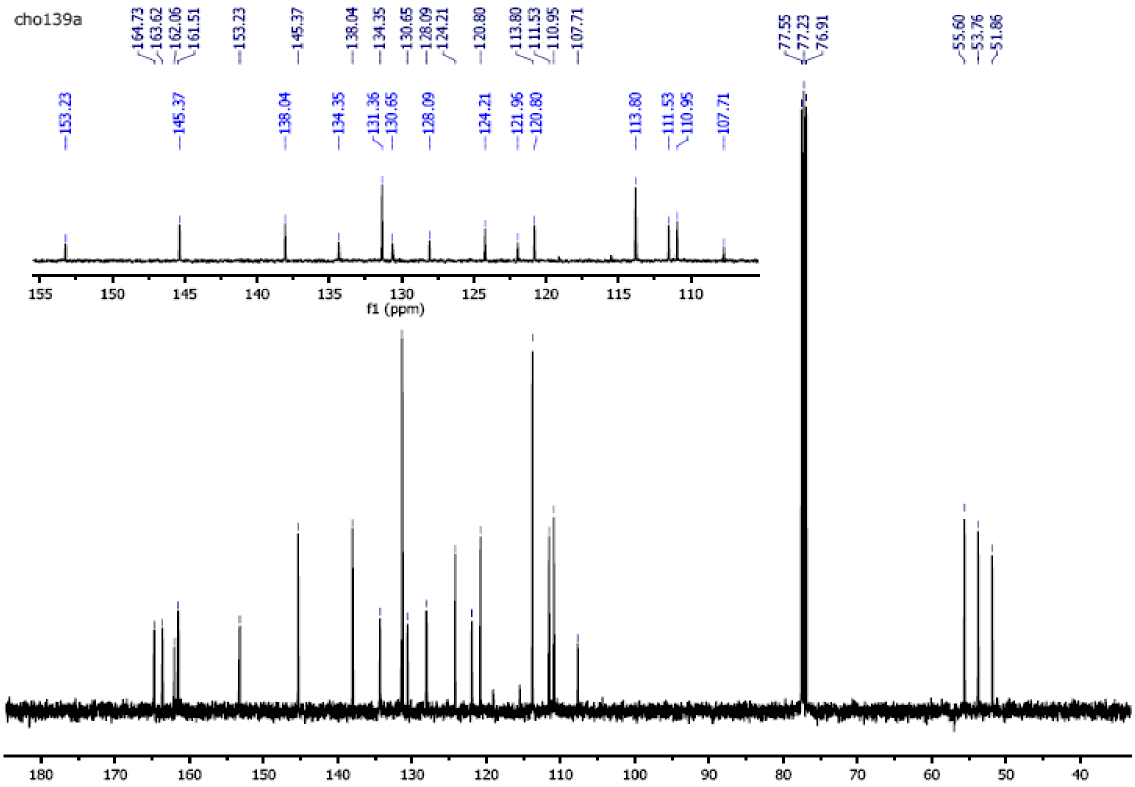




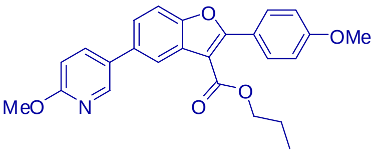
2,3,5-Trisubstituted benzo[*b*]furan 14{*109*}

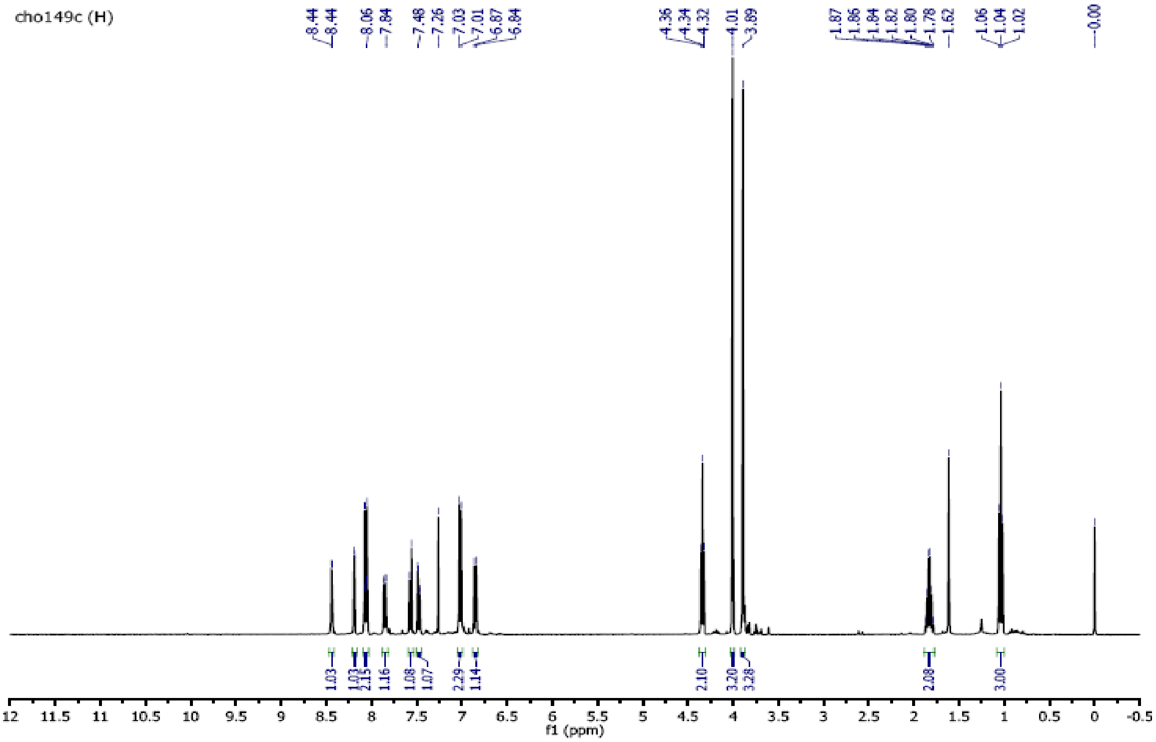


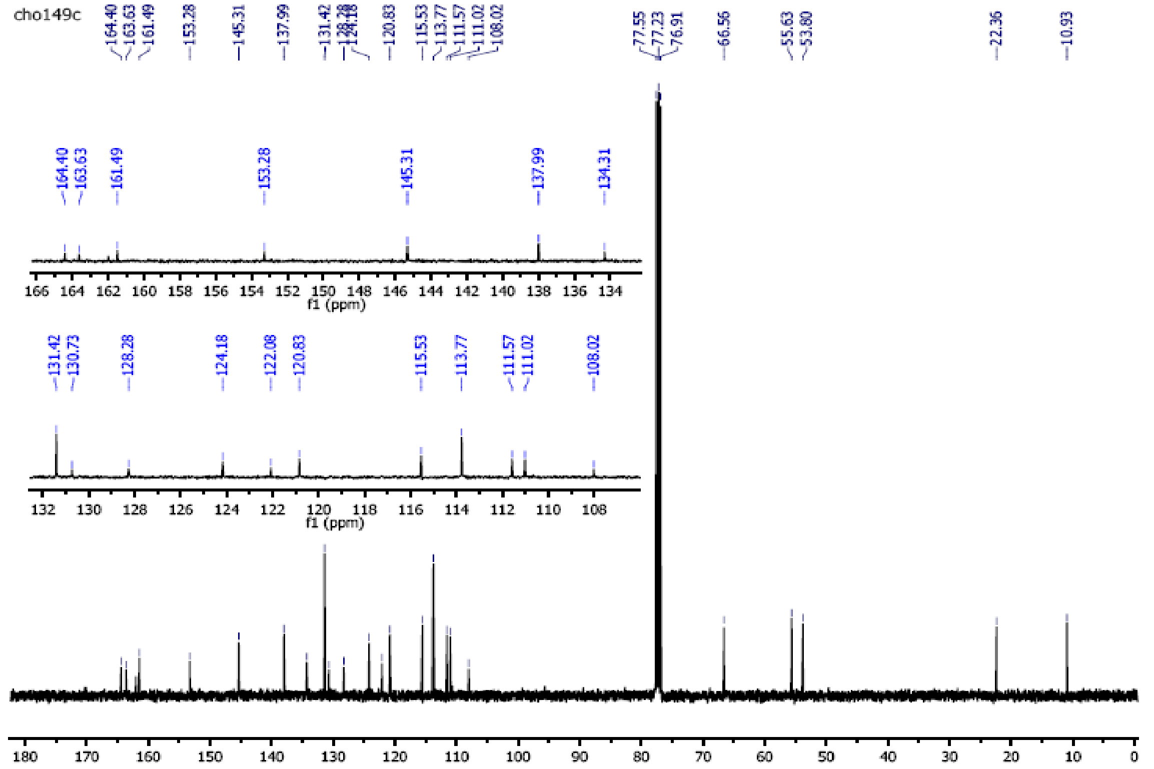




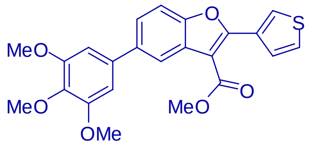
2,3,5-Trisubstituted benzo[*b*]furan 14{*110*}

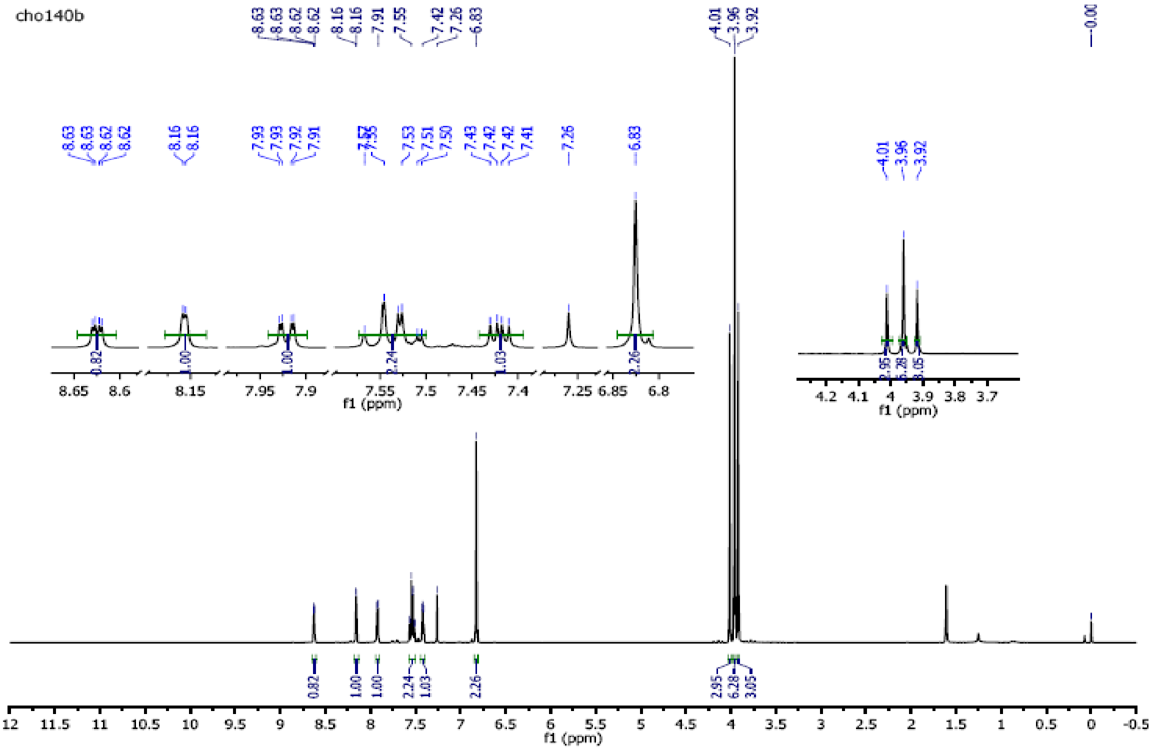


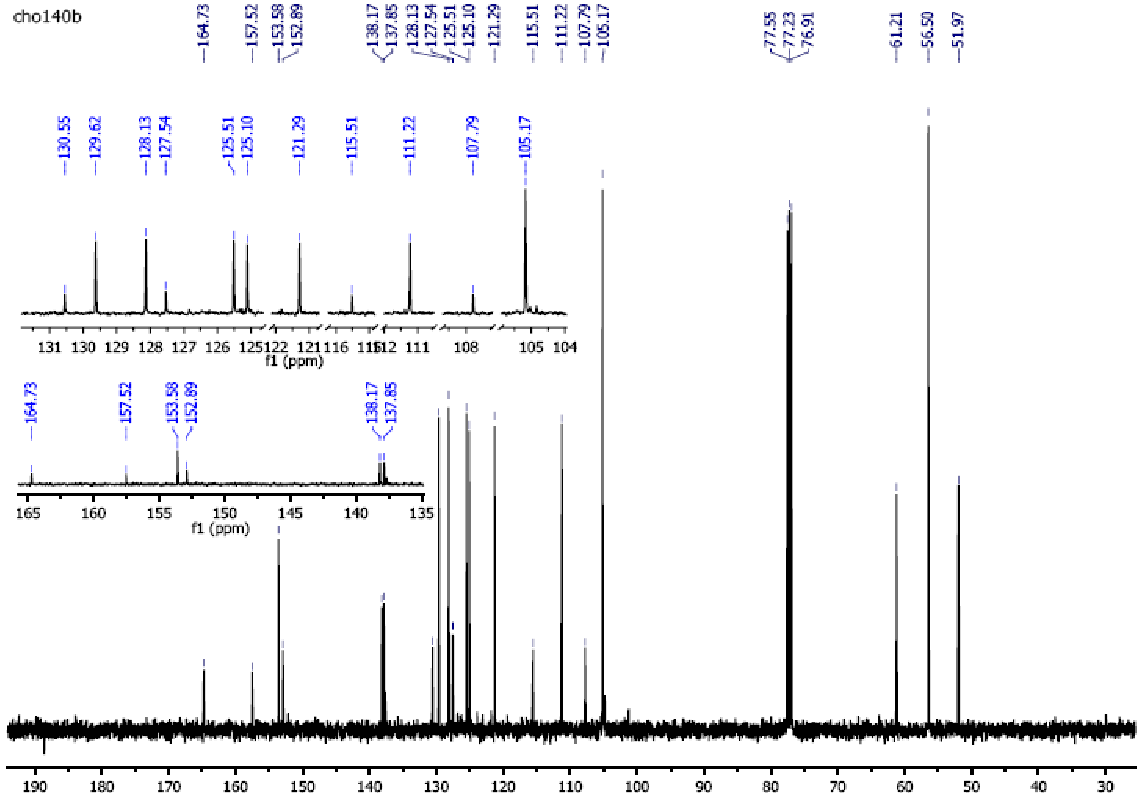




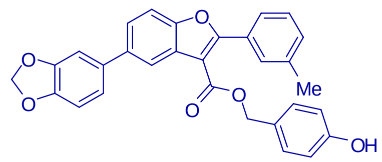
2,3,5-Trisubstituted benzo[*b*]furan 14{*115*}

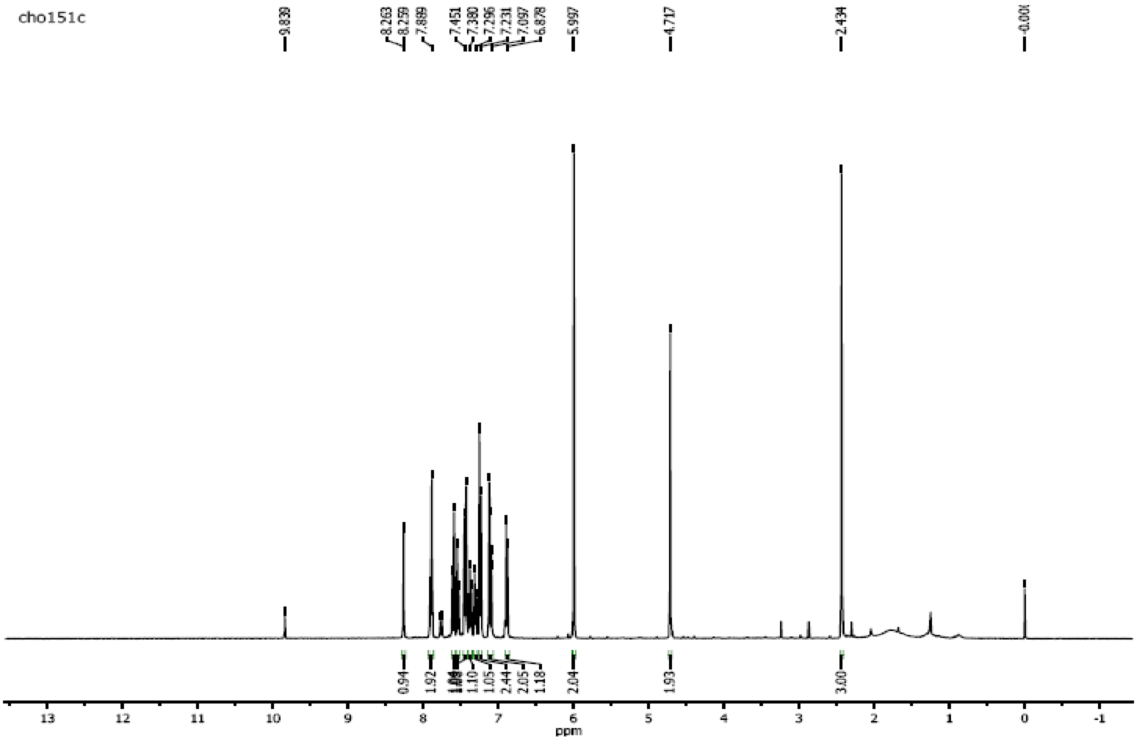


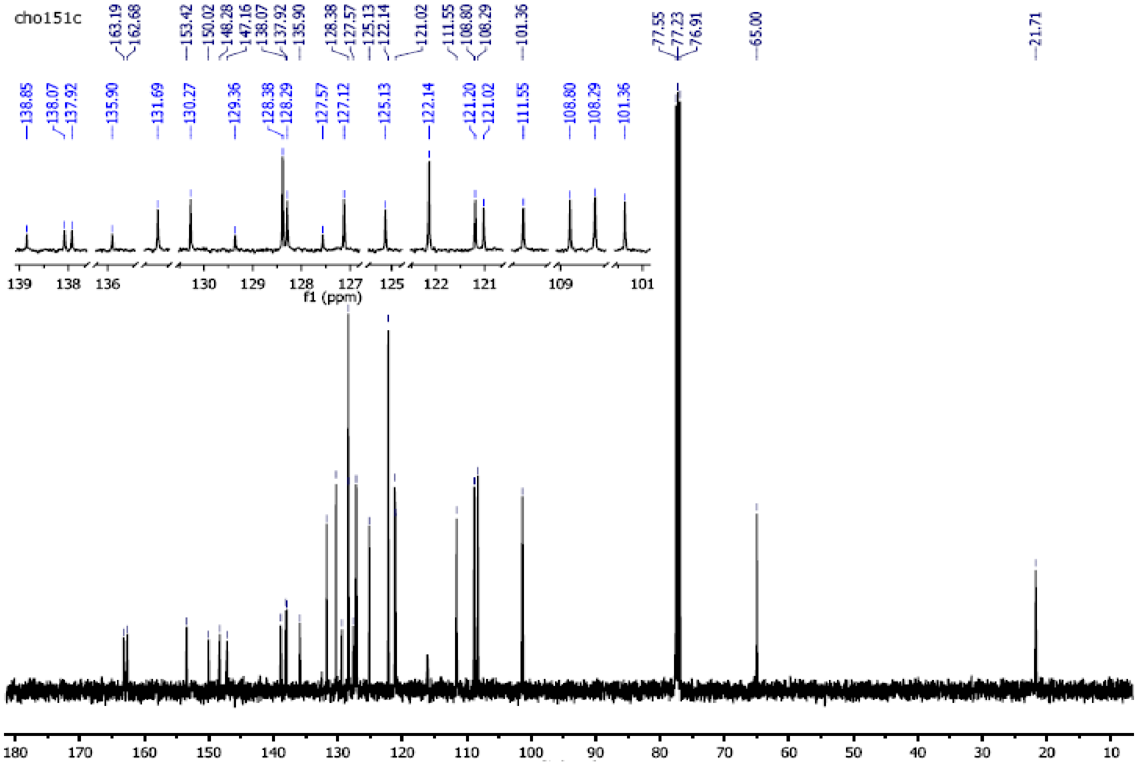




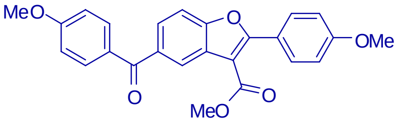
2,3,5-Trisubstituted benzo[*b*]furan 14{*118*}

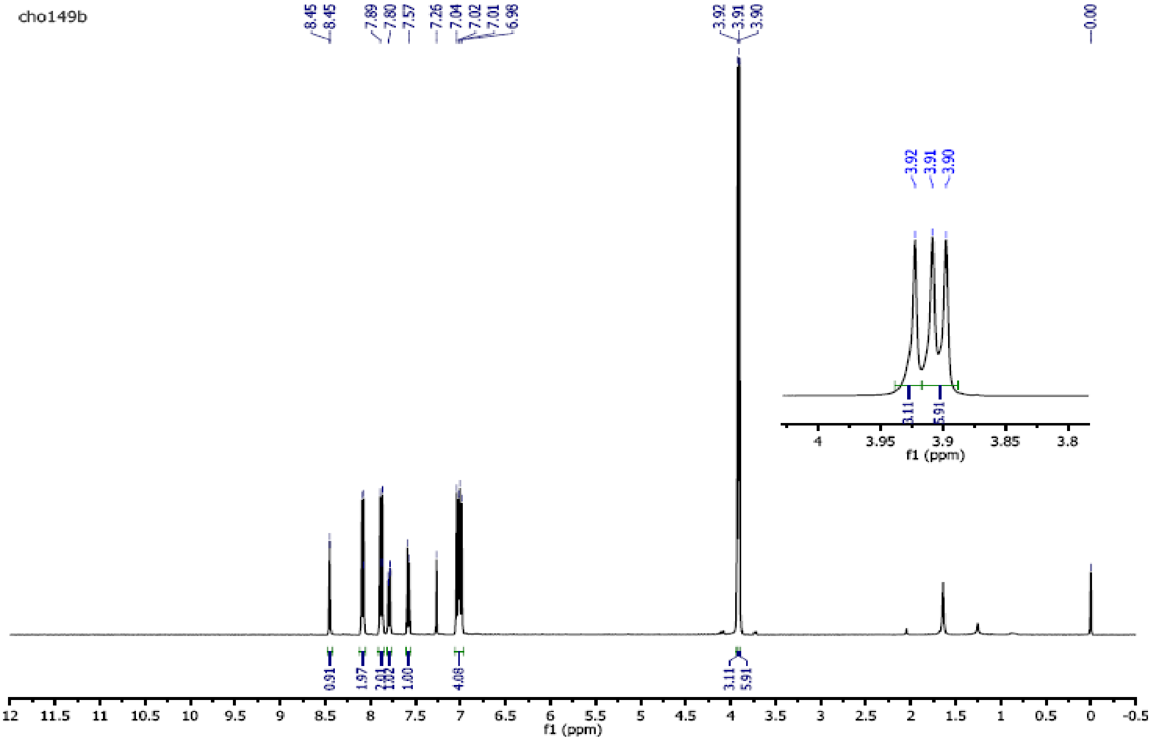


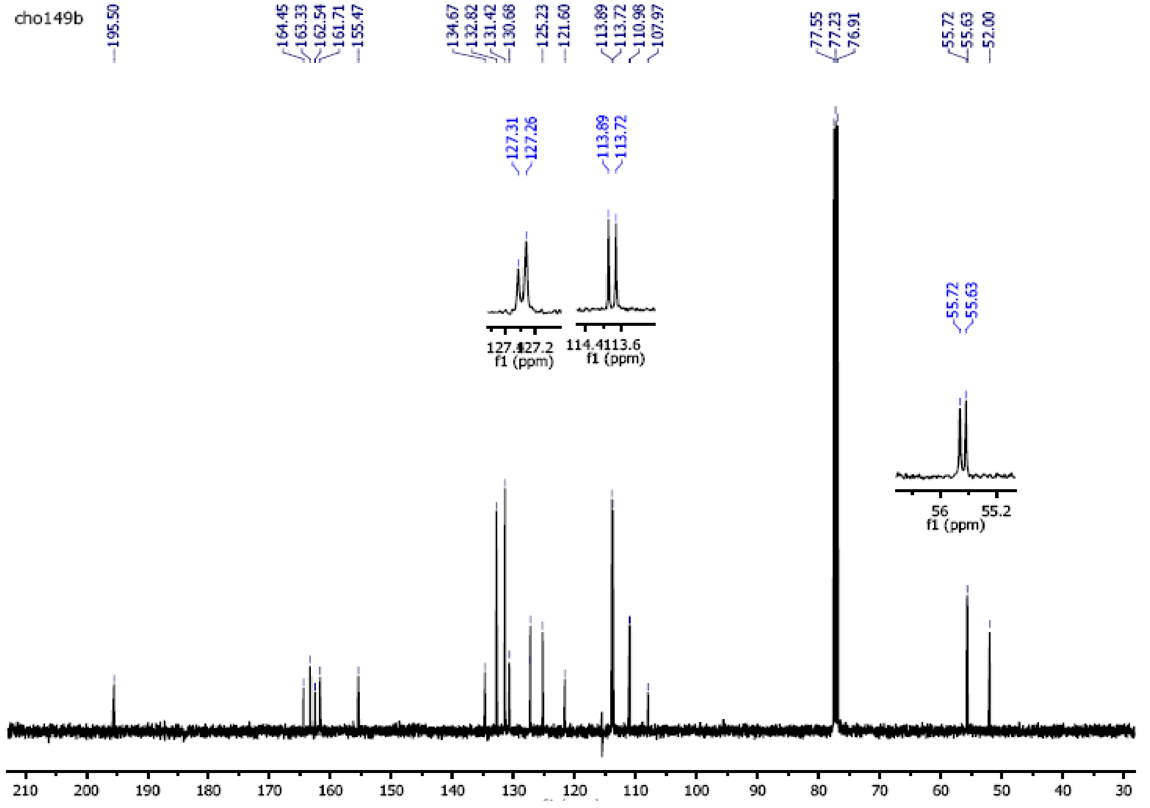




2,3,5-Trisubstituted benzo[*b*]furan 14{*119*}







2,3,5-Trisubstituted benzo[*b*]furan 14{*121*}