Supporting Information

Copper-catalyzed synthesis of 2-acylbenzo[b]thiophenes from 3-(2-iodophenyl)-1-arylpropan-1-ones and potassium sulfide under aerobic conditions

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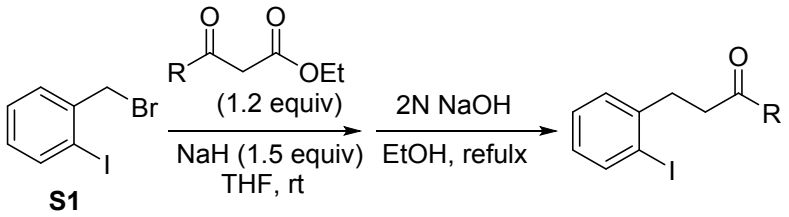
Contents

1) General Information

NMR spectra of the **2a-2v, 3a** were recorded using Bruker Avance-500 instruments, calibrated to TMS (^{1}H NMR spectra) and $CDCl_3$ (^{13}C NMR spectra) as the internal reference (0.00 ppm for ^{1}H NMR spectra and 77.00 ppm for ^{13}C NMR spectra). High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization). Melting points were measured uncorrected. Reactions were monitored by thin-layer chromatography. Column chromatography was performed on silica gel (200-300 mesh).

2) Synthetic Methods of Starting Materials[1]

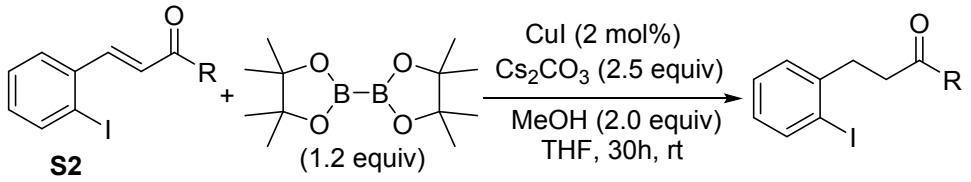
a) General Procedure for the Synthesis of 1a-1e, 1h, 1i, 1l, 1m, 1p-1t



S1

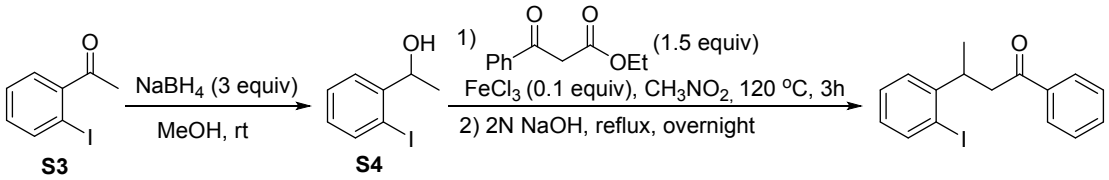
S1 (891.0 mg, 3.0 mmol) was dissolved in dry THF (5 mL) and added to a solution of NaH (60% in paraffin liquid, 180 mg, 4.5 mmol) and ethyl benzoylacetate (700 mg, 3.6 mmol) in dry THF (20 mL), and the resulted mixture was stirred for 1 h at room temperature. After the reaction was quenched with saturated NH_4Cl solution and extracted with EtOAc, the organic layer was dried over Na_2SO_4, filtered and concentrated to give a viscous material. To this material was added 2N NaOH (4 mL) and ethanol (4 mL), and then the reaction mixture was heated at reflux overnight. The solution was cooled to room temperature, poured into 10% aq. HCl (10 mL), and extracted with EtOAc. The combined extracts were dried over Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed with petroleum ether/EtOAc (30:1) to give **1**.

b) General Procedure for the Synthesis of 1f, 1g, 1j, 1k, 1n, 1o, 1v



To a solution of 3-(2-iodophenyl)-1-phenylprop-2-en-1-one (668 mg, 2 mmol) in 15 mL THF at room temperature was added $B_2(pin)_2$ (610 mg, 2.4 mmol), CuI (7.64 mg, 0.04 mmol), Cs_2CO_3 (1.63 g, 5 mmol), MeOH (128 mg, 4 mmol), and the reaction mixture was stirred overnight. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 30:1) to provide **1**.

c) General Procedure for the Synthesis of 1u



$NaBH_4$ (454 mg, 12.0 mmol) was added dropwise to a solution of **S3** (984 mg, 4.0 mmol) in MeOH (20 mL) at 0 °C. The resulting mixture was stirred at room temperature for 3h. After evaporation of MeOH, the solution was extracted with EtOAc, dried over anhydrous Na_2SO_4 and concentrated in vacuo to give **S4**. Anhydrous $FeCl_3$ (16 mg, 0.10 mmol) was added to a solution of **S4** (248 mg, 1.0 mmol) and ethyl benzoylacetate (288 mg, 1.5 mmol) in CH_3NO_2 (4 mL), the mixture was heated at 120 °C for 3 h. The reaction mixture was quenched with water followed by extraction with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated to afford a crude material. To this residual material was added 2N aq. NaOH (5 mL), and the reaction was heated at reflux overnight. The solution was cooled to room temperature, poured into 10% aq. HCl and extracted with EtOAc.

After concentration in vacuo, the residue was chromatographed by petroleum ether/EtOAc (30:1) to give **1u.**

3) Typical experimental procedure

a) Typical experimental procedure for the synthesis of 2-acylbenzo[*b*]thiophenes (Table 2).

The stirred mixture of 3-(2-iodophenyl)-1-phenylpropan-1-one derivatives **1** (0.2 mmol), potassium sulfide (0.6 mmol, 3.0 equiv) and CuI (0.02 mmol, 10%) in DMF (2 mL) at 130 °C for 12 h . After the completion of the reaction (monitored by TLC), the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography to provide the desired products **2**.

b) Deuteration Experiments

The stirred mixture of 3-(2-iodophenyl)-1-phenylpropan-1-one **1a** (0.2 mmol), potassium sulfide (0.6 mmol, 3.0 equiv), D_2O (1.2 mmol, 6 equiv) and CuI (0.02 mmol, 10%) in DMF (2 mL) at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 30:1) to provide the desired products **2a** in 87% **(Scheme 4: eq4)**.

The stirred mixture of 3-(2-iodophenyl)-1-phenylprop-2-en-1-one **4** (0.2 mmol), potassium sulfide (0.6 mmol, 3.0 equiv), D_2O (1.2 mmol, 6 equiv) and CuI (0.02 mmol, 10%) in DMF (2 mL) at 130 °C for 12 h . After the completion of the reaction (monitored by TLC), the reaction mixture was filtered, and concentrated by rotary evaporation. The crude product was purified by column chromatography (petroleum ether : ethyl acetate = 30:1) to provide the desired products **2a** in 87% **(Scheme 4: eq5)**.

4) Characterization Data for All products

benzo[*b*]thiophen-2-yl(phenyl)methanone (2a):[2] pale yellow solid, isolated yield 91% (43.3 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.93-7.85 (m, 5H), 7.63 (t, *J* = 7.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.6, 143.0, 142.6, 139.0, 137.7, 132.4, 132.2, 129.2, 128.4, 127.4, 126.0, 125.0, 122.8.

benzo[*b*]thiophen-2-yl(*o*-tolyl)methanone (2b):[2] pale yellow solid, isolated yield 90% (45.4 mg); **^{1}H NMR** ($CDCl_3$, 500 MHz) δ = 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.63 (s, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.49-7.42 (m, 2H), 7.39 (t, *J* = 7.0 Hz, 1H), 7.34-7.29 (m, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 191.9, 144.3, 143.0, 139.0, 138.0, 136.6, 133.0, 131.1, 130.5, 128.1, 127.5, 126.1, 125.2, 125.0, 122.9, 19.7.

benzo[*b*]thiophen-2-yl(*p*-tolyl)methanone (2c):[2] pale yellow solid, isolated yield 92% (46.3 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.91-7.83 (m, 5H), 7.47 (t, *J* = 7.0 Hz, 1H)), 7.41 (t, *J* = 7.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.2, 143.3, 143.2, 142.5, 139.0, 135.0, 131.8, 129.4, 129.1, 127.2, 125.9, 124.9, 122.8, 21.6.

benzo[*b*]thiophen-2-yl(2-methoxyphenyl)methanone (2d): pale yellow oil, isolated yield 98% (52.5 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.05-7.01 (m, 2H), 3.77 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.6, 157.0, 144.2, 142.9, 138.9, 132.4, 132.0, 129.1, 128.3, 127.3, 126.0, 124.8, 122.9, 120.2, 111.6, 55.6. HRMS (ESI) m/z calcd for $C_{16}H_{13}O_2S^+(M+H)^+$ 269.06308, found 269.06348.

benzo[*b*]thiophen-2-yl(4-methoxyphenyl)methanone (2e):[2] pale yellow solid, isolated yield 80% (42.9 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.95 (d, *J* = 8.5 Hz,

2H), 7.91-7.87 (m, 2H), 7.85 (s, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 188.1, 163.3, 143.3, 142.3, 139.0, 131.7, 131.2, 130.3, 127.1, 125.8, 124.9, 122.8, 113.8, 55.5.

(4-aminophenyl)(benzo[*b*]thiophen-2-yl)methanone (2f): pale yellow solid, isolated yield 70% (35.4 mg); mp: 135.1-136.2 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.90-7.83 (m, 5H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 9.0 Hz, 2H), 4.23 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 187.7, 151.1, 143.6, 142.1, 139.1, 132.1, 130.4, 127.5, 126.8, 125.6, 124.8, 122.7, 113.8. HRMS (ESI) m/z calcd for $C_{15}H_{12}NOS^{+}(M+H)^{+}$ 254.06341, found 269.06357.

benzo[*b*]thiophen-2-yl(4-fluorophenyl)methanone (2g): pale yellow solid, isolated yield 80% (41.0 mg); mp: 94.5-95.2 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.898-7.95 (m, 2H), 7.92-7.88 (m, 2H), 7.84 (s, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.22 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 188.1, 165.4 (d, *J* = 252.7 Hz), 142.7 (d, *J* = 15.0 Hz), 138.9, 134.0 (d, *J* = 2.9 Hz), 131.9, 131.8, 131.8, 127.5, 126.0, 125.1, 122.9, 115.7 (d, *J* = 21.7 Hz). HRMS (ESI) m/z calcd for $C_{15}H_{10}FOS^{+}(M+H)^{+}$ 257.04309, found 257.04343.

benzo[*b*]thiophen-2-yl(4-chlorophenyl)methanone (2h):[2] pale yellow solid, isolated yield 83% (45.2 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.89-7.84 (m, 4H), 7.81 (s, 1H), 7.49-7.45 (m, 3H), 7.40 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 188.3, 142.7, 142.7, 139.0, 139.0, 136.1, 132.2, 130.7, 128.9, 127.7, 126.2, 125.2, 122.9.

benzo[*b*]thiophen-2-yl(naphthalen-1-yl)methanone (2i): pale yellow solid, isolated yield 94% (54.1 mg); mp: 139.0-140.4 ^{o}C;^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.23 (d, *J* = 9.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.95-7.91 (m, 2H), 7.79 (t, *J* = 7.5 Hz, 2H), 7.68 (s, 1H), 7.58-7.53 (m, 3H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 191.3, 144.8, 143.2, 139.0, 135.8, 133.8, 133.3, 131.6,

130.7, 128.5, 127.8, 127.5, 127.4, 126.7, 126.3, 125.5, 125.1, 124.4, 123.1. HRMS (ESI) m/z calcd for $C_{19}H_{13}OS^+(M+H)^+$ 289.06816, found 289.06821.

benzo[*b*]thiophen-2-yl(naphthalen-2-yl)methanone (2j): pale yellow solid, isolated yield 88% (50.6 mg); mp: 139.2-140.3 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ = 8.46 (s, 1H), 7.99-7.93 (m, 6H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.5 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.5, 143.2, 142.7, 139.1, 135.3, 135.1, 132.3, 132.2, 130.7, 129.3, 128.5, 128.3, 127.9, 127.4, 126.9, 126.0, 125.2, 125.0, 122.9. HRMS (ESI) m/z calcd for $C_{19}H_{13}OS^+(M+H)^+$ 289.06816, found 289.06812.

[1,1'-biphenyl]-4-yl(benzo[*b*]thiophen-2-yl)methanone (2k): pale yellow solid, isolated yield 87% (54.6 mg); mp: 143.6-144.4 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ = 8.02 (d, *J* = 8.0 Hz, 2H), 7.93-7.90 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.52-7.48 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.0, 145.2, 143.1, 142.6, 139.8, 139.0, 136.4, 132.0, 129.9, 128.9, 128.2, 127.4, 127.2, 127.1, 126.0, 125.0, 122.8. HRMS (ESI) m/z calcd for $C_{21}H_{15}OS^+(M+H)^+$ 315.08381, found 315.08398.

benzo[*b*]thiophen-2-yl(furan-2-yl)methanone (2l):[3] pale yellow solid, isolated yield 90% (41.0 mg); ^1H NMR ($CDCl_3$, 500 MHz) δ = 8.42 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.72 (s, 1H), 7.47-7.44 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 6.63-6.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 174.5, 152.4, 146.6, 142.3, 141.8, 139.3, 131.1, 127.3, 126.1, 124.9, 122.6, 119.2, 112.5.

benzo[*b*]thiophen-2-yl(thiophen-3-yl)methanone (2m): pale yellow solid, isolated yield 92% (44.9 mg); mp: 127.6-128.9 ^oC; ^1H NMR ($CDCl_3$, 500 MHz) δ = 8.15 (s, 1H), 8.00 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 5.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.43-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 182.5, 143.4, 142.3, 140.8, 138.9, 132.5, 130.7, 128.1, 127.3, 126.5, 125.9, 125.0, 122.8. HRMS (ESI) m/z

calcd for $C_{13}H_9OS_2^+(M+H)^+$ 245.00893, found 245.00894.

benzo[*b*]thiophen-2-yl(1-methyl-1H-pyrrol-2-yl)methanone (2n): pale yellow oil, isolated yield 90% (43.3 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.96 (s, 1H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.45-7.38 (m, 2H), 7.12 (d, *J* = 4.0 Hz, 1H), 6.92 (s, 1H), 6.22-6.21 (m, 1H), 4.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 178.1, 144.3, 141.7, 139.0, 131.7, 130.1, 129.1, 126.6, 125.5, 124.8, 122.7, 121.4, 108.4, 37.1. HRMS (ESI) m/z calcd for $C_{14}H_{12}NOS^+(M+H)^+$ 242.06341, found 242.06340.

benzo[*b*]thiophen-2-yl(1-methyl-1H-indol-3-yl)methanone (2o): pale yellow solid, isolated yield 98% (57.0 mg); mp: 135.0-136.3 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.45 (d, *J* = 5.0 Hz, 1H), 7.94 (s, 1H), 7.91-7.88 (m, 3H), 7.46-7.26 (m, 5H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 182.3, 144.9, 141.5, 139.1, 137.5, 136.5, 127.7, 127.1, 126.4, 125.4, 124.8, 123.8, 122.8, 122.7, 122.7, 115.5, 109.7, 33.6. HRMS (ESI) m/z calcd for $C_{18}H_{14}NOS^+(M+H)^+$ 292.07906, found 292.07901.

1-(benzo[*b*]thiophen-2-yl)ethanone (2p):[2] pale yellow solid, isolated yield 65% (22.9 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.92 (s, 1H), 7.88-7.85 (m, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 192.2, 143.9, 142.6, 139.1, 129.6, 127.4, 125.8, 124.9, 122.9, 26.7.

1-(benzo[*b*]thiophen-2-yl)pentan-1-one (2q):[4] pale yellow solid, isolated yield 50% (21.8 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.95 (s, 1H), 7.87 (t, *J* = 9.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 3.00 (t, *J* = 7.5 Hz, 2H), 1.81-1.75 (m, 2H), 1.48-1.40 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 195.0, 143.9, 142.4, 139.1, 128.7, 127.2, 125.8, 124.9, 122.9, 39.0, 26.8, 22.4, 13.8.

benzo[*b*]thiophen-2-yl(cyclohexyl)methanone (2r): pale yellow solid, isolated yield 92% (44.9 mg); mp: 89.9-90.9 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.96 (s, 1H), 7.89-7.84 (m, 2H), 7.44 (t, *J* = 7.0 Hz, 1H), 7.39 (t, *J* = 7.0 Hz, 1H), 3.26-3.22 (m, 1H), 1.98-1.86 (m, 4H), 1.77-1.74 (m, 1H), 1.63-1.55 (m, 2H), 1.46-1.38 (m, 2H), 1.33-

1.28 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 198.2, 143.3, 142.4, 139.2, 128.4, 127.1, 125.8, 124.8, 122.9, 47.2, 29.6, 25.7, 25.7. HRMS (ESI) m/z calcd for $C_{15}H_{17}OS^+(M+H)^+$ 245.09946, found 245.09943.

(3-methylbenzo[*b*]thiophen-2-yl)(phenyl)methanone (2s):[5] pale yellow solid, isolated yield 78% (39.3 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.90-7.85 (m, 4H), 7.60 t, *J* = 7.5 Hz, 1H), 7.51-7.26 (m, 4H), 2.57 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 191.3, 140.7, 140.2, 139.3, 138.8, 135.0, 132.6, 129.4, 128.3, 127.0, 124.6, 123.7, 122.5, 14.1.

(5-fluorobenzo[*b*]thiophen-2-yl)(phenyl)methanone (2t): pale yellow solid, isolated yield 83% (42.5 mg); mp: 86.9-87.5 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.91 (d, *J* = 7.0 Hz, 2H), 7.86-7.84 (m, 1H), 7.80 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.56-7.52 (m, 3H), 7.25 (td, *J* = 9.0 Hz, 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.4, 160.9 (d, *J* = 242.1 Hz), 145.3, 139.8 (d, *J* = 9.6 Hz), 138.1, 137.5, 132.7, 131.4 (d, *J* = 4.7 Hz), 129.3, 128.6, 124.2 (d, *J* = 9.0 Hz), 116.6 (d, *J* = 25.5 Hz), 110.9 (d, *J* = 22.6 Hz). HRMS (ESI) m/z calcd for $C_{15}H_{10}FOS^+(M+H)^+$ 257.04309, found 257.04327.

(5-chlorobenzo[*b*]thiophen-2-yl)(phenyl)methanone (2u):[4] white solid, isolated yield 88% (48.1 mg); mp: 84-86 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.91 (d, *J* = 7.0 Hz, 2H), 7.85 (d, J= 1.5Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.78 (s, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.44 (dd, *J* = 8.5 Hz, *J* =1.5Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.3, 144.9, 140.6, 140.0, 137.4, 132.7, 131.3, 130.9, 129.3, 128.6, 127.9, 125.3, 124.0.

(5-methoxybenzo[*b*]thiophen-2-yl)(phenyl)methanone (2v): pale yellow solid, isolated yield 95% (50.8 mg); mp: 106-108 ^{o}C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.91 (d, *J* = 7.0 Hz, 2H), 7.79 (s, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 2.5 Hz, 1H), 7.15 (dd, *J* = 9 Hz, *J* =2.5Hz, 1H), 3.87 (s, *J*= 3.87Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.6, 157.8, 144.0, 137.8,

135.5, 132.4, 131.9, 129.2, 128.4, 123.6, 118.6, 106.8, 55.4. HRMS (ESI) m/z calcd for $C_{16}H_{13}O_2S^+$ $(M+H)^+$ 269.06308, found 269.06319.

(7-methylbenzo[*b*]thiophen-2-yl)(phenyl)methanone (2w): pale yellow solid, isolated yield 87% (43.8 mg); mp: 84.7-85.8 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.93 (d, *J* = 7.5 Hz, 2H), 7.89 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 189.7, 143.1, 142.5, 138.9, 137.9, 132.9, 132.5, 132.4, 129.2, 128.5, 127.5, 125.5, 123.7, 20.1. HRMS (ESI) m/z calcd for $C_{16}H_{13}OS^+(M+H)^+$ 253.06816, found 253.06816.

11H-benzo[4,5]thieno[3,2-*b*]thiochromen-11-one (2x):[6] pale yellow solid, isolated yield 93% (49.8 mg); ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.62 (d, *J* = 8.0 Hz, 1H), 7.91-7.87 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 175.7, 141.2, 136.3, 136.2, 135.0, 132.9, 131.5, 129.7, 128.7, 128.6, 127.1, 126.7, 125.0, 123.5, 122.6.

(2,3-dihydrobenzo[*b*]thiophen-2-yl)(phenyl)methanone (3a): pale yellow solid; mp: 87.1-88.6 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 7.94 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.10-7.04 (m, 3H), 5.21 (dd, *J* = 8.5 Hz, *J* = 4.5 Hz, 1H), 3.98 (dd, *J* = 16 Hz, *J* = 4.5 Hz, 1H), 3.46 (dd, *J* = 15.5 Hz, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 193.7, 139.2, 138.4, 135.0, 133.4, 128.7, 128.6, 127.4, 125.0, 124.7, 121.6, 50.0, 36.3. HRMS (ESI) m/z calcd for $C_{15}H_{13}OS^+(M+H)^+$ 241.06816, found 241.06813.

5) References

(1) (a) W.-C. Gao, S. Jiang, R.-L. Wang and C. Zhang, *Chem. Commun.,* 2013, **49**, 4890. (b) Q.-D. Wang, J.-M. Yang, D. F. J. Ren, B. Dong, B. Zhou and B.-B. Zeng,

Tetrahedron Lett., 2016, **57**, 2587.

(2) S. Sangeetha and G. Sekar, *Org. Lett.,* 2017, **19**, 1670.

(3) M. Kuriyama, N. Hamaguchi, K. Sakata and O. Onomura, *Eur. J. Org. Chem.,* 2013, 3378.

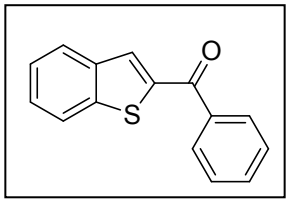
(4) A. J. Eberhart and D. J. Procter, *Angew. Chem. Int. Ed.,* 2013, **52**, 4008.

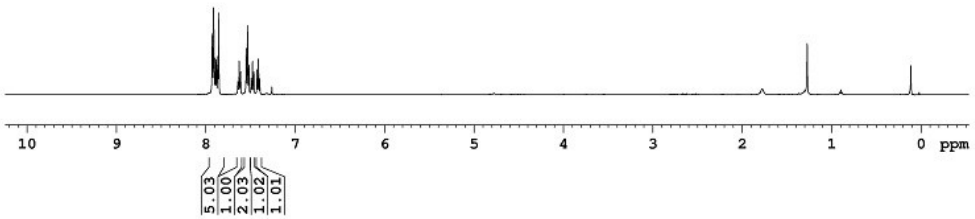
(5) A. Croisy, J. Mispelter, J.-M. Lhoste, F. Zajdela and P. Jacquignon, *J. Heterocyclic Chem.,* 1984, **21**, 353.

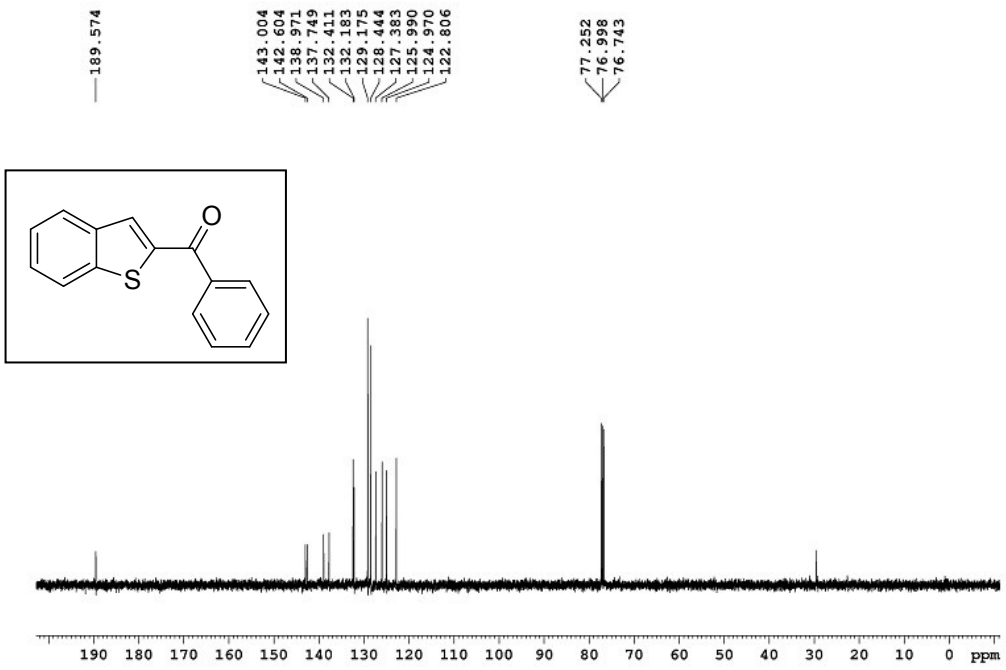
(6) K. Görlitzer and D. Hölscher, *Arch. Pharm.,* 1982, **315**, 193.

6) Scanned ^{1}H NMR and ^{13}C NMR Spectra of All Compounds

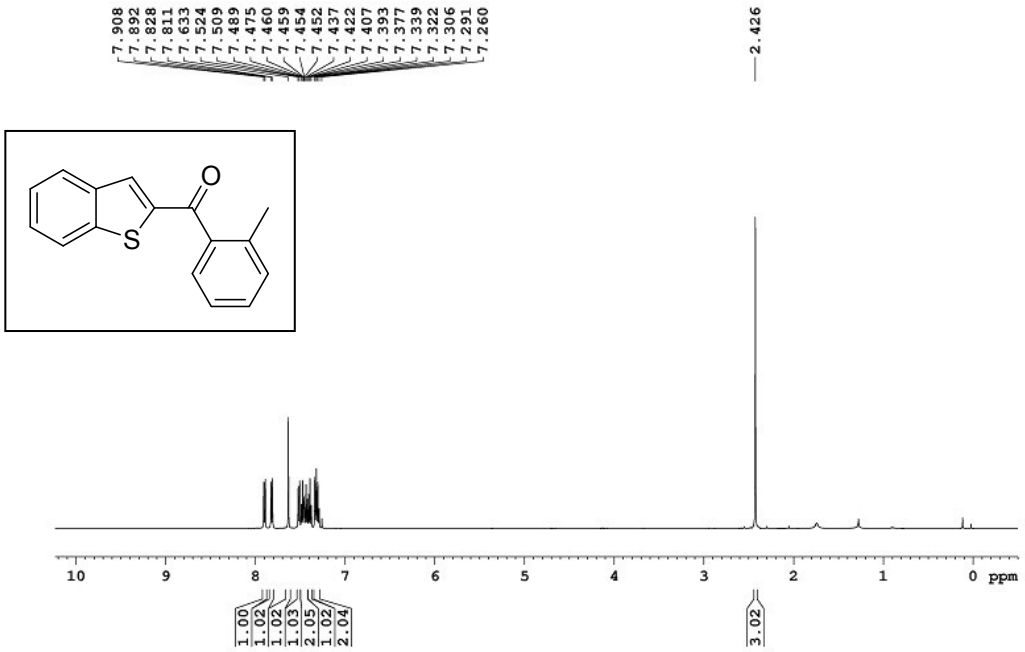
^{1}H and ^{13}C Spectrum of Compound **2a**

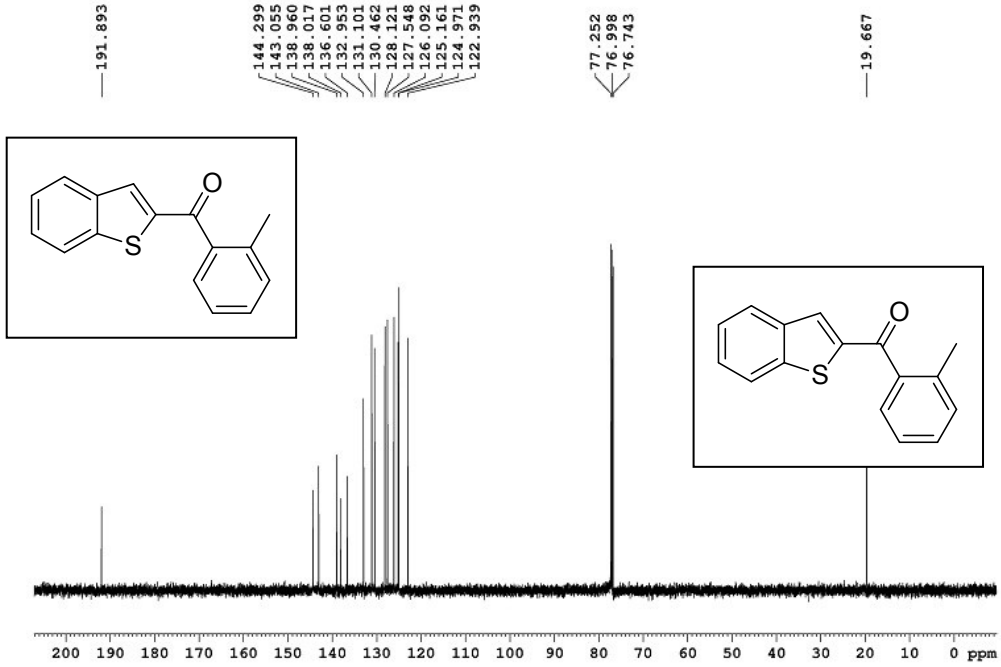




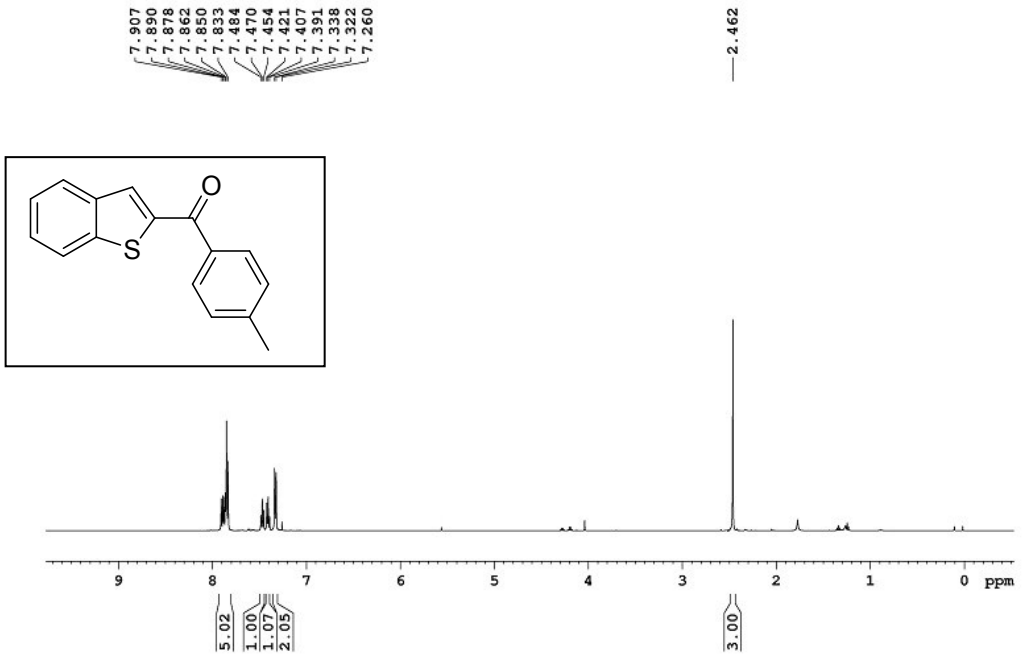


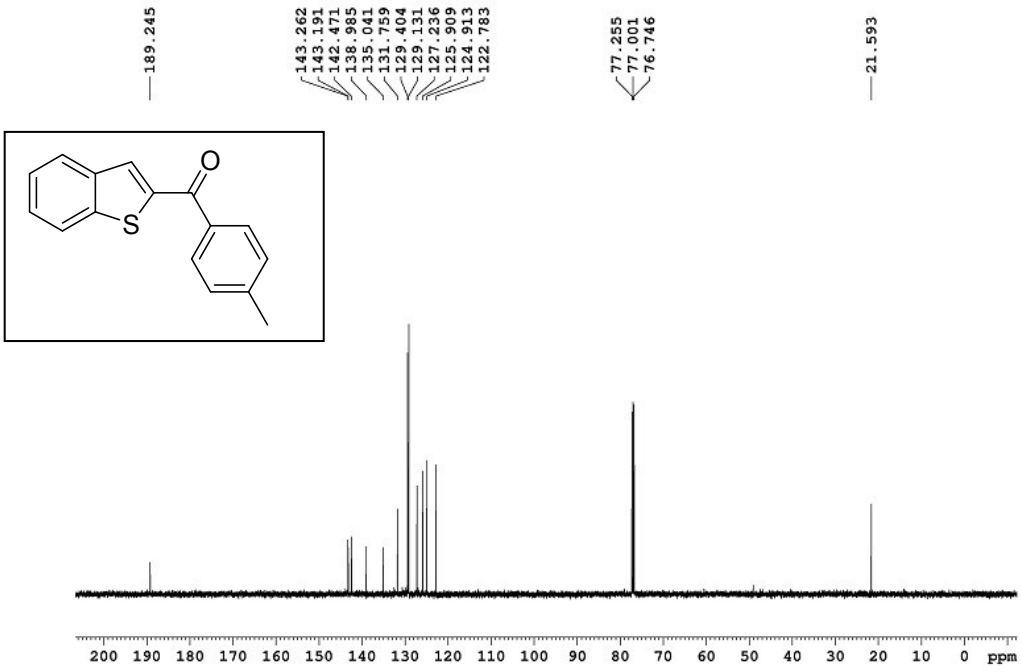
^{1}H and ^{13}C Spectrum of Compound **2b**



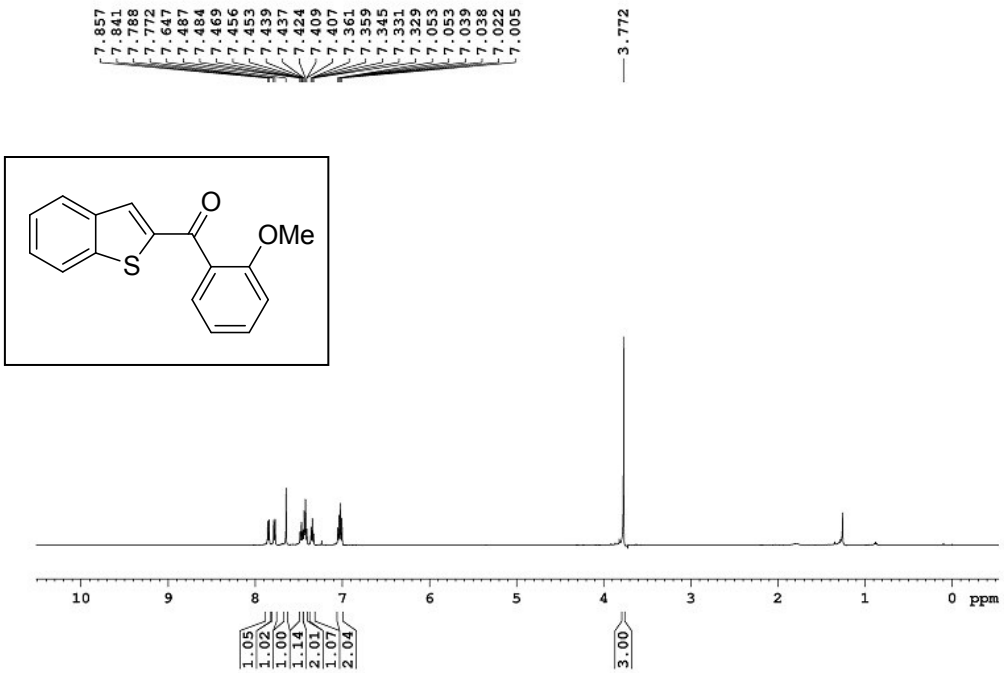


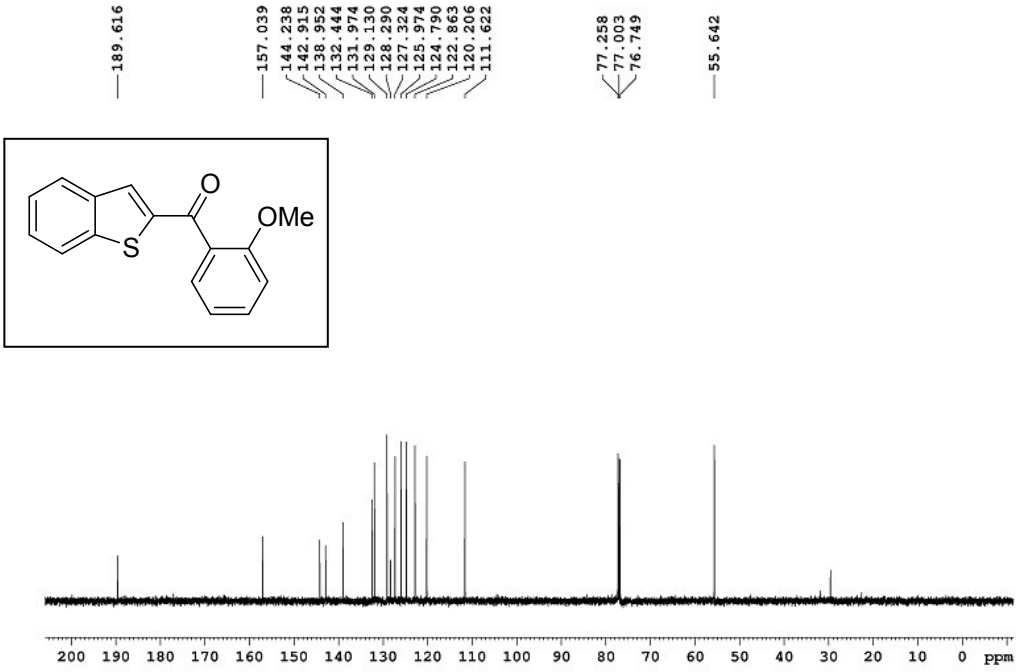
^{1}H and ^{13}C Spectrum of Compound **2c**



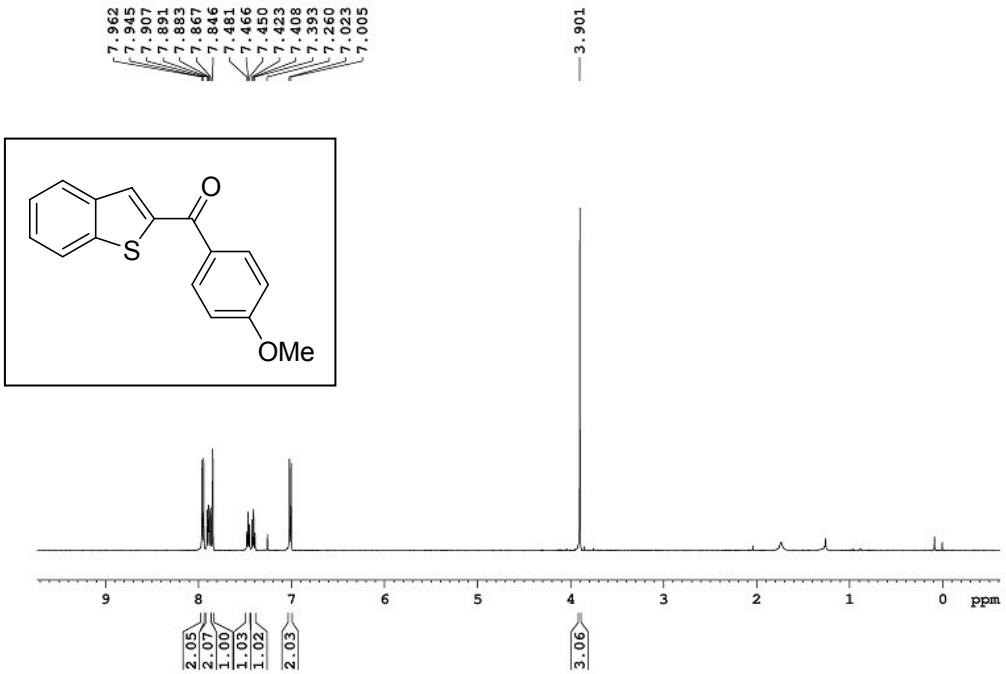


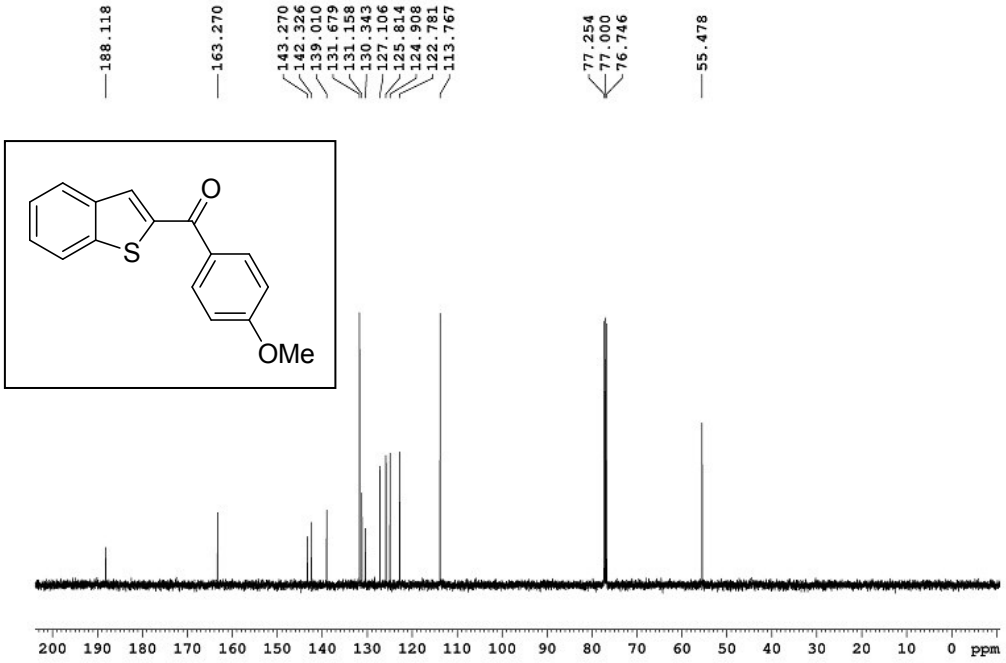
^{1}H and ^{13}C Spectrum of Compound **2d**



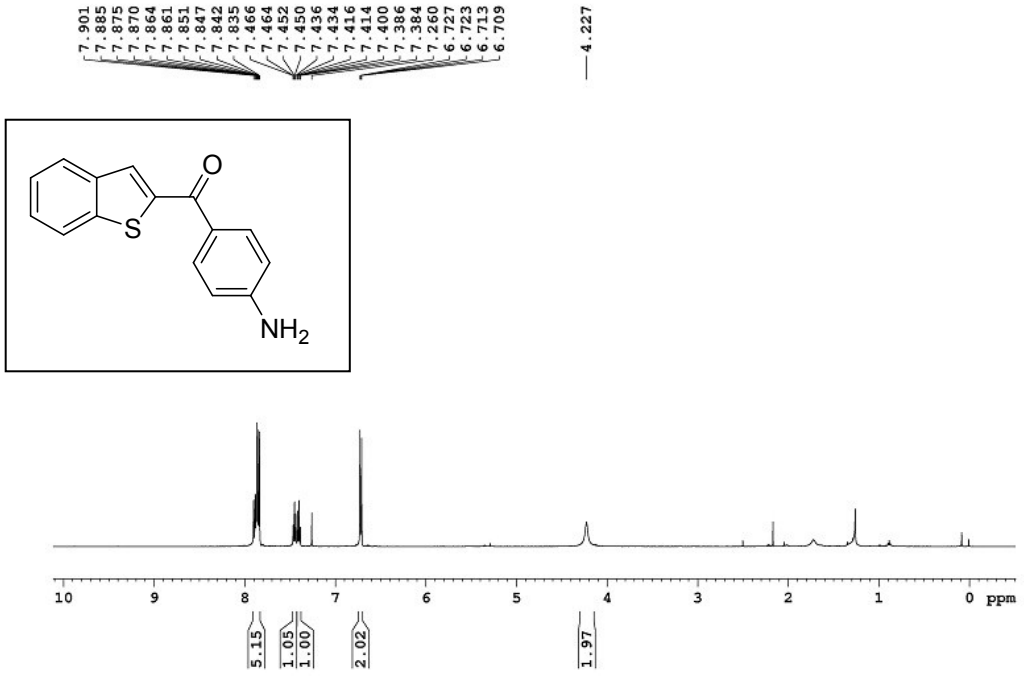


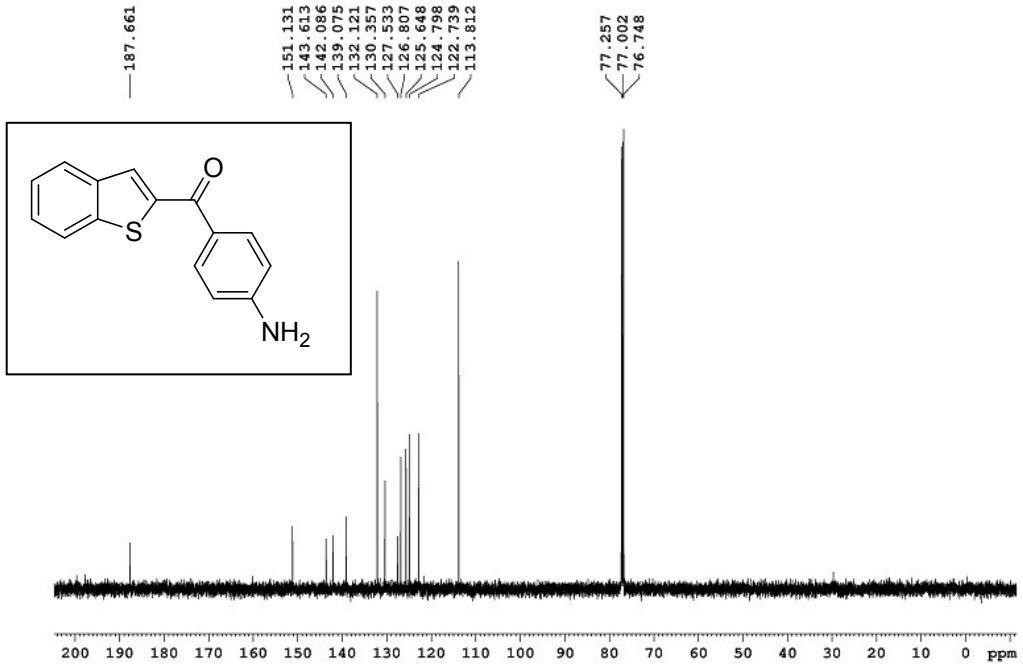
^{1}H and ^{13}C Spectrum of Compound **2e**



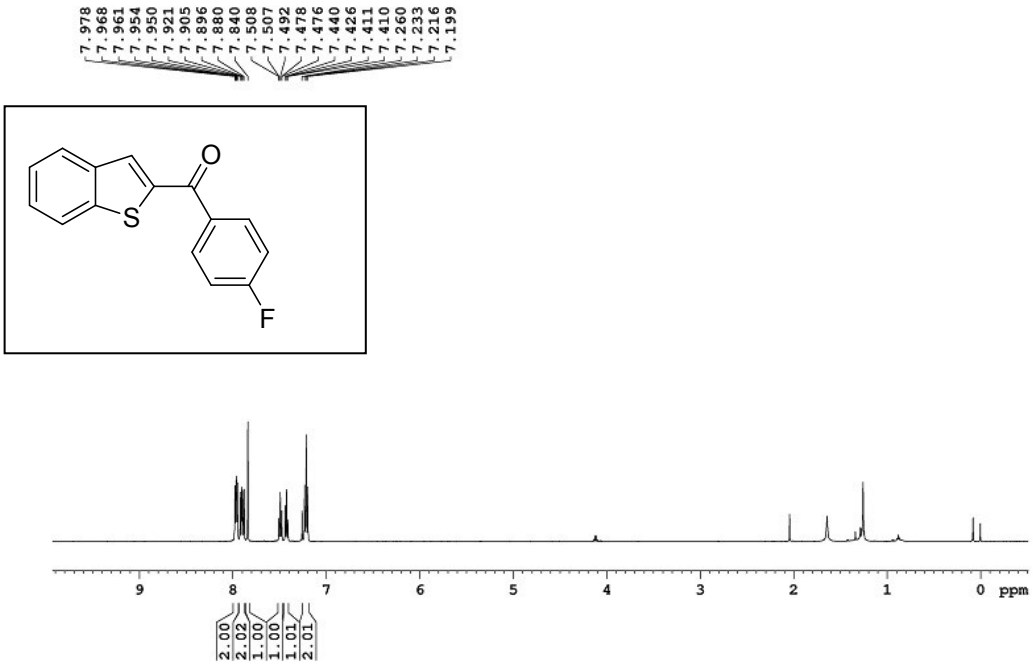


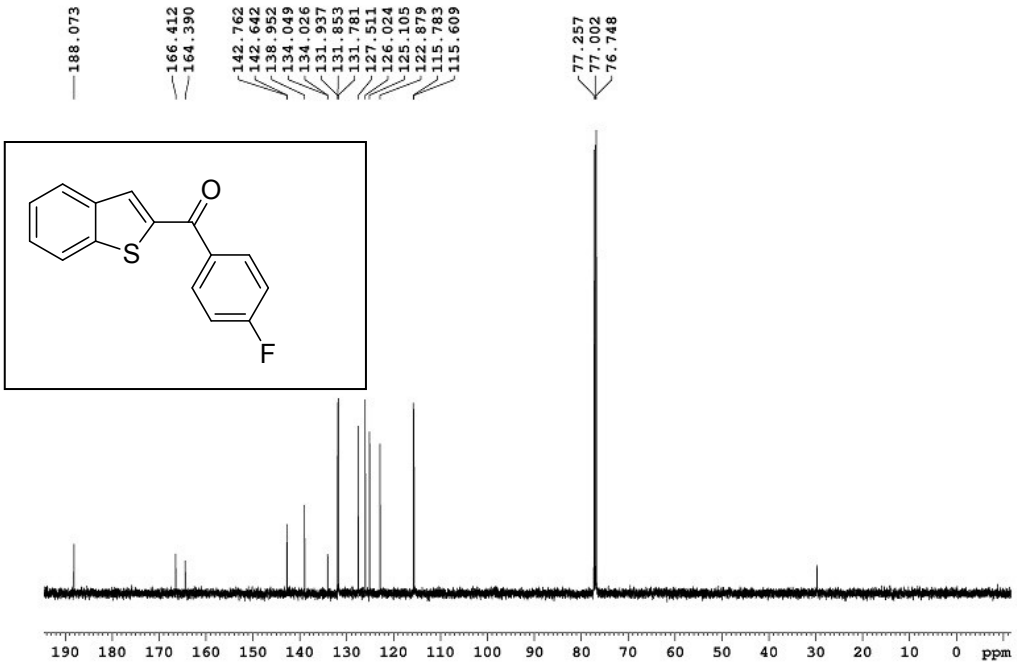
^{1}H and ^{13}C Spectrum of Compound **2f**



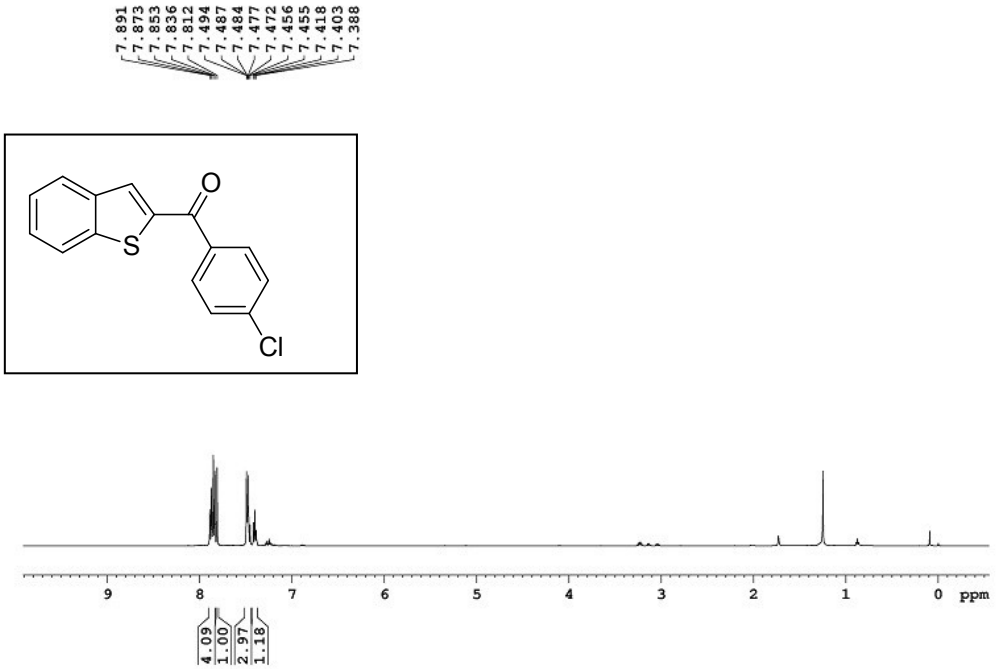


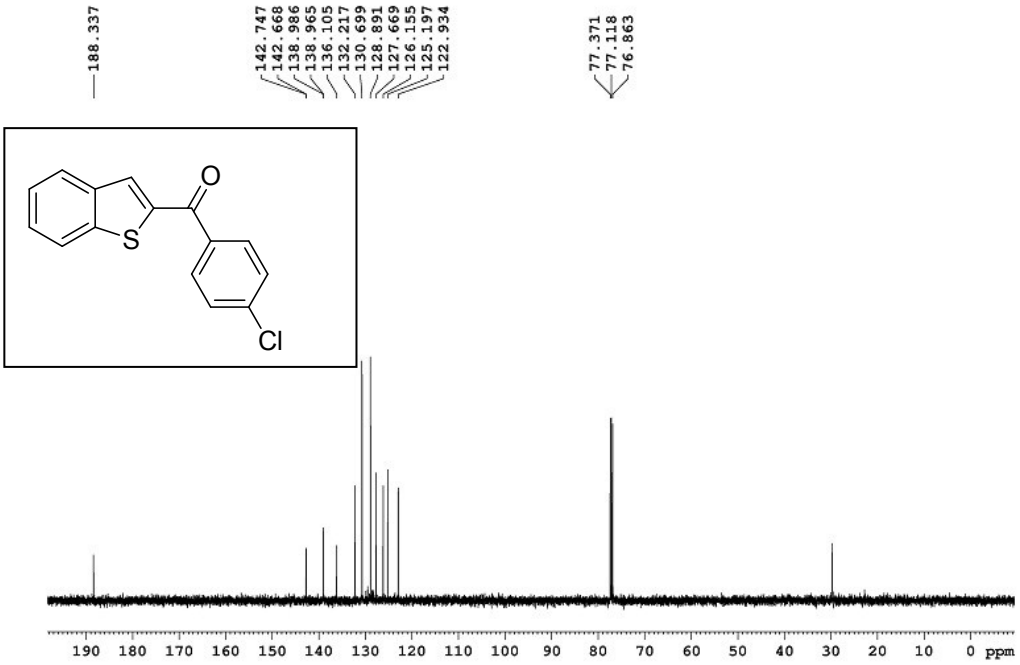
^{1}H and ^{13}C Spectrum of Compound **2g**



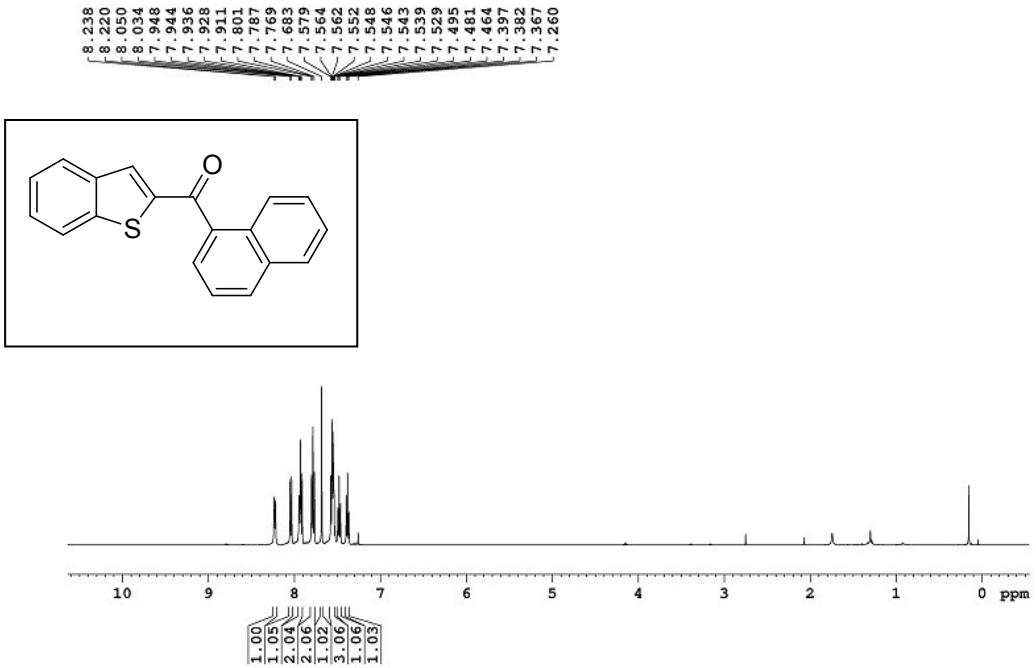


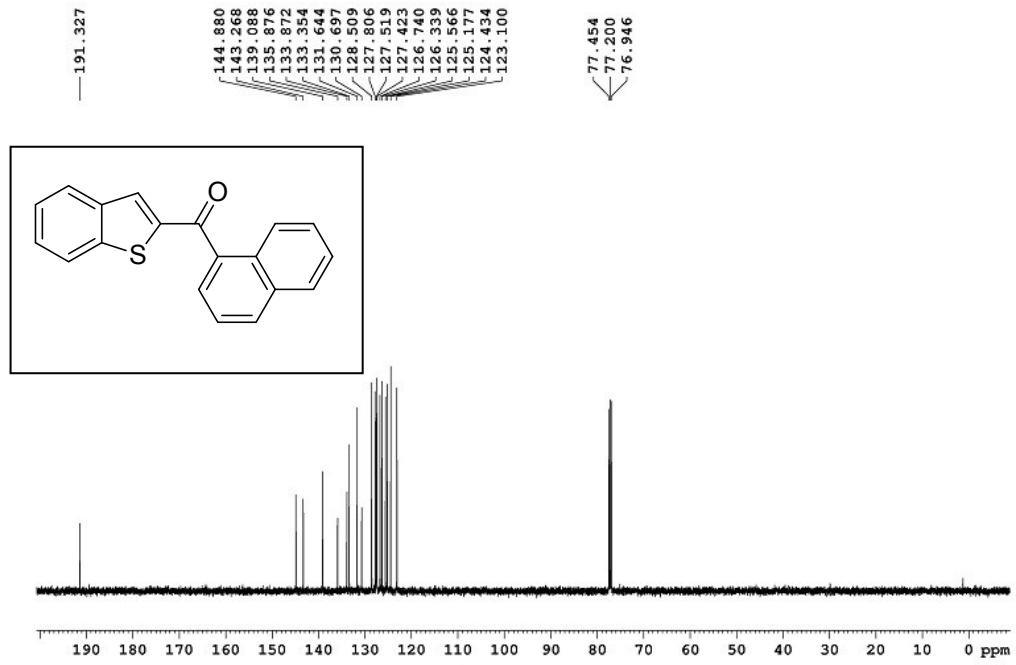
^{1}H and ^{13}C Spectrum of Compound **2h**



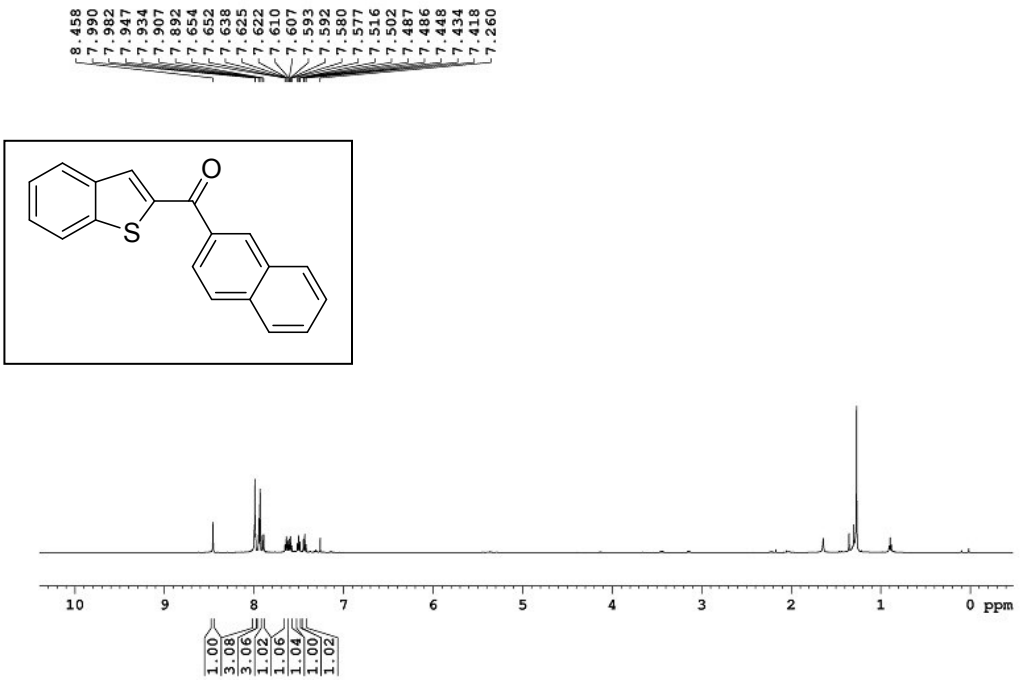


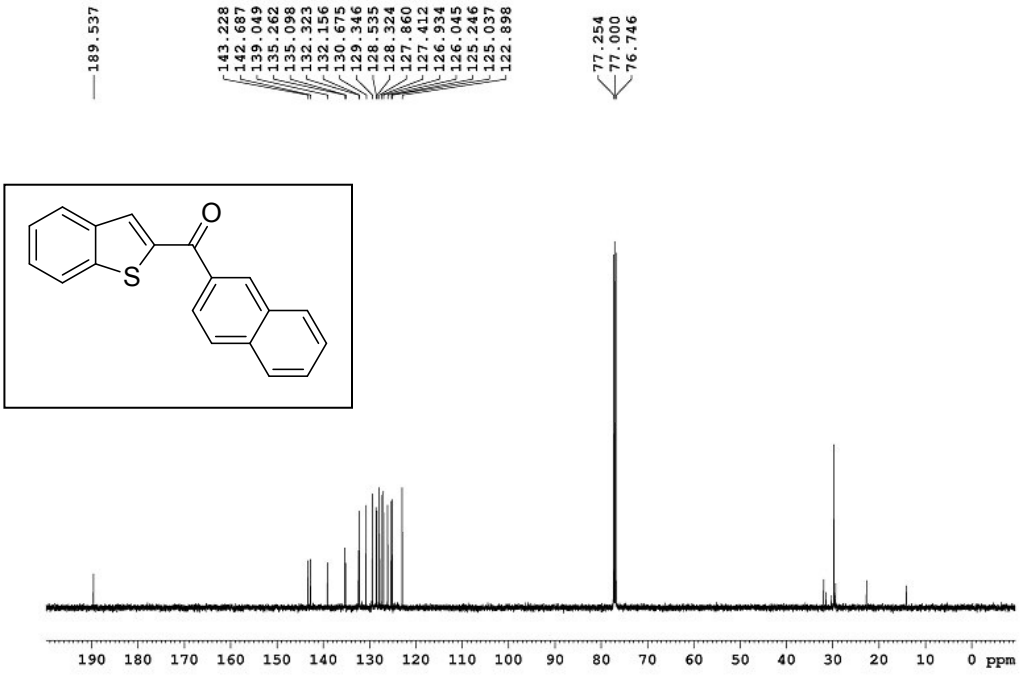
^{1}H and ^{13}C Spectrum of Compound **2i**



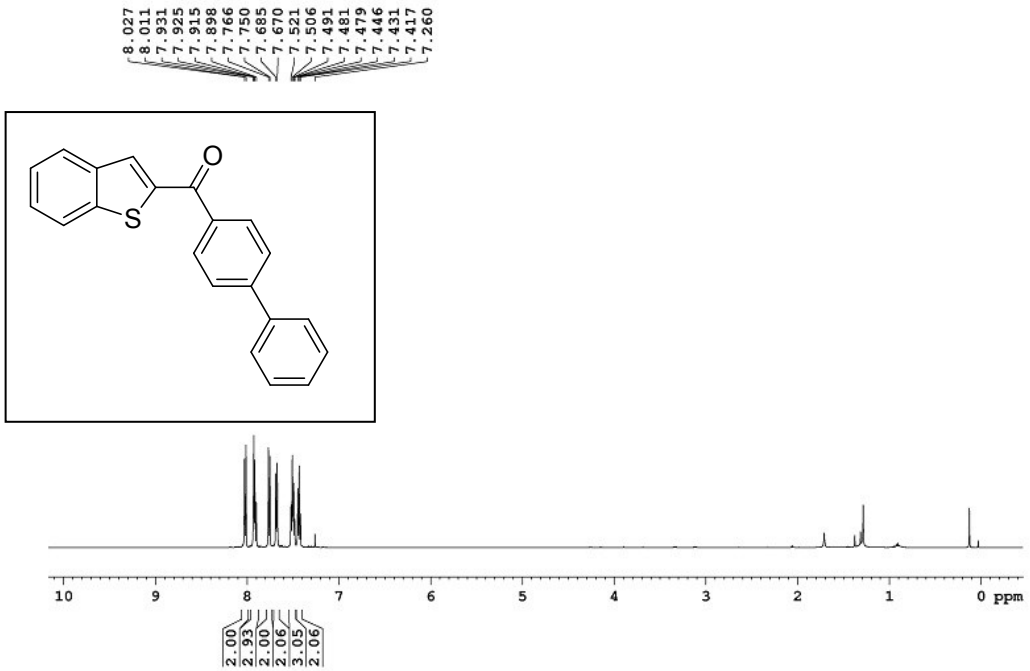


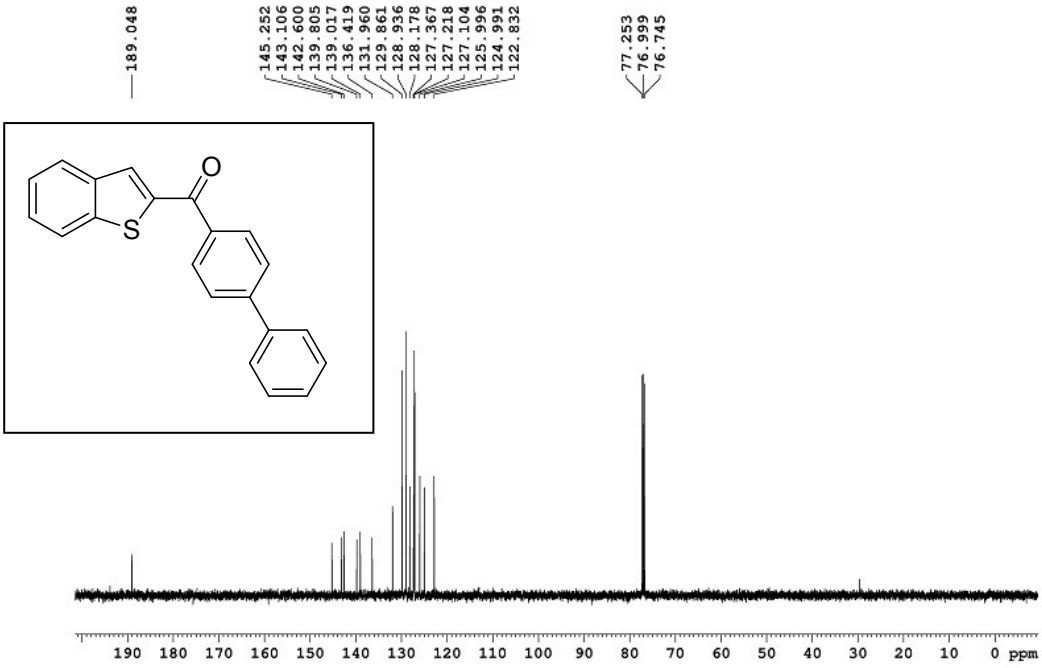
^{1}H and ^{13}C Spectrum of Compound **2j**



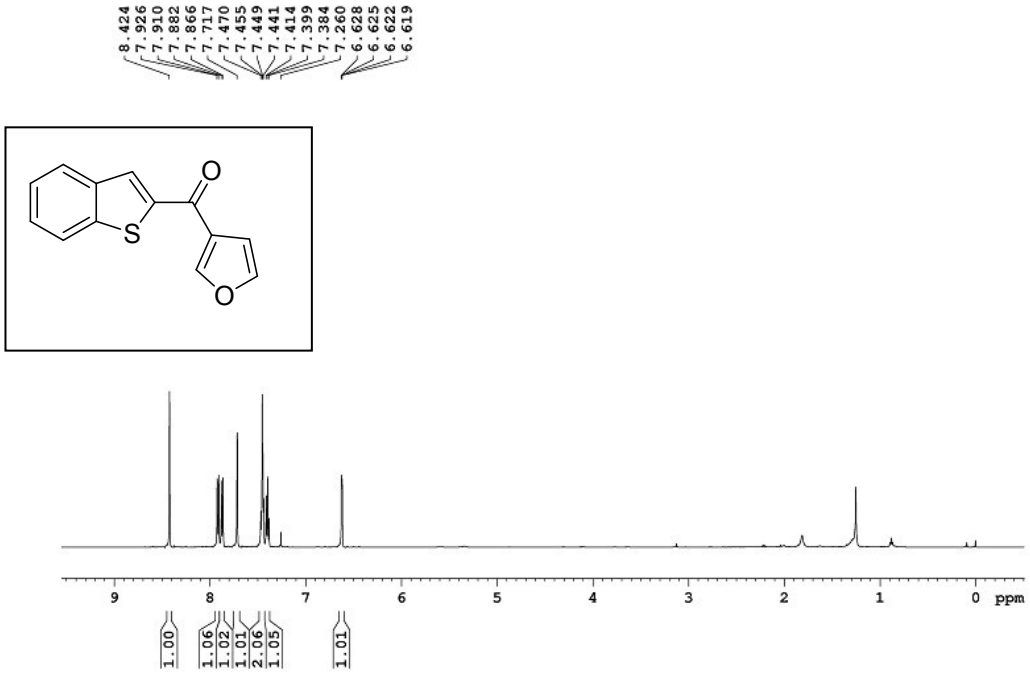


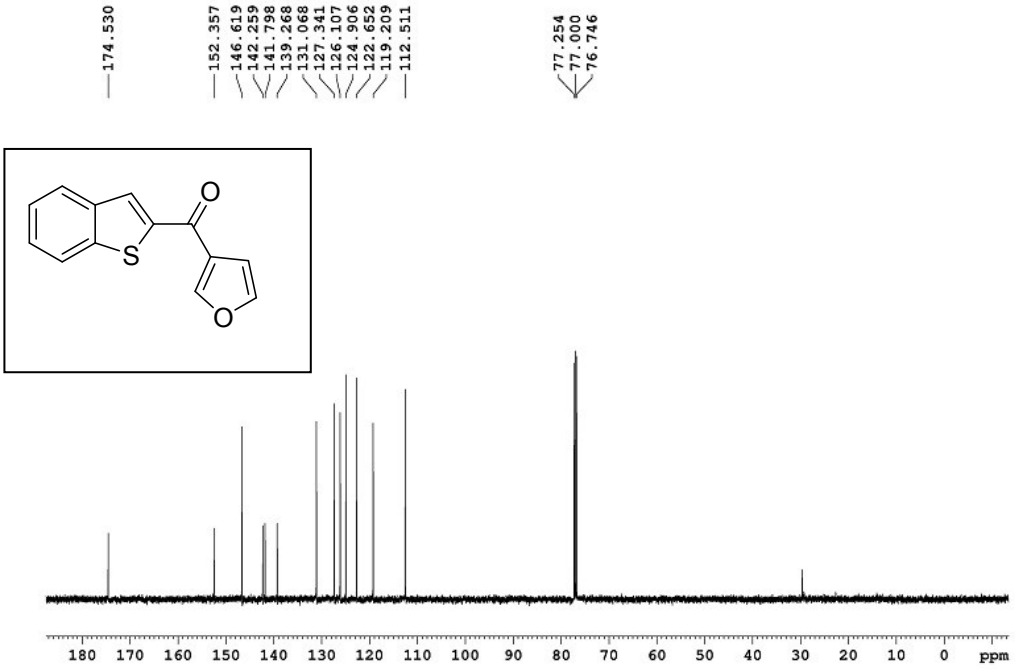
^{1}H and ^{13}C Spectrum of Compound **2k**



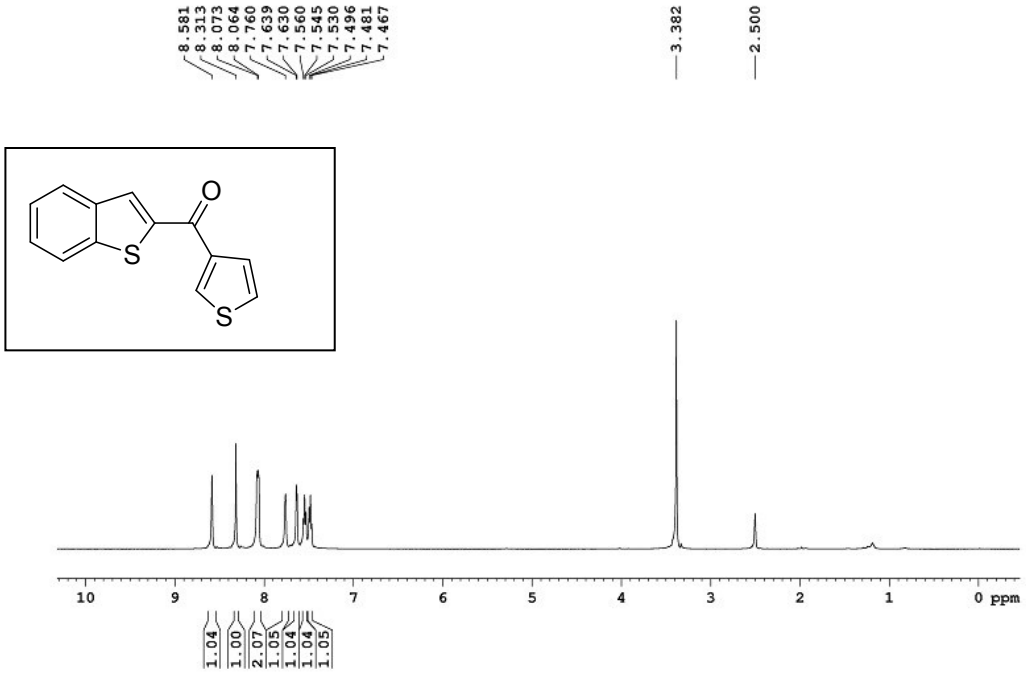


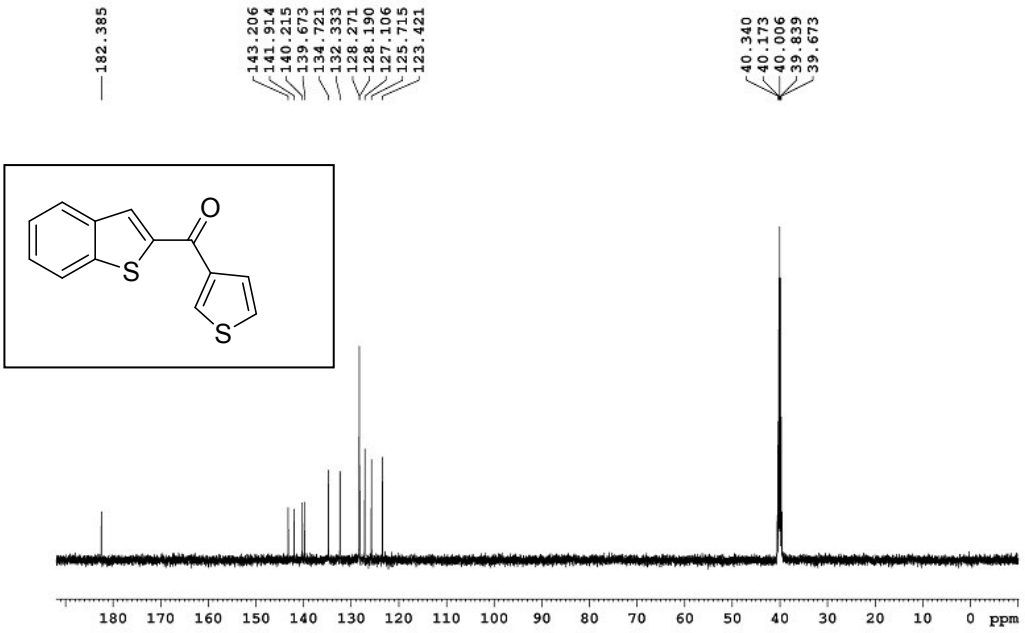
^{1}H and ^{13}C Spectrum of Compound **2l**



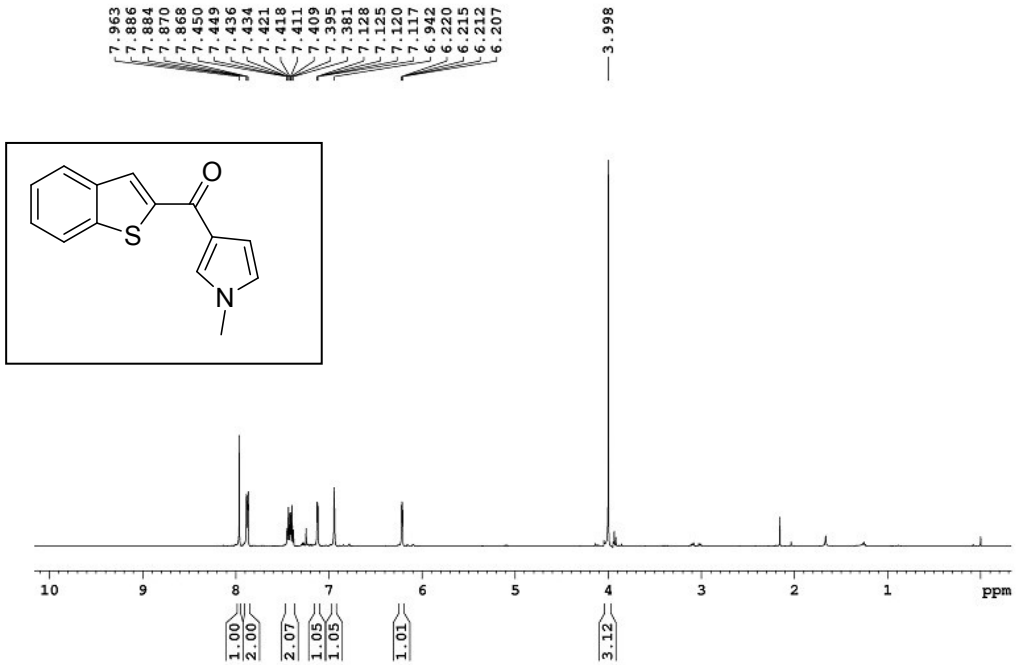


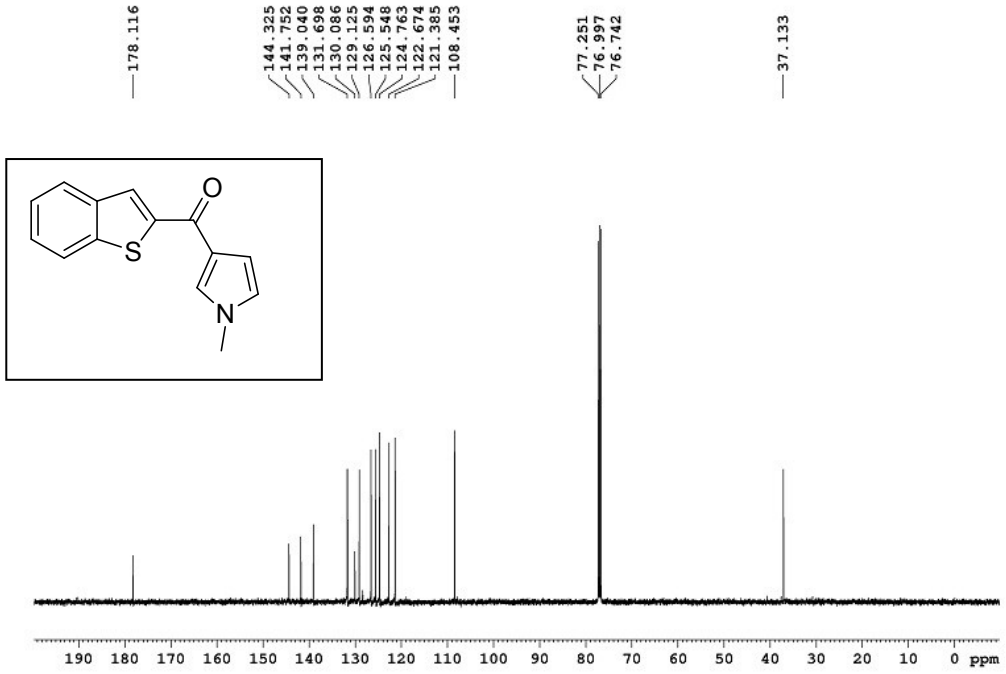
^{1}H and ^{13}C Spectrum of Compound **2m**



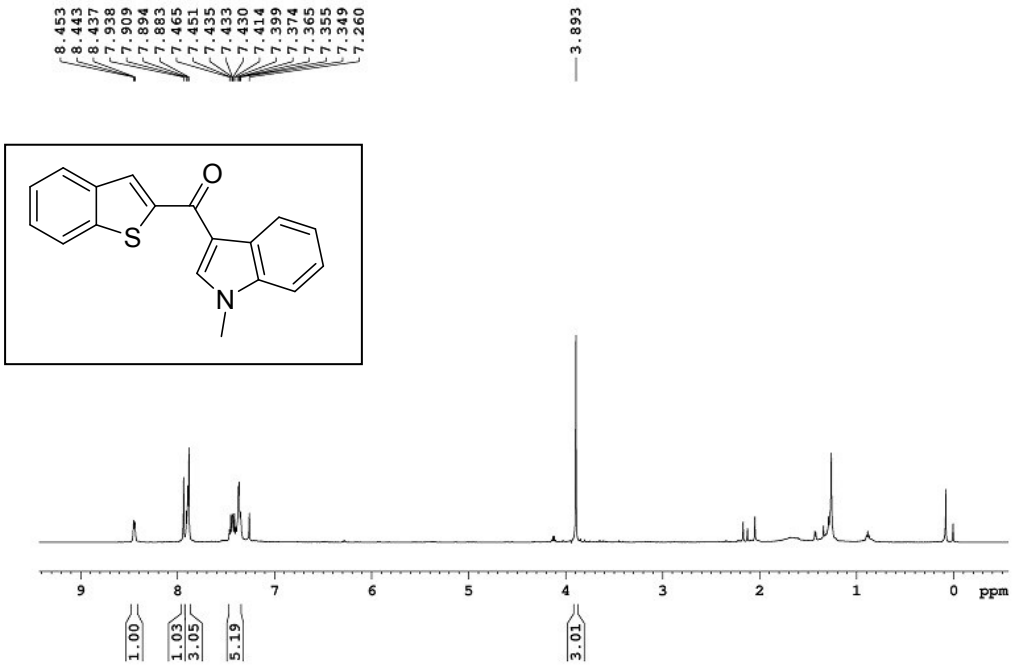


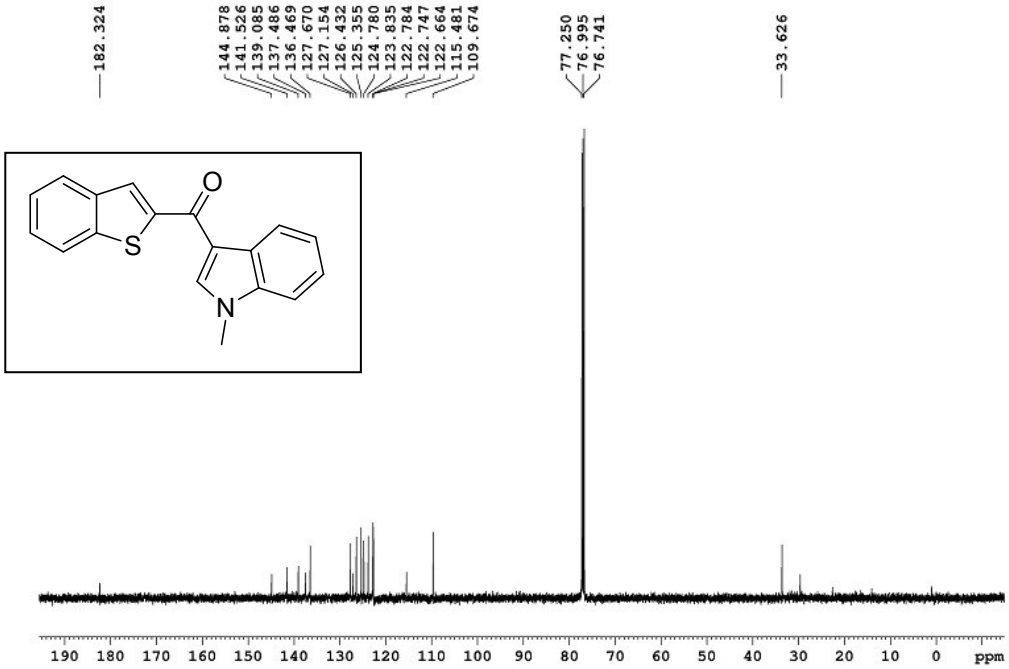
^{1}H and ^{13}C Spectrum of Compound **2n**



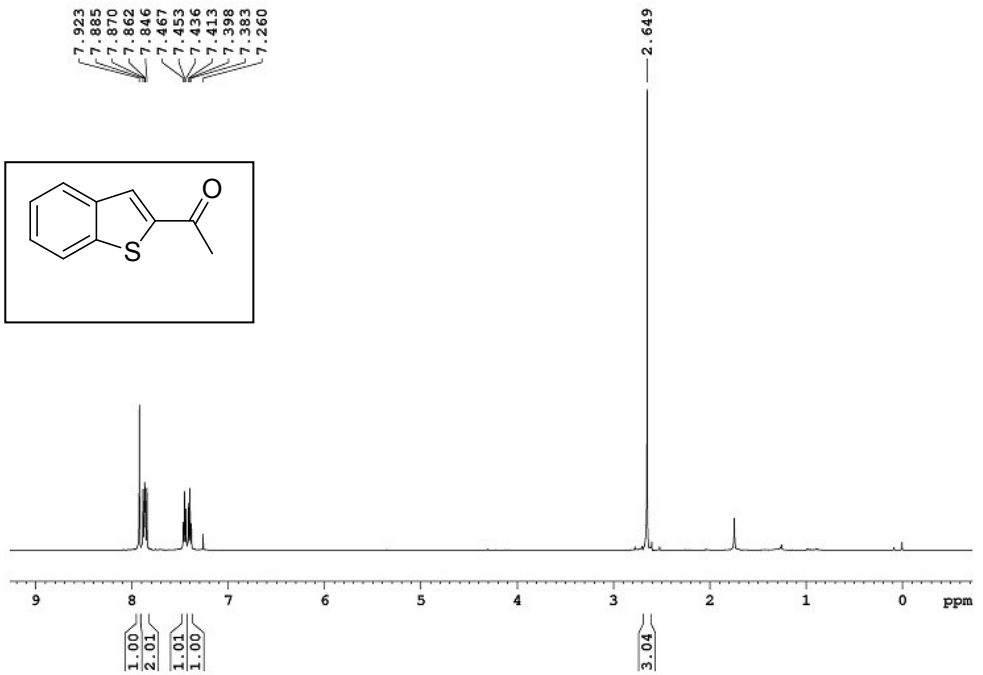


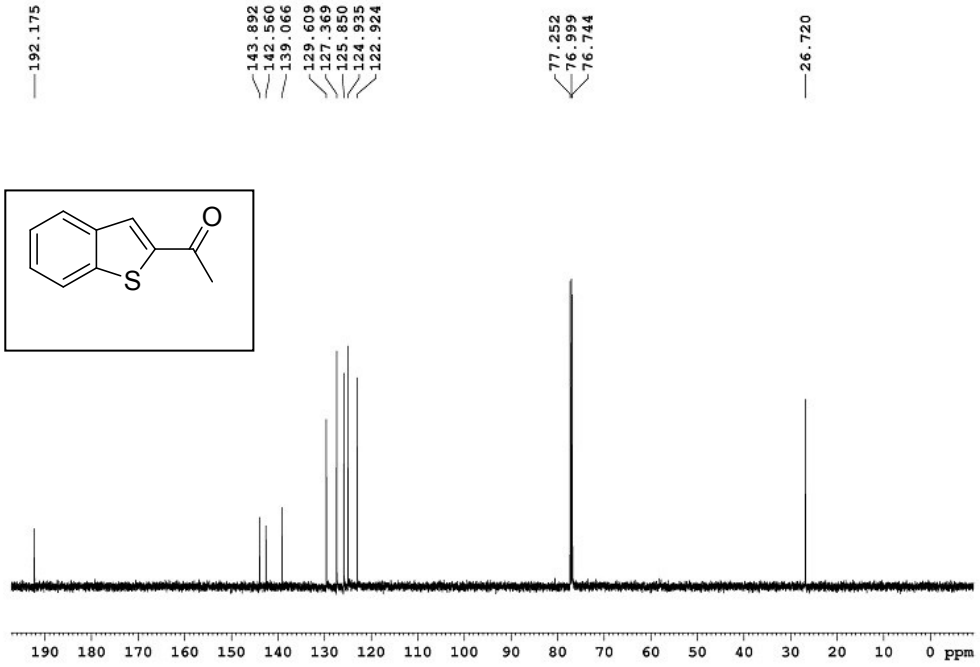
^{1}H and ^{13}C Spectrum of Compound **2o**



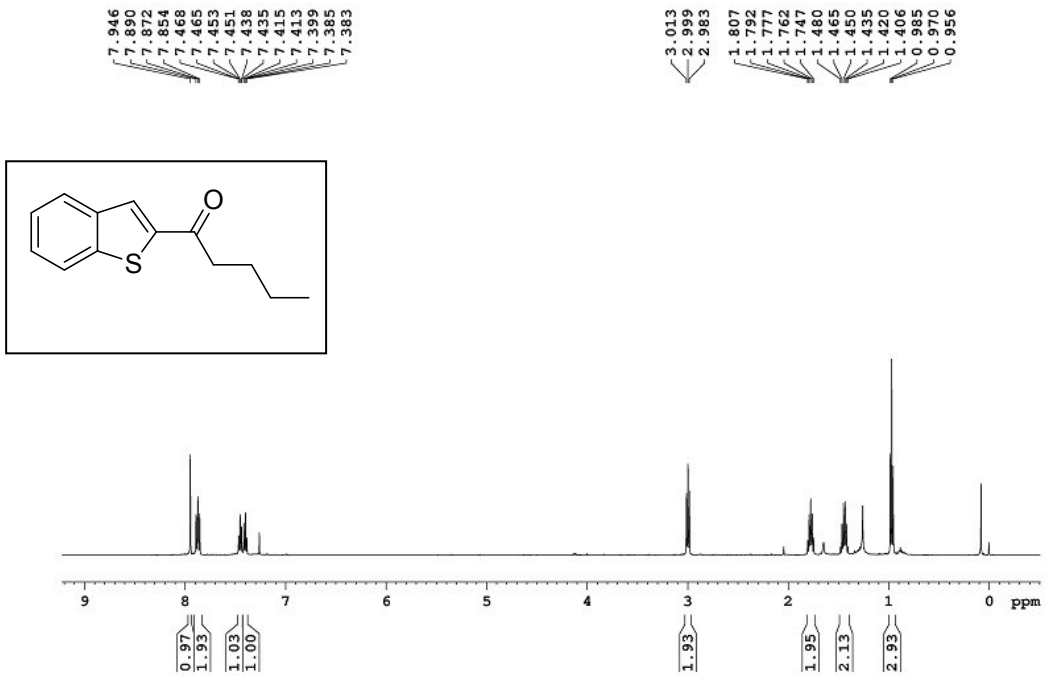


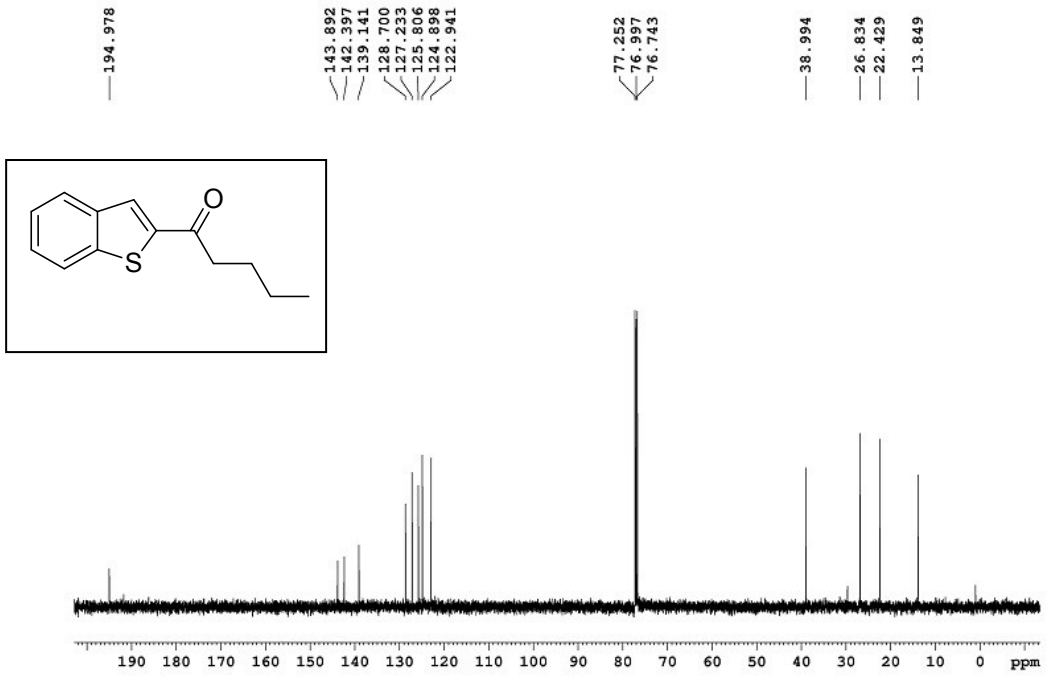
^{1}H and ^{13}C Spectrum of Compound **2p**



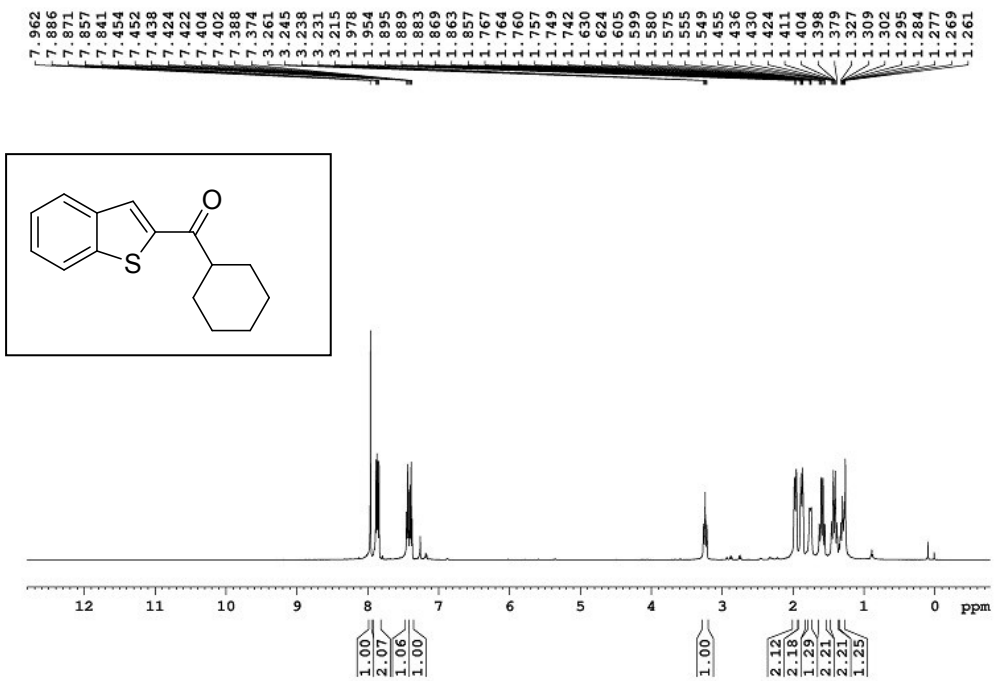


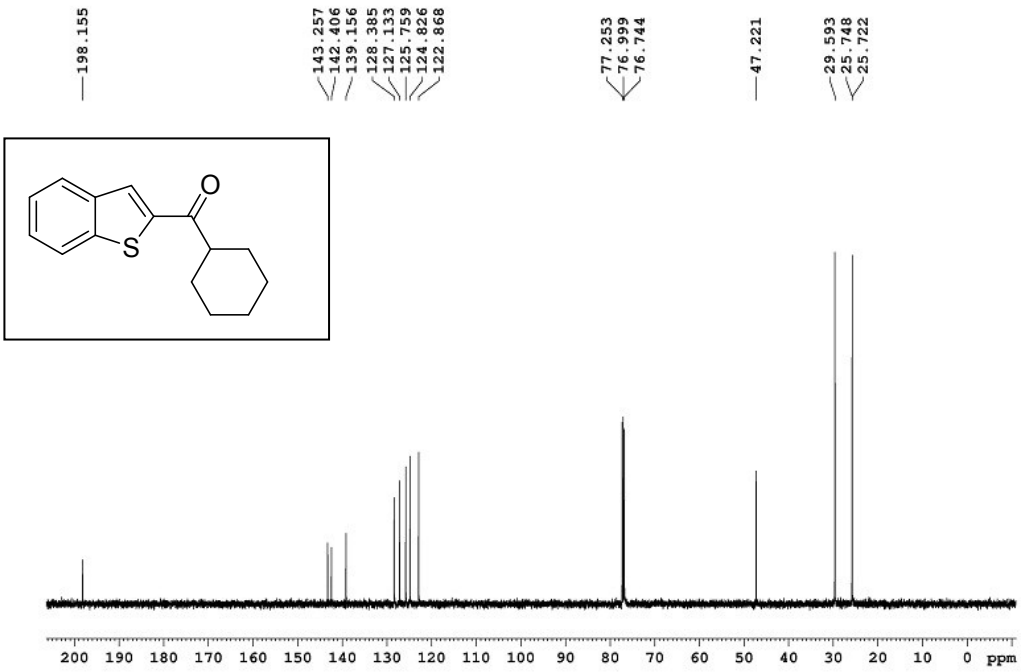
^{1}H and ^{13}C Spectrum of Compound **2q**



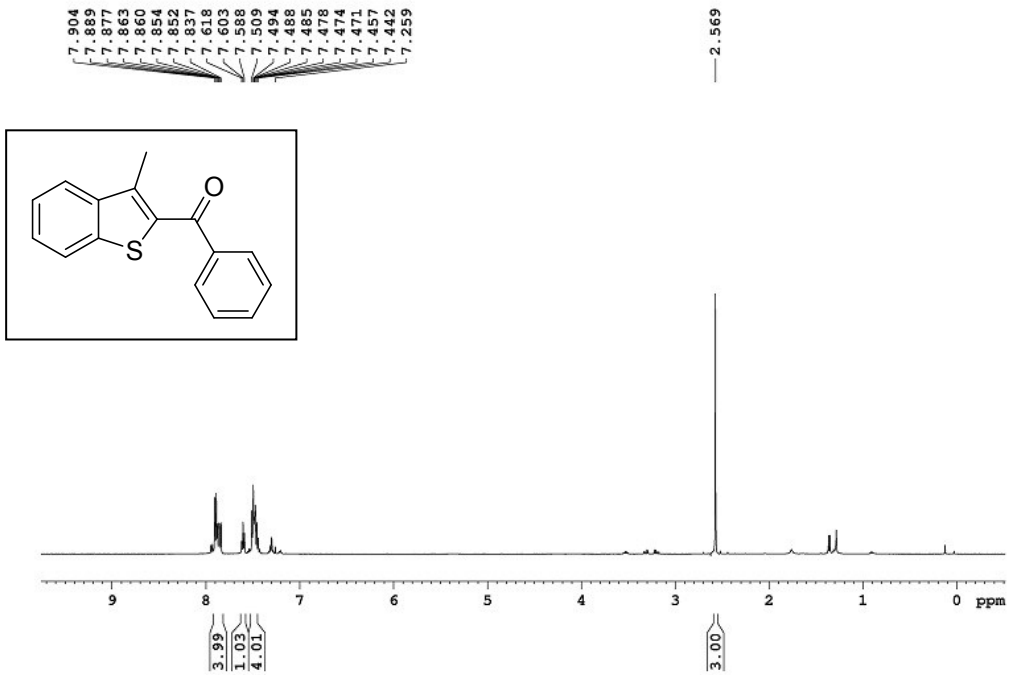


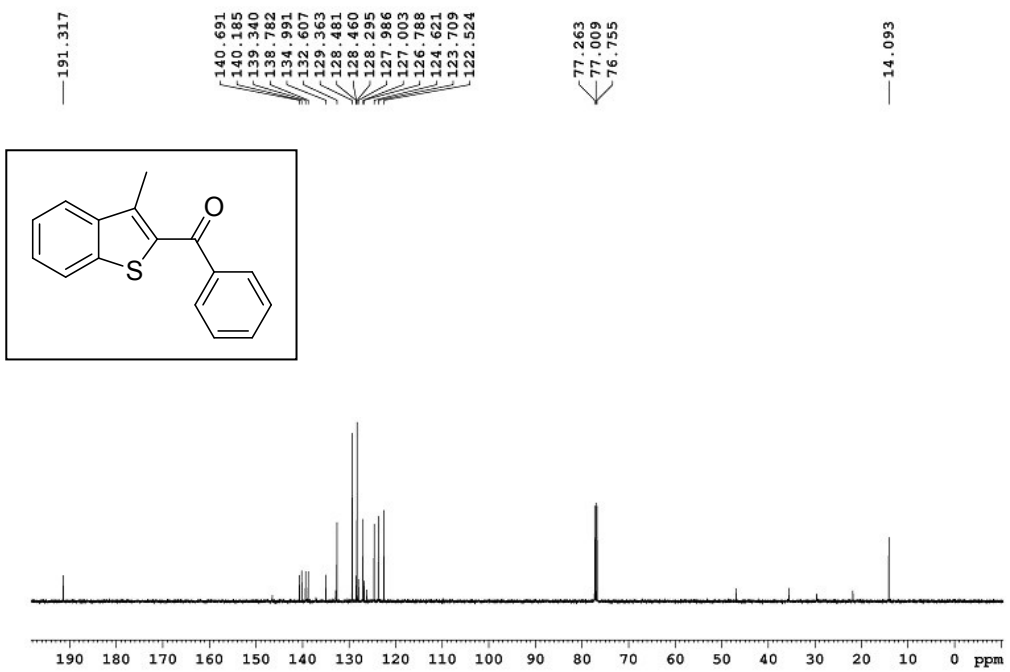
^{1}H and ^{13}C Spectrum of Compound **2r**



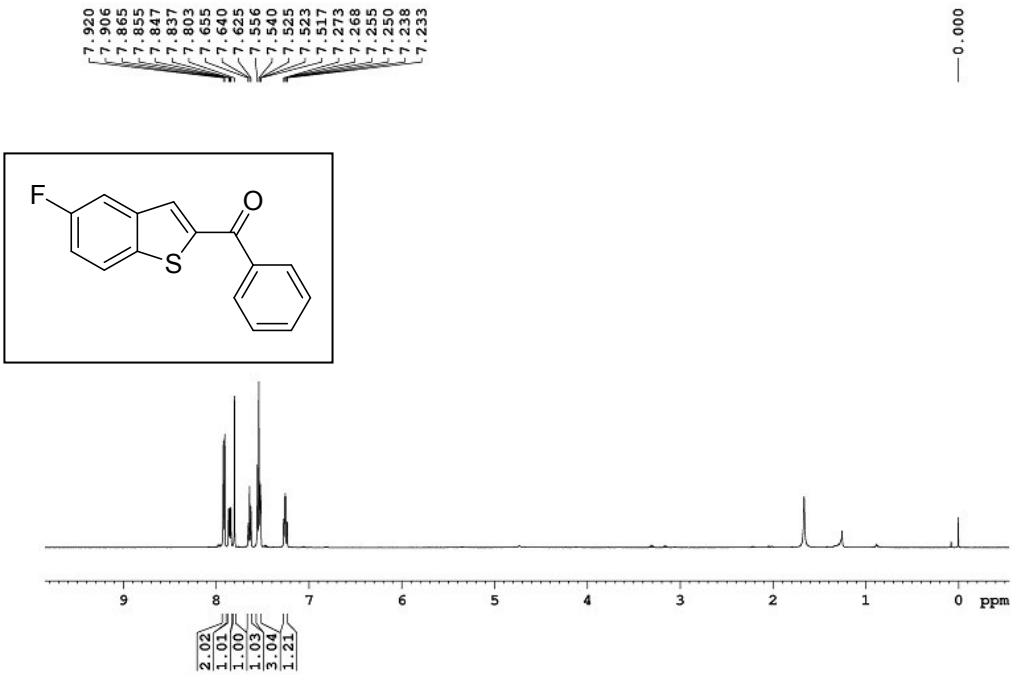


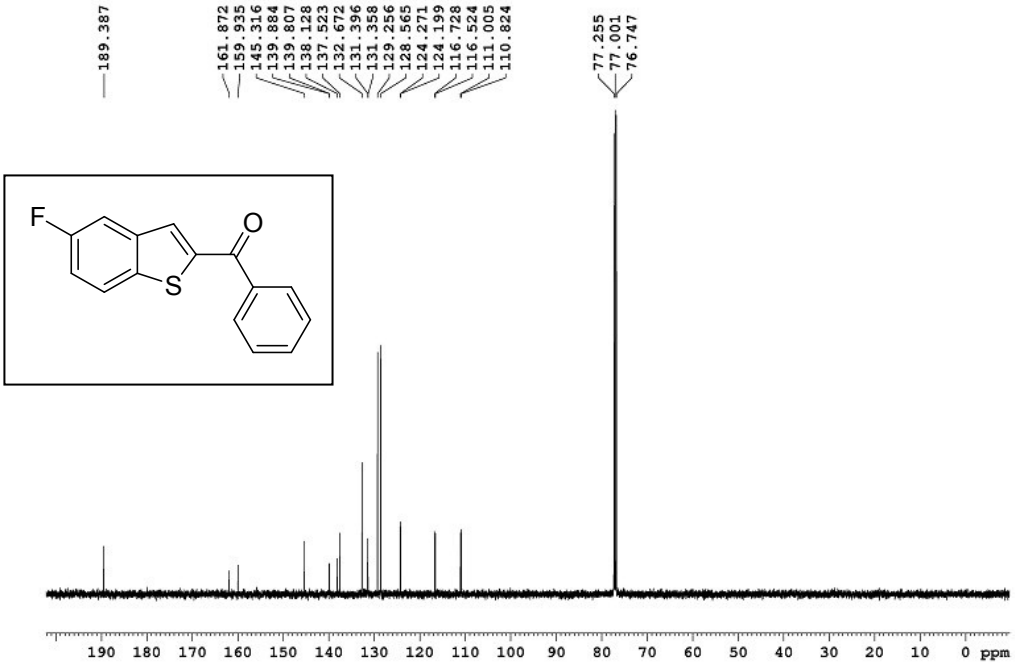
^{1}H and ^{13}C Spectrum of Compound **2s**



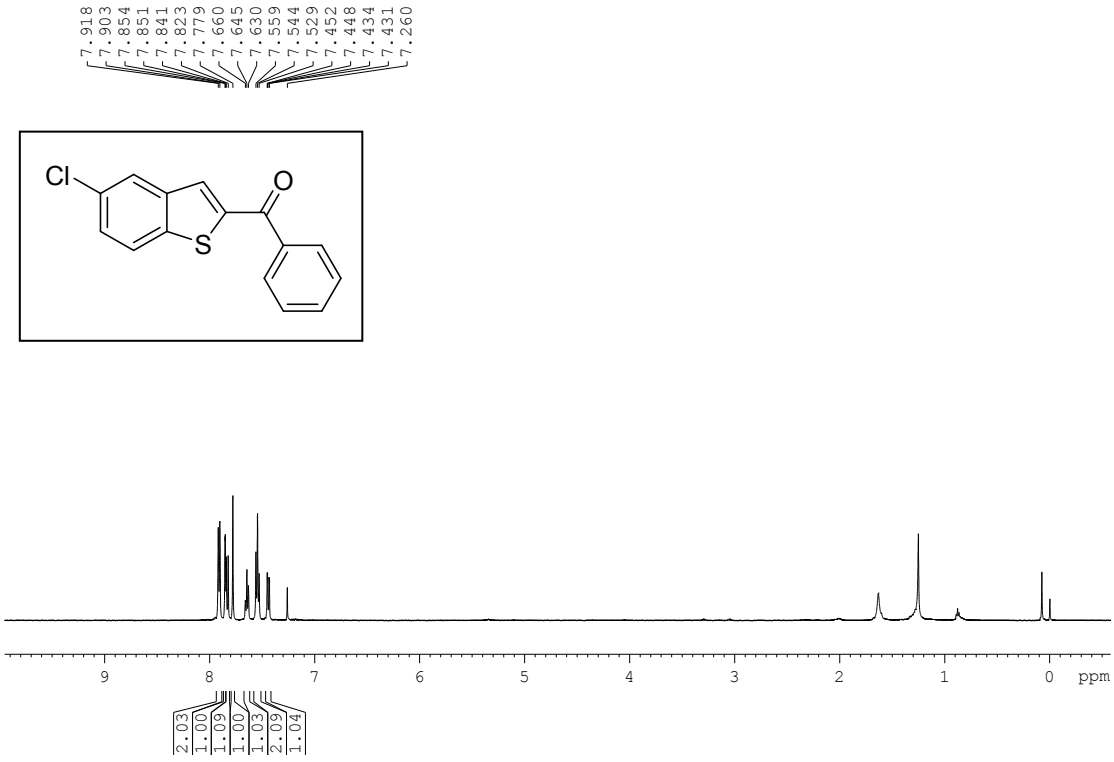


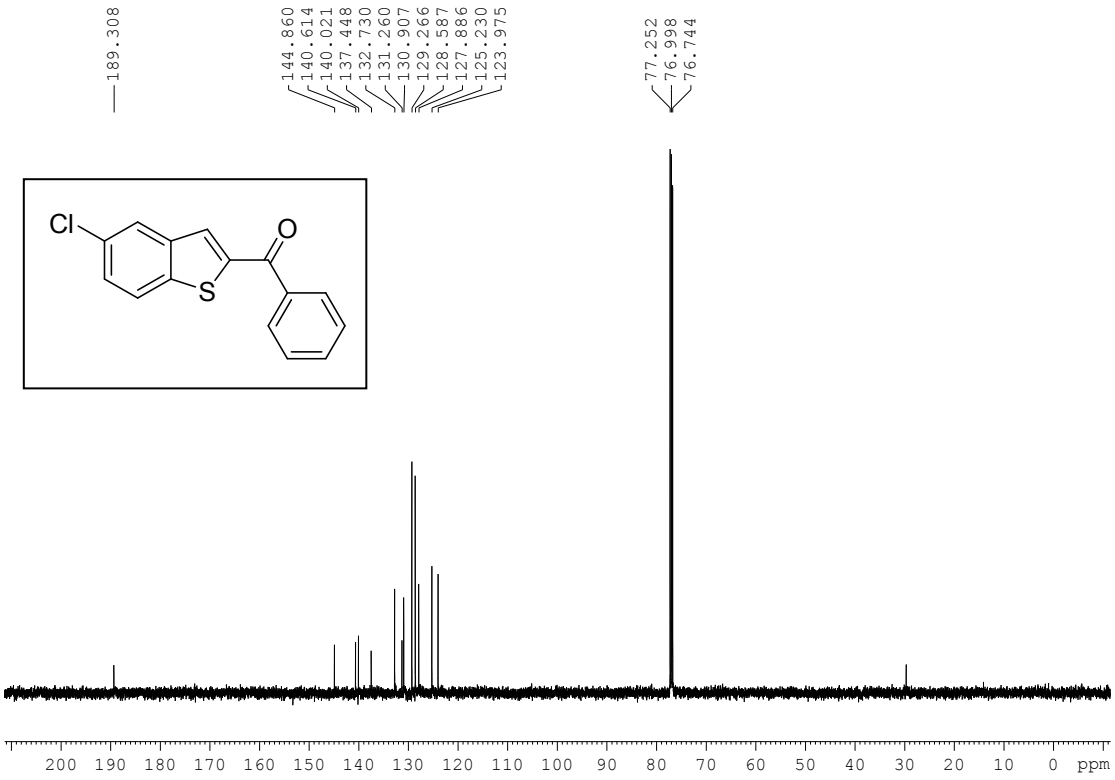
^{1}H and ^{13}C Spectrum of Compound **2t**



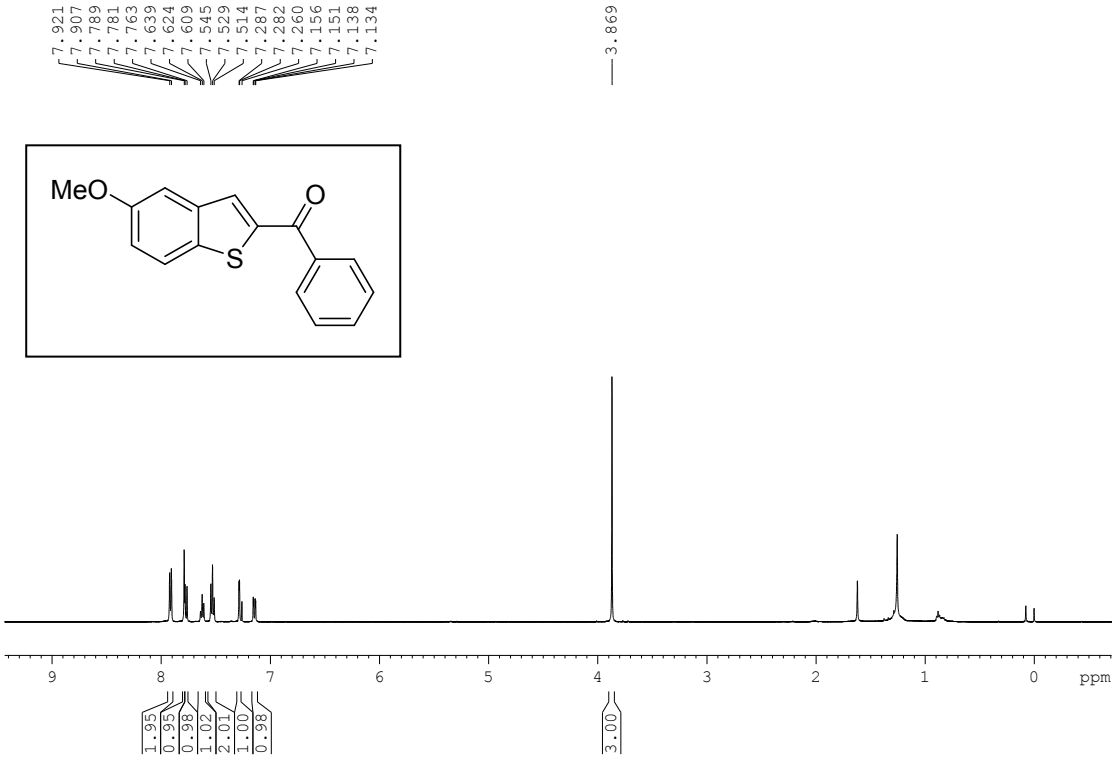


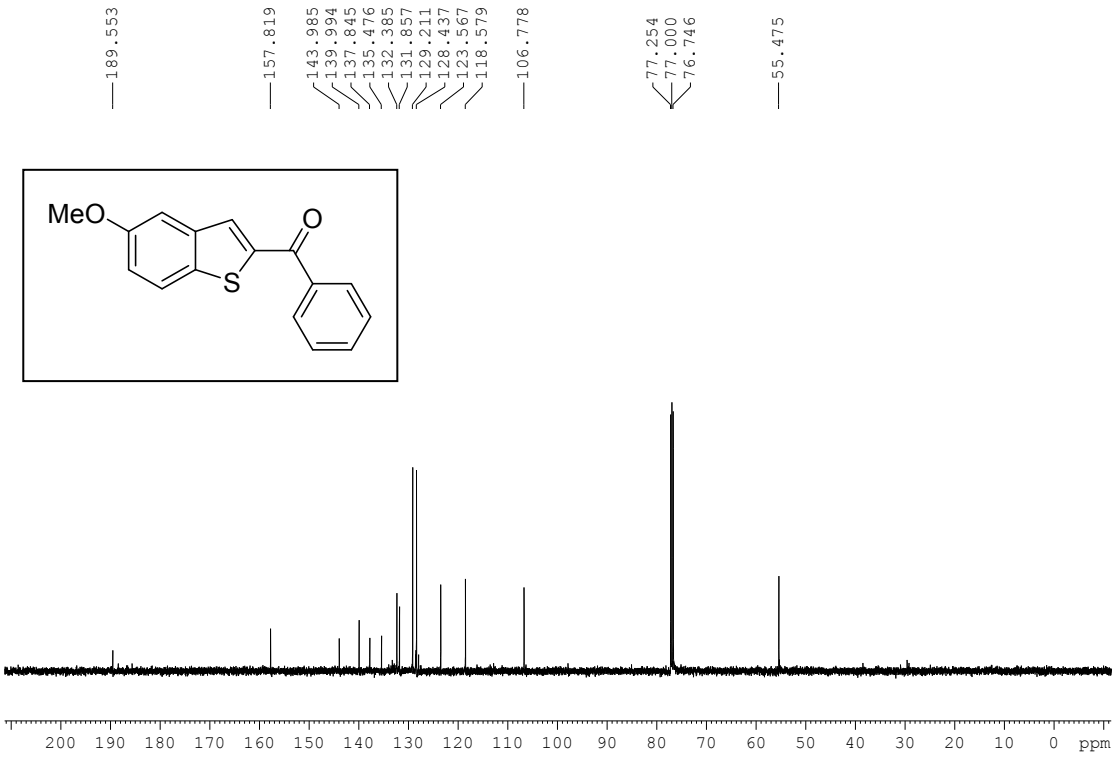
^{1}H and ^{13}C Spectrum of Compound **2u**



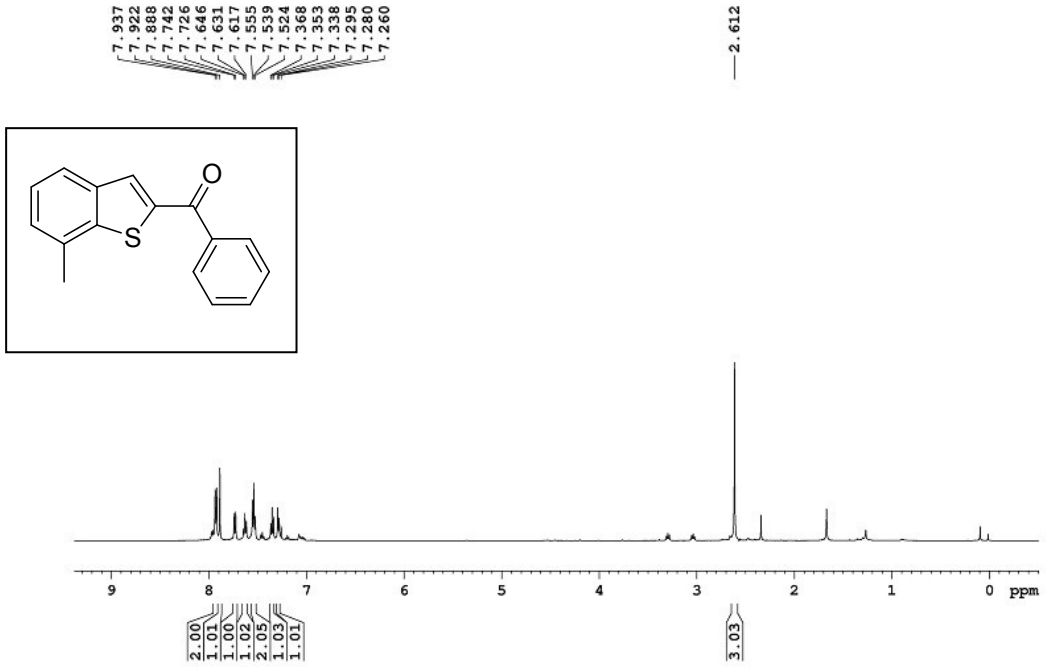


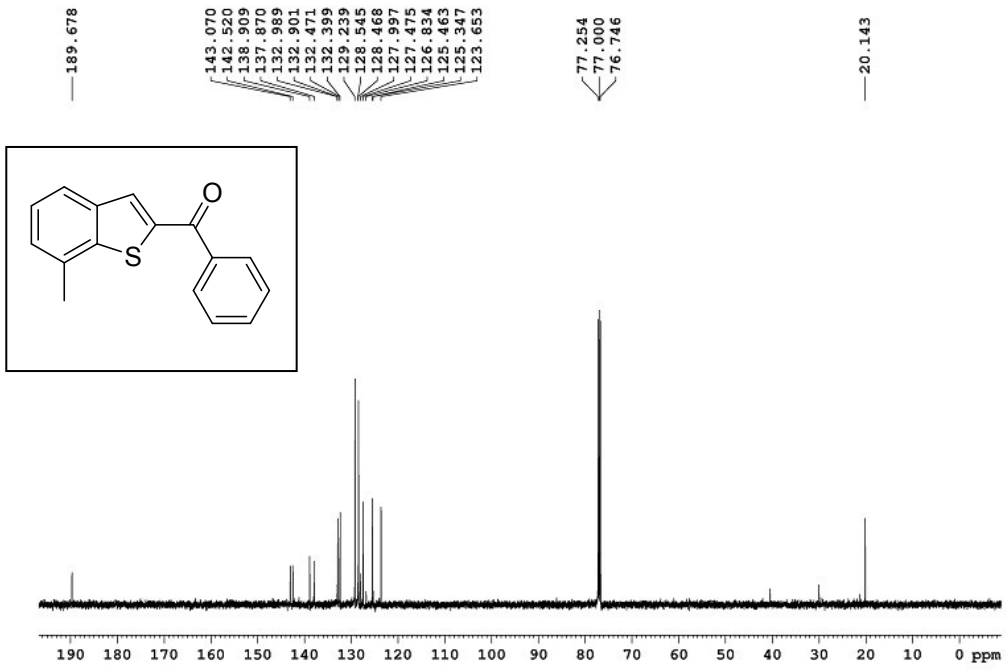
^{1}H and ^{13}C Spectrum of Compound **2v**



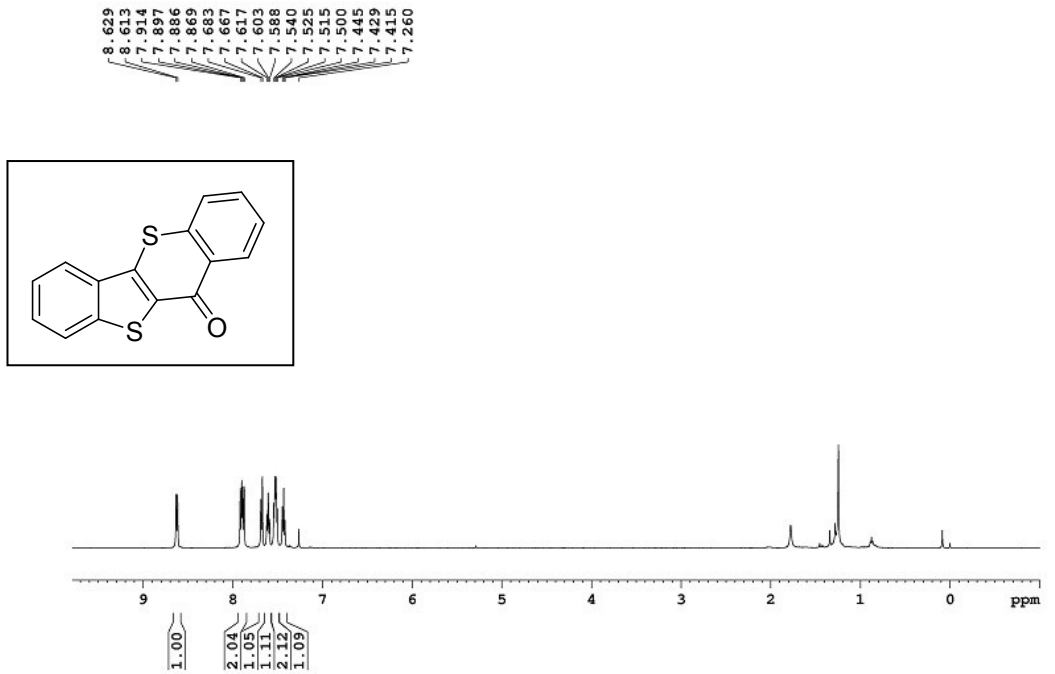


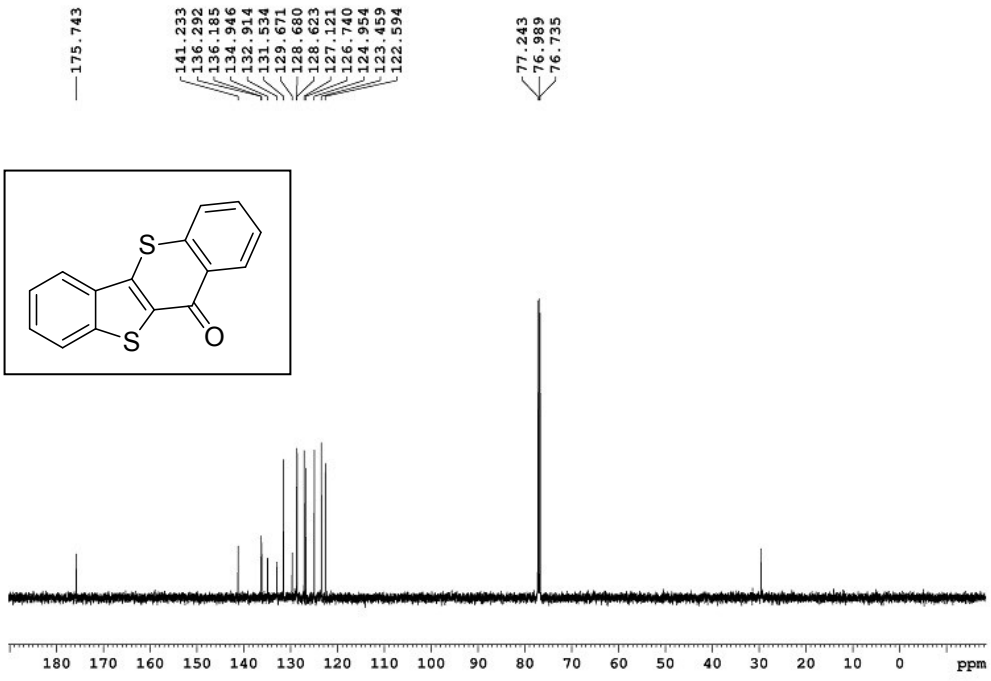
^{1}H and ^{13}C Spectrum of Compound **2w**



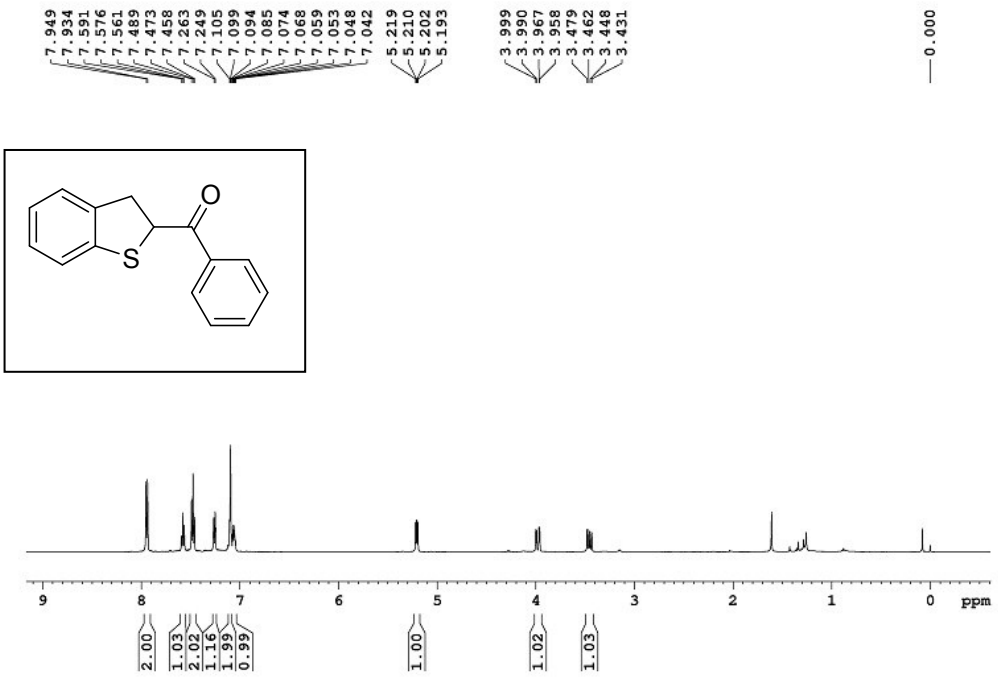


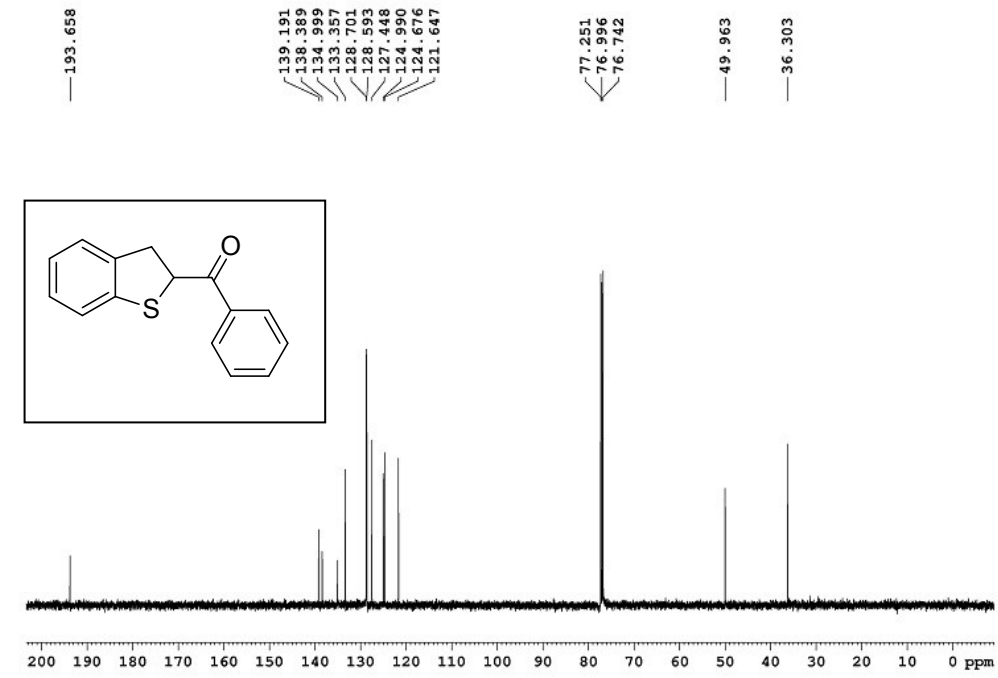
^{1}H and ^{13}C Spectrum of Compound **2x**



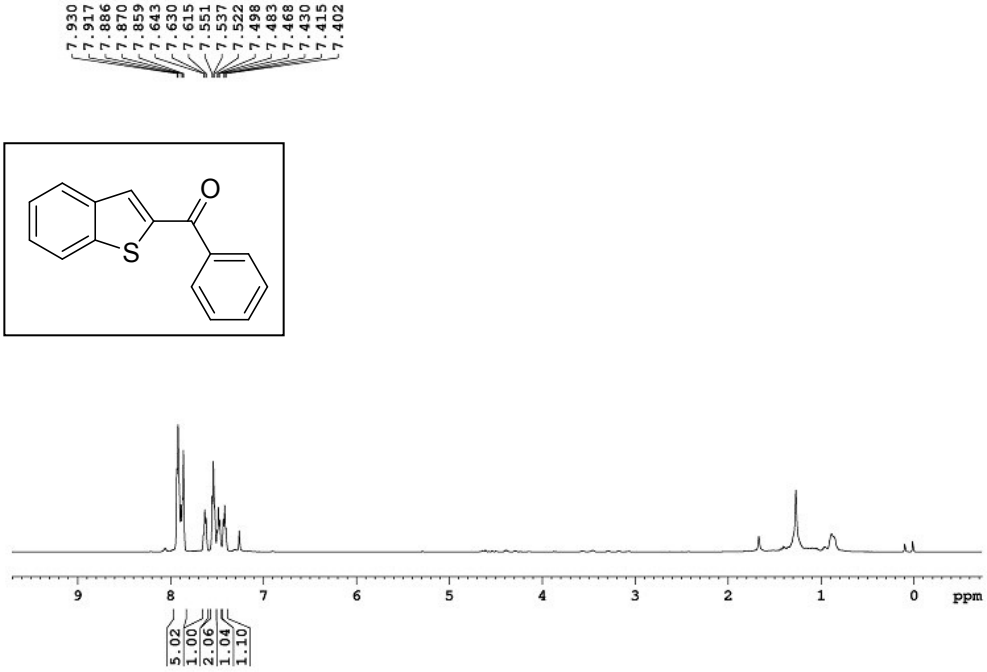


^{1}H and ^{13}C Spectrum of Compound **3a**





Scanned ^{1}H NMR Spectra of Deuteration Experiment 1



Scanned ^{1}H NMR Spectra of Deuteration Experiment 2