Supporting information

As many as six tandem reactions in one step! – Unprecedented formation of highly functionalized benzothiophenes

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General experimental information: All reactions were carried out under nitrogen atmosphere using dry solvents under anhydrous conditions, unless otherwise mentioned. Acetyl acetone, Dimethyl malonate, Diethyl malonate and Ethyl acetoacetate were distilled before use. Triethylamine was dried over calcium hydride and distilled under nitrogen atmosphere. Thin-layer chromatography (TLC) was performed on 0.25 mm silica gel plates (60 F254 grade) from Merck, and were analyzed using a 254 nm UV light. The chromatographic separation was carried out on 100-200 mesh silica gel. Melting points were obtained on electro-thermal apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 MHz instrument, and the chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane, with *J* values in Hertz. The splitting patterns in ^{1}H NMR spectra are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublet; bs = broad singlet; qt = quintet; dt = doublet of triplet; m = multiplet. ^{13}C NMR data are reported with the solvent peak ($CDCl_3$ = 77.0) as the internal standard. High-resolution mass spectra (HRMS) were recorded on a Waters Q-Tof *micro*^{TM} spectrometer with lock spray source. Infrared spectra were recorded using a Nicolet 6700 FT-IR spectrophotometer.

The intensity data collection during X-ray crystallographic analysis was carried out on a Bruker AXS (kappa apex II) diffractometer[1] equipped with graphite monochromated Mo (K_α) radiation. The data were collected for θ up to 25^{o} for Mo (K_α) radiation. ω and ϕ scans were employed to collect the data. The frame width for ω was set to 0.5 deg for data collection. The frames were integrated and data were reduced for Lorentz and polarization correction using SAINT- Plus. The multi-scan

[1] Bruker (2004). APEX-II and SAINT-Plus (Version 7.06a), Bruker AXS Inc., Madison, Wisconsin, USA.

absorption correction[2] was applied to the data. All structures were solved using SIR-92 and refined using SHELXL-97.[3] The molecular and packing diagrams were drawn using ORTEP-32[4] and Mercury 1.4.2. The non-hydrogen atoms were refined with anisotropic displacement parameter. All hydrogen atoms could be located in the difference Fourier map. However, the hydrogen atoms bonded to carbons were fixed at chemically meaningful positions and were allowed to ride with parent atom during the refinement. Structures of compounds **6a**, **7a**, **7b**, **8b**, **9b**, **11d** and **12b** discussed in this manuscript were solved using X-ray crystallographic analysis. Their CCDC numbers respectively are 720188, 720189, 735538, 735540, 738524, 720186 and 720185.

General procedure for the preparation of 2, 3-disubstituted benzothiophenes:

Method A: To a stirred suspension of sodium hydride (4 equiv.) in dry THF (5 mL) was added a solution of the active methylene compound (2.2 equiv.) in dry THF (5 mL) at 0 °C drop-wise. After stirring for half an hour at that temperature, freshly prepared dithiodibenzoyl chloride (1 equiv.) in dry THF (5 mL) was added slowly, the mixture allowed to warm to room temperature, and stirring continued for another 96 hours. The reaction mixture was then admixed with 5N HCl, extracted with EtOAc (80 mL), the organic layer was washed with water (75 mL) and dried over anhydrous Na_2SO_4. It was filtered and the solvent was evaporated under reduced pressure to afford a residue which was chromatographed on silica gel using EtOAc /hexanes in a gradient mode to get substituted benzothiophenes.

Method B: To an azeotropically dried mixture of cyclic 1,3 dione (2.2 equiv.) and $SmCl_3$ (0.2 equiv.) was added toluene (5 mL) followed by triethylamine, and the mixture was stirred at room temperature for 20 min. To this was added a solution of

[2] Bruker (1999). SADABS, Bruker AXS Inc., Madison, Wisconsin, USA.
[3] Sheldrick, G. M. (1997). SHELX97 and SHELXL97. University of Göttingen, Germany.
[4] ORTEP3 for windows. Farrugia, L.J. *J. Appl. Cryst.* **1997**, 30, 565.

dithiodibenzoyl chloride (1 equiv. in Toluene:DMF, 14:1, 15 ml) drop-wise and the mixture was refluxed under anhydrous condition for 3 days. The reaction mixture was worked-up as discussed in Method A and the residue was chromatographed on silica gel using EtOAc /hexanes in a gradient mode to get substituted benzothiophenes.

I) Reaction of dithiodibenzoyl chloride (3) with cyclic 1,3-diones (4a-f)

*a) With 5,5-dimethyl cyclohexane 1,3 dione (**4a**)*

Dimedone (0.196 g, 2.4 mmol) was reacted with dithiodibenzoyl chloride (0.2 g, 0.583 mmol) according to the procedure discussed in Method B to get **6a** (33 mg, 20% yield) and **7a** (85 mg, 49% yield) as white crystalline solids. The same reaction when repeated according to method A, at shorter reaction time (20 min.) exclusively gave the di-O-aroylated product of **4a** with **3** in 50% yield.

Analytical data for **6a**: R_f (5% EtOAc /hexanes) 0.4; mp 118-120 °C; ^{1}H NMR ($CDCl_3$) δ 7.98 (d, 1H, *J* = 8 Hz), 7.87 (d, 1H, *J* = 8 Hz), 7.61 (dd, 1H, *J* = 8 Hz), 7.51 (dd, 1H, *J* = 7.25 Hz), 2.88 (d, 1H, *J* = 16.8 Hz), 2.73 (d, 1H, *J* = 16.8 Hz), 1.35 (s, 3H), 1.34 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 185.6, 177.1, 172.5, 148.9, 130.9, 125.7, 124.9, 123.9, 122.9, 116.4, 113.3, 43.5, 42.7, 22.7, 22.4; IR (neat) cm^{-1}: 2976, 2359, 1813, 1715, 1517, 1412; HRMS (ESI) exact mass calcd. for $C_{15}H_{12}O_4NaS$ $(M+Na)^+$ 311.0354 , found $(M+Na)^+$ 311.0354.

5-(3-hydroxybenzo[b]thiophen-2-yl)-3,3-dimethyl-5-oxopentanoic acid (7a)

Analytical data for **7a:** R_f (25% EtOAc /hexanes) 0.23; mp 106-109 °C; ^{1}H NMR ($CDCl_3$) δ 12.25 (bs, 1H), 8.00 (d, 1H, *J* = 8 Hz), 7.73 (d, 1H, *J* = 8.4 Hz), 7.55 (dd, 1H, *J* = 7.6,6.8 Hz), 7.42 (dd, 1H, *J* = 7.8,8.0 Hz), 2.88 (s, 2H), 2.59 (s, 2H), 1.23 (S, 6H); ^{13}C NMR ($CDCl_3$) δ 198.9, 176.7, 162.5, 139.3, 130.3, 130.1, 124.8, 123.9, 123.2, 112.5, 50.2, 45.3, 34.0, 28.4 (2C); IR (neat) cm^{-1}: 2960, 2359, 1704, 1604, 1521, 1400; HRMS (ESI) exact mass calcd. for $C_{15}H_{16}O_4NaS$ $(M+Na)^+$ 315.0667,

found $(M+Na)^+$ 315.0662.

*b) With 5-Methyl Cyclohexane-1,3-dione (**4b**)*

5-(3-Hydroxy-benzo[b]thiophen-2-yl)-3-methyl-5-oxo-pentanoic acid (7b)

5-Methyl Cyclohexane-1,3-dione (0.40 g, 3.2 mmol) was reacted with dithiodibenzoyl chloride (0.5 g, 1.4 mmol) according to the procedure discussed in Method B to get 7**b** (150 mg, 35%), **8b** (65 mg, 12%) and **9b** (150 mg, 35%) as a pale yellow solids. Analytical data for **7b:** R_f (25% EtOAc /hexanes) 0.2; mp 96-97 °C; ^{1}H NMR ($CDCl_3$) δ 12.3 (bs, 1H), 7.98 (d, 1H, *J* = 8 Hz), 7.23 (d, 1H, *J* = 8.4 Hz), 7.53 (dd, 1H, *J* = 7.4, 7.6 Hz), 7.4 (dd, 1H, *J* = 7.2, 7.6 Hz), 2.89-2.83 (m, 1H), 2.76-2.66 (m, 2H), 2.54 (dd, 1H, *J* = 15.6, 6 Hz), 2.37 (dd, 1H, *J* =15.6, 7.2 Hz), 1.13 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 198.1, 178.0, 162.1, 139.1, 130.4, 129.9, 124.8, 123.8, 123.3, 111.5, 46.9, 40.6, 27.0, 20.1; IR (neat) cm^{-1}: 2924, 1720, 1610; HRMS (ESI) exact mass calcd. for $C_{14}H_{14}O_4SNa$ $(M+Na)^+$ 301.0513, found $(M+Na)^+$ 301.0513.

5-(3-Hydroxy-benzo[b]thiophene-2-carbonyl)-4-methyl-dihydro-furan-2-one (8b)

Analytical data for **8b:** R_f (25% EtOAc /hexanes) 0.25; mp 135-137 °C; ^{1}H NMR ($CDCl_3$) δ 12.4 (bs, 1H), 8.03 (d, 1H, *J* = 8 Hz), 7.74 (d, 1H, *J* = 8.4 Hz), 7.59 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.43 (dd, 1H, *J* = 8.0, 7.6 Hz), 4.79 (d, 1H, *J* = 5.2 Hz), 2.84 (m, 2H), 2.28 (m, 1H), 1.39 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 194.1, 175.0, 165.4, 141.1, 130.8, 129.5, 124.0, 123.9, 123.2, 107.3, 86.2, 35.3, 35.0, 19.0; IR (neat) cm^{-1}: 2924, 1780, 1601, 1515; HRMS (ESI) exact mass calcd. for $C_{14}H_{13}O_4S$ $(M+H)^+$ 277.0535, found $(M+H)^+$ 277.0531.

5-(3-Hydroxy-benzo[b]thiophene-2-carbonyl)-4-methyl-dihydro-furan-2-one (9b)

Analytical data for **9b:** R_f (25% EtOAc /hexanes) 0.2; mp 108 °C; ^{1}H NMR ($CDCl_3$) δ 12.5 (bs, 1H), 8.04 (d, 1H, *J* = 8 Hz), 7.76 (d, 1H, *J* = 8.4 Hz), 7.6 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.5 (dd, 1H, *J* = 7.6, 7.6 Hz), 5.2 (d, 1H, *J* = 5.2 Hz), 3.1 (m, 1H),

2.78 (dd, 1H, *J* = 17.4, 8 Hz) 2.43 (dd , 1H *J* = 17.2, 6.8 Hz), 1.1 (d, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 193.8, 175.3, 165.0, 140.9, 130.9, 129.5, 125.0, 124.1, 123.3, 109.0, 82.9, 35.6, 33.9, 15.0; IR (neat) cm^{-1}: 2926, 1789, 1605, 1514; HRMS (ESI) exact mass calcd. for $C_{14}H_{12}O_4NaS$ $(M+Na)^+$ 299.0354, found $(M+Na)^+$ 299.0361.

*c) With 5-phenyl Cyclohexane-1,3-dione (**4c**)*

5-(3-Hydroxy-benzo[b]thiophen-2-yl)-5-oxo-3-phenyl-pentanoic acid (7c)

5-phenyl Cyclohexane-1,3-dione (1.08 g, 5.77 mmol) was reacted with dithiodibenzoyl chloride (0.9 g, 2.6 mmol) according to the procedure discussed in Method B to get **7c** as a pale brown solid (420 mg, 43%). Analytical data for **7c:** R_f (5% EtOAc /hexanes) 0.35; mp 148 °C; ^{1}H NMR ($CDCl_3$) δ 12.1 (bs, 1H) 7.94 (d, 1H, *J* = 8 Hz), 7.70 (d, 1H, *J* = 8.5 Hz), 7.51 (dd, 1H, *J* = 8, 7.25 Hz), 7.38 (dd, 1H, *J* = 7.75, 7.5 Hz), 7.30-7.25 (m, 4H), 7.22-7.19 (m, 1H), 3.89 (qt, 1H, *J* = 7, 7.5 Hz), 3.15 (dd, 1H, *J* = 16, 7 Hz), 3.11 (dd, 1H, *J* = 16, 7.5 Hz), 2.86 (dd, 1H, *J* = 16.25, 6.5 Hz), 2.74 (dd, 1H, *J* = 16, 8 Hz), ^{13}C NMR ($CDCl_3$) 196.9, 177.0, 162.0, 142.4, 139.1, 130.4, 129.9, 128.8 (2C), 127.3 (2C), 127.1, 124.8, 123.8, 123.3, 111.3, 46.7, 40.2, 37.4; IR (neat) cm^{-1}: 3236, 2923, 2335, 1709, 1606; HRMS (ESI) exact mass calcd. for $C_{19}H_{16}O_4NaS$ $(M+Na)^+$ 363.0667, found $(M+Na)^+$ 363.0662.

*d) With Cyclohexane-1,3-dione (**4e**)*

5-(3-hydroxybenzo[b]thiophen-2-yl)-5-oxopentanoic acid (**7e)**

Cyclohexane-1,3-dione (0.156 g, 1.4 mmol) was reacted with dithiodibenzoyl chloride (0.2 g, 0.583 mmol) according to the procedure discussed in Method B to get **7e** as a pale brown solid. (75 mg, 51%). Analytical data for **7e:** R_f (50% EtOAc /hexanes) 0.29; mp 143-145 °C; ^{1}H NMR ($CDCl_3$+CD_3OD) δ 12.24 (bs, 1H), 8.00 (d, 1H, *J* = 7.6 Hz), 7.74 (d, 1H, *J* = 8.4 Hz), 7.55 (dd, 1H, *J* = 7.6,7.4 Hz), 7.43 (dd, 1H,

J = 7.6,7.6 Hz), 2.89 (t, 2H, *J* = 6.8 Hz), 2.54 (t, 2H, *J* = 6.8 Hz), 2.14 (qt, 2H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$+CD_3OD) δ 198.5, 175.4, 161.1, 138.9, 130.2, 129.7, 124.6, 123.5, 123.1, 111.1, 39.6, 32.9, 19.2; IR (neat) cm^{-1}: 2889, 1701, 1601, 1518, 1430, 1195; HRMS (ESI) exact mass calcd. for $C_{13}H_{12}O_4NaS$ $(M+Na)^+$ 287.0354, found $(M+Na)^+$ 287.0360.

*e) Cyclopentane-1,3-dione (**4f**)*

4-(3-Hydroxy-benzo[b]thiophen-2-yl)-4-oxo-butyric acid (7f)

Cyclopentane-1,3-dione (0.157 g, 1.603 mmol) was reacted with dithiodibenzoyl chloride (0.250 g, 0.728 mmol) according to the procedure discussed in Method B to get **7f** as a pale brown solid (60 mg, 35%). Analytical data for **7f:** R_f (5% EtOAc /hexanes) 0.33; ^{1}H NMR ($CDCl_3$) δ 7.97 (d, 1H, *J* = 8 Hz), 7.76 (d, 1H, *J* = 8 Hz), 7.55 (dd, 1H, *J* = 7.2 Hz), 7.43 (dd, 1H, *J* = 7.4 Hz), 2.89 (t, 2H, *J* = 6.5), 2.14 (t, 2H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$+CD_3OD) δ 197.0, 174.6, 160.7, 138.8, 130.1, 129.6, 124.6, 123.4, 123.1, 110.9, 35.2, 27.5; HRMS (ESI) exact mass calcd. for $C_{12}H_{10}O_4NaS$ $(M+Na)^+$ 273.0198, found $(M+Na)^+$ 273.0190.

II) Reaction of dithiodibenzoyl chloride (3) with acyclic 1,3-diones (10a-d)

*a) With acetyl acetone (**10a**)*

1,1'-(3-oxo-2,3-dihydrobenzo[b]thiophene-2,2-diyl)diethanone (11a)

Acetylacetone (0.056 mL, 0.641 mmol) on reaction with dithiodibenzoyl chloride (0.1 g, 0.291 mmol) according to Method A for 12h to gave **11a** (21 mg, 31% yield) and **13a** (10 mg, 18% yield) as white crystalline solids. Analytical data for **11a:** R_f (10% EtOAc /hexanes) 0.3; mp 175-177 °C; ^{1}H NMR ($CDCl_3$) δ 8.19 (d, 1H, *J* = 7.2 Hz), 7.48 (dd, 1H, *J* = 7.2 ,7.2 Hz), 7.23 (dd, 1H, *J* = 7.2, 7.2 Hz), 7.10 (d, 1H, *J* = 8.4 Hz), 2.30 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 198.6 (2x C=O), 170.9, 143.4, 133.7, 133.0, 125.2, 124.4, 124.1, 101.3, 24.2 (2C); IR (neat) cm^{-1}: 1630, 1550, 1358, 1296, 729;

HRMS (ESI) exact mass calcd. for $C_{12}H_{11}O_3S$ $(M+H)^+$ 235.0429, found $(M+H)^+$ 235.0434.

1-(3-hydroxybenzo[b]thiophen-2-yl)ethanone (13a)

Acetyl acetone (0.056 ml, 0.641 mmol) on reaction with dithiodibenzoyl chloride (0.1 g, 0.291 mmol) according to Method A for 96 h gave **13a** (50 mg, 90% yield) as a white crystalline solid. Analytical data for **13a:** R_f (2% EtOAc /hexanes) 0.48; mp 76-77 °C;^{1}H NMR ($CDCl_3$) δ 12.28 (bs, 1H), 7.97 (d, 1H, *J* = 8 Hz), 7.72 (d, 1H, *J* = 8.0 Hz), 7.52 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.4 (dd, 1H, *J* = 7.6 ,7.6 Hz), 2.48 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 196.7, 161.5, 139.00, 130.4, 129.7, 124.7, 123.7, 123.2, 111.4, 28.1; IR (neat) cm^{-1}: 2921, 1608, 1517, 1469, 1350; HRMS (ESI) exact mass calcd. for $C_{10}H_9O_2S$ $(M+H)^+$ 193.0323, found $(M+H)^+$ 193.0318.

*b) With ethyl acetoacetate (**10b**)*

Ethyl 3-acetoxybenzo[b]thiophene-2-carboxylate (12b)

Ethyl acetoacetate (0.41 mL, 2.9 mmol) on reaction with dithiodibenzoyl chloride (0.55 g, 1.6 mmol) according to Method A for 12h gave **12b** (150 mg, 39% yield) and **13b** (50 mg, 14% yield) as white crystalline solids. Analytical data for **12b:** R_f (10% EtOAc /hexanes) 0.50; mp 96-98 ^{0}C; ^{1}H NMR ($CDCl_3$) δ 7.79 (d, 1H, *J* = 8 Hz), 7.70 (d, 1H, *J* = 8 Hz), 7.49 (dd, 1H, *J* = 7.4,7.2 Hz), 7.42 (dd, 1H, *J* = 7.6,7.4 Hz), 4.36 (q, 2H, *J* = 7.2 Hz), 2.46 (s, 3H), 1.38 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 168.2, 161.2, 145.3, 137.9, 132.8, 127.9, 125.0, 123.0, 122.0, 119.4, 61.4, 20.7, 14.2; IR (neat) cm^{-1}: 1771, 1702, 1363, 1273; HRMS (ESI) exact mass calcd. for $C_{13}H_{12}O_4NaS$ $(M+Na)^+$ 287.0354, found $(M+Na)^+$ 287.0362.

Ethyl 3-hydroxybenzo[b]thiophene-2-carboxylate (13b)

Ethyl acetoacetate (0.45 mL, 3.52 mmol) when reacted with dithiodibenzoyl chloride (0.55 g, 1.6 mmol) according to the procedure discussed in Method A at longer

reaction time (4 days) gave **13b** (260 mg, 73% yield) as the sole product. When diethyl malonate was used instead of ethylacetoacetate, the same product was obtained in 90% yield. Analytical data for **13b:** R_f (2% EtOAc /hexanes) 0.50; mp 64-67 °C; ^{1}H NMR ($CDCl_3$) δ 10.18 (bs, 1H), 7.93 (d, 1H, *J* = 8.4 Hz), 7.71 (d, 1H, *J* = 8 Hz), 7.48 (dd, 1H, *J* = 7.6, 7.6 Hz), 7.38 (dd, 1H, *J* = 7.2 ,7.2 Hz), 4.41 (q, 2H, *J* = 7.2 Hz), 1.40 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 167.3, 159.4, 138.8, 130.5, 128.7, 124.4, 123.1, 122.9, 102.0, 61.3, 14.3; IR (neat) cm^{-1}: 2983, 1657, 1533, 1387; HRMS (ESI) exact mass calcd. for $C_{11}H_{11}O_3S$ $(M+H)^+$ 223.0429, found $(M+H)^+$ 223.0431.

*c) With dimethyl malonate (**10d**)*

Dimethyl 3-oxobenzo[b]thiophene-2,2(3H)-dicarboxylate (11d)

Dimethyl malonate (0.37 mL, 3.2 mmol) on reaction with dithiodibenzoyl chloride (0.5 g, 1.4 mmol) according to Method A for 5h gave **11d** (150 mg, 39% yield) as a white crystalline solid. Analytical data for **11d:** R_f (10% EtOAc /hexanes) 0.26; mp 148 °C; ^{1}H NMR ($CDCl_3$) δ 7.83 (d, 1H, *J* = 7.6 Hz), 7.60 (dd, 1H, *J* = 7.2,7.2 Hz), 7.41 (d, 1H, *J* = 8 Hz), 7.29 (dd, 1H, *J* = 7.4,7.2 Hz), 3.85 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 190.07, 164.79 (2 x C=O), 150.39, 136.6, 128.2, 128.1, 125.9, 123.7 (2C), 54.2 (2C); IR (neat) cm^{-1}: 2959, 1739, 1581, 1442, 1241; HRMS (ESI) exact mass calcd. for $C_{12}H_{10}O_5NaS$ $(M+Na)^+$ 289.0147, found $(M+Na)^+$ 289.0154.

Methyl 3-hydroxybenzo[b]thiophene-2-carboxylate (13d)

Dimethyl malonate (0.37 mL, 3.2 mmol) on reaction with dithiodibenzoyl chloride (0.5 g, 1.4 mmol) according to Method A for 96 h gave **13d** (250 mg, 83% yield) as a white crystalline solid. Analytical data for **13d:** R_f (2% EtOAc /hexanes) 0.46; mp 103-106 °C; ^{1}H NMR ($CDCl_3$) δ 10.20 (bs, 1H), 7.94 (d, 1H, *J* = 8 Hz), 7.73 (d, 1H, *J* = 7.6 Hz), 7.49 (dd, 1H, *J* = 7.6,7.6 Hz), 7.40 (dd, 1H, *J* = 7.6 ,7.5 Hz), 3.95 (s, 3H);

^{13}C NMR ($CDCl_3$) δ 167.6, 159.5, 138.9, 130.4, 128.8, 124.4, 123.1, 122.9, 101.7, 52.1; IR (neat) cm^{-1}: 2983, 1656, 1532, 1386; HRMS (ESI) exact mass calcd. for $C_{10}H_7O_3S$ $(M-H)^-$ 207.0116, found $(M-H)^-$ 207.0112.

III. Preparation of benzothiophenes 7a, 7b and 13a using 2-bromosulfenyl benzoyl chloride.

To a stirred solution of dithiodibenzoyl chloride (2.2 g, 6.41 mmol) in dry dichloromethane (20 mL) was added bromine (0.66 mL, 12.8 mmol) and the mixture was refluxed for 12 h. Dichloromethane and excess bromine were distilled off and the residue was chased with dry benzene (2 x 5 mL) to get 3.2 g of 2-bromosulfenylbenzoyl chloride as a brown solid which was directly subjected to reactions with various diones as follows:

2-bromosulfenylbenzoyl chloride (0.48 g, 1.9 mmol) in dry THF (5 mL) was added drop-wise to a cooled suspension of sodium hydride (2.2 equiv.) and 1,3-dione (1.1 equiv.) in dry THF (5 mL) and the mixture was stirred for 3 days at room temperature. The reaction mixture was then admixed with 5N HCl, extracted with EtOAc (80 mL), the organic layer was washed with water (75 mL) and dried over anhydrous Na_2SO_4. It was filtered and the solvent was evaporated under reduced pressure to afford a residue which was chromatographed on silica gel using EtOAc /hexanes in a gradient mode to get substituted benzothiophenes. Subjecting the diones **4a**, **4b** and **11a** to this reaction led to the formation of benzothiophenes **7a**, **7b** and **13a** in 55%, 40% and 50% yields respectively.

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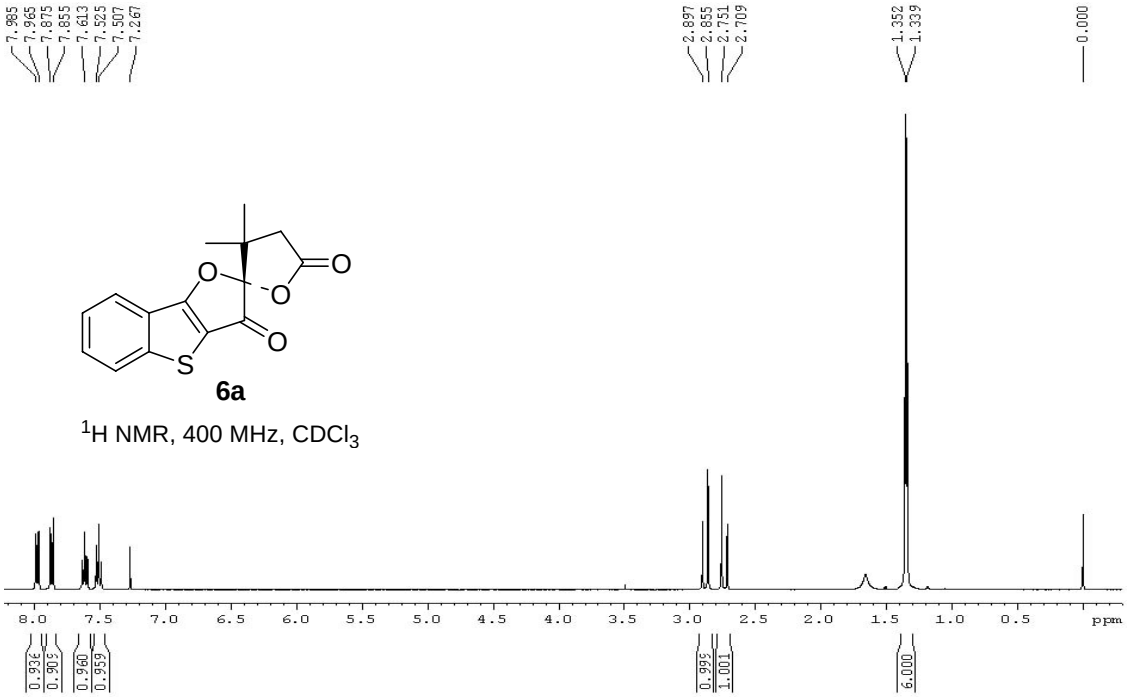
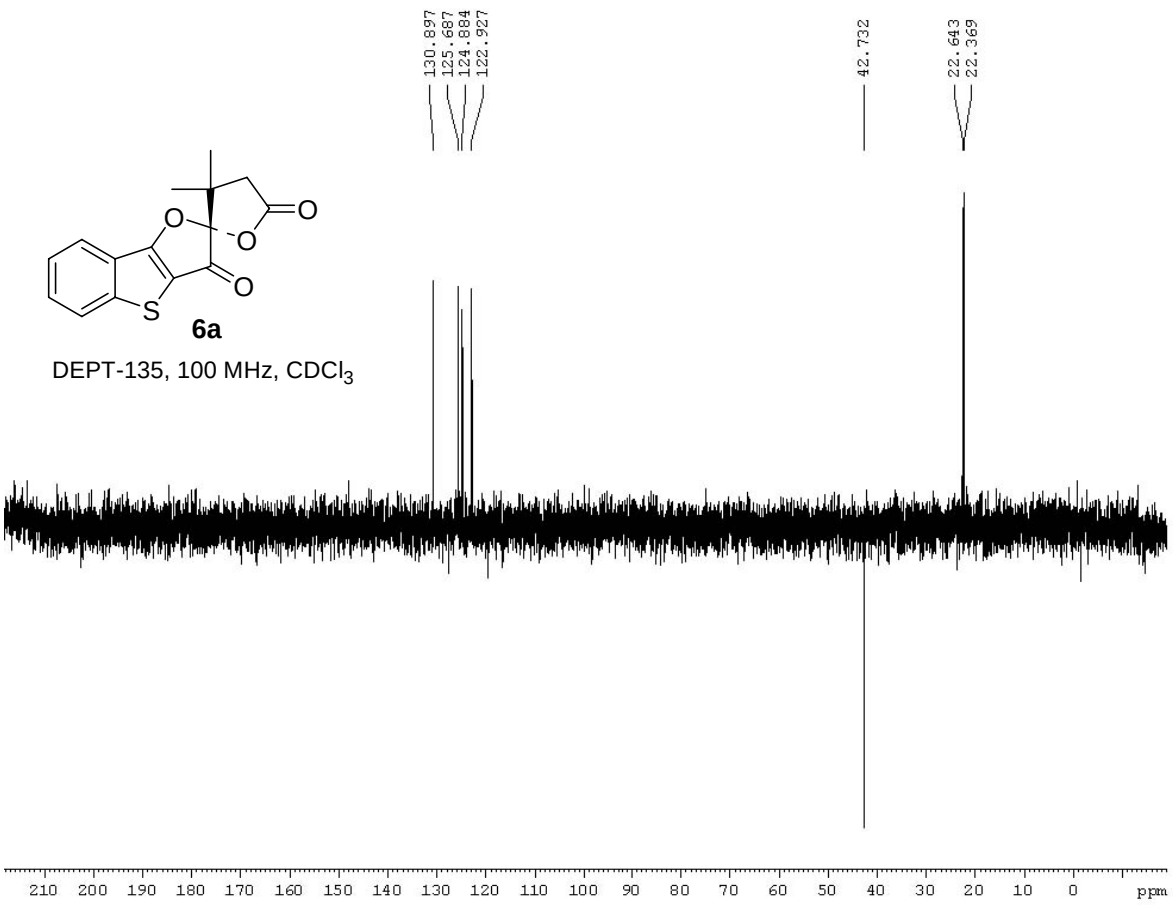


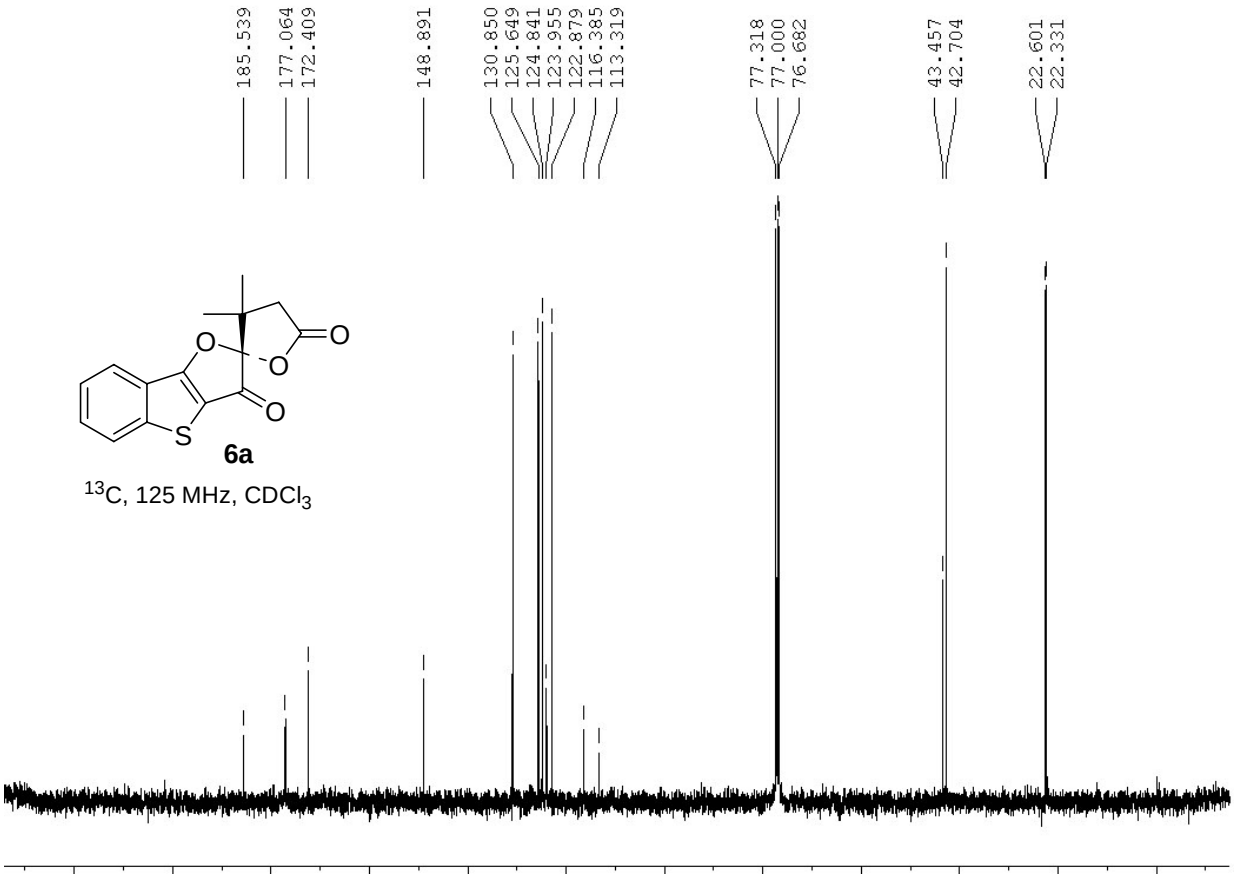
6a

^{1}H NMR, 400 MHz, $CDCl_3$



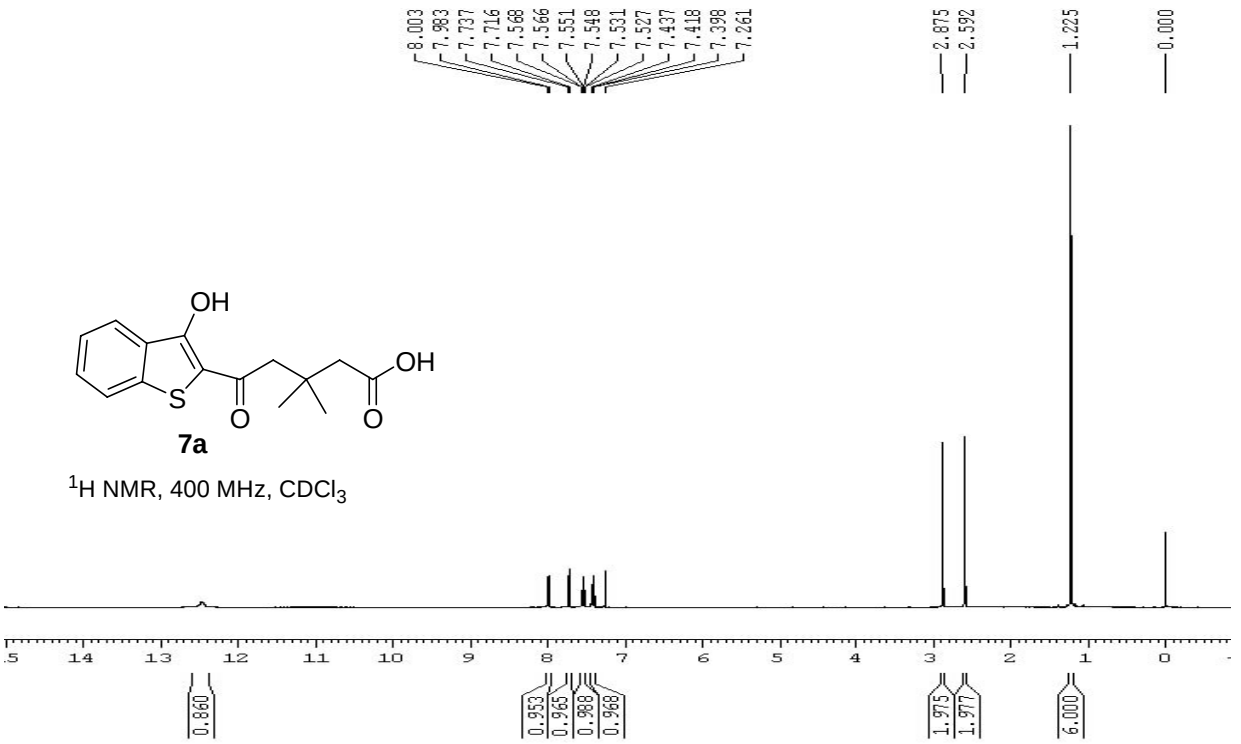
6a

DEPT-135, 100 MHz, $CDCl_3$



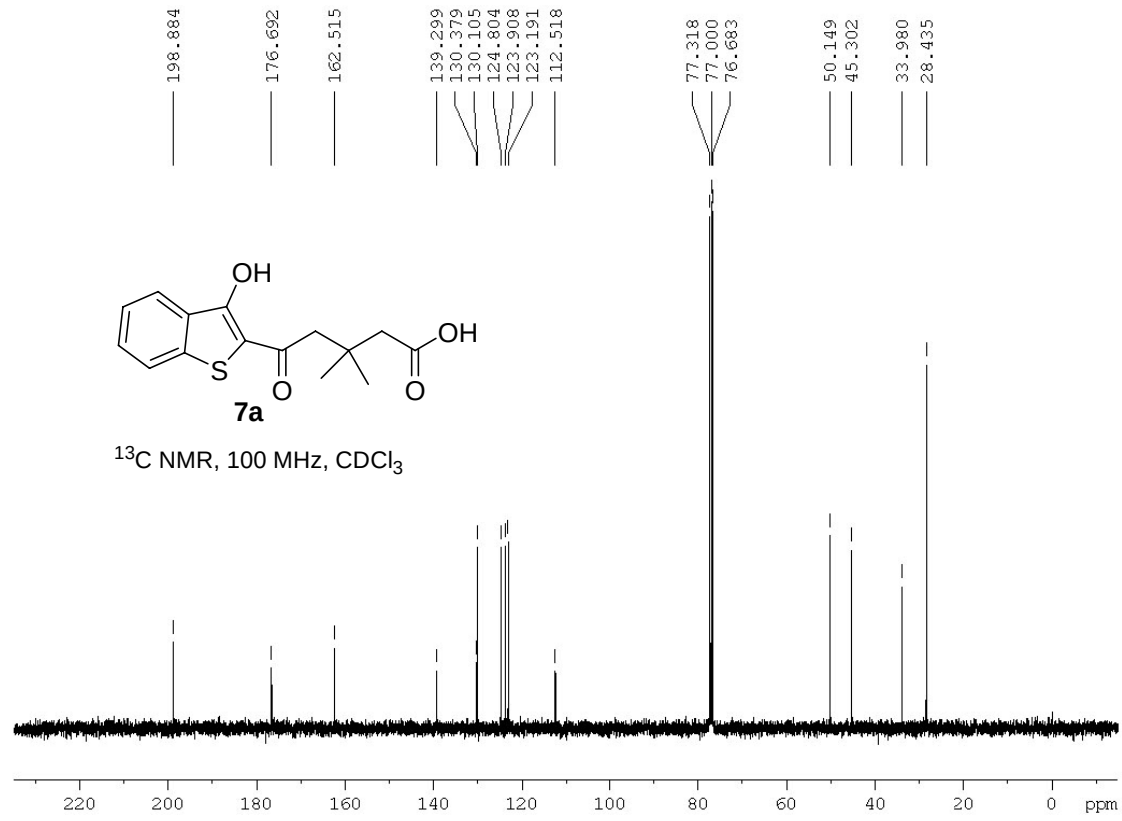
6a

^{13}C, 125 MHz, $CDCl_3$



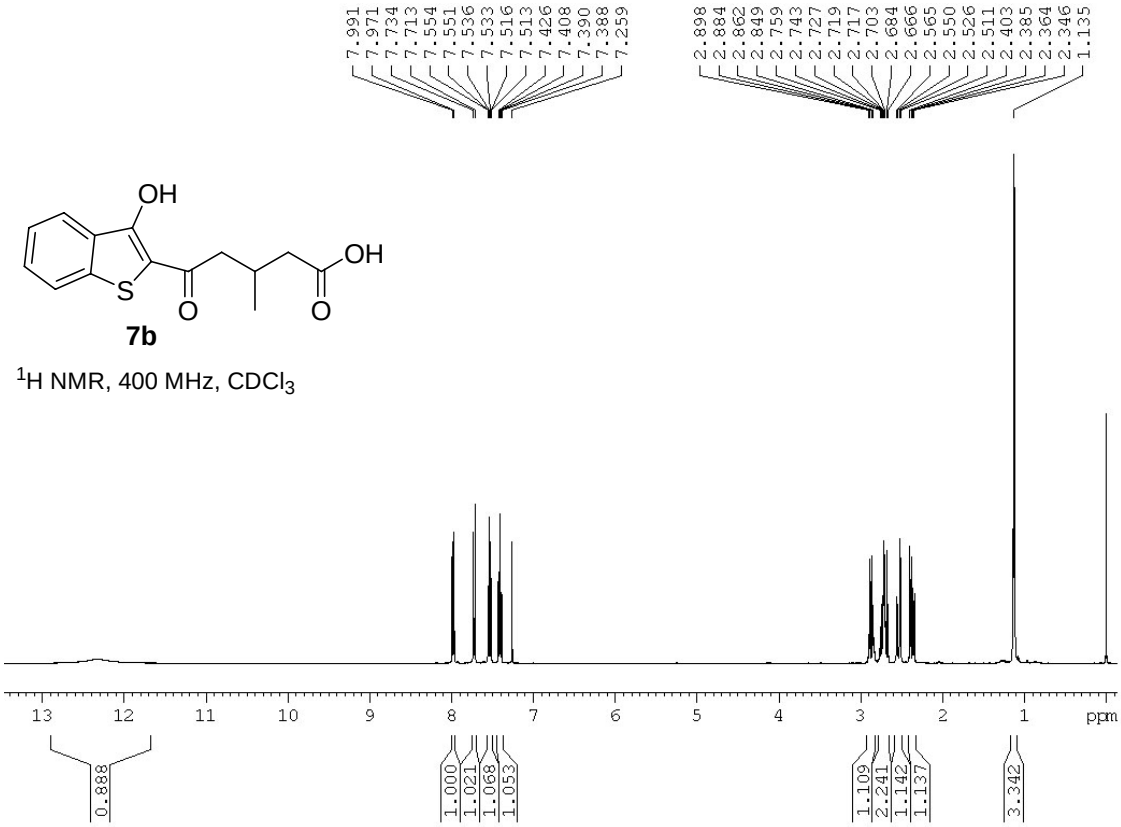
7a

^{1}H NMR, 400 MHz, $CDCl_3$



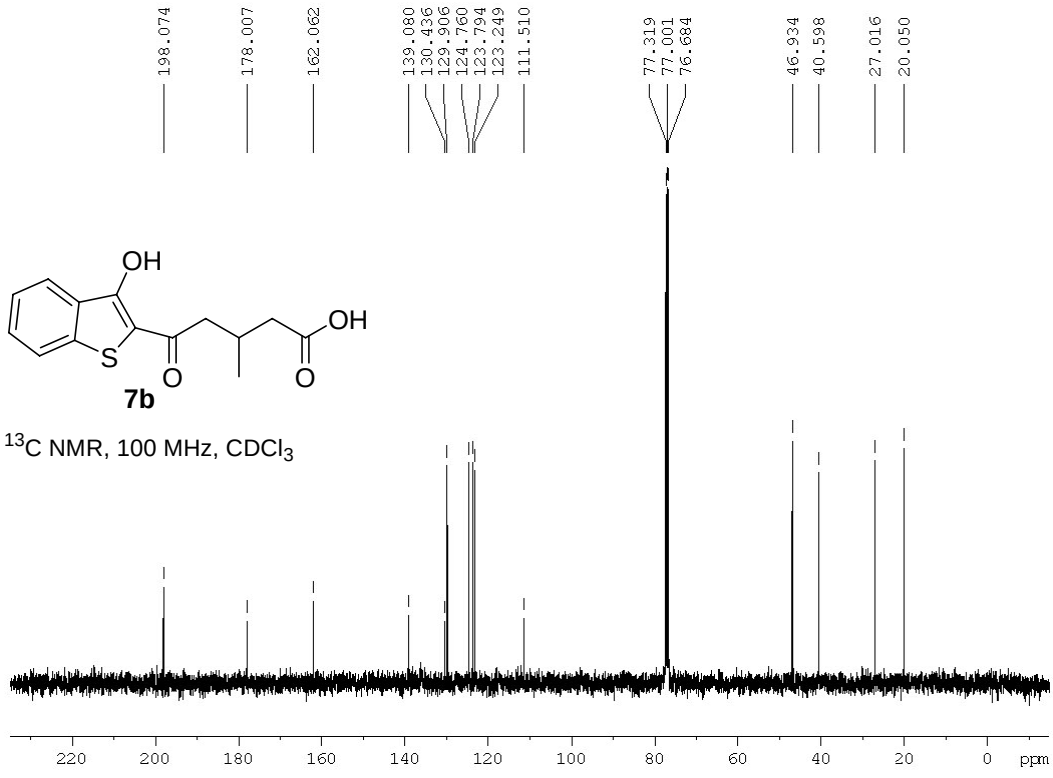
7a

^{13}C NMR, 100 MHz, $CDCl_3$



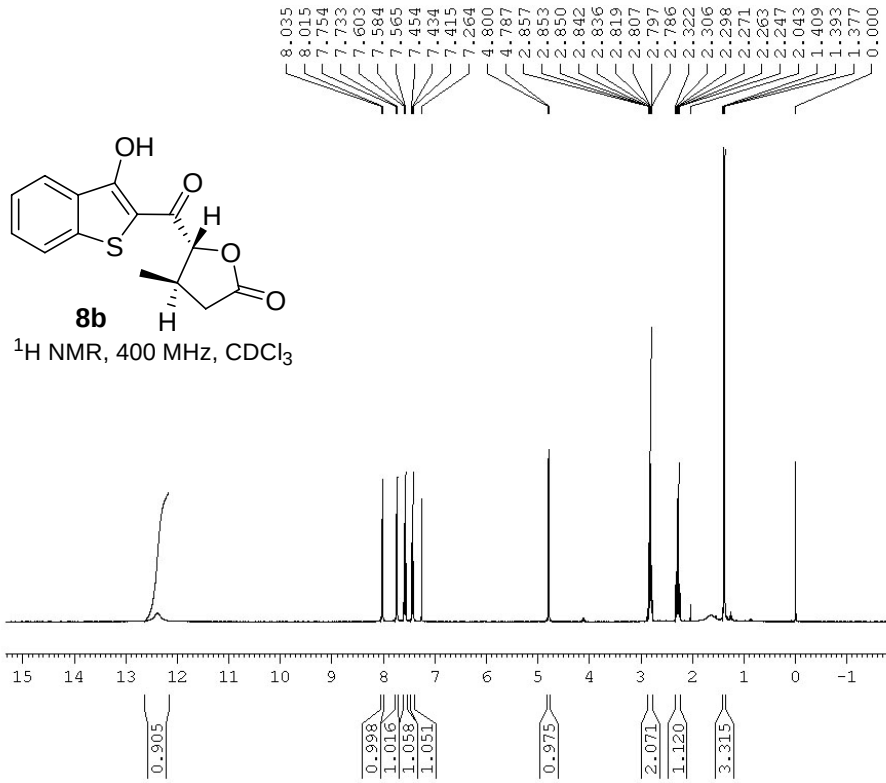
7b

^{1}H NMR, 400 MHz, $CDCl_3$



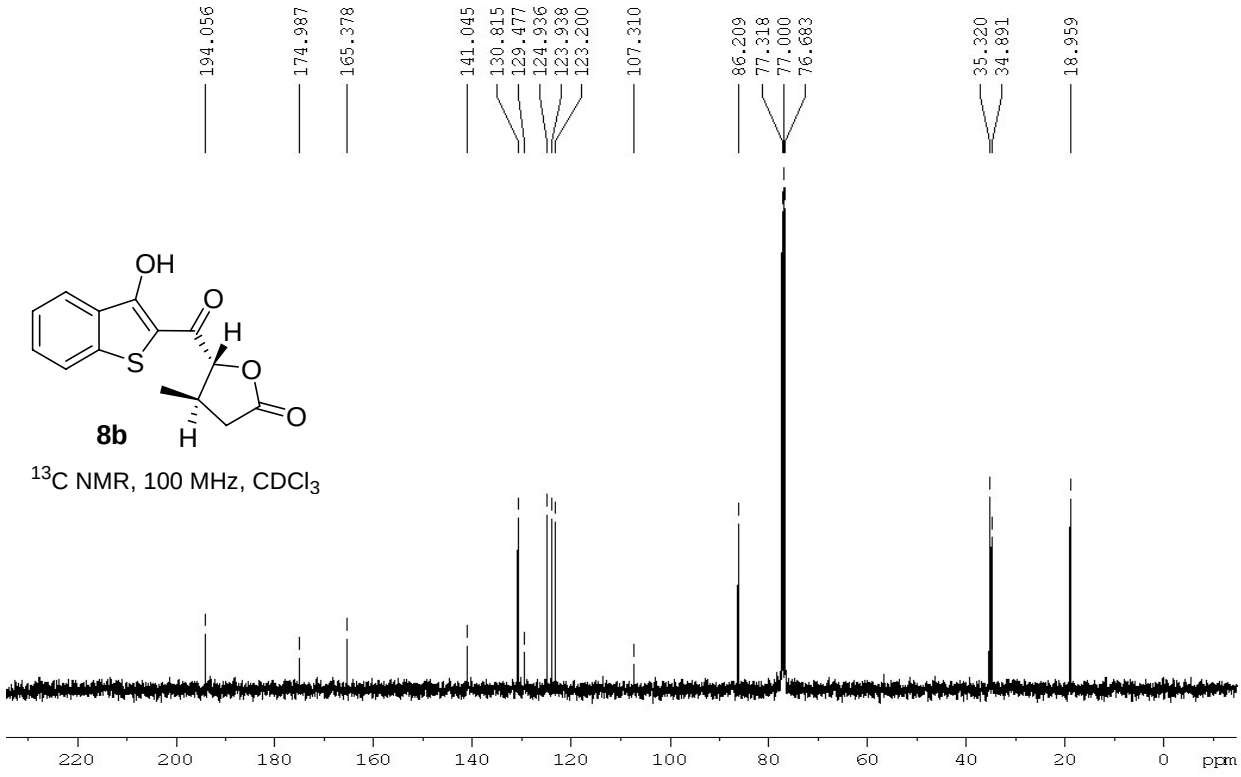
7b

^{13}C NMR, 100 MHz, $CDCl_3$



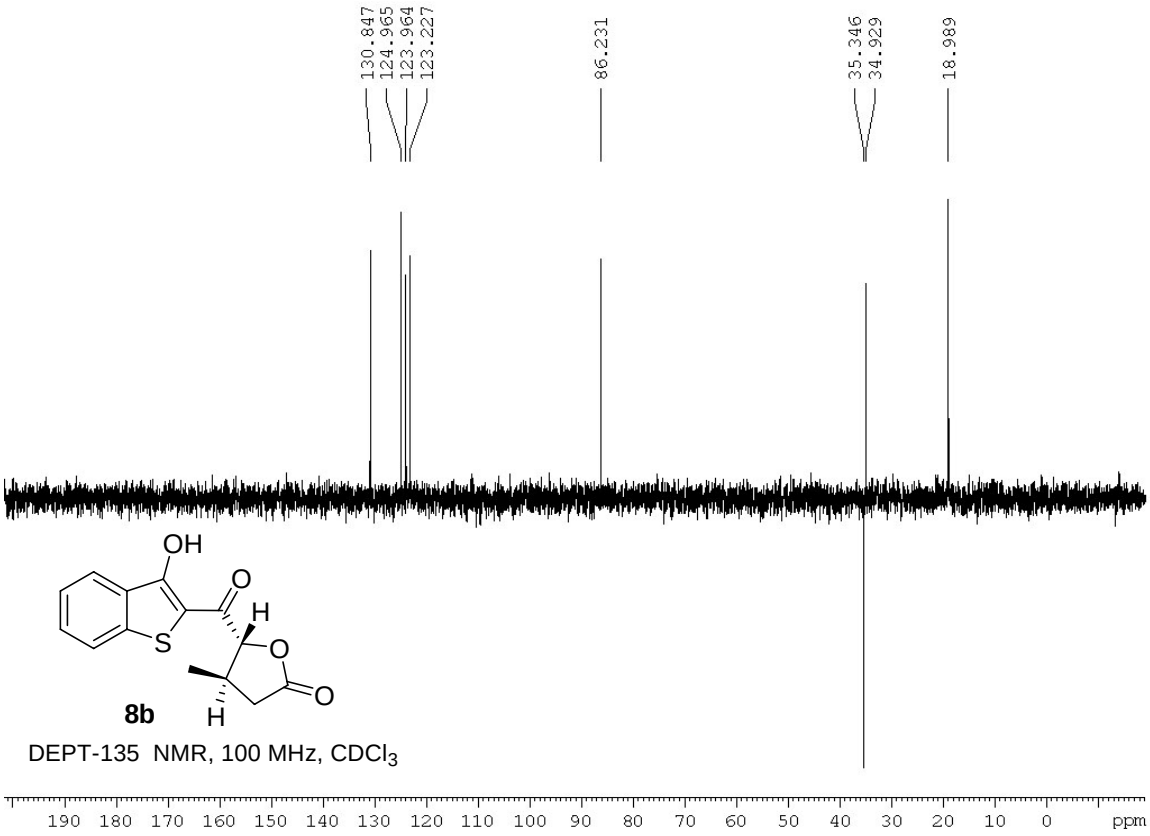
8b

^{1}H NMR, 400 MHz, $CDCl_3$



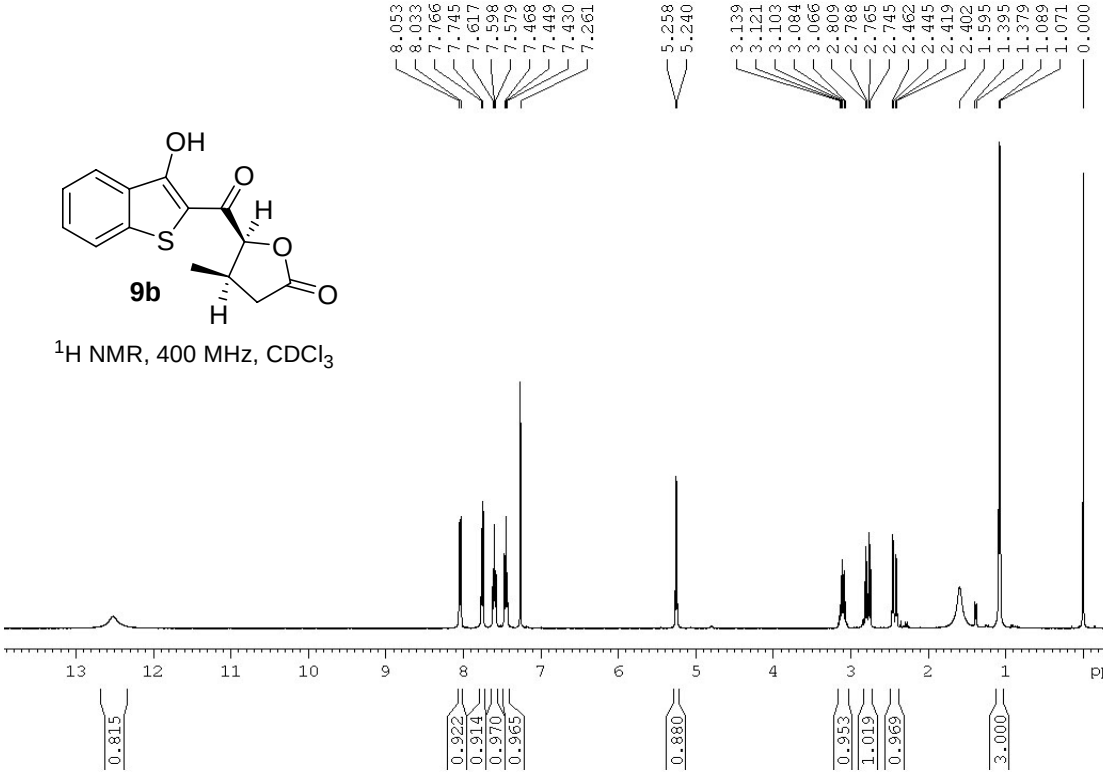
8b

^{13}C NMR, 100 MHz, $CDCl_3$

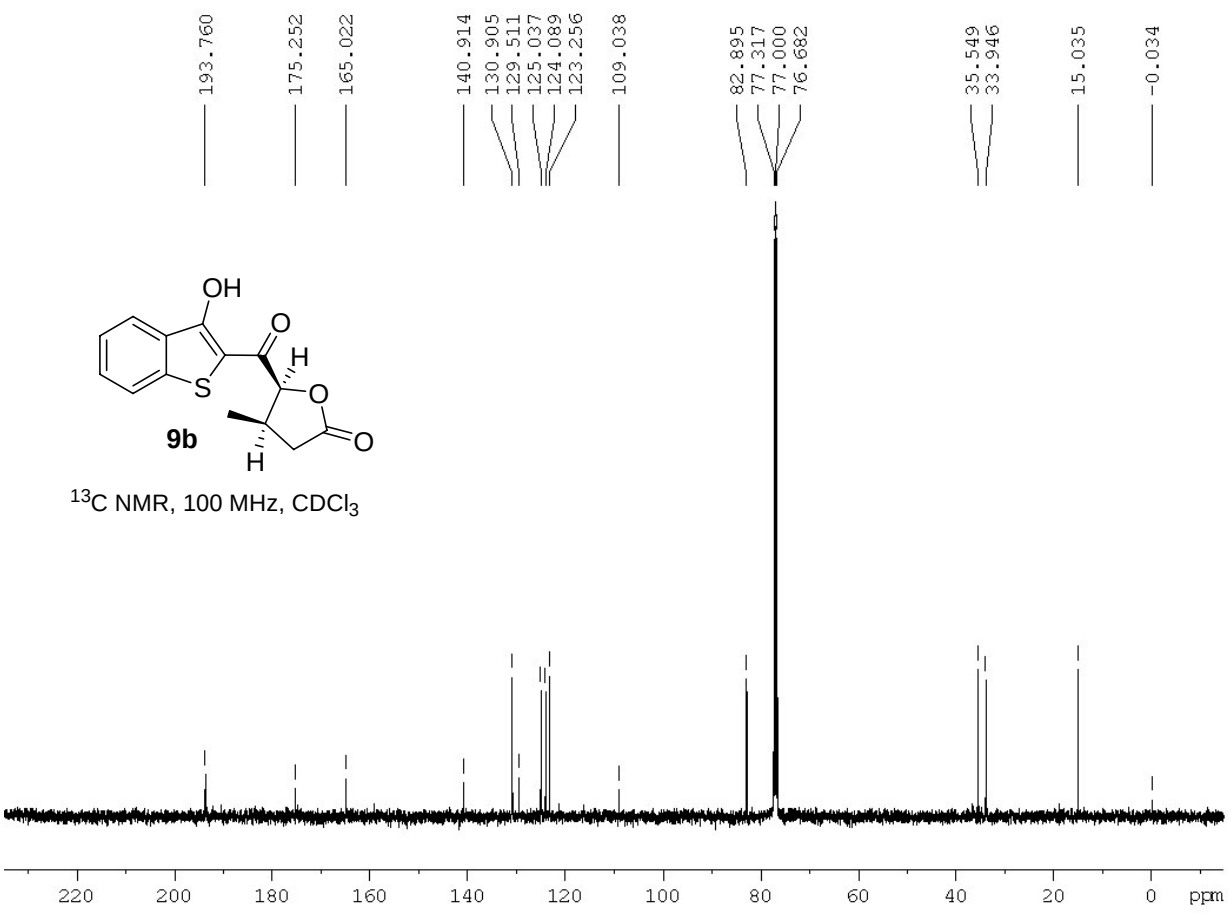


8b

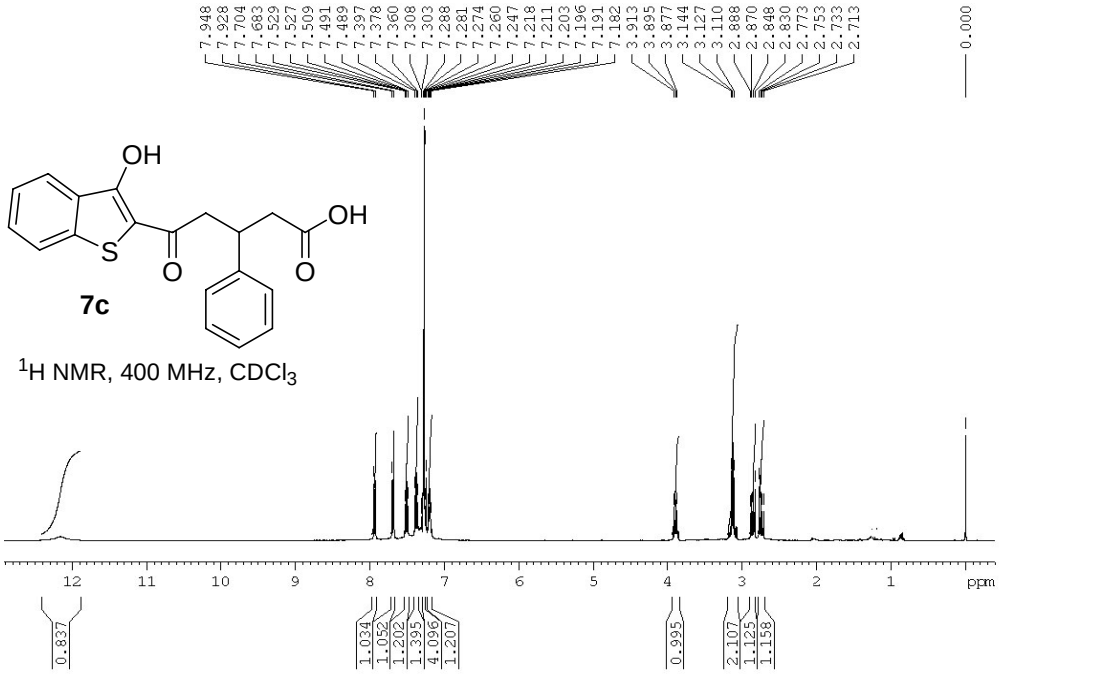
DEPT-135 NMR, 100 MHz, $CDCl_3$

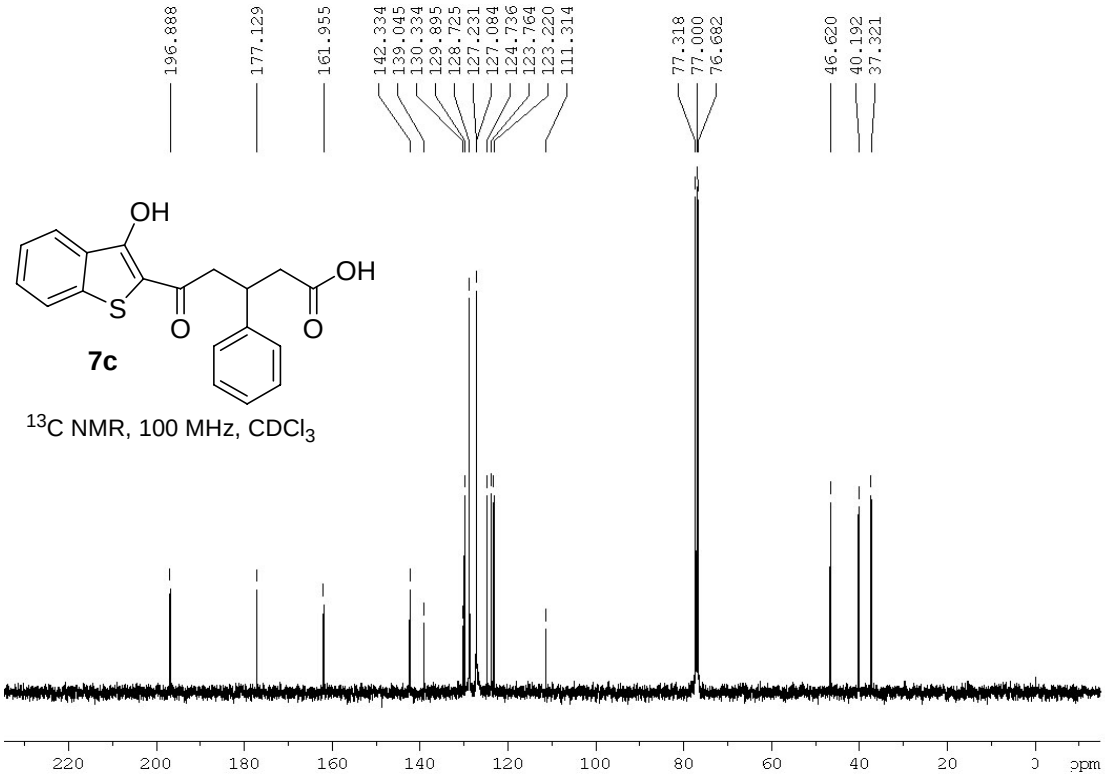


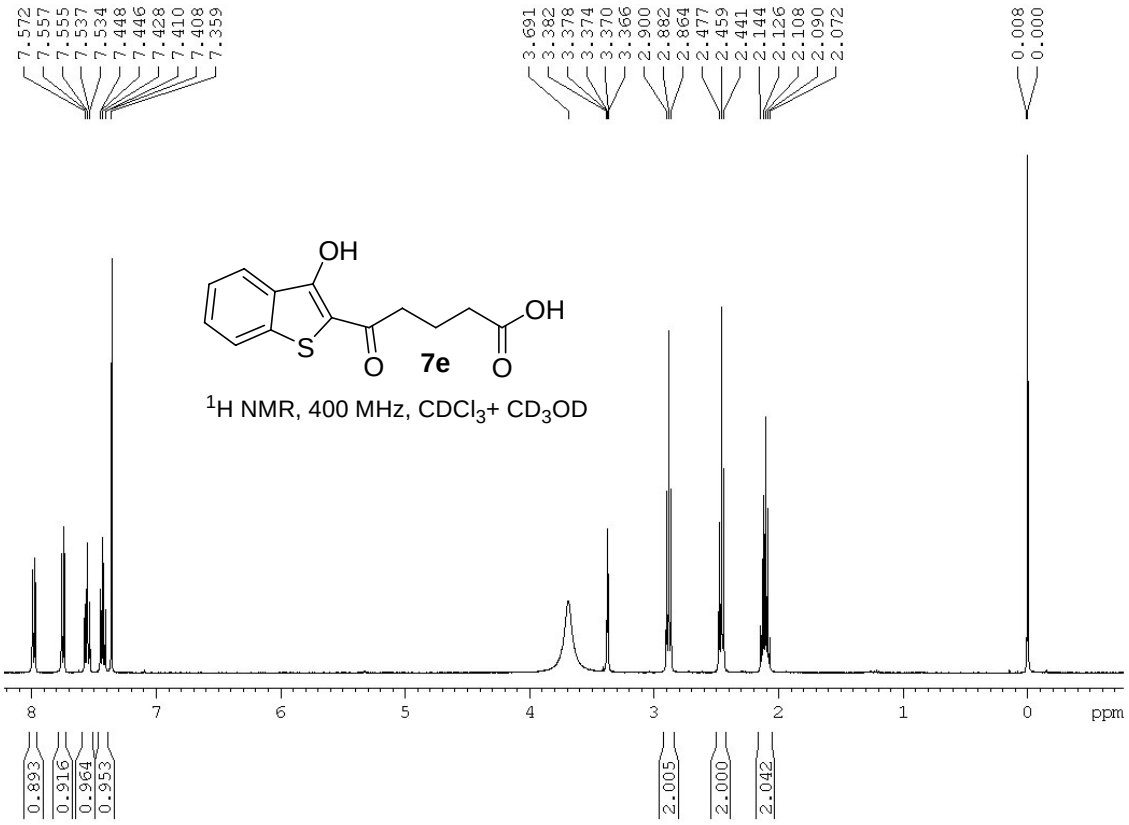
^{1}H NMR, 400 MHz, $CDCl_3$



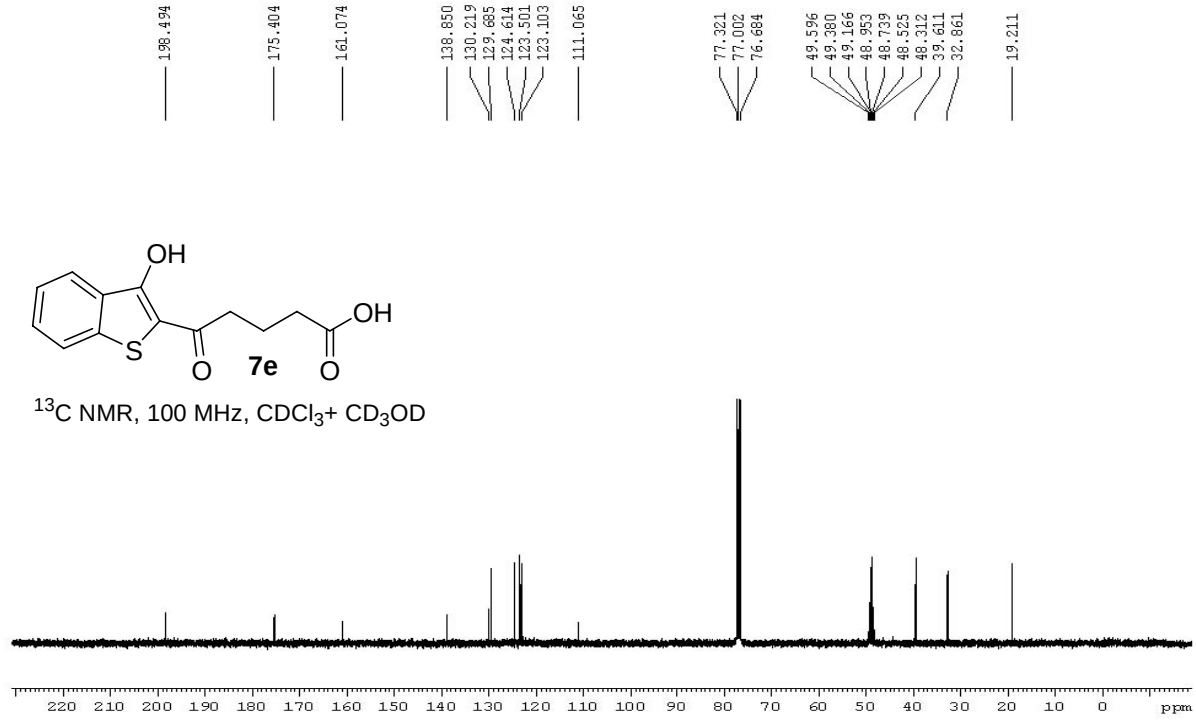
^{13}C NMR, 100 MHz, $CDCl_3$


7.948
7.928
7.704
7.683
7.529
7.527
7.509
7.491
7.489
7.397
7.378
7.360
7.308
7.303
7.288
7.281
7.274
7.260
7.247
7.218
7.211
7.203
7.196
7.191
7.182
3.913
3.895
3.877
3.144
3.127
3.110
2.888
2.870
2.848
2.830
2.773
2.753
2.733
2.713
0.000
OH
OH
S
O
O
7c
1H NMR, 400 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.837
1.024
1.052
1.202
1.395
4.096
1.207
0.995
2.107
1.125
1.158

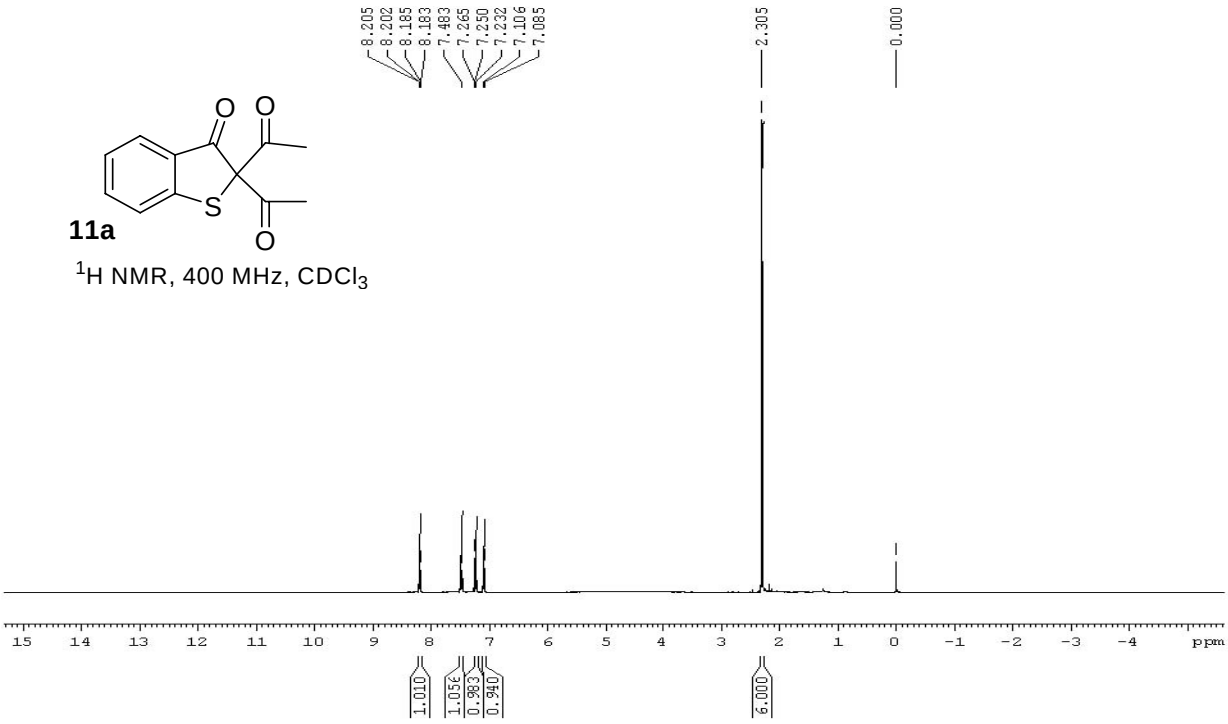

196.888
177.129
161.955
142.334
139.045
130.334
129.895
128.725
127.231
127.084
124.736
123.764
123.220
111.314
77.318
77.000
76.682
46.620
40.192
37.321
OH
OH
S
O
O
7c
13C NMR, 100 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm



^{1}H NMR, 400 MHz, $CDCl_3$+ CD_3OD

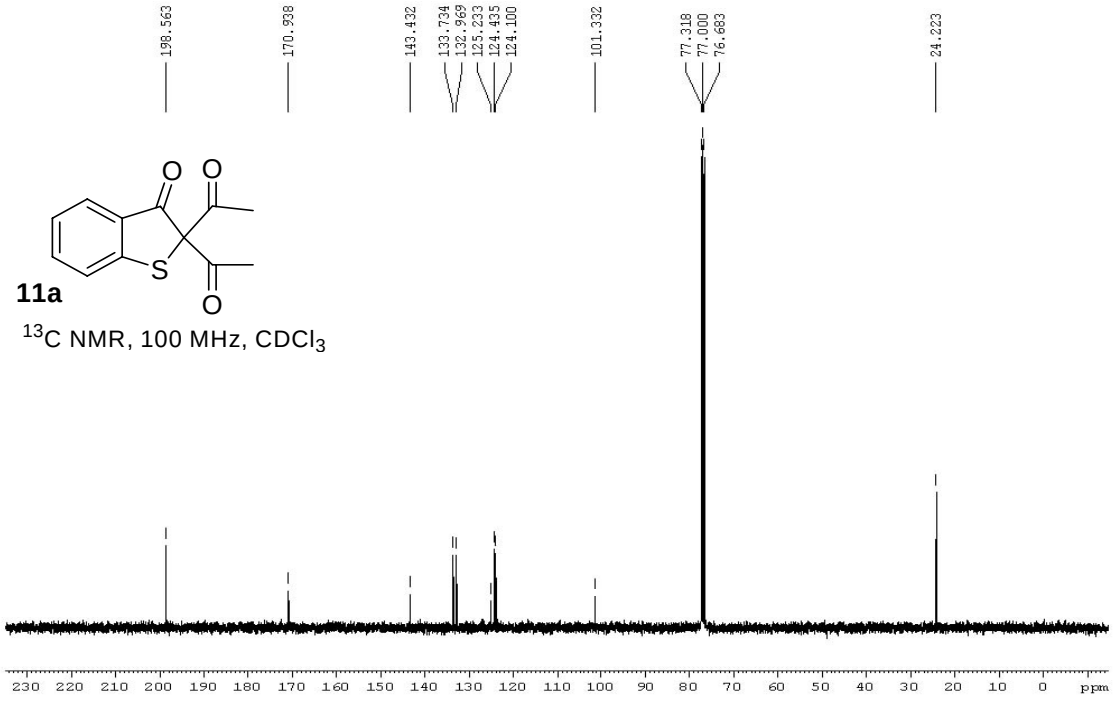


^{13}C NMR, 100 MHz, $CDCl_3$+ CD_3OD



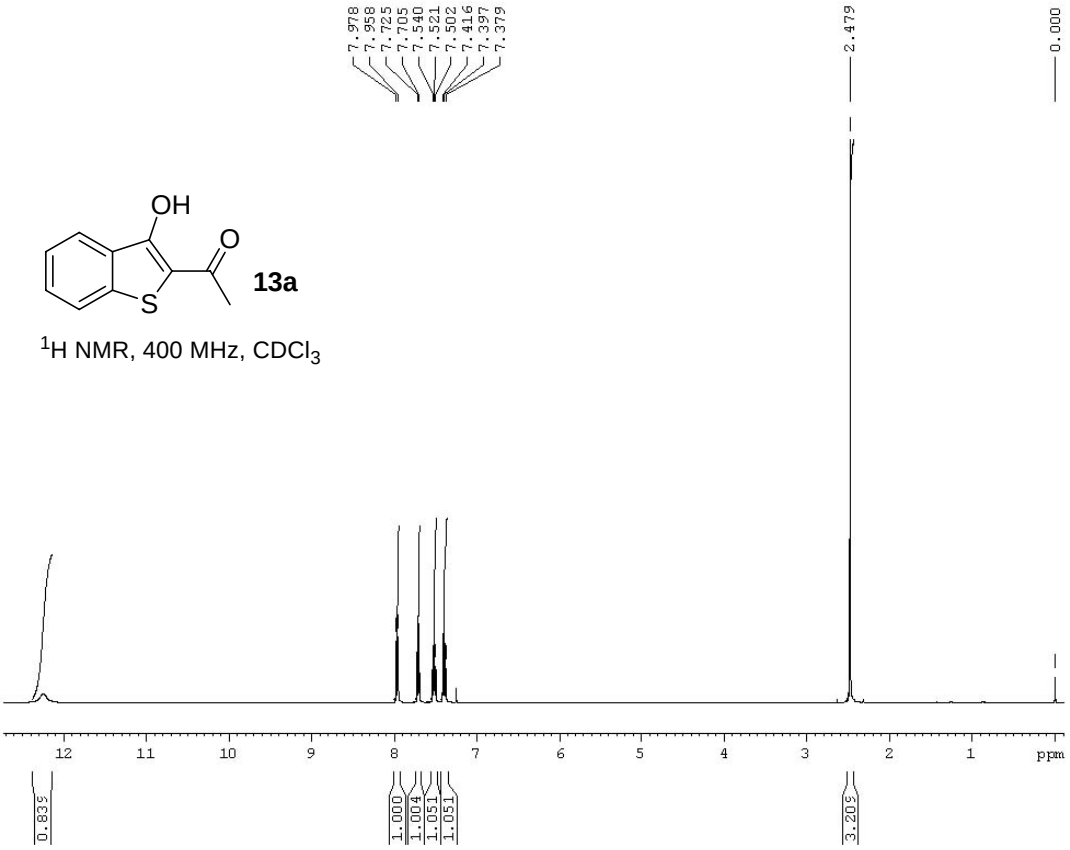
11a

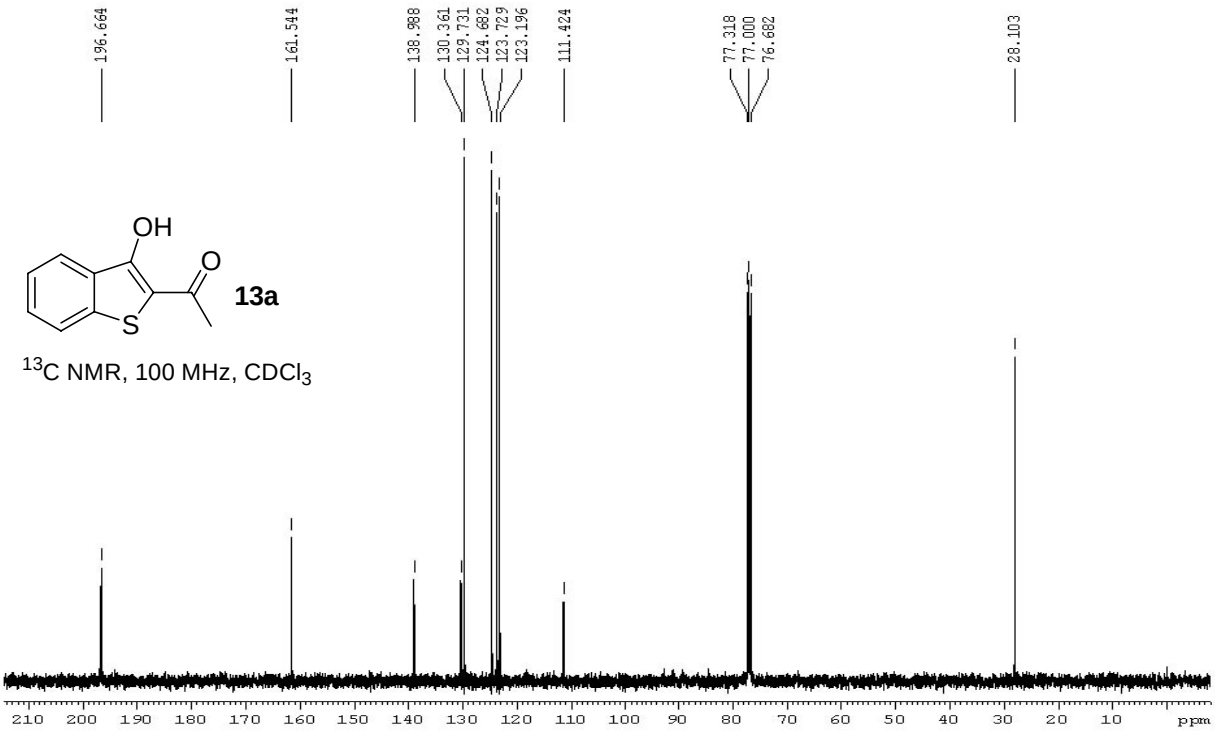
^{1}H NMR, 400 MHz, $CDCl_3$

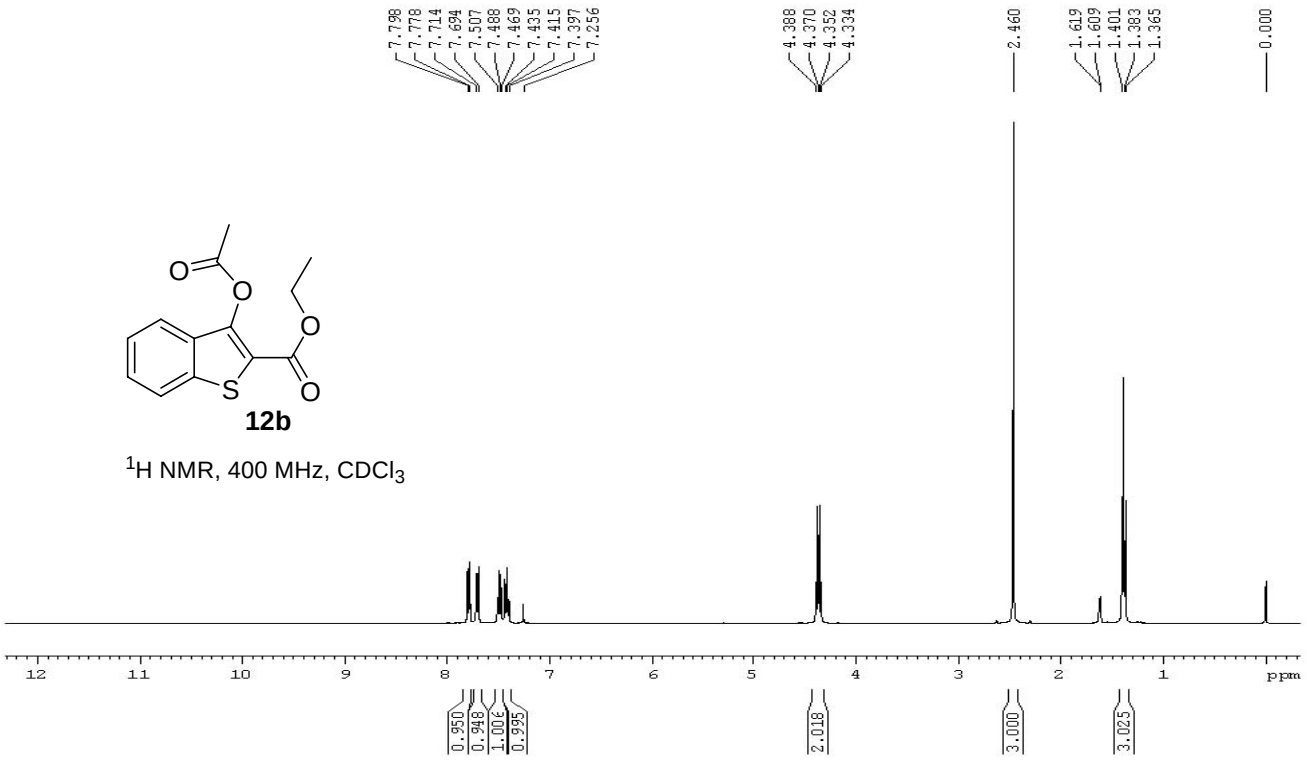


11a

^{13}C NMR, 100 MHz, $CDCl_3$

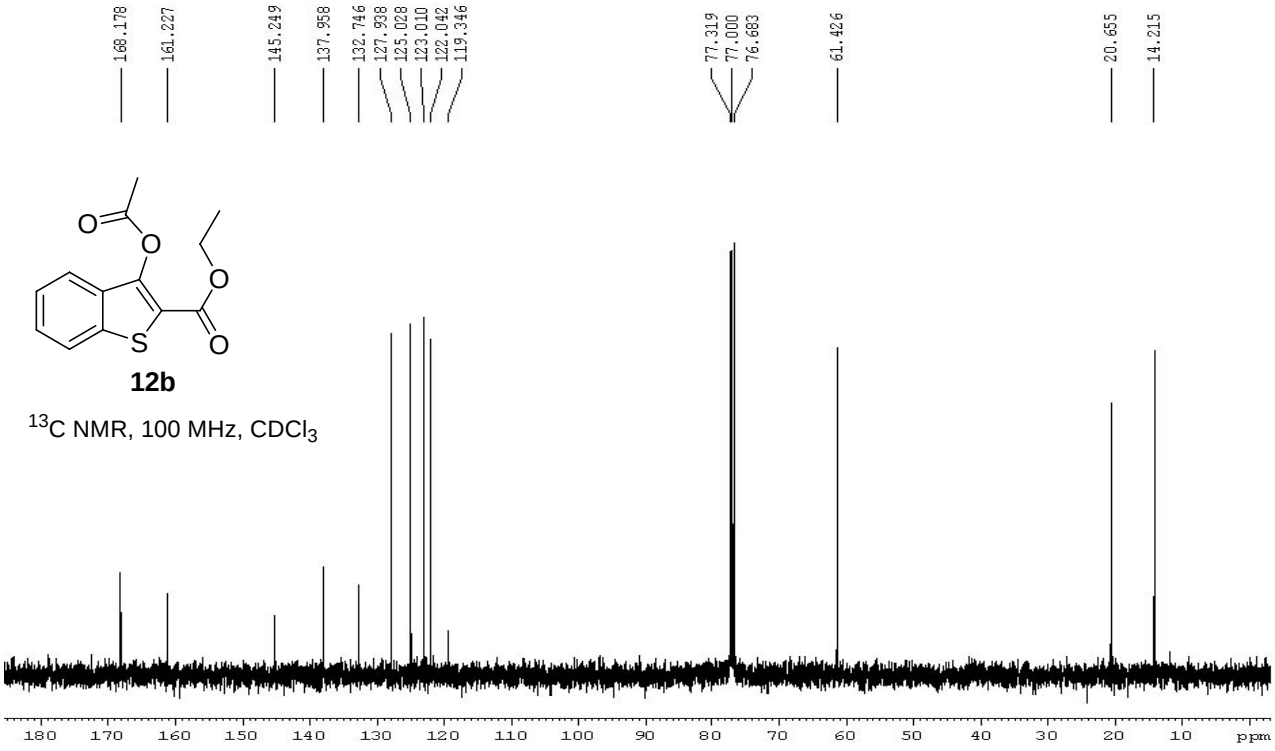

7.978
7.958
7.725
7.705
7.540
7.521
7.502
7.416
7.397
7.379
2.479
0.000
OH
O
S
13a
1H NMR, 400 MHz, CDCl3
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.839
1.000
1.004
1.051
1.051
3.209


196.664
161.544
138.988
130.361
129.731
124.682
123.729
123.196
111.424
77.318
77.000
76.682
28.103
OH
O
S
13a
13C NMR, 100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



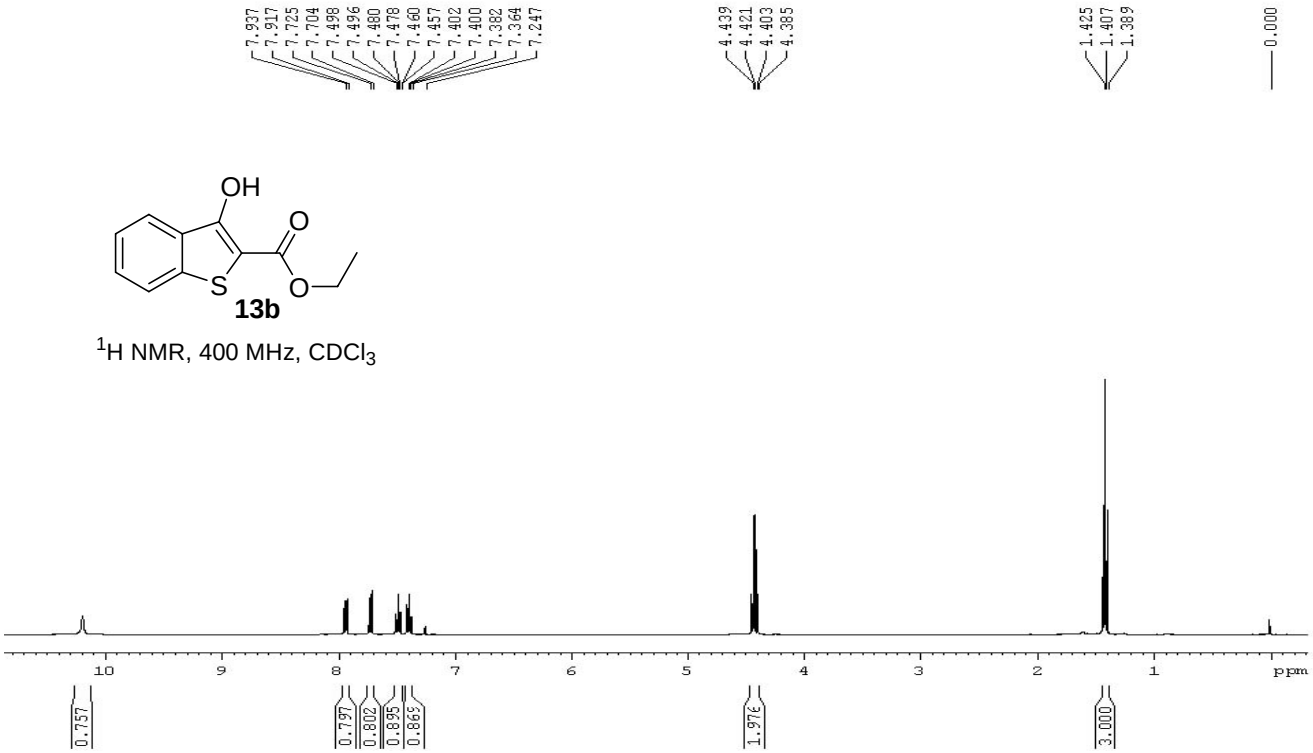
12b

^{1}H NMR, 400 MHz, $CDCl_3$

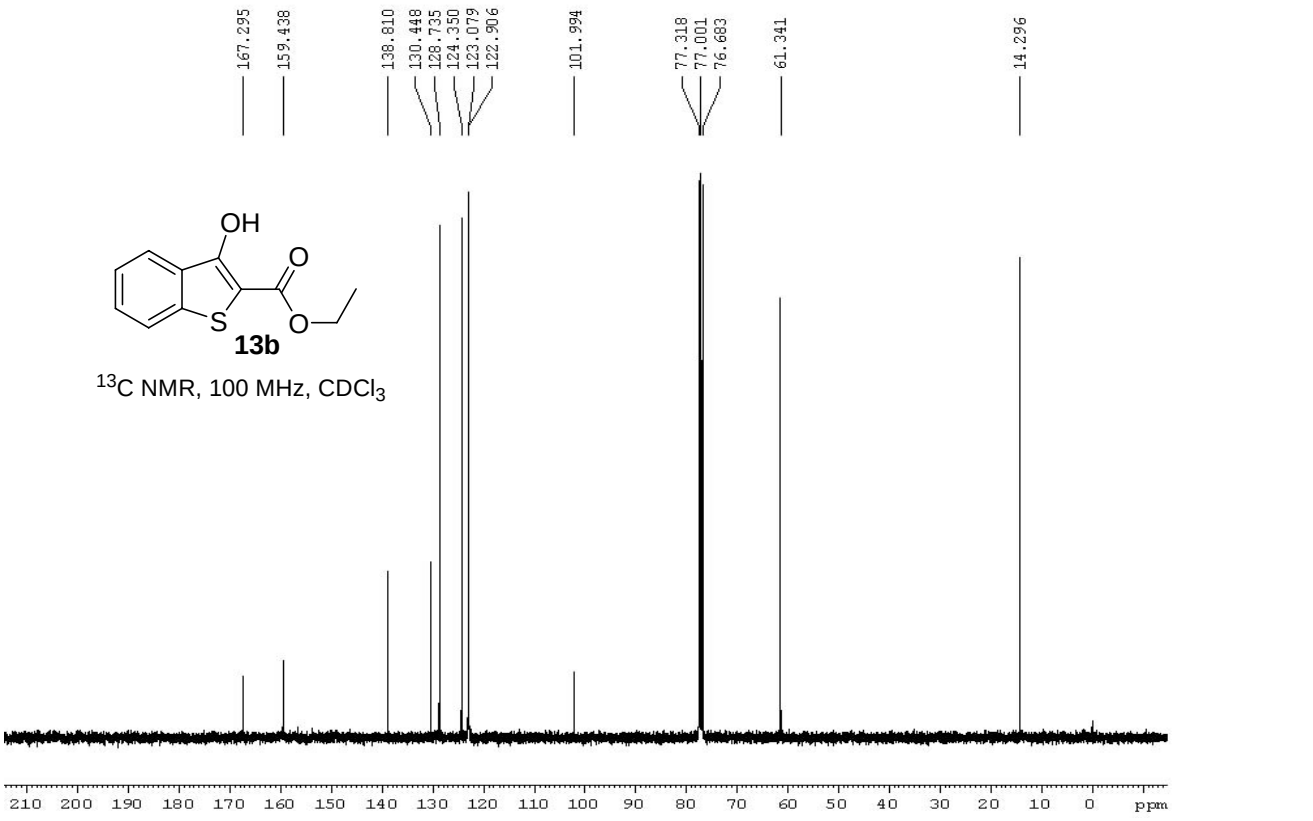


12b

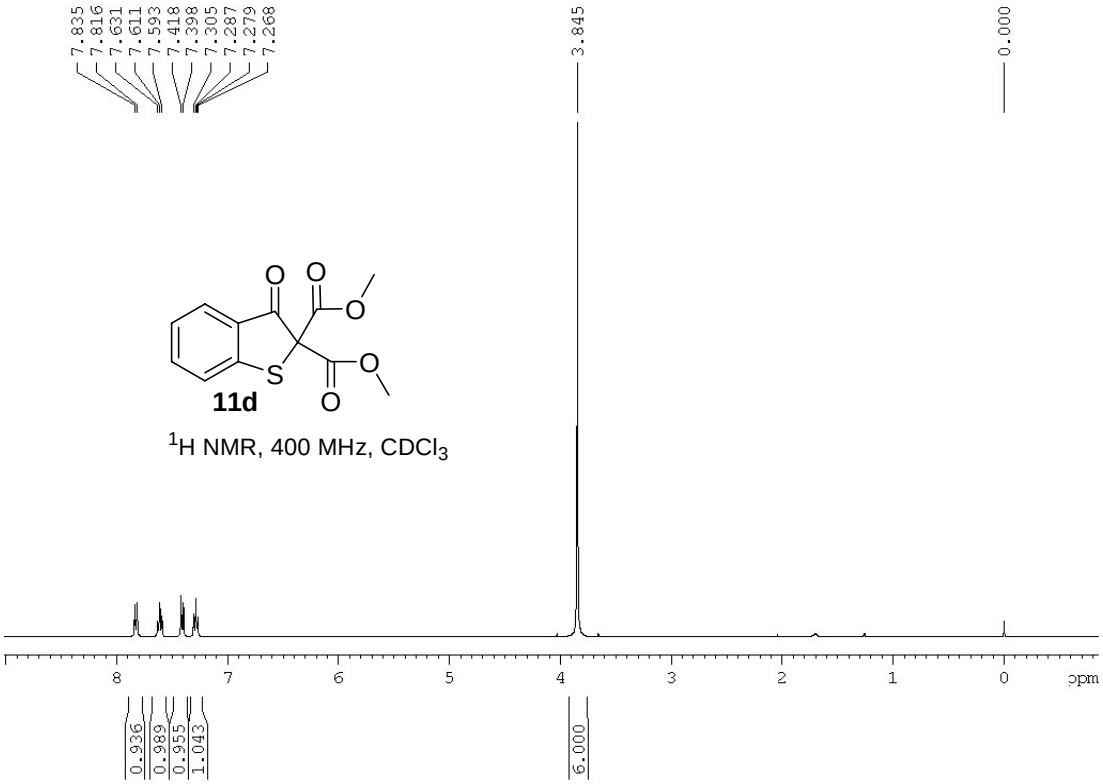
^{13}C NMR, 100 MHz, $CDCl_3$



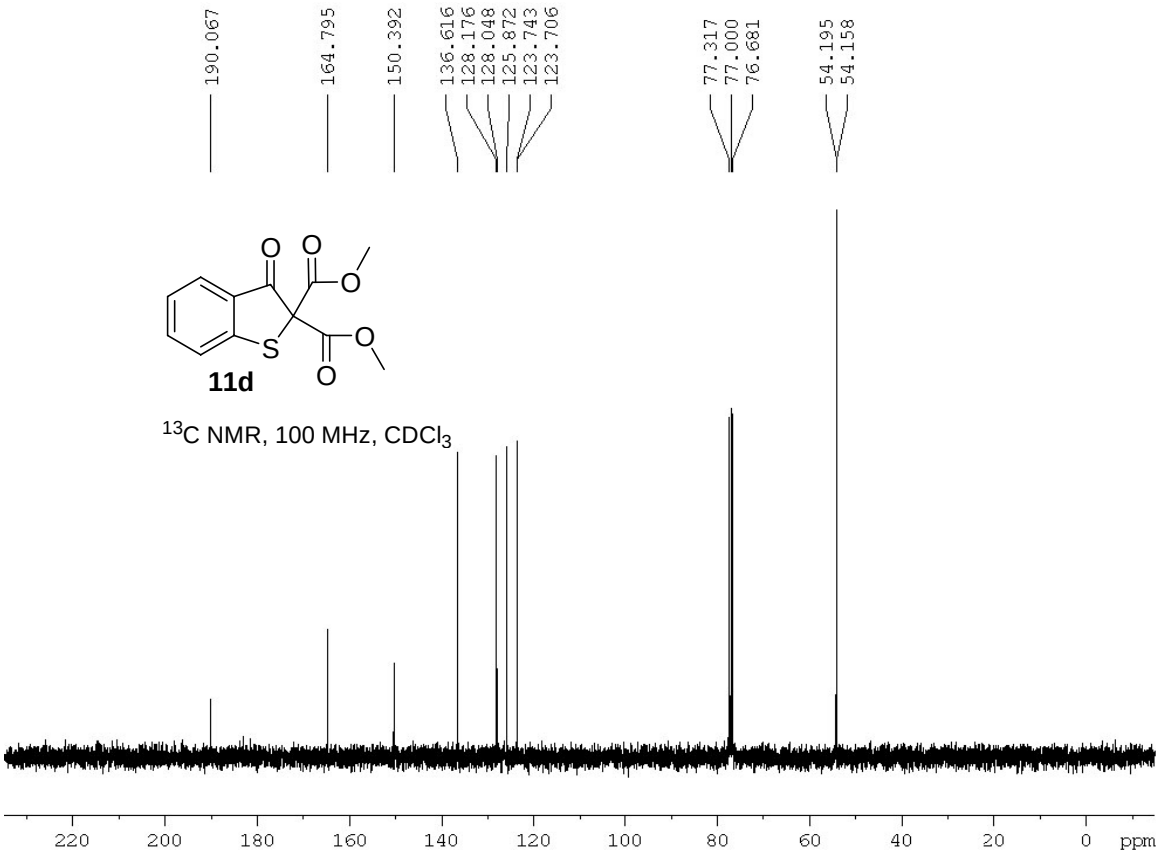
^{1}H NMR, 400 MHz, $CDCl_3$



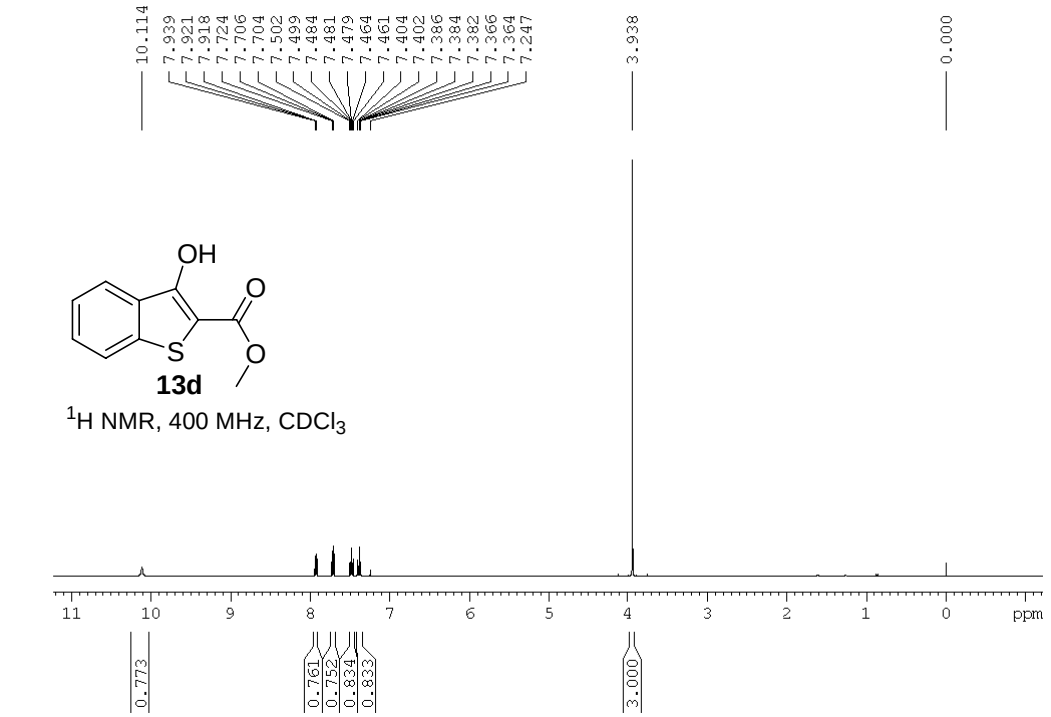
^{13}C NMR, 100 MHz, $CDCl_3$

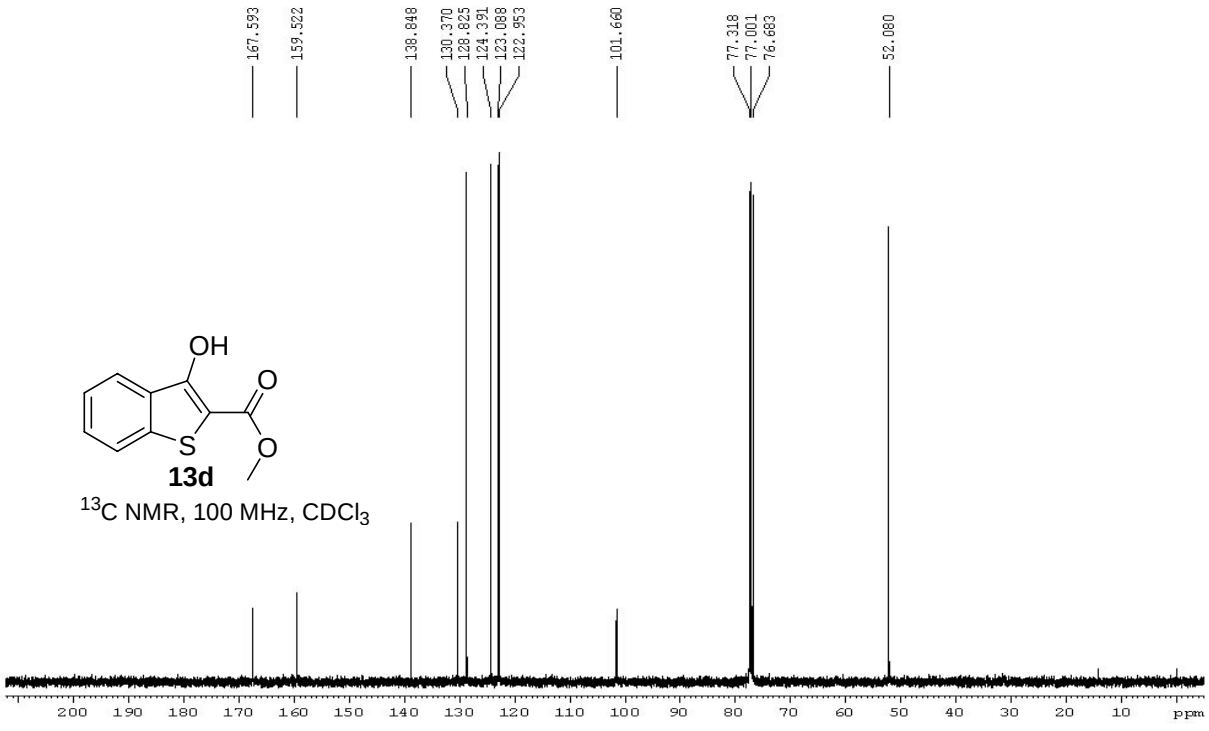


^{1}H NMR, 400 MHz, $CDCl_3$

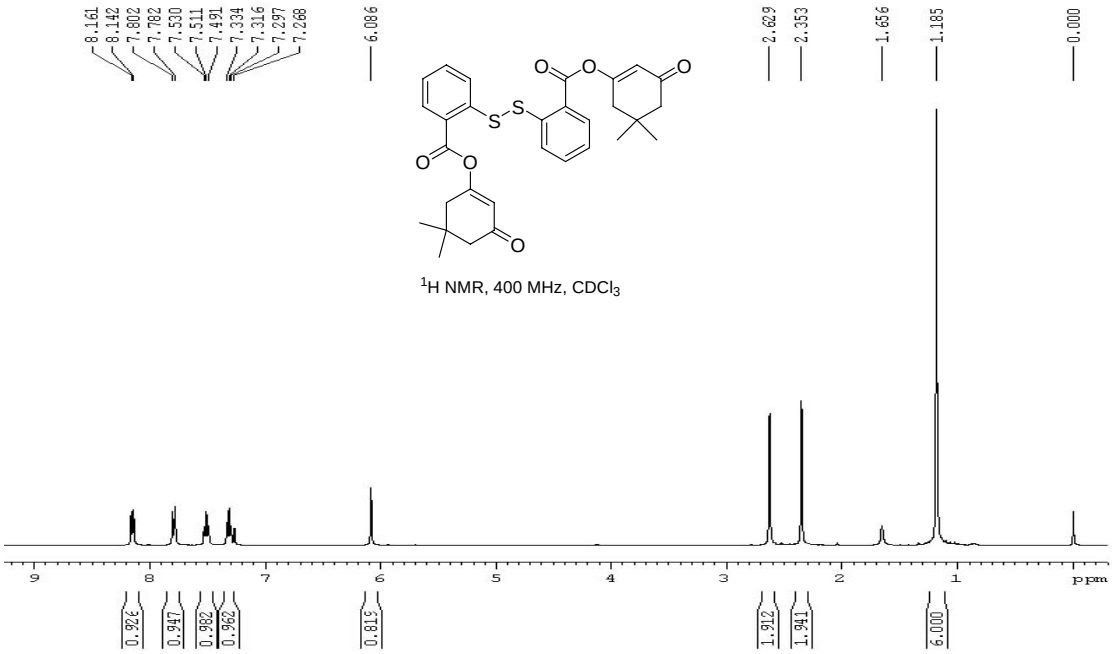


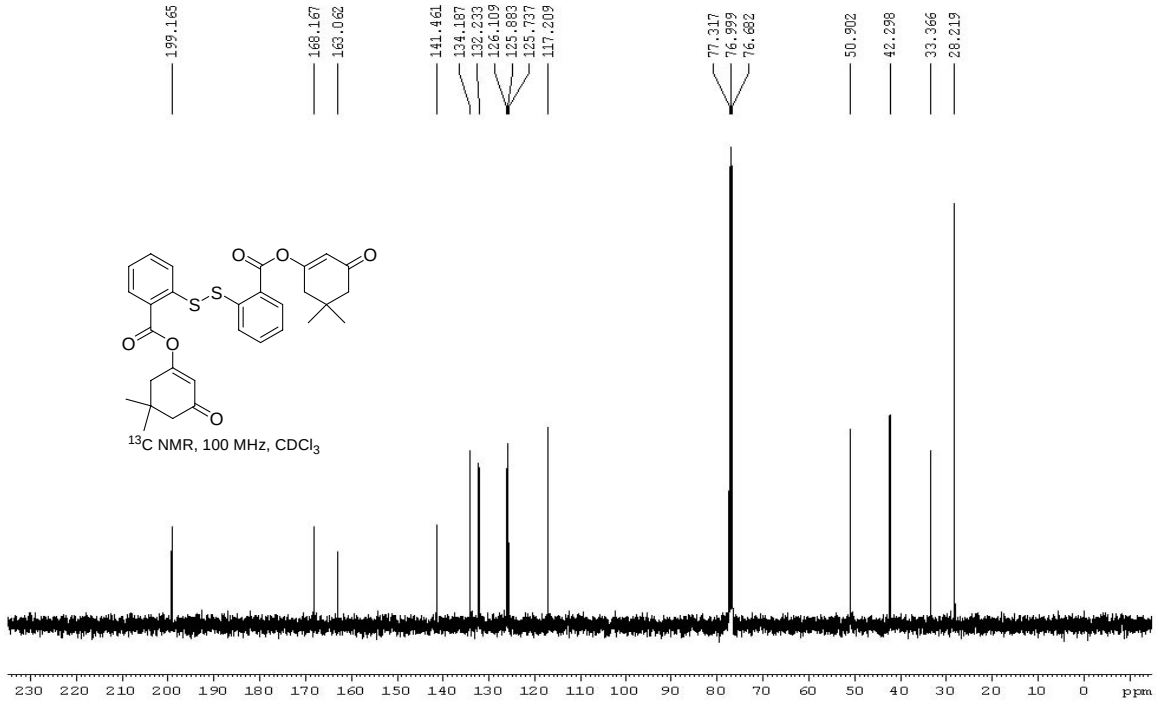
^{13}C NMR, 100 MHz, $CDCl_3$


10.114
7.939
7.921
7.918
7.724
7.706
7.704
7.502
7.499
7.484
7.481
7.479
7.464
7.461
7.404
7.402
7.386
7.384
7.382
7.366
7.364
7.247
3.938
0.000
OH
O
S
O
13d
1H NMR, 400 MHz, CDCl3
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.773
0.761
0.752
0.834
0.833
3.000


167.593
159.522
138.848
130.370
128.825
124.391
123.088
122.953
101.660
77.318
77.001
76.683
52.080
OH
O
S
O
13d
13C NMR, 100 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Structure and spectral details of the di-O-aroylated product of dimedone (**4a**) with dithodibenzoyl chloride (**3**), that is obtained by quenching the reaction after 20 minutes:



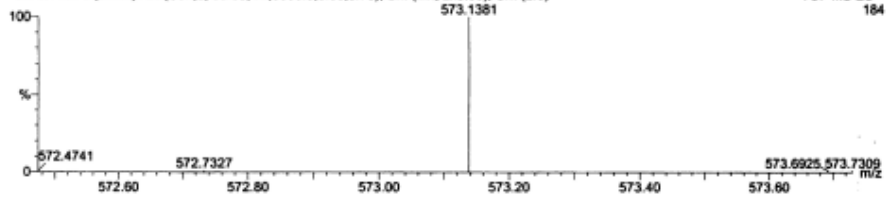


Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 200.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
37 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

PGN-02-163 Dept of Chemistry - IITM - Chennai CE =10 eV
QTOF - Micromass-UK 25-Nov-2008
PGN-02-163 6 (0.247) AM (Cen,2, 80.00, Ht,5000.0,0.00,0.70); Sm (Mn, 2x3.00); Cm (2:6) TOF MS ES+
184



Minimum:				-1.5		
Maximum:		200.0	5.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
573.1381	573.1382	-0.1	-0.2	15.5	1	C30 H30 O6 Na S2

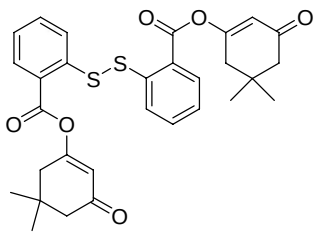


Table 1. Crystallographic summary for compounds **6a**, **7a**, **7b**, **8b**, **9b**, **11d** and **12b**.

Compound	**6a**	**7a**	**7b**	**8b**	**9b**	**11d**	**12b**
Chemical formula	$C_{15}H_{12}O_4S$	$C_{15}H_{16}O_4S$	$C_{14}H_{14}O_4S$	$C_{14}H_{12}O_4S$	$C_{14}H_{12}O_4S$	$C_{12}H_{10}O_5S$	$C_{13}H_{12}O_4S$
Formula weight	288.31	292.34	278.31	276.30	276.30	266.26	264.29
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
a (A)	8.8103(3)	20.0834(10)	18.9046(9)	7.2014(9)	10.3417(4)	10.8201(6)	8.4664(3)
B (A)	7.9336(2)	5.9233(3)	5.6296(3)	9.5258(12)	9.8285(4)	7.8657(4)	8.7330(4)
C (A)	38.3842(11)	12.5540(6)	13.0661(8)	18.552(2)	12.6105(4)	14.7561(8)	9.3615(4)
α (^{o})	90	90	90	90	90	90	90.151(2)
β (^{o})	90	102.986(2)	103.761(3)	92.133(4)	91.270(2)	105.514(2)	106.357(2)
γ (^{o})	90	90	90	90	90	90	105.808(2)
Temperature	RT	RT	RT	RT	RT	RT	RT
V (A^3)	2682.96(14)	1455.23(12)	1350.65(13)	1271.8(3)	1281.46(8)	1210.10(11)	636.66(5)
Space group (No)	Pbca	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/c	P2(1)/n	P-1
Z	8	4	4	4	4	4	2
Total reflections	20215	9564	9308	7891	9635	8429	8096
Independent reflections	3257	2981	3206	2682	3643	2802	2929
R_{int}	0.0593	0.0175	0.0371	0.0553	0.0197	0.0245	0.0199
Final R value	0.0465	0.0381	0.0506	0.0522	0.0404	0.0605	0.0330
CCDC numbers	720188	720189	735538	735540	738524	720186	720185