

Electronic Supporting Information

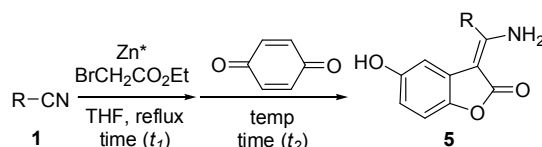
Tandem Blaise-Nenitzescu reaction: One-Pot synthesis of 5-Hydroxy- α -(aminomethylene)benzofuran-2(3H)-ones from nitriles

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General. All reactions were performed in a nitrogen atmosphere. The reaction solvents were distilled prior to used (THF was distilled from sodium benzophenone ketyl). All purchased reagents were used without further purification. Flasks were flames dried under a stream of nitrogen. The NMR spectra were recorded at 250 MHz (¹H) and 62.9 MHz (¹³C).

Typical procedure for the synthesis of 5.



To a stirred suspension of zinc dust (1.0 g, 15.3 mmol) was added methanesulfonic acid (3.7 mg) in anhydrous THF (4.0 mL). After 10 min reflux, nitrile **1** (7.6 mmol) was added all at once. While maintaining reflux temperature, ethyl bromo acetate (11.4 mmol) was slowly added over 1 hr, and the reaction mixture was refluxed for the given time (t_1) in Table 1 to afford the Blaise reaction intermediate **2** (>98% conversion by GC analysis). To this Blaise reaction intermediate, a solution of 1,4-benzoquinone (7.6 mmol) in anhydrous THF (8.0 mL) was added for 10 min at either reflux or room temperature. The reaction was continued for the given time (t_1) in Table 1, and quenched by addition of saturated aqueous NH₄Cl. The reaction mixture was extracted with ethyl acetate (3 x 40 mL), and the combined organic layer was dried with anhydrous MgSO₄, filtered, and concentrated. The residue was purified by silica column chromatography to afford benzofuranone **5**.

3-(Amino-phenyl-methylene)-5-hydroxy-3H-benzofuran-2-one (5a)

Yield: 90 %; Yellow solid; mp: 110-115 °C; ¹H NMR (250 MHz, Acetone-d₆) δ 5.79(d, J = 2.6 Hz, 1H), 6.47(dd, J = 2.6 Hz, J = 8.5 Hz, 1H), 6.85(d, J = 8.5 Hz, 1H), 7.57 ~ 7.67(m, 6H), 7.83(d, J = 1.1 Hz, 1H), 8.95(brs, 1H) ppm; ¹³C NMR (62.9 MHz, Acetone-d₆) δ 90.3, 106.1, 110.4, 111.0, 127.3, 128.5, 130.0, 131.5, 135.8, 143.9, 153.8, 163.3, 171.7 ppm; IR (KBr pallet) 3427, 3360, 3289, 3196, 1686, 1631, 1549, 1459, 1203, 1135, 1096, 811 cm⁻¹; HRMS Cal. for [M-H]⁺: C₁₅H₁₀NO₃: 252.0661. Found: 252.0654.

3-(Amino-*o*-tolyl-methylene)-5-hydroxy-3*H*-benzofuran-2-one (5b)

Yield: 86 %; Yellow solid; mp: 198-200 °C; ¹H NMR (250 MHz, Acetone-*d*₆) δ 2.29 (s, 3H), 5.33(d, *J* = 2.6 Hz, 1H), 6.46(dd, *J* = 2.6, *J* = 8.5 Hz, 1H), 6.75(d, *J* = 8.5 Hz, 1H), 7.31 ~ 7.53(m, 4H), 7.61 (brs, 1H), 7.82(brs, 1H), 8.88(brs, 1H) ppm; ¹³C NMR (62.9 MHz, Acetone-*d*₆) δ 19.0, 91.0, 105.5, 110.4, 110.9, 116.6, 127.5, 128.2, 131.0, 131.5, 135.5, 135.8, 143.9, 154.0, 162.7, 171.4 ppm; IR (KBr pallet) 3379, 3295, 3207, 1691, 1621, 1512, 1459, 1204, 1140, 1095, 1001, 849, 811 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₆H₁₂NO₃: 266.0817. Found: 266.0810.

3-(Amino-*m*-tolyl-methylene)-5-hydroxy-3*H*-benzofuran-2-one (5c)

Yield: 78 %; Yellow solid; mp: 186-188 °C; ¹H NMR (250 MHz, Acetone-*d*₆) δ 2.43(s, 3H), 5.86(d, *J* = 2.3 Hz, 1H), 6.47(dd, *J* = 2.5, *J* = 8.5 Hz, 1H), 6.85(d, *J* = 8.5 Hz, 1H), 7.36 ~ 7.52(m, 5H), 7.55(brs, 1H), 7.81(s, 1H), 8.94(brs, 1H) ppm; ¹³C NMR (62.9 MHz, acetone) δ 21.3, 90.2, 106.1, 110.4, 111.0, 125.6, 127.4, 129.0, 129.8, 132.1, 135.7, 139.8, 143.9, 153.8, 163.5, 171.7 ppm; IR (KBr pallet) 3394, 3286, 3212, 1680, 1631, 1539, 1462, 1292, 1202, 1153, 1005, 859, 813 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₆H₁₂NO₃: 266.0817. Found: 266.0816.

3-(Amino-*p*-tolyl-methylene)-5-hydroxy-3*H*-benzofuran-2-one (5d)

Yield: 80 %; Yellow solid; mp: 190-192 °C; ¹H NMR (250 MHz, Acetone-*d*₆) δ 2.46(s, 3H), 5.92(d, *J* = 2.5 Hz, 1H), 6.47(dd, *J* = 2.6, *J* = 8.5 Hz, 1H), 6.85(d, *J* = 8.5 Hz, 1H), 7.42(d, *J* = 8.0 Hz, 2H), 7.50(dd, *J* = 1.9Hz, *J* = 6.4 Hz, 2H), 7.55(brs, 1H), 7.81(s, 1H), 8.96(brs, 1H) ppm; ¹³C NMR (62.9 MHz, acetone) δ 21.5, 90.2, 106.2, 110.4, 110.9, 127.4, 128.6, 130.5, 132.9, 141.8, 143.9, 153.7, 163.5, 171.7 ppm; IR (KBr pallet) 3452, 3325, 3218, 1674, 1628, 1540, 1458, 1199, 1130, 1050, 999, 834 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₆H₁₂NO₃: 266.0817. Found: 266.0783.

3-[Amino-(4-fluoro-phenyl)-methylene]-5-hydroxy-3*H*-benzofuran-2-one (5e)

Yield: 88 %; Pale yellow solid; mp: 206-208 °C; ¹H NMR (250 MHz, Acetone-*d*₆) δ 5.81(d, *J* = 2.5 Hz, 1H), 6.48(dd, *J* = 2.6 Hz, *J* = 8.5 Hz, 1H), 6.86(d, *J* = 8.5Hz, 1H), 7.35 ~ 7.43(m, 2H), 7.63 ~ 7.70(m, 2H), 7.86(s, 1H), 8.92(brs, 1H) ppm; ¹³C NMR (62.9 MHz, acetone) : δ 90.6, 105.9, 110.6, 111.1, 116.9(d, *J* = 22.0 Hz), 127.1, 131.2(d, *J* = 8.7 Hz), 132.0(d, *J* = 3.4 Hz), 143.9, 153.8, 162.1, 164.8(d, *J* = 248.2 Hz), 171.5 ppm; IR (KBr pallet) 3382, 3307, 3206, 1658, 1628, 1536, 1502, 1453, 1135, 1096, 855 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₅H₉FNO₃: 270.0566. Found: 270.0556.

3-[Amino-(4-trifluoromethyl-phenyl)-methylene]-5-hydroxy-3*H*-benzofuran-2-one (5f)

Yield: 84 %; Yellow solid; mp: 216-218 °C; ¹H NMR (250 MHz, Acetone-*d*₆) δ 5.76(d, *J* = 2.5 Hz, 1H), 6.52(dd, *J* = 2.6 Hz, *J* = 8.5 Hz, 1H), 6.89(d, *J* = 8.5 Hz, 1H), 7.73(brs, 1H), 7.78(brs, 1H) 7.85(d, *J* = 8.0 Hz, 1H), 7.97(d, *J* = 8.2 Hz, 1H), 8.97(brs, 1H) ppm; ¹³C NMR (62.9 MHz, acetone) 90.8,

150.9, 110.7, 111.5, 116.6, 126.9(q, $J = 8.7$ Hz), 129.7, 132.6(q, $J = 32.3$ Hz), 139.5, 144.0, 151.1, 153.7, 161.3, 171.5 ppm; IR (KBr pallet) 3381, 3294, 3212, 1681, 1637, 1458, 1324, 1138, 1066, 761 cm^{-1} ; HRMS Cal. for $[\text{M-H}]^-$: $\text{C}_{16}\text{H}_9\text{F}_3\text{NO}_3$: 320.0535. Found: 320.0528.

3-[Amino-(4-methoxy-phenyl)-methylene]-5-hydroxy-3H-benzofuran-2-one (5g)

Yield: 80 %; Yellow solid; mp: 244-246 °C; ^1H NMR (250 MHz, Acetone- d_6) δ 3.92(s, 3H), 6.00(d, $J = 2.5$ Hz, 1H), 6.47(dd, $J = 2.6$, $J = 8.5$ Hz, 1H), 6.85(d, $J = 8.5$ Hz, 1H), 7.14(dt, $J = 2.5$ Hz, $J = 9.3$ Hz, 2H), 7.55 (brs, 1H), 7.56 (dt, $J = 2.5$ Hz, $J = 9.3$ Hz, 2H) 7.85(s, 1H), 8.94(brs, 1H) ppm; ^{13}C NMR (62.9 MHz, acetone) δ 55.9, 90.1, 106.1, 110.4, 110.8, 115.2, 127.6, 127.8, 130.4, 143.8, 153.7, 162.6, 163.3, 171.8 ppm; IR (KBr pallet) 3449, 3309, 3251, 1677, 1620, 1552, 1505, 1460, 1383, 1131, 1014, 835 cm^{-1} ; HRMS Cal. for $[\text{M-H}]^-$: $\text{C}_{16}\text{H}_{12}\text{NO}_4$: 282.0766. Found: 282.0759.

3-(Amino-pyridin-3-yl-methylene)-5-hydroxy-3H-benzofuran-2-one (5h)

Yield: 82 %; Yellow solid; mp: 266 - 270 °C; ^1H NMR (250 MHz, Acetone- d_6) δ 5.70(d, $J = 2.5$ Hz, 1H), 6.50(dd, $J = 2.5$ Hz, $J = 8.5$ Hz, 1H), 6.88((d, $J = 8.6$ Hz, 1H), 7.64(ddd, $J = 0.9$ Hz, $J = 4.8$ Hz, $J = 7.8$ Hz, 1H), 7.74(brs, 1H), 7.92(s, 1H), 8.00(ddd, $J = 1.8$ Hz, $J = 2.2$ Hz, $J = 7.9$ Hz, 1H), 8.80(dd, $J = 0.8$ Hz, $J = 2.3$ Hz, 1H), 8.84(dd, $J = 1.6$ Hz, $J = 4.9$ Hz, 1H), 8.93(brs, 1H) ppm; ^{13}C NMR (62.9 MHz, acetone) 104.9, 109.9, 110.6, 123.8, 126.0, 130.8, 135.6, 143.2, 148.3, 151.6, 153.0, 159.0, 170.5 ppm; IR (KBr pallet) 3376, 3274, 3195, 1711, 1625, 1558, 1469, 1377, 1212, 1135, 996, 814 cm^{-1} ; HRMS Cal. for $[\text{M-H}]^-$: $\text{C}_{14}\text{H}_9\text{N}_2\text{O}_3$: 253.0613. Found: 253.0607.

3-(Amino-furan-2-yl-methylene)-5-hydroxy-3H-benzofuran-2-one (5i)

Yield: 74 %; Yellow solid; mp: 188-192 °C; ^1H NMR (250 MHz, Acetone- d_6) δ 6.58(dd, $J = 2.6$ Hz, $J = 8.5$ Hz, 1H), 6.81(dd, $J = 1.8$ Hz, $J = 3.5$ Hz, 1H), 6.86 (d, $J = 2.5$ Hz, 1H), 6.91 (d, $J = 8.5$ Hz, 1H), 7.31(dd, $J = 0.7$ Hz, $J = 3.5$ Hz, 1H), 7.55(brs, 1H), 7.95(d, $J = 1.1$ Hz, 1H), 7.98(s, 1H), 8.95(brs, 1H) ppm; ^{13}C NMR (62.9 MHz, Acetone- d_6) δ 90.3, 107.2, 110.6, 111.6, 113.2, 115.9, 126.5, 143.9, 146.4, 147.9, 150.1, 154.1, 172.3 ppm; IR (KBr pallet) 3376, 3274, 3195, 1711, 1625, 1558, 1469, 1212, 1135, 996, 814 cm^{-1} ; HRMS Cal. for $[\text{M-H}]^-$: $\text{C}_{13}\text{H}_8\text{NO}_4$: 242.0453. Found: 242.0451.

3-(1-Amino-2-phenyl-ethylidene)-5-hydroxy-3H-benzofuran-2-one (5j)

Yield: 78 %; Pale yellow solid; mp: 180-182 °C; ^1H NMR (250 MHz, Acetone- d_6) δ 4.18(s, 2H), 6.54(dd, $J = 2.5$ Hz, $J = 8.5$ Hz, 1H), 6.80(d, $J = 2.5$ Hz, 1H), 6.89(d, $J = 8.5$ Hz, 1H), 7.22 ~ 7.40(m, 5H), 7.45(brs, 1H), 7.97(s, 1H), 9.04(brs, 1H) ppm; ^{13}C NMR (62.9 MHz, Acetone- d_6) δ 39.6, 90.6, 106.8, 110.4, 110.5, 127.5, 128.0, 129.5, 129.8, 135.9, 143.7, 154.3, 164.4, 171.7 ppm; IR (KBr pallet) 3395, 3284, 3219, 1679, 1634, 1538, 1468, 1203, 1154, 1009, 812 cm^{-1} ; HRMS Cal. for $[\text{M-H}]^-$: $\text{C}_{16}\text{H}_{12}\text{NO}_3$: 266.0817. Found: 266.0810.

3-(1-Amino-propylidene)-5-hydroxy-3*H*-benzofuran-2-one (5k)

Yield: 82 %; Pale yellow solid; mp: 178-180 °C; ¹H NMR (250 MHz, Acetone-d₆) δ 1.34(t, *J* = 7.6 Hz, 3H), 2.78(q, *J* = 7.6 Hz, 2H), 6.55(dd, *J* = 2.5 Hz, *J* = 8.5 Hz, 1H), 6.80(d, *J* = 2.5 Hz, 1H), 6.88(d, *J* = 8.5 Hz, 1H), 7.61(brs, 1H), 7.99(s, 1H), 8.90(brs, 1H) ppm; ¹³C NMR (62.9 MHz, Acetone-d₆) δ 11.6, 27.7, 88.9, 106.4, 110.0, 110.3, 127.5, 143.5, 154.3, 168.7, 171.7 ppm; IR (KBr pallet) 3395, 3298, 3223, 2979, 1685, 1635, 1546, 1464, 1206, 1153, 1000, 911, 845 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₁H₁₀NO₃: 204.0661. Found: 204.0659.

3-(1-Amino-3-methyl-butylidene)-5-hydroxy-3*H*-benzofuran-2-one (5l)

Yield: 80 %; Pale yellow solid; mp: 220-222 °C; ¹H NMR (250 MHz, Acetone-d₆) δ 1.08(d, *J* = 6.6 Hz, 6H), 2.07 ~ 2.20(m, 1H), 2.64(d, *J* = 7.4 Hz, 2H), 6.53(dd, *J* = 2.5 Hz, *J* = 8.5 Hz, 1H), 6.78(d, *J* = 2.4 Hz, 1H), 6.88(d, *J* = 8.5 Hz, 1H), 7.61(brs, 1H), 8.05(s, 1H), 9.01(brs, 1H) ppm; ¹³C NMR (62.9 MHz, Acetone-d₆) : δ 22.5, 27.7, 43.1, 89.7, 106.5, 110.2, 110.4, 127.6, 143.5, 154.2, 166.6, 171.7 ppm; IR (KBr pallet) 3395, 3294, 3231, 2964, 1678, 1643, 1536, 1466, 1152, 1006, 846 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₃H₁₄NO₃: 232.0974. Found: 232.0971.

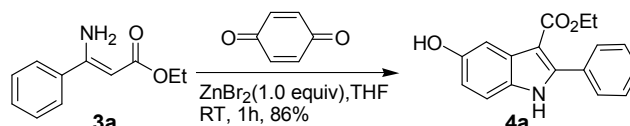
3-(Amino-phenyl-methylene)-5-hydroxy-4,6-dimethyl-3*H*-benzofuran-2-one (5m)

Yield: 76 %; Pale yellow solid; mp: 240-242 °C; ¹H NMR (250 MHz, Acetone-d₆) δ 1.20(s, 3H), 2.23(s, 3H) 6.73(s, 1H), 6.75(s, 1H), 7.31(brs, 1H) 7.50 ~ 7.58(m, 5H), 9.04(brs, 1H) ppm; ¹³C NMR (62.9 MHz, Acetone-d₆) : δ 15.01, 17.04, 92.2, 109.4, 117.5, 121.2, 124.0, 129.6, 129.9, 131.6, 139.0, 144.6, 150.2, 162.2, 172.3 ppm; IR (KBr pallet) 3363, 3277, 3195, 1692, 1624, 1533, 1488, 1214, 1034, 847 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₇H₁₄NO₃: 280.0974. Found: 280.0980.

3-(Amino-phenyl-methylene)-5-hydroxy-4,7-dimethyl-3*H*-benzofuran-2-one (5n)

Yield: 82 %; Pale yellow solid; mp: 238-240 °C; ¹H NMR (250 MHz, Acetone-d₆) δ 1.16(s, 3H), 2.23(s, 3H) 6.46(s, 1H), 7.36(brs, 1H) 7.49 ~ 7.61(m, 6H), 9.13(brs, 1H) ppm; ¹³C NMR (62.9 MHz, Acetone-d₆) : δ 14.2, 14.8, 92.4, 112.7, 114.3, 117.1, 126.0, 129.5, 129.7, 131.6, 138.9, 142.7, 152.2, 163.0, 172.2 ppm; IR (KBr pallet) 3417, 3320, 3225, 1675, 1627, 1533, 1267, 1207, 1056, 912 cm⁻¹; HRMS Cal. for [M-H]⁻: C₁₇H₁₄NO₃: 280.0974. Found: 280.0978.

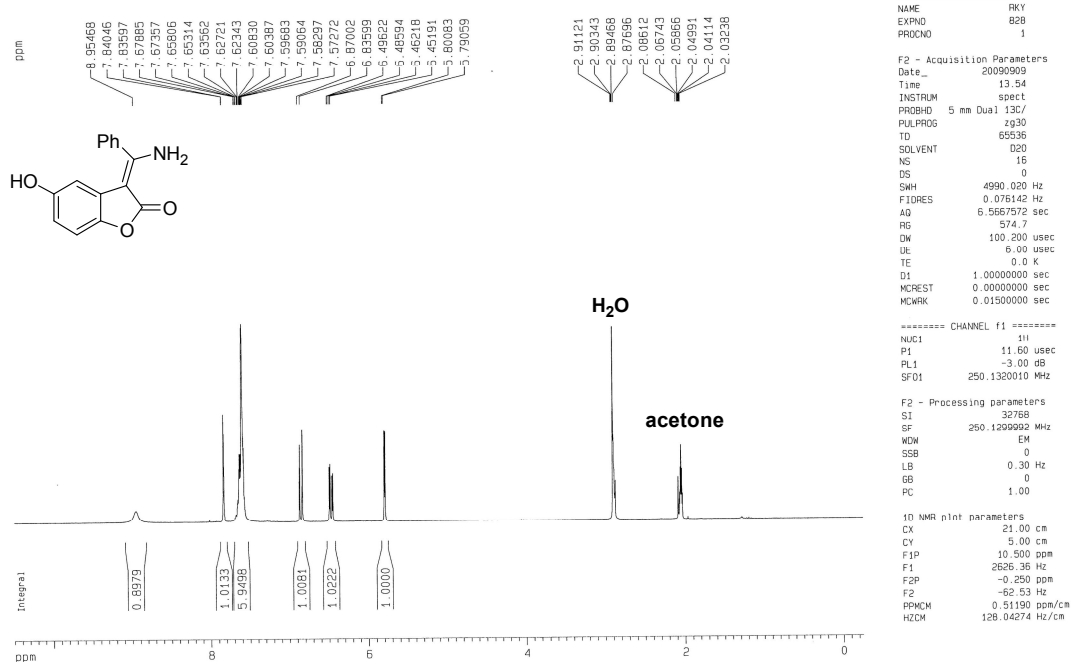
Synthesis of indole 4a from the isolated β-enaminoester 3a.



To a solution of the isolated β-enaminoesters **3a** (0.191 g, 1 mmol) in anhydrous THF (2 mL) were added anhydrous ZnBr₂ (0.225 g, 1 mmol) and a solution of 1,4-benzoquinone (0.108 g, 1mmol) in anhydrous THF (2 mL) successively at room temperature. After stirring for 1h, the reaction was

quenched with saturated aqueous NH_4Cl , and extracted with ethyl acetate (3 x 10 mL). The combined organic layer was dried with anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica chromatography to afford **4a** (86 %, 0.244 g). Yield: 86 %; white solid; mp: 174-176 °C; ^1H NMR (250 MHz, Acetone- d_6) δ 1.25(t, $J = 7.1\text{ Hz}$, 3H), 4.22(q, $J = 7.1\text{ Hz}$, 2H) 6.67(s, 1H), 6.82(dd, $J = 2.4\text{ Hz}$, $J = 8.7\text{ Hz}$, 1H), 7.42 ~ 7.46 (m, 2H), 7.67 ~ 7.73 (m, 3H), 8.01 (brs, 1H) 10.82 (brs, 1H) ppm; ^{13}C NMR (62.9 MHz, Acetone- d_6) : δ 13.8, 58.7, 106.1, 112.0, 112.7, 115.7, 127.7, 128.6, 129.2, 129.8, 130.5, 132.7, 144.7, 152.8, 164.8 ppm; IR (KBr pallet) 3380, 3282, 1655, 1624, 1454, 1377, 1294, 1234, 1190, 1045, 871 cm^{-1} ; HRMS Cal. for $[\text{M-H}]^-$: $\text{C}_{17}\text{H}_{14}\text{NO}_3$: 280.0974. Found: 280.0984.

^1H and ^{13}C NMR spectra of **5a**



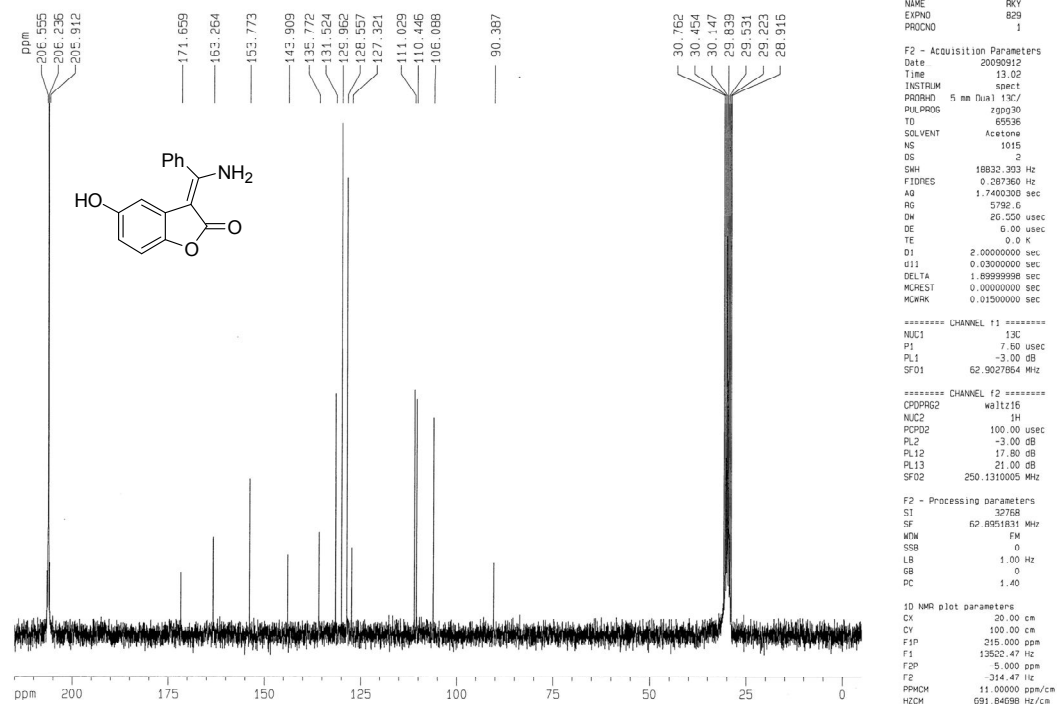
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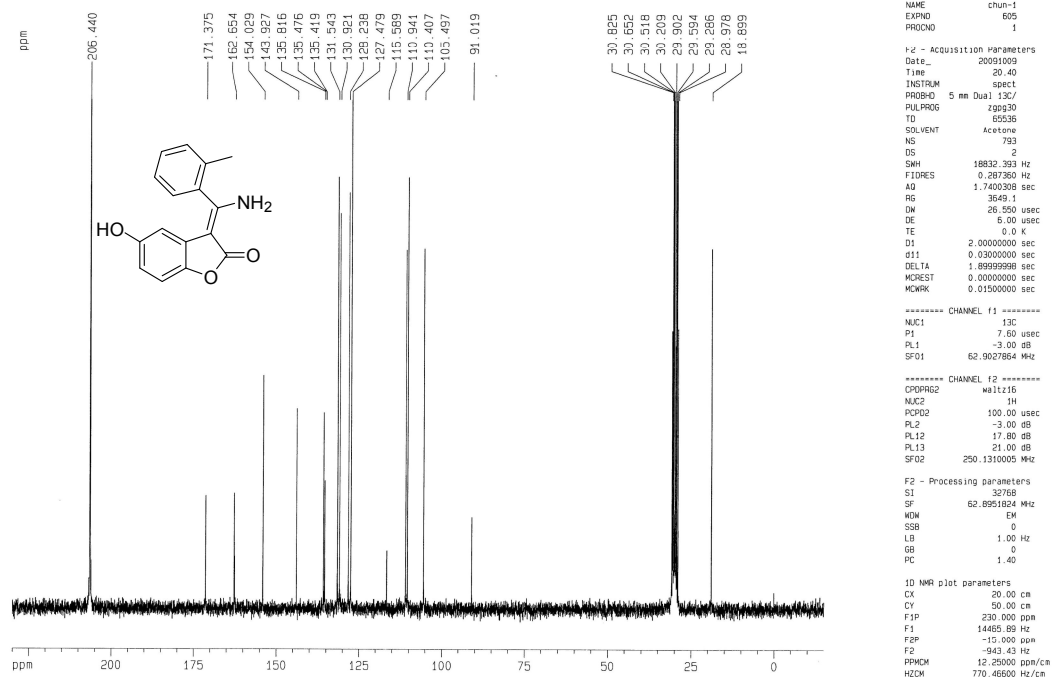
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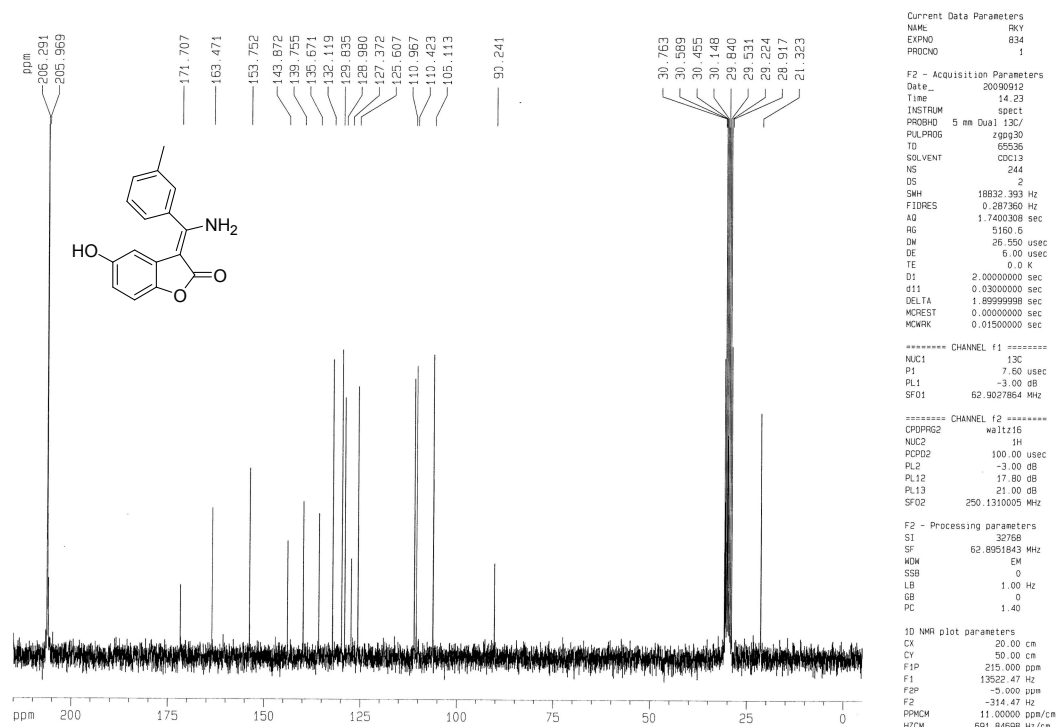
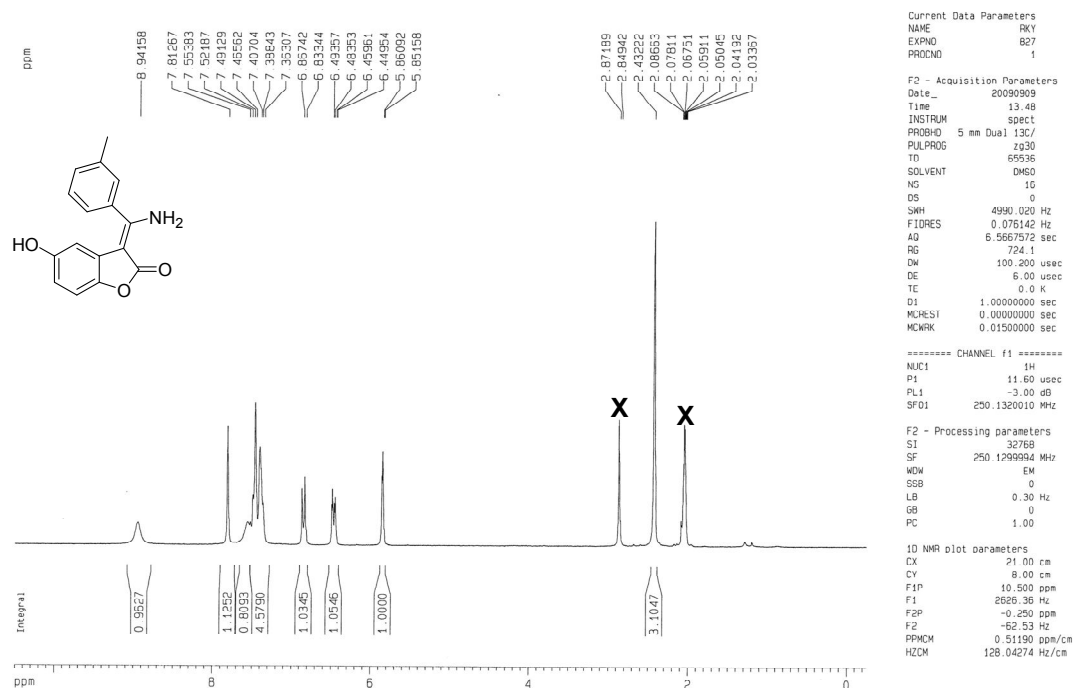
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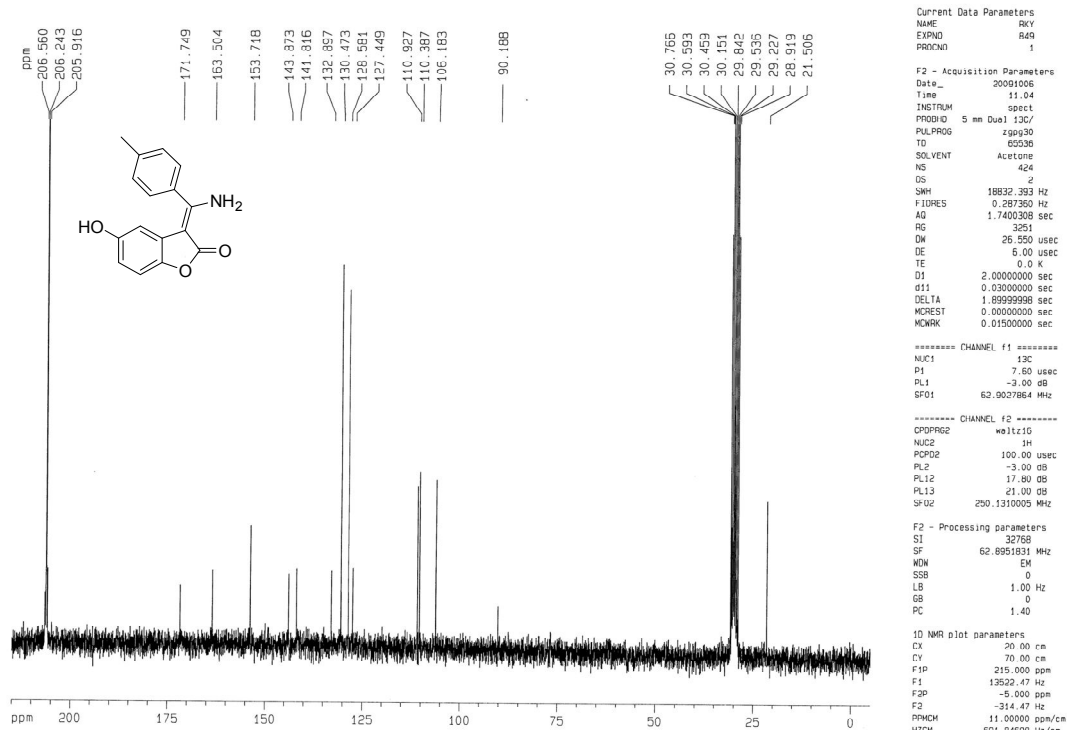
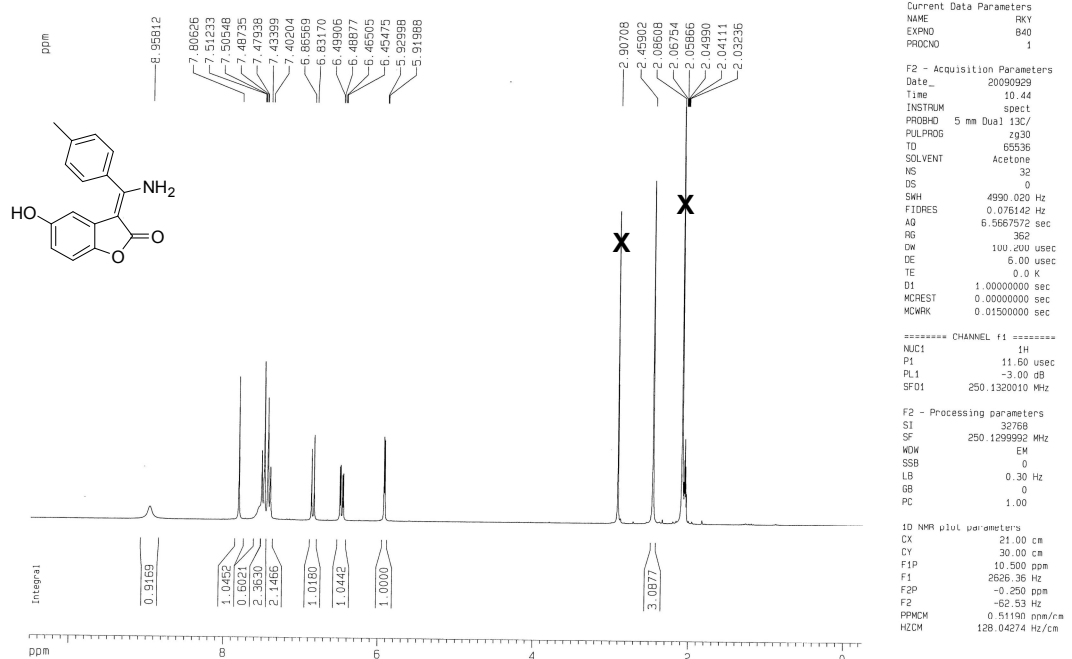
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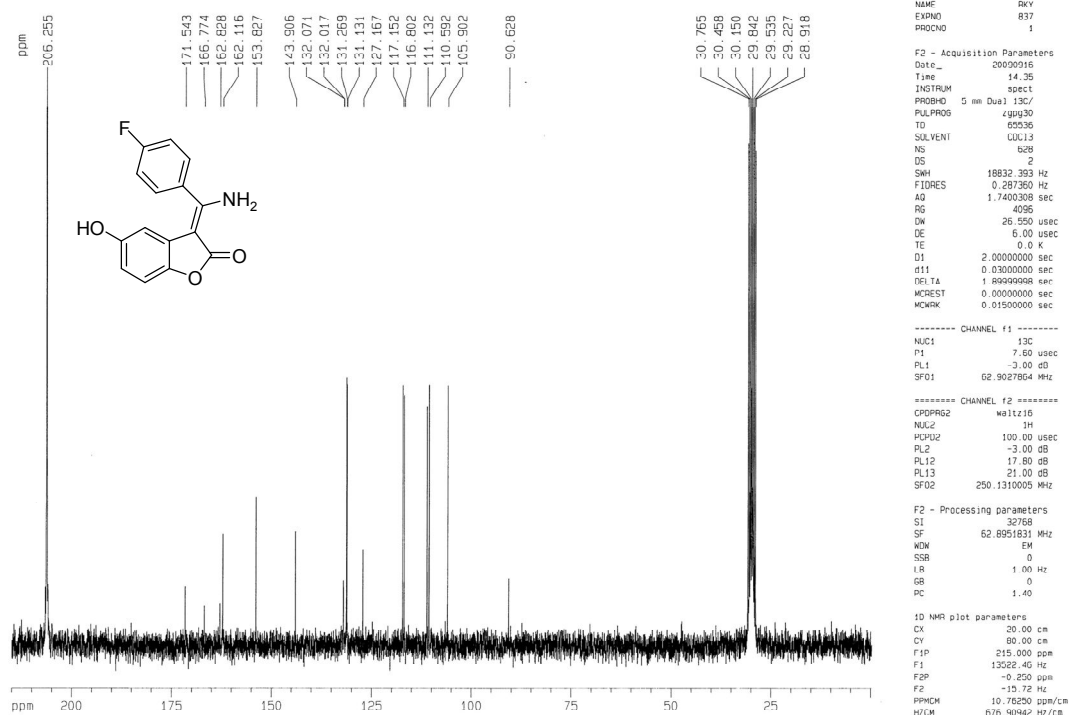
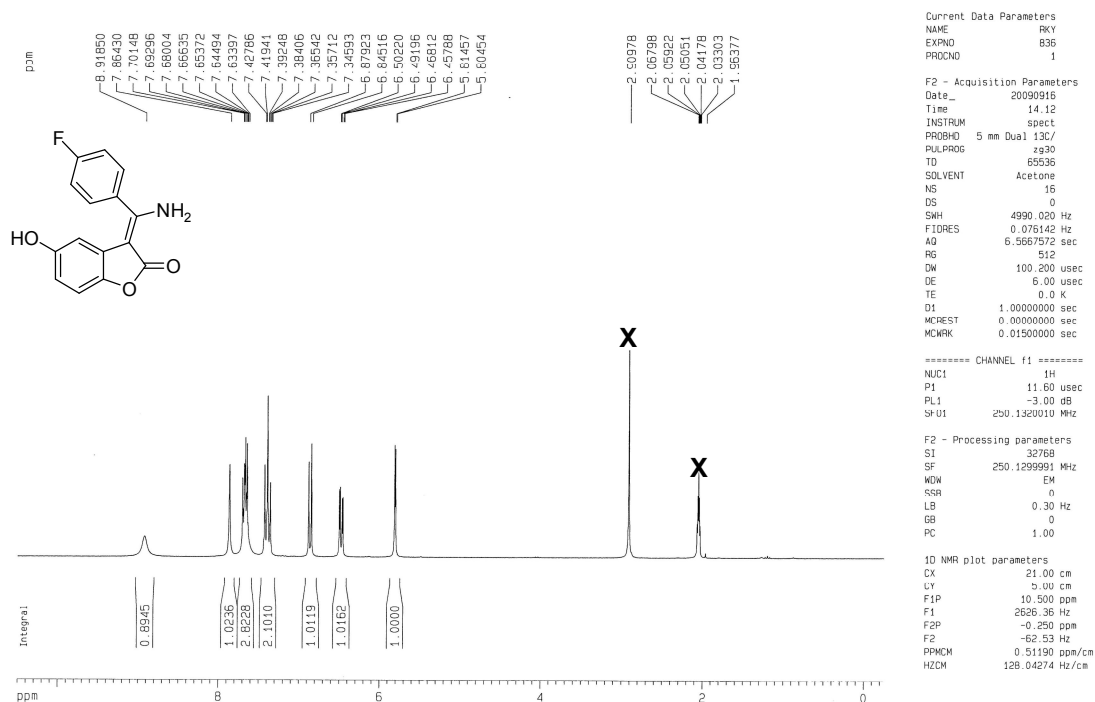
^1H and ^{13}C NMR spectra of **5c**



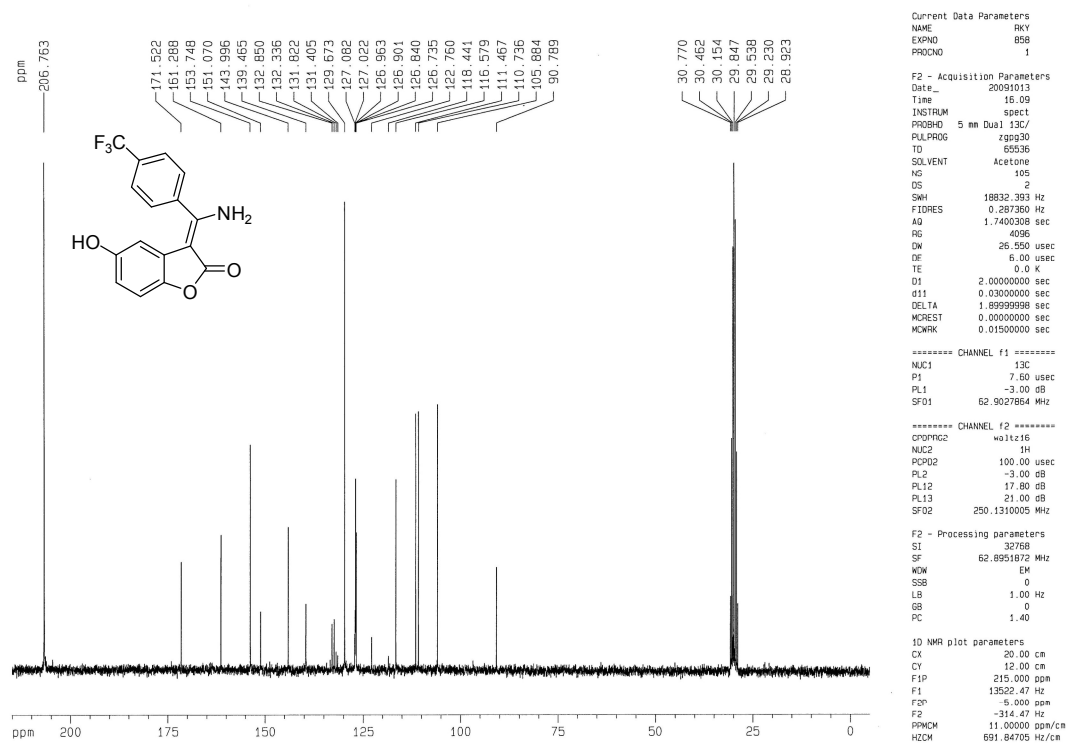
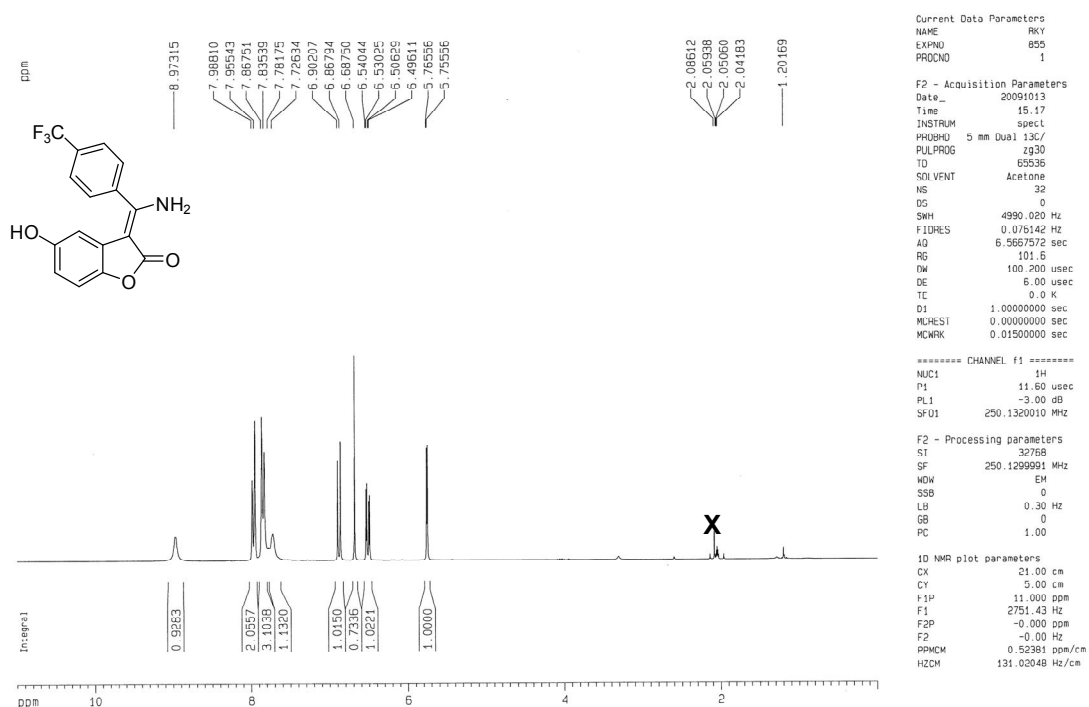
^1H and ^{13}C NMR spectra of **5d**



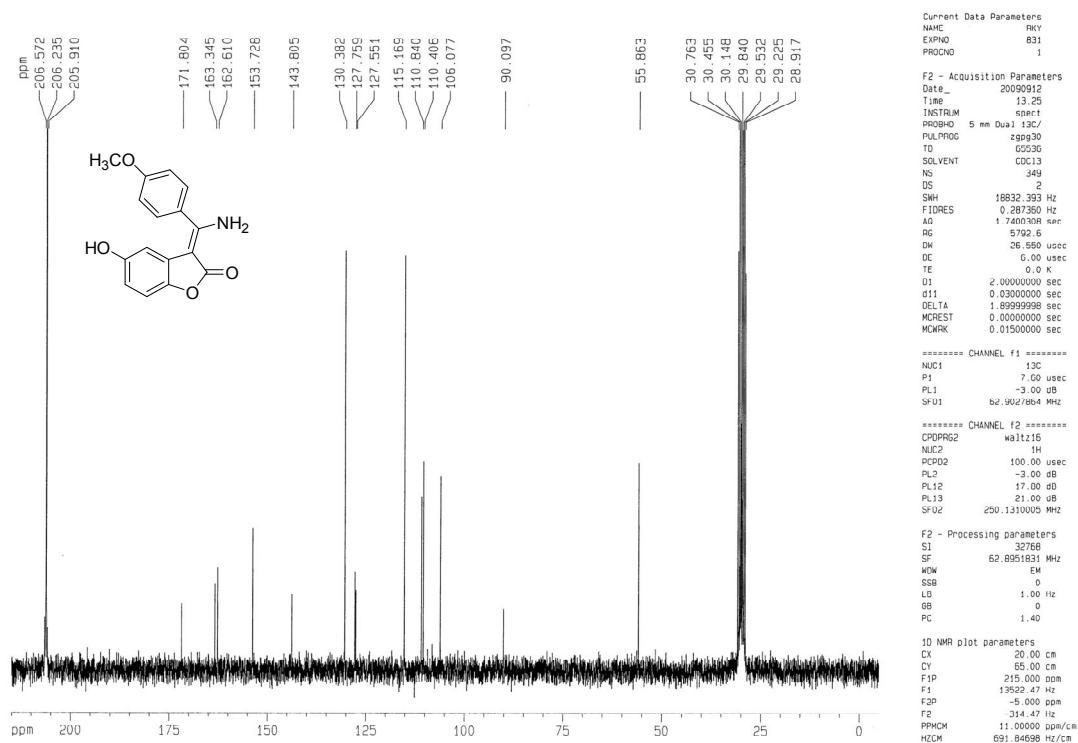
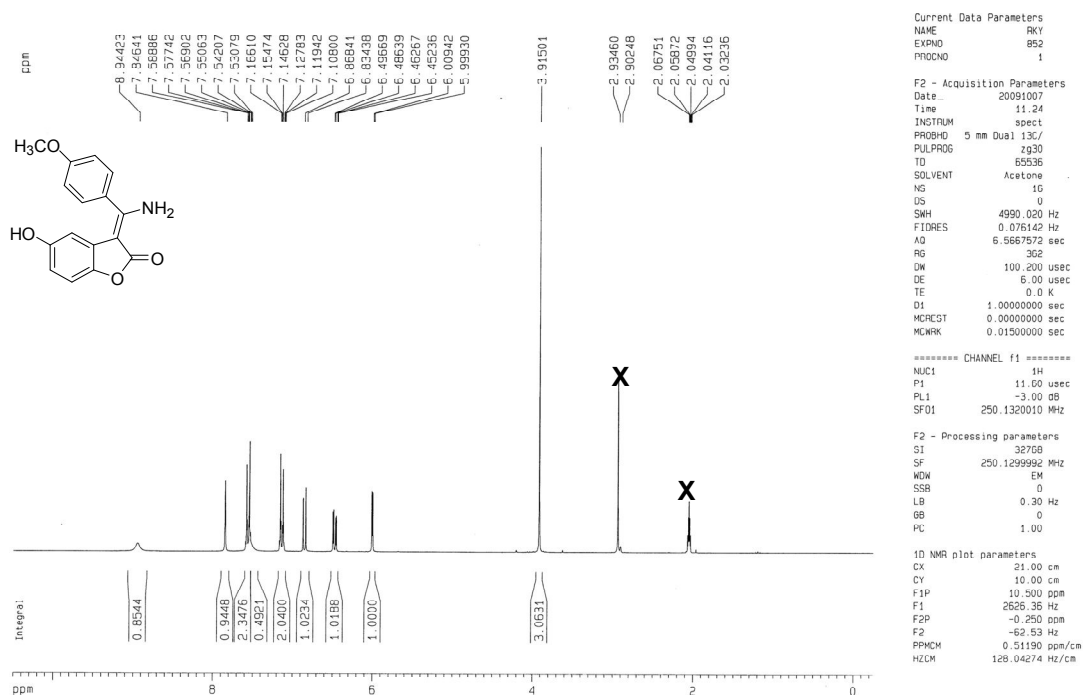
^1H and ^{13}C NMR spectra of **5e**



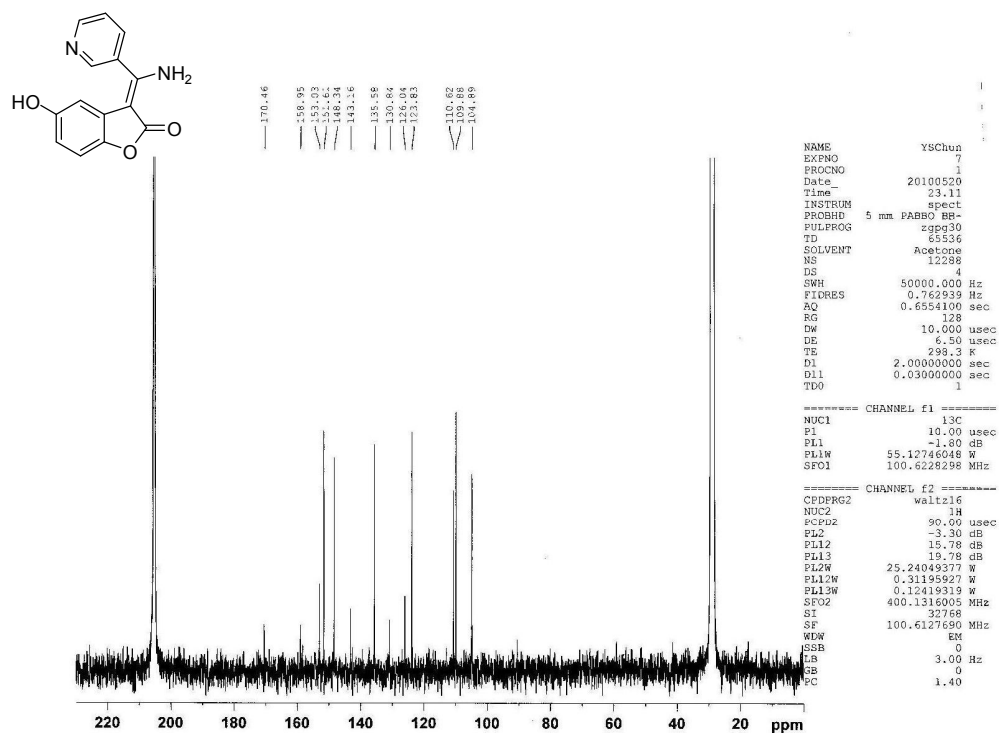
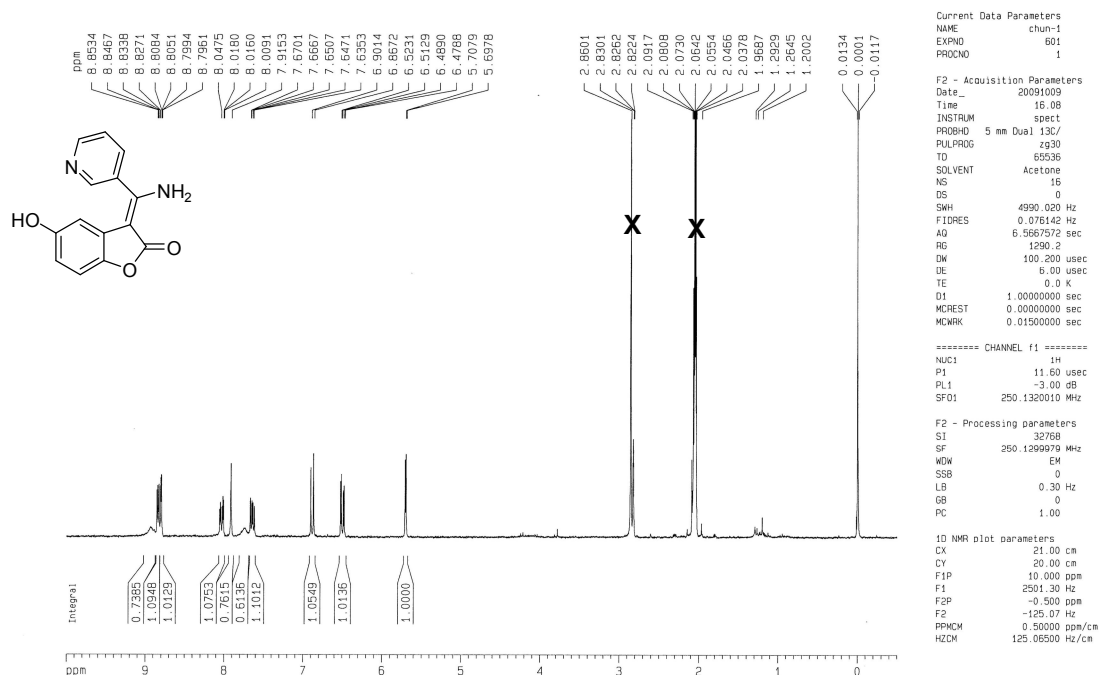
^1H and ^{13}C NMR spectra of **5f**



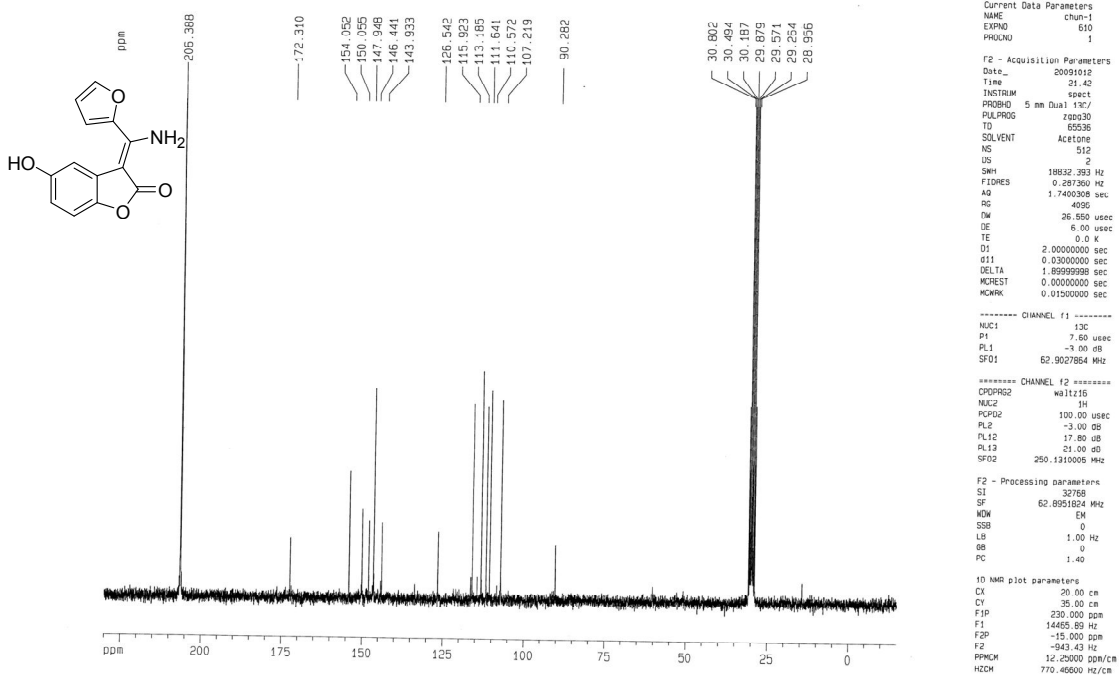
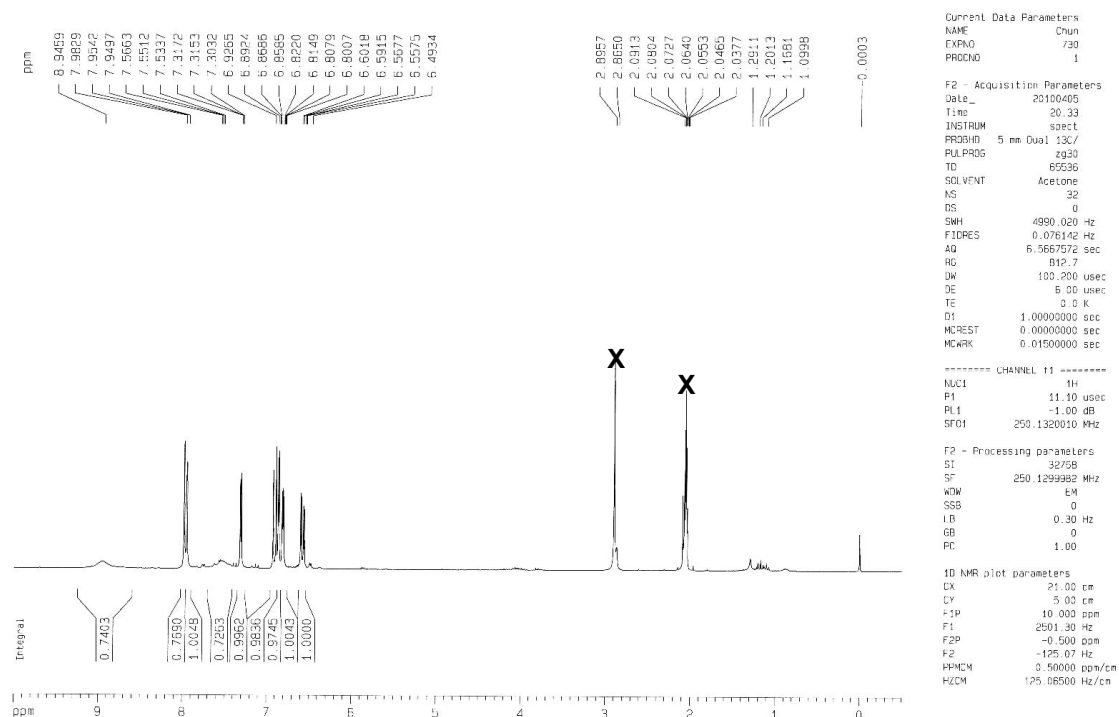
^1H and ^{13}C NMR spectra of **5g**



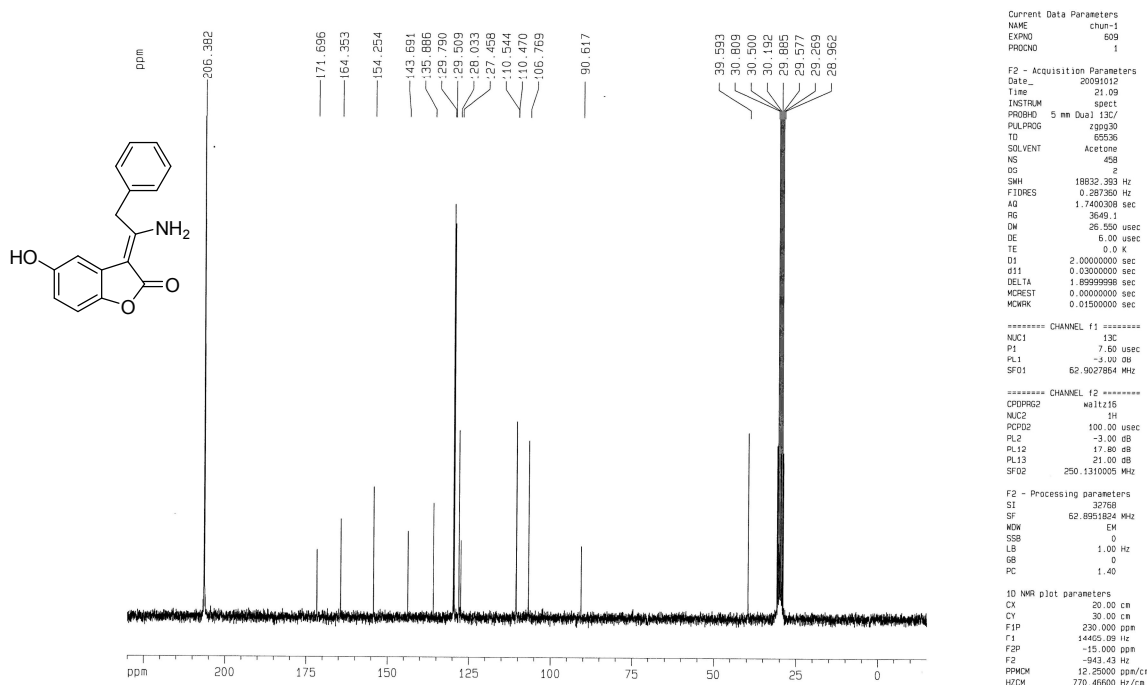
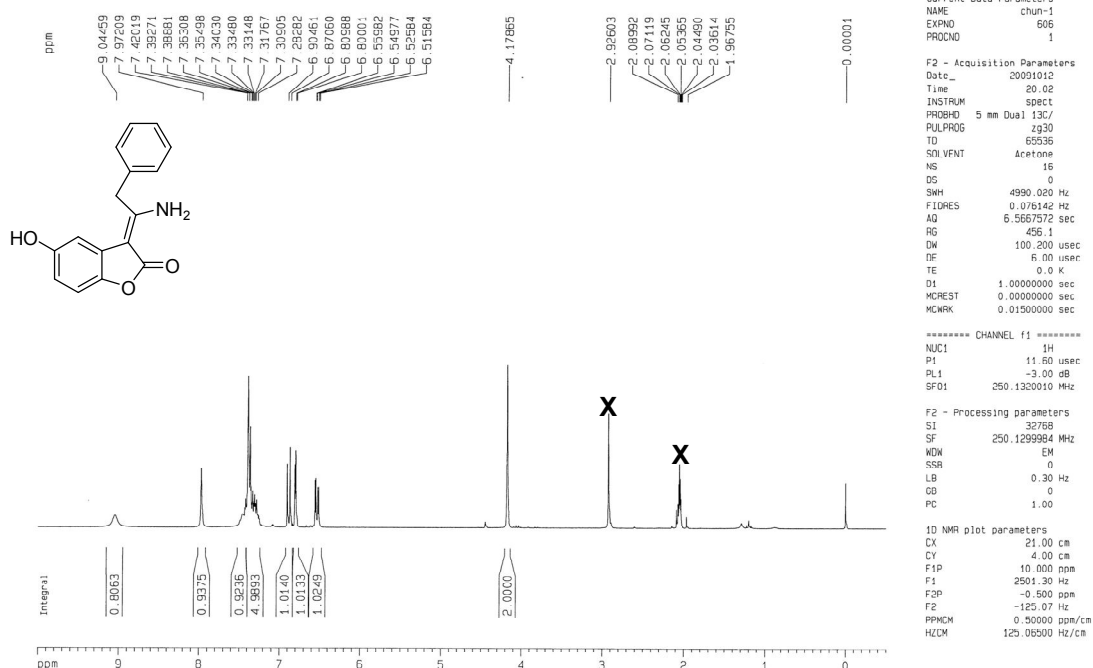
^1H and ^{13}C NMR spectra of **5h**



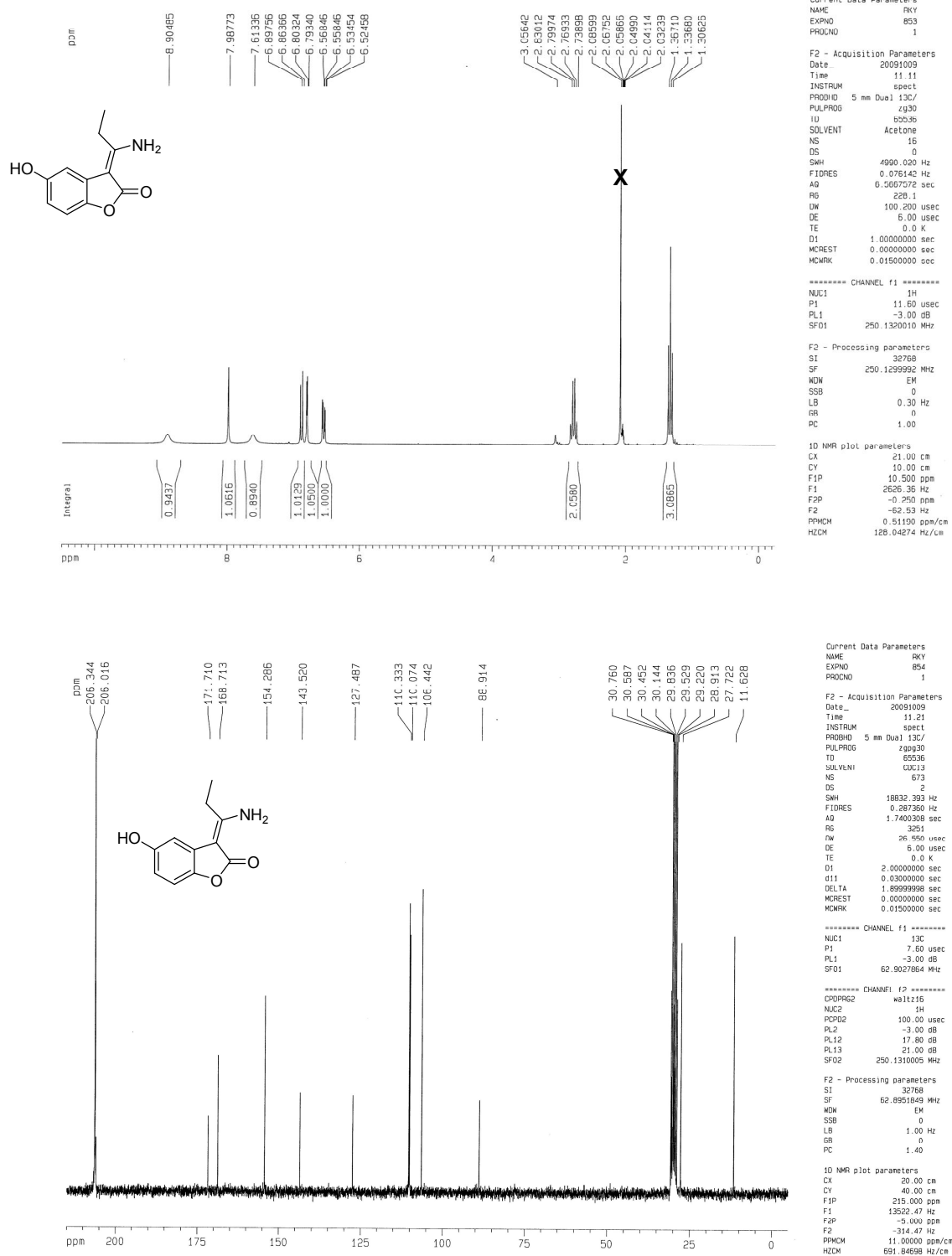
^1H and ^{13}C NMR spectra of **5i**



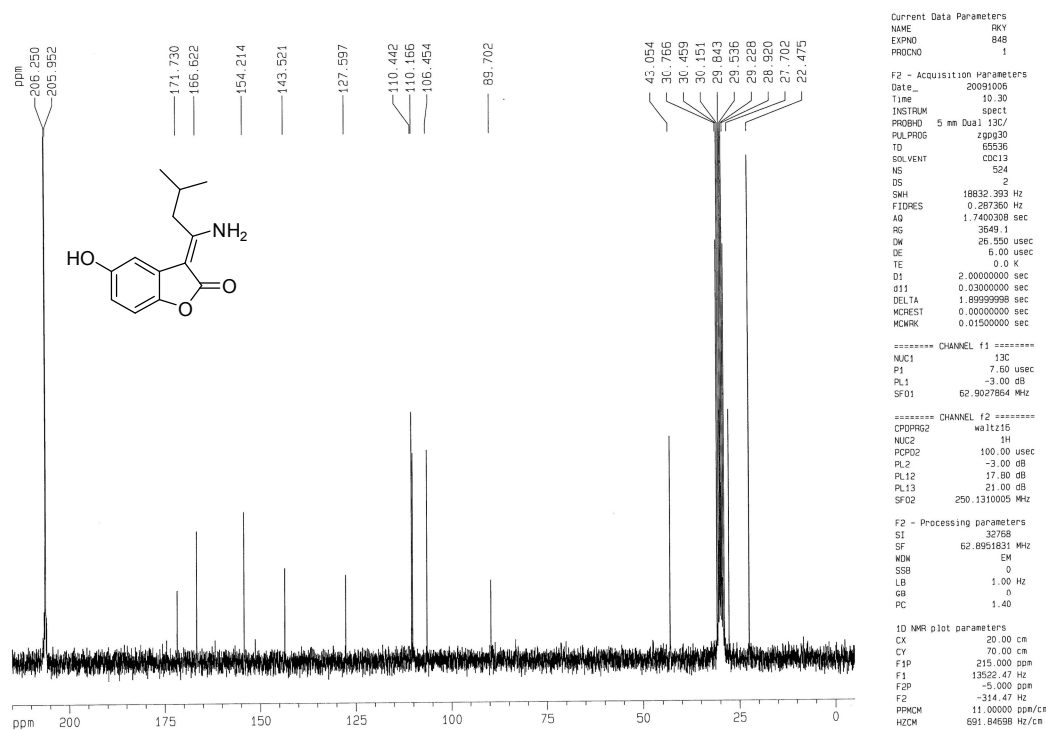
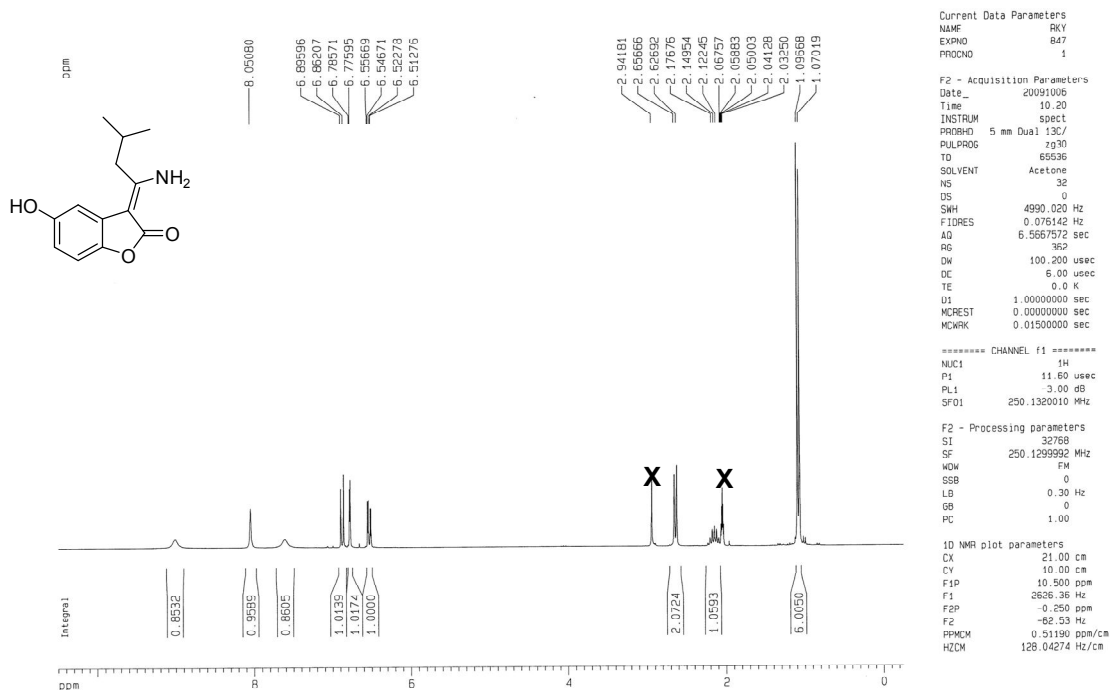
^1H and ^{13}C NMR spectra of **5j**



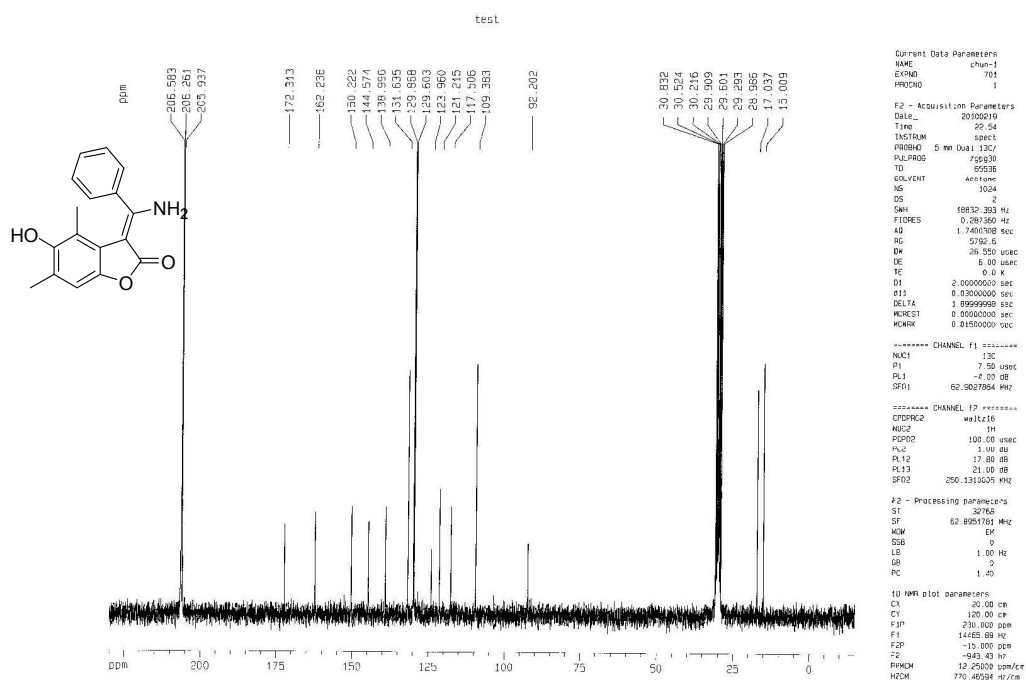
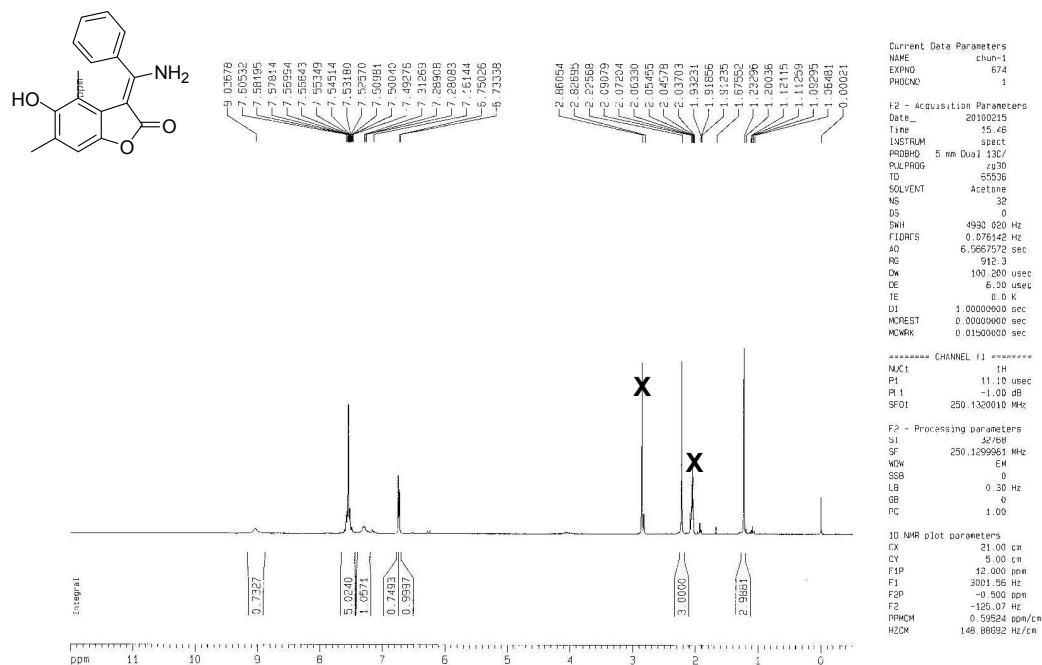
^1H and ^{13}C NMR spectra of **5k**



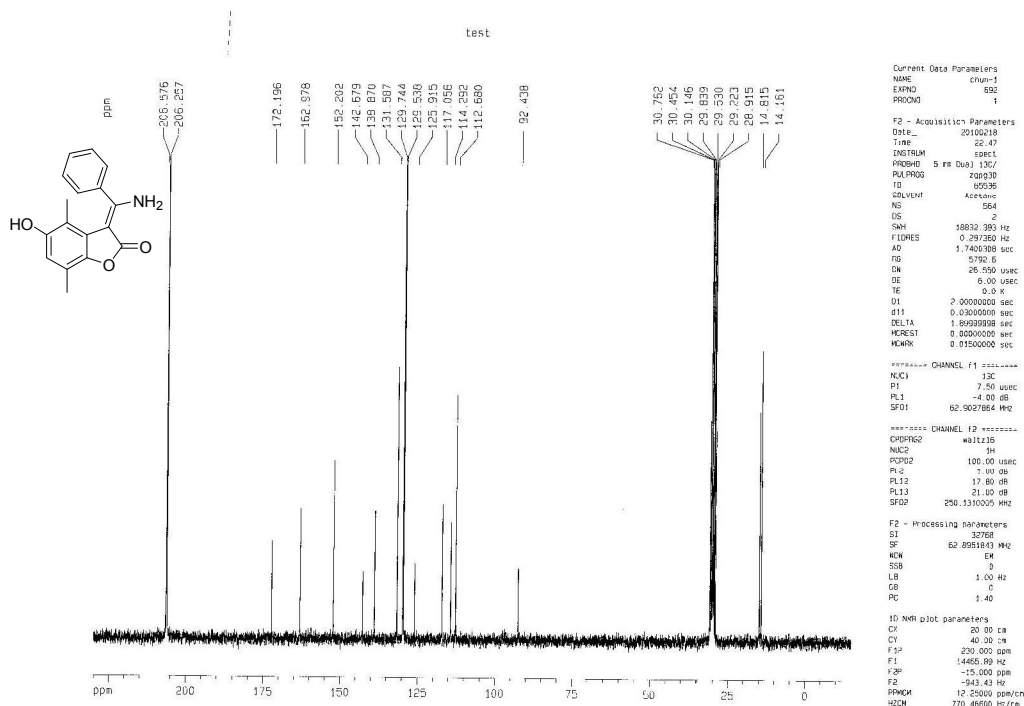
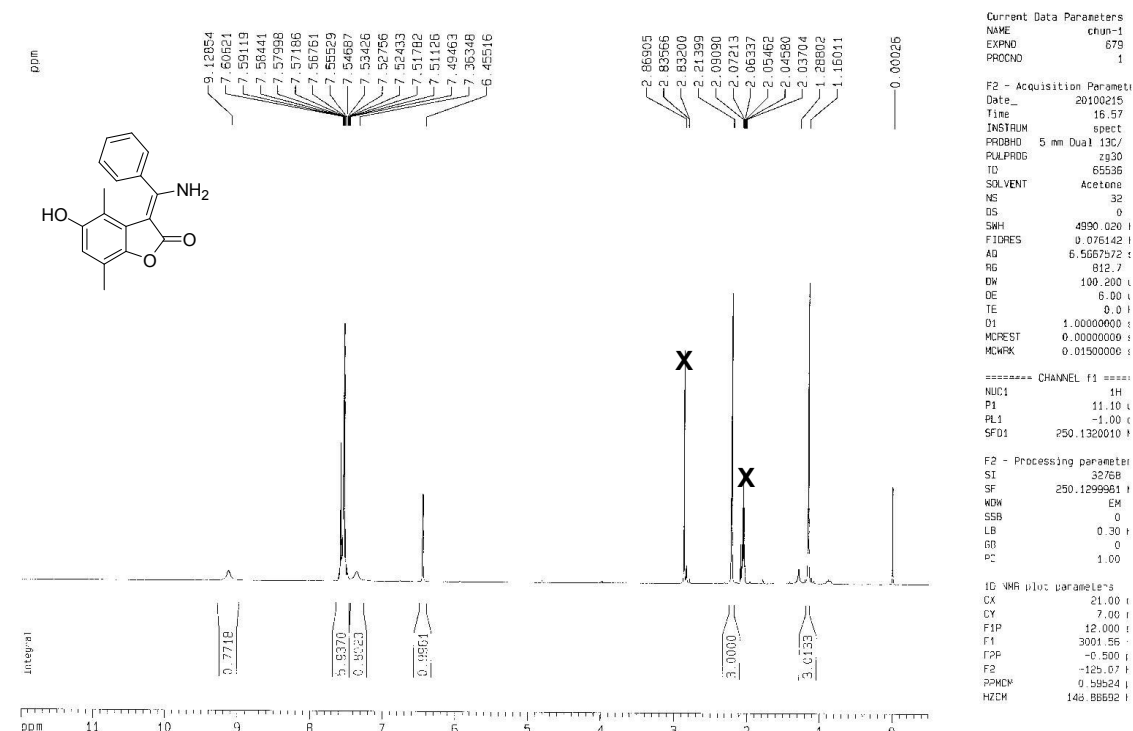
^1H and ^{13}C NMR spectra of **51**



^1H and ^{13}C NMR spectra of **5m**



^1H and ^{13}C NMR spectra of **5n**



^1H and ^{13}C NMR spectra of **4a**

