Supporting Information

for

Magnetic metal-organic framework as a highly active heterogeneous catalyst for one-pot synthesis of 2-substituted alkyl and aryl(indolyl)kojic acid derivatives

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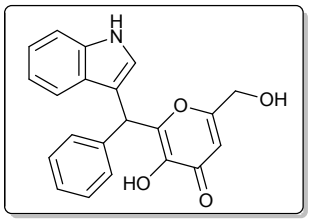
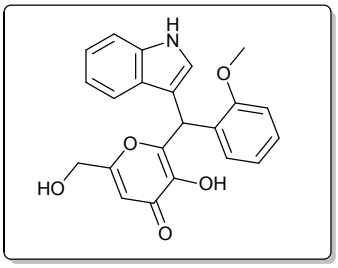
2-((1*H*-Indol-3-yl)(phenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4a)



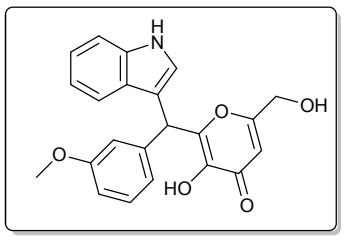
Brown solid; IR (KBr): 3387, 3269, 2924, 2850, 1655, 1621, 1456, 1228, 738 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.06 (s, 1 H), 9.15 (s, 1 H), 7.23-7.37 (m, 8 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 6.93 (t, *J* = 7.5 Hz, 1 H), 6.31 (s, 1 H), 5.98 (s, 1 H), 5.66 (s, 1 H), 4.25 (d, *J* = 5.0 Hz, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.6, 151.5, 141.4, 141.0, 136.6, 128.9, 128.7,127.2, 126.2, 124.5, 121.7, 119.1, 118.9, 113.3, 112.1, 109.5, 60.0. ESI-MS: m/z = 348.3 $(M+1)^+$.

2-((1*H*-Indol-3-yl)(2-methoxyphenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4b)



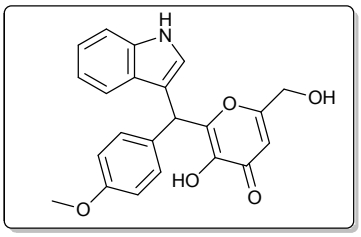
Brown solid; IR (KBr): 3436, 2919, 1658, 1624, 1460, 1252, 1094, 756 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 10.96 (s, 1 H), 8.88 (s, 1 H), 7.35 (d, *J* = 8.0 Hz, 1 H), 7.28 (t, *J* = 7.0 Hz, 2 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.00-7.07 (m, 3 H), 6.92 (t, *J* = 7.5 Hz, 1 H), 6.86 (t, *J* = 7.5 Hz, 1 H), 6.34 (s, 1 H), 6.30 (s, 1 H), 5.63 (s, 1 H), 4.22 (s, 2 H), 3.79 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.5, 156.9, 151.5, 141.4, 136.7, 129.9, 128.7, 128.5, 126.9, 124.3, 121.6, 120.8, 119.1, 118.7, 113.9, 112.0, 111.5, 109.4, 60.1, 56.2, 33.3. ESI-MS: m/z = 378.3 $(M+1)^+$.

2-((1*H*-Indol-3-yl)(3-methoxyphenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4c)



Brown solid; IR (KBr): 3409, 2926, 2838, 1618, 1453, 1239, 1047, 749 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.05 (s, 1 H), 9.15 (s, 1 H), 7.36 (t, *J* = 8.5 Hz, 1 H), 7.23 (d, *J* = 7.5 Hz, 2 H), 7.07 (d, *J* = 7.5 Hz, 2 H), 6.89-6.95 (m, 3 H), 6.81 (d, *J* = 8.5 Hz, 1 H), 6.31 (s, 1 H), 5.94 (s, 1 H), 5.66 (s, 1 H), 4.25 (s, 2 H), 3.69 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.5, 159.7, 151.4, 142.5, 141.4, 136.6, 129.9, 126.9, 124.5, 121.7, 121.0, 119.2, 118.9, 114.7, 113.2, 112.3, 112.1, 109.5, 60.1, 55.4. ESI-MS: m/z = 378.3 $(M+1)^+$.

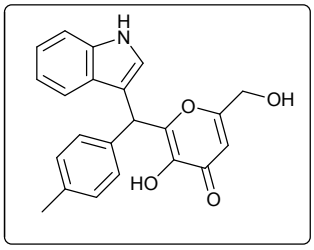
2-((1*H*-Indol-3-yl)(4-methoxyphenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4d)



Brown solid; IR (KBr): 3422, 2926, 1611, 1460, 1245, 1178,

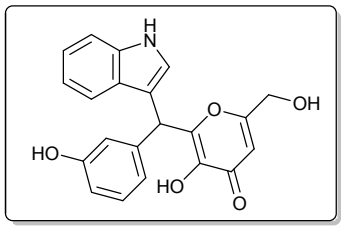
1027, 792 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.03 (s, 1 H), 9.09 (s, 1 H), 7.36 (d, *J* = 8.5 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 1 H), 7.27 (d, *J* = 8.5 Hz, 2 H), 7.20 (s, 1 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.92 (t, *J* = 7.5 Hz, 1 H), 6.86 (d, *J* = 8.0 Hz, 2 H), 6.30 (s, 1 H), 5.91 (s, 1 H), 5.65 (s, 1 H), 4.24 (s, 2 H), 3.71 (s, 3 H). ^{13}C NMR (125MHz, DMSO-d_6): δ = 174.2, 167.6, 158.5, 151.8, 141.2, 136.7, 132.9, 129.7, 126.8, 124.3, 121.7, 119.1, 119.0, 114.3, 113.7, 112.0, 109.4, 60.0, 55.5, 21.2, 14.6. ESI-MS: m/z = 378.3 $(M+1)^+$.

2-((1*H*-Indol-3-yl)(p-tolyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4e)



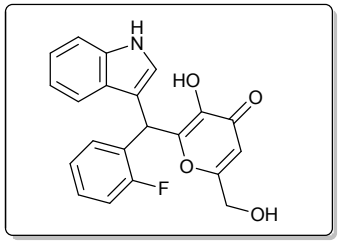
Brown solid; IR (KBr): 3400, 2924, 2856, 1650, 1620, 1456, 1311, 1227, 1076, 995, 738 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.04 (s, 1 H), 9.11 (s, 1 H), 7.23-7.38 (m, 5 H), 7.05-7.11 (m, 3 H), 6.92 (t, *J* = 7.5 Hz, 1 H), 6.31 (s, 1 H), 5.94 (s, 1 H), 5.66 (s, 1 H), 4.25 (s, 2 H), 2.25 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.6, 151.7, 141.3, 138.0, 136.7, 136.2, 129.5, 128.6, 126.9, 124.4, 121.7, 119.1, 119.0, 113.5, 112.0, 109.5, 60.1, 21.1. ESI-MS: m/z = 362.3 $(M+1)^+$.

3-Hydroxy-6-(hydroxymethyl)-2-((3-hydroxyphenyl)(1*H*-indol-3-yl)methyl)-4*H*-pyran-4-one (4f)



Brown solid; IR (KBr): 3409, 2926, 2851, 1618, 1453, 1232, 1198, 736 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.05 (s, 1 H), 9.31 (s, 1 H), 9.12 (s, 1 H), 6.60-7.38 (m, 9 H), 6.31 (s, 1 H), 5.89 (s, 1 H),5.66 (t, *J* = 6.0Hz, 1 H), 4.25 (d, J = 5.5Hz, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.6, 157.8, 151.6, 142.4, 141.4, 136.6, 129.8, 126.9, 124.5, 121.7, 119.2, 119.1, 119.0, 115.5, 114.2, 113.1, 112.0, 109.4, 60.0. ESI-MS: m/z = 364.3 $(M+1)^+$.

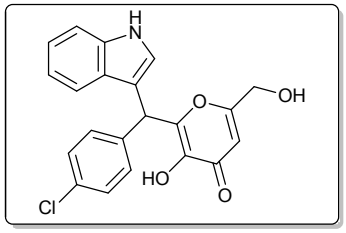
2-((2-Fluorophenyl)(1H-indol-3-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one(4g)



Brown solid; IR (KBr): 3395, 2926, 2858, 1645, 1611, 1466, 1212,1087, 997, 742 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.09 (s, 1 H), 9.16 (s, 1 H), 7.18-7.42 (m, 6 H), 7.13 (t, *J* = 7.5 Hz, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 6.95 (t, *J* = 7.5 Hz, 1 H), 6.32 (s, 1 H), 6.24 (s, 1 H), 5.66 (t, *J* = 6.0 Hz, 1 H),4.24 (d, *J* = 5.5 Hz, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.7, 160.2 (d, $^1J_{FC}$ = 243.3 Hz),

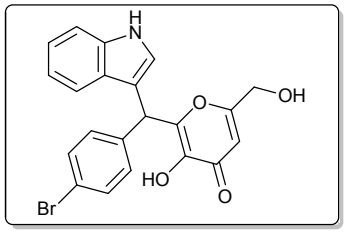
150.2, 141.5, 136.7, 130.9, 129.4 (d, $^{3}J_{FC}$ = 8.2Hz), 127.5 (d, $^{3}J_{FC}$ = 13.8Hz), 126.6, 124.9 (d, $^{4}J_{FC}$ = 2.8Hz), 124.6, 121.8, 119.3, 118.4, 115.7 (d, $^{2}J_{FC}$ = 21.9Hz), 112.3 (d, $^{2}J_{FC}$ = 26.6Hz), 109.6, 60.0, 33.0. ESI-MS: m/z = 366.3 $(M+1)^{+}$.

2-((4-Chlorophenyl)(1H-indol-3-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one(4h)



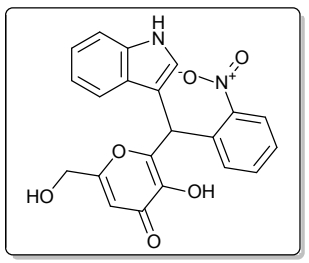
Brown solid; IR (KBr): 3409, 2926, 1617, 1460, 1225, 1094, 1018, 742 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.11 (s, 1 H), 9.23 (s, 1 H), 7.33-7.40 (m, 7 H), 7.27 (s, 1 H), 7.09 (t, *J* = 7.5 Hz, 1 H), 6.94 (t, *J* = 7.5 Hz, 1 H), 6.34 (s, 1 H), 6.00 (s, 1 H), 4.27 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.8, 151.0, 141.5, 140.0, 136.7, 131.9, 131.6, 130.5, 129.2, 128.9, 126.7, 124.6, 121.8, 119.3, 119.0,112.9, 112.1, 109.5, 60.0, 31.1. ESI-MS: m/z = 382.3$(M+1)^{+}$.

2-((4-Bromophenyl)(1H-indol-3-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one(4i)



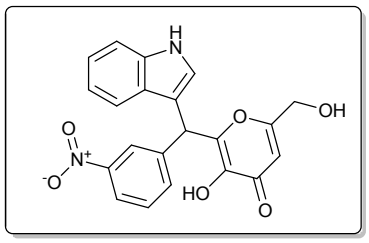
Brown solid; IR (KBr): 3415, 2975, 2926, 1624, 1460, 1232, 1198, 1067, 1004, 749 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.11 (s, 1 H), 9.24 (s, 1 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 7.40 (d, *J* = 8.5 Hz, 1 H), 7.31-7.35 (m, 3 H), 7.28 (s, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 6.95 (t, *J* = 7.5 Hz, 1 H), 6.35 (s, 1 H), 5.99 (s, 1 H), 4.27 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.7, 150.9, 141.5, 140.4, 136.7, 131.8, 130.9, 126.7, 124.6, 121.8, 120.4, 119.3, 118.9, 112.8, 112.1, 109.5, 60.1. ESI-MS: m/z = 426.2 $(M+1)^{+}$.

2-((1*H*-Indol-3-yl)(2-nitrophenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4j)



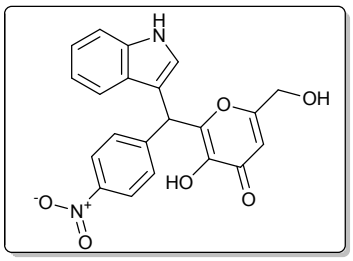
Brown solid; IR (KBr): 3415, 2975, 2926, 1667, 1617, 1527, 1356, 1225, 1087, 741 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.13 (s, 1 H), 9.21 (s, 1 H), 7.90 (d, *J* = 7.5 Hz, 1 H), 6.94-7.64 (m, 8 H), 6.47 (s, 1 H), 6.32 (s, 1 H), 5.63 (s, 1 H), 4.19 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.7, 149.8, 149.1, 142.1, 136.7, 133.7, 133.3, 131.4, 128.9, 126.6, 125.1, 124.6, 121.9, 119.5, 118.4,112.2, 109.6, 59.9, 35.8, 31.2. ESI-MS: m/z = 393.3 $(M+1)^{+}$.

2-((1*H*-Indol-3-yl)(3-nitrophenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4k)



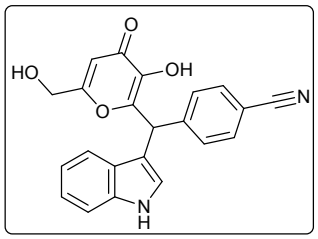
Brown solid; IR (KBr): 3409, 2970, 2920, 1643, 1498, 1406, 1225, 749 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.20 (s, 1 H), 9.37 (s, 1 H), 6.94-8.18 (m, 9 H), 6.37 (s, 1 H), 6.19 (s, 1 H), 5.71 (s, 1 H), 4.28 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.8, 150.3, 148.4, 143.2, 141.8, 136.8, 135.4, 130.5, 126.6, 124.9, 123.2, 122.4, 122.0, 119.4, 118.9,112.3, 112.2, 109.6, 60.0, 31.2. ESI-MS: m/z = 393.3 $(M+1)^+$.

2-((1*H*-Indol-3-yl)(4-nitrophenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4l)



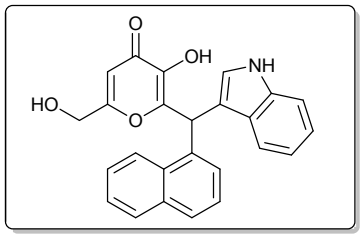
Brown solid; IR (KBr): 3420, 2980, 2925, 1670, 1620, 1456, 1230, 750 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.18 (s, 1 H), 9.35 (s, 1 H), 8.18 (d, *J* = 8.5 Hz, 2 H), 7.61 (d, *J* = 8.5 Hz, 2 H), 7.39 (d, *J* = 9.0 Hz, 1 H), 7.32-7.35 (m, 2 H), 7.09 (t, *J* = 7.5 Hz, 1 H), 6.95 (t, *J* = 7.5 Hz, 1 H), 6.35 (s, 1 H), 6.14 (s, 1 H), 4.27 (s, 2 H) . ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.9, 150.1, 148.7, 146.9, 141.8, 136.7, 130.0, 126.6, 124.9, 124.1, 121.9, 119.4, 118.9, 112.2, 109.6, 60.0. ESI-MS: m/z = 393.3 $(M+1)^+$.

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(1*H*-indol-3-yl)methyl)benzonitrile (4m)



Brown solid; IR (KBr): 3366, 2230, 1718, 1687, 1598, 1541, 1441, 746 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.06 (s, 1 H), 9.29 (s, 1 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 1 H), 7.28 (s, 1 H), 7.08 (t, *J* = 7.5 Hz, 1 H), 6.93 (t, *J* = 7.5 Hz, 1 H), 6.32 (s, 1 H), 6.06 (s, 1 H), 5.65 (s, 1 H), 4.24 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.8, 150.2, 146.7, 141.8, 136.7, 132.9, 129.7, 126.6, 124.8, 121.9, 119.4, 119.3, 118.9, 112.3, 112.2, 110.1, 109.6, 60.0, 6.99. ESI-MS: m/z = 373.3 $(M+1)^+$.

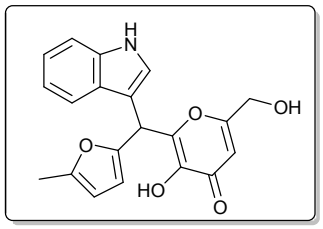
2-((1*H*-Indol-3-yl)(naphthalen-1-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4n)



Brown solid; IR (KBr): 3415, 3251, 2926, 2858, 1645, 1611, 1460, 1205, 749 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ =

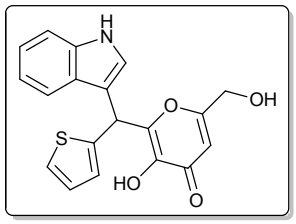
11.10 (s, 1 H), 9.38 (s, 1 H), 6.69-8.29 (m, 13 H), 6.30 (s, 1 H), 5.60 (s, 1 H), 4.12-4.22 (m, 2 H) . ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.7, 151.3, 141.2, 136.8, 136.4, 133.9, 131.6, 129.3, 128.0, 127.0, 126.9, 126.8, 126.2, 126.0, 125.1, 123.4, 121.8, 119.3, 118.6, 113.3, 112.2, 109.6, 60.0, 36.6. ESI-MS: m/z = 398.3 $(M+1)^+$.

2-((1*H*-Indol-3-yl)(4-methylcyclopenta-1,3-dien-1-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4o)



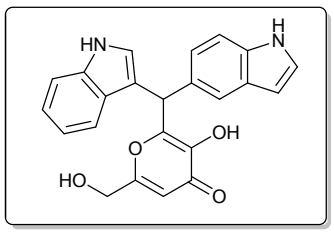
Brown solid; IR (KBr): 3409, 2919, 1624, 1453, 1232, 1191, 1087, 742 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.08 (s, 1 H), 9.23 (s, 1 H), 6.99-7.52 (m, 5 H), 6.31 (s, 1 H), 6.11 (s, 1 H), 6.00 (s, 1 H), 5.95 (s, 1 H), 5.66 (s, 1 H), 4.22-4.30 (m, 2 H), 2.21 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.5, 151.4, 151.0, 149.6, 141.4, 136.6, 126.6, 124.5, 121.7, 119.2, 118.9, 112.1, 111.4, 109.5, 108.5, 107.0, 60.0, 34.7, 13.8. ESI-MS: m/z = 352.3 $(M+1)^+$.

2-((1*H*-Indol-3-yl(thiophen-2-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4p)



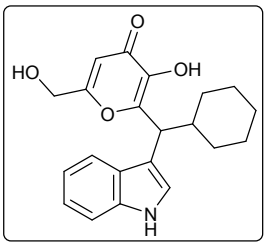
Brown solid; IR (KBr): 3389, 2990, 1630, 1466, 1224, 860, 753 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.09 (s, 1 H), 9.29 (s, 1 H), 7.47 (d, *J* = 8.0Hz, 1 H), 7.37-7.40 (m, 2 H), 7.29 (s, 1 H), 6.96-7.10 (m, 4 H), 6.32 (s, 1 H), 6.23 (s, 1 H), 5.67 (s, 1 H), 4.28 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.7, 150.5, 143.8, 140.9, 136.6, 127.2, 126.5, 126.2, 125.5, 124.4, 121.8, 119.3, 118.9, 113.6, 112.1, 109.5, 60.0, 35.7. ESI-MS: m/z = 354.3 $(M+1)^+$.

2-((1*H*-Indol-3-yl)(1*H*-indol-5-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one(4q)



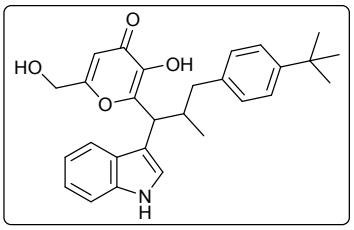
Brown solid; IR (KBr): 3409, 2926, 2851, 1624, 1453, 1232, 1205, 749 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 10.97 (s, 2 H), 9.12 (s, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.23 (s, 2 H), 7.06 (t, *J* = 7.5 Hz, 2 H), 6.95 (t, *J* = 7.5 Hz, 2 H), 6.29 (s, 1 H), 6.22 (s, 1 H), 5.65 (s, 1 H), 4.25 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.5, 152.3, 140.6, 136.7, 126.9, 124.3, 121.6, 119.0, 113.9, 112.0, 109.4, 60.2, 60.1, 32.0. ESI-MS: m/z = 387.3 $(M+1)^+$.

2-(Cyclohexyl(1*H*-indol-3-yl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4r)



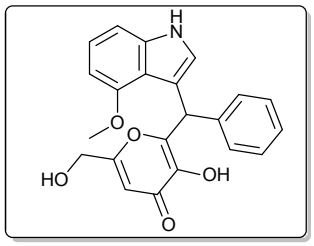
Brown solid; IR (KBr): 3429, 2924, 1624, 1453, 1258, 1087, 1024, 809, 746 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 10.96 (s, 1 H), 8.73 (s, 1 H), 7.62 (d, *J* = 7.5 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 1 H), 7.29 (s, 1 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 6.97 (t, *J* = 7.5 Hz, 1 H), 6.22 (s, 1 H), 4.25-4.36 (m, 4 H), 2.17-2.21 (m, 1H), 1.58-1.81 (m, 10H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 177.1, 173.8, 167.3, 152.6, 141.6, 136.4, 127.5, 123.7, 121.4, 119.2, 119.0, 113.1, 111.9, 109.1, 60.1, 31.6, 31.5, 29.1, 26.5, 26.0, 25.4. ESI-MS: m/z = 354.4 $(M+1)^+$.

2-(3-(4-(tert-Butyl)phenyl)-1-(1*H*-indol-3-yl)-2-methylpropyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4s)



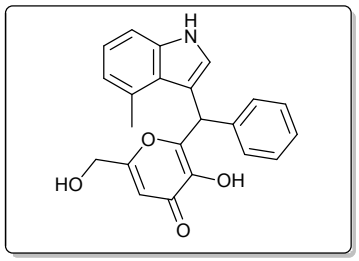
Brown solid; IR (KBr): 3366, 2230, 1718, 1687, 1598, 1541, 1441, 746 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 10.99 (s, 1 H), 8.82 (s, 1 H), 6.67 (d, *J* = 8.0 Hz, 1 H), 7.31-7.34 (m, 2 H), 7.26 (d, *J* = 8.5 Hz, 2 H), 7.04-7.09 (m, 3H), 6.99 (t, *J* = 7.5 Hz, 1 H), 6.21 (s, 1 H), 5.69 (s, 1 H), 4.32-4.37 (m, 3 H), 2.67 (d, *J* = 10.5 Hz, 2 H), 2.27-2.32(m, 1H), 1.24 (s, 9H), 0.71 (d, *J* = 6.0 Hz, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 173.9, 167.1, 152.5, 148.4, 141.6, 138.1, 136.4, 129.1, 129.0, 127.3, 125.3, 123.8, 121.5, 119.3, 119.0, 113.5, 112.0, 109.2, 60.2, 41.5, 41.1, 37.7, 34.5, 31.7, 18.4. ESI-MS: m/z = 446.4 $(M+1)^+$.

3-Hydroxy-6-(hydroxymethyl)-2-((4-methoxy-1*H*-indol-3-yl)(phenyl)methyl)-4*H*-pyran-4-one(4t)



Brown solid; IR (KBr): 3409, 2925, 2850, 1710, 1618, 1460, 1203, 740 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.00 (s, 1 H), 8.89 (s, 1 H), 6.93-7.30 (m, 8 H), 6.41 (t, *J* = 8.0 Hz, 2 H), 6.30 (s, 1 H), 5.68 (s, 1H), 4.23-4.32 (m, 2 H), 3.69 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.3, 154.5, 152.5, 142.5, 141.1, 137.9, 128.8, 128.6, 126.8, 123.0, 122.6, 116.9, 113.7, 109.5, 105.4, 99.7, 60.1, 55.4, 21.2, 14.6. ESI-MS: m/z = 378.3 $(M+1)^+$.

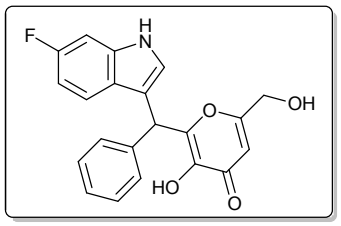
3-Hydroxy-6-(hydroxymethyl)-2-((4-methyl-1*H*-indol-3-yl)(phenyl)methyl)-4*H*-pyran-4-one(4u)



Brown solid; IR (KBr): 3409, 2926, 1735, 1645, 1618, 1460,

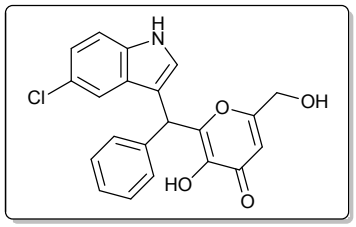
1198, 736 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.08 (s, 1 H), 9.12 (s, 1 H), 7.17-7.32 (m, 8 H), 6.94 (t, *J* = 7.5 Hz, 1 H), 6.67 (d, *J* = 7.0 Hz, 1 H), 6.32 (d, *J* = 7.5 Hz, 2 H), 4.17-4.28 (m, 2 H), 2.44 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.2, 167.5, 152.4, 142.3, 141.0, 136.9, 129.5, 128.9, 128.7, 127.1, 125.5, 125.0, 121.7, 121.1, 113.6, 110.2, 109.6, 60.1, 20.4. ESI-MS: m/z = 362.3 $(M+1)^+$.

2-((6-Fluoro-1H-indol-3-yl)(phenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one(4v)



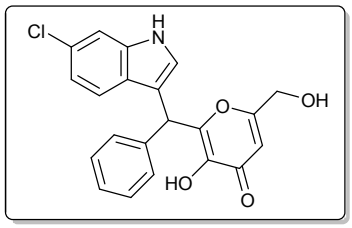
Brown solid; IR (KBr): 3348, 2926, 2851, 1631, 1453, 1198, 1142, 1101, 799, 709 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.13 (s, 1 H), 9.18 (s, 1 H), 7.13-7.36 (m, 8 H), 6.80 (t, *J* = 8.5 Hz, 1 H), 6.31 (s, 1 H), 5.96 (s, 1 H), 5.66 (s, 1H), 4.24 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.7, 159.3 (d, $^1J_{FC}$ = 233.1 Hz), 151.2, 141.5, 140.8, 136.5 (d, $^2J_{FC}$ = 12.6Hz), 128.9, 128.6, 127.3, 125.2, 123.7, 120.0 (d, $^2J_{FC}$ = 10.3Hz) 113.6, 109.5, 107.8, 107.6, 98.1, 97.9, 60.0. ESI-MS: m/z = 366.3 $(M+1)^+$.

2-((5-Chloro-1*H*-indol-3-yl)(phenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4w)



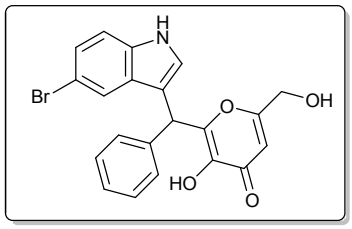
Brown solid; IR (KBr): 3409, 2919, 2851, 1708, 1624, 1453, 1205, 1087, 695 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.28 (s, 1 H), 9.20 (s, 1 H), 7.06-7.40 (m, 9 H), 6.31 (s, 1 H), 5.95 (s, 1 H), 5.66 (t, *J* = 6.5 Hz, 1 H), 4.25 (d, *J* = 5.5Hz, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.7, 151.1, 141.5, 140.6, 135.2, 133.3, 129.7, 129.0, 128.6, 127.9, 127.3, 126.4, 123.8, 121.7, 118.2, 113.7, 113.3, 109.5, 60.0. ESI-MS: m/z = 382.3 $(M+1)^+$.

2-((6-Chloro-1*H*-indol-3-yl)(phenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4x)



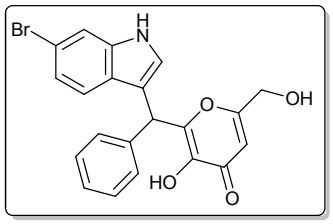
Brown solid; IR (KBr): 3422, 2919, 2845, 1618, 1460, 1205, 698 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.21 (s, 1 H), 9.19 (s, 1 H), 7.24-7.41 (m, 8 H), 6.95 (d, *J* = 8.0Hz, 1 H), 6.31 (s, 1 H), 5.96 (s, 1 H), 5.66 (s, 1H), 4.24 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.7, 151.1, 141.5, 140.7, 137.1, 129.0, 128.6, 127.3, 126.5, 125.7, 125.6, 120.4, 119.5, 113.7, 111.7, 109.5, 60.0. ESI-MS: m/z = 382.3 $(M+1)^+$.

2-((5-Bromo-1H-indol-3-yl)(phenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one(4y)



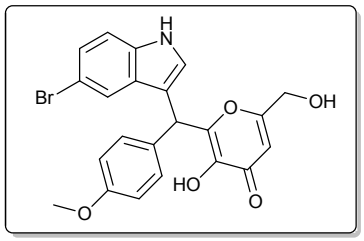
Brown solid; IR (KBr): 3422, 2919, 2845, 1618, 1460, 1198, 1081, 695 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.30 (s, 1 H), 9.20 (s, 1 H), 7.47 (s, 1 H), 7.30-7.36 (m, 6 H), 7.25 (t, *J* = 7.0Hz, 1 H), 7.18 (d, *J* = 8.5Hz, 1 H), 6.31 (s, 1 H), 5.95 (s, 1 H), 5.66 (s, 1 H), 4.25 (s, 2 H) . ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.7, 151.1, 141.5, 140.6, 135.4, 133.3, 129.7, 129.0, 128.6, 127.3, 126.3, 124.2, 121.2, 114.2, 113.1, 111.8, 109.5, 60.0. ESI-MS: m/z = 427.3 $(M+1)^+$.

2-((6-Bromo-1H-indol-3-yl)(phenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (4z)



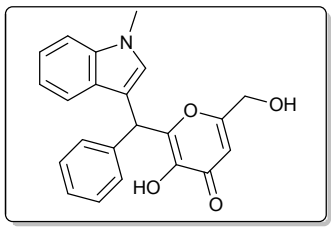
Brown solid; IR (KBr): 3415, 2926, 2858, 1618, 1453, 1198, 702 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.22 (s, 1 H), 9.20 (s, 1 H), 7.56 (s, 1 H), 7.23-7.35 (m, 8 H), 7.06-7.08 (m, 1 H), 6.32 (s, 1 H), 5.96 (s, 1 H), 4.24 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.7, 151.1, 141.5, 140.7, 137.6, 129.7, 129.0, 128.6, 127.3, 125.9, 125.7, 122.1, 120.8, 114.6, 114.5, 113.7, 109.5, 60.0. ESI-MS: m/z = 427.3 $(M+1)^+$.

2-((5-Bromo-1H-indol-3-yl)(4-methoxyphenyl)methyl)-3-hydroxy-6-(hydroxymethyl)-4H-pyran-4-one (4aa)



Brown solid; IR (KBr): 3422, 2919, 2845, 1618, 1460, 1198, 1081, 695 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 11.28 (s, 1 H), 9.15 (s, 1 H), 7.46 (s, 1 H), 7.25-7.36 (m, 4 H), 7.17-7.20 (m, 1 H), 6.87 (d, *J* = 9.0 Hz, 2 H),6.31 (s, 1 H), 5.89 (d, *J* = 8.5 Hz, 1 H), 6.31 (s, 1 H), 5.89 (s, 1 H), 4.25 (s, 2 H), 3.71 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.6, 158.6, 151.4, 141.2, 135.4, 132.5, 129.7, 128.6, 126.1, 124.2, 121.2, 114.3, 114.1, 113.5, 111.7, 109.4, 60.2, 60.0, 55.5. ESI-MS: m/z = 456.3 $(M+1)^+$.

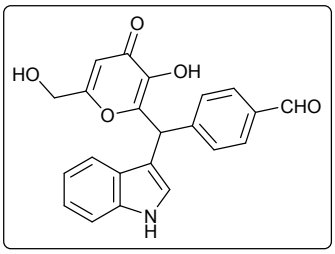
3-Hydroxy-6-(hydroxymethyl)-2-((1-methyl-1H-indol-3-yl)(phenyl)methyl)-4*H*-pyran-4-one (4ab)



Brown solid; IR (KBr): 2919, 2854, 1622, 1573, 1452, 1202, 867, 732 cm^{-1}. ^1H NMR (500 MHz, DMSO-d_6): δ = 9.14 (s, 1 H), 7.41 (d, *J* = 8.5Hz, 1 H), 7.29-7.37 (m, 5 H), 7.24 (t, *J* = 7.5Hz, 2 H),

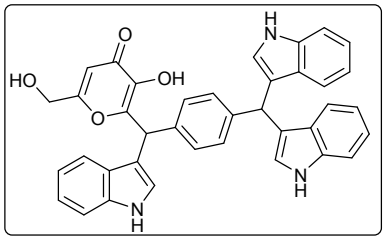
7.14 (t, *J* = 7.5 Hz, 1 H), 6.97 (t, *J* = 7.5 Hz, 1 H), 6.31 (s, 1 H), 5.97 (s, 1 H), 5.64 (s, 1 H), 4.26 (s, 2 H), 3.76 (s, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.8, 151.2, 141.4, 140.8, 137.1, 128.9, 128.8, 128.7, 127.3, 127.2, 121.8, 119.3, 119.1, 112.6, 110.3, 109.4, 60.0, 32.9. ESI-MS: m/z = 362.3 $(M+1)^+$.

4-((3-Hydroxy-6-(hydroxymethyl)-4-oxo-4*H*-pyran-2-yl)(1*H*-indol-3-yl)methyl)benzaldehyde (4ac)



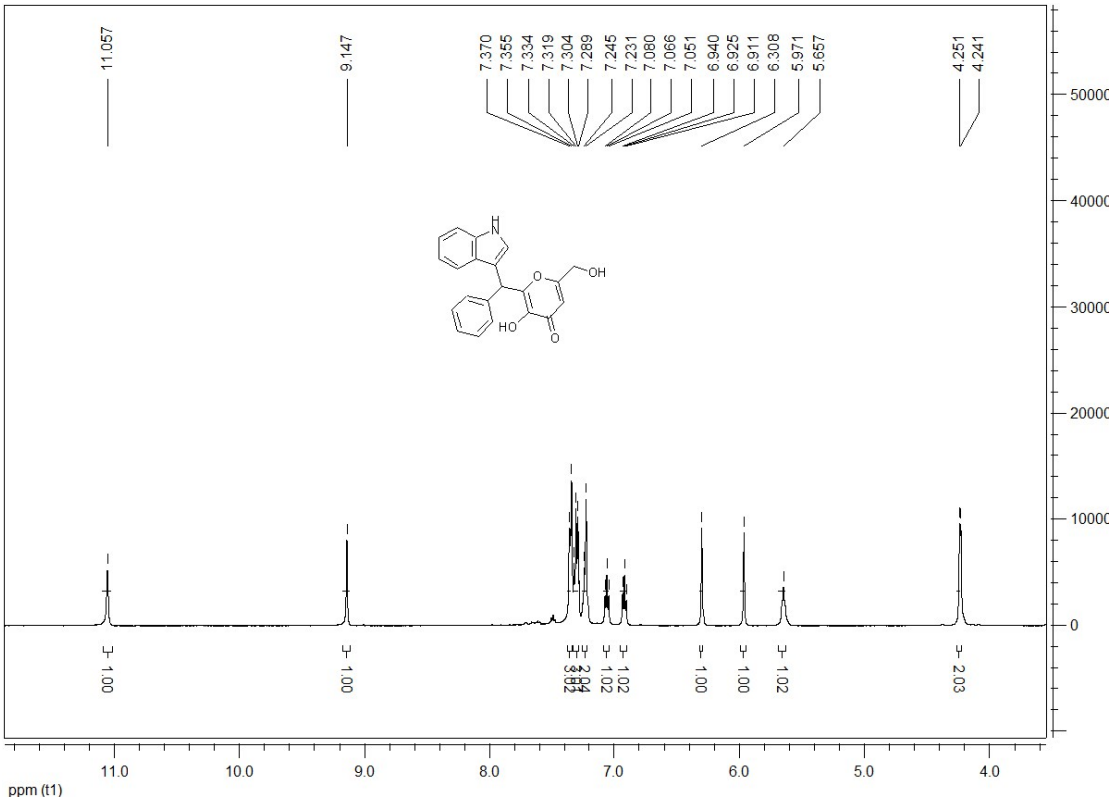
Red solid; IR (KBr): 3417, 2930, 1712, 1630, 1459, 1258, 1094, 1018, 809, 753 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.18 (s, 1 H), 9.96 (s, 1 H), 7.85 (d, *J* = 7.5 Hz, 1 H), 7.56 (d, *J* = 8.0 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 1 H), 7.29 (s, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 6.93 (t, *J* = 7.5 Hz, 1 H), 6.32 (s 1 H), 6.09 (s, 1 H), 4.25(s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 193.1, 174.2, 172.7, 167.8, 150.6, 147.9, 141.9, 141.8, 136.7, 135.4, 130.2, 129.4, 126.7, 124.7, 121.8, 119.3, 118.9, 112.5, 112.2, 109.6, 60.3, 60.0, 29.5. ESI-MS: m/z = 376.4 $(M+1)^+$.

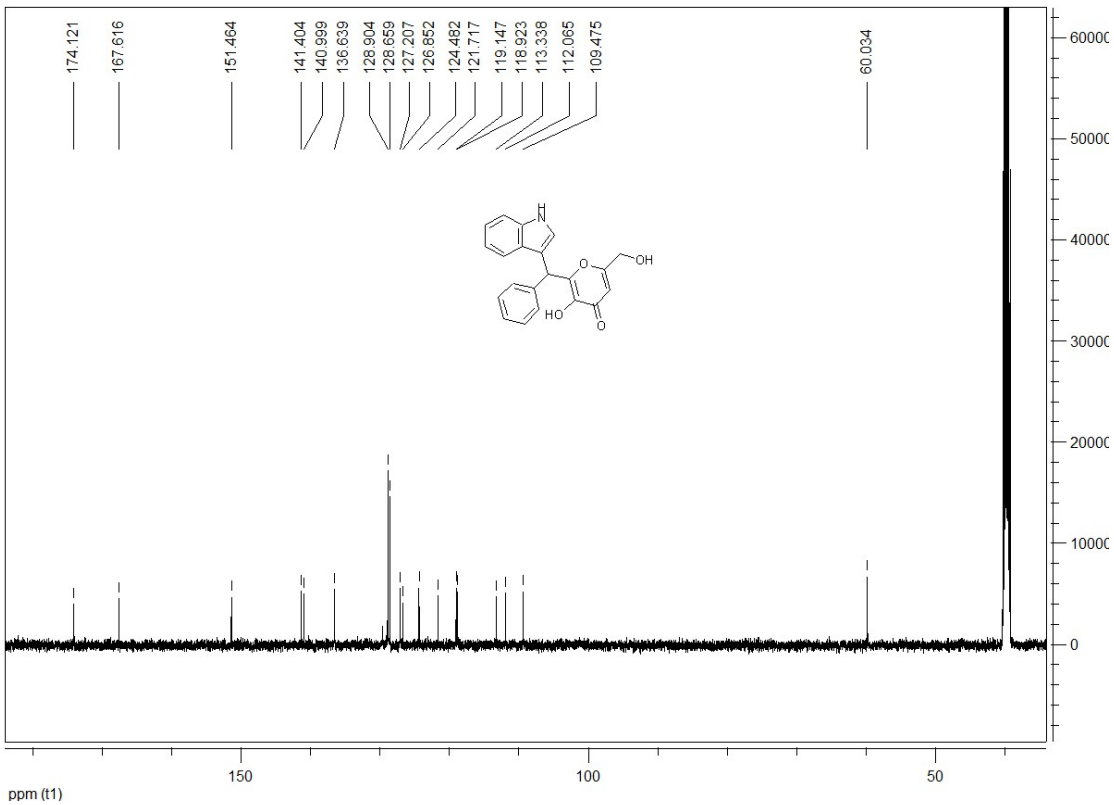
2-((4-(Di(1*H*-indol-3-yl)methyl)phenyl)(1*H*-indol-3-yl)methyl-3-hydroxy-6-(hydroxymethyl)-4*H*-pyran-4-one (5)



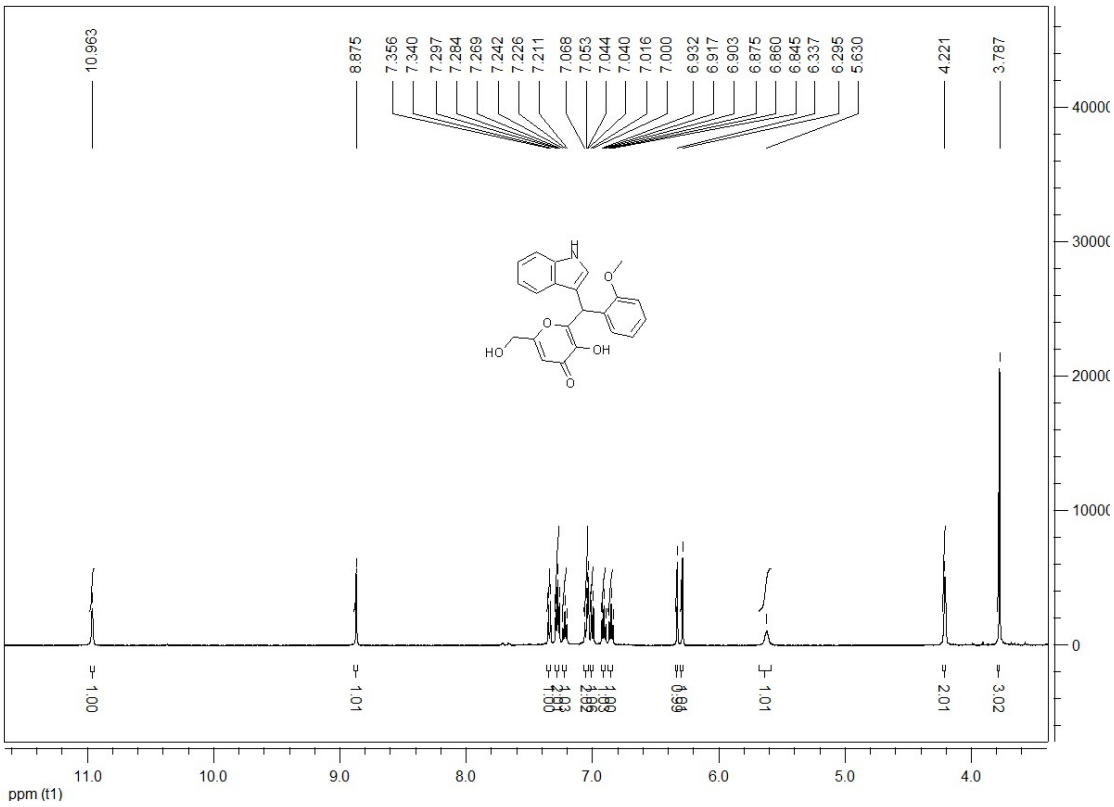
Red solid; IR (KBr): 3423, 2924, 1718, 1624, 1453, 746 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.01 (s, 1 H), 10.79 (s, 2 H), 9.08 (s, 1 H), 7.24-7.36 (m, 11 H), 7.16 (s, 1 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 7.01 (t, *J* = 7.5 Hz, 2 H), 6.91 (t, *J* = 7.0 Hz, 1 H), 6.83 (t, *J* = 7.5 Hz, 3 H), 6.28 (s 1 H), 5.93 (s, 1 H), 5.79(s, 1H), 5.60 (s, 1H), 4.21 (s, 2 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 174.1, 167.6, 143.9, 141.4, 138.3, 137.1, 128.8, 128.4, 127.1, 126.9, 124.4, 124.0, 121.7, 121.3, 119.5, 119.1, 118.6, 118.5, 118.4, 113.7, 112.0, 111.9, 109.4, 60.0, 29.5, 22.6. ESI-MS: m/z = 592.4 $(M+1)^+$.

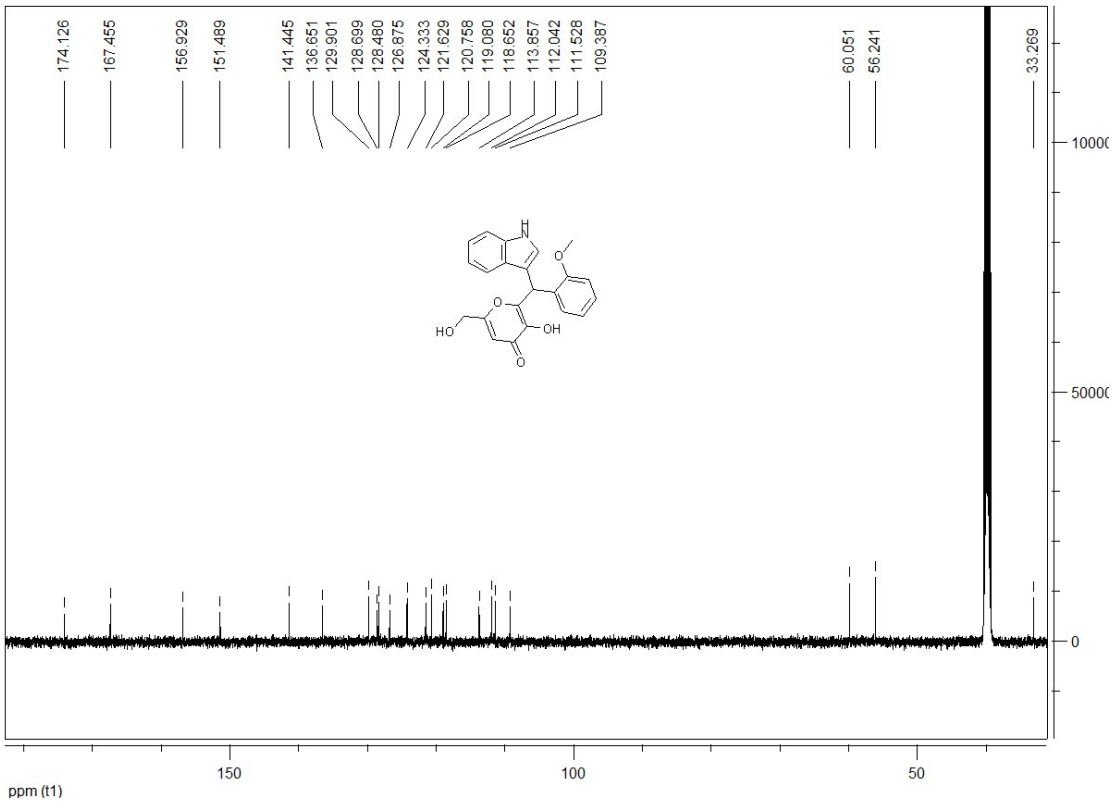
^{1}H NMR and ^{13}C NMR of compound **4a**



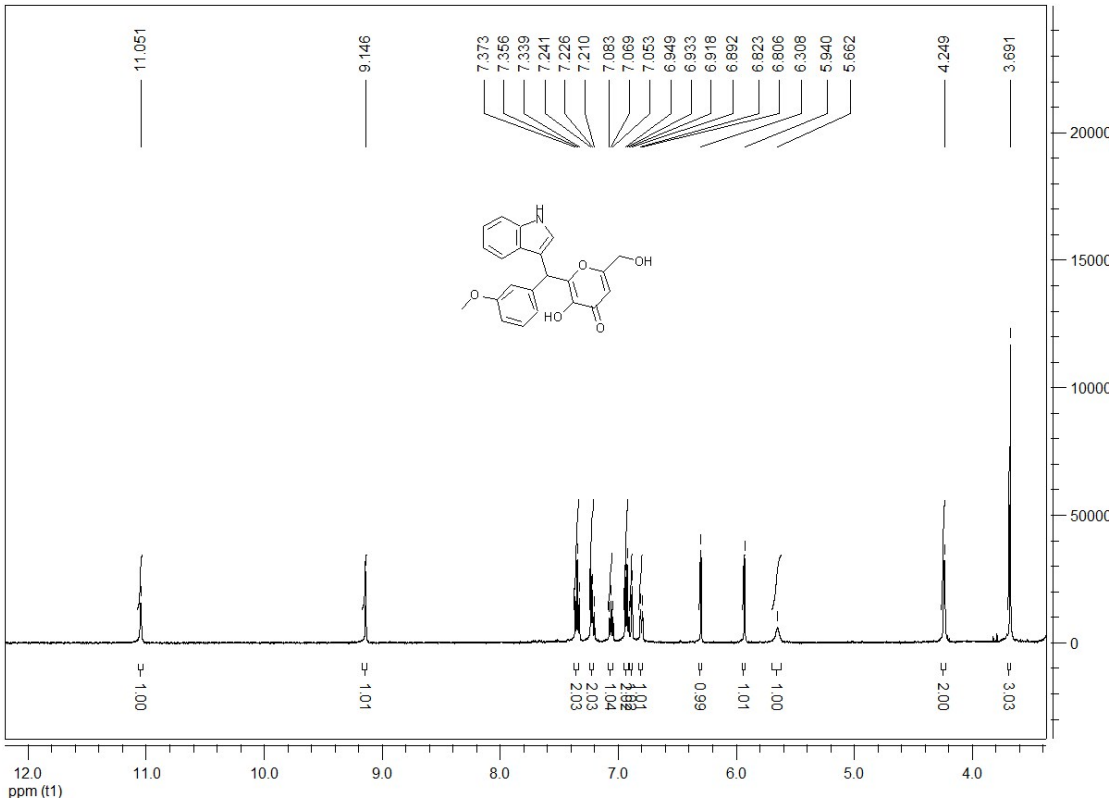


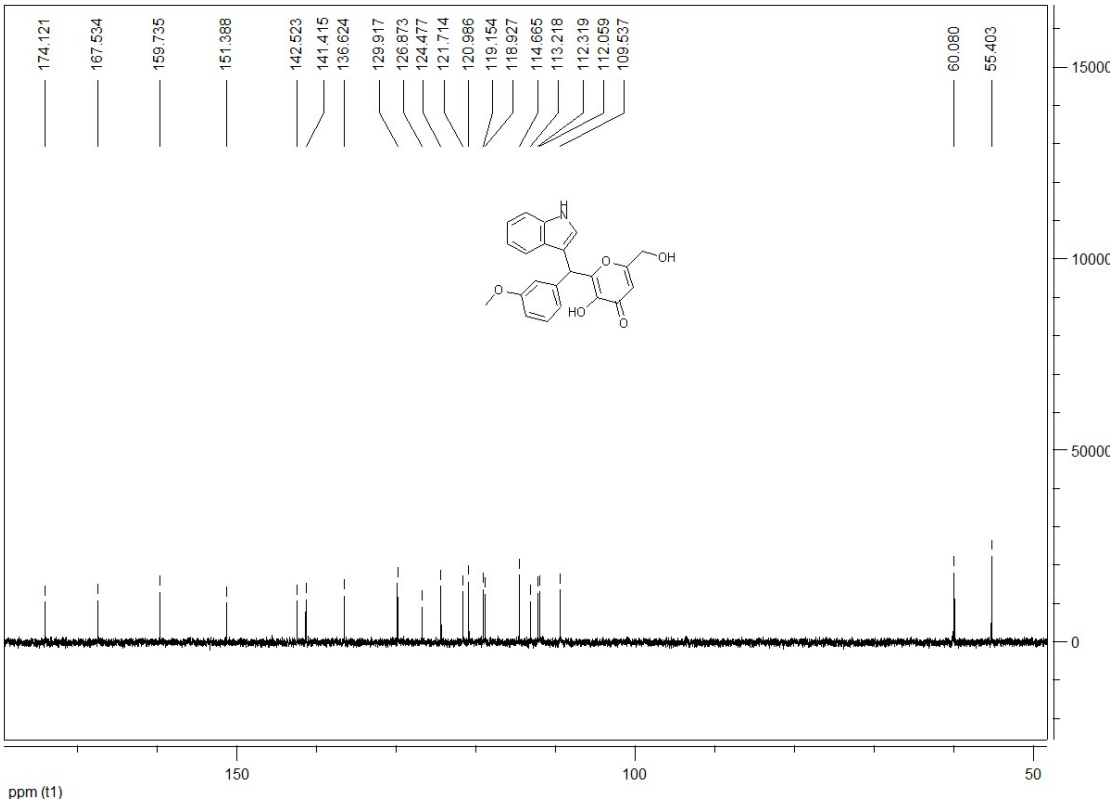
^{1}H NMR and ^{13}C NMR of compound **4b**



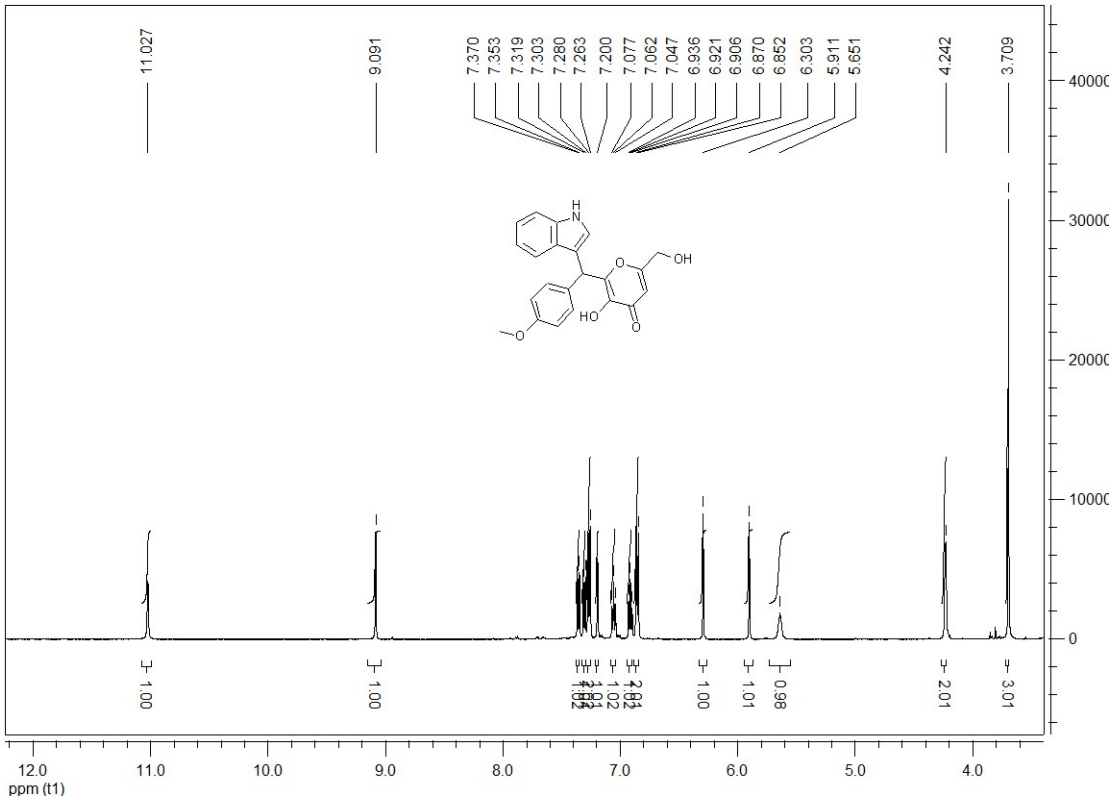


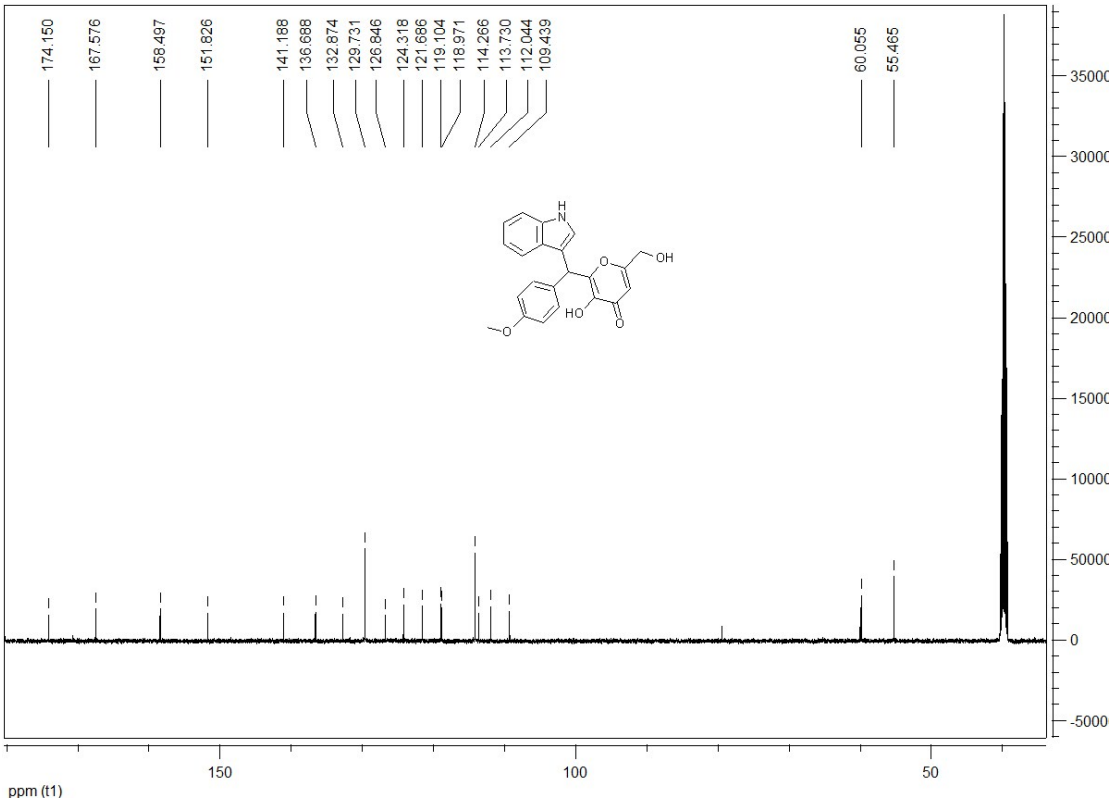
^{1}H NMR and ^{13}C NMR of compound **4c**



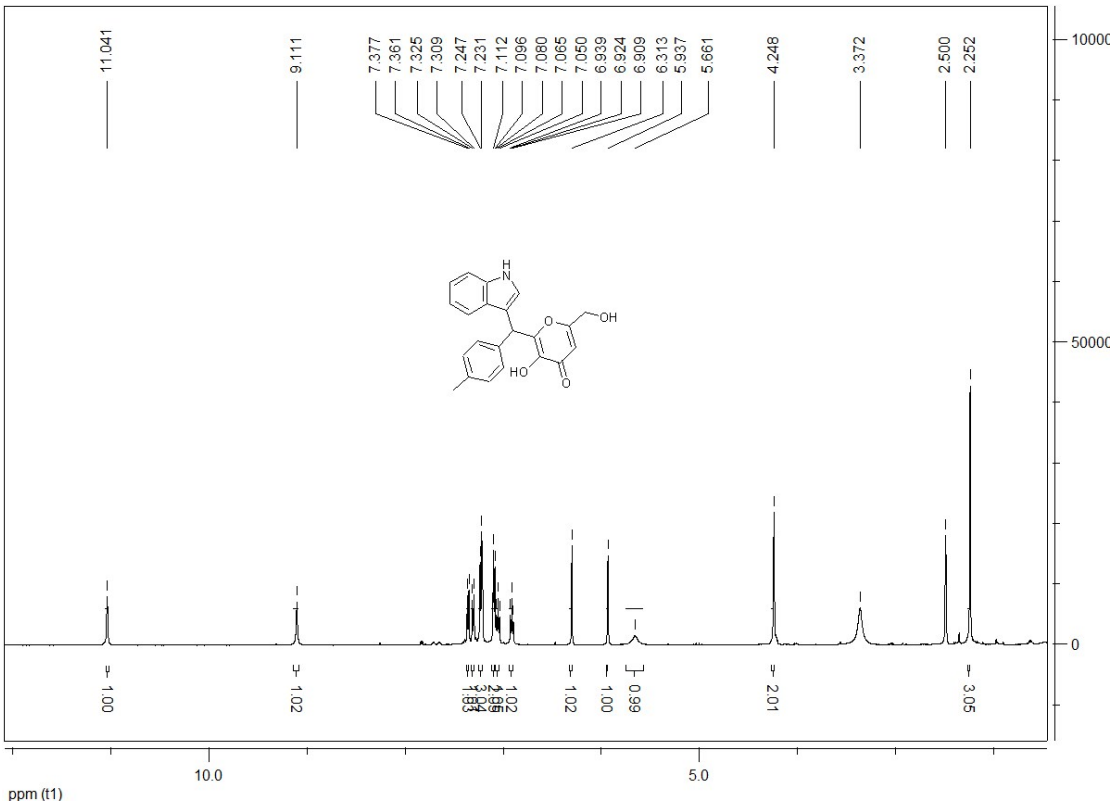


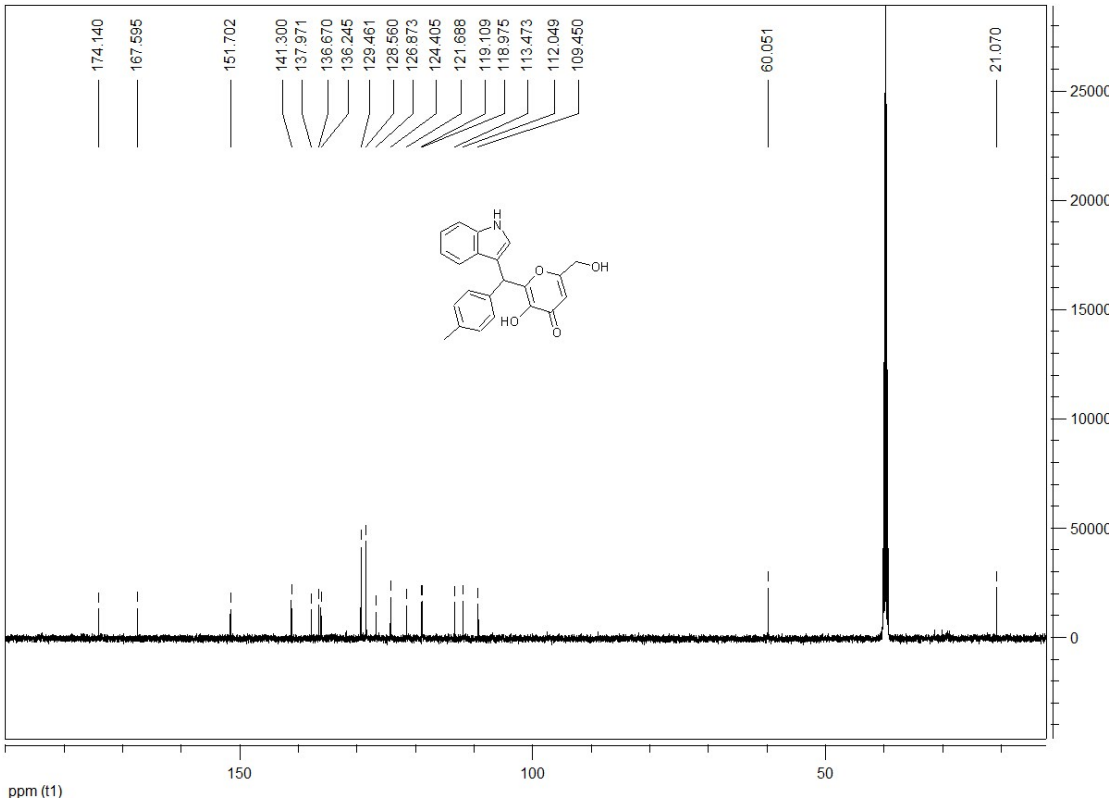
^{1}H NMR and ^{13}C NMR of compound **4d**



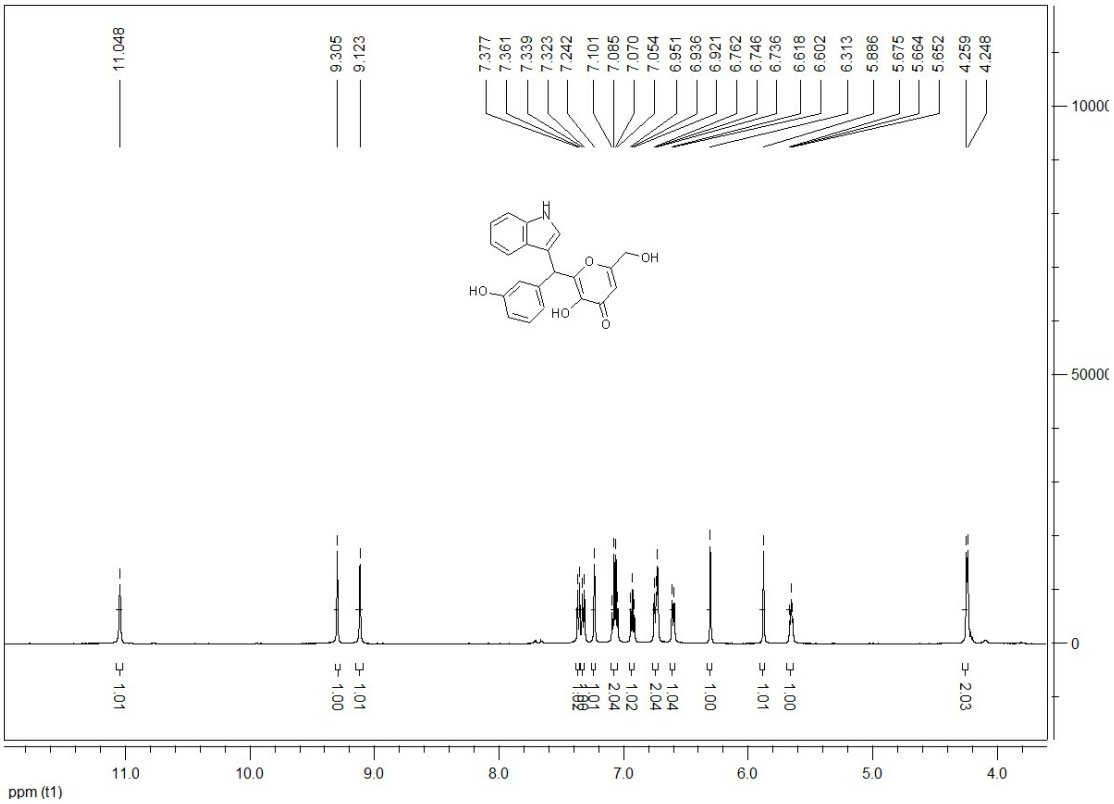


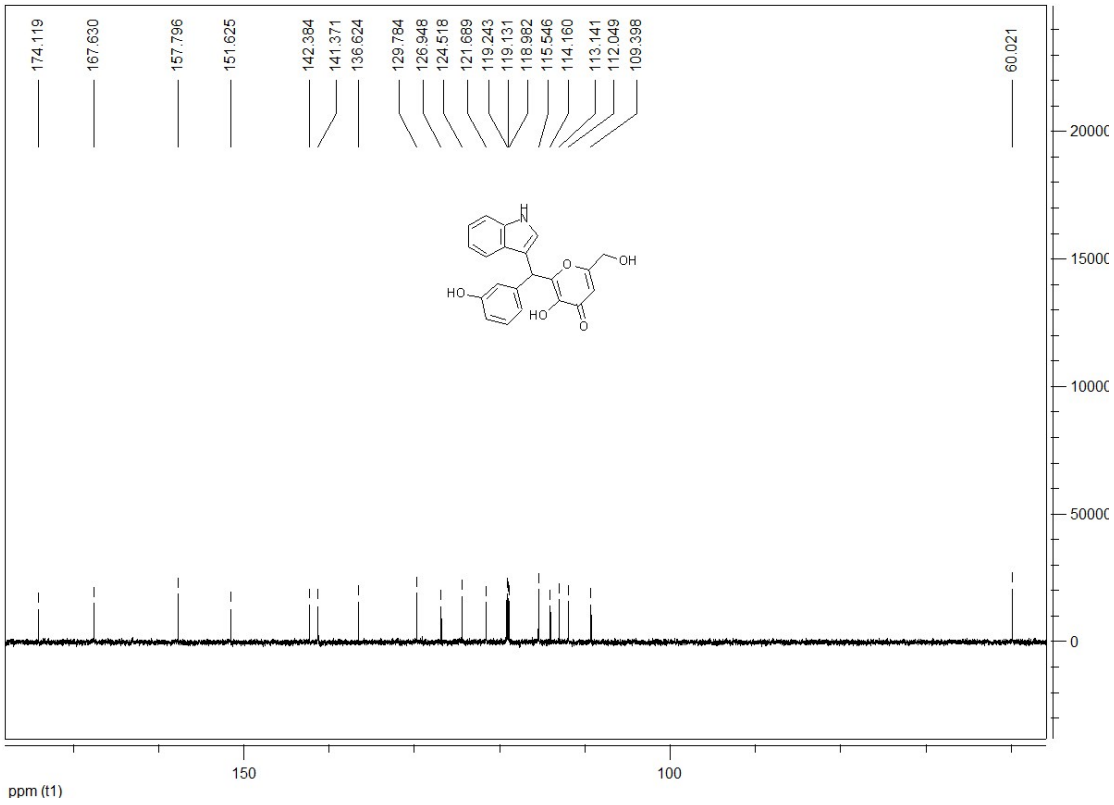
^{1}H NMR and ^{13}C NMR of compound **4e**



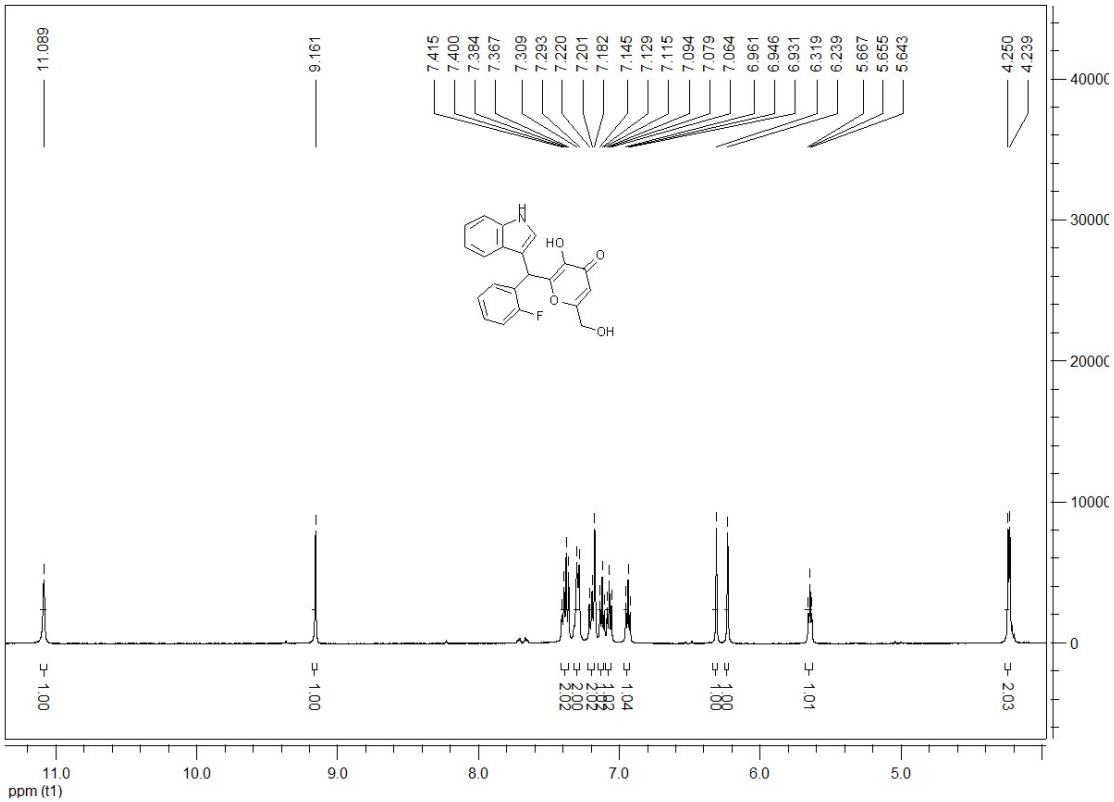


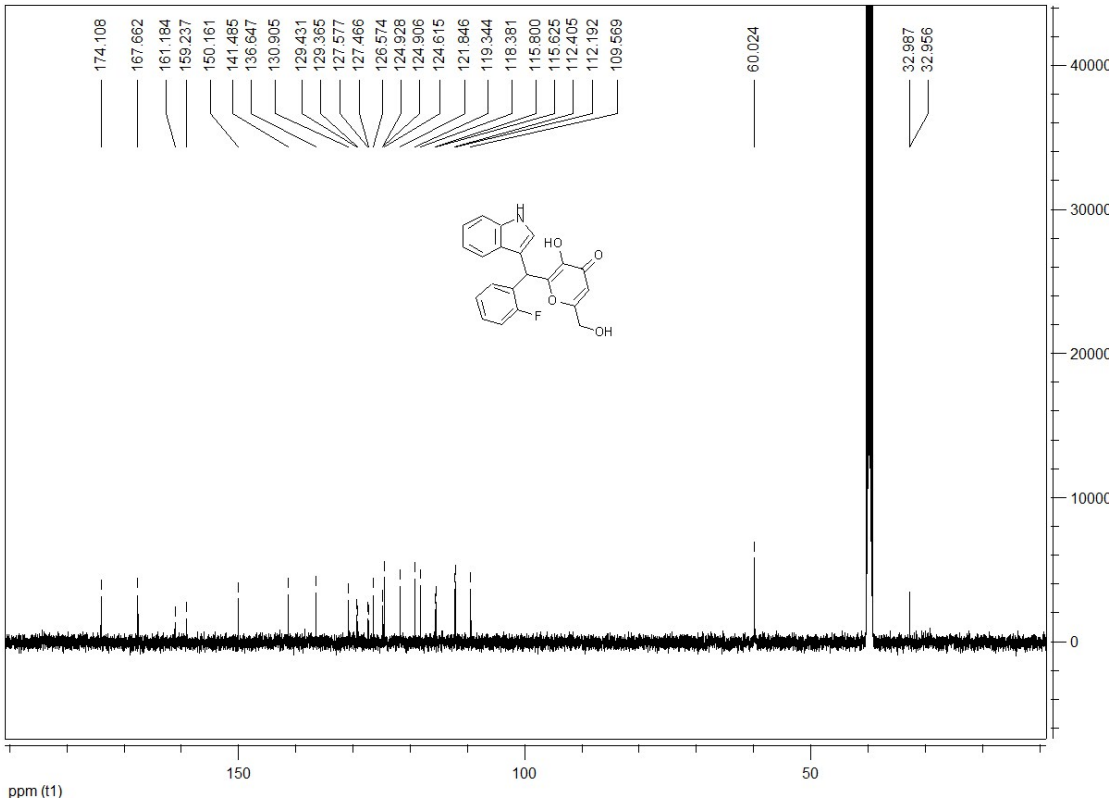
^{1}H NMR and ^{13}C NMR of compound **4f**



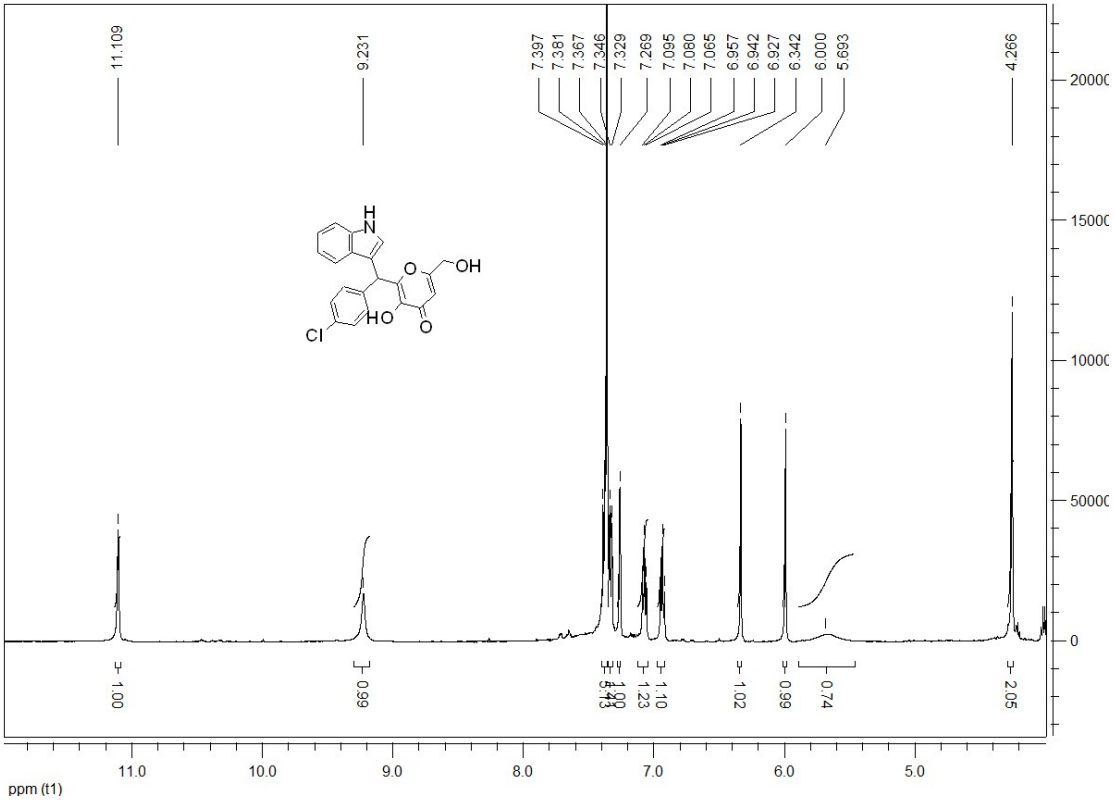


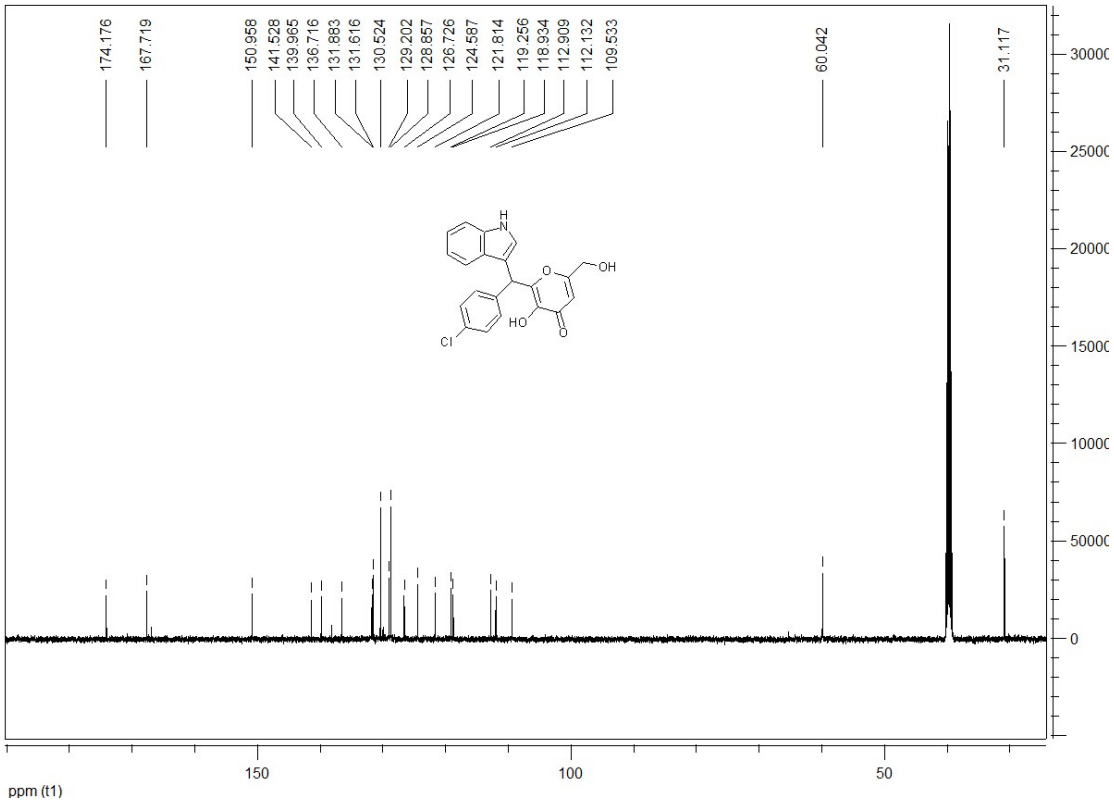
^{1}H NMR and ^{13}C NMR of compound **4g**



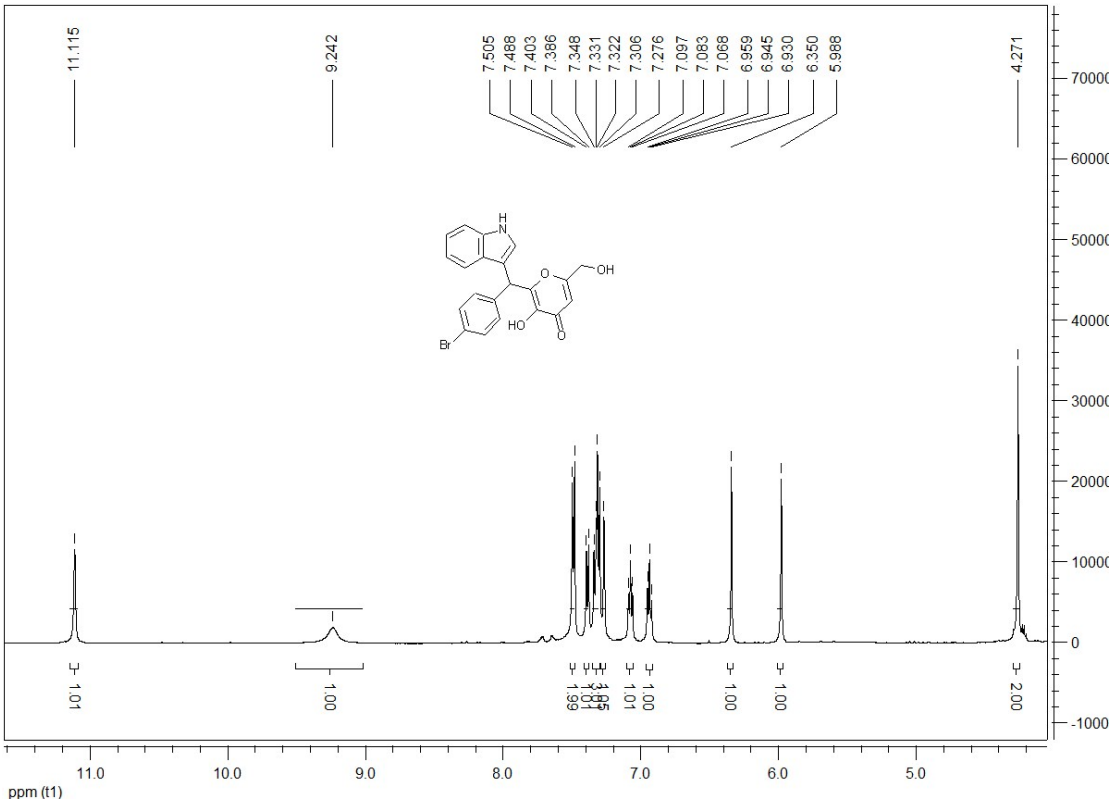


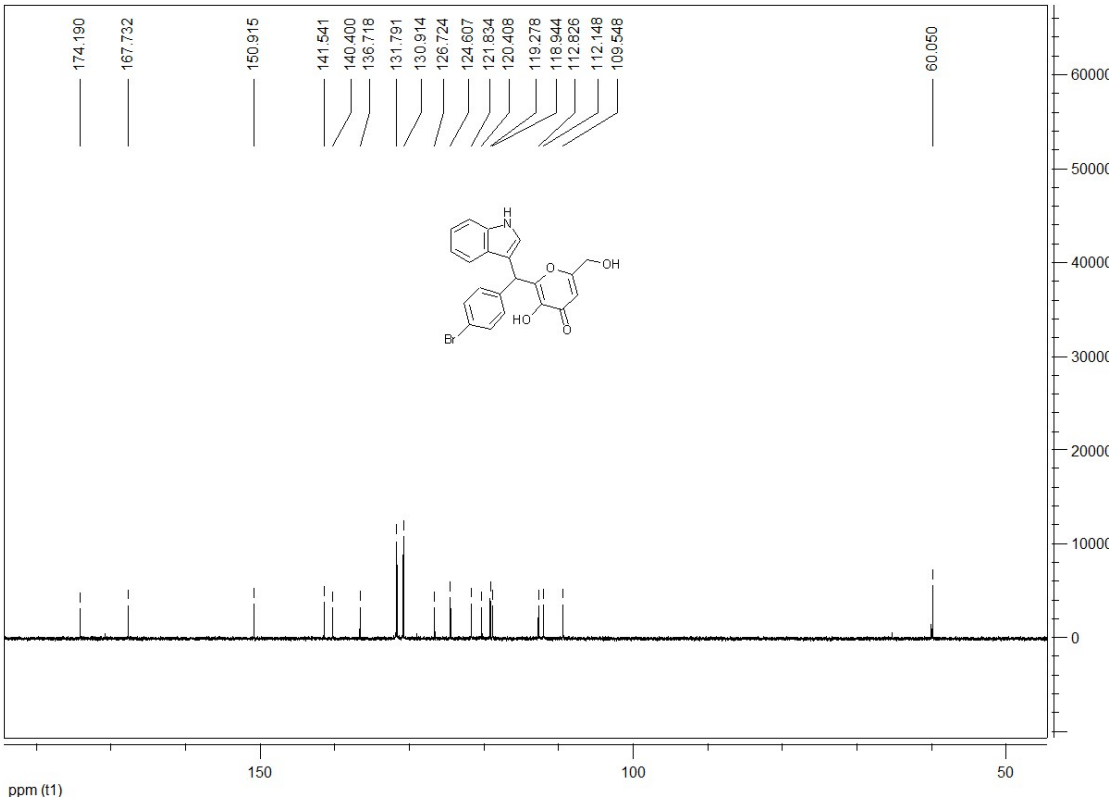
^{1}H NMR and ^{13}C NMR of compound **4h**



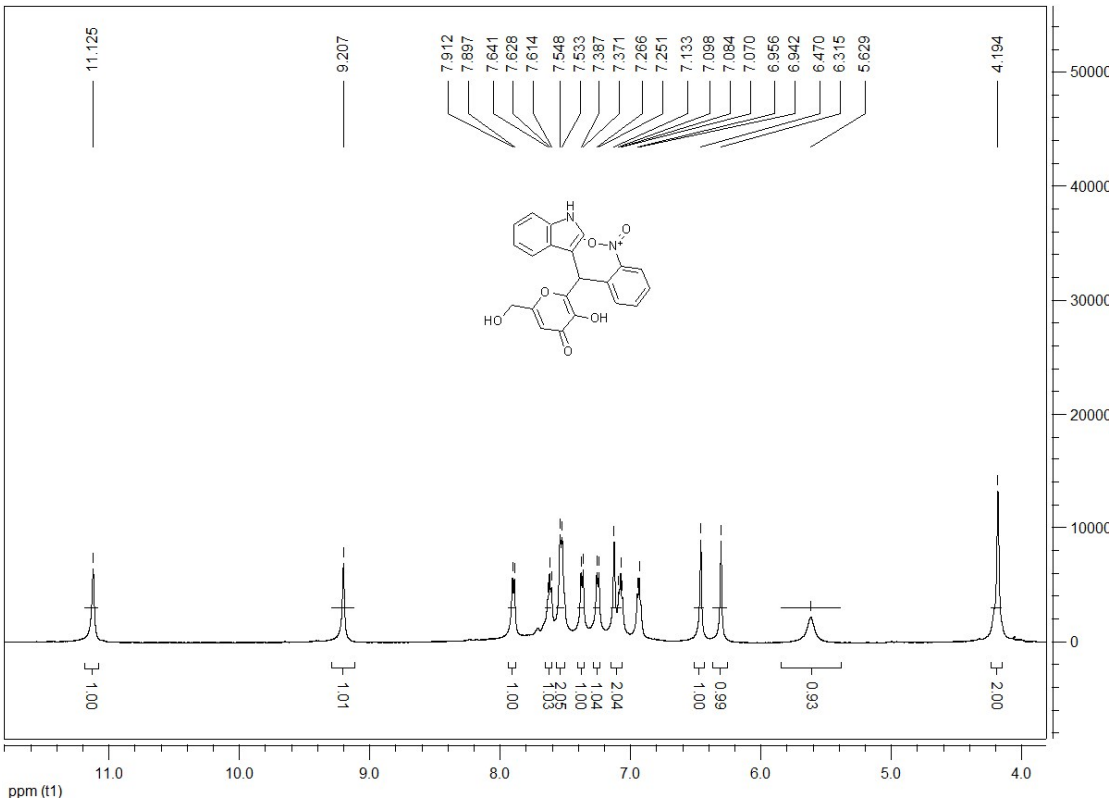


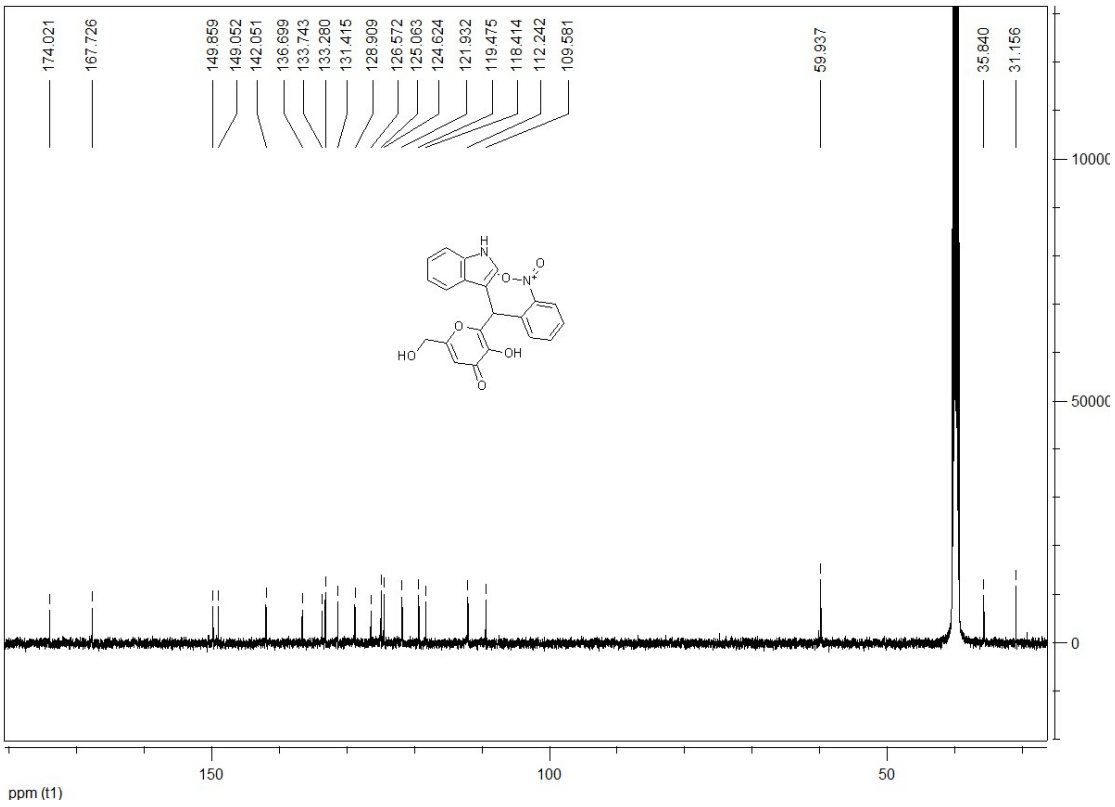
^{1}H NMR and ^{13}C NMR of compound **4i**



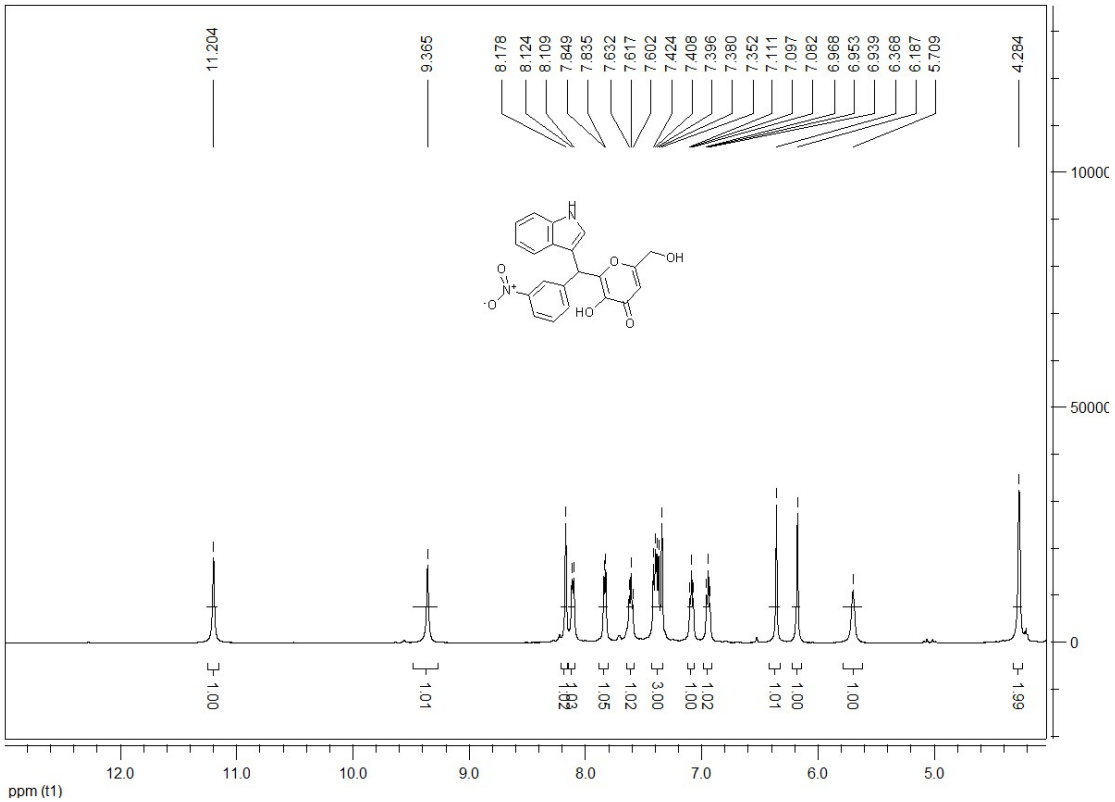


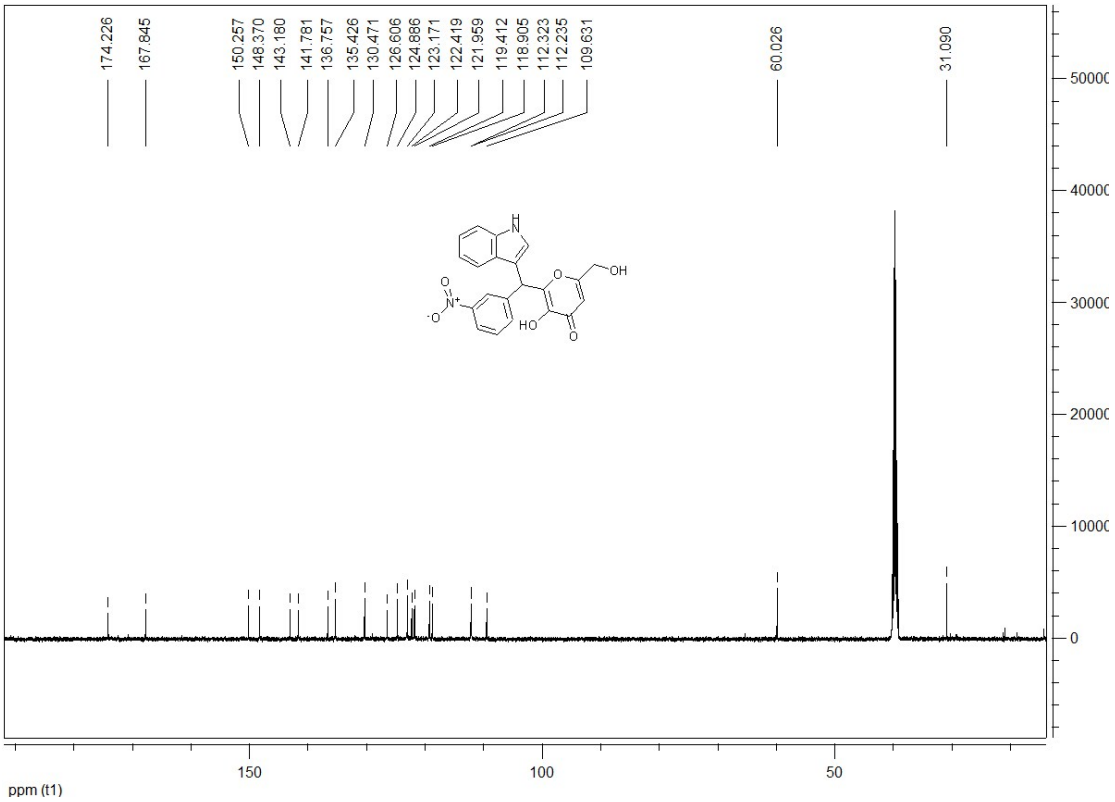
^{1}H NMR and ^{13}C NMR of compound **4j**



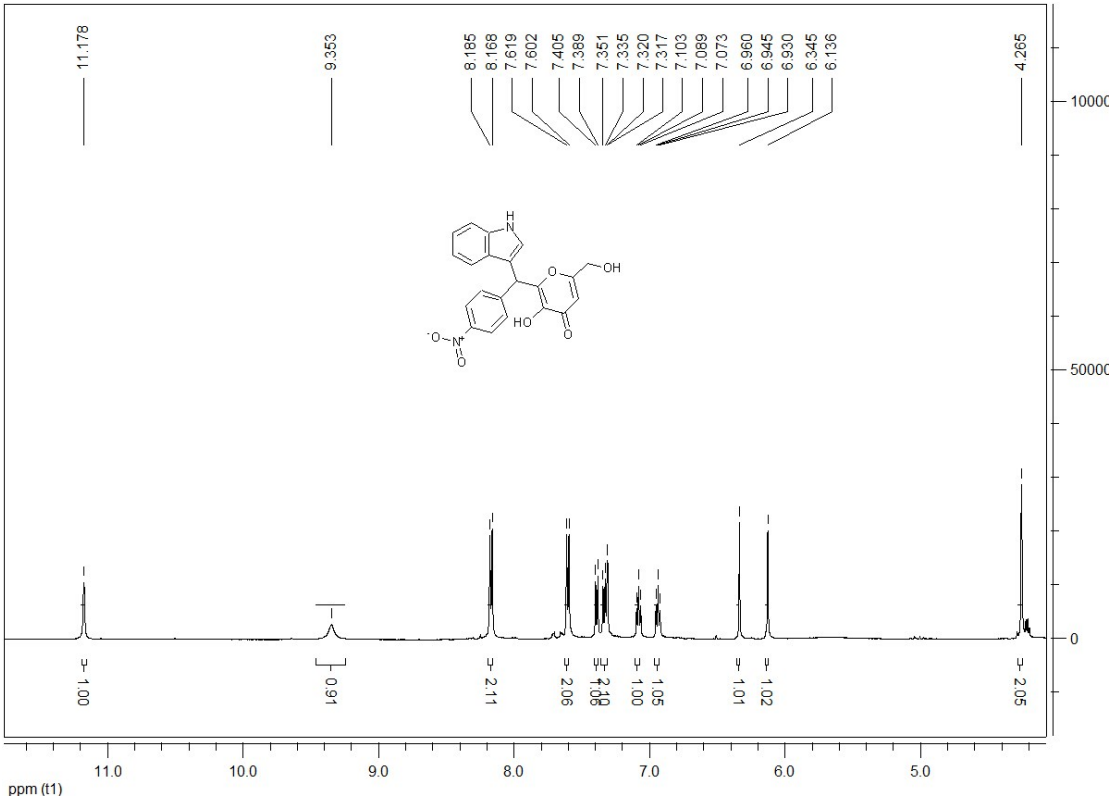


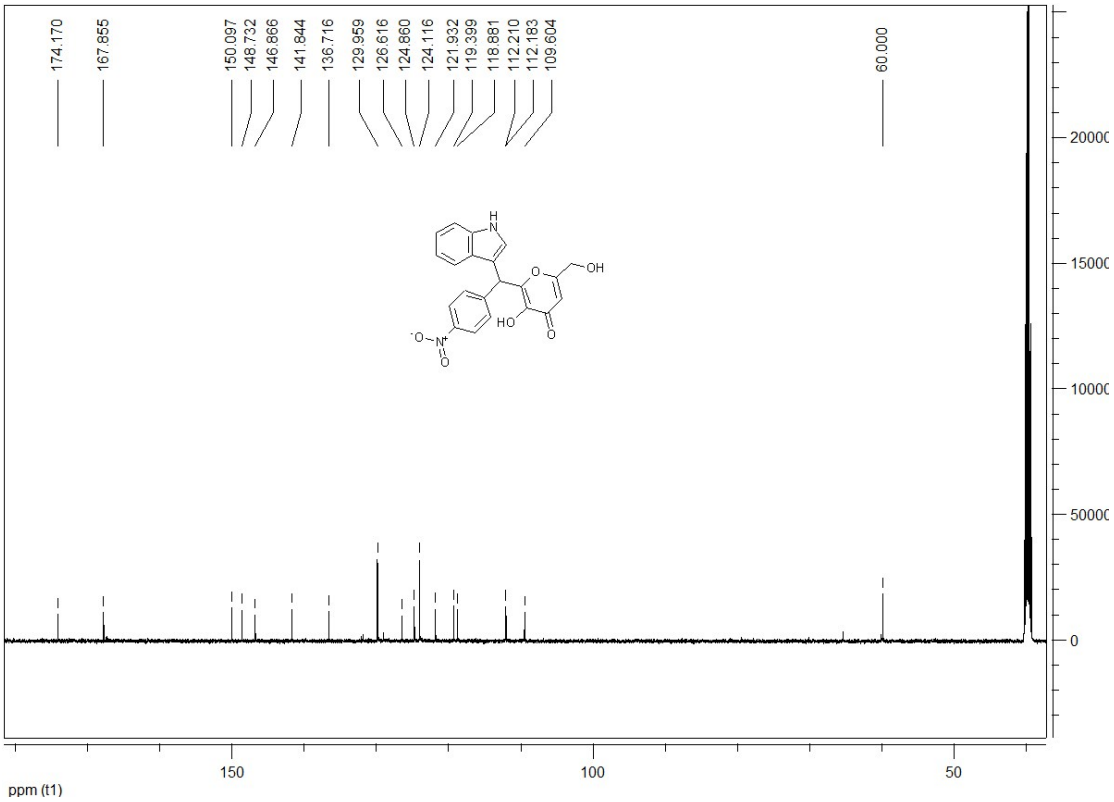
^{1}H NMR and ^{13}C NMR of compound **4k**



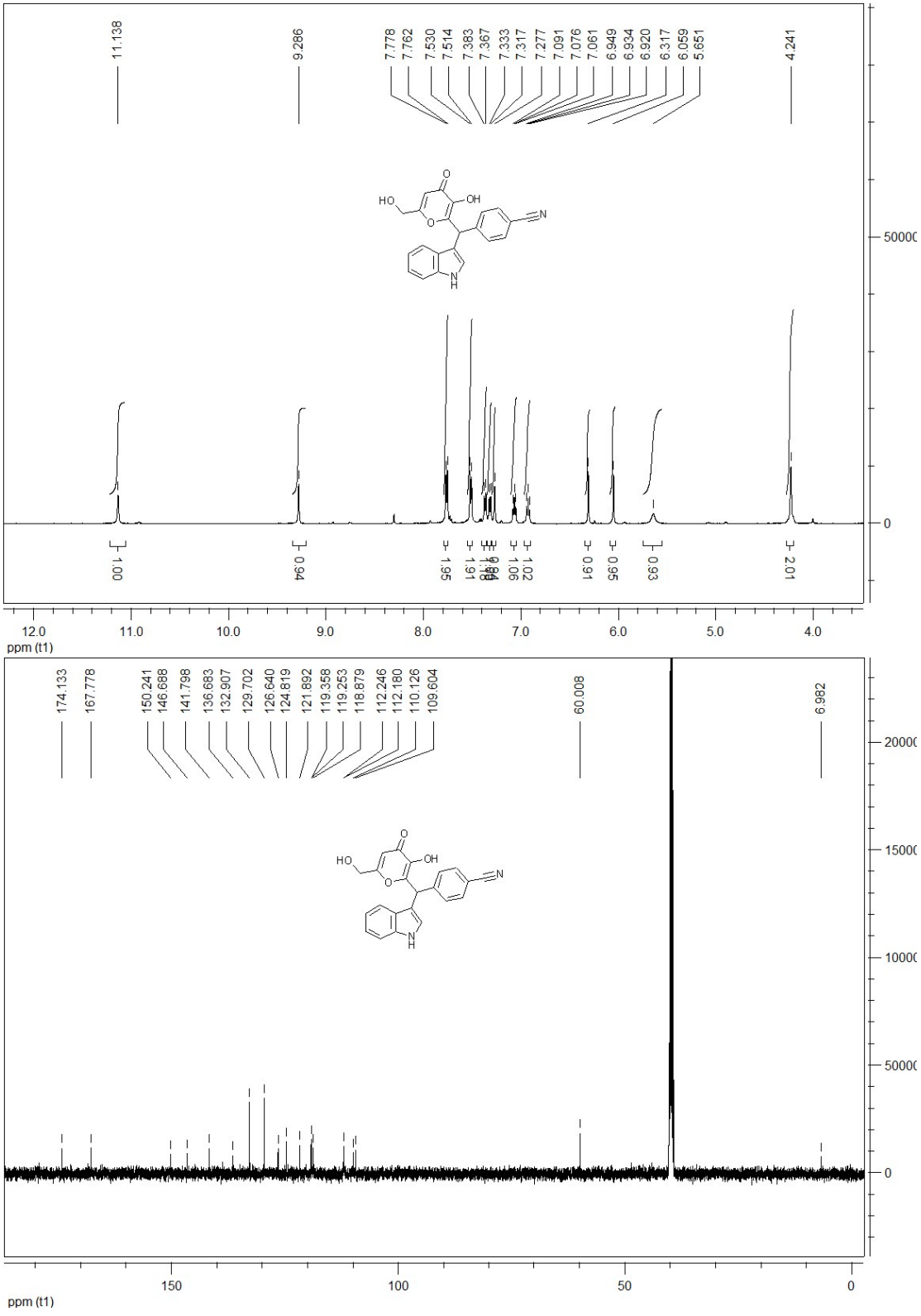


^{1}H NMR and ^{13}C NMR of compound **4l**

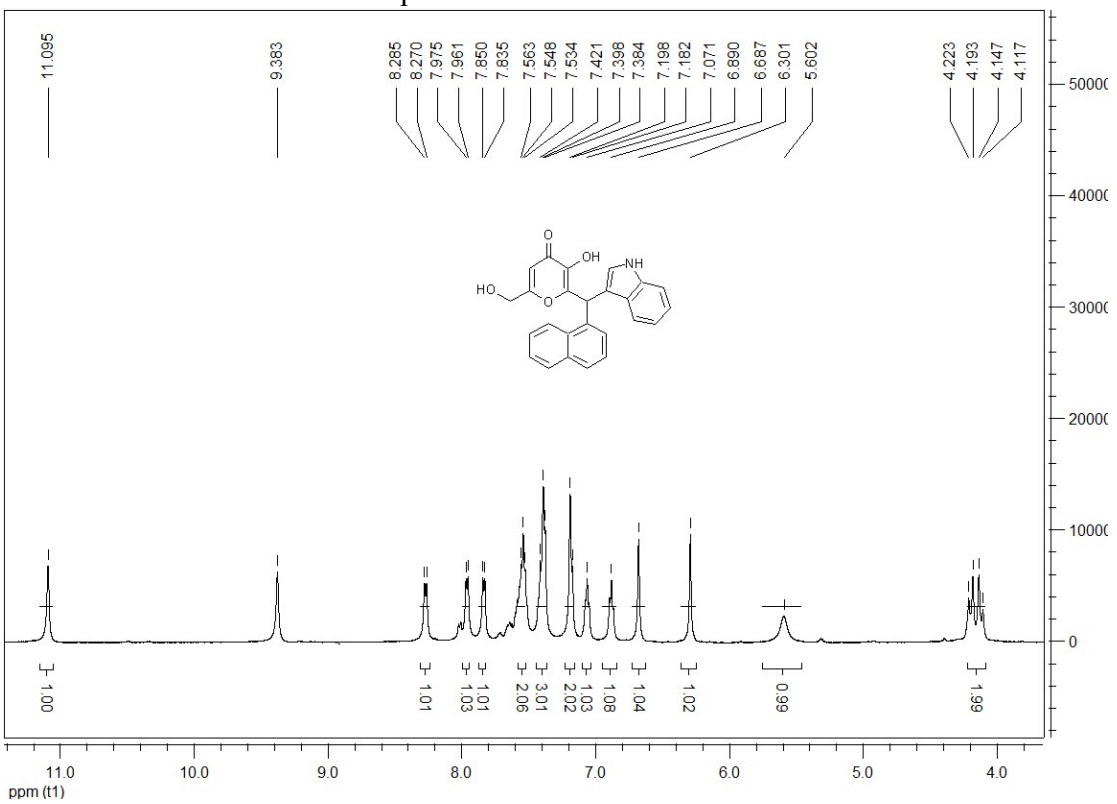


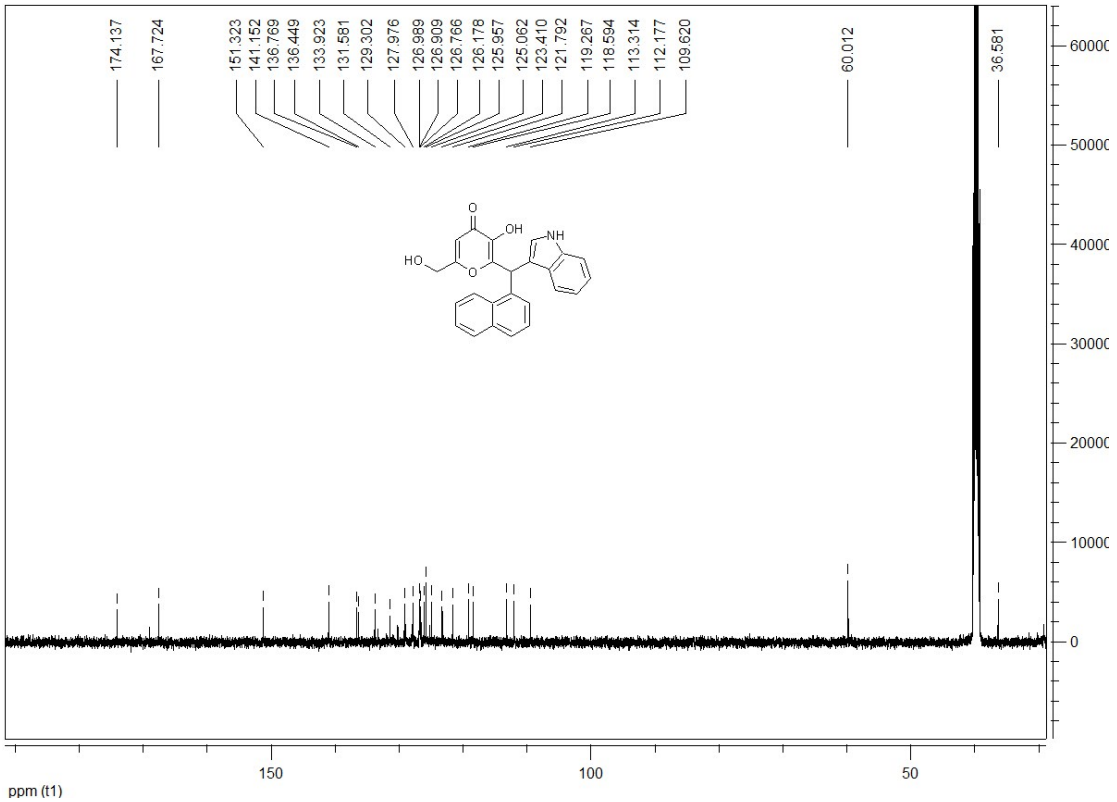


^{1}H NMR and ^{13}C NMR of compound **4m**

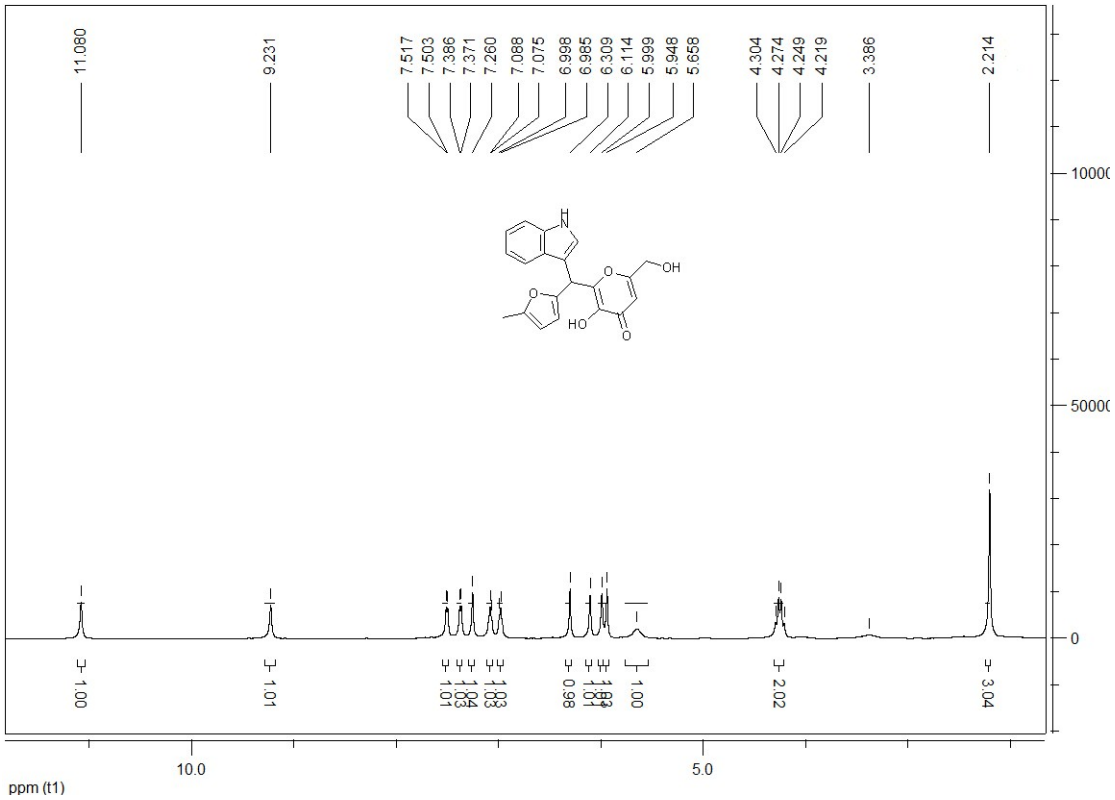


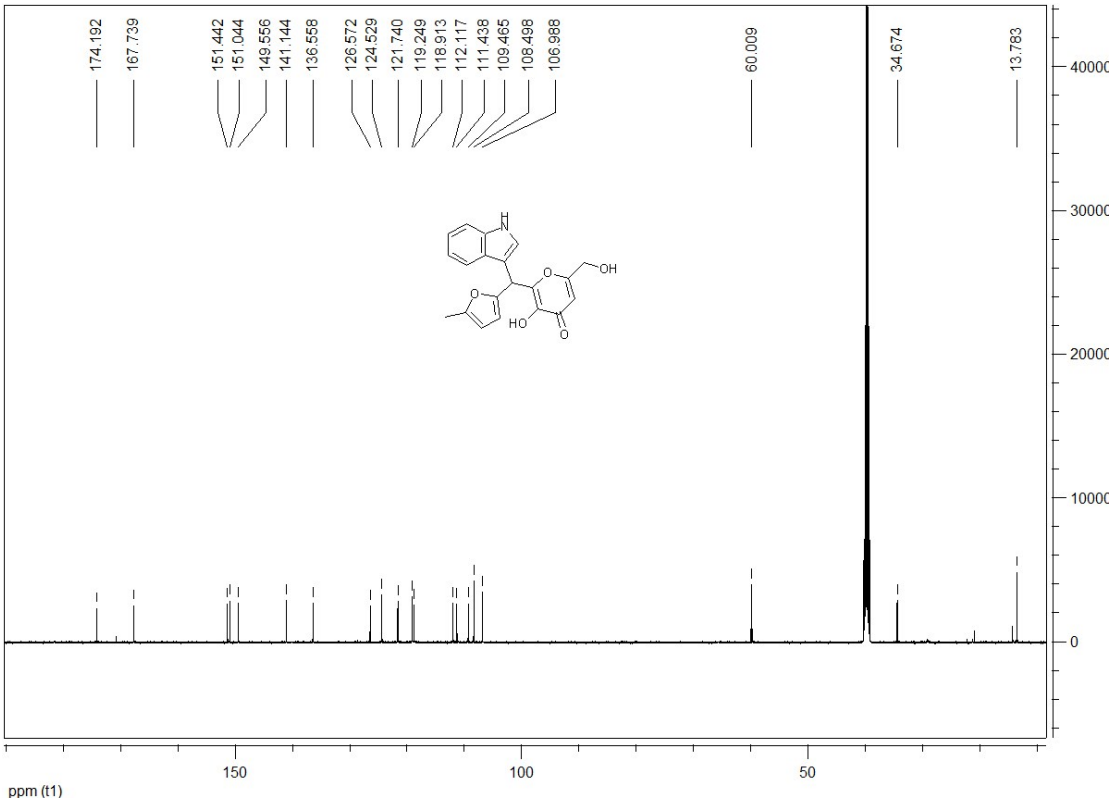
^{1}H NMR and ^{13}C NMR of compound **4n**



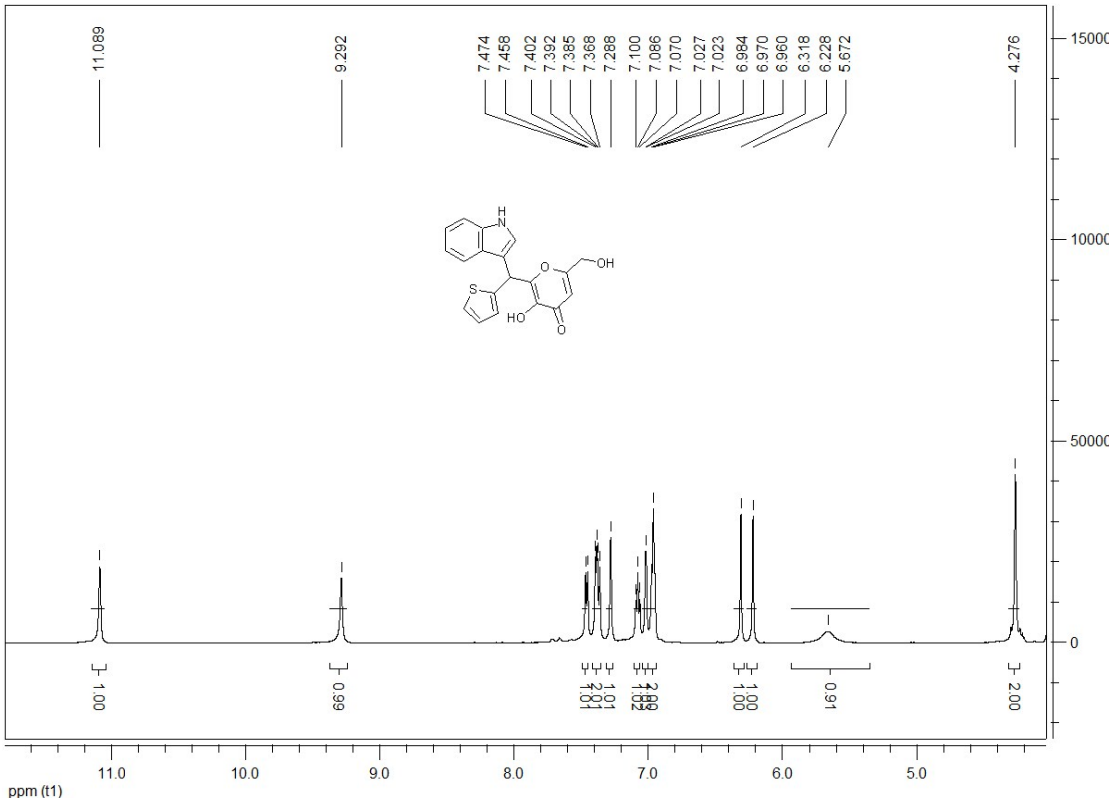


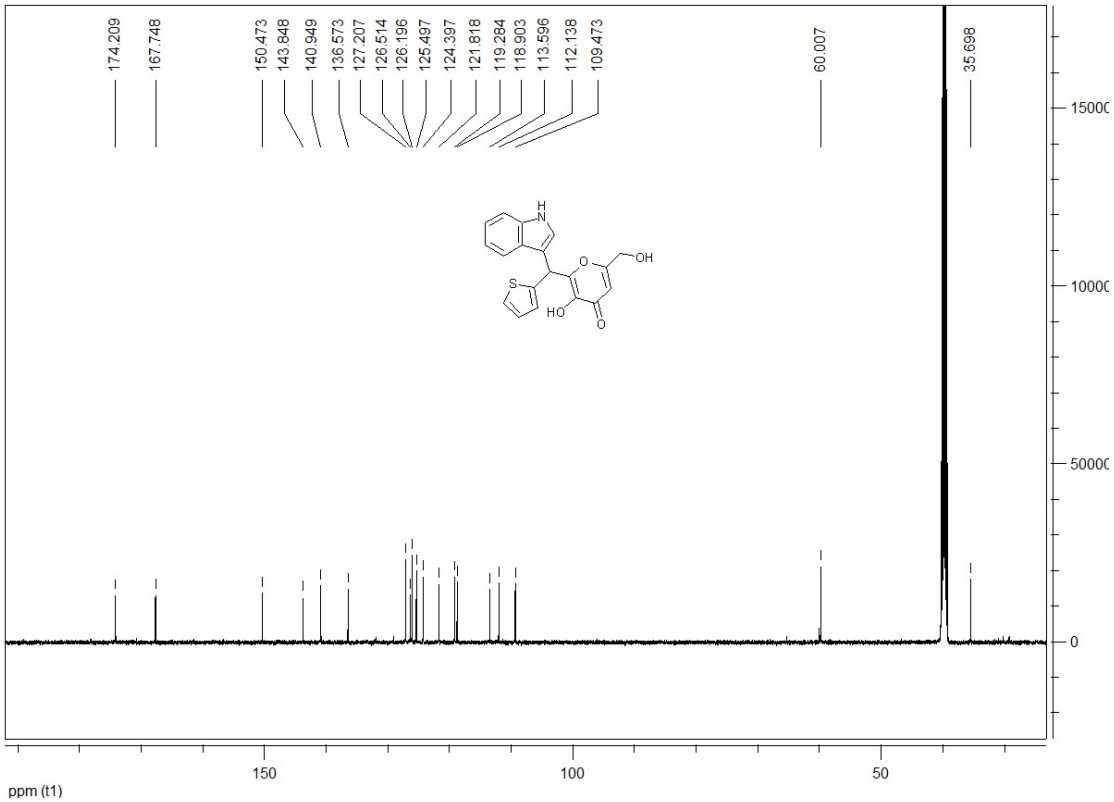
^{1}H NMR and ^{13}C NMR of compound **4o**



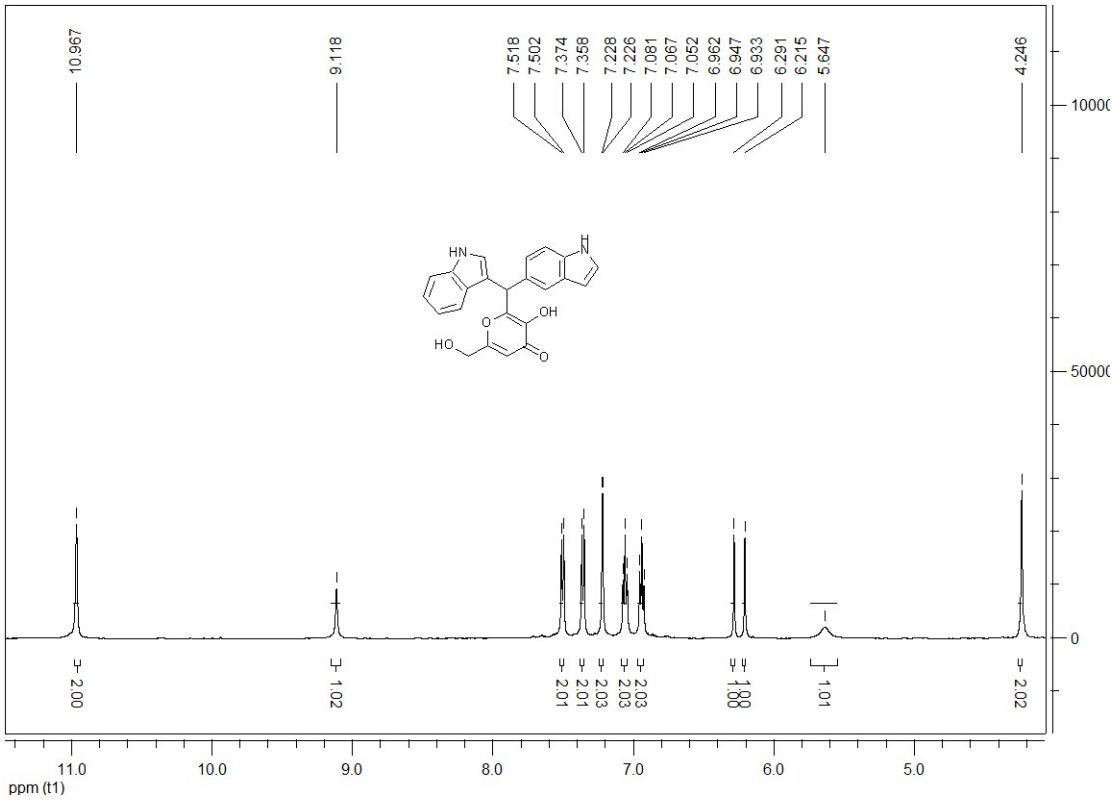


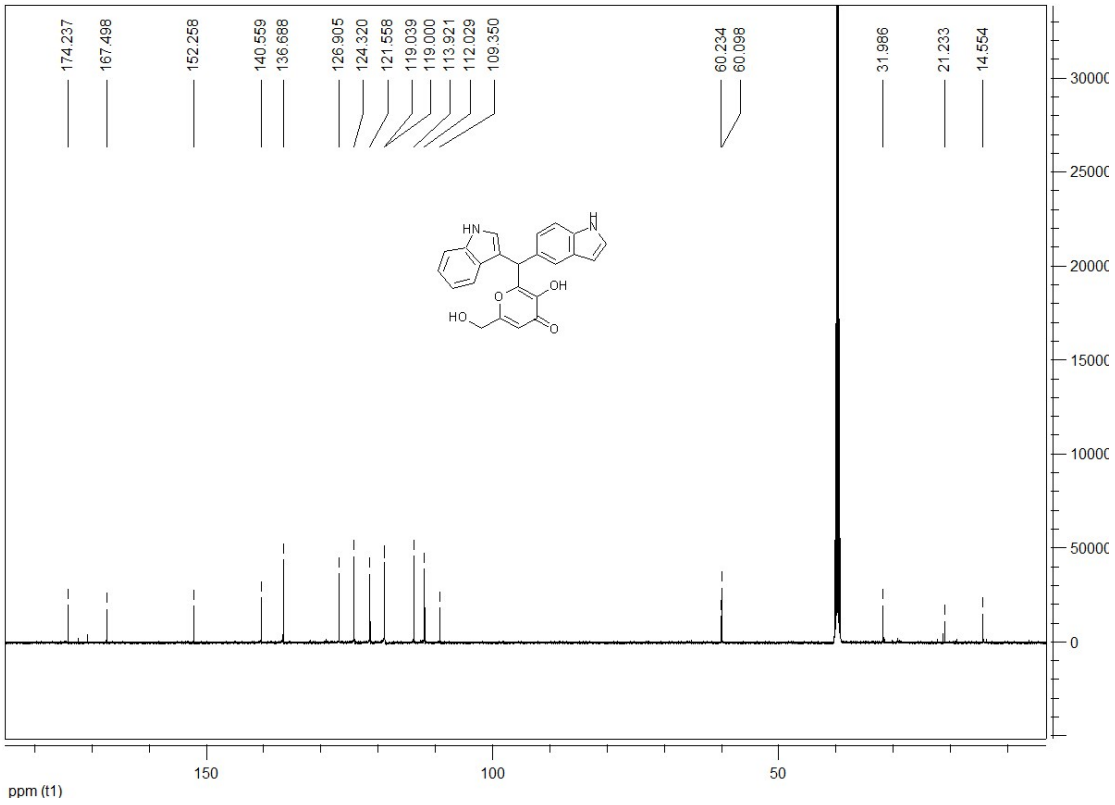
^{1}H NMR and ^{13}C NMR of compound **4p**



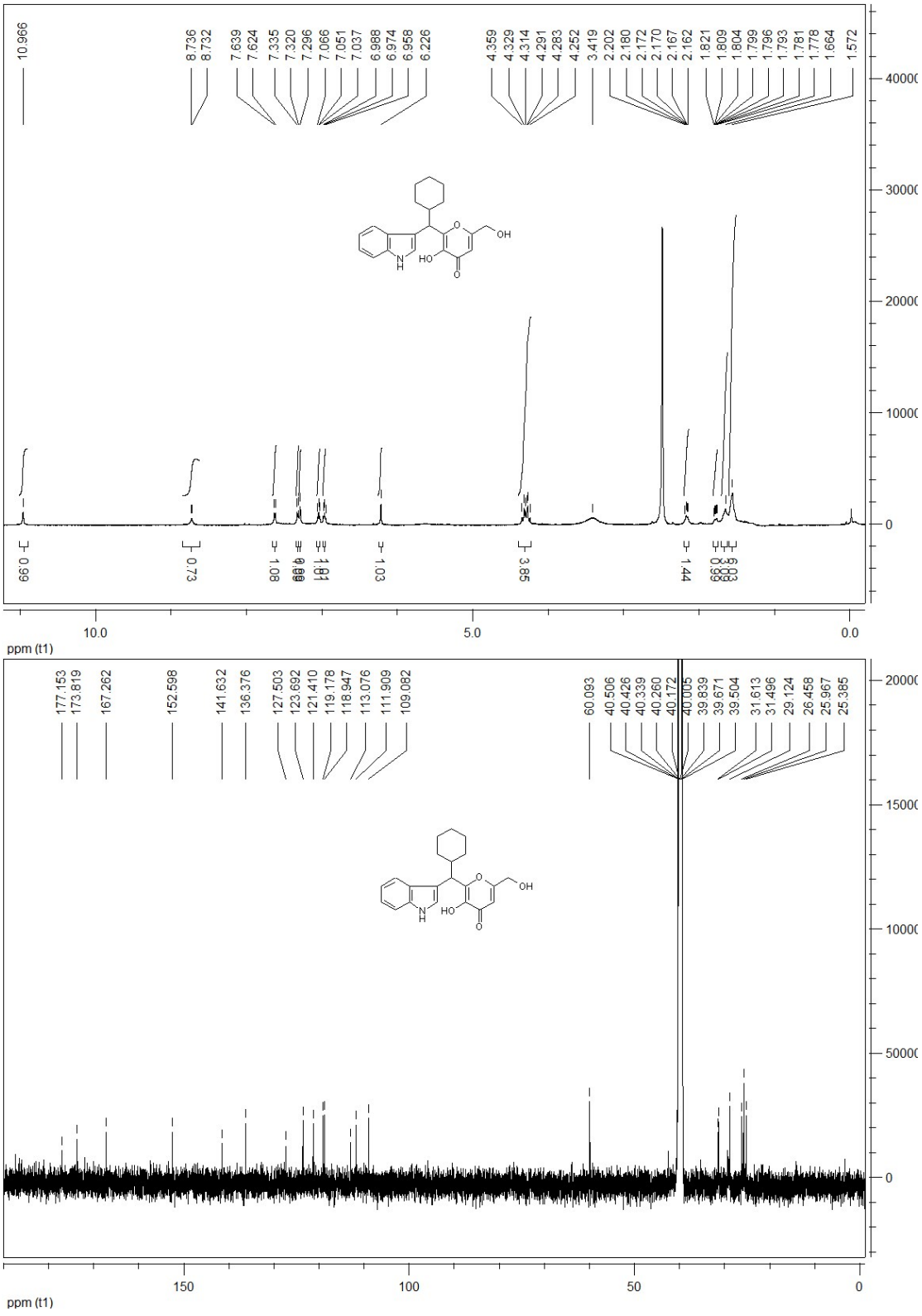


^{1}H NMR and ^{13}C NMR of compound **4q**

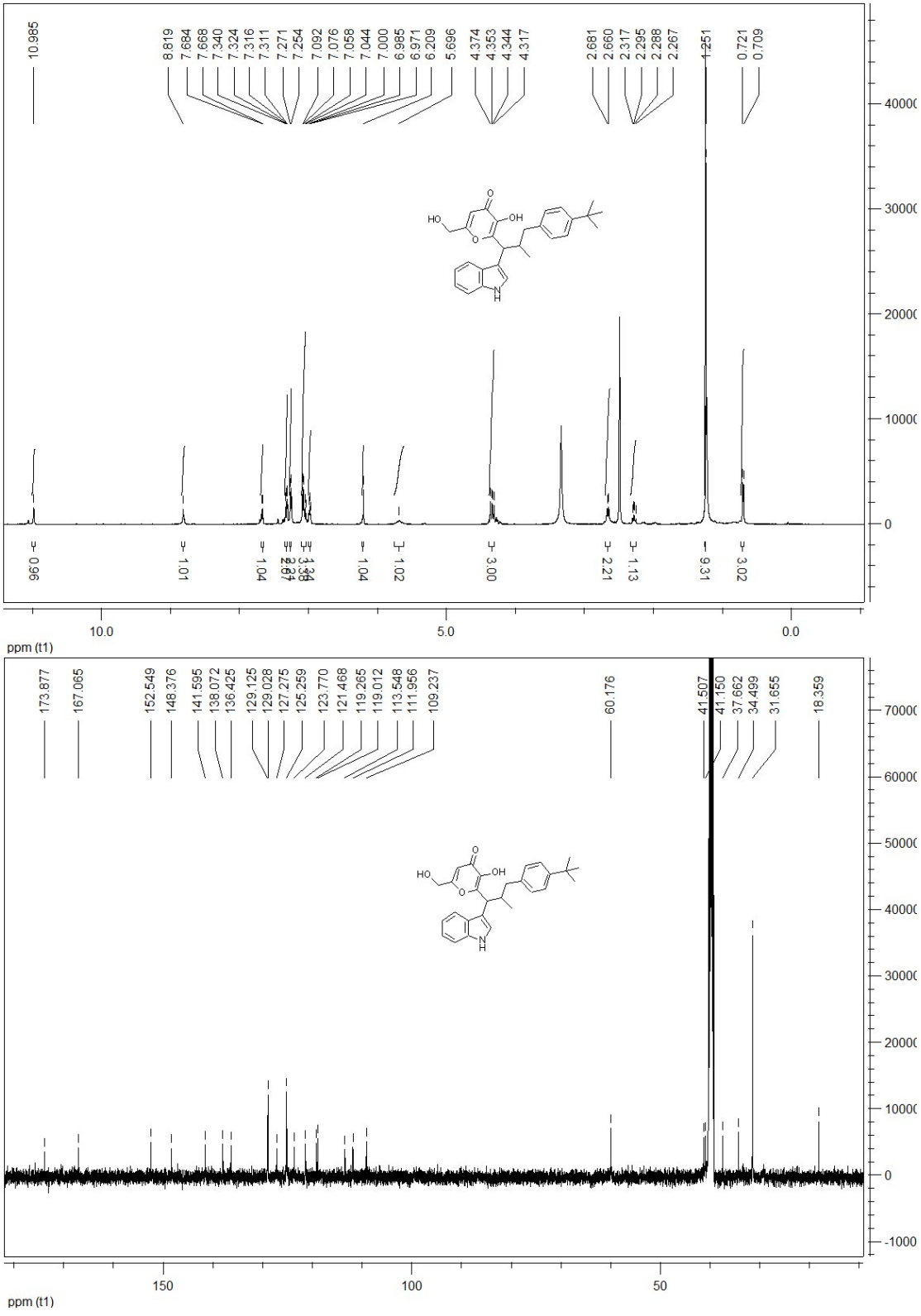




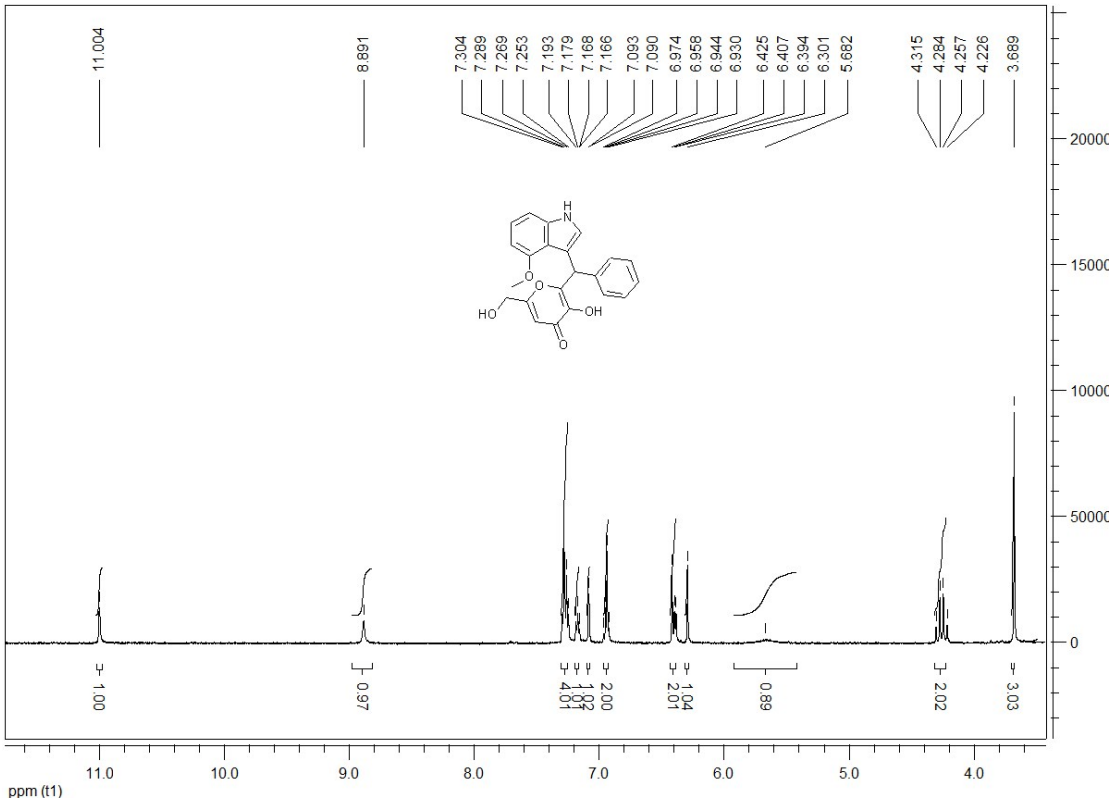
^{1}H NMR and ^{13}C NMR of compound **4r**

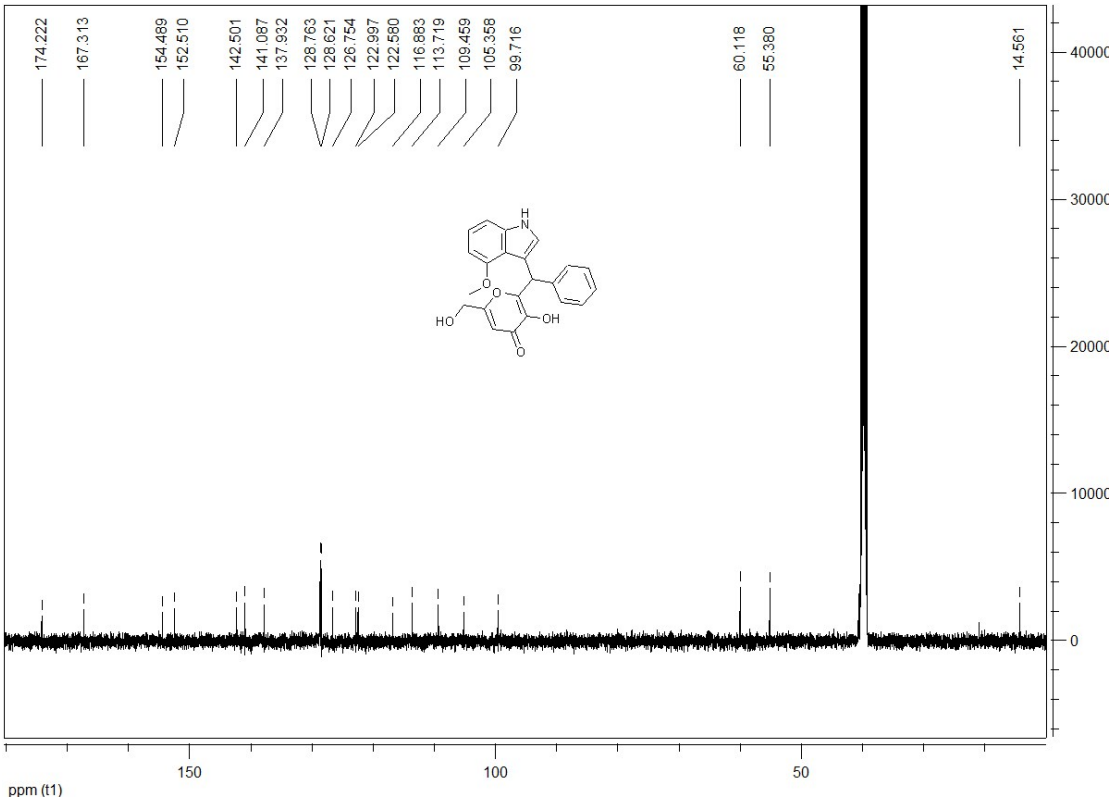


^{1}H NMR and ^{13}C NMR of compound **4s**

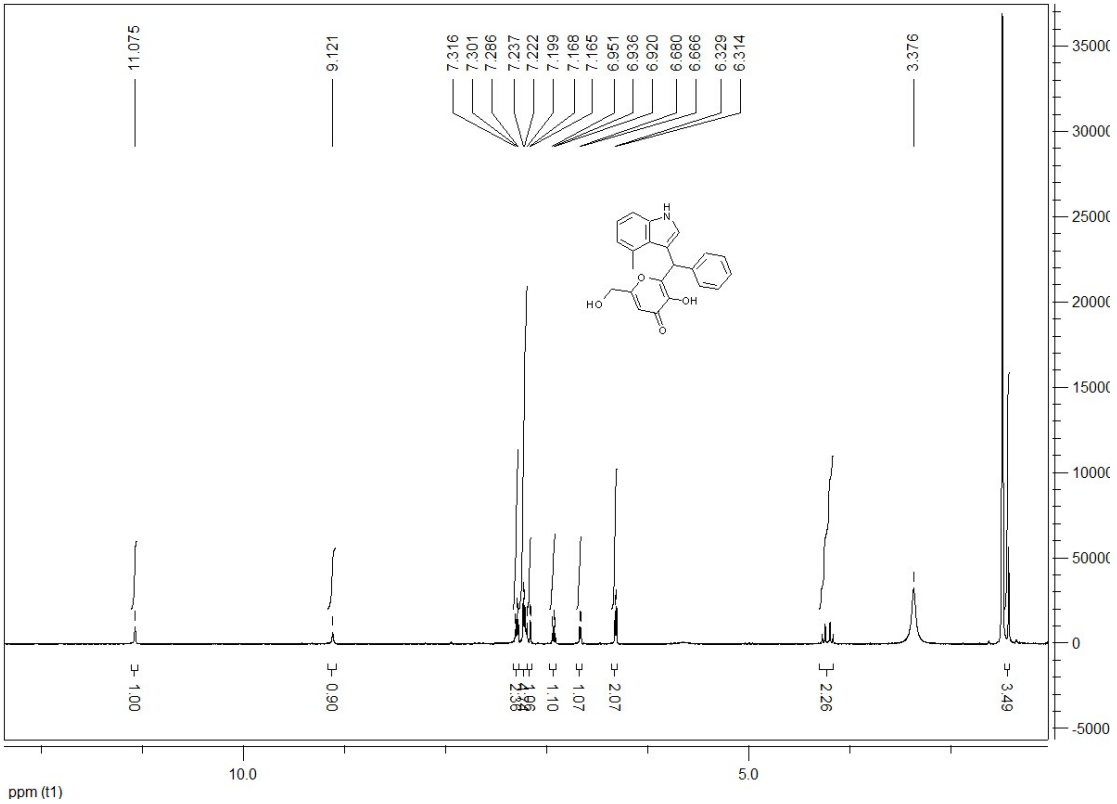


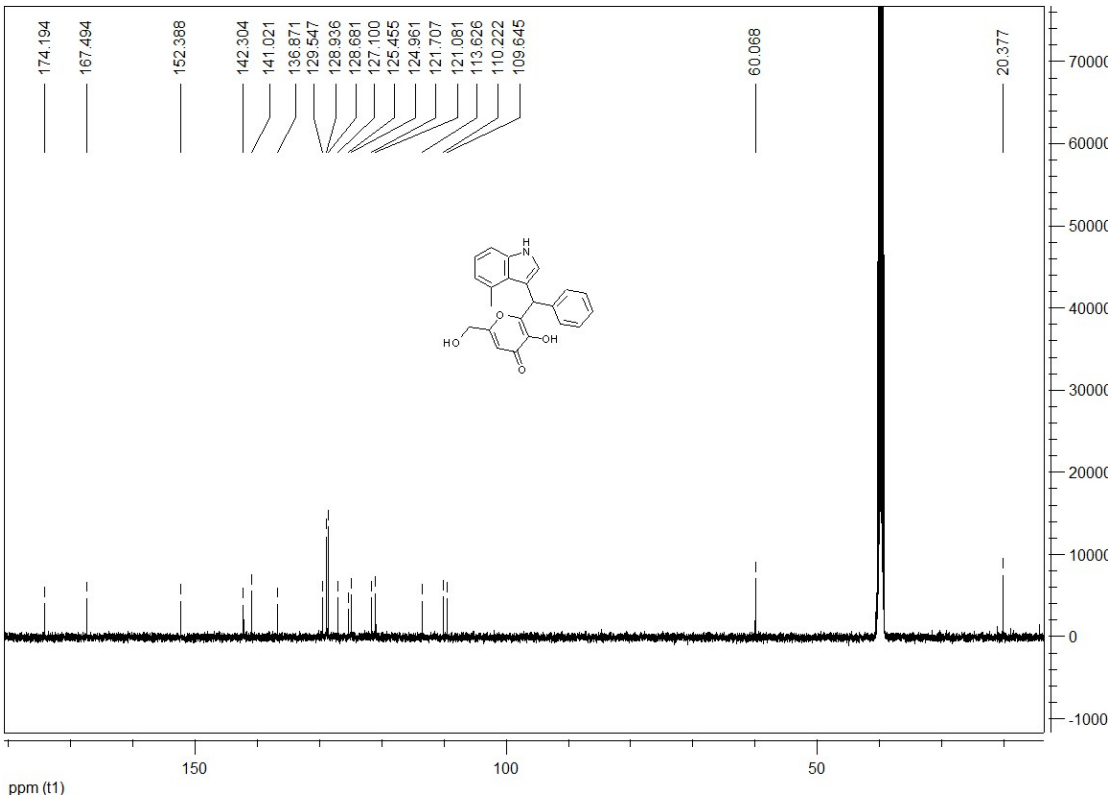
^{1}H NMR and ^{13}C NMR of compound **4t**



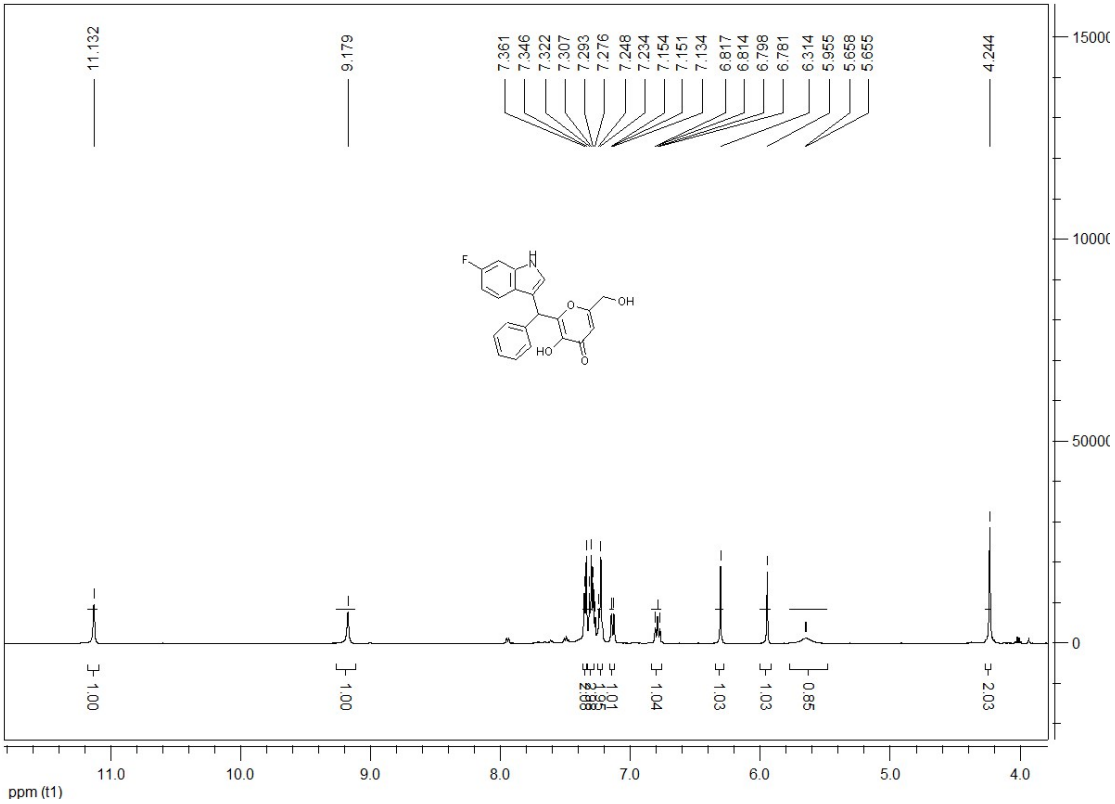


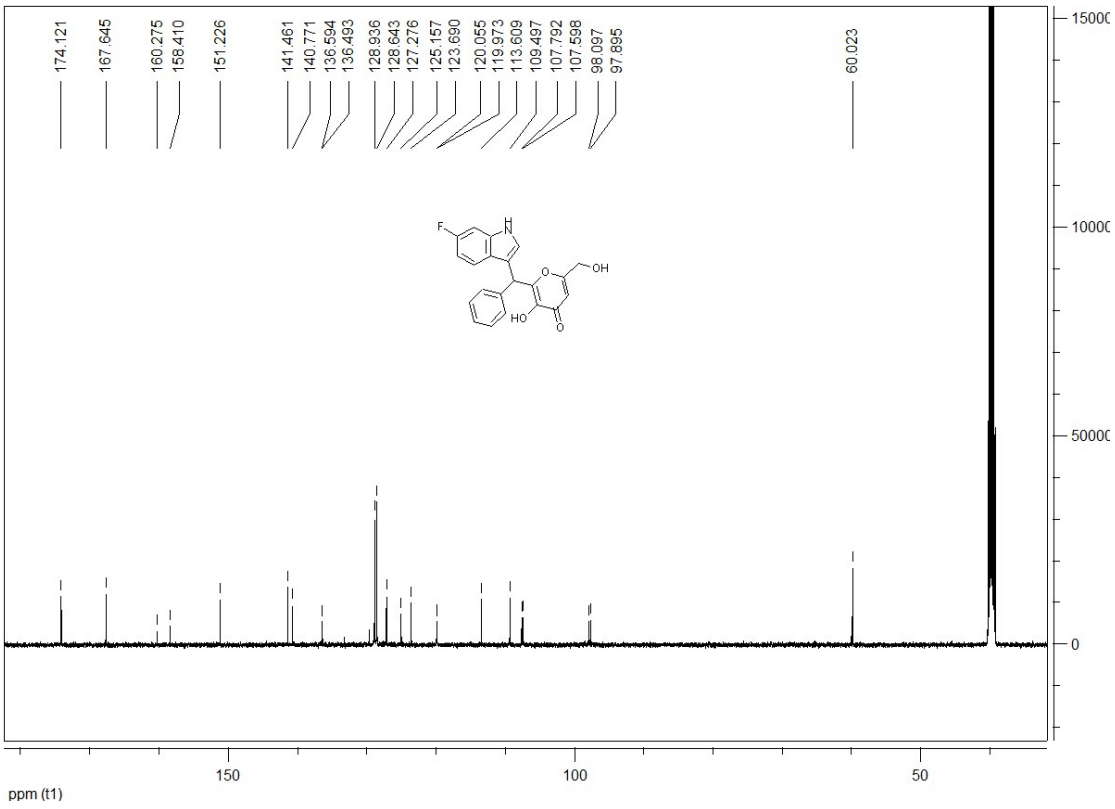
^{1}H NMR and ^{13}C NMR of compound **4u**



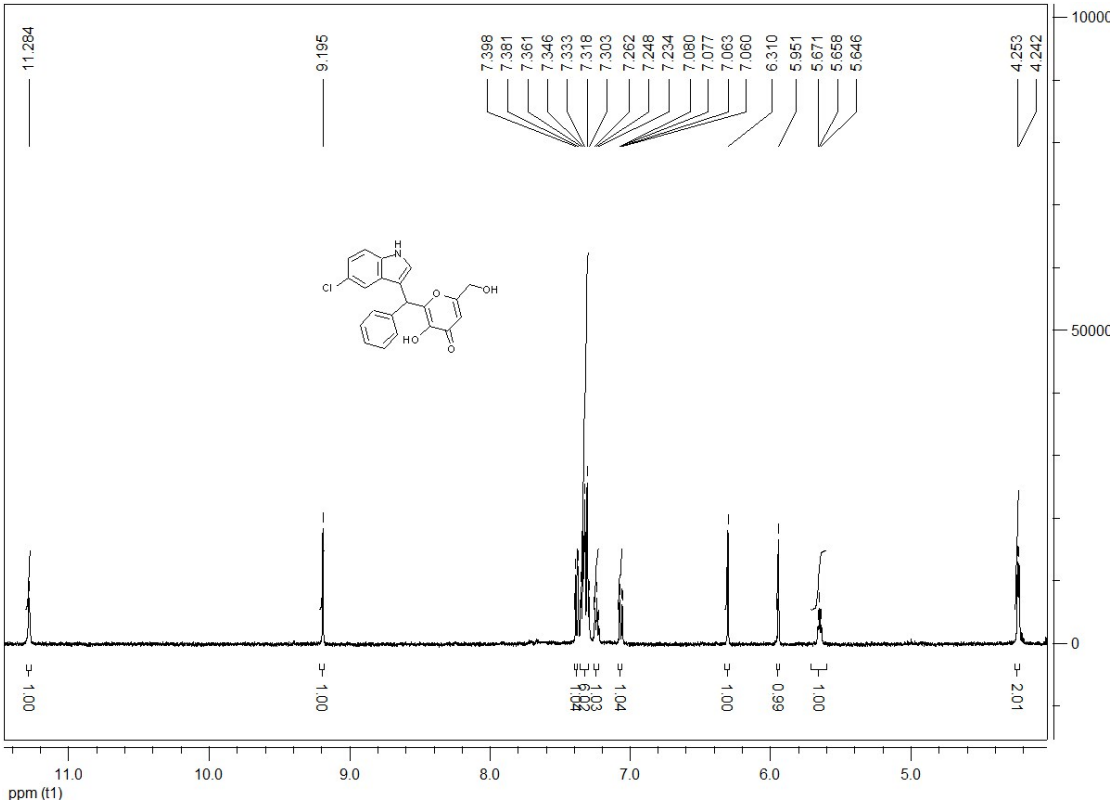


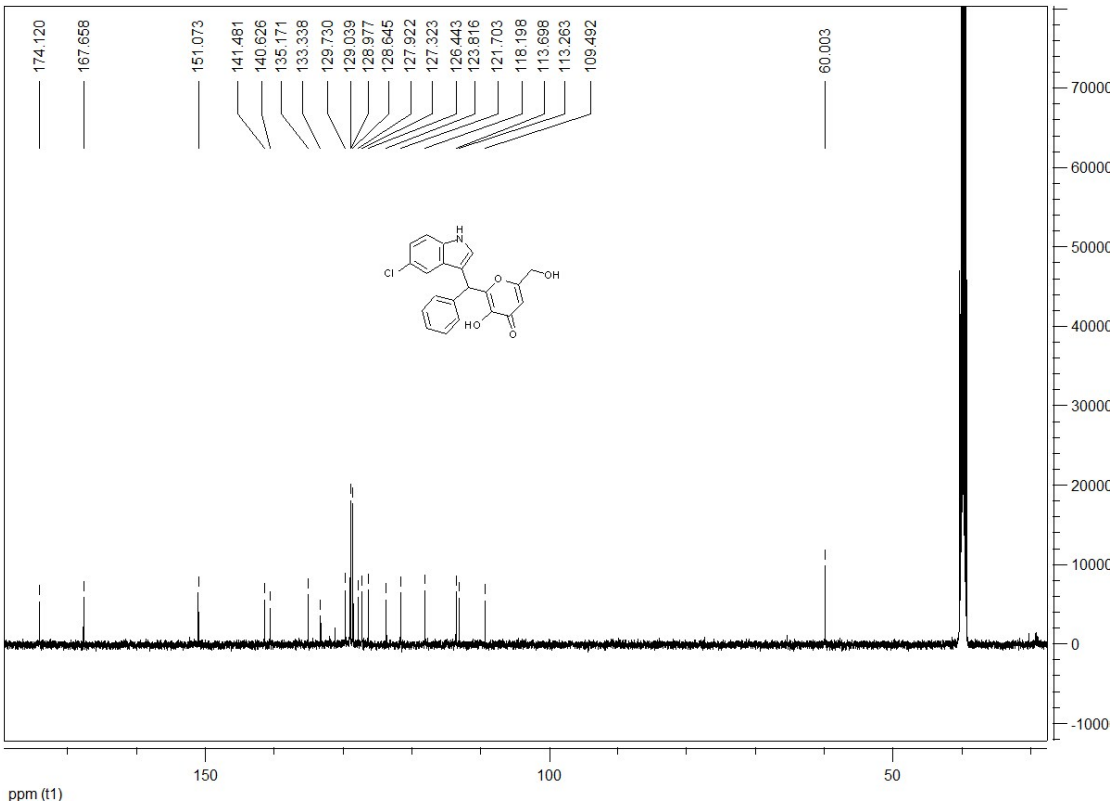
^{1}H NMR and ^{13}C NMR of compound **4v**



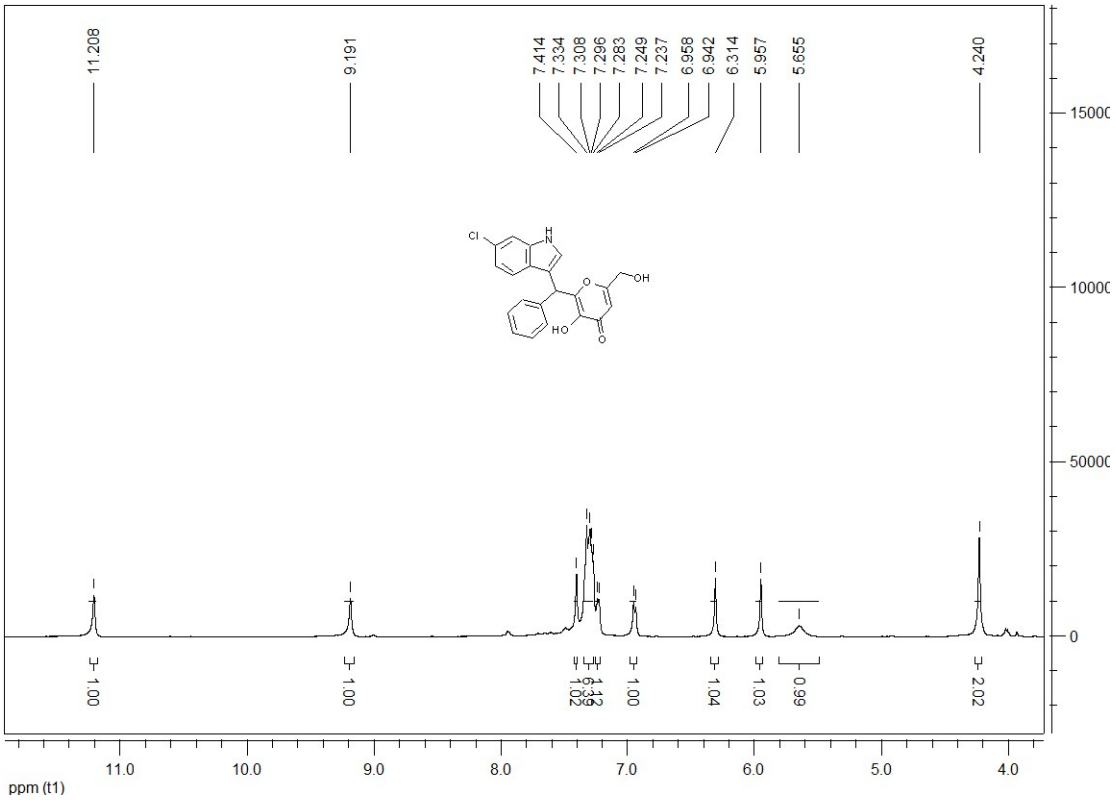


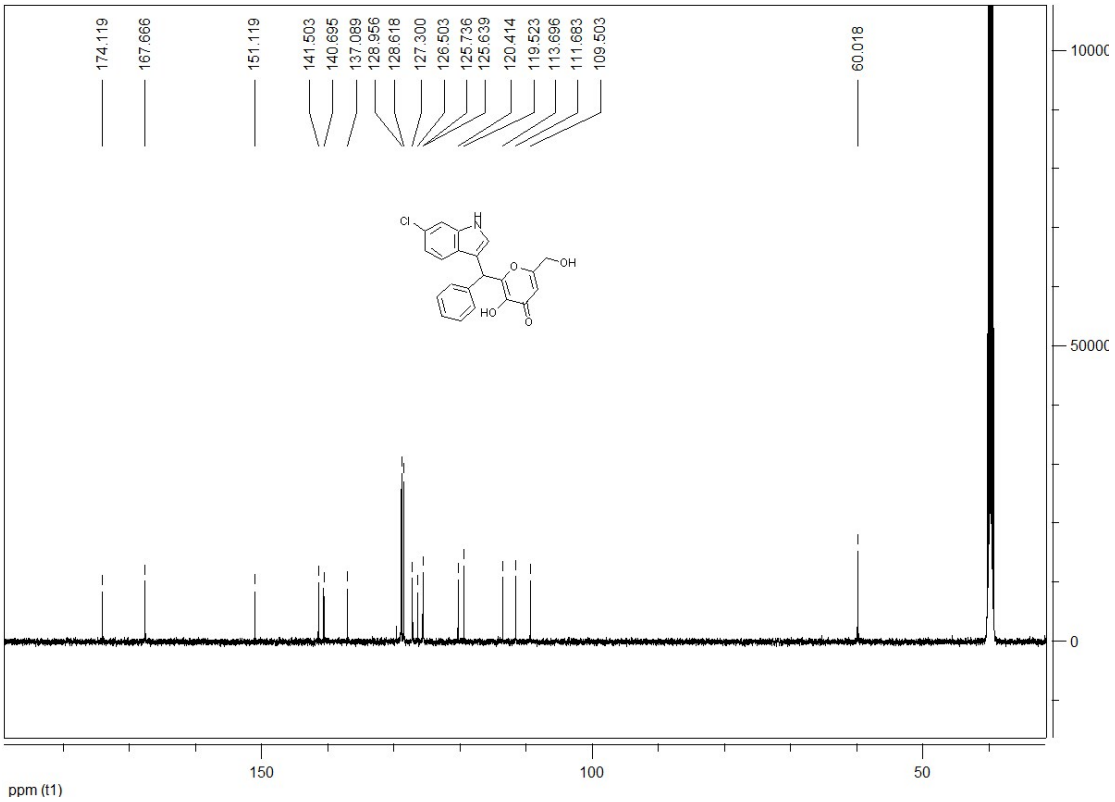
^{1}H NMR and ^{13}C NMR of compound **4w**



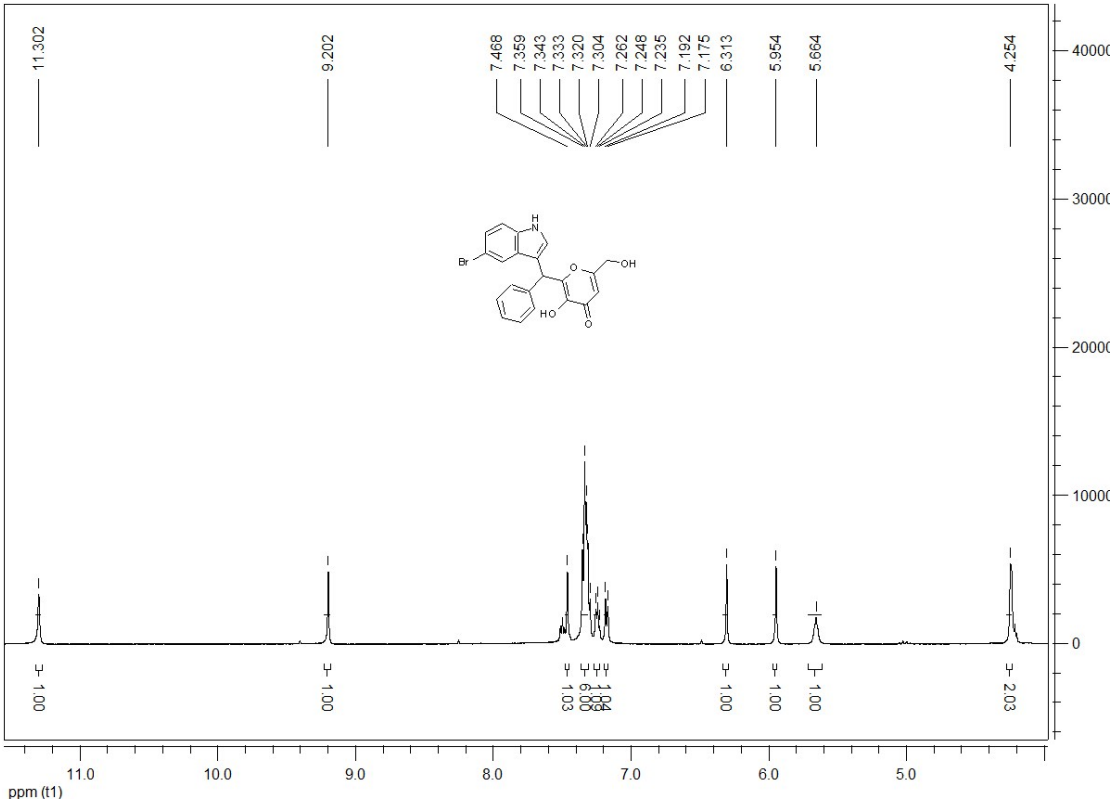


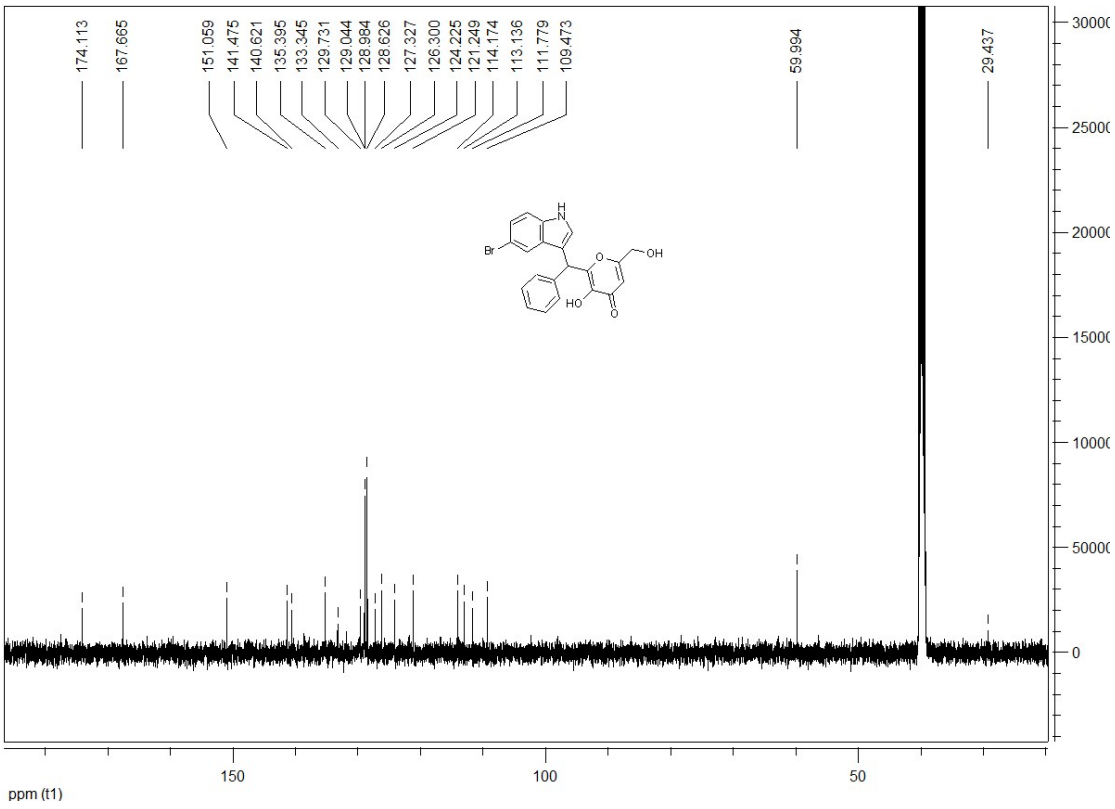
^{1}H NMR and ^{13}C NMR of compound **4x**



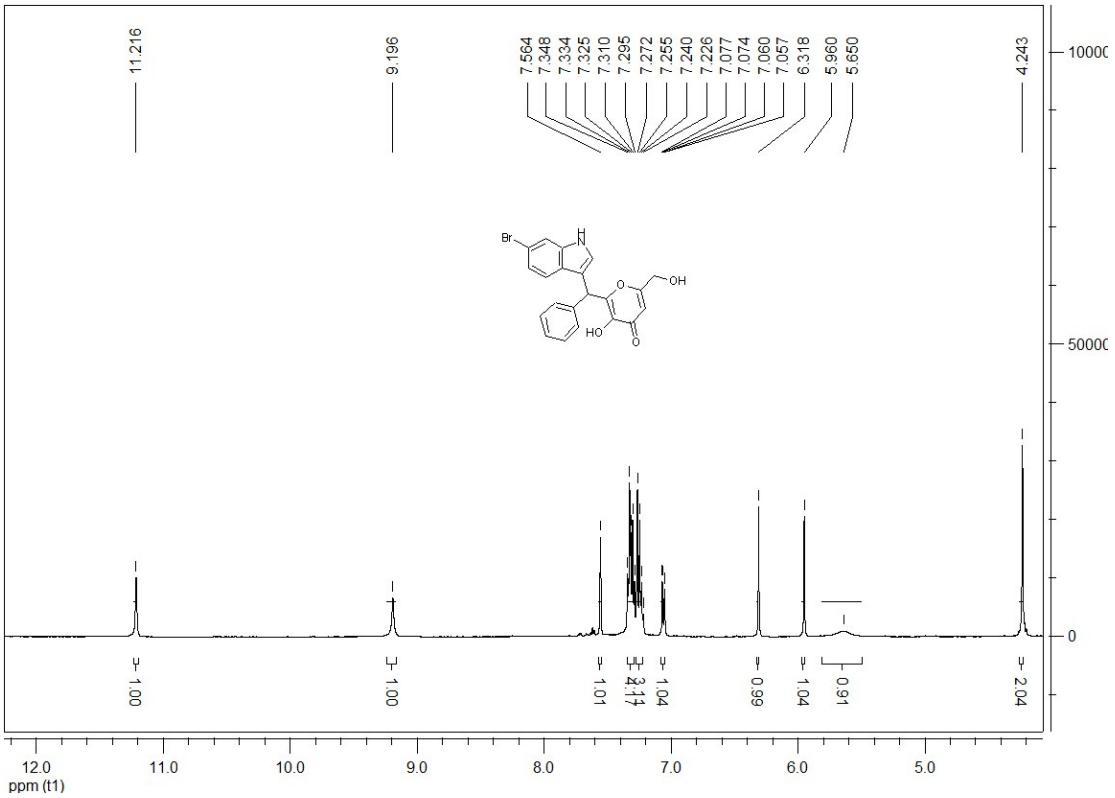


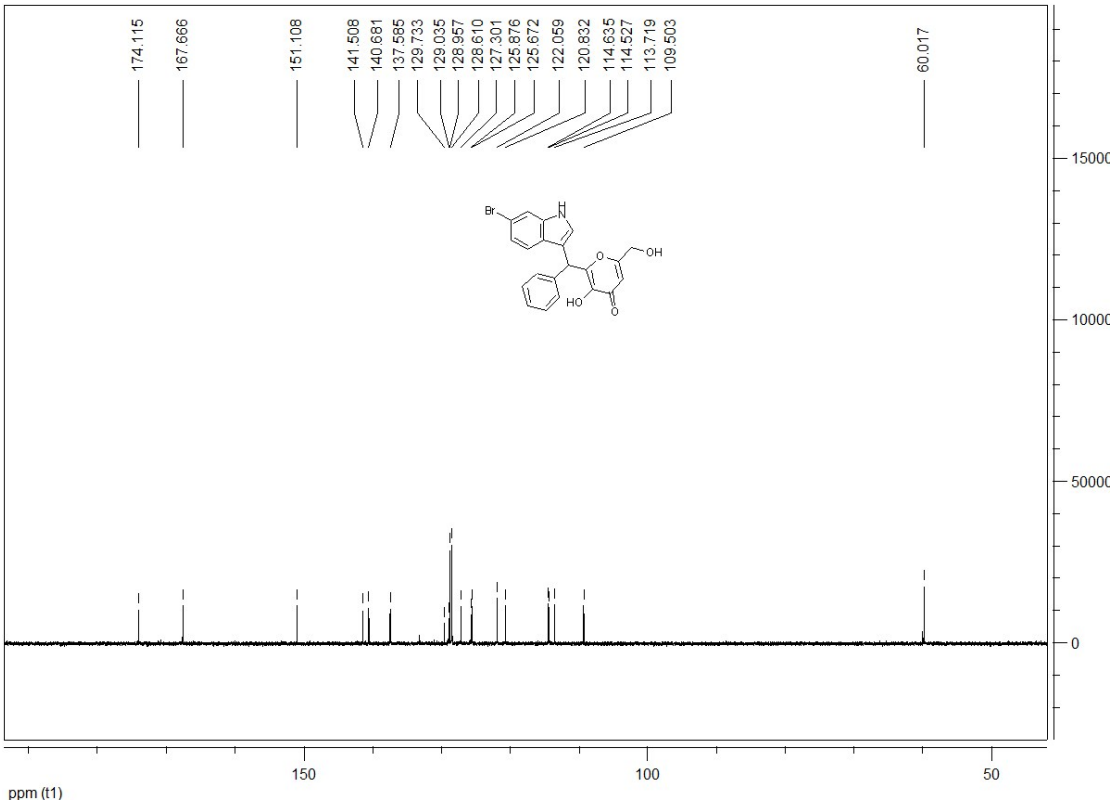
^{1}H NMR and ^{13}C NMR of compound **4y**



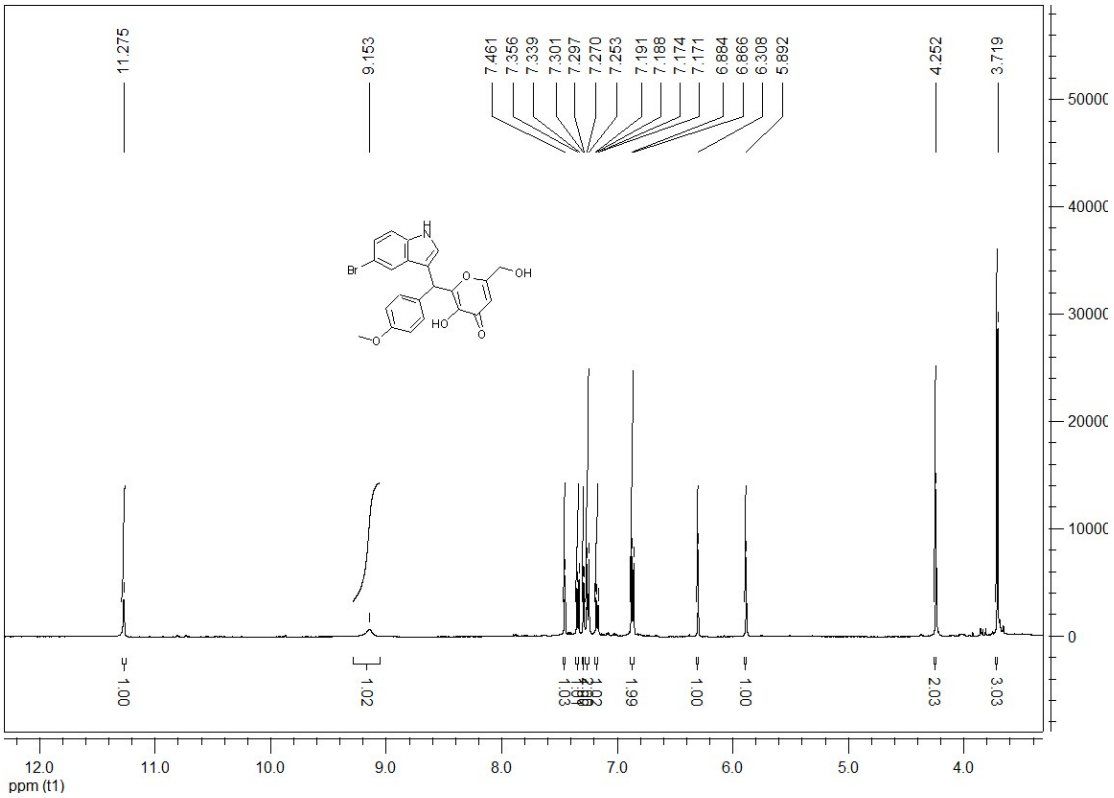


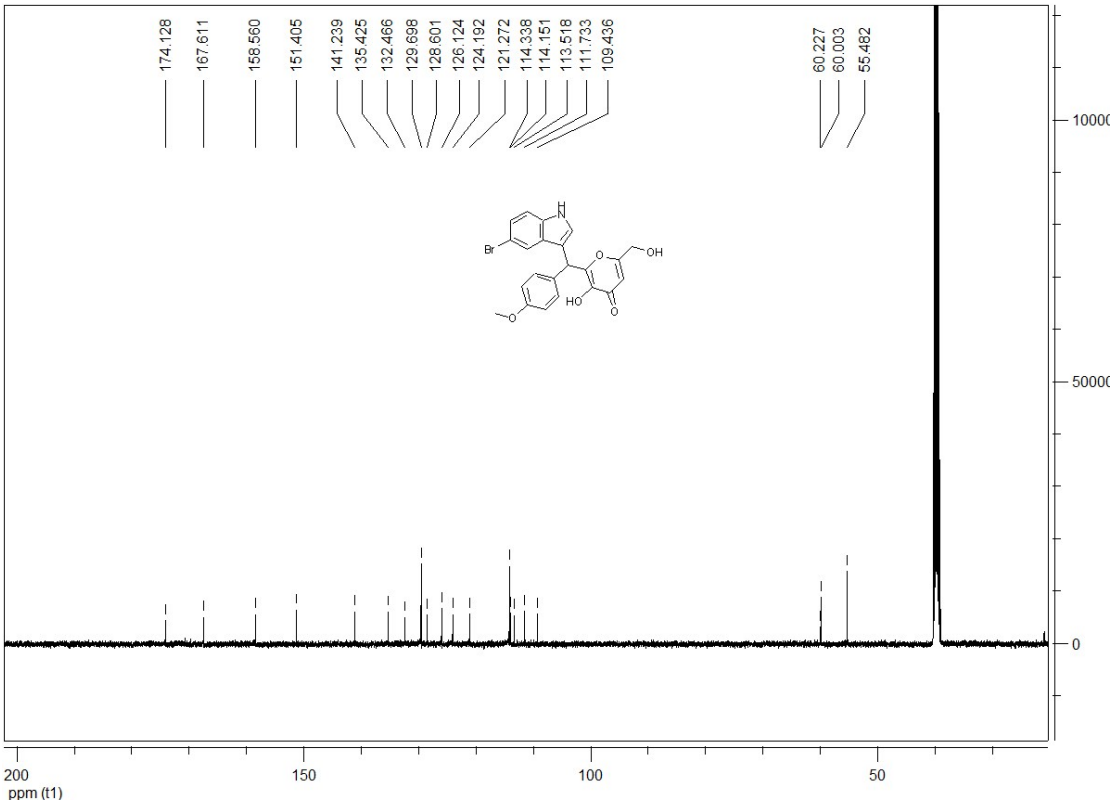
^{1}H NMR and ^{13}C NMR of compound **4z**



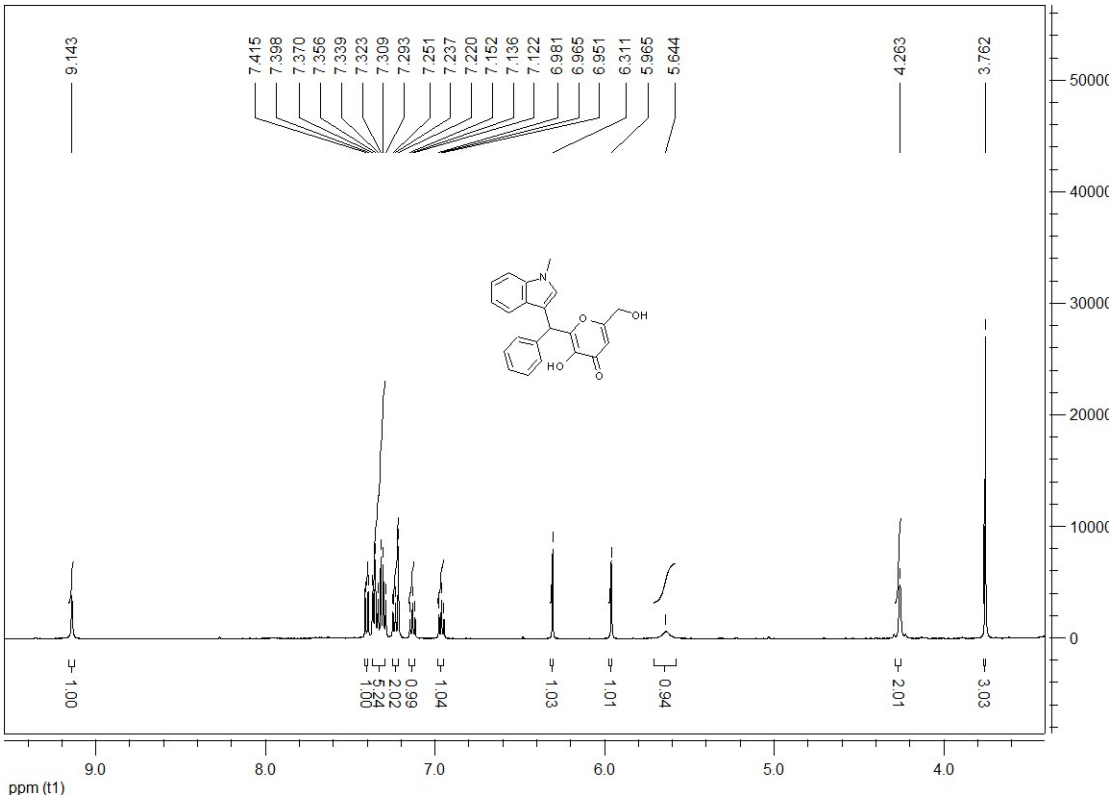


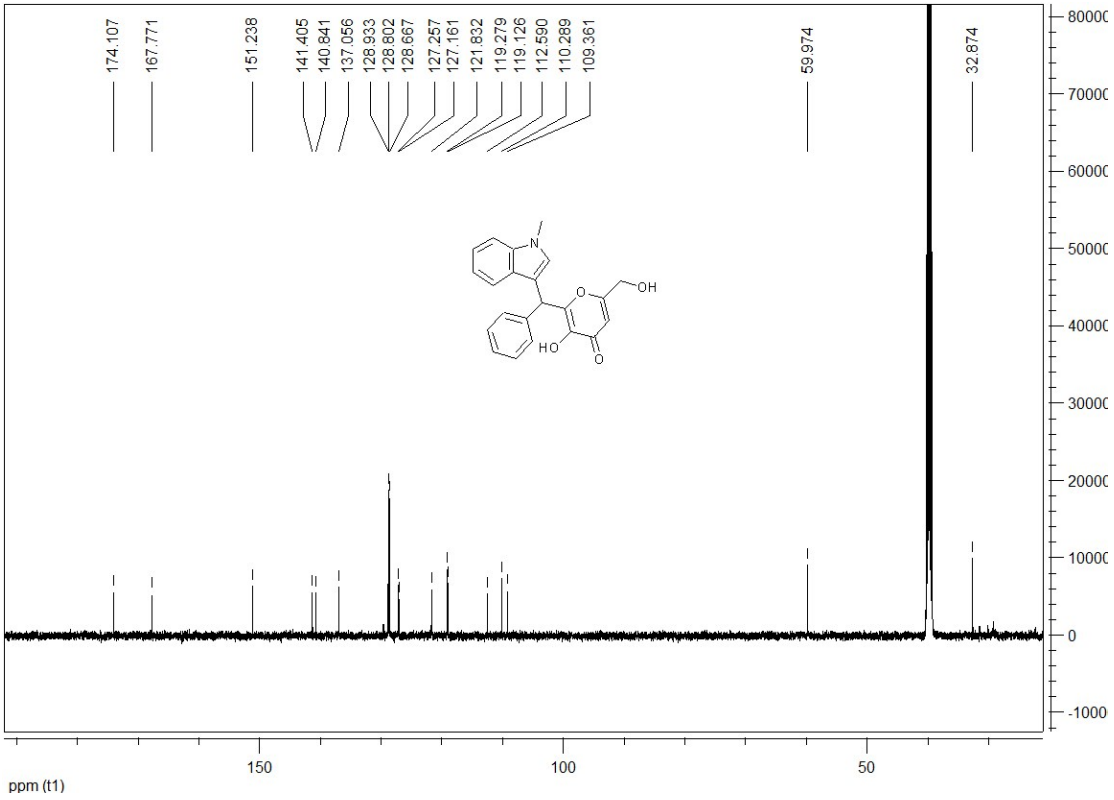
^{1}H NMR and ^{13}C NMR of compound **4aa**



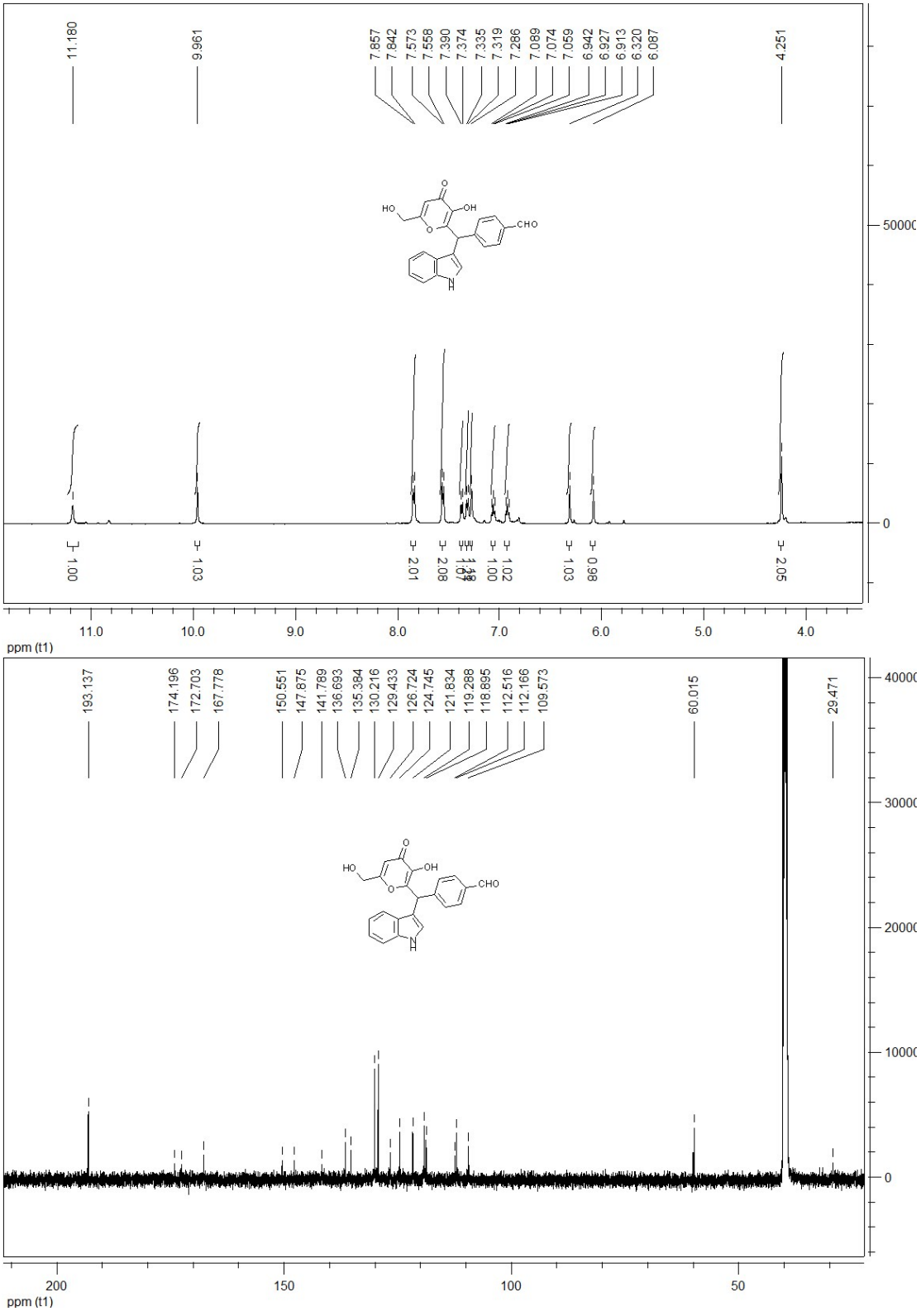


^{1}H NMR and ^{13}C NMR of compound **4ab**

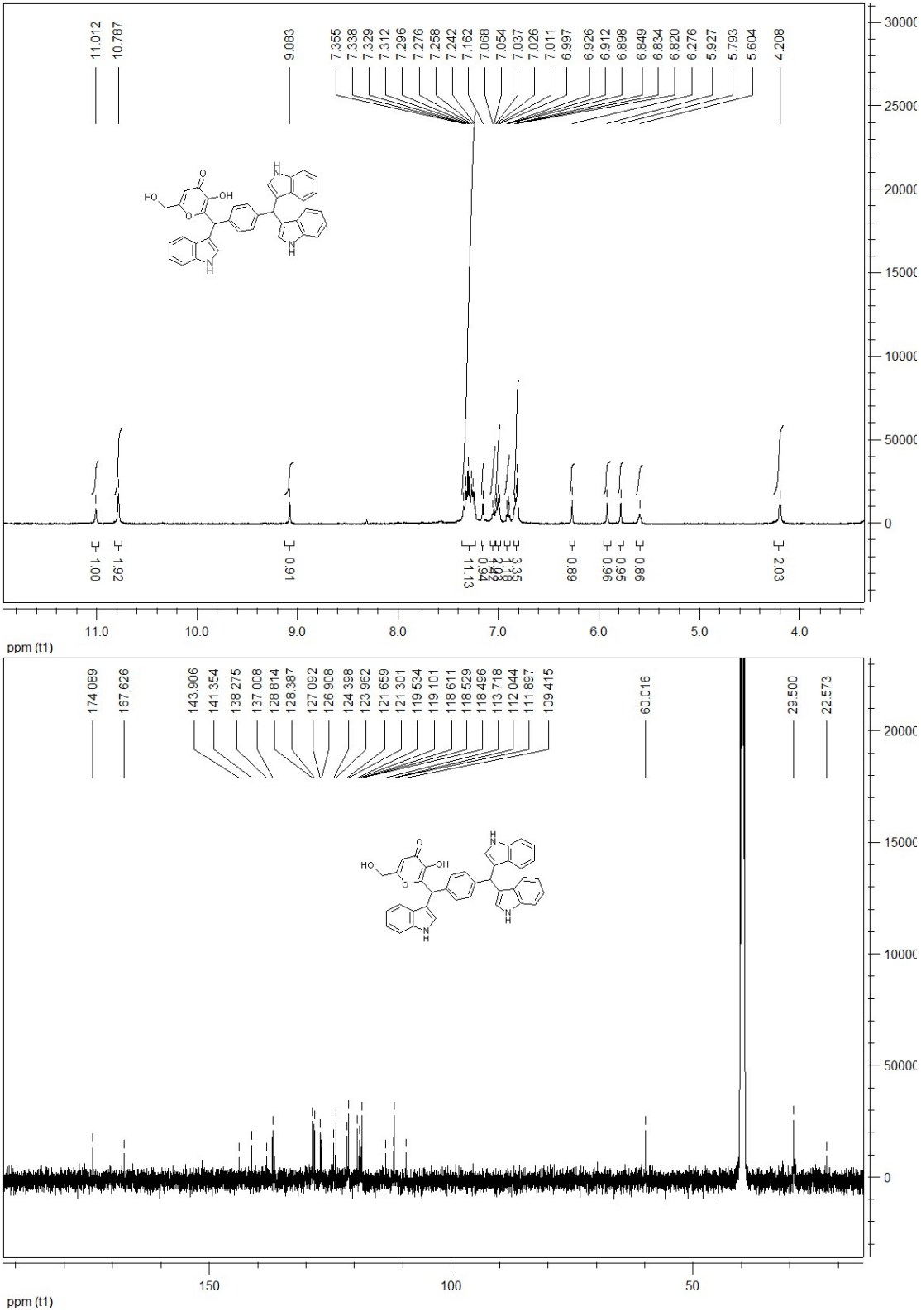




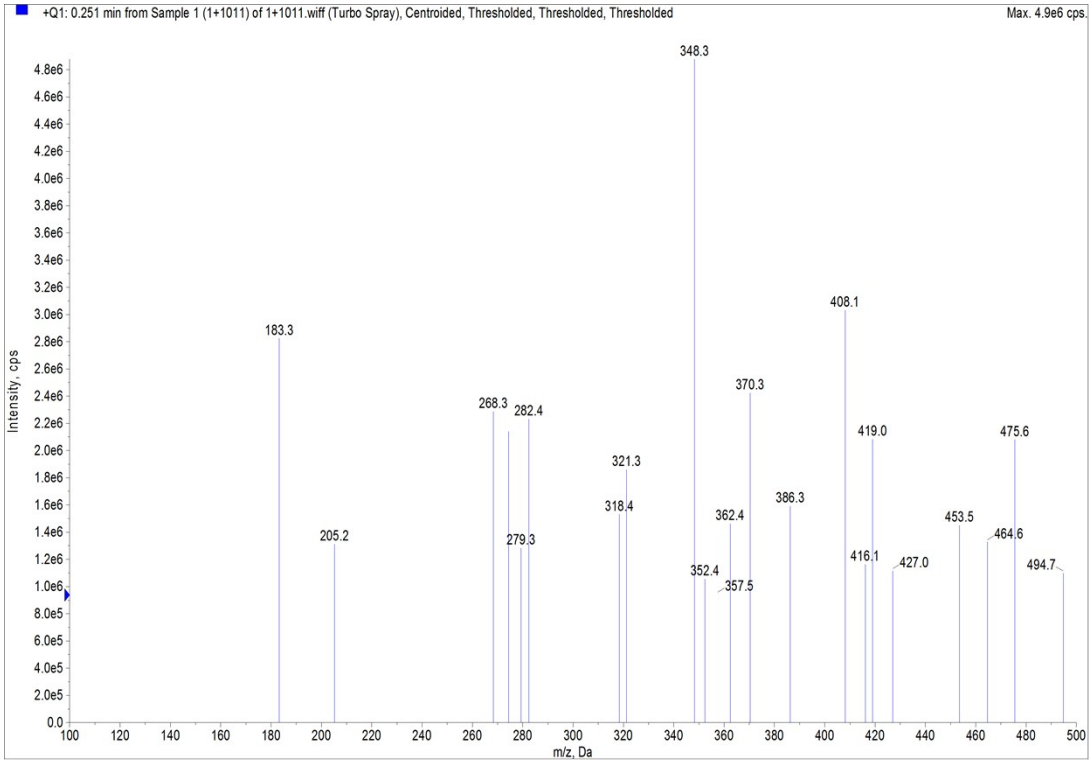
^{1}H NMR and ^{13}C NMR of compound **4ac**



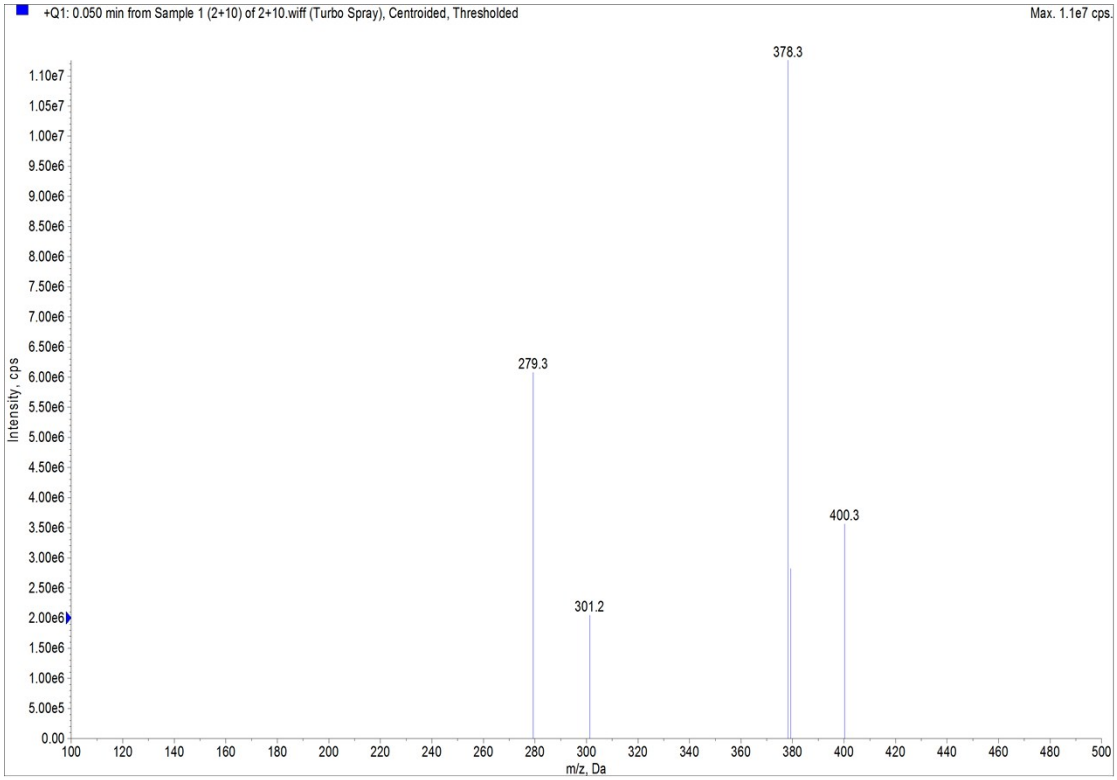
^{1}H NMR and ^{13}C NMR of compound **5**



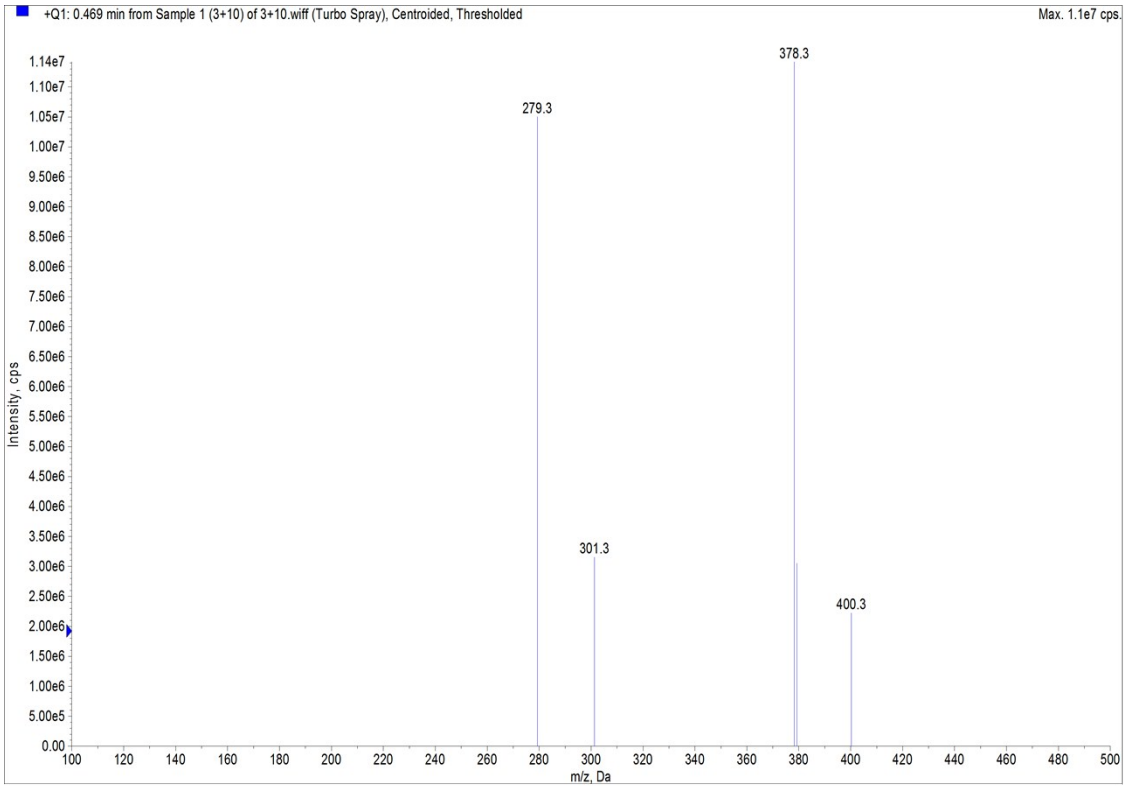
ESI-MS of compound **4a**



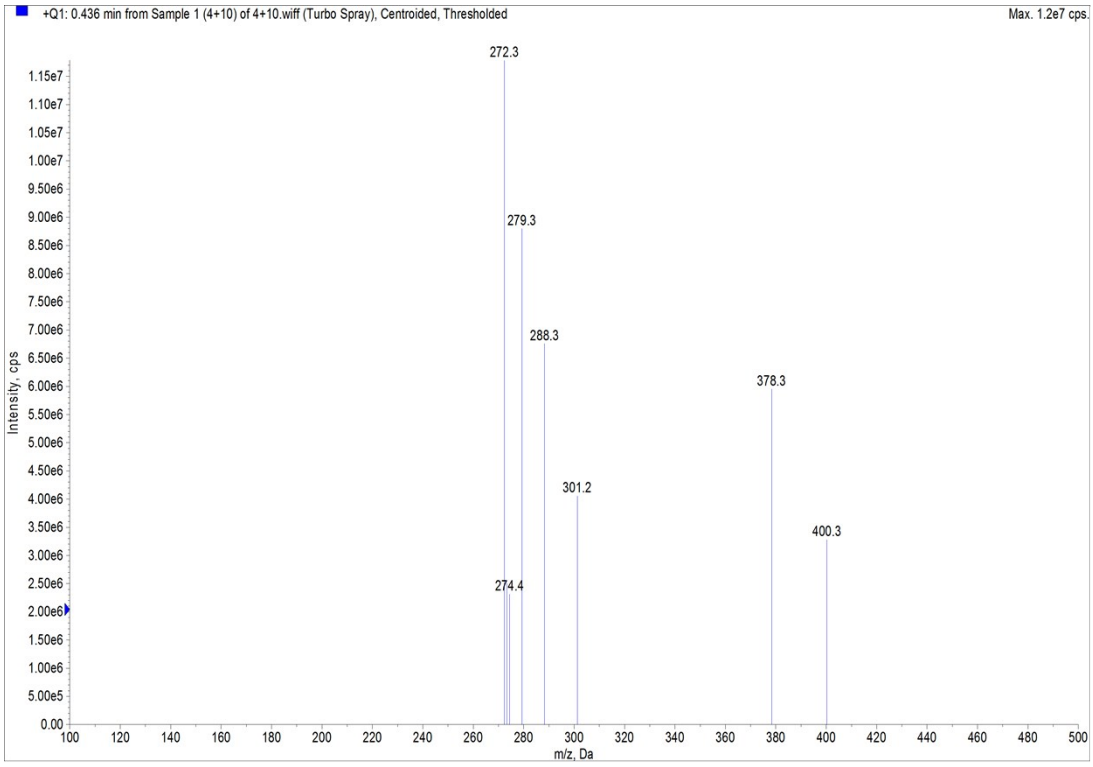
ESI-MS of compound **4b**



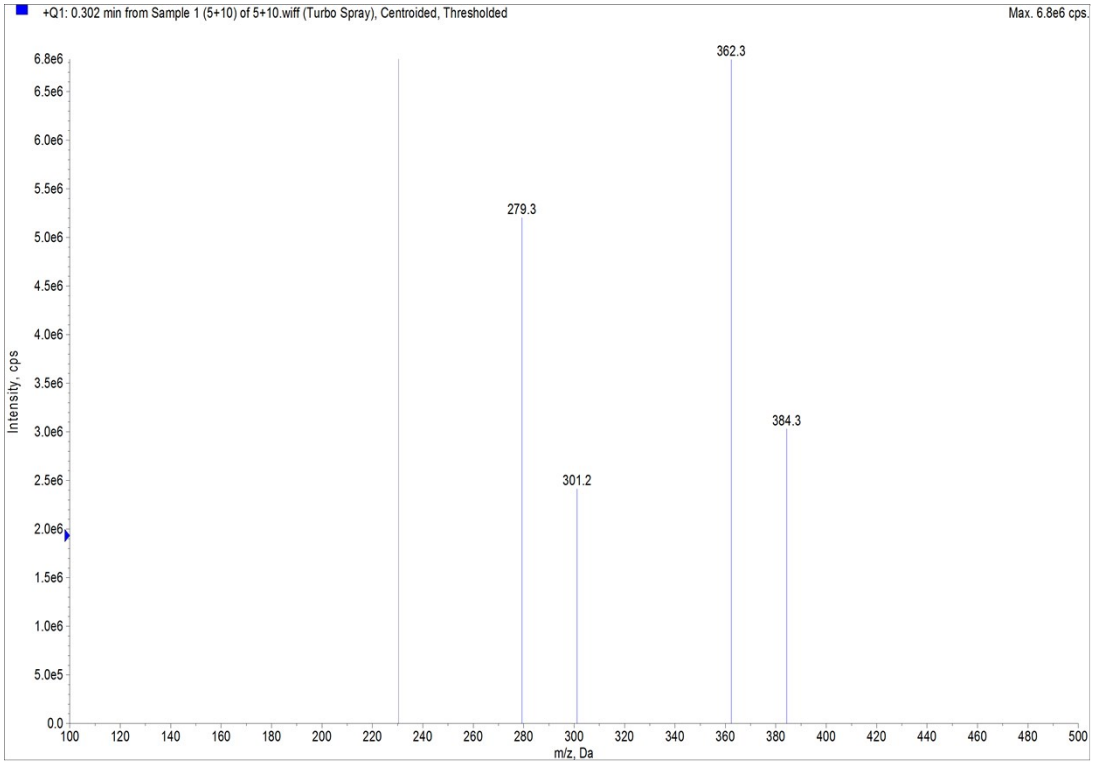
ESI-MS of compound **4c**



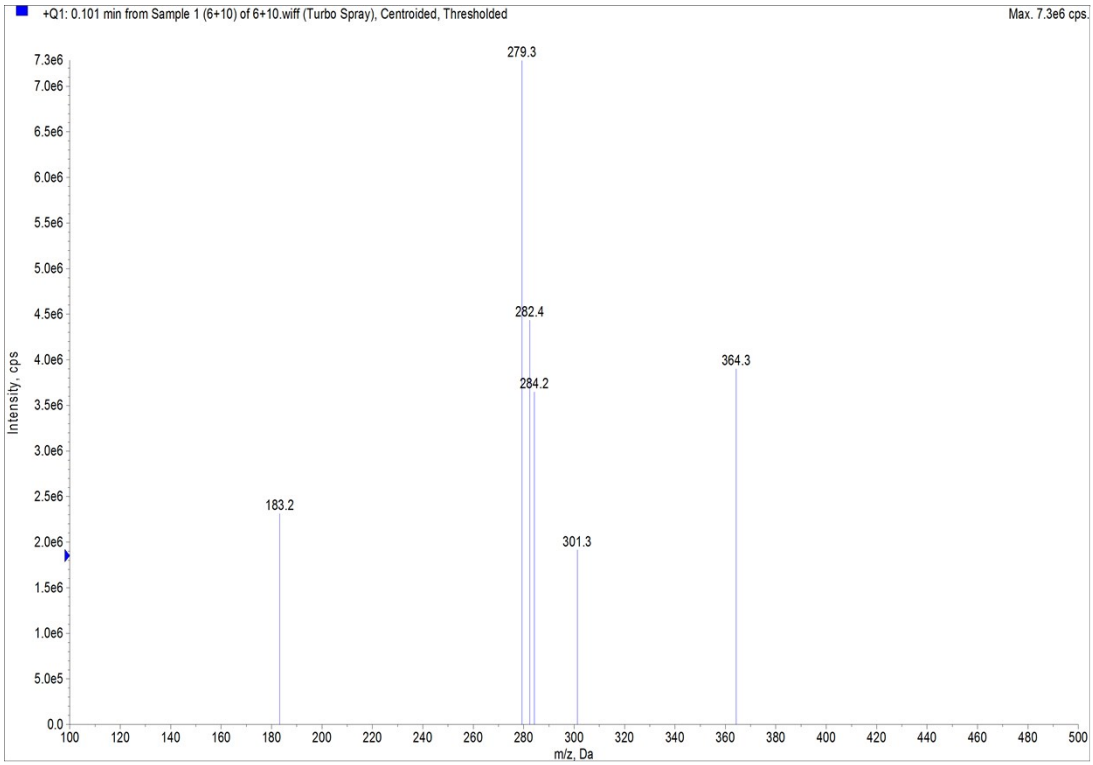
ESI-MS of compound **4d**



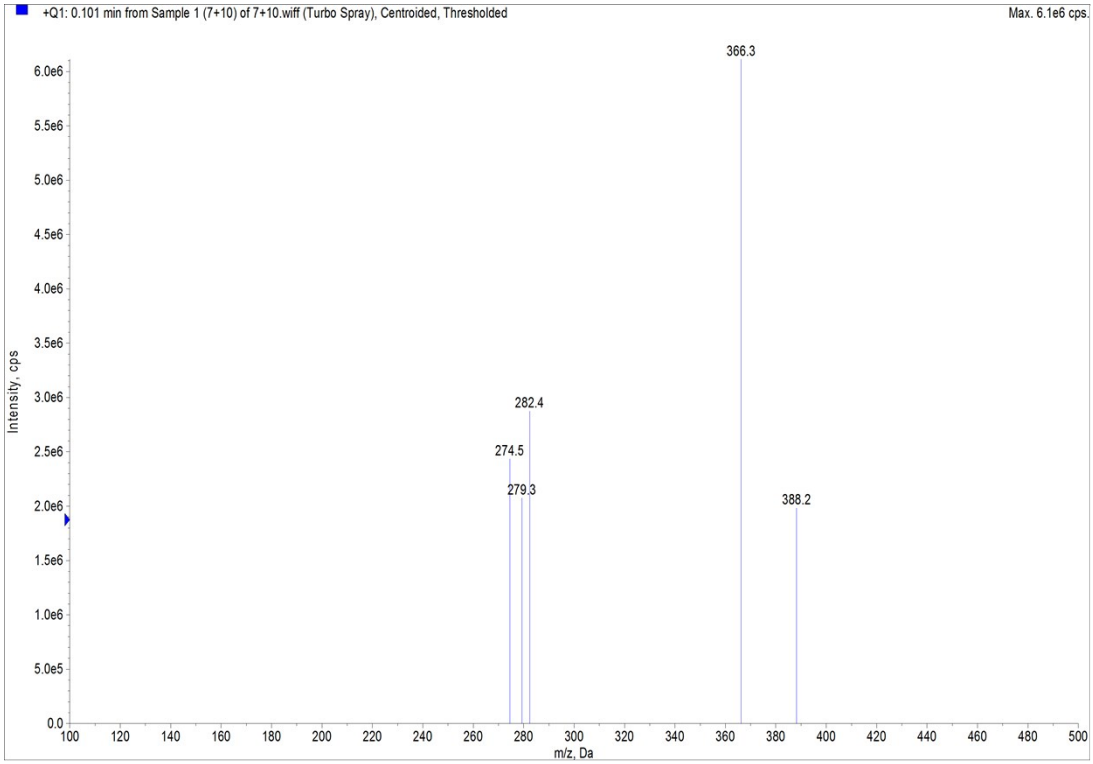
ESI-MS of compound **4e**



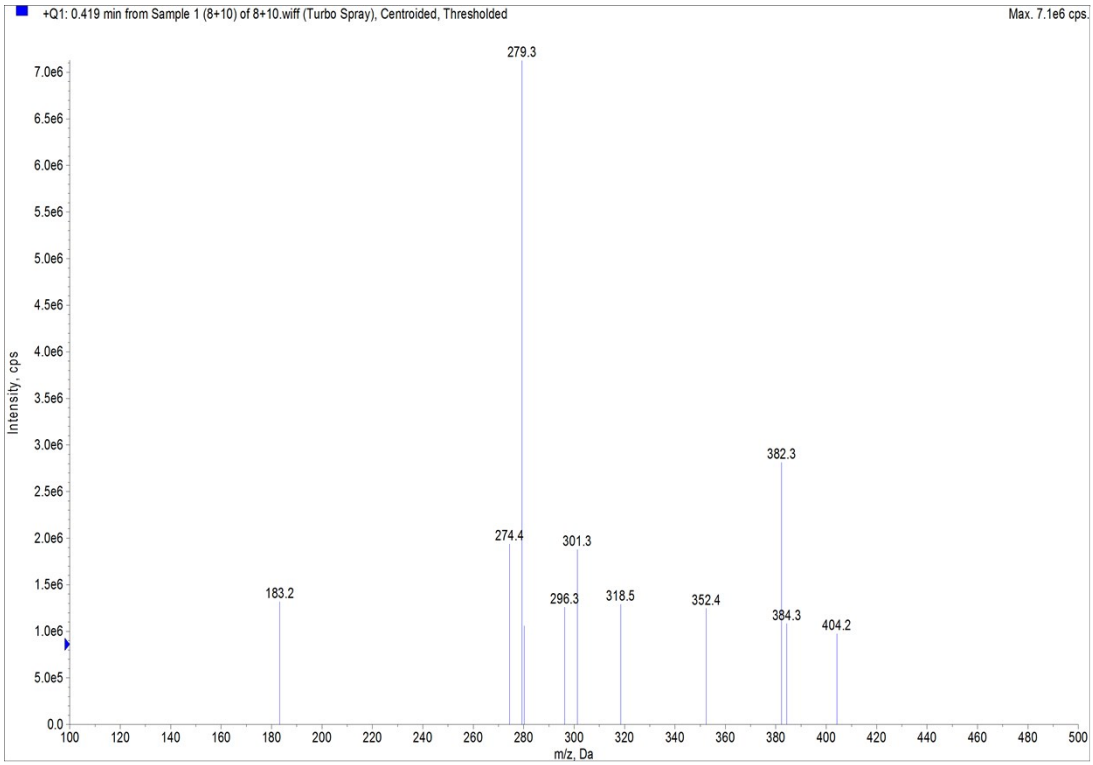
ESI-MS of compound **4f**



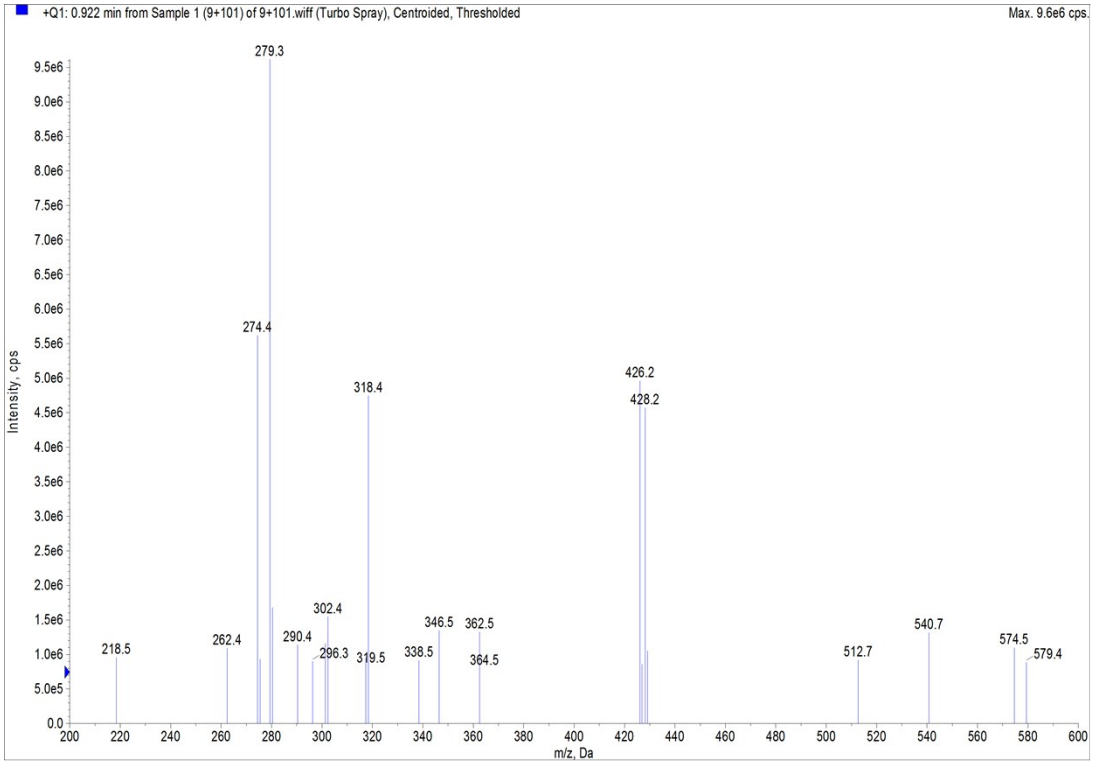
ESI-MS of compound **4g**



ESI-MS of compound **4h**



ESI-MS of compound **4i**



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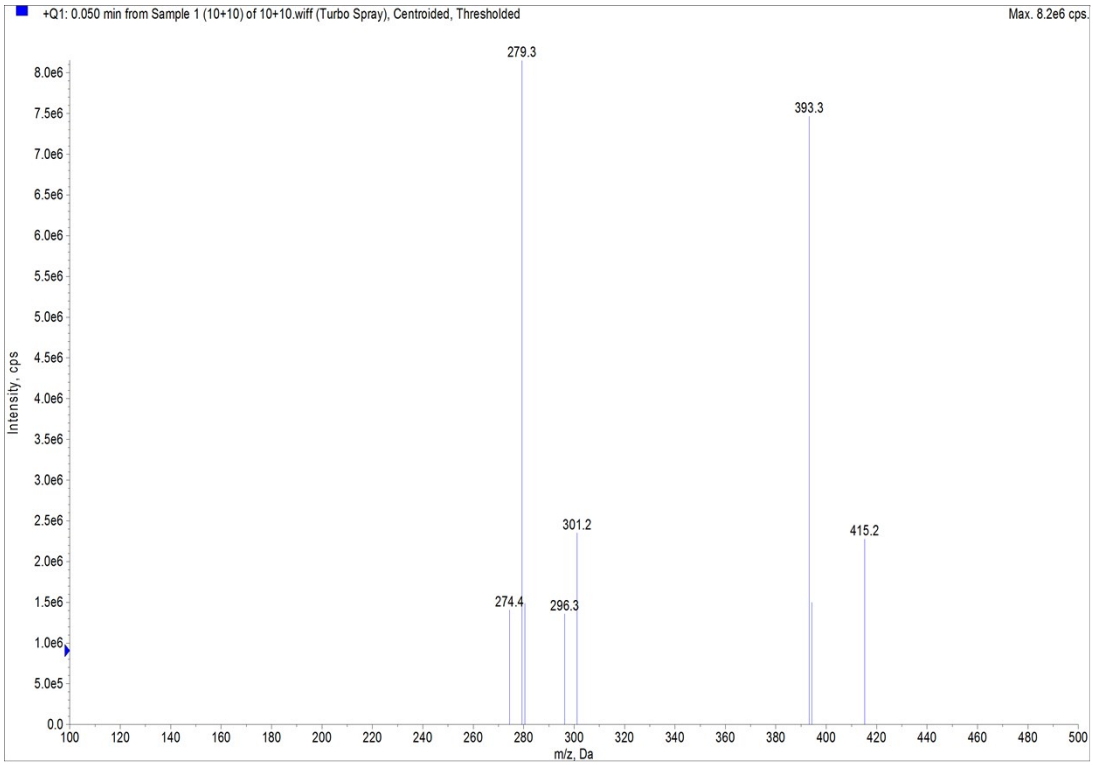
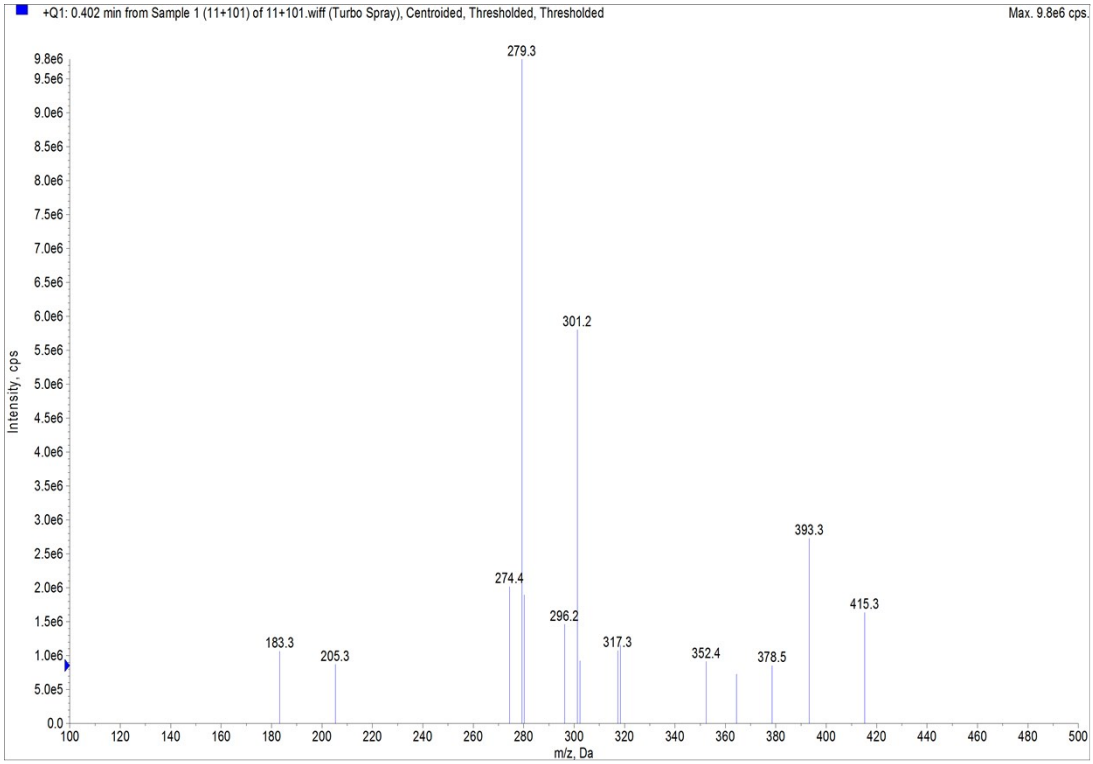
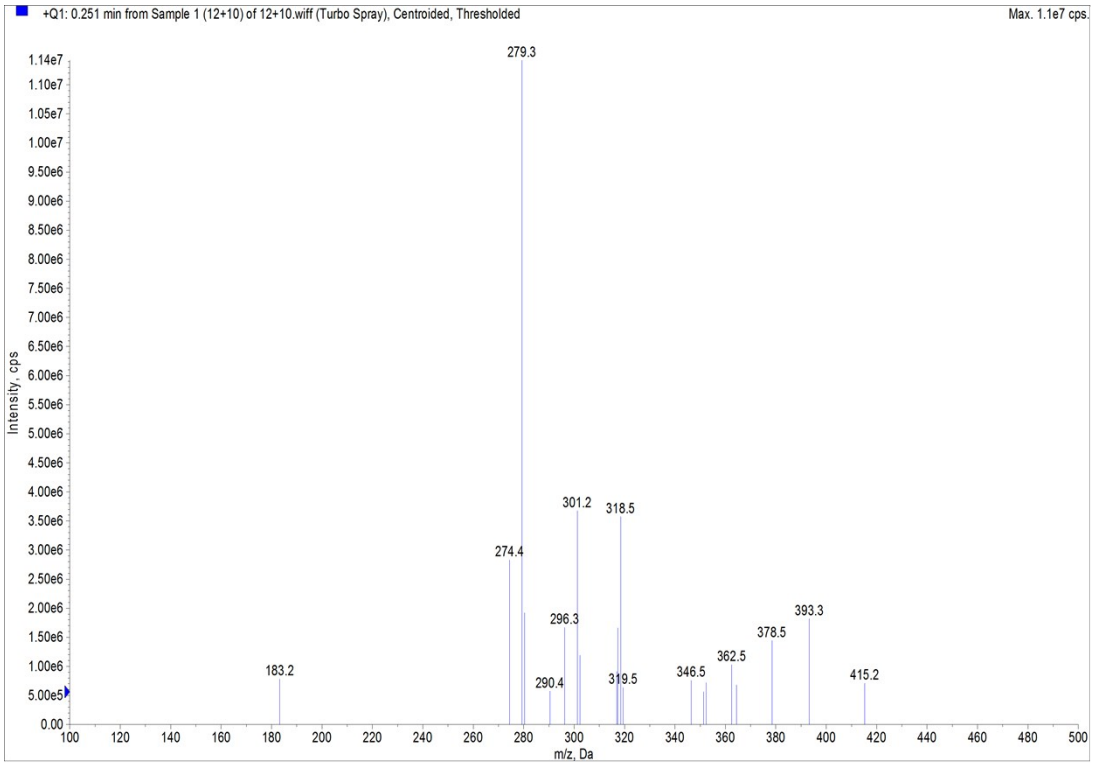


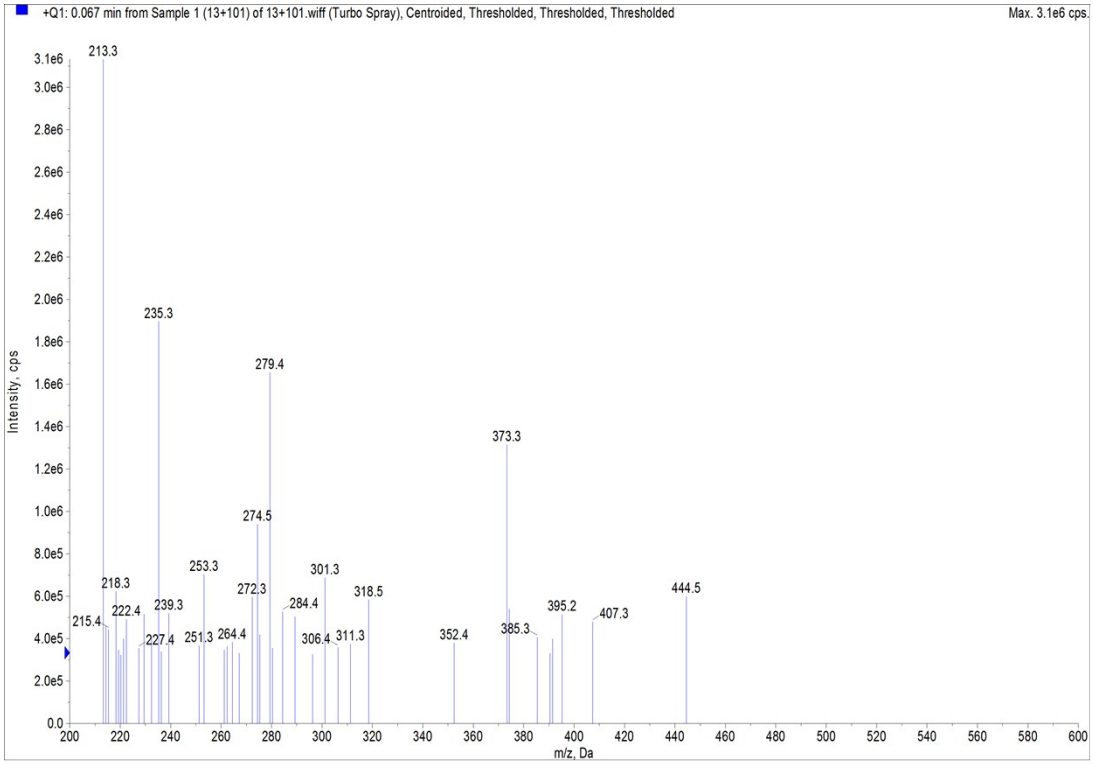
ESI-MS of compound **4k**



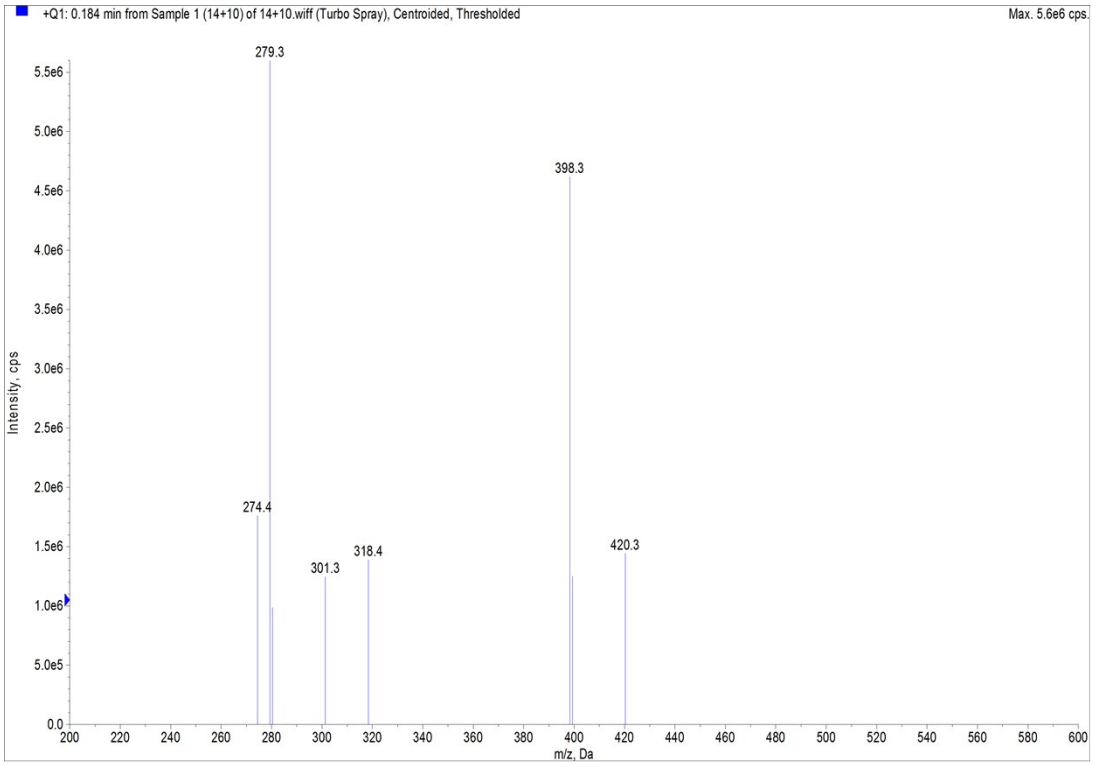
ESI-MS of compound **4l**



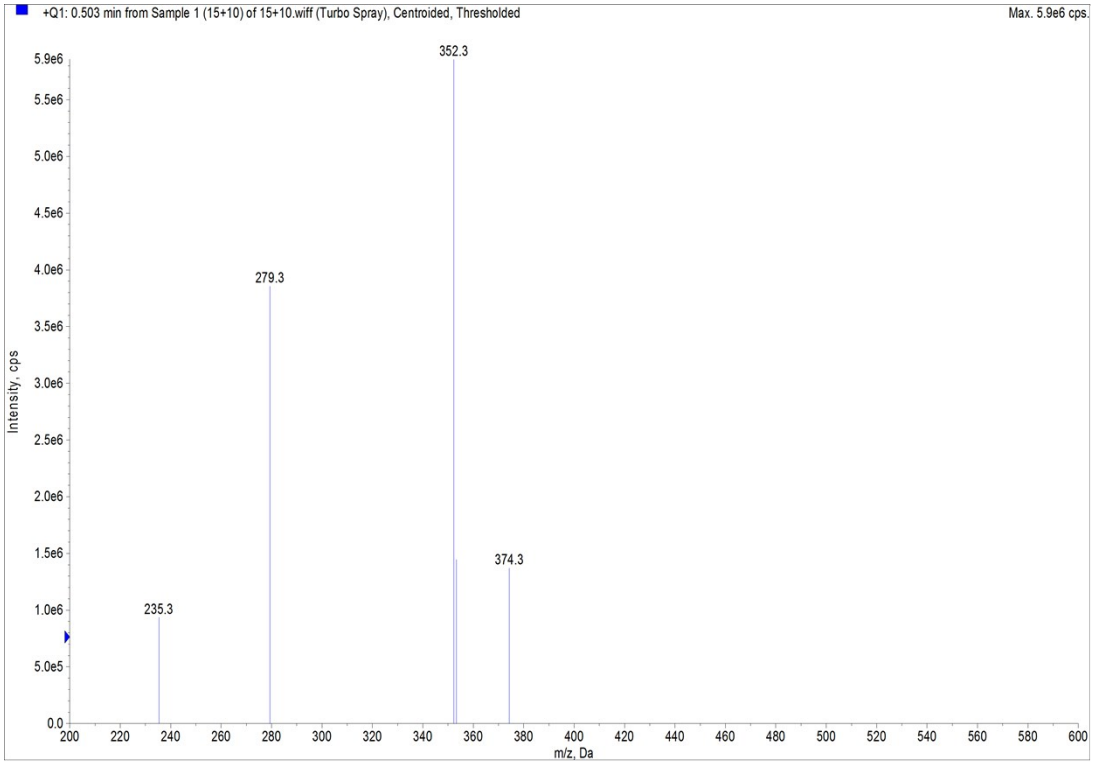
ESI-MS of compound **4m**



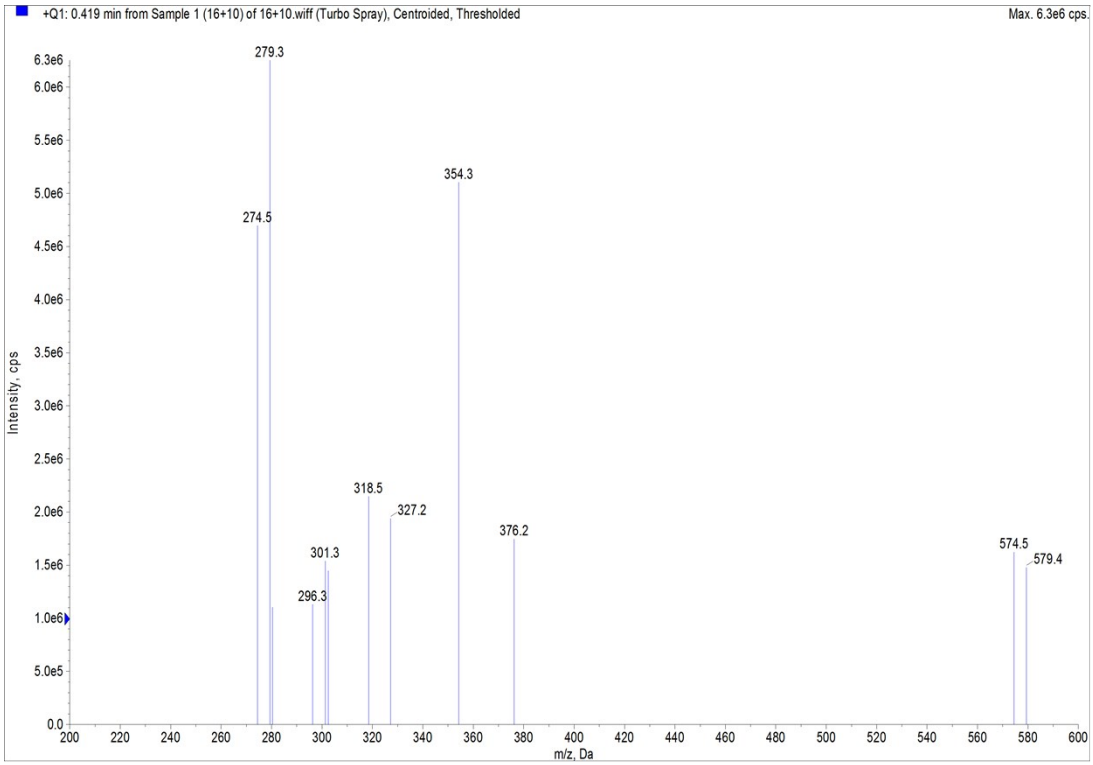
ESI-MS of compound **4n**



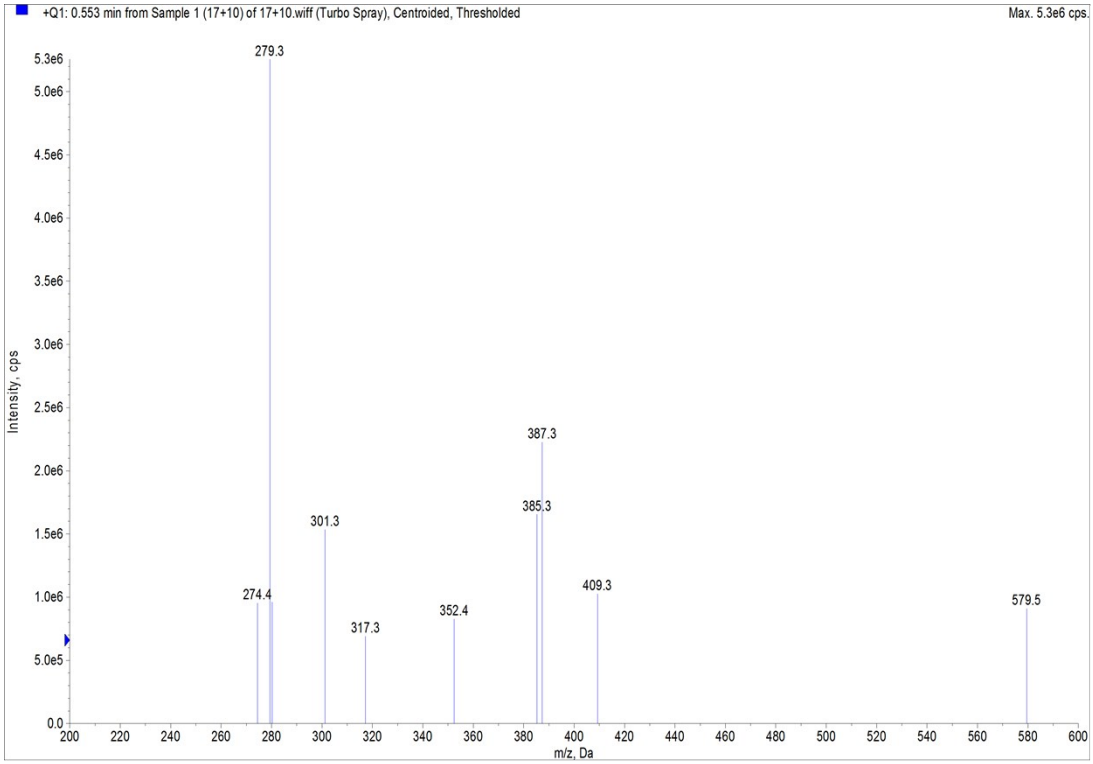
ESI-MS of compound **4o**



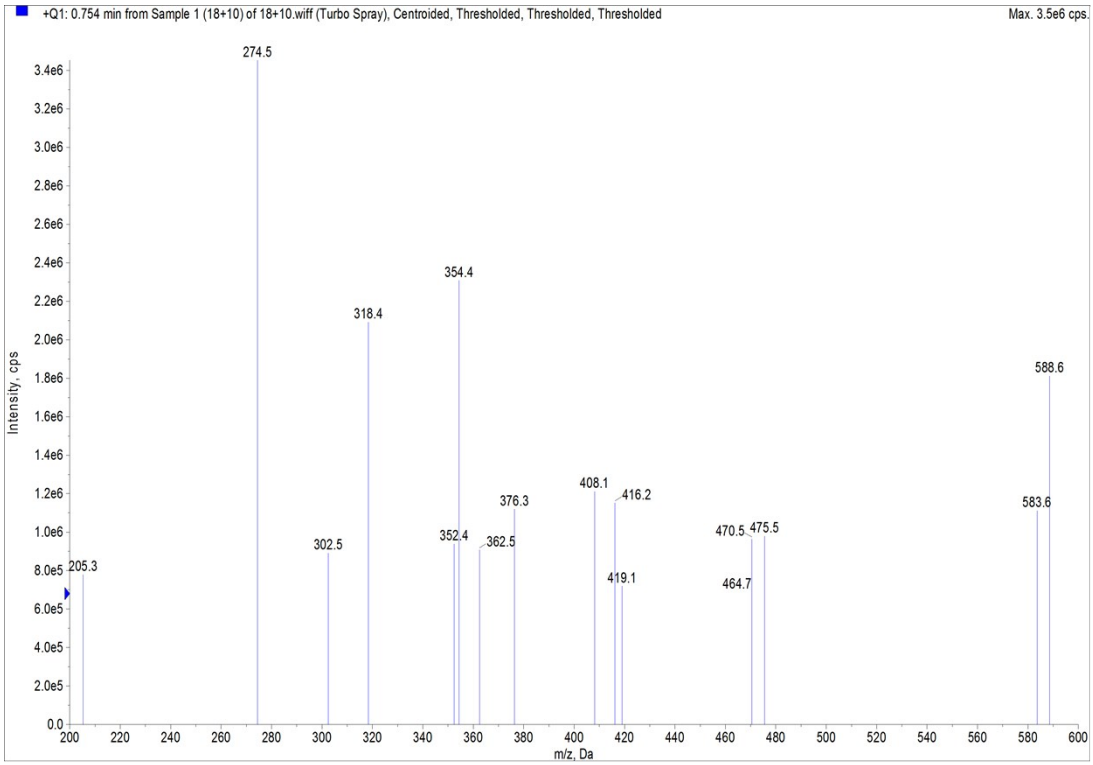
ESI-MS of compound **4p**



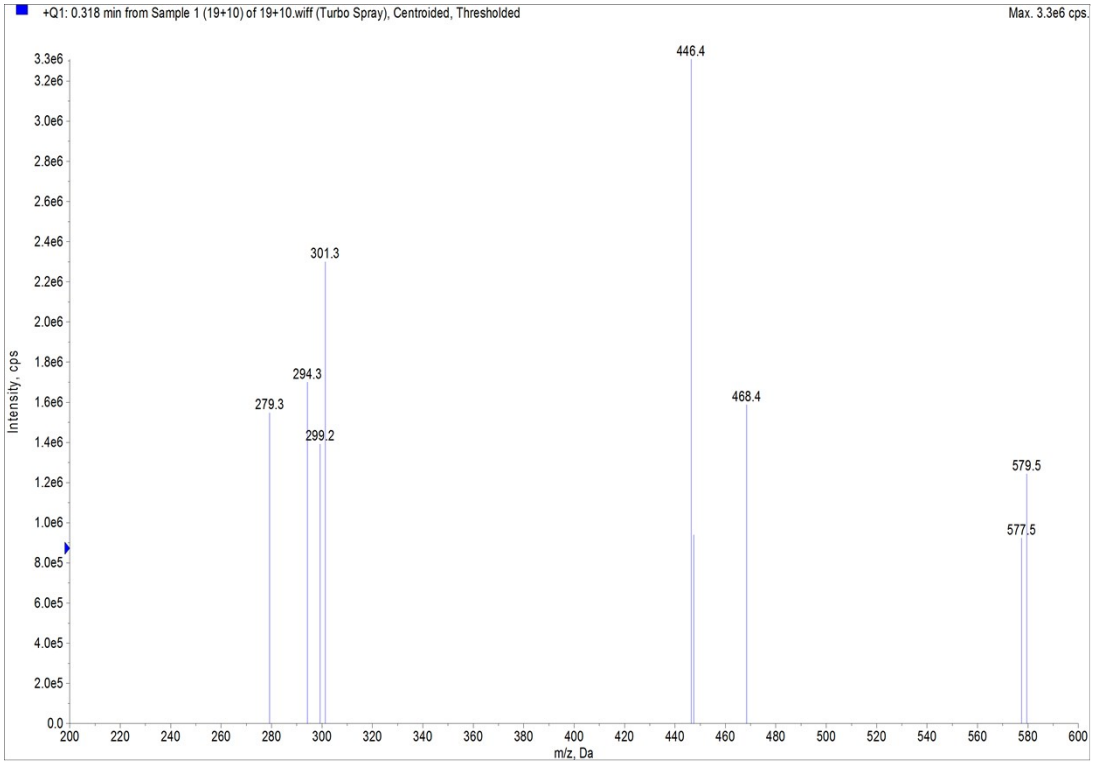
ESI-MS of compound **4q**



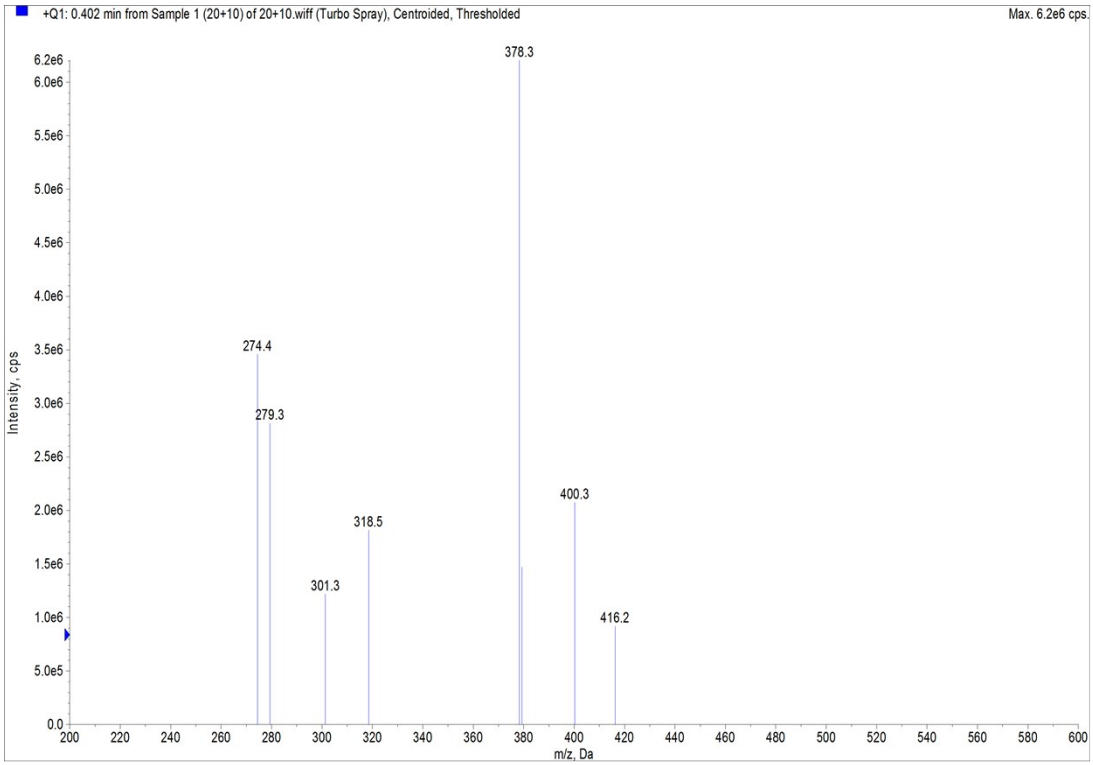
ESI-MS of compound **4r**



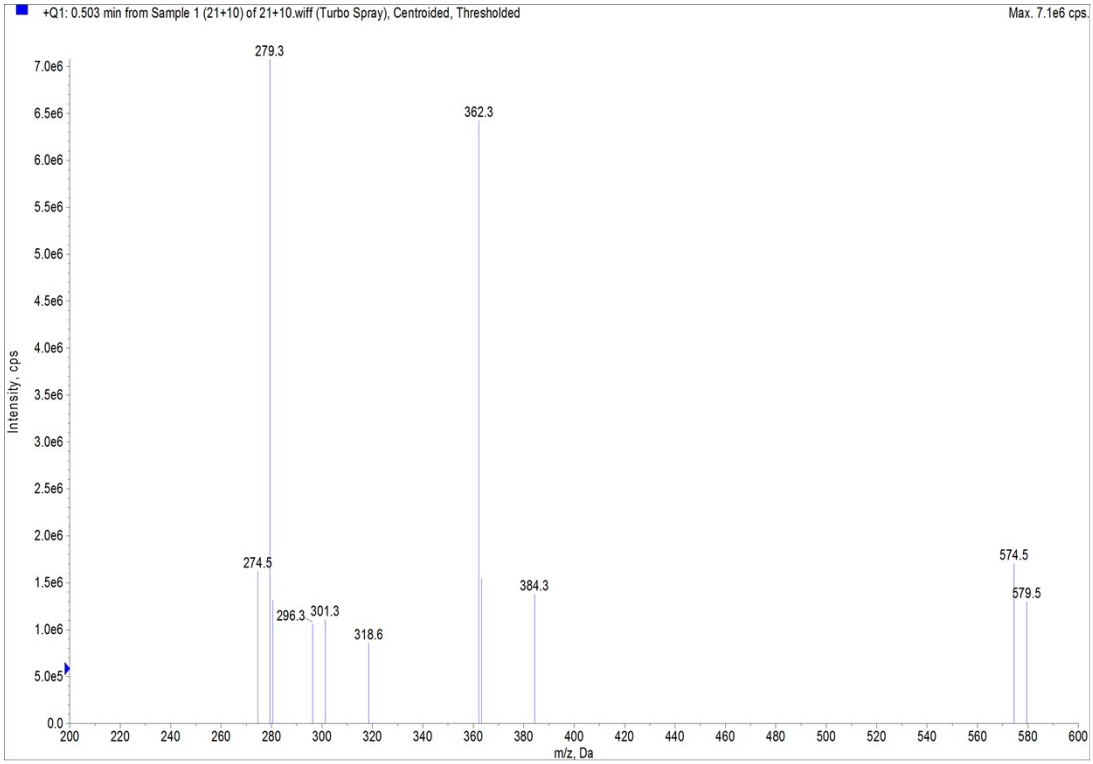
ESI-MS of compound **4s**



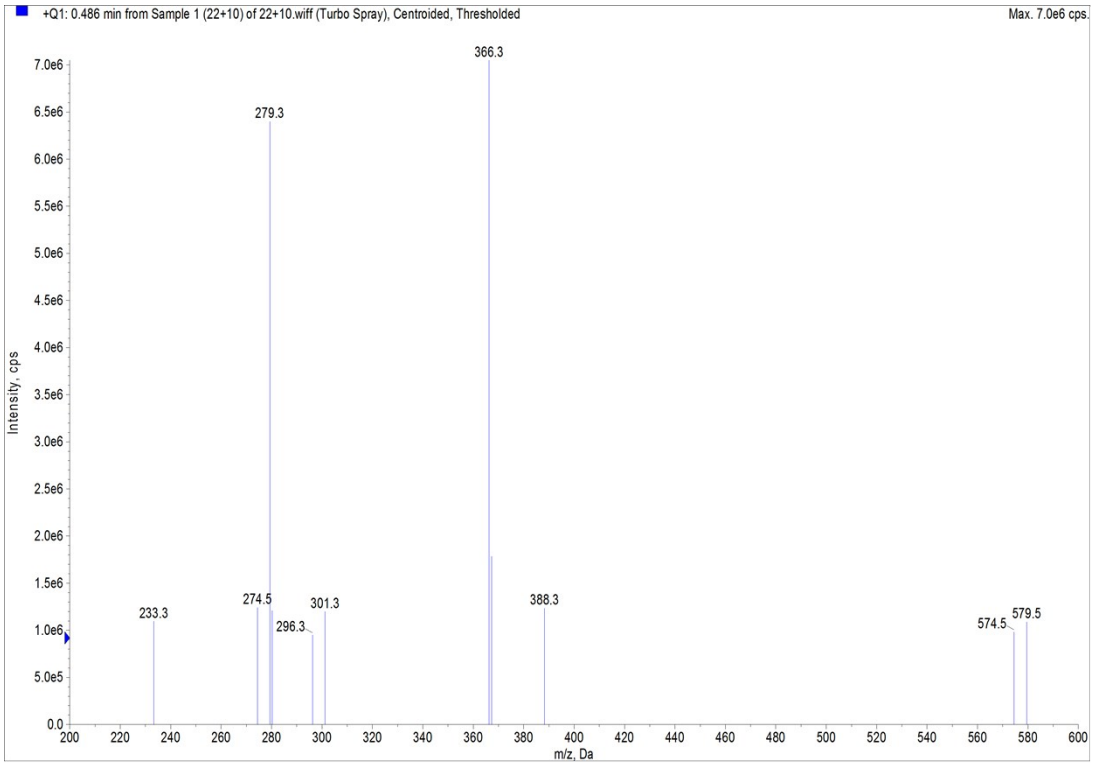
ESI-MS of compound **4t**



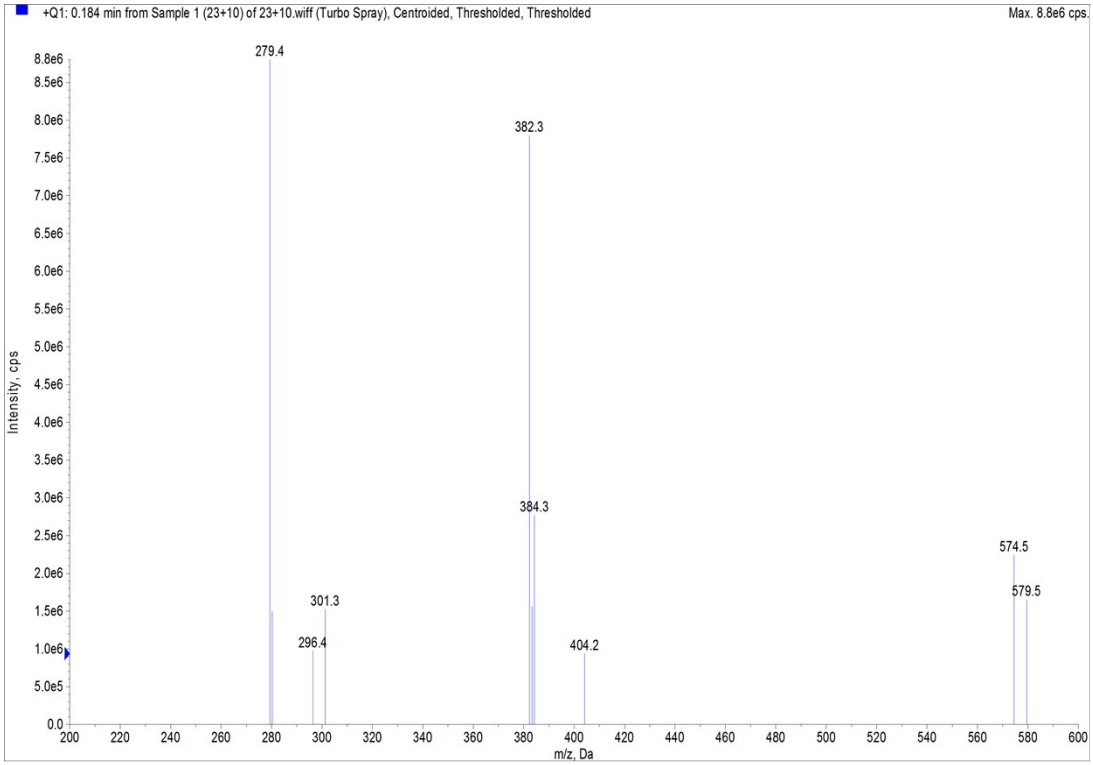
ESI-MS of compound **4u**



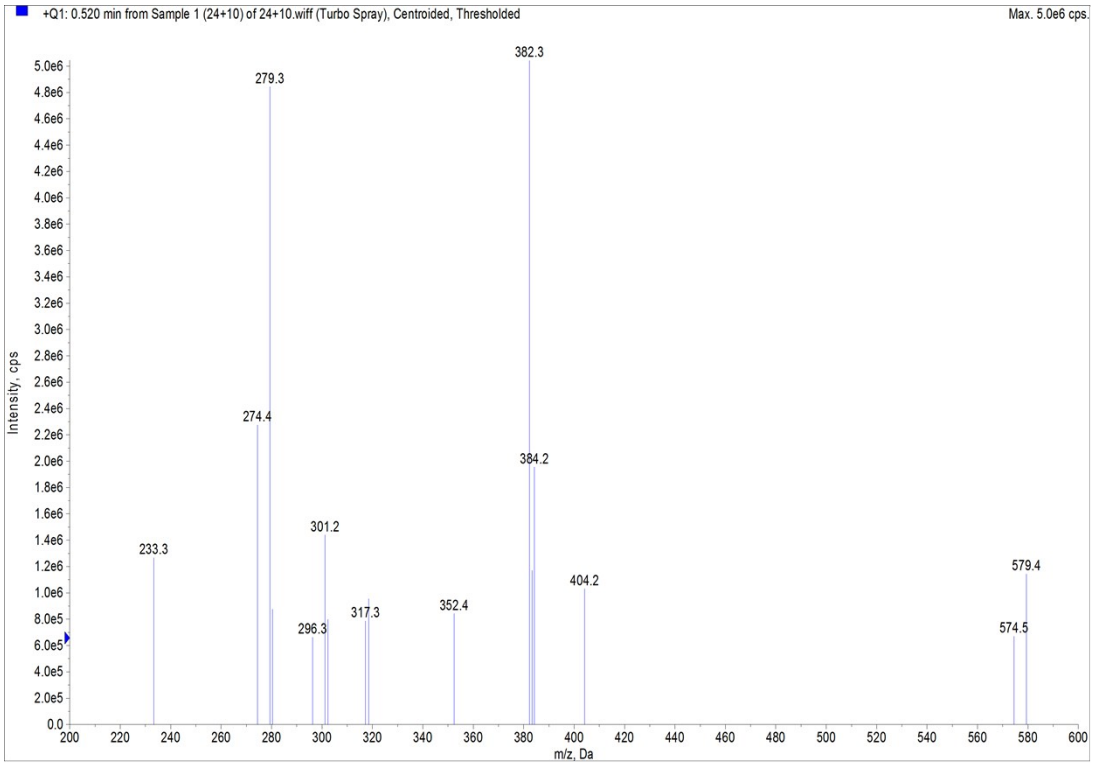
ESI-MS of compound **4v**



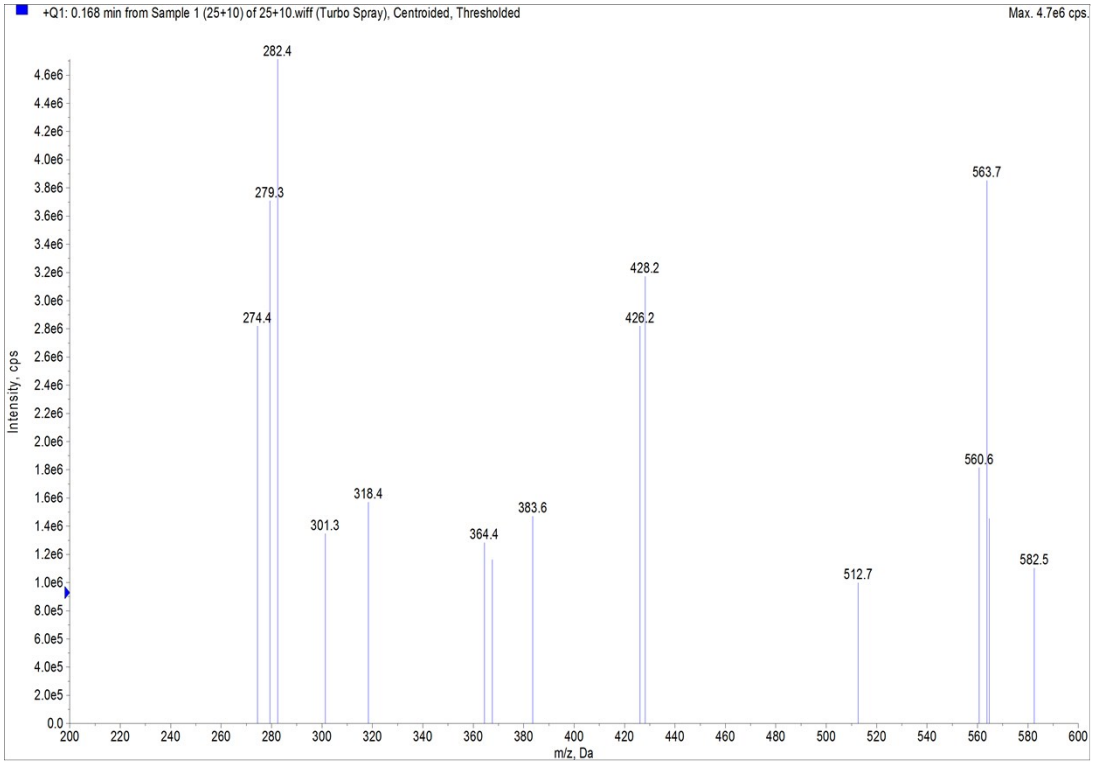
ESI-MS of compound **4w**



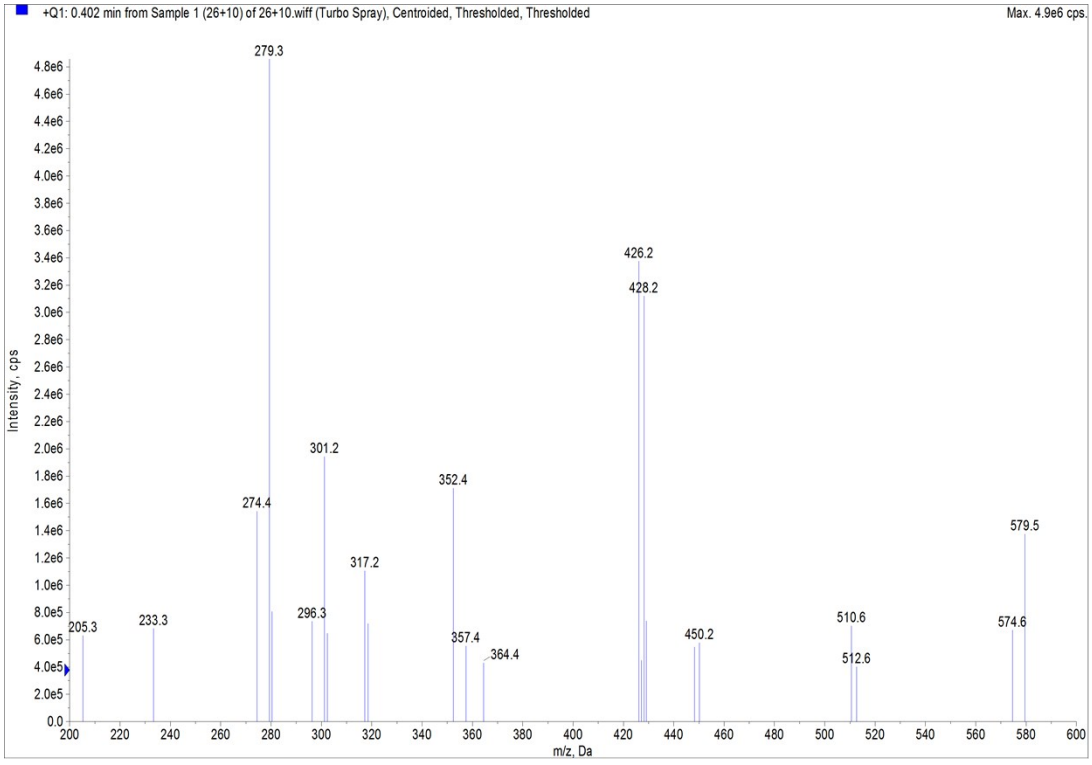
ESI-MS of compound **4x**



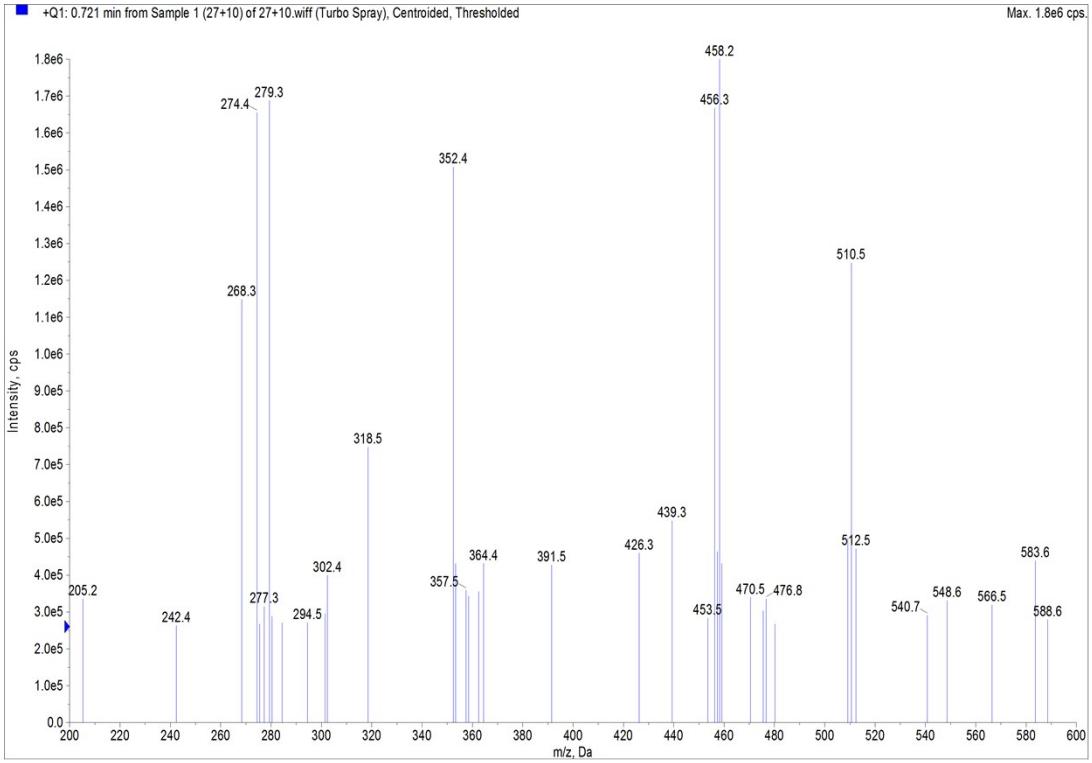
ESI-MS of compound **4y**



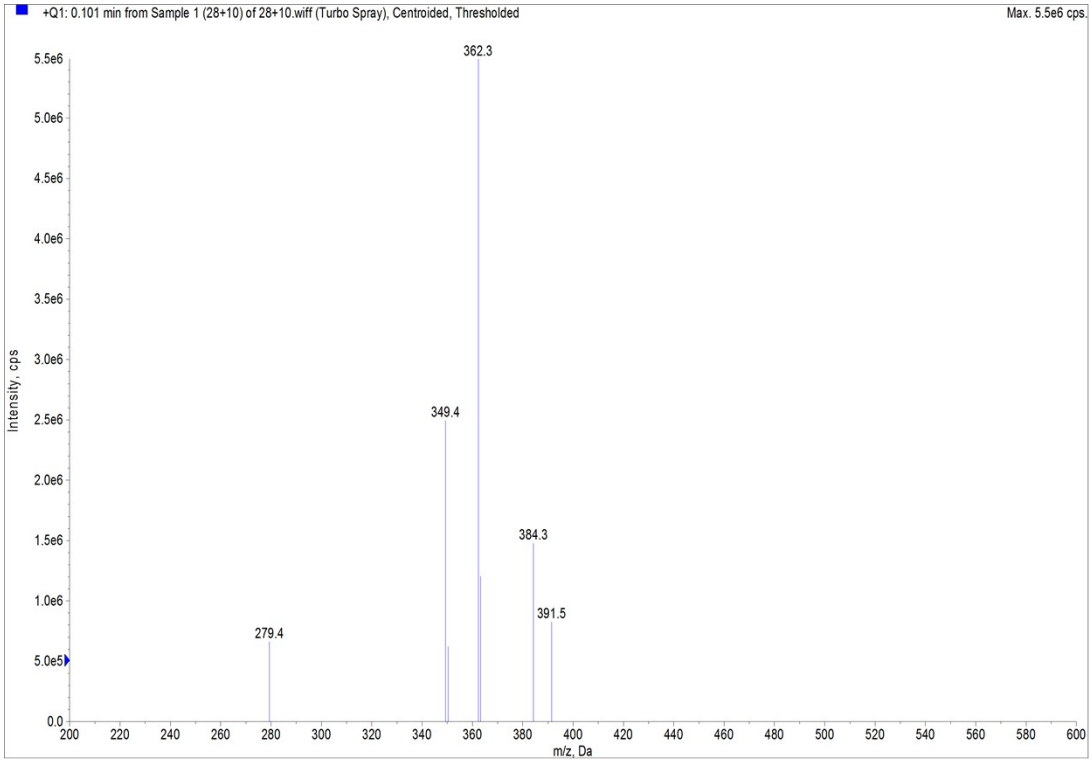
ESI-MS of compound **4z**



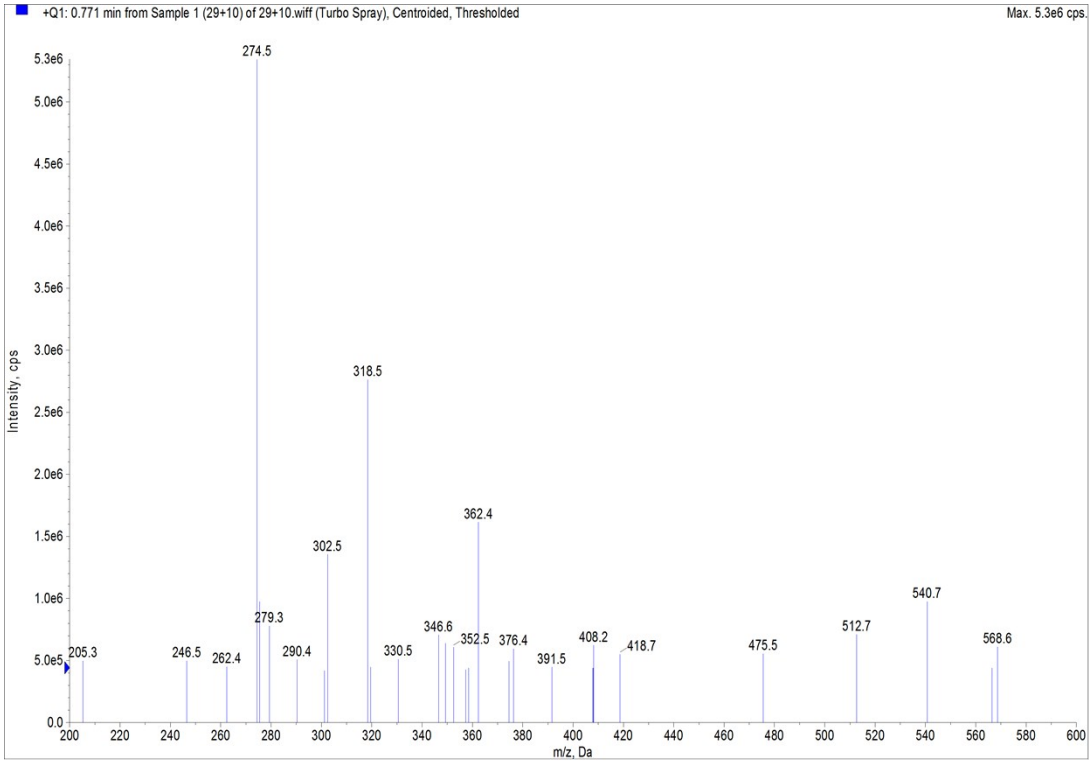
ESI-MS of compound **4aa**



ESI-MS of compound **4ab**



ESI-MS of compound **4ac**



ESI-MS of compound **5**