Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Microwave-Assisted C-3 Selective Oxidative Radical Alkylation of Flavones.

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1. Experimental

General Information

^{1}H NMR spectra were recorded on Varian Gemini-200 MHz and Eclipse 300 MHz JEOL spectrometers in deuterated chloroform (CDCl3) solutions with internal TMS standard (0 ppm). Chemical shifts were reported in parts per million (δ/ppm). Multiplicities of the signals are described using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were recorded at 50 MHz and 75 MHz on the same instruments. IR spectra were obtained using a FT-IR Tensor 27 Bruker spectrometer on KBr pellets, in chloroform solution, or in solid film. Mass spectra were recorded on a JEOL JEM-AX505HA spectrometer by electronic impact (EI) at 70 eV. High resolution mass spectra (HRMS) were obtained using the same spectrometer by FAB^{+} ionization. Flash column chromatography was carried out with silica gel 60 (230–400 mesh ASTM). Dry 1,2-dichoroethane was purchased from Aldrich. Laboratory materials (glassware, stir bars, syringes, etc) were dried left them in an oven at 120°C for 12 hours.

Typical procedure for the C-3 oxidative radical addition to flavones.

Conventional heating reaction. Flavone substrate (1 equivalent) and the corresponding xanthate (2 equivalents) were dissolved in dry 1,2-dicloroethane (0.06 M with respect of the flavone) in a round bottomed flask provided with a stir bar. The resulting solution was deaerated with a current of argon under ultrasonic agitation for 20 minutes. Then, the reaction flask was equipped with a condenser and the solution was heated to reflux (keeping an argon atmosphere). Subsequently 0.3 equivalents of DLP (dilauroyl peroxide) were added every hour until addition of 1.5 equivalents of the peroxide had been completed.

Microwave assisted reaction. Flavone substrate (1 equivalent) and the corresponding xanthate (2 equivalents) were dissolved in dry 1,2-dicloroethane (0.06 M with respect of the flavone) in a round bottomed flash provided with a stir bar. The resulting solution was deaerated with a current of argon under ultrasonic agitation for 20 minutes. Then, 0.3 equivalents of DLP were added, the reaction flask was equipped with a condenser and the mixture was irradiated with microwaves (300 w, 80 °C) for 6 minutes using a CEM Discover microwave reactor. Next, 0.3 equivalents of DLP were added every 6 minutes (maintaining microwave irradiation and argon atmosphere) until addition of 1.5 equivalents of the peroxide had been completed.

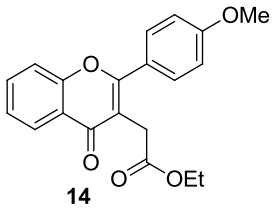
Workup. The solvent is evaporated under reduced pressure. The mixture is dissolved in cold acetonitrile at 0 °C, after DLP is precipitated the reaction mixture is filtered. This procedure is repeated 2 times. Then, solvent is evaporated under reduced pressure and mixture is added on top of a silica gel column that is eluted with hexanes/ethyl acetate. If product is solid and still contains DLP residues it is possible to recrystalize from hexanes/ethyl acetate.

Synthesis of testosterone dirived xanthate 30.

A 10 ml round-bottomed flask equipped with a magnetic stir bar was charged with 0.5 g of testosterone (1.734 mmol) and 2.5 mL of anhydrous DCM. The resulting solution was cooled to 0 °C on an ice bath and 0.24 mL of Et_3N (0.175g, 1.734 mmol) were added. Mixture was then stirred for 30 minutes. Then 0.28 ml (1.734 mmol) of chloroacetil chloride were added dropwise. Mixture was left at room temperature in agitation over night. The resulting solution was deluted in 2.5ml of DCM and was washed with HCl 0.5N and with H_2O. Organic phase was dried over Na_2SO_4, filtered and concentrated under reduced pressure, giving the acetylated compound (0.501g, 79%) as a white solid (f.p 122-123 °C). Product was carried over to the next step without further purification. Analytical sample can be obtained by flash chromatography on silica gel, using hexanes/$CHCl_3$ (30:70). Spectral Data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72 – 5.74 (m, 1H), 4.70 (dd, *J* = 9.2, 7.8 Hz, 1H), 4.06 (s, 2H), 2.48 – 2.16 (m, 5H), 2.03 (ddd, *J* = 13.4, 5.0, 3.3 Hz, 1H), 1.89-1.53 (m, 7H), 1.48-1.33 (m, 2H), 1.26-1.16 (m, 1H), 1.19 (s, 3H), 1.13 –0.91 (m, 3H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.45, 170.80, 167.41, 124.13, 84.45, 53.76, 50.28, 42.85, 41.17, 38.71, 36.66, 35.83, 35.50, 34.03, 32.80, 31.57, 27.44, 23.55, 20.62, 17.52, 12.08. IR ν/cm^{-1}: 2974, 2945, 2916, 2853, 1731, 1668, 1612, 1448, 1389, 1333, 1282, 1261, 1226, 1161, 1042, 1017, 867, 782.

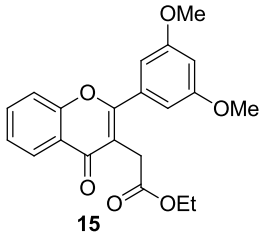
A 50 mL round bottomed flask, equipped with a magnetic stir bar was charged with the product obtained from the previous reaction in 10 ml of DMF. Stirring was begun and then potassium ethyl xanthogenate (0.834 g, 5.2 mmol, 3.0 eq) was added in one portion. After 10 min, the reaction mixture was quenched with water (30 mL) and transferred to a 250 mL separatory funnel. Then, the mixture was extracted with EtOAc (4x40 mL). The combined organic phase was washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel, using hexanes/EtOAc (90:10), giving the title compund as a colorless liquid (0.607 g, 78% yield, 2 steps). FTIR (cm^{-1}) 2938, 2852, 1735, 1673, 1616, 1294, 1269, 1228, 1158, 1113, 1051, 1008. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (bs, 1H), 4.65 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 2.48 – 2.13 (m, 5H), 2.02 (ddd, *J* = 13.4, 5.0, 3.3 Hz, 1H), 1.89 – 1.52 (m, 7H), 1.46-1.31 (m, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.23-1.14 (m, 1H), 1.19 (s, 3H), 1.11 – 0.88 (m, 3H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.94, 199.51, 170.92, 167.90, 124.12, 84.15, 70.71, 53.81, 50.30, 42.86, 38.74, 38.21, 36.70, 35.85, 35.53, 34.06, 32.84, 31.61, 27.43, 23.61, 20.67, 17.54, 13.87, 12.15.

Compounds 14-31



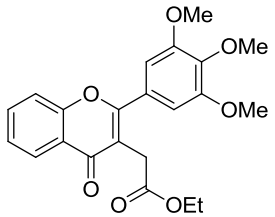
14

Ethyl 2-(2-(4-methoxyphenyl)-4-oxo-4*H*-chromen-3-yl)acetate (14). ^{1}H NMR ($CDCl_3$, 200 MHz) δ/ppm: 1.28 (t, 3H, J= 7.2), 3.58 (s, 2H), 3.86 (s, 3H), 4.21 (q, 2H, J= 7.2), 7.02 (d, 2H, J=9.0), 7.43 (m, 2H, J= 7.4), 7.65 (m, 3H), 8.23 (m, 3H, J= 1.6, 7.8). ^{13}C NMR ($CDCl_3$, 50 MHz) δ/ppm: 14.2, 32.3, 55.4, 61.0, 114.1, 115.4, 117.9, 122.6, 124.9, 125.1, 125.9, 130.3, 133.6, 156.2, 161.4, 163.3, 171.5, 177.9. IR (KBr), ν/cm^{-1}: 3075, 2978, 2934, 2838, 1719, 1624. MS (EI) m/z= M^{+}: 338 (33%), 292 (100%). HRMS-FAB^{+} m/z: observed: 339.1237, calcd. for $C_{20}H_{19}O_5$: 339.1232.



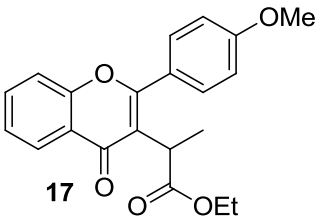
15

Ethyl 2-(2-(3,5-dymethoxyphenyl)-4-oxo-4*H*-chromen-3-yl)acetate (15). ^{1}H NMR ($CDCl_3$, 200 MHz) δ/ppm: 1.23 (t, 3H, J= 7.2), 3.40 (s, 2H), 3.79 (s, 3H), 3.88 (s, 3H), 4.12 (q, 2H, J= 7.2), 6.58 (m, 2H), 7.41 (m, 2H), 7.65 (m, 1H, J= 1.6, 7.7), 8.25 (m, 1H, J= 1.6, 7.8). ^{13}C NMR ($CDCl_3$, 50 MHz) δ/ppm: 14.2, 32.0, 55.5, 60.7, 98.7, 104.8, 114.5, 117.7, 118.0, 122.9, 124.7, 125.9, 131.5, 133.4, 156.6, 158.2, 161.3, 162.9, 171.1, 177.8. IR (KBr), ν/cm^{-1}: 3079, 2924, 2851, 1742, 1707, 1637, 1606. MS (EI) m/z= M^{+}: 368 (100%). HRMS-FAB^{+} m/z: observed: 369.1338, calcd. for $C_{21}H_{21}O_6$: 369.1338.



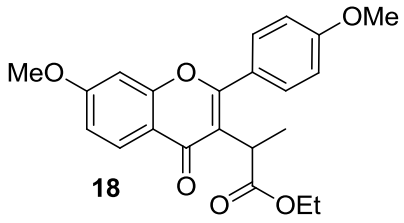
16

Ethyl 2-(2-(3,4,5-trimethoxyphenil)-4-oxo-4*H*-chromen-3-yl)acetate (16). ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 1.26 (t, 3H, J= 7.2), 3.59 (s, 2H), 3.90 (s, 6H), 3.93 (s, 3H), 4.20 (q, 2H, J= 7.2), 6.93 (s, 2H), 7.45 (m, 2H), 7.69 (m, 1H, J= 1.8, 7.7), 8.24 (m, 1H, J= 1.5, 7.8). ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm: 14.2, 32.4, 56.2, 60.1, 61.0, 106.1, 115.7, 117.9, 122.6, 125.1, 125.1, 125.9, 127.9, 133.7, 139.9, 153.3, 156.1, 163.3, 171.6, 177.8. MS (EI) m/z= M^+: 398 (14%), 206 (100%). HRMS-FAB$^+$ m/z: observed: 399.1448, calcd. for $C_{22}H_{23}O_7$: 399.1444.



17

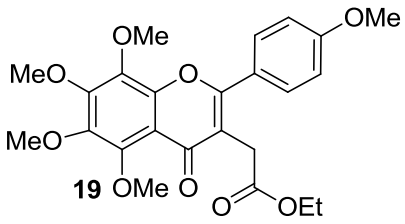
Ethyl 2-(2-(4-methoxyphenyl)-4-oxo-4H-chromen-3-yl)propanoate (17): 1H NMR (300 MHz, *CDCl$_3$*) δ/ppm: 8.25-8.21 (m, 1H), 7.70-7.59 (m, 1H), 7.49-7.45 (m, 1H), 7.43-7.37 (m, 1H), 7.05-7.03 (m, 1H), 7.02-6.99 (m, 1H), 4.20 (q, *J* = 7.1 Hz, 1H), 3.89 (s, 1H), 3.58 (s, 1H), 1.28 (t, *J* = 7.1 Hz, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 177.96, 171.49, 163.24, 161.42, 156.21, 133.58, 130.31, 125.93, 125.13, 124.91, 122.66, 117.90, 115.49, 114.09, 77.42, 77.00, 76.58, 60.99, 55.44, 32.36, 29.68, 14.19. IR (film *CHCl$_3$*) cm^{-1} ν: 2959, 2927, 2853, 1733, 1639, 1608, 1511, 1467, 1388, 1256, 1177, 1031, 762 MS (EI) m/z= M^+: 292 (100%).



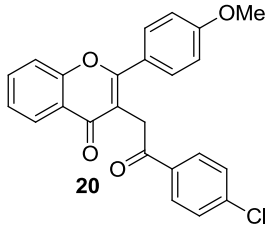
18

Ethyl 2-(7-methoxy-2-(4-methoxyphenyl)-4-oxo-4H-chromen-3-yl)propanoate (18). ^{1}H NMR (300 MHz, CDCl3) δ/ppm: 8.12 (d, J = 8.9 Hz, 1H), 7.61 (d, J = 2.1 Hz, 1H), 7.59 (d, J = 2.1 Hz, 1H), 7.05 (d, J = 2.1 Hz, 1H), 7.03 (d, J = 2.1 Hz, 1H), 6.85 (d, J = 2.3 Hz, 1H), 4.16 (dd, J = 7.1, 2.31 Hz, 1H), 3.90 (s, 1H), 3.63 (q, J = 7.0 Hz, 1H), 2.36 (t, J = 7.5 Hz, 1H), 1.48 (d, J = 7.0 Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$) δ/ppm: 179, 176, 173, 164, 161, 157, 130, 127, 125, 122, 117, 114, 99, 60, 55, 38, 33, 31, 24, 22, 15, 14. IR (film CHCl3) cm-1 ν: 2918, 2851, 1734, 1701, 1612 1504, 1441, 1385, 1301, 1252, 1171, 1030, 952, 838,

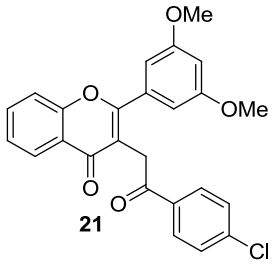
755. MS (EI) m/z= M^+: 383 (5%), 57 (100%). HRMS Calcd for C22H22O6 382.14, FAB+ Found m/z 383. 1503



Ethyl 2-(5,6,7,8-tetramethoxy-2-(4-methoxyphenyl)-4-oxo-4H-chromen-3-yl)acetate (19): ^{1}H NMR (300 MHz, *$CDCl_3$)* δ/ppm 7.62 (d, *J* = 8.9 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.08 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.53 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, *$CDCl_3$)* δ/ppm 176.62, 171.58, 161.36, 161.21, 151.33, 148.25, 147.77, 143.93, 137.73, 130.25, 130.25, 125.01, 115.58, 114.12, 114.12, 113.66, 62.17, 61.91, 61.81, 61.65, 60.97, 55.43, 32.28, 14.19. IR (*film $CHCl_3$)* cm^{-1} ν: 2937, 1728, 1636, 1378, 1257, 1174, 1061, 987.76. MS (EI) m/z= M^+: 459 (60%), 397 (100%). HRMS calc. for $C_{24}H_{26}O_9$ 458.15, FAB+ Found m/z 459.1655



3-(2-(4-chlorophenyl)-2-oxoethyl)-2-(4-methoxyphenyl)-4*H*-chromen-4-one (20). ^{1}H NMR ($CDCl_3$, 200MHz) δ/ppm: 3.85 (s, 3H), 4.19 (s, 2H), 6.78 (m, 2H, J= 2.2, 9.0), 7.52 (m, 7H), 8.00 (m, 2H, J=2.4, 8.8), 8.20 (m, 1H, J= 0.4, 1.8, 8.0). ^{13}C NMR ($CDCl_3$, 50MHz) δ/ppm: 36.5, 55.4, 114.1, 116.2, 118.0, 122.5, 125.0, 125.2, 125.9, 128.9, 129.8, 130.2, 133.7, 135.3, 139.6, 156.3, 161.4, 163.5, 177.9, 196.5. IR (KBr), ν/cm^{-1}: 2957.6, 2922.7, 2852.6, 1702.1, 1629.5, 1610.2. MS (EI) m/z= M^+: 404 (19%), 265 (100%). HRMS-FAB^+ m/z: observed: 405.0899, calcd. for $C_{24}H_{18}ClO_4$: 405.0894.



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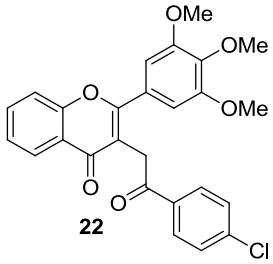
3-(2-(4-chlorophenyl)-2-oxoethyl)-2-(3,5-dimethoxyphenyl)-4*H*-chromen-4-one (21). ^{1}H NMR ($CDCl_3$, 200 MHz) δ/ppm: 3.72 (s, 3H), 3.85 (s, 3H), 4.01 (s, 2H), 6.52 (m, 1H, J= 2.4, 5.4), 6.57 (m, 1H, J= 2.4), 7.40 (m, 5H), 7.66 (m, 1H, J= 1.6, 7.8), 7.90 (m, 2H, J=2.4, 8.6), 8.23 (m, 1H, J= 1.4, 8.0). ^{13}C NMR ($CDCl_3$, 50 MHz) δ/ppm: 36.3, 55.6, 98.8, 104.8, 114.6, 118.01, 118.4, 122.8, 124.8, 125.9, 128.7, 129.6, 131.5, 133.4, 135.4, 139.2, 156.7, 158.2, 161.5, 162.9, 177.7, 195.6. IR (film), ν/cm^{-1}: 2960.8, 2926.6, 2852.3, 1691.1, 1632.9, 1612.1, 1588.0, 1577.0. MS (EI). m/z= M^{+}: 434 (36%), 295 (100%).



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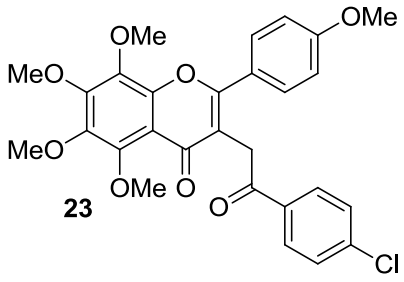
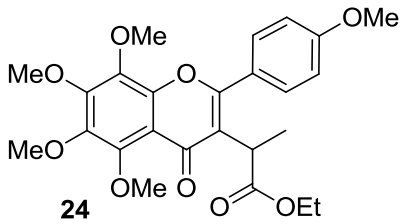
3-(2-(4-chlorophenyl)-2-oxoethyl)-2-(3,4,5-trimethoxyphenyl)-4*H*-chromen-4-one (22). ^{1}H NMR ($CDCl_3$, 200 MHz)δ/ppm: 3.80 (s, 6H), 3.90 (s, 3H), 4.20 (s, 2H), 6.89 (s, 2H), 7.47 (m, 4H),7.7 (m, 1H, J=1.8, 7.8),8.01 (m, 2H, J= 2.4, 9.0),8.22 (m, 1H, J= 0.4, 1.4 8.0). RMN^{13}C ($CDCl_3$, 50 MHz) δ/ppm: 36.7, 56.2, 61.0, 105.8, 116.5, 118.0, 122.5, 125.1, 125.9, 127.9, 129.0, 129.7, 133.8, 135.2, 139.8, 146.5, 154.3, 156.2, 177.8, 196.7. IR (KBr) ν/cm^{-1}: 3074.3, 2921.6, 2846.8, 1696.6, 1671.2, 1633.8, 1585.6. MS (EI). m/z= M^{+}: 464 (48%), 325 (100%). HRMS-FAB^{+} m/z: observed: 465.1113, calcd. for $C_{26}H_{22}ClO_6$: 465.1105.



23

3-(2-(4-chlorophenyl)-2-oxoethyl)-5,6,7,8-tetramethoxy-2-(4-methoxyphenyl)-4H-chromen-4-one (23): ^{1}H NMR (300 MHz, *$CDCl_3$)* δ/ppm: 8.00 (d, *J* = 8.79 Hz, 2H), 7.59 (d, *J* = 8.96 Hz, 2H), 7.44 (d, *J* = 8.79 Hz, 2H), 6.97 (d, *J* = 8.94 Hz, 2H), 4.14 (s, 2H),

4.09 (s, 3H), 3.94 (s, 3H), 3.92 (s, 3H), 3.90 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, *CDCl$_3$*) δ/ppm: 196.503, 176.452, 161.412, 161.361, 151.369, 148.228, 147.865, 143.914, 139.443, 137.747, 135.359, 130.066, 130.066, 129.855, 129.855, 128.783, 128.783, 125.081, 116.226, 14.121, 114.121, 113.569, 62.119, 61.919, 61.776, 61.646, 55.383, 36.453. IR (*film CHCl$_3$*) cm^{-1} ν: 2940, 1626, 1374, 1252, 1178, 1152, 1047, 836. MS (EI) m/z= M$^+$: 525 (30%), 509 (100%). HRMS calc. for $C_{28}H_{25}ClO_8$ 524.12, FAB+ Found m/z 525.1315



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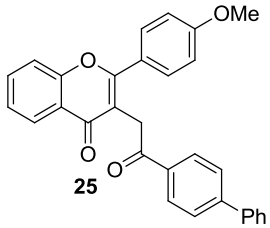
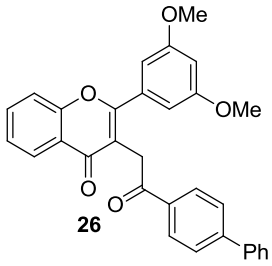
Ethyl 2-(5,6,7,8-tetramethoxy-2-(4-methoxyphenyl)-4-oxo-4H-chromen-3-yl)propanoate (24): 1H NMR (300 MHz, *CDCl$_3$*) δ/ppm 7.60 (d, *J* = 8.7 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 4.07 (s, 1H), 3.93 (d, *J* = 3.2 Hz, 1H), 3.89 (s, 1H), 3.60 (q, *J* = 6.8 Hz, 1H), 1.47 (d, *J* = 6.9 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$) δ/ppm: 175.8, 173.5, 161.2, 160.1, 154.9, 151.2 148.2, 147.6, 143.7, 137.6, 130.1, 125.1, 122.3, 114.1, 110, 105.2, 62.1, 61.8, 61.6, 60.7, 60.6, 55.4, 38.3, 29.6, 15.4, 14.2. IR (film *CHCl$_3$*) cm^{-1} ν: 2980, 2936, 2872, 2851, 1736, 1639, 1607, 1511, 1464, 1408, 1303, 1256, 1201, 1085, 1028, 840, 814, 768. MS (EI) m/z= M$^+$: 473 (40%), 188 (100%). HRMS Calcd for $C_{25}H_{28}O_9$ 472.48, FAB+ Found m/z 473.18.



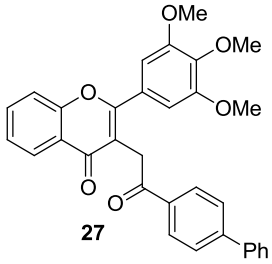
25

3-(2-(biphenyl-4-yl)-2-oxoethyl)-2-(4-methoxyphenyl)-4*H*-chromen-4-one (25). ^{1}H NMR ($CDCl_3$, 300 MHz) δ/ppm: 3.85 (s, 3H), 4.27 (s, 2H), 6.98 (m, 2H, J= 2.1, 9.0), 7.45 (m, 5H), 7.65 (m, 7H), 8.13 (m, 2H, J= 8.4), 8.22 (m, 1H, J= 1.5, 7.8). ^{13}C NMR ($CDCl_3$, 75 MHz) δ/ppm: 36.6, 55.4, 114.1, 116.4, 117.9, 122.7, 124.9, 125.4, 126.0, 127.2, 127.3, 128.2, 128.9, 129.0, 130.2, 133.6, 135.7, 140.0, 145.8, 156.4, 161.4, 163.4, 177.9, 197.1. IR (KBr), ν/cm^{-1}: 3067.7, 3034.0, 2958.3, 2923.6, 2853.6, 1707.4, 1666.4, 1634.2, 1606.9, 1574.4. MS (EI) m/z= M$^+$: 446 (37%), 181 (100%). HRMS-FAB$^+$ m/z: observed: 447.1606, calcd. for $C_{30}H_{23}O_4$: 447.1596.



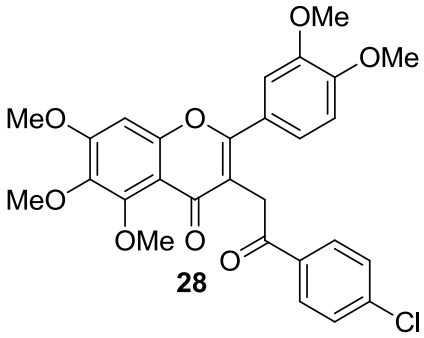
26

3-(2-(biphenyl-4-yl)-2-oxoethyl)-2-(3,5-dimethoxyphenyl)-4*H*-chromen-4-one (26). ^{1}H NMR ($CDCl_3$, 200 MHz) δ/ppm: 3.74 (s, 3H), 3.84 (s, 3H), 4.09 (s, 2H), 6.52 (m, 1H, J= 2.2), 6.58 (d, 1H, J= 2.2), 7.43 (m, 6H), 7.63 (m, 5H), 8.04 (m, 2H, J= 8.6), 8.25 (m, 1H, J= 1.4, 8.0). ^{13}C NMR ($CDCl_3$, 50 MHz) δ/ppm: 36.4, 55.6, 98.8, 104.8, 114.7, 118.0, 118.6, 122.9, 124.7, 126.0, 127.1, 127.2, 128.1, 128.8, 128.9, 131.6, 133.4, 135.8, 140.0, 145.4, 156.7, 158.2, 161.5, 162.8, 177.8, 196.4. IR (KBr), ν/cm^{-1}: 3063.2, 2925.4, 2854.3, 1683.9, 1637.2, 1607.9, 1576.6. MS (EI). m/z= M^+: 476 (54%), 181 (100%). HRMS-FAB$^+$ m/z: observed: 477.1694, calcd. for $C_{31}H_{25}O_5$: 477.1702.



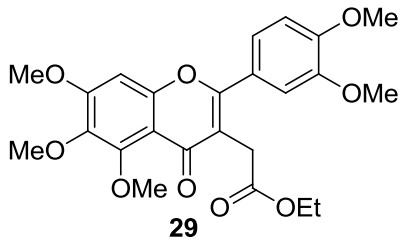
27

3-(2-(biphenyl-4-yl)-2-oxoethyl)-2-(3,4,5-trimethoxyphenyl)-4*H*-chromen-4-one (27). ^{1}H NMR ($CDCl_3$, 200MHz) δ/ppm: 3.80 (s, 6H), 3.90 (s, 3H), 4.28 (s, 2H), 6.93 (s, 2H), 7.37-7.75 (m, 10H), 8.14 (m, 2H, J= 8.6), 8.24 (m, 1H, J= 1.6, 8.0). ^{13}C NMR ($CDCl_3$, 50MHz) δ/ppm: 36.7, 56.2, 60.9, 105.8, 107.8, 116.7, 118.0, 122.6, 125.1, 126.0, 127.3, 128.1, 128.2, 128.9, 133.7, 135.5, 139.8, 146.0, 153.3, 156.2, 163.4, 177.9, 197.4. IR (KBr), ν/cm^{-1}: 3062.8, 2998.7, 2929.9, 2839.6, 1674.6, 1632.2, 1606.2, 1574.7. MS (EI). m/z= M^+: 506 (55%), 181 (100%). HRMS-FAB$^+$ m/z: observed: 507.1803, calcd. for $C_{32}H_{27}O_6$: 507.1808.



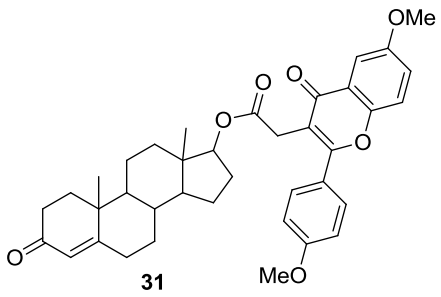
28

3-(2-(4-chlorophenyl)-2-oxoethyl)-5,6,7-trimethoxy-2-(4-methoxyphenyl)-4H-chromen-4-one (28): ^{1}H NMR (300 MHz, *CDCl*$_3$) δ/ppm 7.98 (d, *J* = 8.74 Hz, 2H), 7.43 (d, *J* = 8.74 Hz, 2H), 7.19 (dd, *J* = 8.26 Hz, 2.04 Hz, 1H), 7.15 (d, *J* = 2.00 Hz, 1H), 6.91 (d, *J* = 8.34 Hz, 1H), 6.73 (s, 1H), 4.12 (s, 2H), 3.95 (s, 6H), 3.91 (s, 3H), 3.90 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (75 MHz, *CDCl*$_3$) δ/ppm 196.79, 176.18, 161.39, 157.87, 154.57, 152.56, 150.86, 148.93, 140.33, 139.48, 135.44, 129.81, 129.81, 128.83, 128.83, 125.33, 121.59, 116.52, 111.71, 111.47, 110.98, 96.07, 62.06, 61.50, 56.26, 55.98, 36.53, 29.69. IR (*film CHCl*$_3$) cm^{-1} ν: 2960, 2931, 1729, 1274, 1123, 1072, 743. MS (EI) m/z= M^{+}: 149 (100%). HRMS calc. for $C_{28}H_{25}ClO_8$ 524.12, FAB+ Found m/z 525.130



29

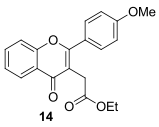
Ethyl 2-(2-(3,4-dimethoxyphenyl)-5,6,7-trimethoxy-4-oxo-4H-chromen-3-yl)acetate (29): ^{1}H NMR (300 MHz, *CDCl*$_3$) δ/ppm 7.23 (dd, *J* = 8.35, 1.83 Hz, 1H), 7.20 (d, *J* = 1.76 Hz, 1H), 6.97 (d, *J* = 8.27 Hz, 1H), 6.72 (s, 1H), 4.19 (q, *J* = 7.13 Hz, 2H), 3.98 (s, 3H), 3.95 (s, 3H), 3.95 (s, 3H), 3.91 (s, 3H), 3.91 (s, 3H), 3.52 (s, 2H), 1.27 (t, *J* = 7.02 Hz, 3H). **^{13}C NMR** (75 MHz, *CDCl*$_3$) δ/ppm 196.79, 176.18, 161.39, 157.87, 154.57, 152.56, 150.86, 148.93, 140.33, 139.48, 135.44, 129.81, 129.81, 128.83, 128.83, 125.33, 121.59, 116.52, 111.71, 111.47, 110.98, 96.07, 62.06, 61.50, 56.26, 55.98, 36.53, 29.69. **IR** (*film CHCl*$_3$) cm^{-1} ν: 2936, 1728, 1631, 1605, 1462, 1331, 1252, 1238, 1170, 1026, 995. MS (EI) m/z= M^{+}: 459 (60%), 397 (100%). **HRMS** calc. for $C_{24}H_{26}O_9$ 458.15, FAB+ Found m/z 459.1645



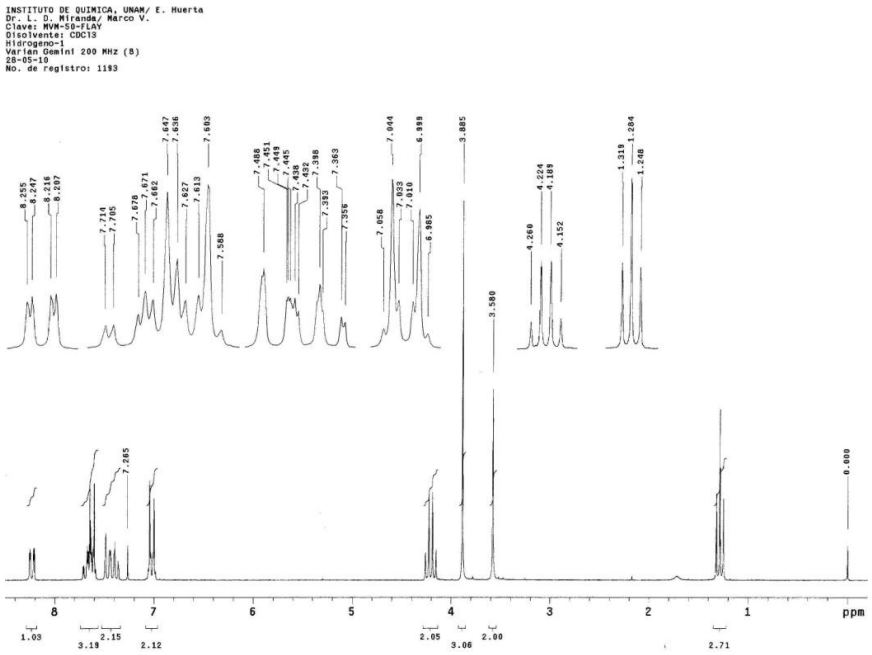
31

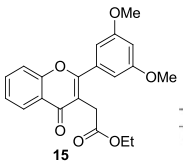
(8R,9S,10R,13S,14S,17S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl 2-(7-methoxy-2-(4-methoxyphenyl)-4-oxo-4H-chromen-3-yl)acetate (31): 1H NMR (300 MHz, *$CDCl_3$* δ/ppm 8.13 (d, *J* = 8.9 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.07-6.93 (m, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 5.73 (s, 1H), 4.75-4.60 (m, 1H), 4.26-4.16 (m, 1H), 4.05 (s, 1H), 3.89 (d, *J* = 4.0 Hz, 1H), 3.55 (s, 1H), 2.47-0.66 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm 199.38, 171.48, 170.94, 164.05, 130.84, 130.24, 128.79, 127.34, 123.93, 115.40, 114.34, 114.06, 100.02, 82.95, 77.41, 76.99, 76.56, 68.16, 55.76, 55.45, 53.72, 50.29, 42.74, 38.63, 36.66, 35.72, 35.44, 33.94, 32.76, 32.35, 31.52, 29.69, 27.38, 23.52, 22.97, 20.61, 17.40, 11.98, 10.95. IR (film *$CHCl_3$*) cm^{-1} ν: 2938, 2852, 1731, 1671, 1631, 1611, 1512, 1441, 1386, 1256, 1164, 1031, 838, 753. MS (EI) m/z= M^+: 611 (10%), 323 (100%). HRMS Calcd for $C_{38}H_{42}O_7$ 611, FAB+ Found 611.3 m/z

^{1}H and NMR Spectra

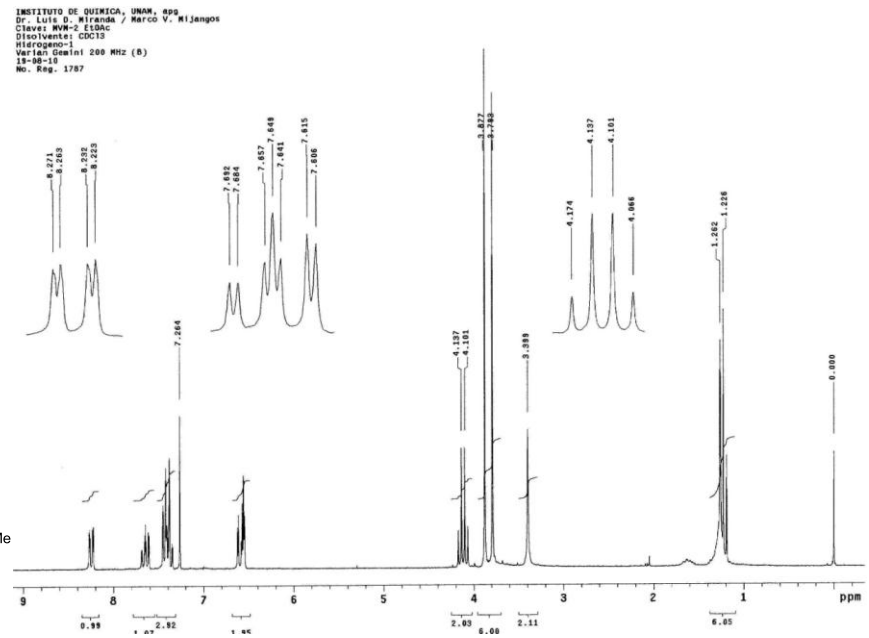


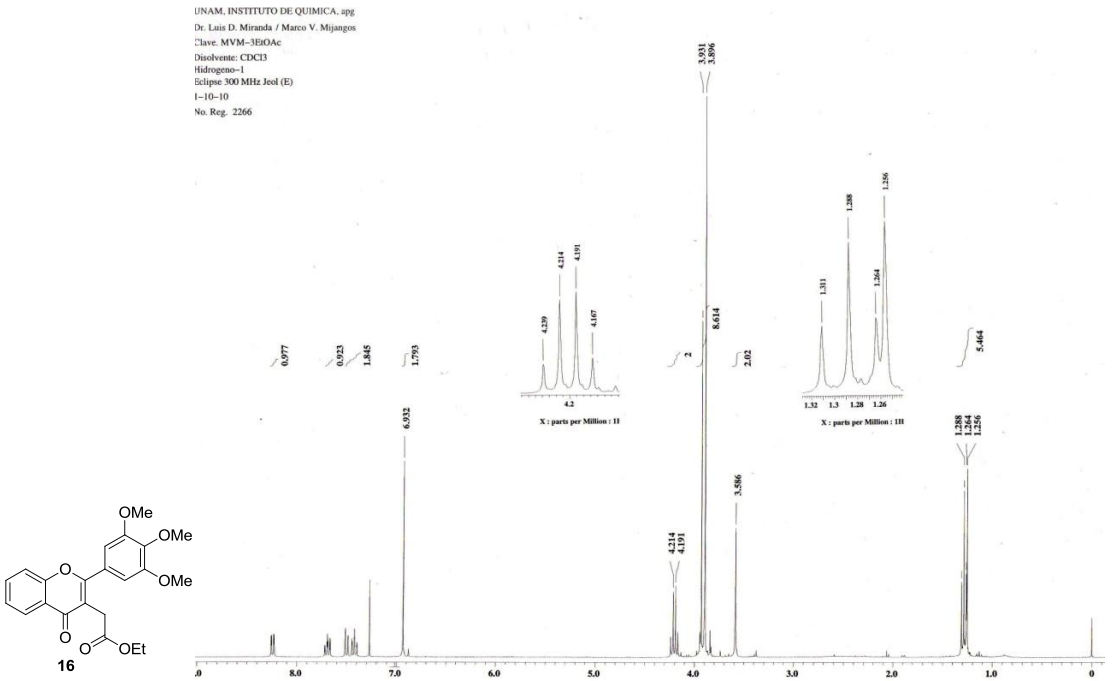
14

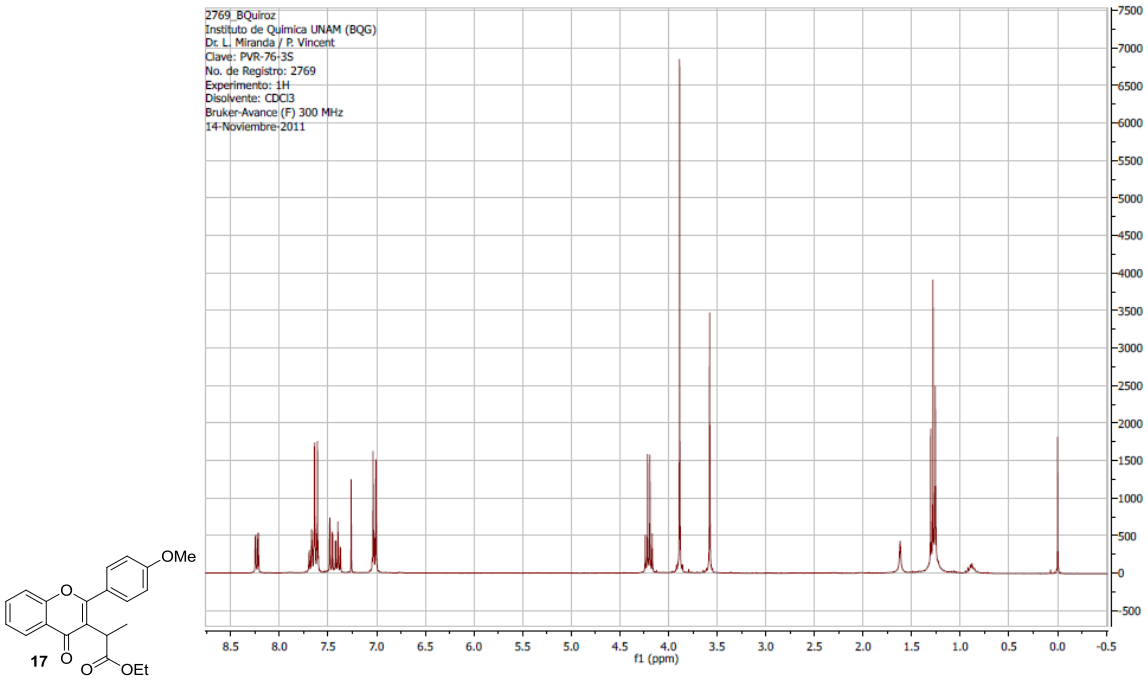


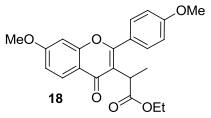


15

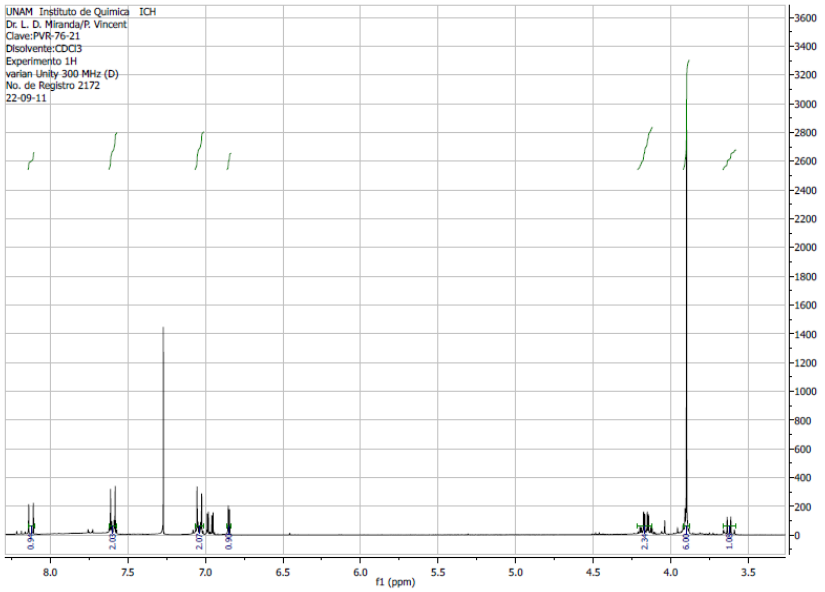


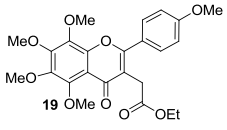

UNAM, INSTITUTO DE QUIMICA, apg
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MVM-3EtOAc
Disolvente: CDCl3
Hidrogeno-1
Eclipse 300 MHz Jeol (E)
1-10-10
No. Reg. 2266
OMe
OMe
OMe
O
O
OEt
16


2769_BQuiroz
Instituto de Quimica UNAM (BQG)
Dr. L. Miranda / P. Vincent
Clave: PVR-76-3S
No. de Registro: 2769
Experimento: 1H
Disolvente: CDCl3
Bruker-Avance (F) 300 MHz
14-Noviembre-2011
OMe
O
O
OEt
17
f1 (ppm)

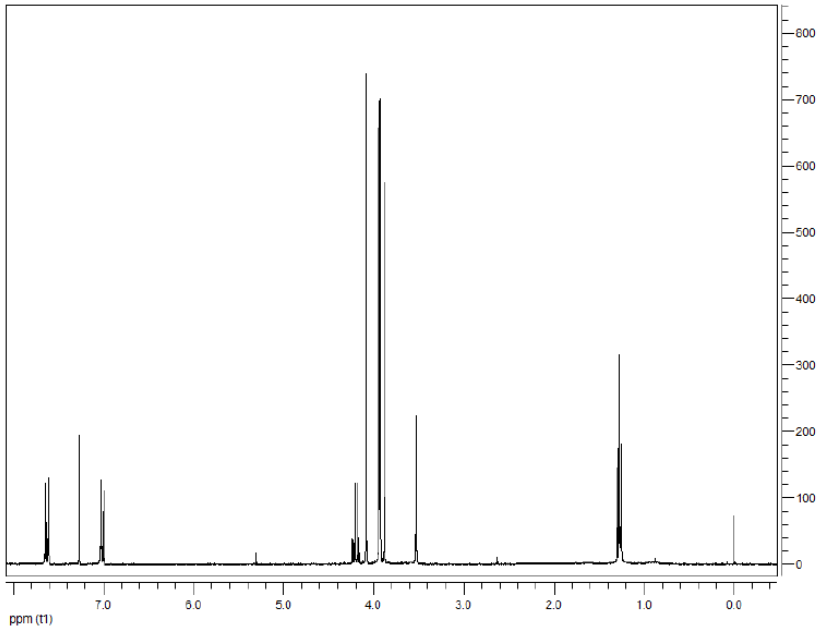

MeO
OMe
O
O
OEt

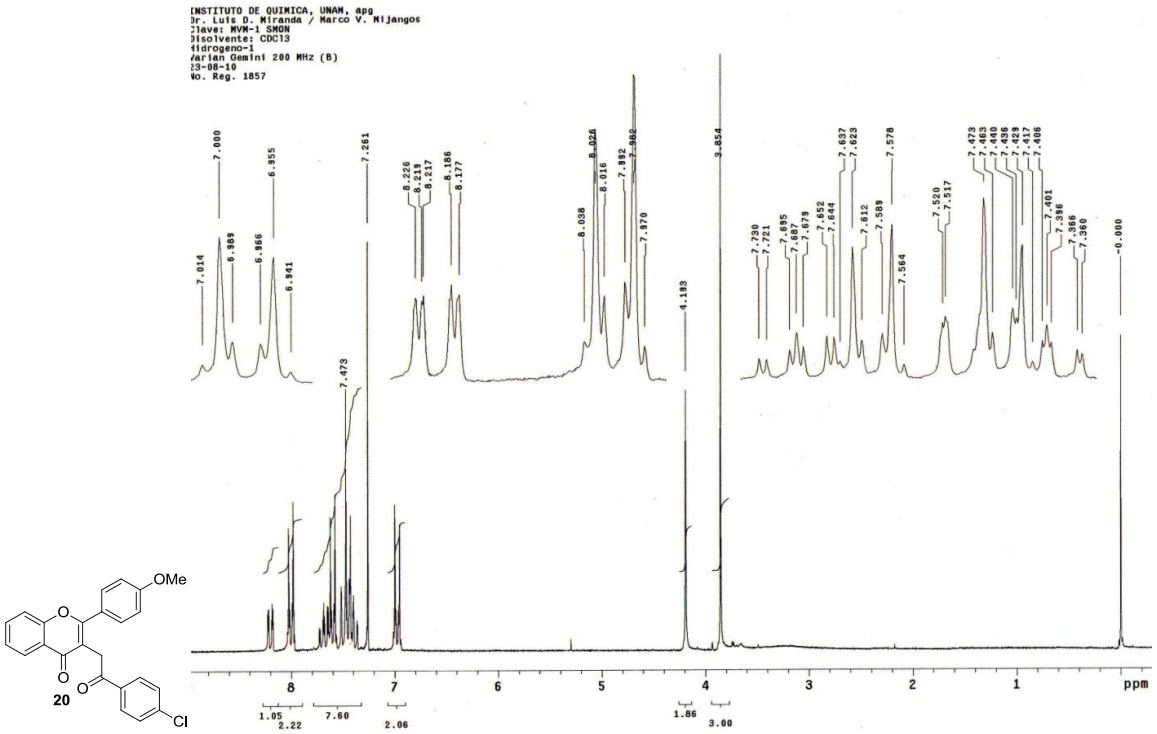
18

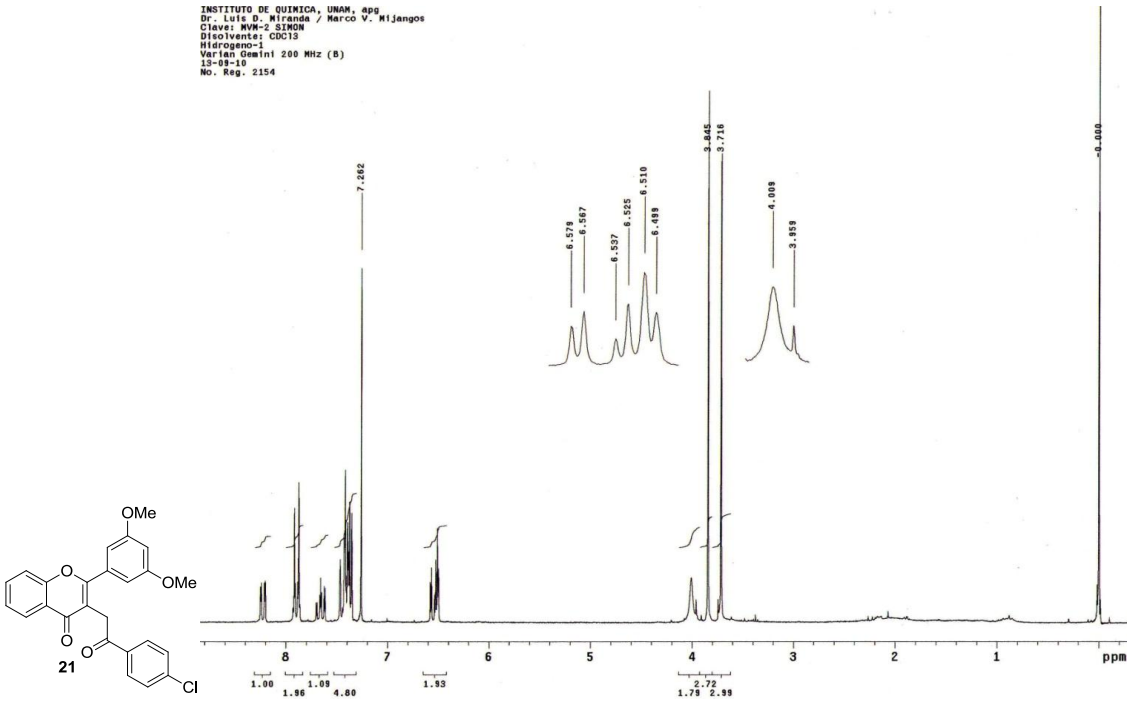

UNAM Instituto de Química ICH
Dr. L. D. Miranda/P. Vincent
Clave:PVR-76-21
Disolvente:CDCl3
Experimento 1H
varian Unity 300 MHz (D)
No. de Registro 2172
22-09-11
f1 (ppm)

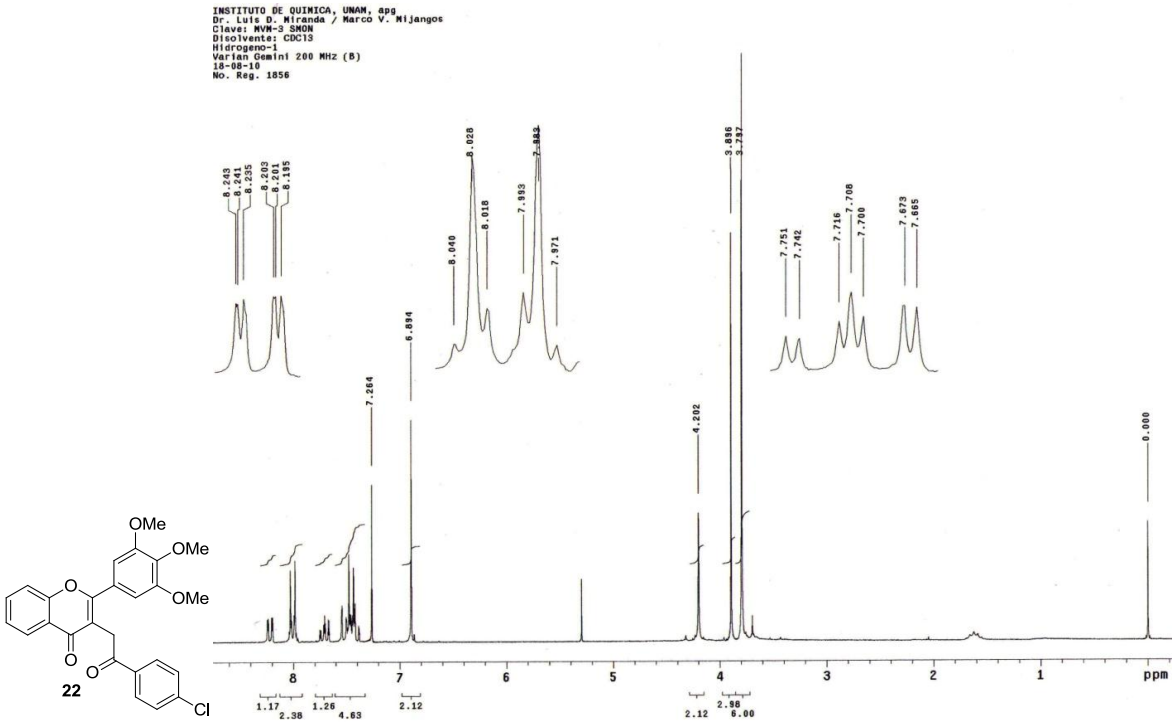

MeO
OMe
MeO
OMe
OMe
O
O
OEt

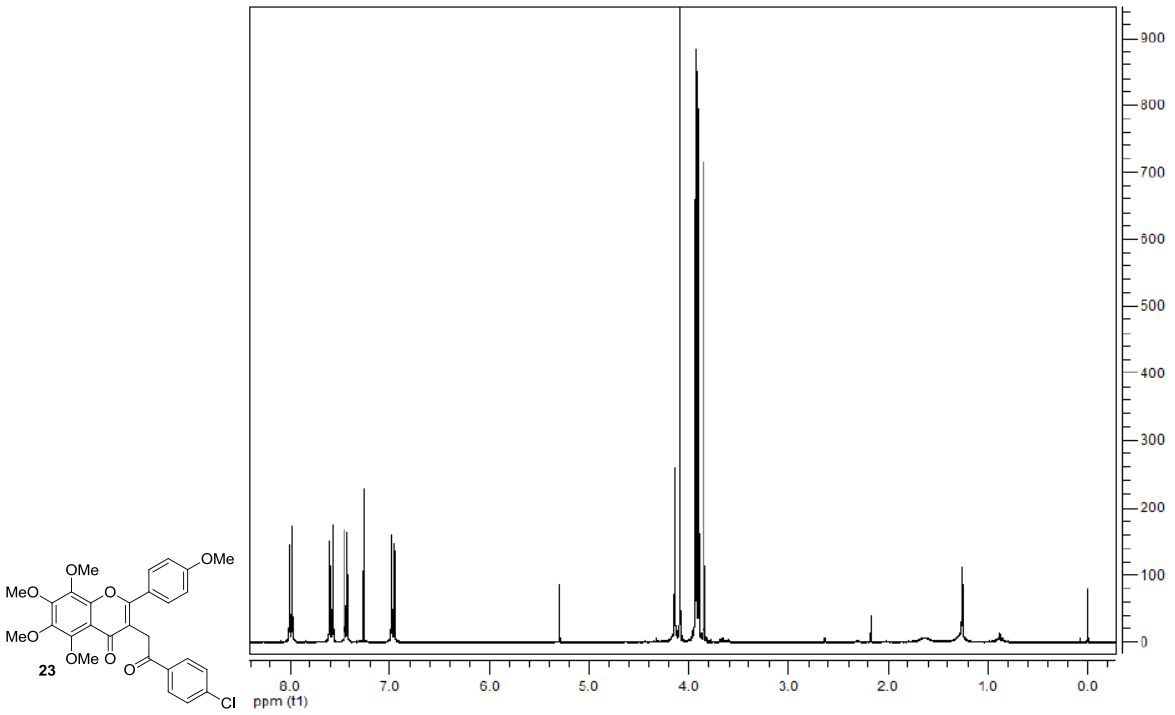
19


ppm (t1)


INSTITUTO DE QUIMICA, UNAM, apg
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MVM-1 SIMON
Disolvente: CDCl3
Hidrogeno-1
Varian Gemini 200 MHz (B)
23-08-10
No. Reg. 1857
OMe
O
O
O
Cl
20
ppm


INSTITUTO DE QUIMICA, UNAM, apg
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MVM-2 SIMON
Disolvente: CDCl3
Hidrogeno-1
Varian Gemini 200 MHz (B)
13-09-10
No. Reg. 2154
OMe
OMe
O
O
O
Cl
21
ppm


INSTITUTO DE QUIMICA, UNAM, dpg
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MVM-3 SMON
Disolvente: CDCl3
Hidrogeno-1
Varian Gemini 200 MHz (B)
18-08-10
No. Reg. 1856
8.243
8.241
8.235
8.203
8.201
8.195
8.028
8.018
8.040
7.993
7.971
7.751
7.742
7.716
7.708
7.700
7.673
7.665
7.264
6.894
4.202
3.886
3.237
0.000
OMe
OMe
OMe
O
O
O
Cl
22
8
7
6
5
4
3
2
1
ppm
1.17
2.38
1.26
4.63
2.12
2.12
2.98
6.00


OMe
MeO
MeO
OMe
OMe
O
O
O
Cl
23
900
800
700
600
500
400
300
200
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0
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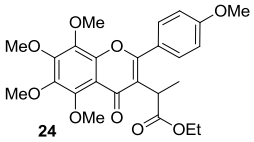
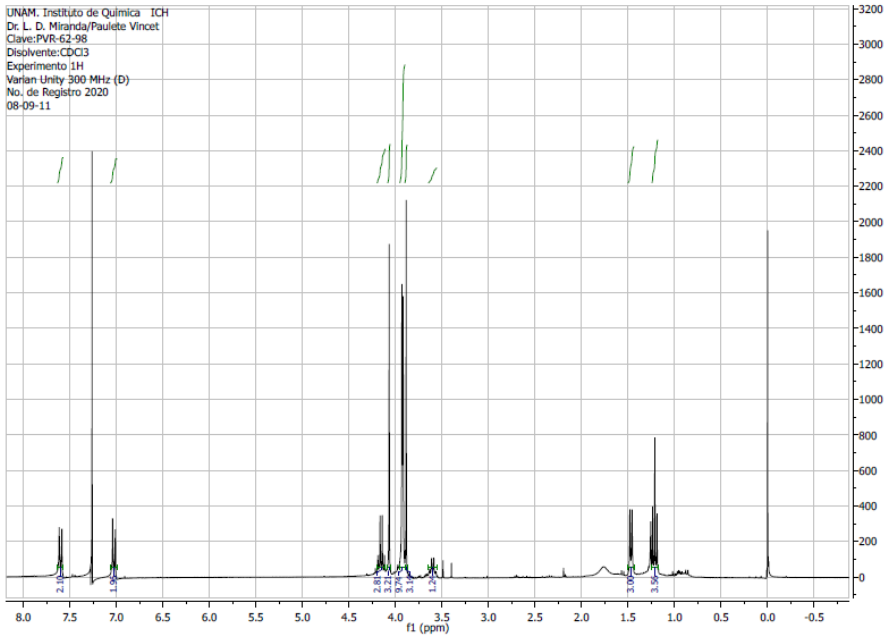
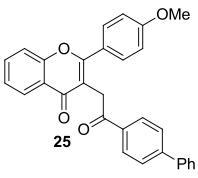
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

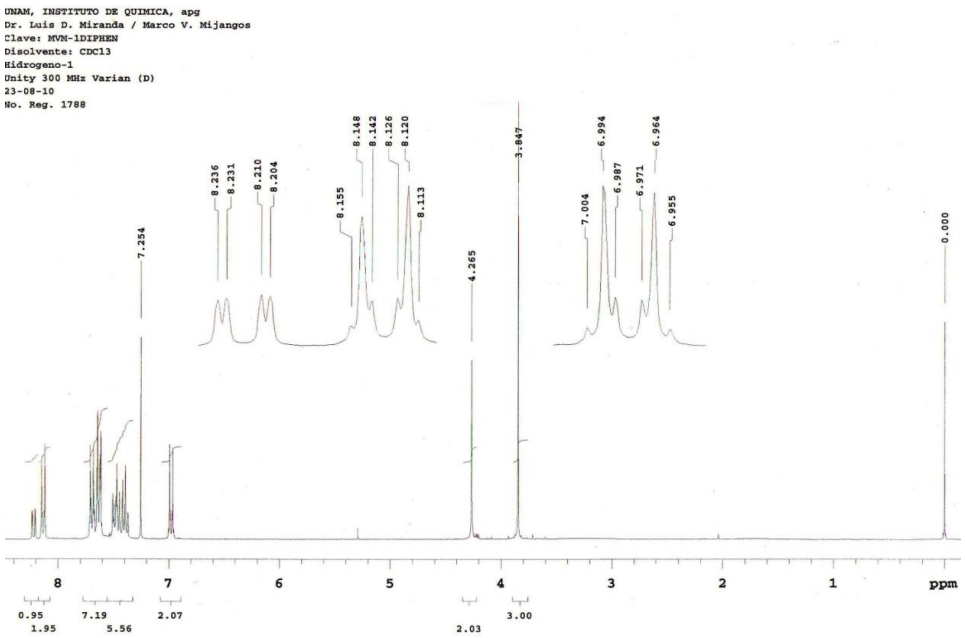

OMe
MeO
MeO
OMe
O
O
OEt
OMe

24


UNAM. Instituto de Química ICH
Dr. L. D. Miranda/Paulete Vincet
Clave:PVR-62-98
Disolvente:CDCl3
Experimento 1H
Varian Unity 300 MHz (D)
No. de Registro 2020
08-09-11
f1 (ppm)


OMe
O
O
O
Ph

25


UNAM, INSTITUTO DE QUIMICA, apg
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MVM-1DIPHEN
Disolvente: CDCl3
Hidrogeno-1
Unity 300 MHz Varian (D)
23-08-10
No. Reg. 1788
8.236
8.231
8.210
8.204
8.155
8.148
8.142
8.126
8.120
8.113
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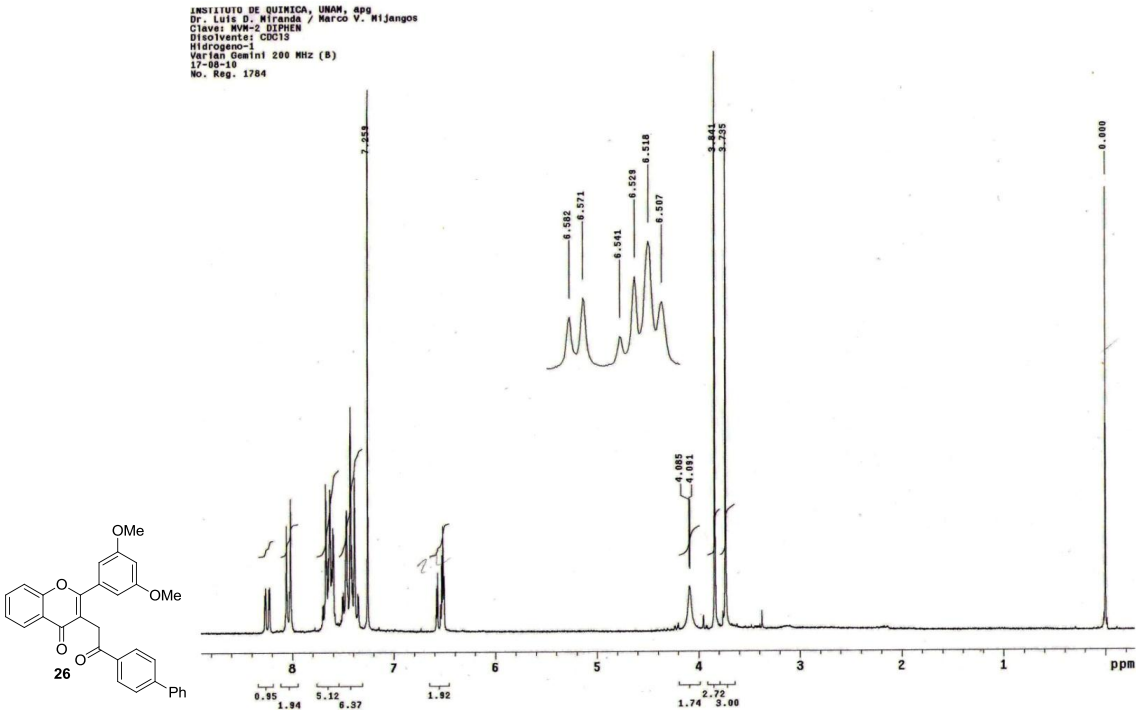
7.004
6.994
6.987
6.971
6.964
6.955
0.000
ppm


INSTITUTO DE QUIMICA, UNAM, apg
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MVM-2 DIPHEN
Disolvente: CDCl3
Hidrogeno-1
Varian Gemini 200 MHz (B)
17-08-10
No. Reg. 1784
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6.582
6.571
6.541
6.528
6.518
6.507
4.085
4.081
3.841
3.735
0.000
OMe
OMe
O
O
O
26
Ph
8
7
6
5
4
3
2
1
ppm
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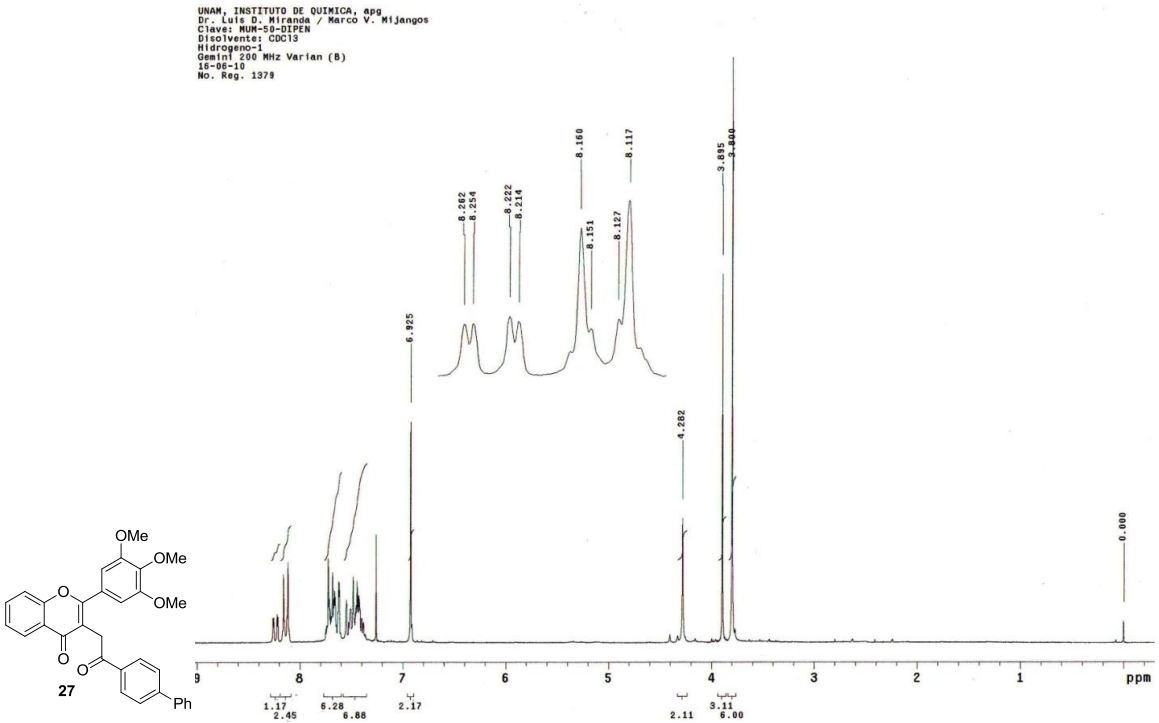
1.94
5.12
6.37
1.92
1.74
2.72
3.00


UNAM, INSTITUTO DE QUIMICA, apg
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MUM-50-DIPEN
Disolvente: CDCl3
Hidrogeno-1
Gemini 200 MHz Varian (B)
16-06-10
No. Reg. 1379
8.262
8.254
8.222
8.214
8.160
8.151
8.127
8.117
7.925
4.282
3.895
3.880
0.000
OMe
OMe
OMe
O
O
O
27
Ph
8
7
6
5
4
3
2
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ppm
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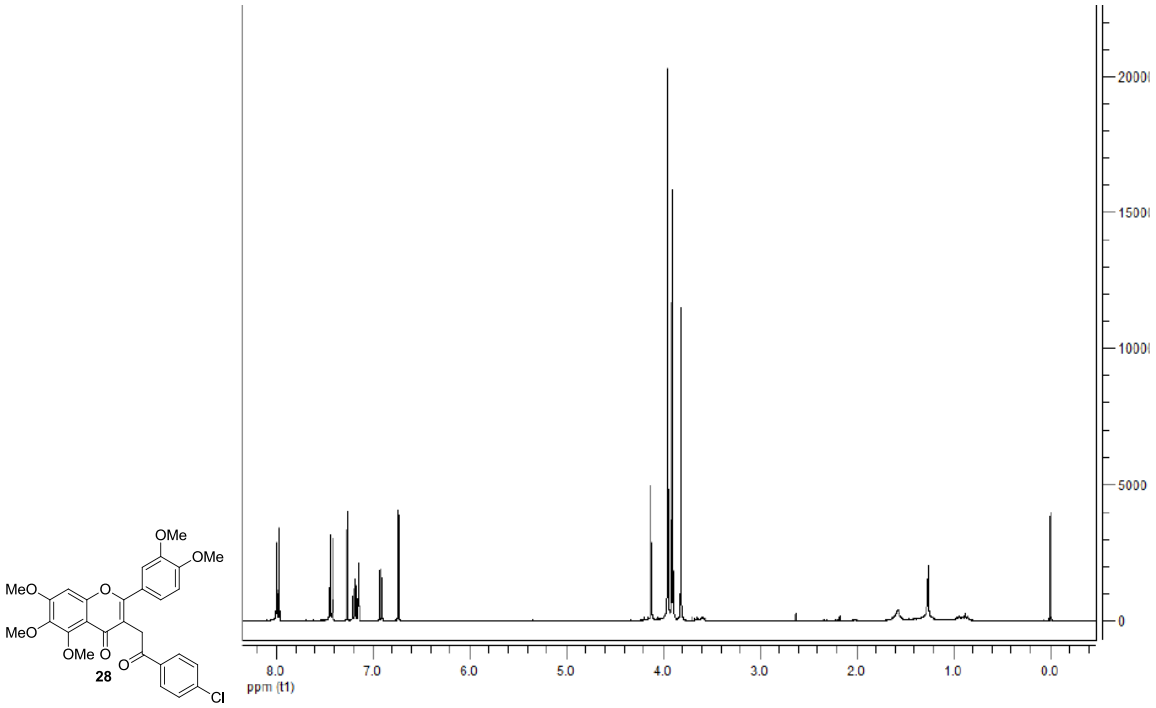
2.45
6.28
6.88
2.17
2.11
3.11
6.00


OMe
OMe
MeO
MeO
OMe
O
O
Cl
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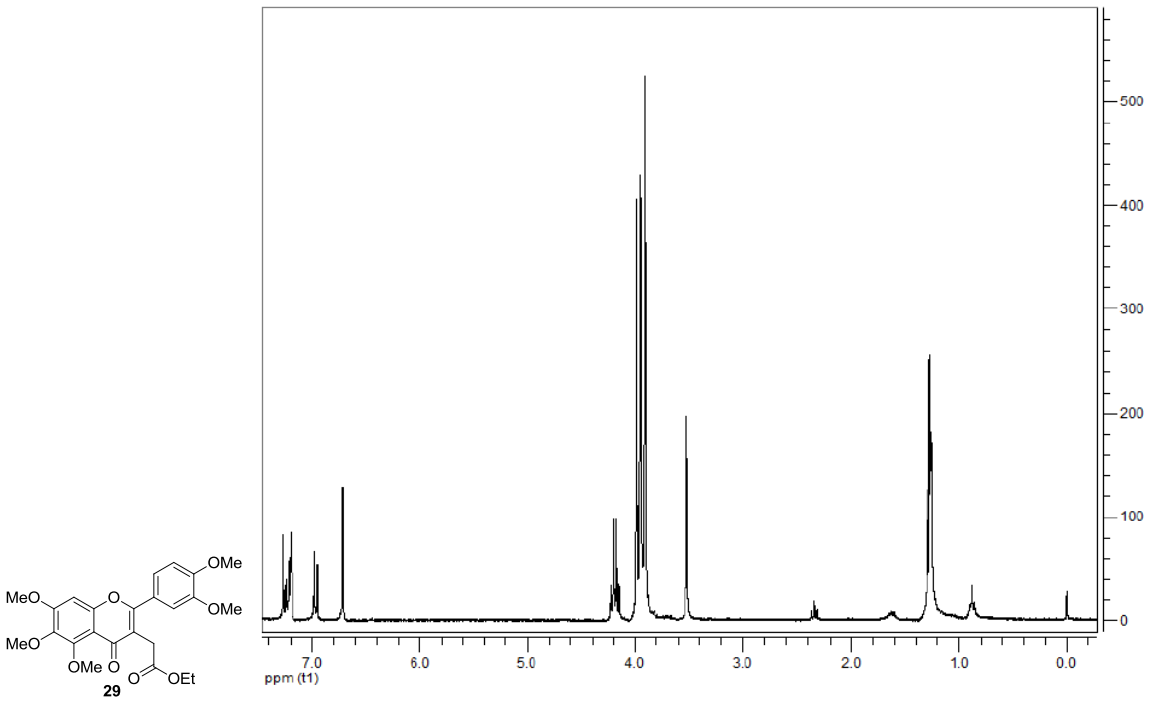
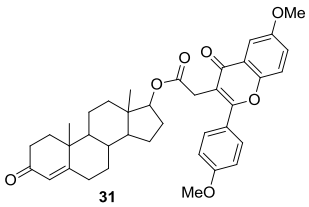
2000
1500
1000
5000
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


OMe
OMe
MeO
MeO
OMe
O
O
OEt
29
500
400
300
200
100
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)



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