Electronic Supplementary Material (ESI) for Chemical Communications

Tandem Synthesis of 3-Allyl-chromones from Alkynones and Allylic Alcohols under Metal-free Conditions

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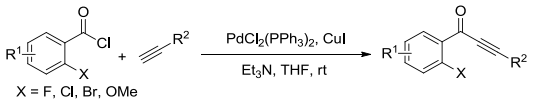
Page S2-S8: Materials and Methods. Page S9-S32: the ^{1}H NMR and ^{13}C NMR spectra for compounds **1k, 1t, c** and **3a-3u.**

List of ^{1}H NMR and ^{13}C NMR spectra for compounds

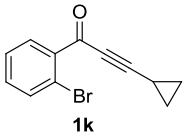
Experimental Section

All commercially available chemicals were obtained from Adamas-beta and used without further purifications. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All melting points were determined on a Beijing Science Instrument Dianguang Instrument Factory XT4B melting point apparatus and uncorrected. ^{1}H and ^{13}C NMR spectra were measured on a 400 MHz Bruker spectrometer (^{1}H 400 MHz, ^{13}C100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. HRMSESI spectra were obtained on Agilent 6450 spectrometer. IR data were recorded on a Nicolet IS10 spectrometer. The products listed below were determined by ^{1}H, ^{13}C NMR. PE is petroleum ether (60-90 ^{o}C).

General Procedure for the Preparation of alkynones:[1]



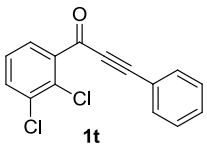
To a solution of the acyl chloride (1.0 mmol) and terminal alkyne (1.1 mmol) in anhydrous THF (5 mL) under N_2 protection, was added $PdCl_2(PPh_3)_2$ (14 mg, 2 mol %) and CuI (7.6 mg, 4 mol %). After stirring for 1 min, Et_3N (1.5 mmol) was added and the mixture was stirred for 15 h at r.t. When the reaction was complete (Monitored by TLC), distilled H_2O was added. The mixture was extracted with CH_2Cl_2. The organic phase was collected, dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography [silica gel, PE/EtOAc (50:1)].



1k

1-(2-bromophenyl)-3-cyclopropylprop-2-yn-1-one (**1k**); 85% yield.

yellow liquid; IR (KBr) 2203, 1649 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.92 (m, 1H), 7.64 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.42-7.38 (m, 1H), 7.35-7.31 (m, 1H), 1.53-1.47 (m, 1H), 1.04-0.99 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.3, 137.7, 134.7, 132.9, 132.4, 127.2, 120.8, 102.5, 9.8, 0.1; HRMS m/z (ESI) calcd for $C_{12}H_9OBr$ $(M + H)^+$ 248.9915, found 248.9912.

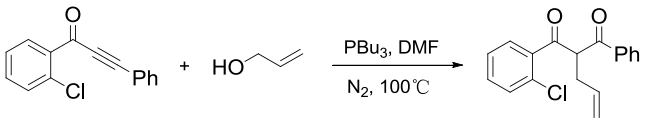


1t

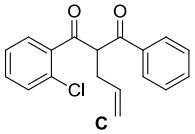
1-(2, 3-dichlorophenyl)-3-phenylprop-2-yn-1-one (**1t**); 88% yield.

yellow solid; mp: 74-76℃; IR (KBr) 2200, 1638 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.91-7.88 (m, 1H), 7.67-7.63 (m, 3H), 7.51-7.47 (m, 1H), 7.43-7.40 (m, 2H), 7.37-7.33 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.3, 138.4, 135.0, 133.9, 133.2, 131.5, 131.2, 130.0, 128.7, 127.3, 119.8, 94.7, 88.2; HRMS m/z (ESI) calcd for $C_{15}H_8OCl_2$ $(M + H)^+$ 275.0030, found 275.0027.

Procedure for the synthesis of intermediate C:



A mixture of *o*-chlorophenylynone (1.0 mmol), allyl alcohol (1.2 mmol) and PBu_3 (0.1 mmol) in N,N-dimethylformamide (2 mL) was stirred at 100 °C for 8 h under nitrogen atmosphere (without base). After cooling to room temperature, water was added (10 mL). Then the aqueous solution was extracted with ethyl acetate (3× 10mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography [eluent: PE/EtOAc (50:1)] on silica gel to give the compound **C**.



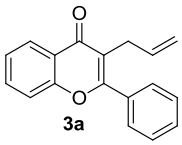
C

2-allyl-1-(2-chlorophenyl)-3-phenylpropane-1,3-dione (**c**); 94% yield.

yellow liquid; IR (KBr) 3069, 1708, 1676, 1593, 1434, 1263, 1235, 999, 923, 759, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 7.89 (d, 2H), 7.54 (m, 1H), 7.41 (m, 3H), 7.32 (m, 2H), 7.24 (m, 1H), 5.85 (m, 1H), 5.45 (m, 1H), 5.05 (m, 2H), 2.76-2.93 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 197.8, 195.5, 138.5, 136.2, 134.6, 133.5, 131.9, 130.6, 130.3, 129.6, 128.7, 128.5, 127.0, 117.5, 59.8, 33.2; HRMS m/z (ESI) calcd for $C_{18}H_{15}O_2Cl$ $(M + Na)^+$ 321.0658, found 321.0660.

General Procedure for the synthesis of substituted chromones 3a-3u:

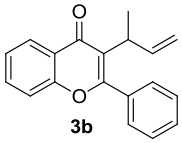
A mixture of alkynones (0.5 mmol), allylic alcohol (0.6 mmol), K_2CO_3(0.5 mmol) and PBu_3 (0.05 mmol) in N,N-dimethylformamide (2 mL) was stirred at 100 °C for 8-24 h under nitrogen. After cooling to room temperature, water was added (10 mL). Then the aqueous solution was extracted with ethyl acetate. The organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography [eluent: PE/EtOAc (30:1)] on silica gel to provide the desired product.



3a

3-allyl-2-phenyl-4*H*-chromen-4-one (**3a**)

yellow solid; mp: 50-52℃; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.26 (dd, J = 8.0, 1.5 Hz, 1H), 7.70-7.64 (m, 3H), 7.52-7.38 (m, 5H), 6.11-6.05 (m, 1H), 5.05 (m, 2H), 3.32 (d, J = 5.70 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 178.0, 162.3, 156.1, 135.9, 133.4, 133.2, 130.4, 128.5, 128.4, 126.0, 124.8, 122.9, 119.4, 117.9, 115.4, 30.0.

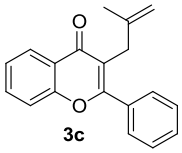


3b

3-(but-3-en-2-yl)-2-phenyl-4*H*-chromen-4-one (**3b**)

yellow solid; mp: 54-56℃; IR (KBr) 3087, 2966, 1654, 1605, 1426, 1371, 1130, 1074, 927, 854,

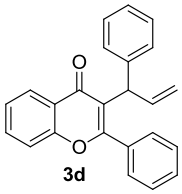
767, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.23 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.65-7.58 (m, 5H), 7.42-7.36 (m, 3H), 6.41-6.32 (m, 1H), 4.96 (t, *J* = 13.6 Hz, 2H), 3.46 (p, *J* = 6.9 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.8, 162.1, 155.9, 141.5, 133.6, 133.3, 130.2, 128.7, 128.5, 125.9, 124.7, 124.3, 123.9, 117.8, 113.5, 38.0, 18.7; HRMS m/z (ESI) calcd for $C_{19}H_{16}O_2$ $(M + H)^+$ 277.1229, found 277.1229.



3c

3-(2-methylallyl)-2-phenyl-4*H*-chromen-4-one (**3c**)

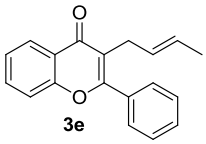
yellow solid; mp: 58-60℃; IR (KBr) 3072, 2978, 1640, 1621, 1466, 1386, 1123, 889, 768, 670 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.26 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.71-7.65 (m, 3H), 7.52-7.47 (m, 4H), 7.41 (m, 1H), 4.84 (dt, *J* = 2.8, 1.3 Hz, 1H), 4.59 (s, 1H), 3.23 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 178.1, 162.5, 156.2, 143.9, 133.4, 133.3, 130.4, 128.4, 128.3, 126.1, 124.8, 122.8, 119.6, 117.9, 110.2, 33.5, 23.4; HRMS m/z (ESI) calcd for $C_{19}H_{16}O_2$ $(M + H)^+$ 277.1229, found 277.1228.



3d

2-phenyl-3-(1-phenylallyl)-4*H*-chromen-4-one (**3d**)

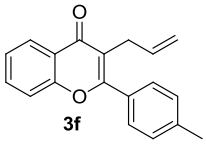
yellow solid; mp: 111-113℃; IR (KBr) 3059, 3043, 1640, 1624, 1466, 1379, 1219, 903, 758, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66-7.59 (m, 3H), 7.55-7.43 (m, 4H), 7.38-7.34 (m, 1H), 7.26-7.21 (m, 4H), 7.17-7.13 (m, 1H), 6.71 (m, 1H), 5.20 (m, 1H), 5.10-5.05 (m, 1H), 4.67 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.2, 163.2, 156.0, 142.1, 138.4, 133.5, 133.3, 130.4, 128.7, 128.6, 128.1, 127.2, 126.1, 124.8, 123.9, 123.1, 117.8, 116.8, 48.3; HRMS m/z (ESI) calcd for $C_{24}H_{18}O_2$ $(M + H)^+$ 339.1385, found 339.1382.



3e

3-(but-2-en-1-yl)-2-phenyl-4*H*-chromen-4-one (**3e**)

yellow solid; mp: 74-76℃; IR (KBr) 3064, 2931, 1639, 1610, 1469, 1390, 1122, 959, 765 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.26 (d, *J* = 7.7 Hz, 1H), 7.66 (m, 3H), 7.52-7.38 (m, 5H), 5.68-5.41 (m, 2H), 3.25 (dd, *J* = 30.3, 5.1 Hz, 2H), 1.65 (t, *J* = 10.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 178.2, 162.0, 156.2, 133.4, 130.3, 128.6, 128.4, 126.0, 124.7, 123.0, 120.3, 117.9, 28.8, 17.9; HRMS m/z (ESI) calcd for $C_{19}H_{16}O_2$ $(M + H)^+$ 277.1229, found 277.1227.

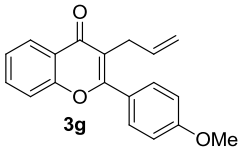


3f

3-allyl-2-(*p*-tolyl)-4*H*-chromen-4-one (**3f**)

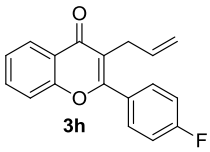
white solid; mp: 70-72℃; IR (KBr) 3073, 2975, 1643, 1613, 1470, 1384, 1133, 903, 759 cm^{-1}; ^1H

NMR (400 MHz, $CDCl_3$) δ ppm 8.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (m, 1H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.46-7.37 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.11-6.01 (m, 1H), 5.06 (m, 2H), 3.33 (dt, *J* = 5.7, 1.7 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 178.1, 162.6, 156.2, 140.7, 136.1, 133.4, 130.4, 129.1, 128.5, 126.0, 124.7, 122.9, 119.2, 117.9, 115.3, 30.1, 21.5; HRMS m/z (ESI) calcd for $C_{19}H_{16}O_2$ $(M + H)^+$ 277.1229, found 277.1225.



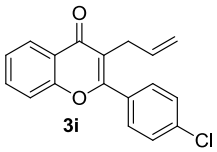
3-allyl-2-(4-methoxyphenyl)-4*H*-chromen-4-one (**3g**)

white solid; mp: 64-66℃; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.25 (dd, *J* = 7.95 Hz, *J* = 1.40 Hz, , 1H), 7.65 (m, 3H), 7.46 (dd, J = 10.3, 6.0 Hz, 1H), 7.39 (tt, J = 12.2, 3.0 Hz, 1H), 7.01 (m, 2H), 6.09 (m, 1H), 5.07 (m, 2H), 3.89 (s, 3H), 3.35 (dt, J = 5.6, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 178.1, 162.3, 161.2, 156.1, 136.1, 133.3, 130.2, 126.0, 125.6, 124.7, 122.8, 118.8, 117.8, 115.3, 113.8, 55.4, 30.2.



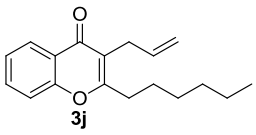
3-allyl-2-(4-fluorophenyl)-4*H*-chromen-4-one (**3h**)

yellow solid; mp: 93-95℃; IR (KBr) 3060, 2960, 1635, 1610, 1508, 1478, 1387, 1238, 1138, 907, 851, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.26 (m, 1H), 7.71-7.65 (m, 3H), 7.47-7.39 (m, 2H), 7.22-7.18 (m, 2H), 6.11-6.01 (m, 1H), 5.05 (m, 2H), 3.31 (dt, J = 5.6, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.9, 163.8 (d, J_{C-F} = 249.98 Hz), 161.3, 156.1, 135.8, 133.5, 130.7 (d, J_{C-F} = 8.54 Hz), 129.3 (d, J_{C-F} = 3.25 Hz), 126.0, 124.9, 122.8, 119.5, 117.8, 115.7, 115.5 (d, J_{C-F} = 4.47 Hz), 30.0; HRMS m/z (ESI) calcd for $C_{18}H_{13}O_2F$ (M + H)+ 281.0978, found 281.0975.



3-allyl-2-(4-chlorophenyl)-4*H*-chromen-4-one (**3i**)

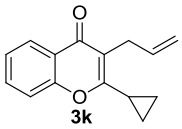
yellow solid; mp: 101-103℃; IR (KBr) 3074, 2959, 1636, 1607, 1468, 1384, 1137, 1095, 907, 828, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.26 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70-7.62 (m, 3H), 7.51-7.39 (m, 4H), 6.05 (m, 1H), 5.05 (m, 2H), 3.30 (dt, *J* = 5.6, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.9, 161.1, 156.1, 136.7, 135.8, 133.6, 131.6, 130.0, 128.8, 126.1, 125.0, 122.8, 119.7, 117.9, 115.6, 30.0; HRMS m/z (ESI) calcd for $C_{18}H_{13}O_2Cl$ $(M + H)^+$ 297.0682, found 297.0680.



3-allyl-2-hexyl-4*H*-chromen-4-one (**3j**)

yellow liquid; IR (KBr) 3077, 2930, 1640, 1575, 1468, 1390, 1227, 1160, 911, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ ppm 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63-7.59 (m, 1H), 7.40-7.33 (m, 2H), 5.90 (m, 1H), 5.04 (m, 2H), 3.34 (dt, *J* = 6.1, 1.6 Hz, 2H), 2.68 (m, 2H), 1.75 (m, 2H), 1.43-1.28

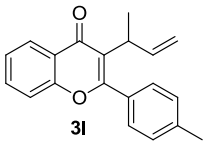
(m, 6H), 0.90 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.4, 166.7, 156.0, 135.5, 133.0, 125.9, 124.5, 122.9, 118.6, 117.6, 115.0, 31.9, 31.5, 29.0, 28.4, 27.2, 22.5, 14.0; HRMS m/z (ESI) calcd for $C_{18}H_{22}O_2$ $(M + H)^+$ 271.1698, found 271.1698.



3k

3-allyl-2-cyclopropyl-4*H*-chromen-4-one (**3k**)

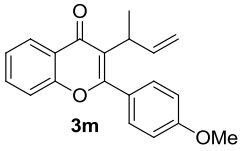
yellow solid; mp: 46-48℃; IR (KBr) 3010, 2969, 1617, 1570, 1466, 1398, 1225, 1169, 1118, 1063, 913, 891, 762, 629 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.19 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.60-7.56 (m, 1H), 7.35-7.26 (m, 2H), 5.95 (m, 1H), 5.07 (m, 2H), 3.48 (dt, *J* = 6.0, 1.6 Hz, 2H), 2.12 (tt, *J* = 8.3, 5.0 Hz, 1H), 1.26 (m, 2H), 1.10-1.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.6, 165.9, 155.3, 135.4, 132.8, 126.0, 124.5, 123.0, 118.1, 117.2, 115.0, 27.9, 12.0, 8.2; HRMS m/z (ESI) calcd for $C_{15}H_{14}O_2$ $(M + H)^+$ 227.1072, found 227.1069.



3l

3-(but-3-en-2-yl)-2-(*p*-tolyl)-4*H*-chromen-4-one (**3l**)

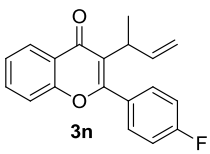
yellow solid; mp: 80-82℃; IR (KBr) 3067, 2990, 1641, 1621, 1467, 1385, 1221, 1090, 903, 822, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.22 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65-7.60 (m, 1H), 7.48 (t, *J* = 9.2 Hz, 2H), 7.40 (m, 4H), 6.37 (m, 1H), 4.96 (m, 2H), 3.48 (p, *J* = 7.0 Hz, 1H), 2.45 (s, 3H), 1.45 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.8, 162.3, 155.9, 141.7, 140.5, 133.2, 130.7, 129.2, 128.6, 125.8, 124.6, 124.1, 123.9, 117.8, 113.4, 38.0, 21.5, 18.8; HRMS m/z (ESI) calcd for $C_{20}H_{18}O_2$ $(M + H)^+$ 291.1385, found 291.1383.



3m

3-(but-3-en-2-yl)-2-(4-methoxyphenyl)-4*H*-chromen-4-one (**3m**)

yellow solid; mp: 72-74℃; IR (KBr) 3063, 2940, 1639, 1619, 1513, 1466, 1381, 1253, 1176, 838, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.22 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.64-7.60 (m, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.41-7.35 (m, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.38 (m, 1H), 5.00-4.94 (m, 2H), 3.89 (s, 3H), 3.51 (p, *J* = 7.0 Hz, 1H), 1.46 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.8, 162.1, 161.0, 155.8, 141.7, 133.2, 130.2, 125.9, 125.8, 124.6, 123.9, 123.8, 117.7, 113.9, 113.4, 55.4, 38.0, 18.8; HRMS m/z (ESI) calcd for $C_{20}H_{18}O_3$ $(M + H)^+$ 307.1334, found 307.1333.

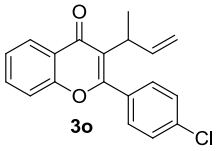


3n

3-(but-3-en-2-yl)-2-(4-fluorophenyl)-4*H*-chromen-4-one (**3n**)

yellow solid; mp: 54-56℃; IR (KBr) 3067, 2936, 1631, 1615, 1506, 1468, 1380, 1230, 1093, 1013, 917, 841, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.23 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.66-7.57 (m, 3H), 7.41-7.37 (m, 2H), 7.23-7.19 (m, 2H), 6.35 (m, 1H), 4.96 (m, 2H), 3.43 (m, 1H), 1.45 (d,

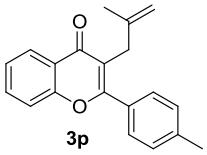
J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.7, 163.7 (d, J_{C-F} = 249.5 Hz), 161.1, 155.8, 141.4, 133.4, 130.8 (d, J_{C-F} = 8.43 Hz), 129.6 (d, J_{C-F} = 4.0 Hz), 125.9, 124.8, 124.4, 123.8, 117.7, 115.7 (d, J_{C-F} = 21.79 Hz), 113.6, 38.0, 18.8; HRMS m/z (ESI) calcd for $C_{19}H_{15}O_2F$ $(M + H)^+$ 295.1134, found 295.1136.



3o

3-(but-3-en-2-yl)-2-(4-chlorophenyl)-4*H*-chromen-4-one (**3o**)

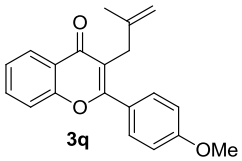
yellow solid; mp: 98-100℃; IR (KBr) 3065, 2989, 1642, 1620, 1467, 1383, 1089, 838, 767 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.22 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.64 (m, 1H), 7.55-7.49 (m, 4H), 7.41-7.37 (m, 2H), 6.35 (m, 1H), 4.95 (m, 2H), 3.42 (m, 1H), 1.45 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.6, 160.8, 155.8, 141.3, 136.5, 133.5, 131.9, 130.1, 128.8, 125.9, 124.9, 124.5, 123.8, 117.7, 113.7, 38.0, 18.8; HRMS m/z (ESI) calcd for $C_{19}H_{15}O_2Cl$ $(M + H)^+$ 311.0839, found 311.0837.



3p

3-(2-methylallyl)-2-(*p*-tolyl)-4*H*-chromen-4-one (**3p**)

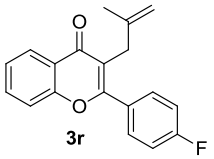
yellow solid; mp: 86-88℃; IR (KBr) 3071, 2918, 1635, 1618, 1466, 1384, 1337, 1171, 1114, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 (m, 1H), 7.69 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.39 (tt, *J* = 7.9, 3.9 Hz, 1H), 7.30 (m, 2H), 4.83 (dt, *J* = 2.8, 1.3 Hz, 1H), 4.59 (d, *J* = 0.8 Hz, 1H), 3.23 (s, 2H), 2.44 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 178.1, 162.6, 156.2, 143.9, 140.7, 133.3, 130.5, 129.1, 128.3, 126.1, 124.7, 122.8, 119.3, 117.9, 110.2, 33.6, 23.4, 21.5; HRMS m/z (ESI) calcd for $C_{20}H_{18}O_2$ $(M + H)^+$ 291.1385, found 291.1384.



3q

2-(4-methoxyphenyl)-3-(2-methylallyl)-4*H*-chromen-4-one (**3q**)

white solid; mp: 100-102℃; IR (KBr) 3079, 3004, 1637, 1608, 1510, 1466, 1387, 1253, 1178, 1028, 836, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.25 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68-7.63 (m, 3H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.41-7.37 (m, 1H), 7.00 (m, 2H), 4.85 (m, 1H), 4.60 (s, 1H), 3.88 (s, 3H), 3.24 (s, 2H), 1.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 178.1, 162.4, 161.2, 156.1, 144.0, 133.3, 130.0, 126.1, 125.6, 124.7, 122.8, 118.9, 117.8, 113.8, 110.2, 55.4, 33.7, 23.5; HRMS m/z (ESI) calcd for $C_{20}H_{18}O_3$ $(M + H)^+$ 307.1334, found 307.1331.

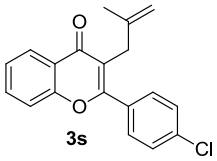


3r

2-(4-fluorophenyl)-3-(2-methylallyl)-4*H*-chromen-4-one (**3r**)

yellow solid; mp: 76-78℃; IR (KBr) 3061, 2967, 1637, 1605, 1508, 1469, 1382, 1227, 1163, 854, 758 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.26 (m, 1H), 7.73-7.66 (m, 3H), 7.47 (m, 1H),

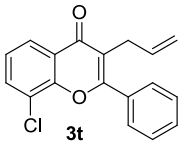
7.43-7.39 (m, 1H), 7.18 (m, 2H), 4.84 (m, 1H), 4.58 (d, *J* = 0.7 Hz, 1H), 3.21 (s, 2H), 1.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.9, 163.8 (d, J_{C-F} = 249.9 Hz), 161.4, 156.1, 143.8, 133.5, 130.5 (d, J_{C-F} = 8.49 Hz), 129.4, 125.5 (d, J_{C-F} = 123.9 Hz), 122.7, 119.5, 117.8, 115.7 (d, J_{C-F} = 21.66 Hz), 115.5, 110.3, 33.5, 23.4; HRMS m/z (ESI) calcd for $C_{19}H_{15}O_2F$ $(M + H)^+$ 295.1134, found 295.1135.



3s

2-(4-chlorophenyl)-3-(2-methylallyl)-4*H*-chromen-4-one (**3s**)

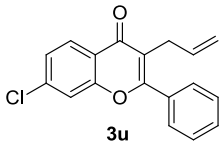
white solid; mp: 112-114℃; IR (KBr) 3076, 2890, 1638, 1619, 1464, 1385, 1126, 1091, 839, 764 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.25 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70-7.64 (m, 3H), 7.49-7.46 (m, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 4.84 (dt, *J* = 2.7, 1.3 Hz, 1H), 4.58 (d, *J* = 0.6 Hz, 1H), 3.21 (s, 2H), 1.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.9, 161.2, 156.1, 143.8, 136.6, 133.6, 131.6, 129.7, 128.8, 126.2, 125.0, 122.8, 119.7, 117.8, 110.4, 33.5, 23.4; HRMS m/z (ESI) calcd for $C_{19}H_{15}O_2Cl$ $(M + H)^+$ 311.0839, found 311.0836.



3t

3-allyl-8-chloro-2-phenyl-4*H*-chromen-4-one (**3t**)

yellow solid; mp: 98-100℃; IR (KBr) 3065, 2978, 1650, 1623, 1439, 1379, 1166, 1115, 913, 768, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.16 (m, 1H), 7.78-7.72 (m, 3H), 7.53 (m, 3H), 7.34 (m, 1H), 6.08 (m, 1H), 5.08 (m, 2H), 3.36 (dt, *J* = 5.6, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.6, 162.2, 151.9, 135.6, 133.6, 132.7, 130.7, 128.8, 128.5, 124.8, 124.6, 124.1, 123.0, 119.6, 115.7, 30.0; HRMS m/z (ESI) calcd for $C_{18}H_{13}O_2Cl$ $(M + H)^+$ 297.0682, found 297.0680.



3u

3-(but-3-en-2-yl)-7-chloro-2-phenyl-4*H*-chromen-4-one (**3u**)

yellow solid; mp: 81-83℃; IR (KBr) 3087, 2966, 1655, 1605, 1427, 1371, 1130, 1075, 927, 854, 767, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.19 (d, *J* = 8.6 Hz, 1H), 7.66 (m, 2H), 7.53-7.49 (m, 4H), 7.36 (m, 1H), 6.04 (m, 1H), 5.07 (m, 2H), 3.30 (dt, *J* = 5.7, 1.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.3, 162.5, 156.3, 139.5, 135.7, 132.8, 130.6, 128.5, 128.5, 127.4, 125.7, 121.4, 119.8, 117.9, 115.6, 30.0; HRMS m/z (ESI) calcd for $C_{18}H_{13}O_2Cl$ $(M + H)^+$ 297.0682, found 297.0679.

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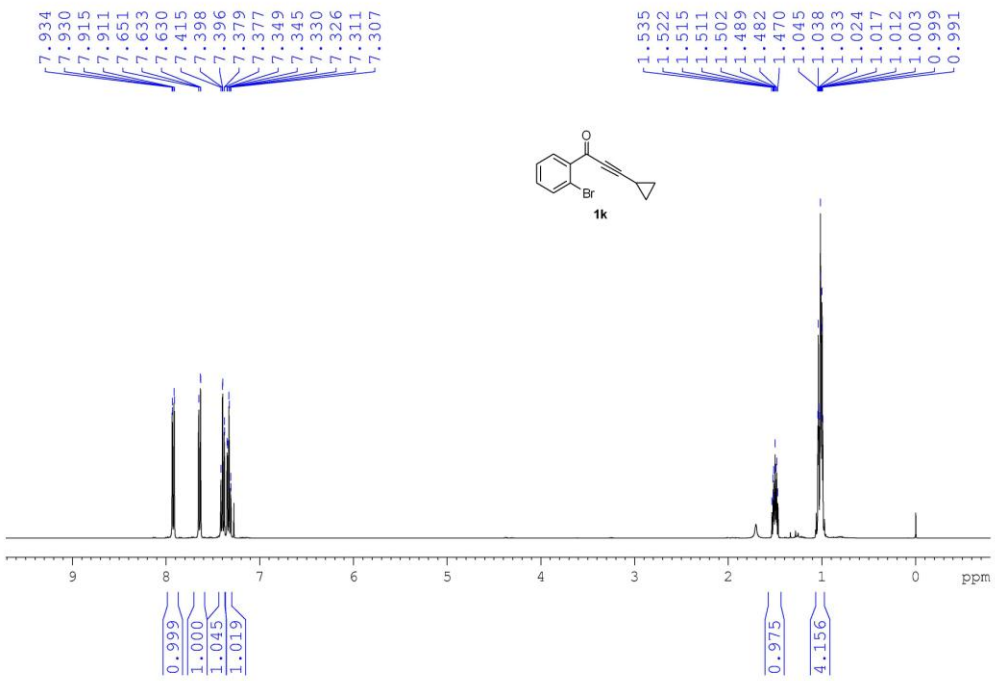
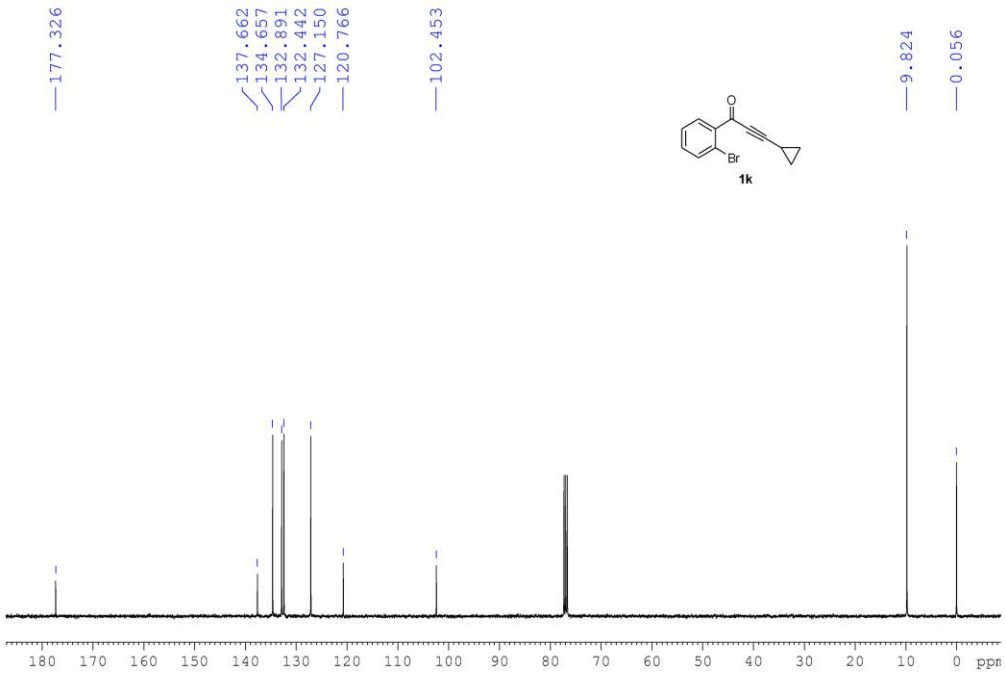
1 (a) V. O. Iaroshenko, S. Mkrtchyan and A. Villinger, *Synthesis*, 2013, **45**, 208; (b) Z. She, D. Niu, L. Chen, M. A. Gunawan, X. Shanja, W. H. Hersh and Y. Chen, *J. org. chem.* 2012, **77**, 3627. (c) S. S. Palimkar, P. H. Kumar, N. R. Jogdand, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *Tetrahedron lett.*, 2012, **47**, 5527. (d) S. Santra, K. Dhara, P. Ranjan, P. Bera, J. Dash and S. K. Mandal, *Green Chem.*, 2011, ***13***, 3238.

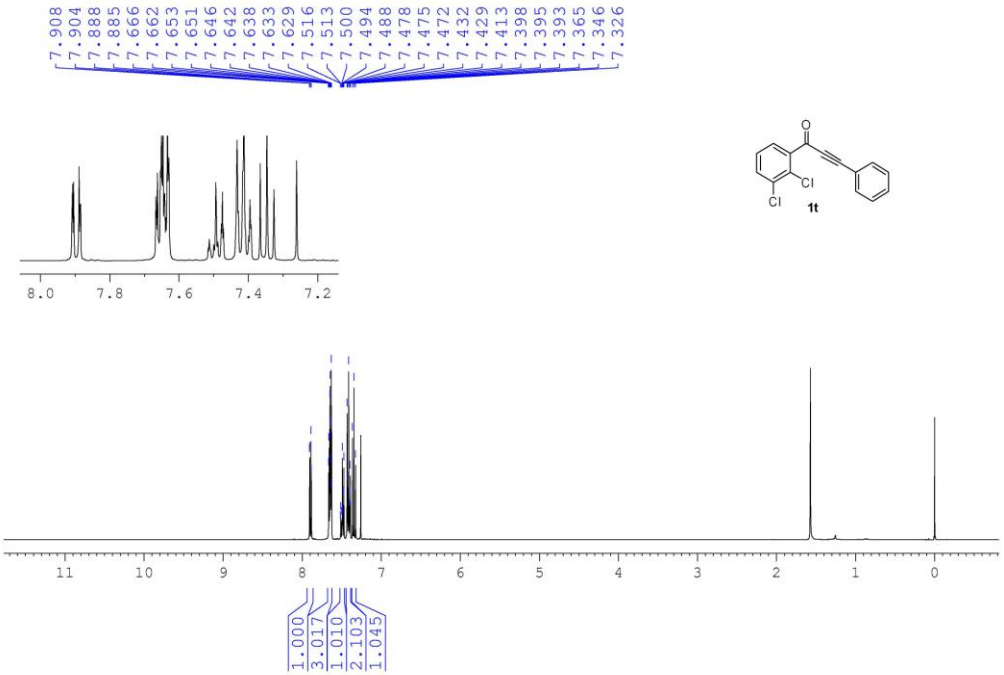
^{1}H NMR spectrum of **1k**



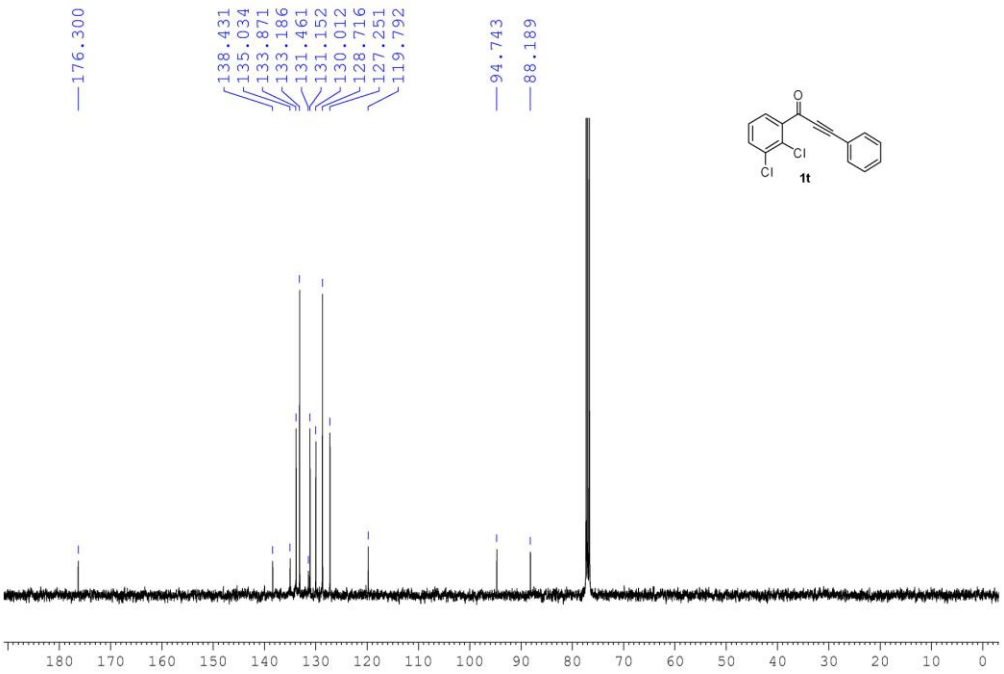
^{13}C NMR spectrum of **1k**

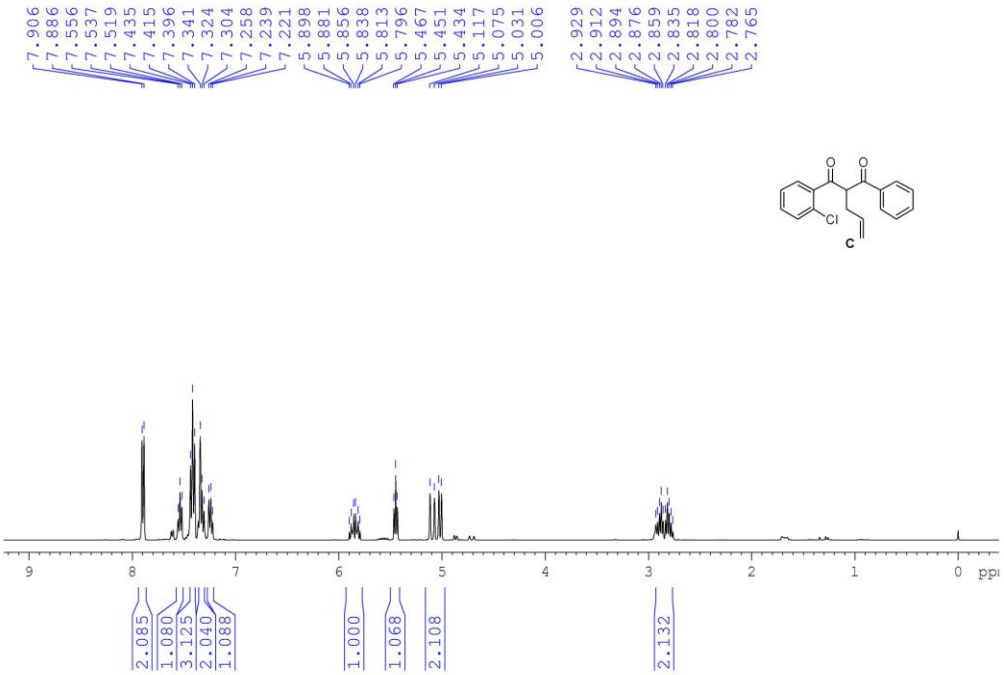


^{1}H NMR spectrum of **1t**



^{13}C NMR spectrum of **1t**

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7.239
7.221
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5.881
5.856
5.838
5.813
5.796
5.467
5.451
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5.117
5.075
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2.835
2.818
2.800
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2.765
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O
Cl
c
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8
7
6
5
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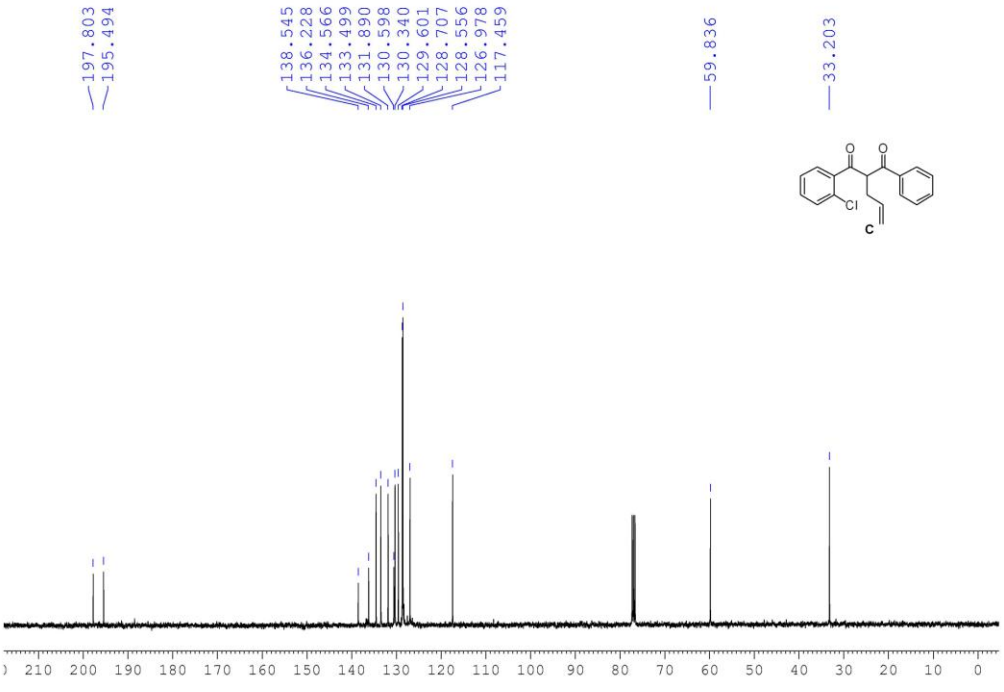
2.132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Cl
c
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200
190
180
170
160
150
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130
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110
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70
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50
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30
20
10
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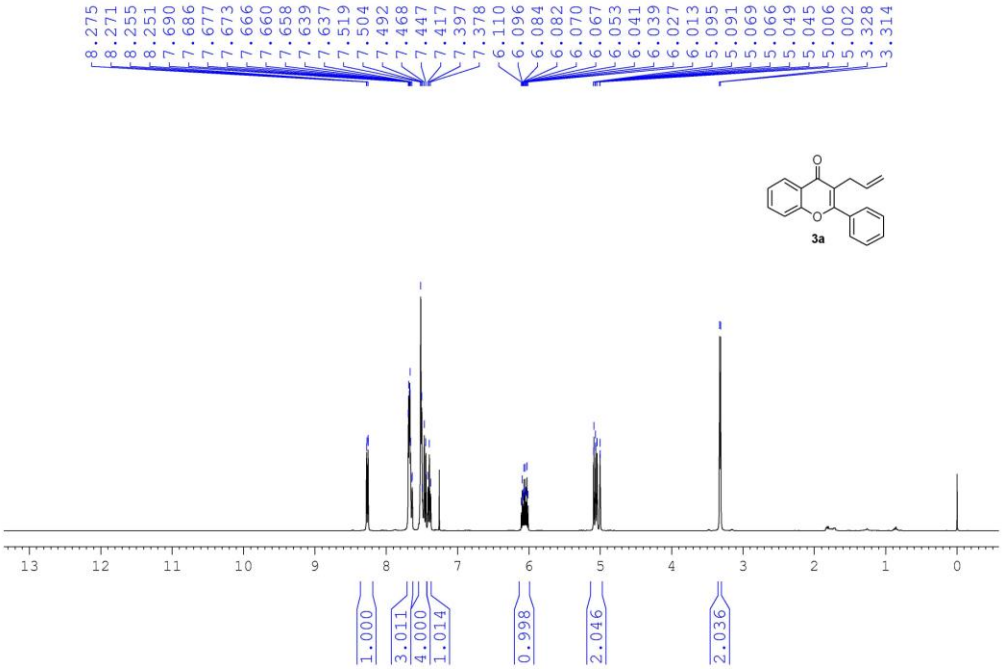
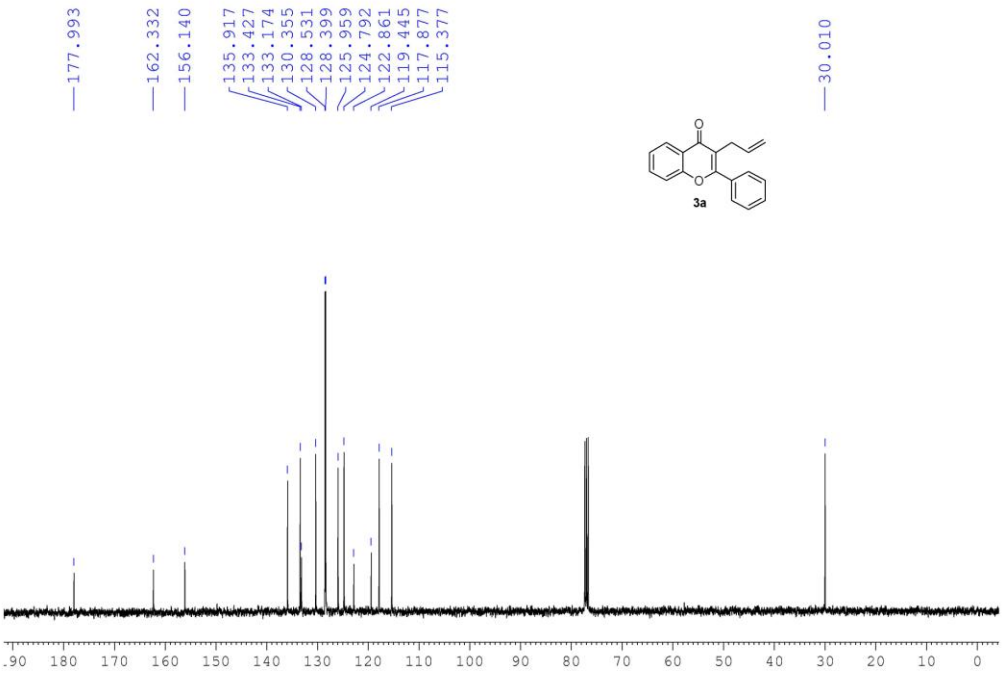
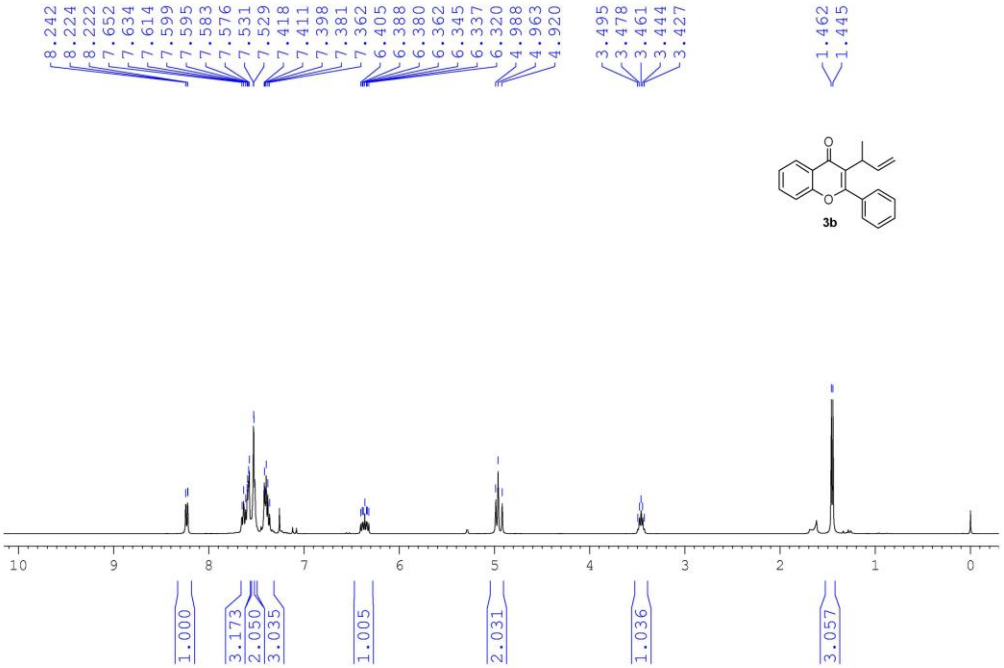
^{1}H NMR spectrum of **3a**



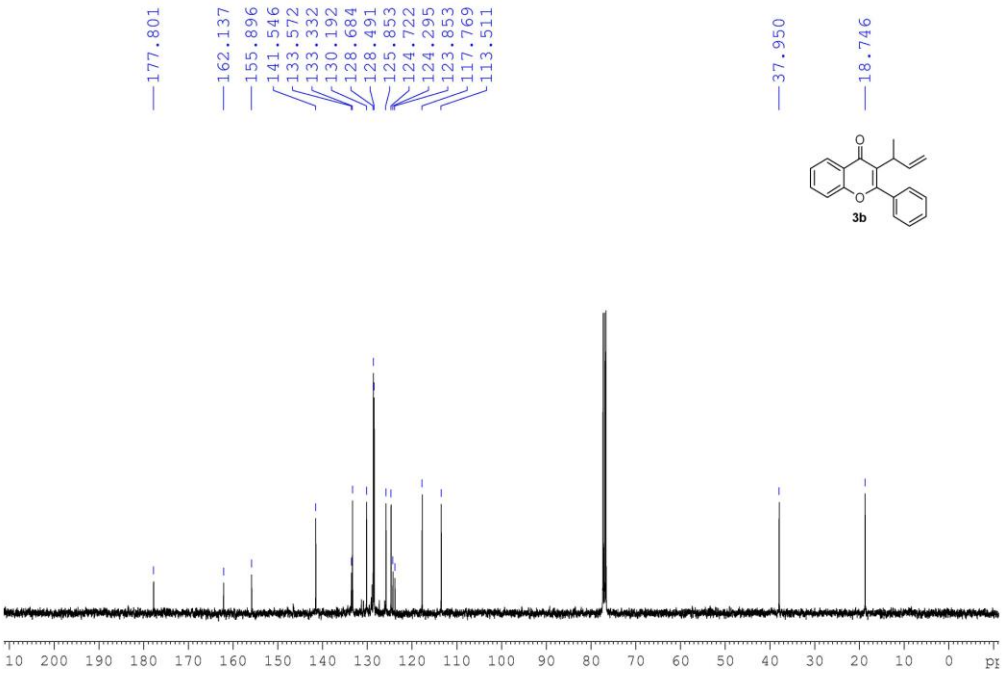
^{13}C NMR spectrum of **3a**



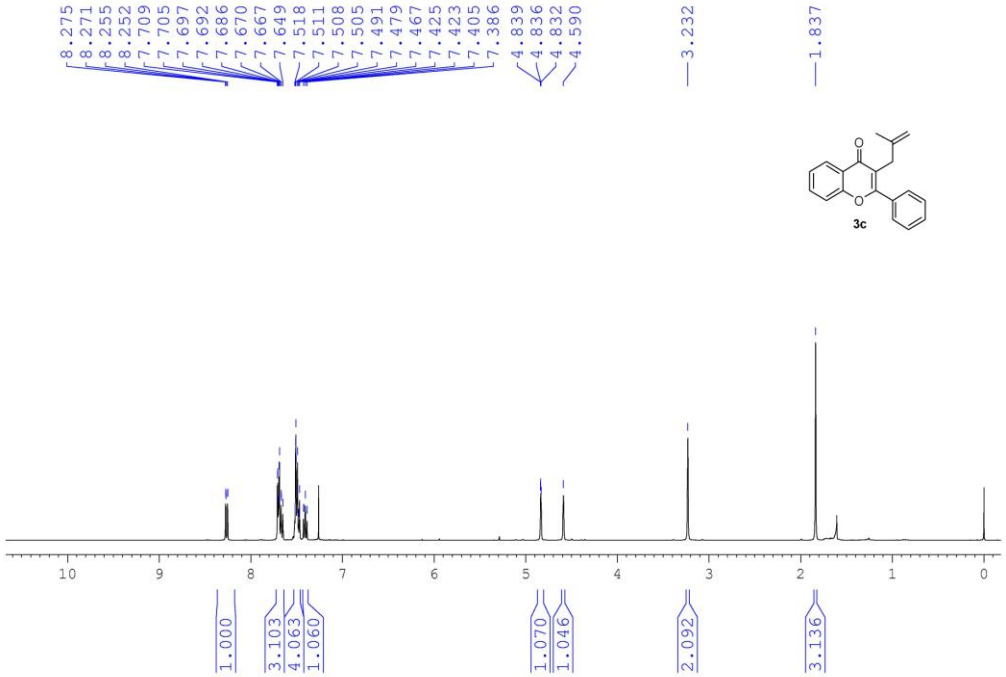
^{1}H NMR spectrum of **3b**



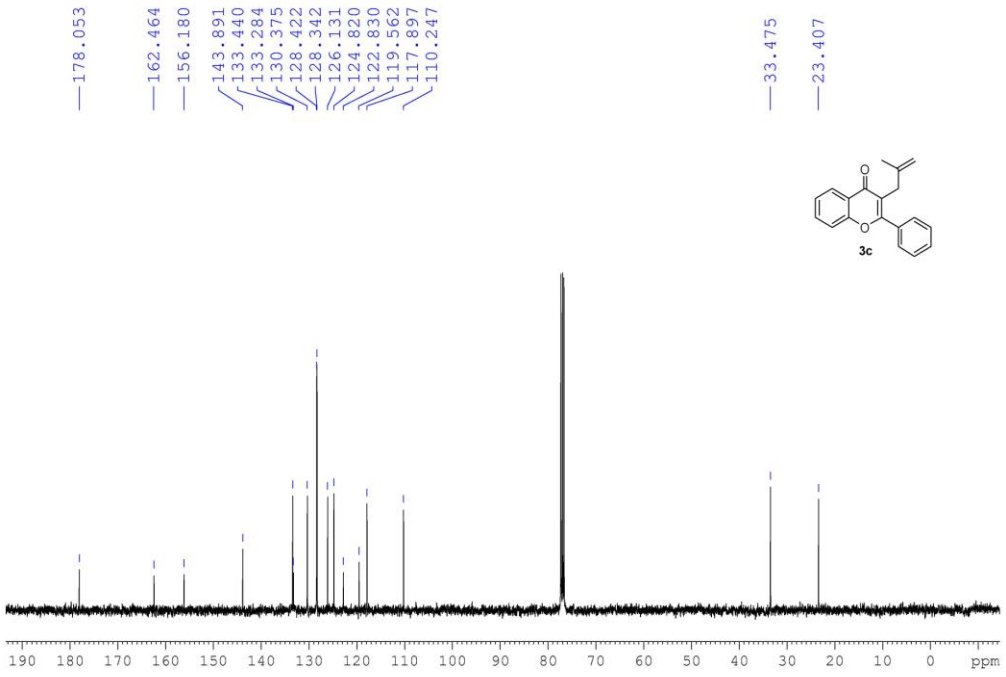
^{13}C NMR spectrum of **3b**



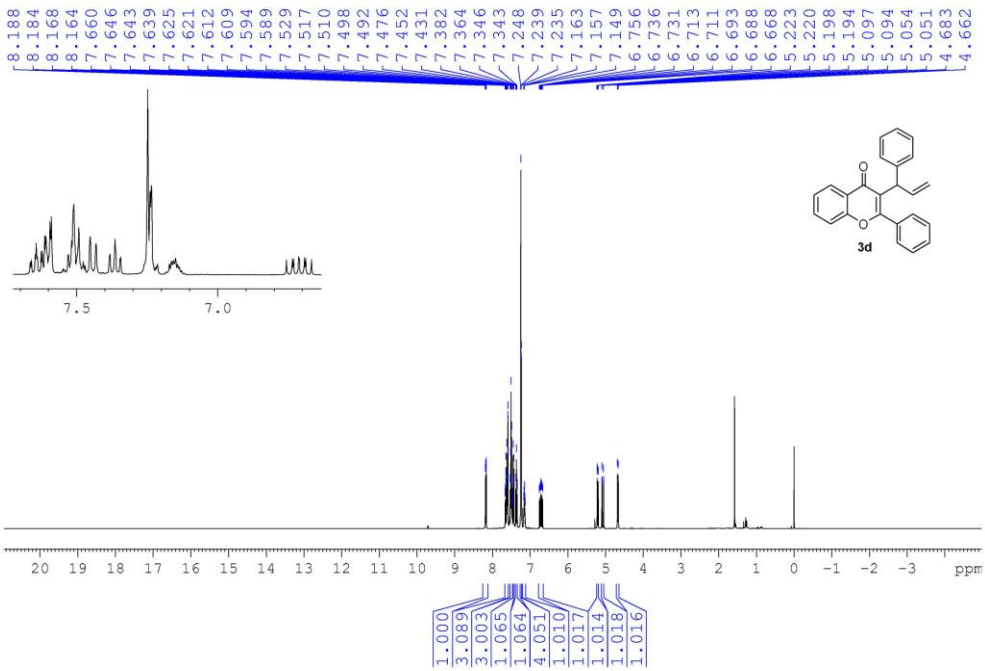
^{1}H NMR spectrum of **3c**



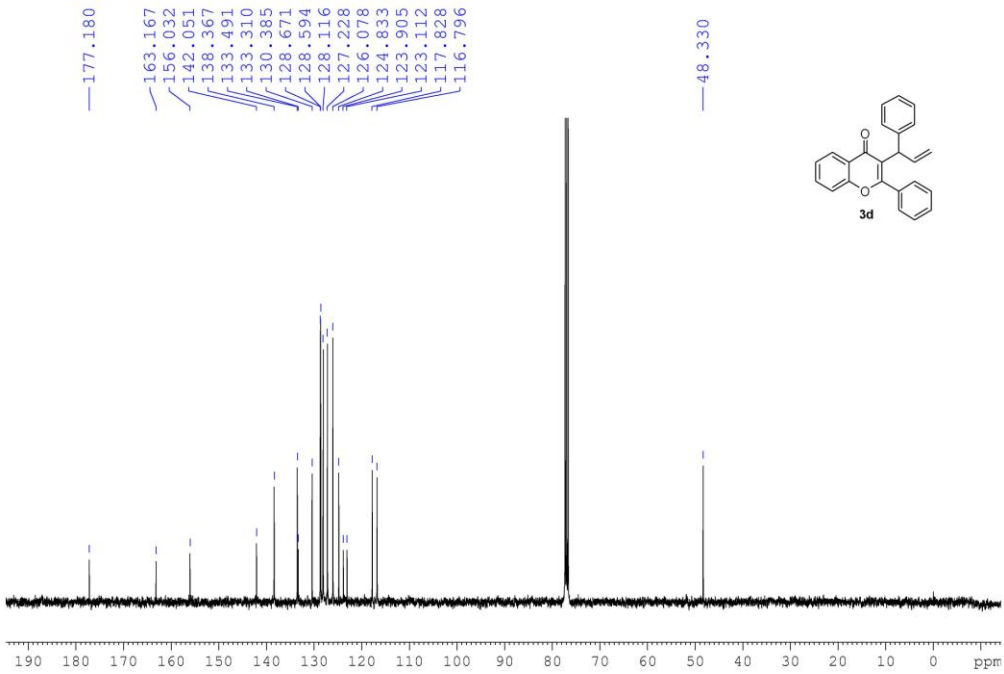
^{13}C NMR spectrum of **3c**



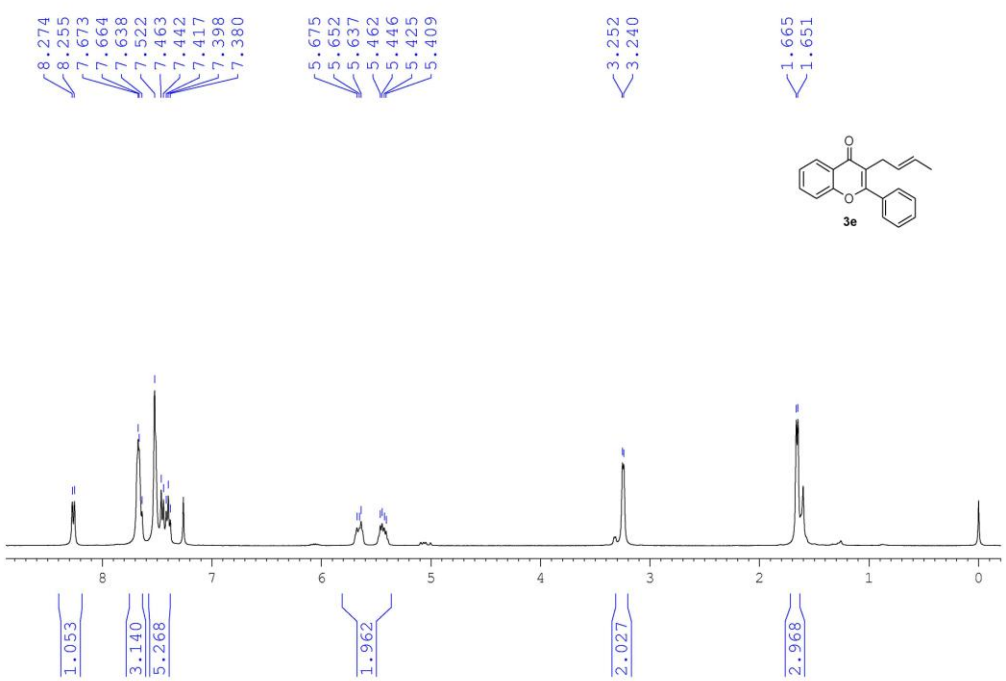
^{1}H NMR spectrum of **3d**



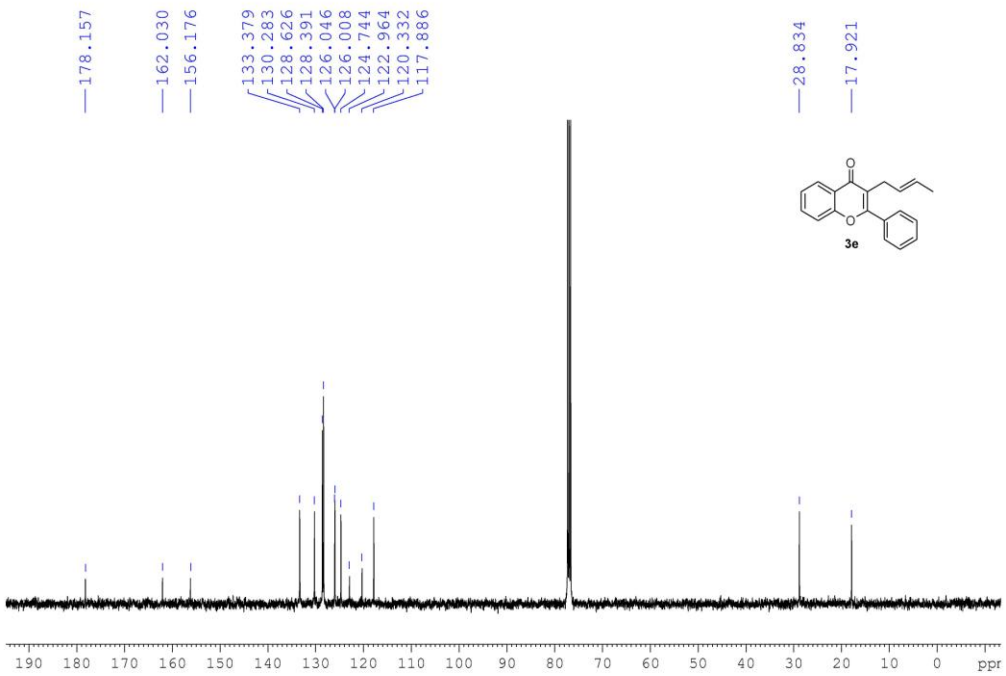
^{13}C NMR spectrum of **3d**



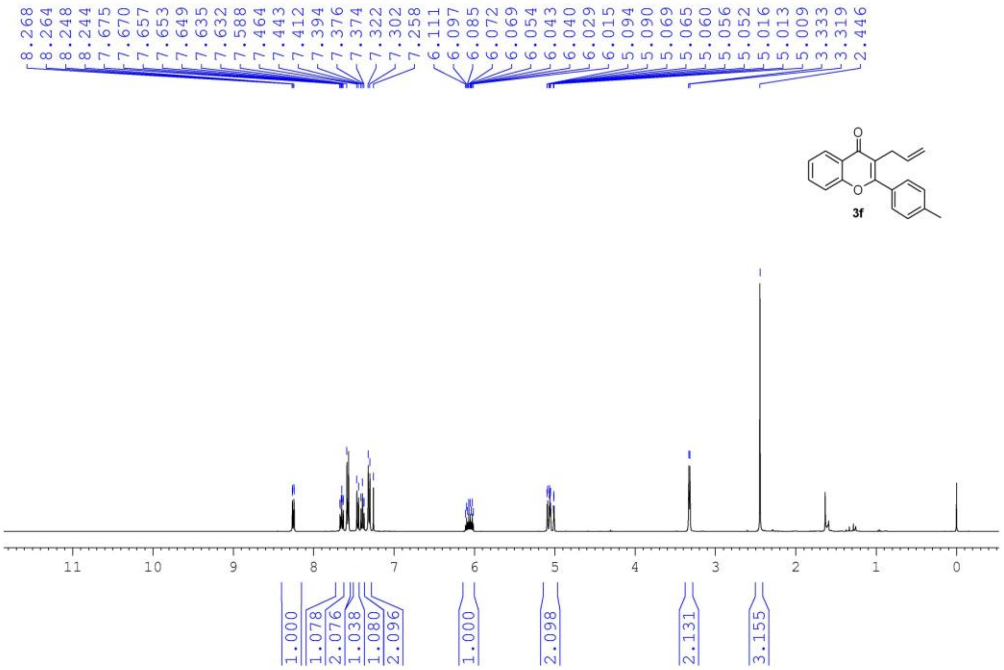
^{1}H NMR spectrum of **3e**



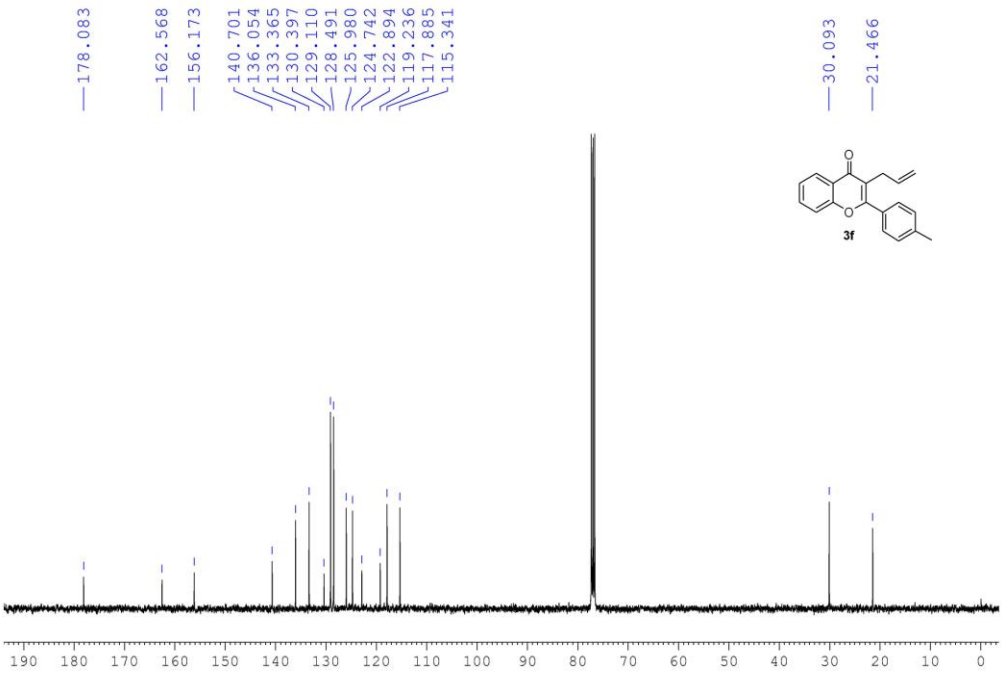
^{13}C NMR spectrum of **3e**



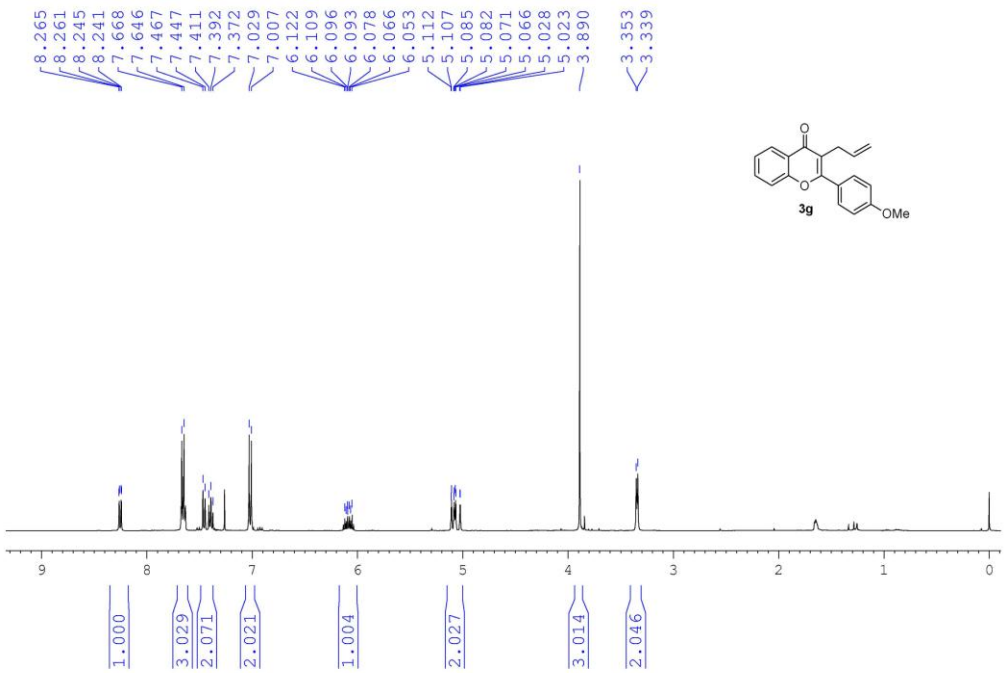
^{1}H NMR spectrum of **3f**



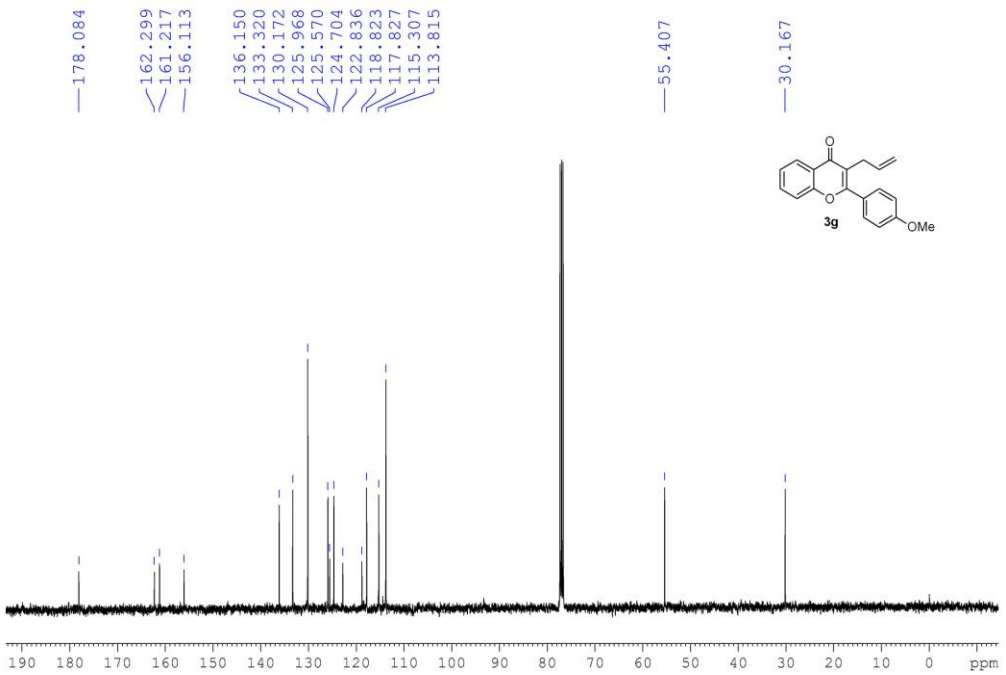
^{13}C NMR spectrum of **3f**



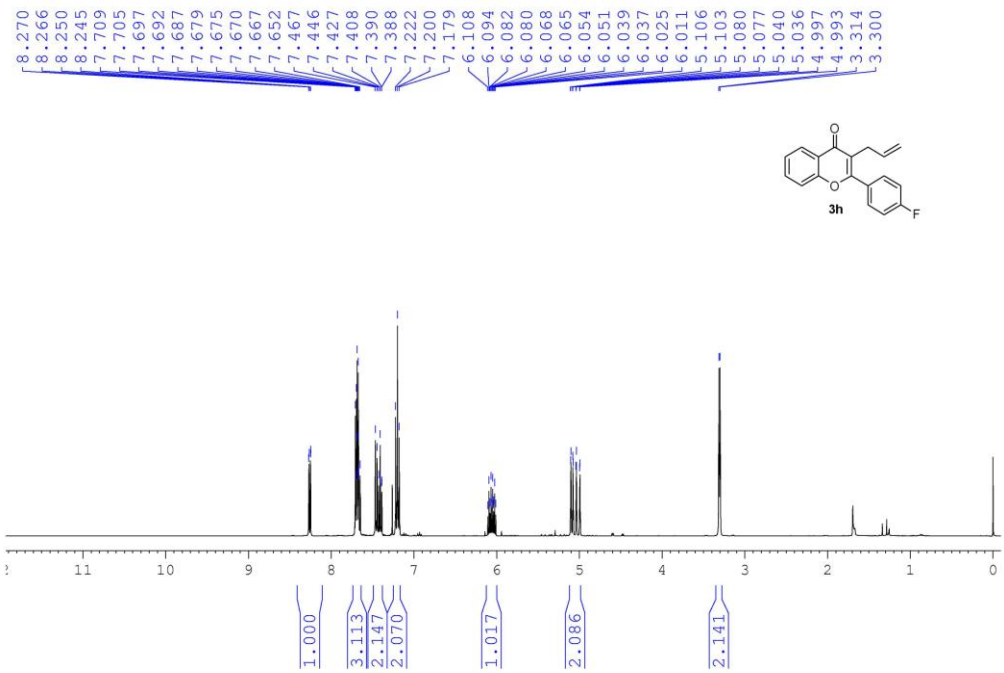
^{1}H NMR spectrum of **3g**



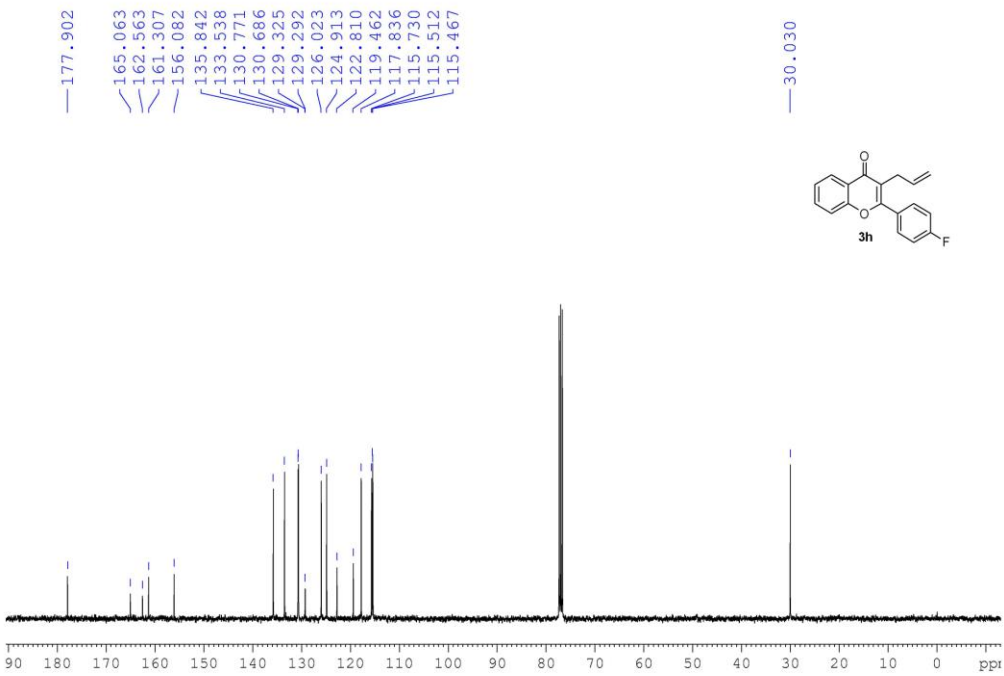
^{13}C NMR spectrum of **3g**



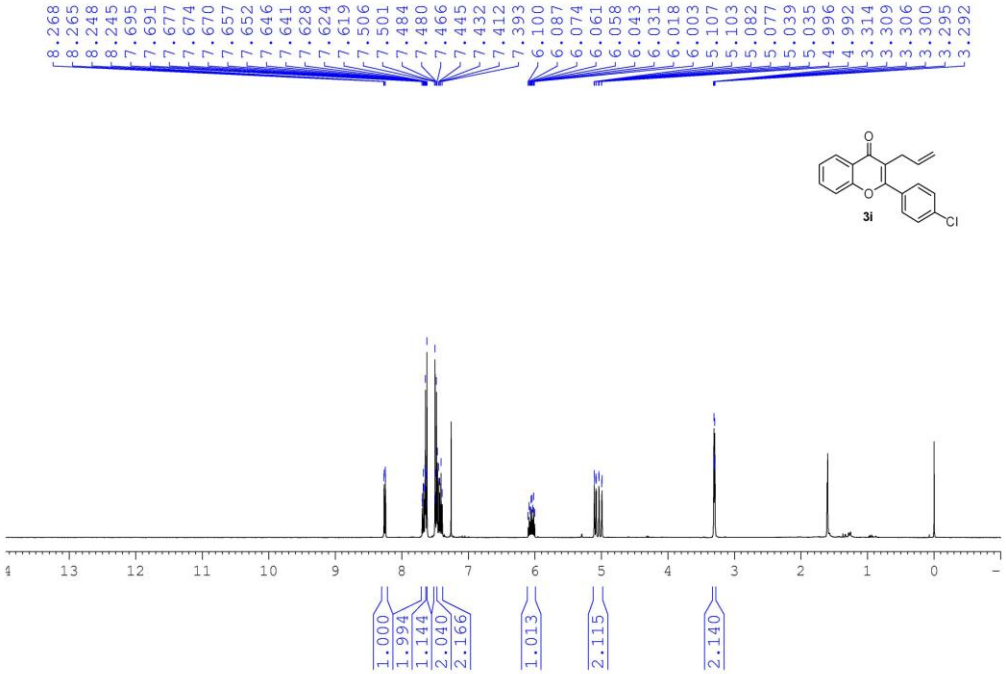
^{1}H NMR spectrum of **3h**



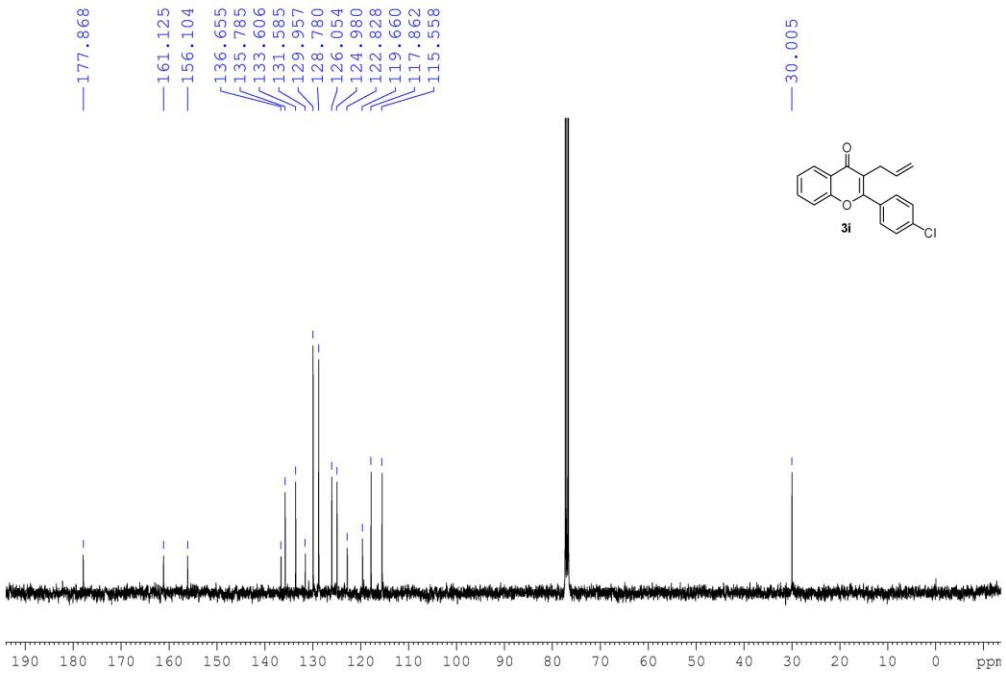
^{13}C NMR spectrum of **3h**



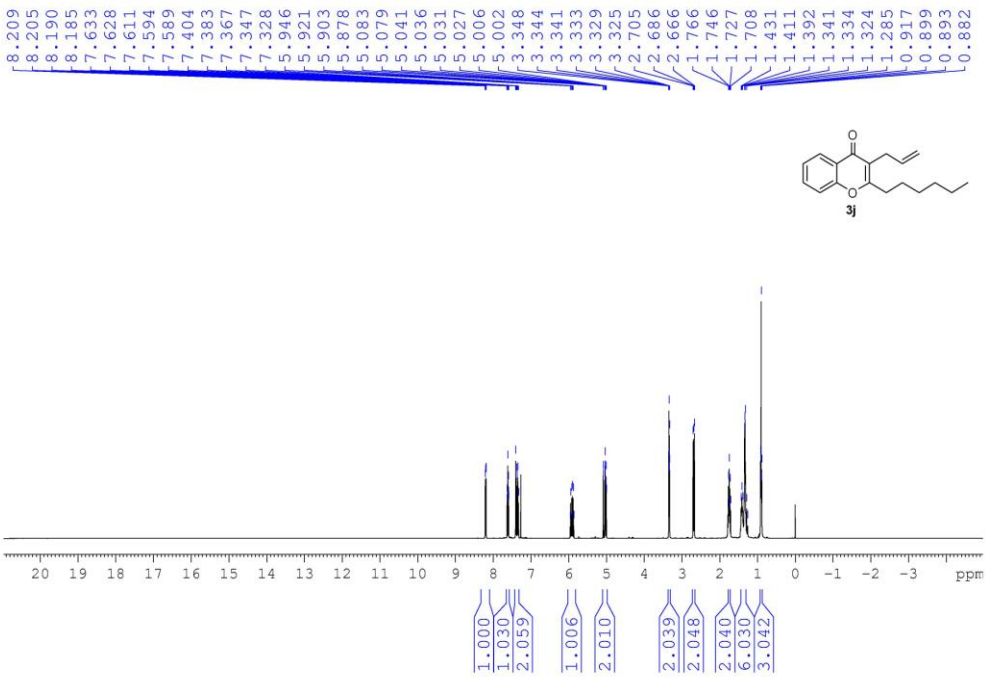
^{1}H NMR spectrum of **3i**



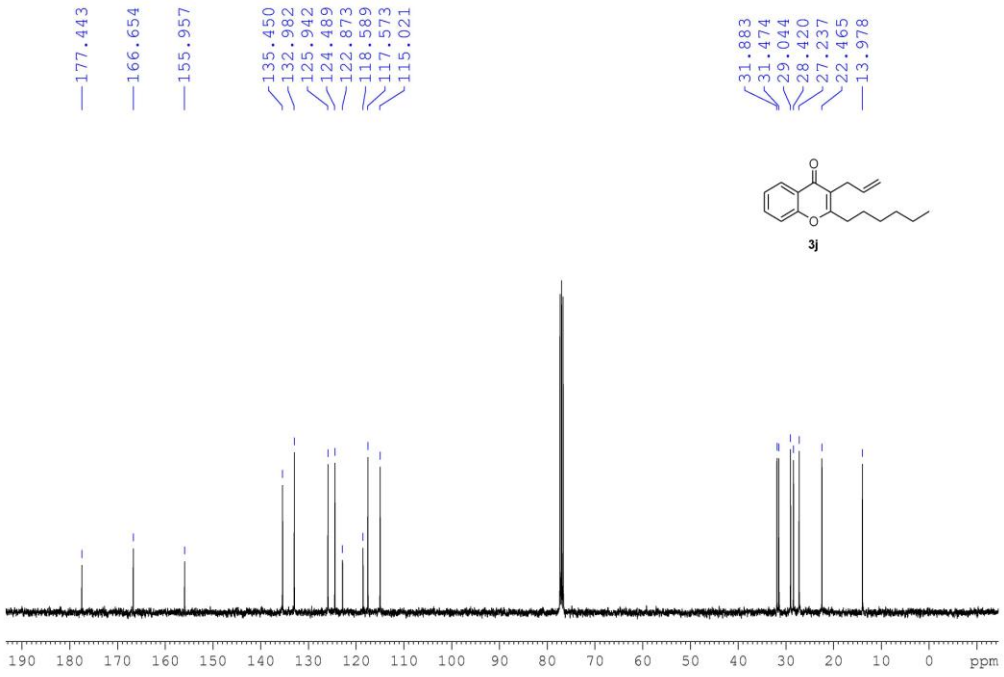
^{13}C NMR spectrum of **3i**



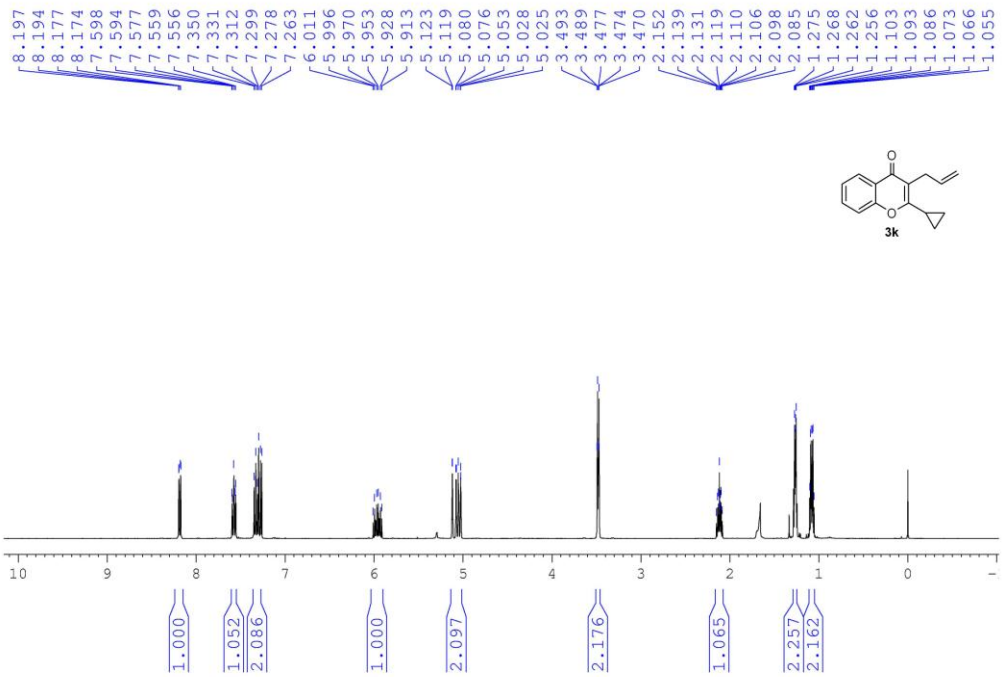
^{1}H NMR spectrum of **3j**



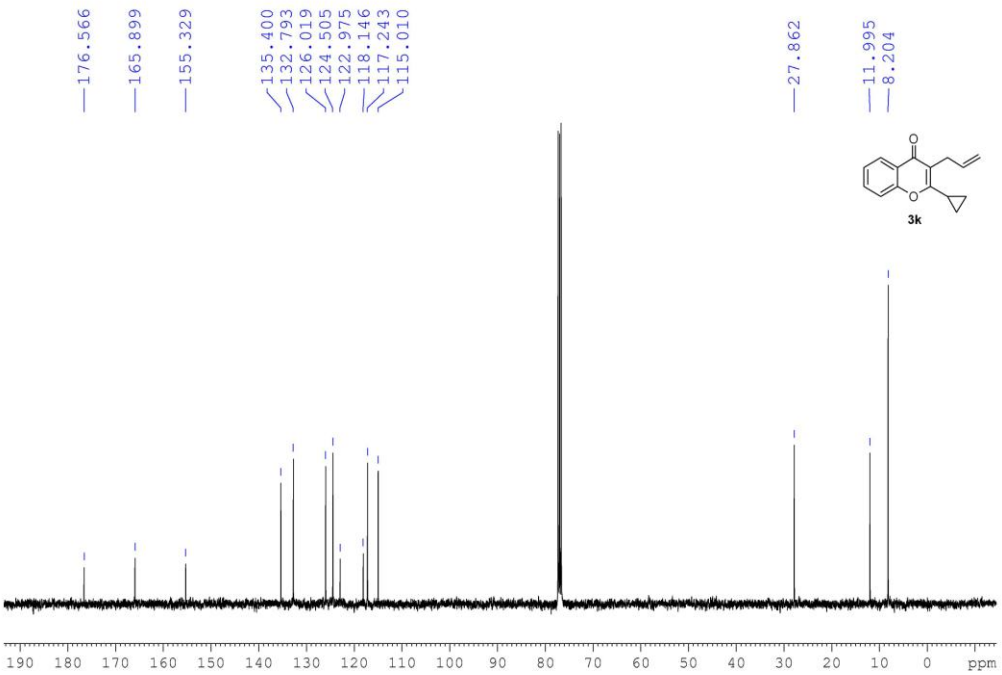
^{13}C NMR spectrum of **3j**



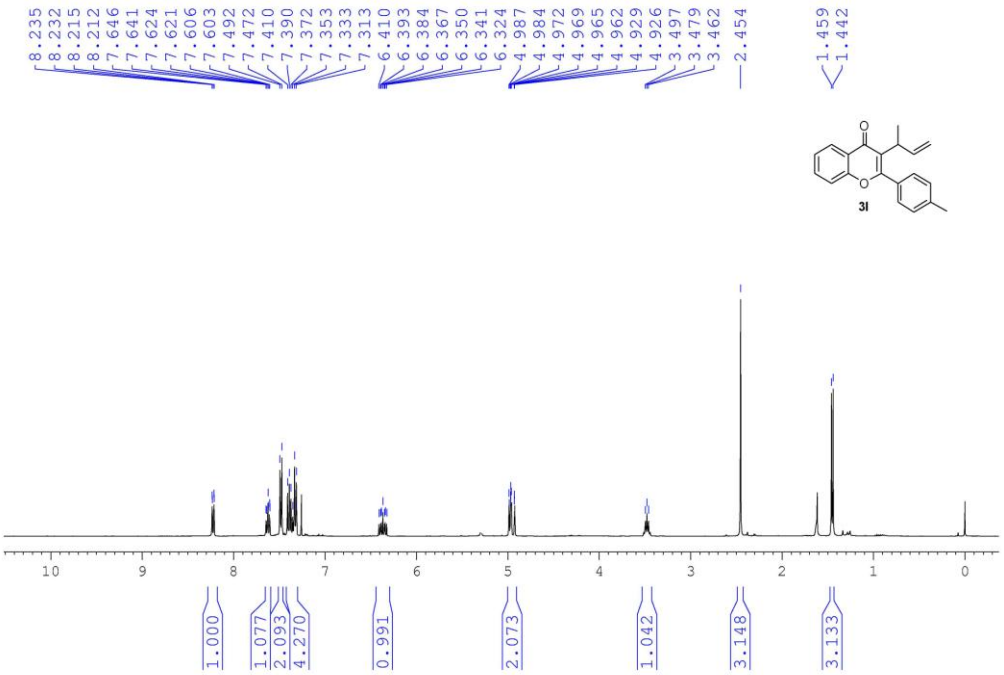
^{1}H NMR spectrum of **3k**



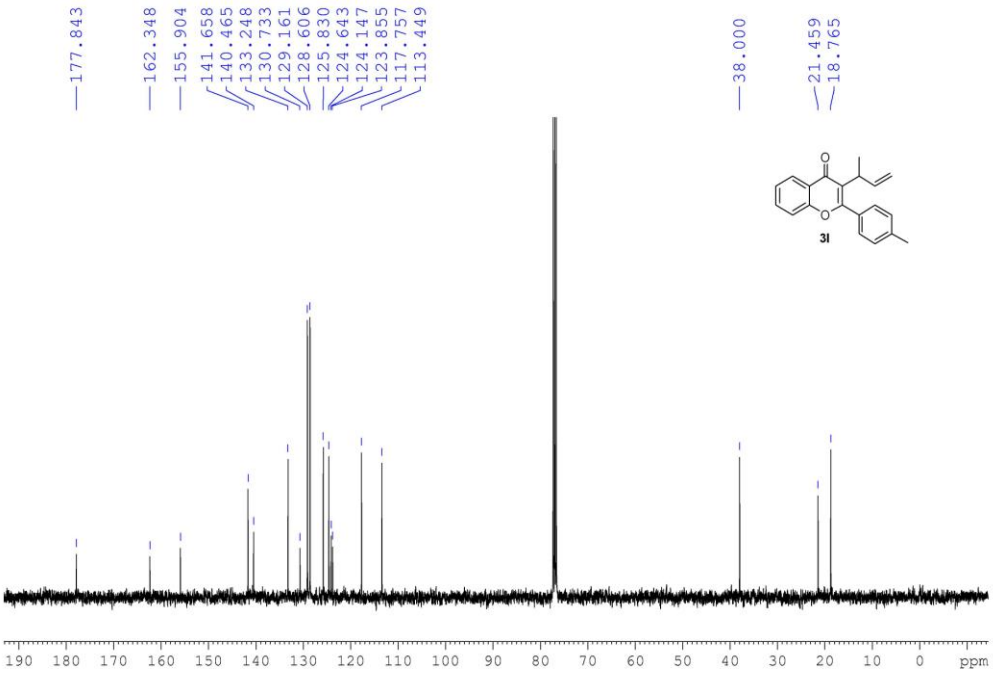
^{13}C NMR spectrum of **3k**



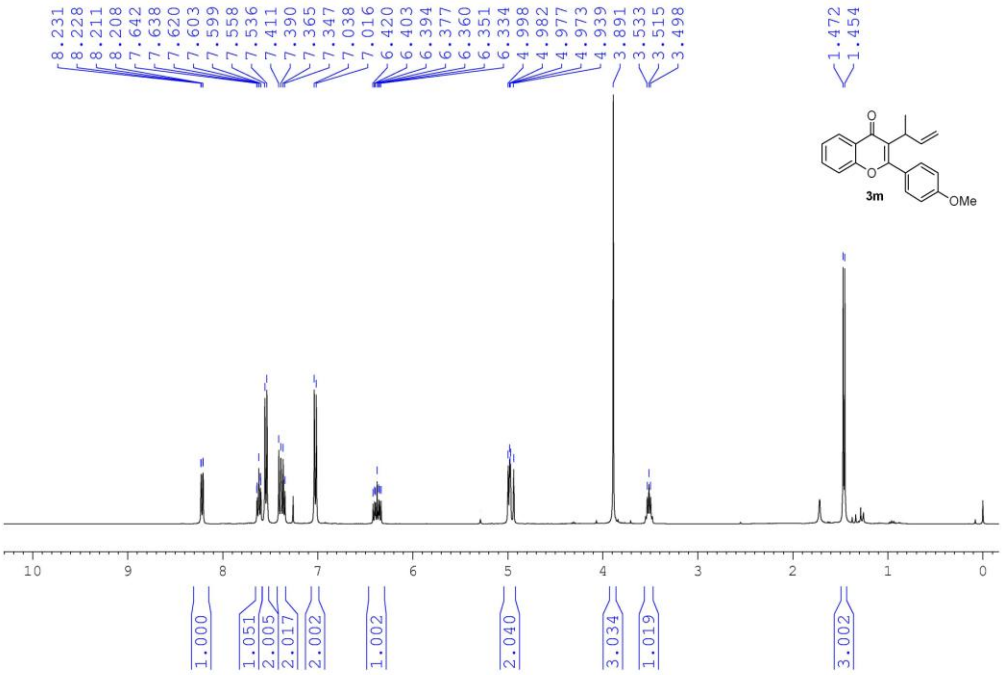
^{1}H NMR spectrum of **3l**



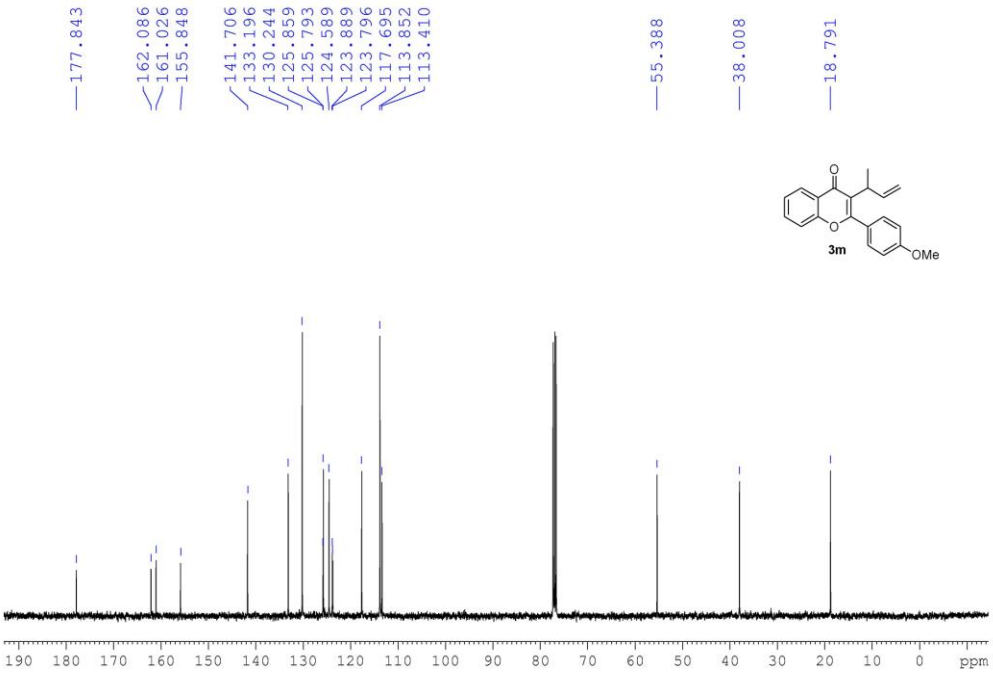
^{13}C NMR spectrum of **3l**



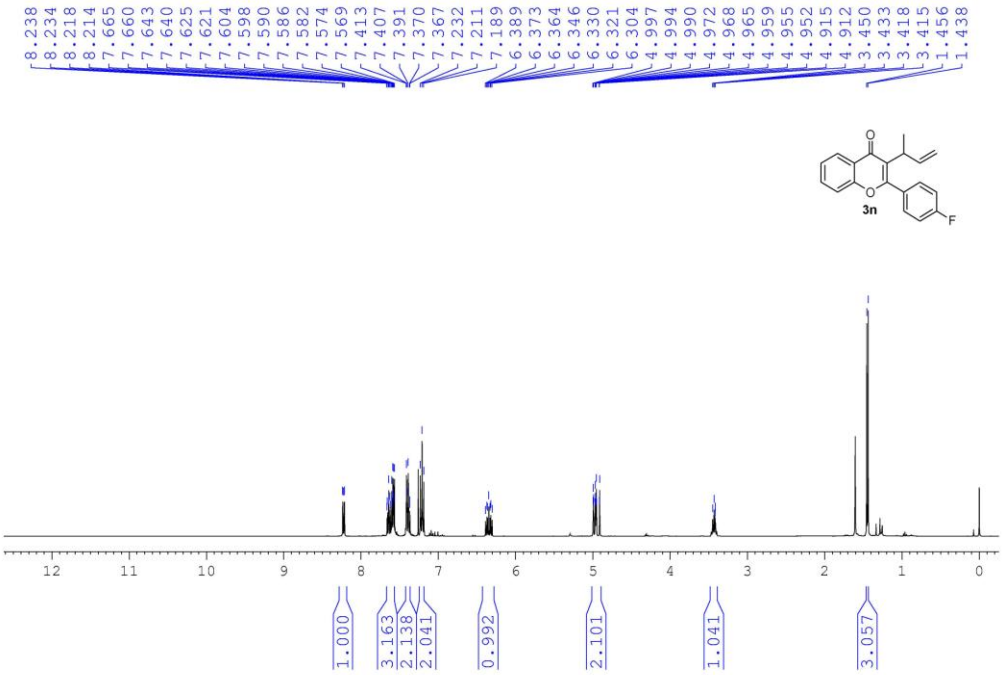
^{1}H NMR spectrum of **3m**



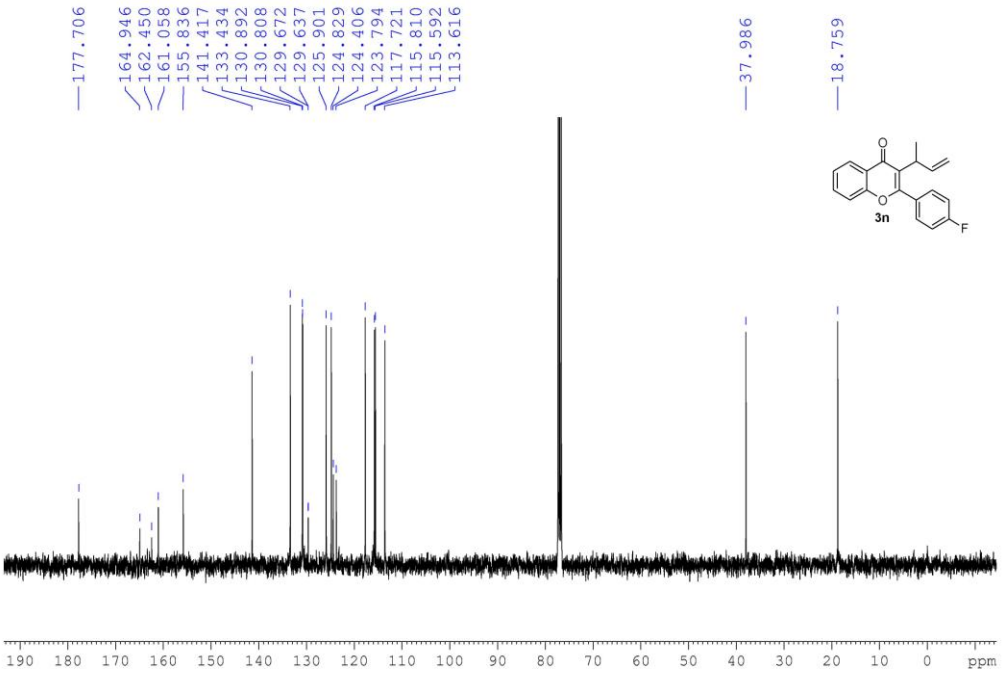
^{13}C NMR spectrum of **3m**



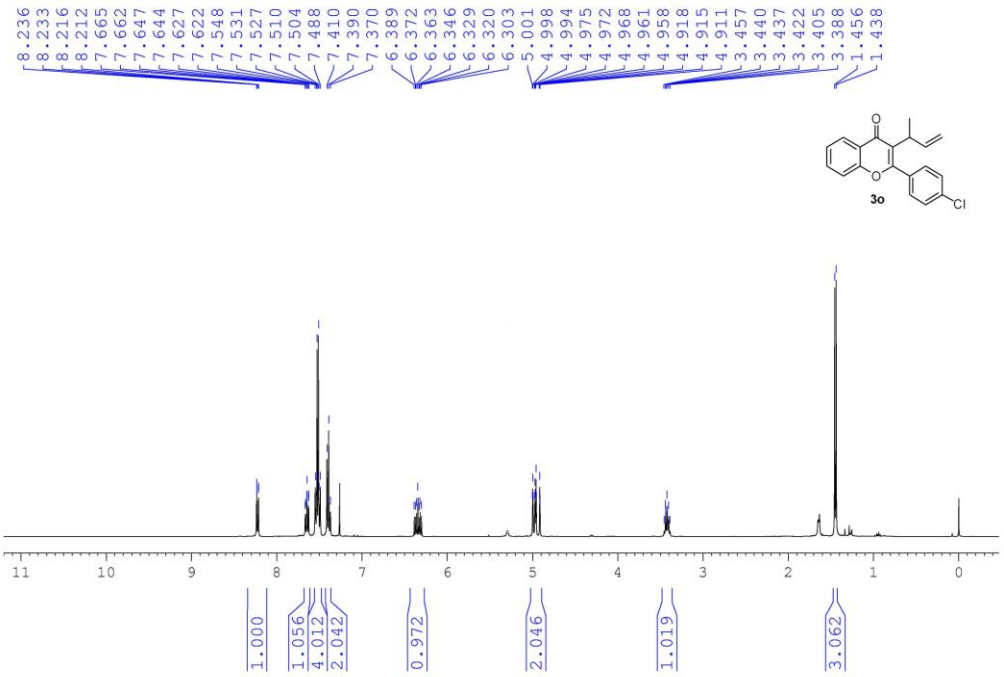
^{1}H NMR spectrum of **3n**



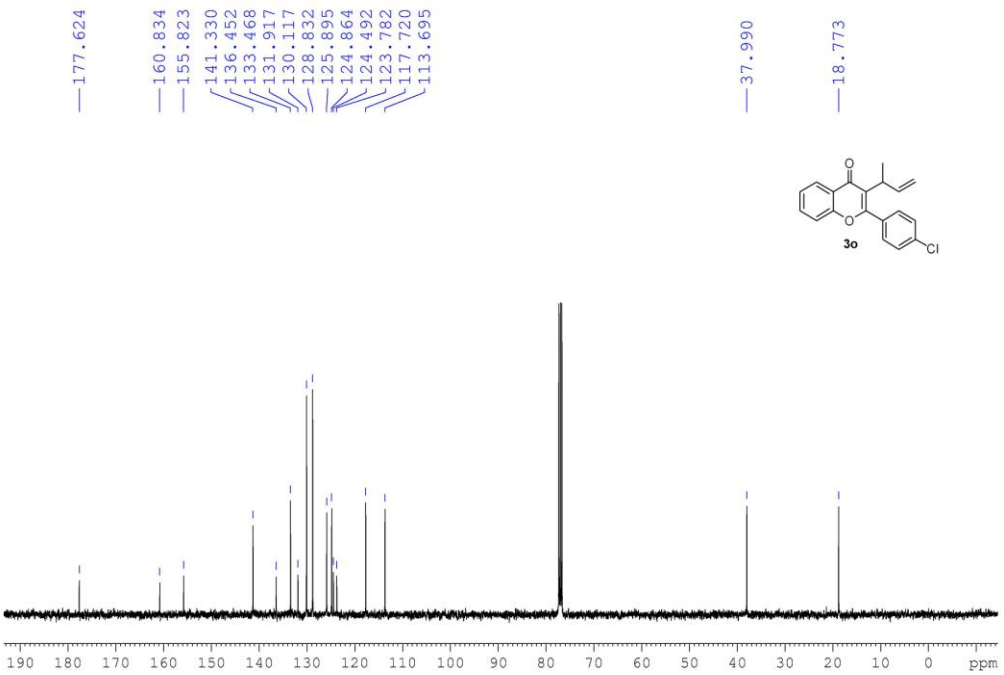
^{13}C NMR spectrum of **3n**



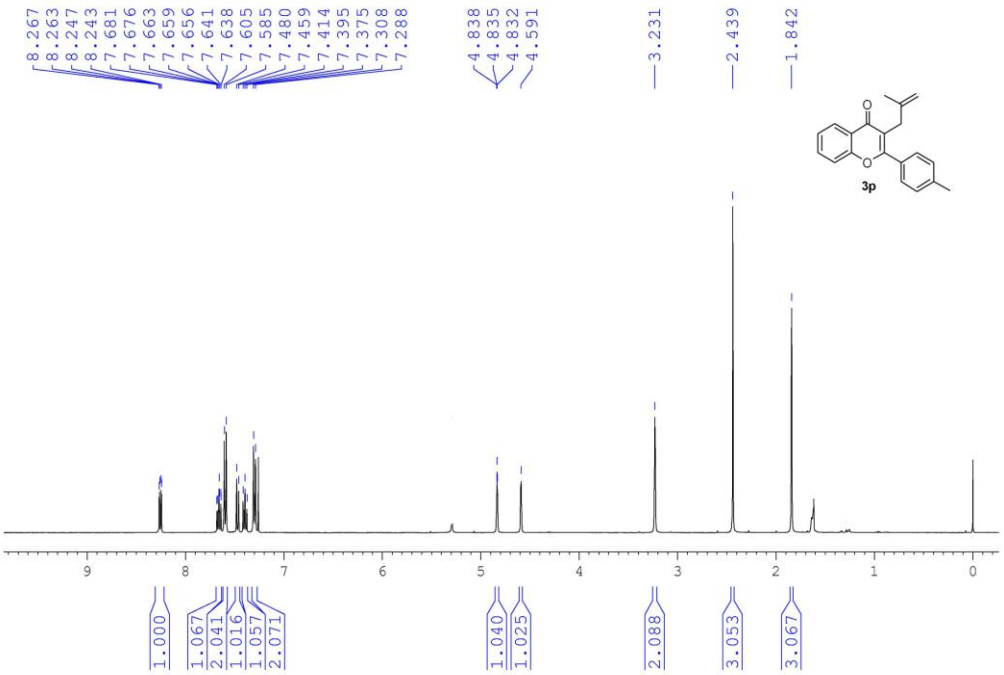
^{1}H NMR spectrum of **3o**



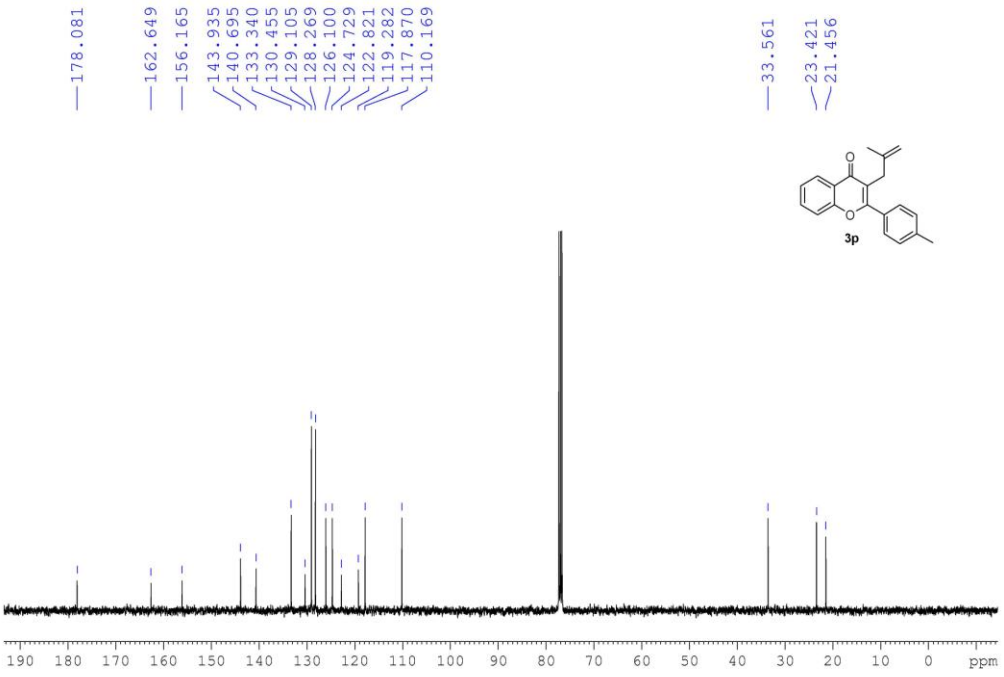
^{13}C NMR spectrum of **3o**



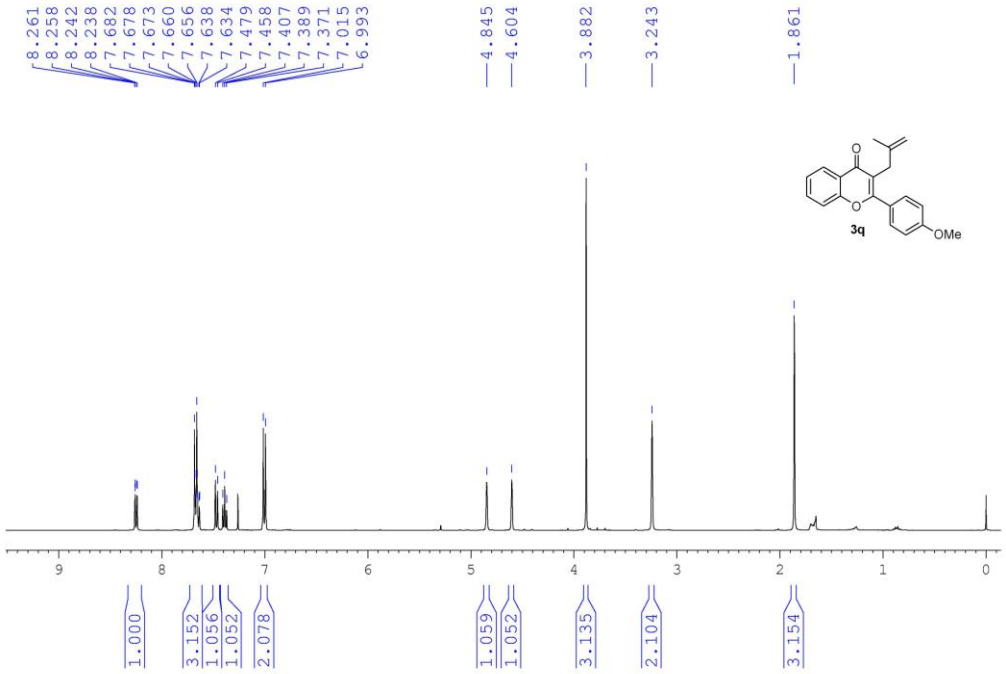
^{1}H NMR spectrum of **3p**



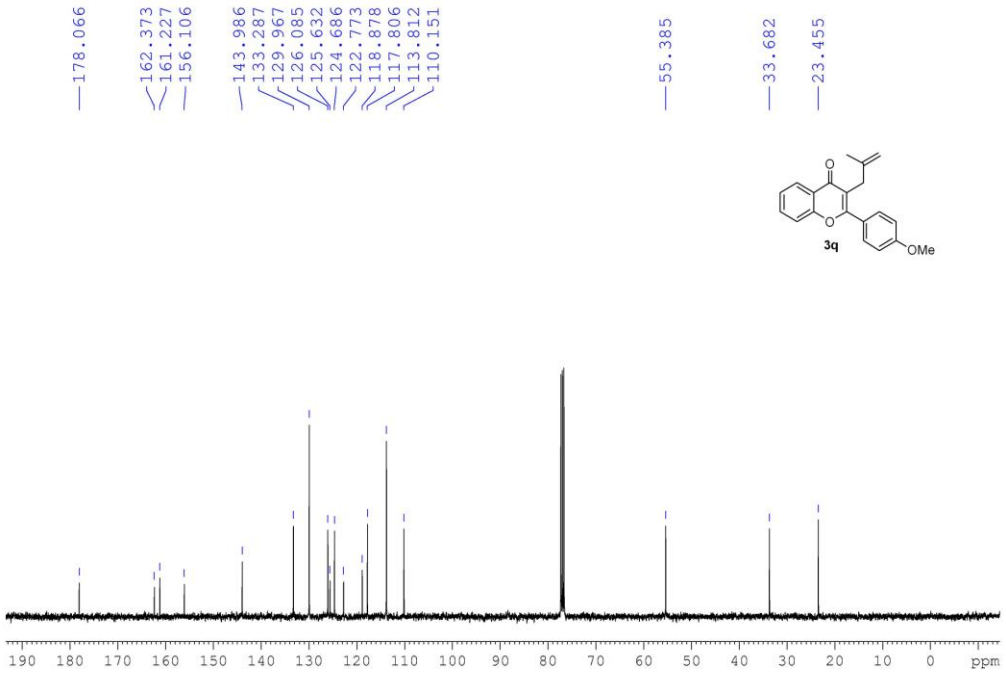
^{13}C NMR spectrum of **3p**



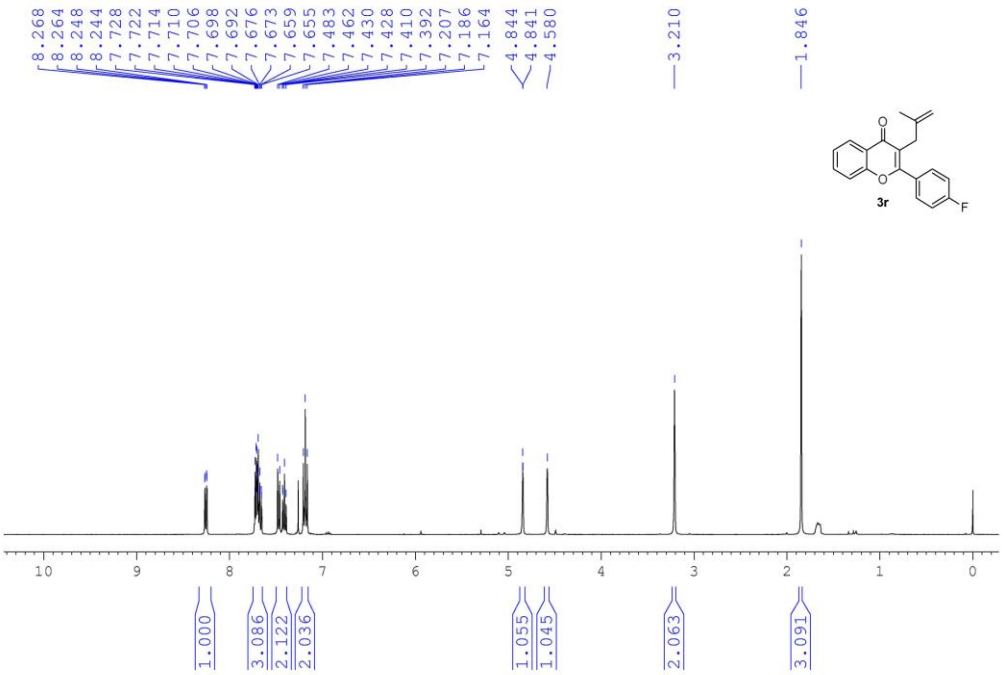
^{1}H NMR spectrum of **3q**



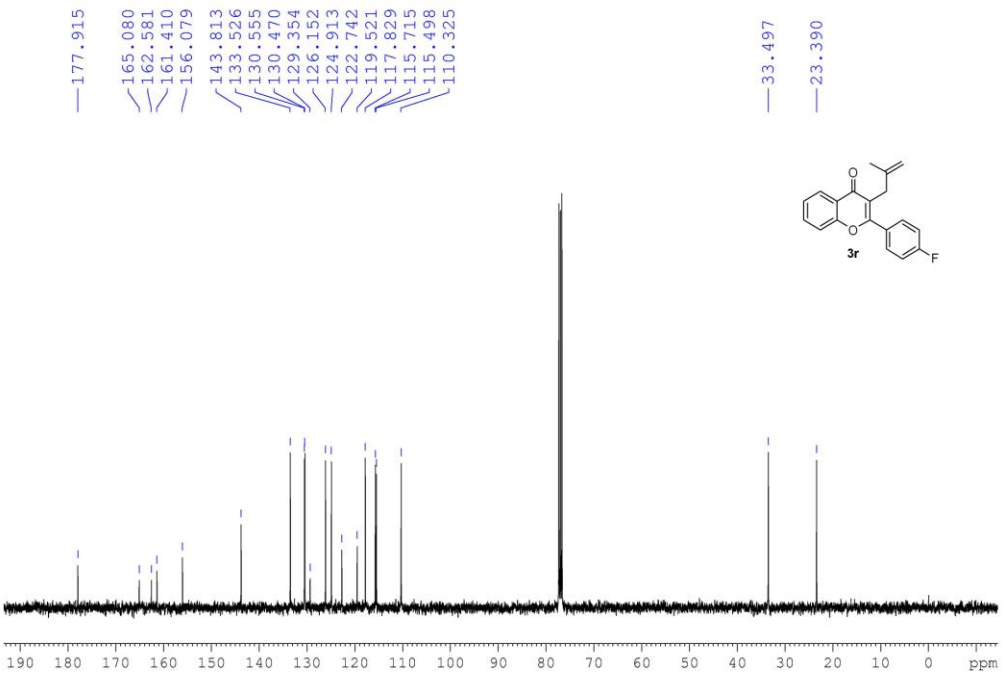
^{13}C NMR spectrum of **3q**



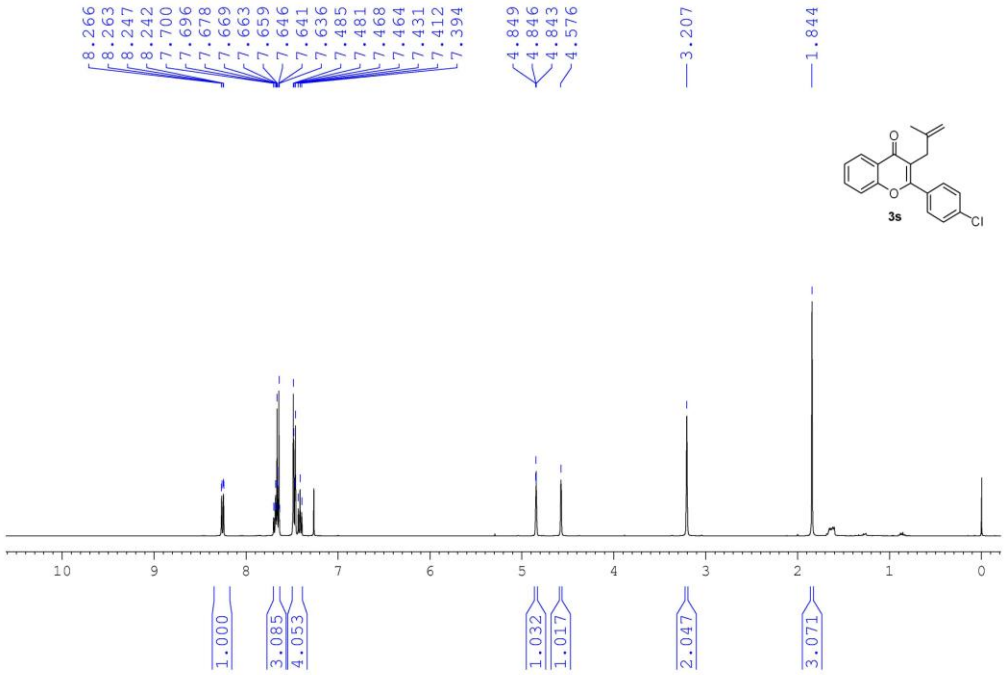
^{1}H NMR spectrum of **3r**



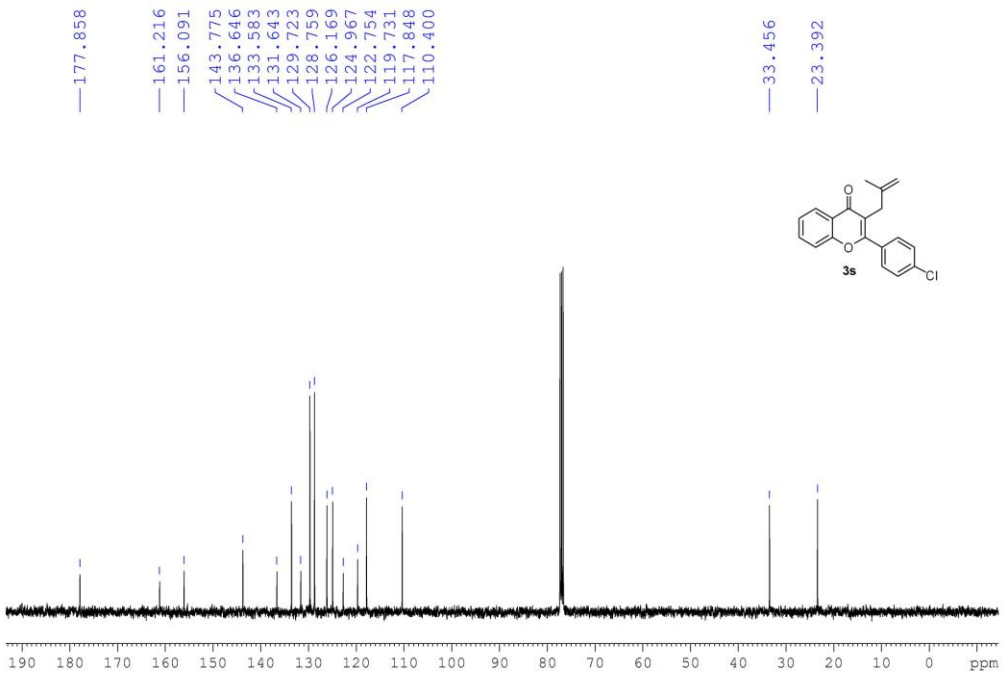
^{13}C NMR spectrum of **3r**



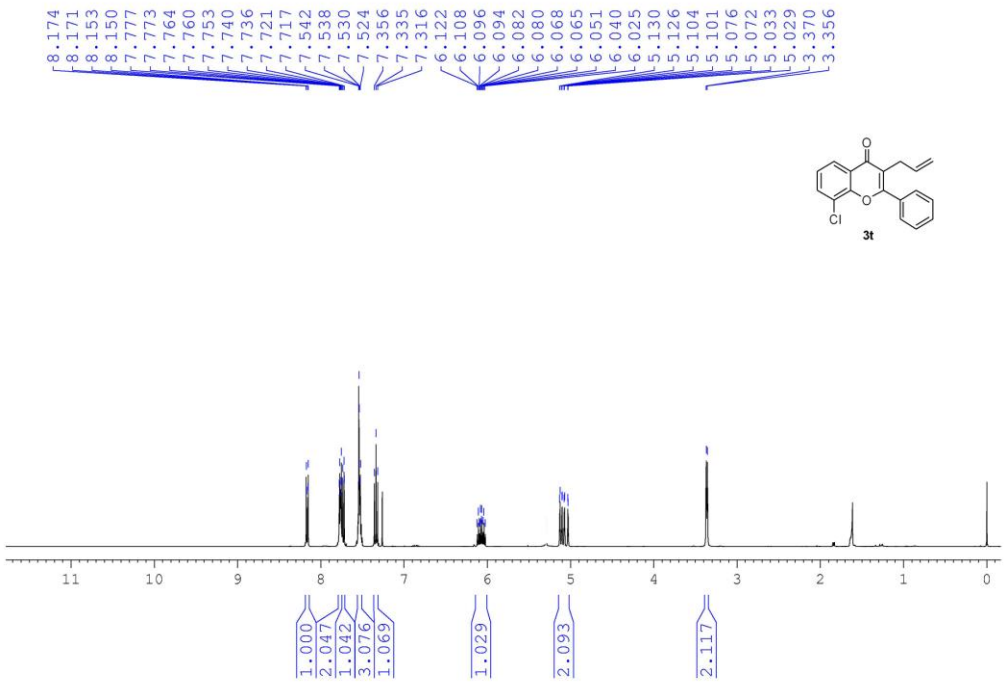
^{1}H NMR spectrum of **3s**



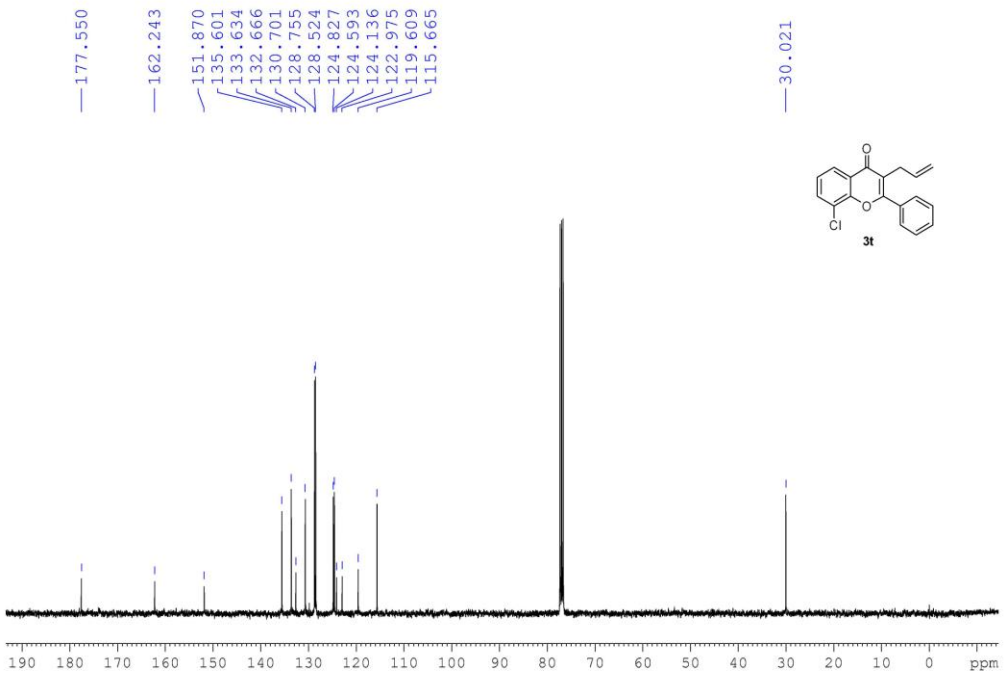
^{13}C NMR spectrum of **3s**



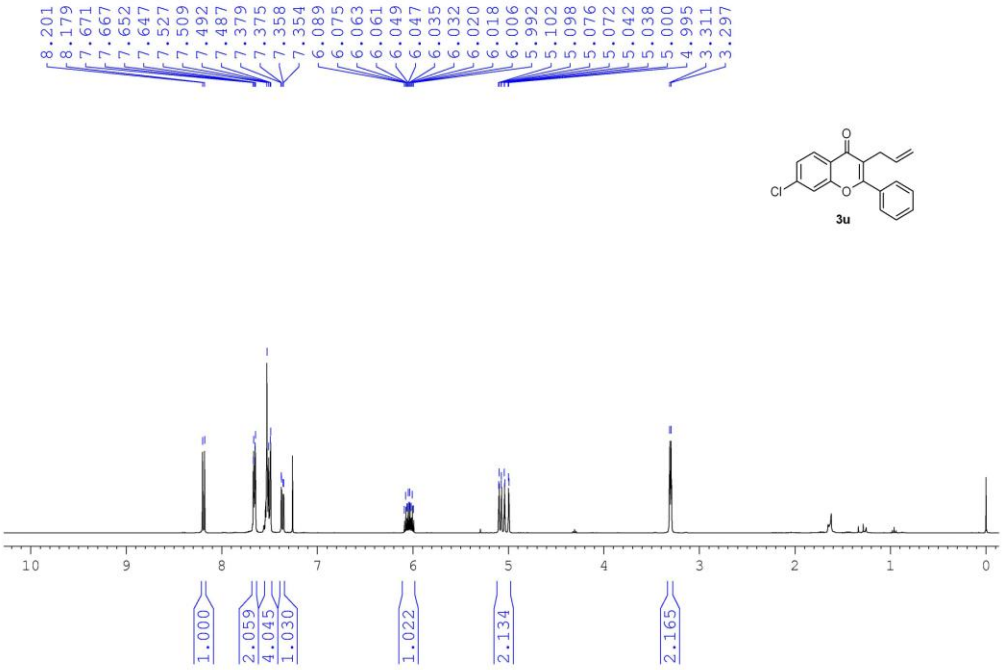
^{1}H NMR spectrum of **3t**



^{13}C NMR spectrum of **3t**



^{1}H NMR spectrum of **3u**



^{13}C NMR spectrum of **3u**