

Supplementary Material (ESI)

Direct Michael Addition/Decarboxylation Reaction of Coumarin-3-Carboxylic Acid to Cyclic 1,3-Diketones by Copper Ferrite Oxide Nanoparticles Immobilized on Microcrystalline Cellulose

Bhupender Kumar^a, Biplob Borah^a, J. Nagendra Babu^b and L. Raju Chowhan^{a*}

^aSchool for Applied Material Sciences, Central University of Gujarat, Sector 30, Gandhinagar, Gujarat, 382021, India.

^bDepartment of Chemical Sciences, School for Basic and Applied Sciences, Central University of Punjab, Ghudda, Bathinda, 151401, India.

E-mail address: rajuchowhan@gmail.com, rchowhan@cug.ac.in

Table of contents

Sr. No.	Section	Page No.
1.	General Experimental Details	S1
2.	DTG of CuFe ₂ O ₄ @MCC nanocomposite	S2
3.	Brunauer–Emmett–Teller (BET) Analysis of CuFe ₂ O ₄ @MCC	S2
4.	General experimental procedure for the reaction	S3
5.	Spectral data for products (3a-z)	S3
6.	Copies of ¹ H and ¹³ C NMR spectra of products (3a-z)	S12

Experimental Section

1. General Experimental Details

All commercially available chemicals were used without further purification. Field Emission Scanning Electron Microscope (FESEM) (Carl Zeiss Merlin compact equipped with Oxford X-maxⁿ), High-resolution Transmission Electron Microscopy (HR-TEM) of JEOL model JEM 2100 TEM HR LaB6 and X-ray diffraction (XRD) of Bruker D8 Advance X-ray diffractometer were used for the characterization of Cu₂O immobilized on microcrystalline cellulose (Cu₂O@MCC). The thermal stability of the catalyst was analyzed using TG/DTA 7300 of EXSTAR. Brunauer–Emmett–Teller (BET) analysis was carried out to examine the surface area of composite material by using Belsorp_{max} of Microtrac BEL Corp. Detection of copper was measured from inductively coupled plasma (ICP) emission spectroscopy of 7300 DV, Perkin Elmer. ¹H NMR spectra were obtained on Bruker 500 MHz NMR and 400, 600 MHz JEOL NMR spectrometers. ¹³C NMR spectra were recorded at 100, 125, and 150 MHz. Chemical shifts are reported relative to the TMS signal. Multiplicity is indicated as follows: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets), etc. TOF and quadrupole mass analyzer types are used for the HRMS measurements. FT-IR spectrometer (Shimadzu) in the range of 400–4000 cm⁻¹. The melting point of organic molecules was observed from the melting point apparatus. Thin Layer Chromatography (TLC) was performed by using silica gel 60 F₂₅₄ plates (Merck).

2. DTG of CuFe₂O₄@MCC nanocomposite

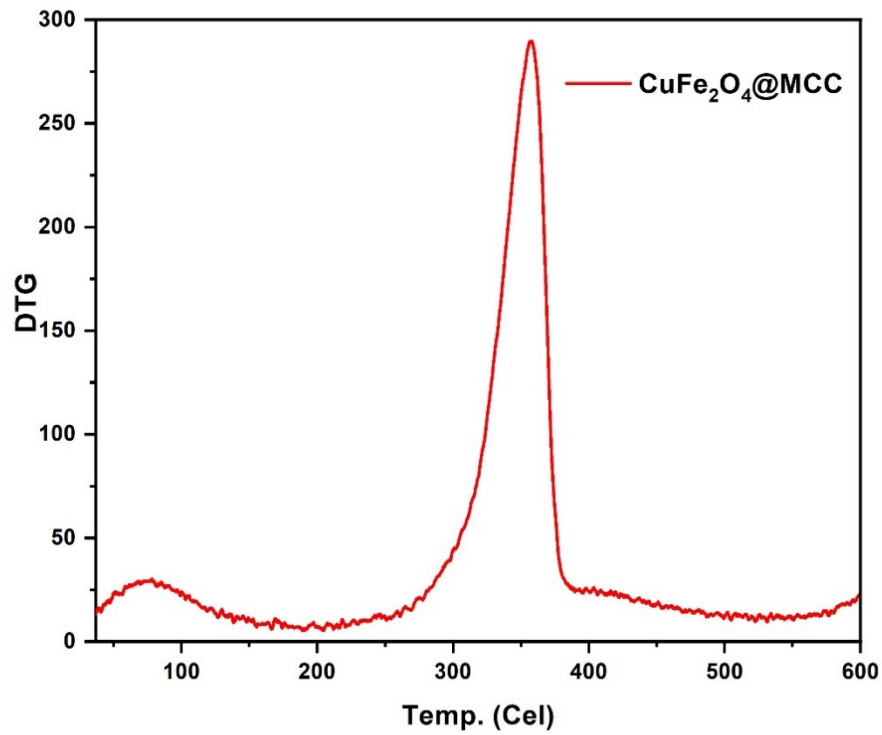


Figure: SI.1:- DTG of CuFe₂O₄@MCC

3. Brunauer–Emmett–Teller (BET) Analysis of CuFe₂O₄@MCC

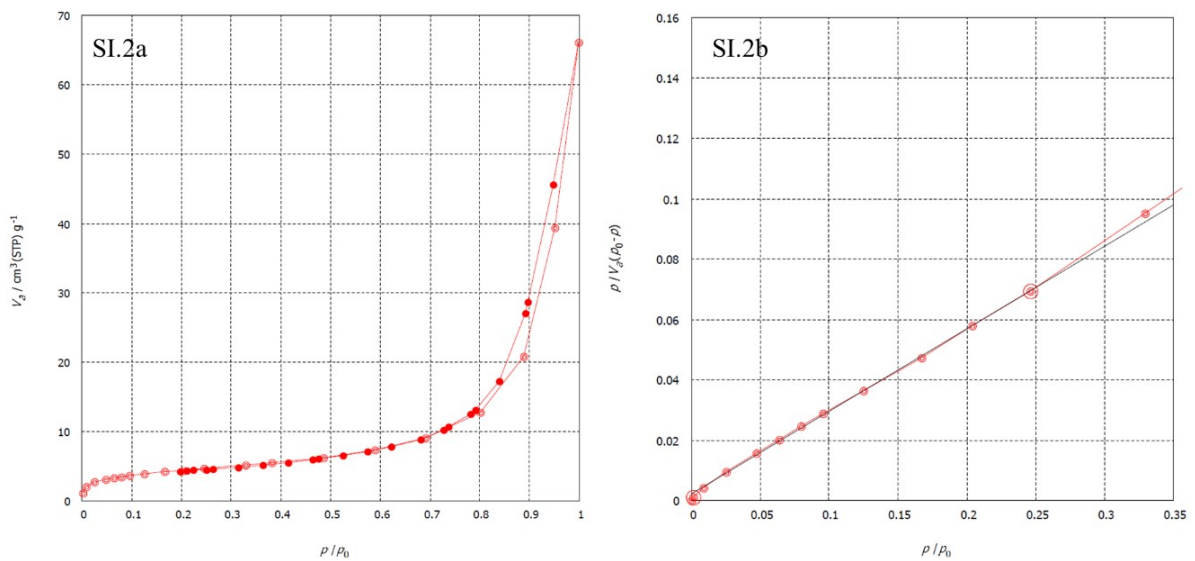


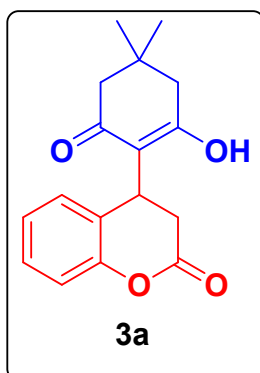
Figure: SI.2a and 2b:- Adsorption-desorption isotherm & BET plot

Composite	Surface area (m ² /g)	Average Pore Diameter (Å)
CuFe ₂ O ₄ @MCC	15.77	28.186

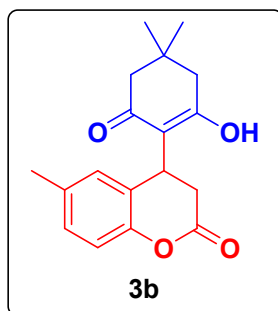
4. General Procedure for Michael Addition/decarboxylation of 1,3 diketone cyclohexanone with 1mmol coumarin 3-carboxylic acid

In a 10ml round bottom flask 1mmol of dimedone (**1a**) with 1mmol coumarin 3-carboxylic acid (**2a**) in DMSO: H₂O (1:1) 3 ml with catalyst (20mg) was stirred for 7 hours at 60°C. The progress of the reaction was examined by thin-layer chromatography (TLC). After completion of the reaction, 10 ml of water was added and extracted with ethyl acetate (3 X 10 ml). A combined organic layer passed through filter paper for removing the catalyst. The organic layer was washed with brine(20 ml), dried over anhydrous Na₂SO₄(10 gm), and concentrated under reduced pressure. Thus, obtained crude was washed with diethyl ether (3 ml) to remove nonpolar impurities. Further purification was done by recrystallization in ethyl acetate if necessary.

5. Spectral data for products (3a-p)

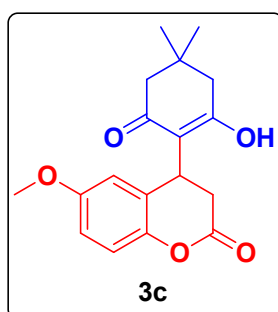


4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)chroman-2-one (3a): White solid; 86% yield; Melting Point: 178-180 °C; IR (KBr) ν_{\max} (cm⁻¹): 2947, 1758, 1558, 1373, 1288, 1226, 1180, 1041, 933, 756, 609; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.19 (dd, *J* = 14.0, 3.0 Hz, 1H), 7.04 – 7.00 (m, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 4.57 (dd, *J* = 8.5, 4.9 Hz, 1H), 2.95 (dd, *J* = 16.6, 8.5 Hz, 1H), 2.68 (dd, *J* = 16.6 Hz, 1H), 2.32 – 2.15 (m, 4H), 0.97 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.88, 151.67, 128.20, 127.94, 125.39, 124.34, 116.64, 115.39, 33.61, 32.17, 28.44, 28.31. HRMS(ESI⁺): *m/z* calculated for C₁₇H₁₉O₄ [M+H]⁺ 287.1283; Found: 287.1318.



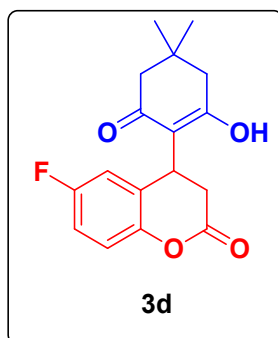
4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-6-methylchroman-2-one

(3b): White solid; 82% yield; Melting Point: 182-184°C; IR (KBr) ν_{\max} (cm⁻¹): 2954, 1743, 1566, 1481, 1365, 1249, 1226, 1157, 1041, 879, 817, 663, 609; ¹H NMR (500 MHz, DMSO-*d*₆) δ 6.98 (d, *J* = 7.1 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.80 (s, 1H), 4.53 (dd, *J* = 8.4, 4.8 Hz, 1H), 2.91 (dd, *J* = 16.6, 8.6 Hz, 1H), 2.65 (dd, *J* = 16.6, 4.8 Hz, 1H), 2.24 (s, 4H), 2.19 (s, 3H), 0.97 (s, 6H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 172.72, 154.38, 144.65, 137.84, 133.09, 129.72, 121.08, 120.09, 111.52, 61.82, 38.41, 36.85, 33.11, 33.00, 25.54, 12.12. HRMS(ESI⁺): *m/z* calculated for C₁₈H₂₁O₄ [M+H]⁺ 301.1440; Found: 301.1479.



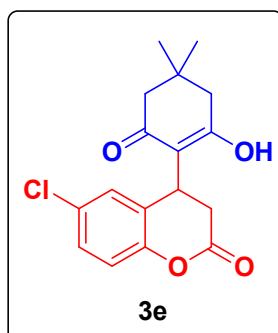
4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-6-methoxychroman-2-one

(3c): White solid; 79% yield; Melting Point: 180-182°C; IR (KBr) ν_{\max} (cm⁻¹): 2954, 1765, 1563, 1365, 1248, 1268, 1176, 1048, 1020, 879, 814, 673, 609; ¹H NMR (500 MHz, CDCl₃) δ 7.07 (d, *J* = 8.8 Hz, 1H), 6.92 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.65 (d, *J* = 2.8 Hz, 1H), 4.67 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.80 (s, 3H), 3.02 (dd, *J* = 16.6, 8.3 Hz, 1H), 2.85 (dd, *J* = 16.6, 5.7 Hz, 1H), 2.52 – 2.27 (m, 4H), 1.12 (s, 6H). ¹³C NMR (126 MHz, DMSO) δ 168.09, 155.84, 145.66, 126.52, 117.33, 114.79, 112.93, 112.88, 55.75, 33.39, 32.14, 28.74, 28.28.



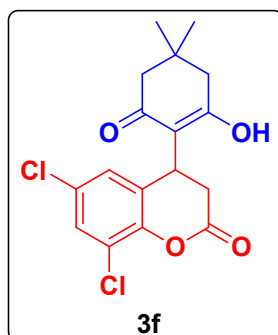
6-fluoro-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)chroman-2-one

(3d): White solid; 83% yield; Melting Point: 184-186°C; IR (KBr) ν_{\max} (cm^{-1}): 2954, 1766, 1558, 1373, 1296, 1249, 1180, 1041, 925, 879, 810, 694, 617; ^1H NMR (600 MHz, $\text{CDCl}_3 + \text{DMSO-}d_6$) δ 7.75 – 7.68 (m), 7.14 (d, $J = 8.4$ Hz, 1H), 7.05 (s, 1H), 6.95 – 6.91 (m, 1H), 4.69 (t, $J = 6.9$ Hz, 1H), 2.99 (dd, $J = 16.5, 8.7$ Hz, 1H), 2.83 (dd, $J = 16.4$ Hz, 1H), 2.31 (d, $J = 6.9$ Hz, 4H), 1.07 (s, 6H). ^{13}C NMR (151 MHz, $\text{DMSO-}d_6$) δ 168.03, 149.69, 133.15, 128.39 (d, $J_{\text{C-F}} = 2.7$ Hz), 125.02, 116.40, 115.44, 33.72, 32.18, 28.41, 28.31, 20.86. ^{19}F NMR (500 MHz, $\text{CDCl}_3 + \text{DMSO-}d_6$) δ -114.90. HRMS(ESI+): m/z calculated for $\text{C}_{17}\text{H}_{18}\text{FO}_4$ $[\text{M}+\text{H}]^+$ 305.1189; Found: 305.1227.



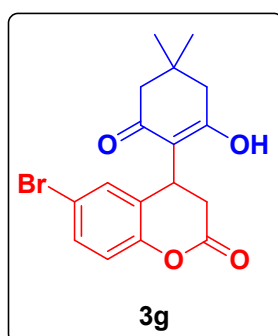
6-chloro-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)chroman-2-one

(3e): White solid; 83% yield; Melting Point: 172-174°C; IR (KBr) ν_{\max} (cm^{-1}): 2954, 1728, 1581, 1488, 1373, 1257, 1141, 871, 802, 756, 686, 609; ^1H NMR (500 MHz, DMSO) δ 7.27 (dd, $J = 8.7, 2.5$ Hz, 1H), 7.05 (d, $J = 8.7$ Hz, 1H), 7.00 (d, $J = 2.1$ Hz, 1H), 4.59 (dd, $J = 8.5, 4.8$ Hz, 1H), 2.99 (dd, $J = 16.7, 8.7$ Hz, 1H), 2.69 (dd, $J = 16.7, 4.8$ Hz, 1H), 2.37 – 2.18 (m, 4H), 0.99 (s, 6H). ^{13}C NMR (126 MHz, DMSO) δ 167.26, 150.53, 127.88, 127.80, 127.64, 127.54, 118.59, 114.85, 33.12, 32.16, 28.51, 28.25. HRMS(ESI+): m/z calculated for $\text{C}_{17}\text{H}_{18}\text{ClO}_4$ $[\text{M}+\text{H}]^+$ 321.0894; Found: 321.0934.



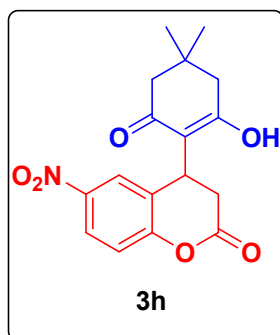
6,8-dichloro-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)chroman-2-one

(3f): White solid; 80% yield; Melting Point: 178-180°C; IR (KBr) ν_{\max} (cm⁻¹): 2955, 1734, 1424, 1558, 1448, 1373, 1248, 1158, 1041, 874, 612; ¹H NMR (500 MHz, DMSO) δ 7.72 (d, J = 2.4 Hz, 1H), 7.64 (d, J = 2.2 Hz, 1H), 4.23 (t, J = 4.4 Hz, 1H), 2.76 (t, J = 10.3 Hz, 3H), 2.60 (d, J = 17.6 Hz, 1H), 2.50 (d, J = 16.1 Hz, 1H), 2.34 (d, J = 16.1 Hz, 1H), 1.22 (s, 3H), 1.19 (s, 3H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 196.88, 172.65, 165.82, 145.41, 128.59, 128.32, 128.05, 121.67, 111.01, 50.58, 32.22, 29.47, 28.80, 26.62. HRMS(ESI⁺): m/z calculated for C₁₇H₁₈NO₆ [M+H]⁺ 355.0504; Found: 355.0501.



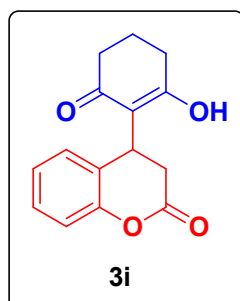
6-bromo-4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)chroman-2-one

(3g): White solid; 81% yield; Melting Point: 174-176 °C; IR (KBr) ν_{\max} (cm⁻¹): 2954, 1766, 1558, 1342, 1257, 1226, 1157, 1041, 871, 601; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.38 (dd, J = 8.6, 2.4 Hz, 1H), 7.12 (d, J = 2.2 Hz, 1H), 6.98 (d, J = 8.6 Hz, 1H), 4.58 (dd, J = 8.6, 4.7 Hz, 1H), 2.98 (dd, J = 16.7, 8.7 Hz, 1H), 2.67 (dd, J = 16.7, 4.8 Hz, 1H), 2.46 – 1.97 (m, 4H), 0.98 (s, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.22, 151.01, 130.71, 130.49, 128.06, 119.04, 115.80, 114.99, 33.15, 32.19, 28.46, 28.25. HRMS(ESI⁺): m/z calculated for C₁₇H₁₈BrO₄ [M+H]⁺ 365.0461; Found: 365.0448.



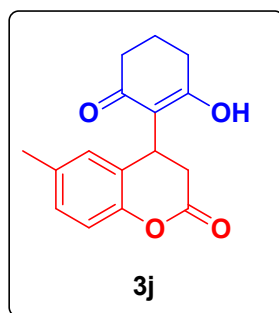
4-(2-hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)-6-nitrochroman-2-one (3h):

White solid; 80% yield; Melting Point: 184-186°C; IR (KBr) ν_{\max} (cm^{-1}): 2954, 1712, 1620, 1527, 1388, 1342, 1234, 1203, 1157, 1033, 925, 833, 794, 748, 671, 648, 594; ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 8.30 (d, $J = 2.6$ Hz, 1H), 8.11 (dd, $J = 9.0, 2.7$ Hz, 1H), 8.07 (s, 1H), 7.22 (d, $J = 9.0$ Hz, 1H), 4.24 (s, 1H), 2.65 (t, $J = 5.8$ Hz, 1H), 2.60 – 2.58 (m, 1H), 2.50 (d, $J = 17.6$ Hz, 1H), 2.34 (d, $J = 16.1$ Hz, 1H), 2.27 (d, $J = 16.1$ Hz, 1H), 1.12 (d, $J = 8.0$ Hz, 6H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 194.66, 170.69, 163.65, 153.02, 142.38, 138.05, 124.28, 109.31, 104.92, 55.22, 48.82, 30.27, 27.53, 26.47, 25.15, 5.52. HRMS(ESI+): m/z calculated for $\text{C}_{17}\text{H}_{18}\text{NO}_6$ $[\text{M}+\text{H}]^+$ 332.1134; Found: 332.1133.

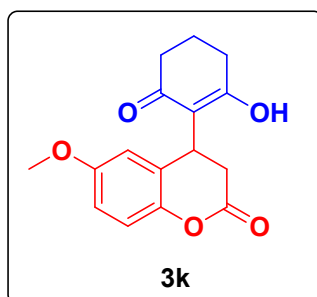


4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)chroman-2-one (3i): White solid; 85% yield;

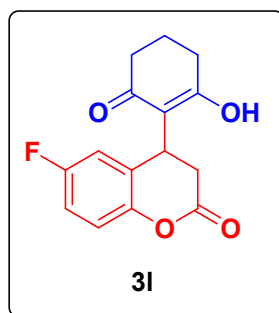
Melting Point: 176-178°C; IR (KBr) ν_{\max} (cm^{-1}): 3440, 2561, 1766, 1635, 1550, 1488, 1450, 1365, 1296, 1172, 1103, 1072, 995, 945, 925, 864, 756, 709, 648; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.22 – 7.16 (m, 1H), 7.02 (d, $J = 6.2$ Hz, 2H), 6.96 (d, $J = 7.9$ Hz, 1H), 4.63 – 4.53 (m, 1H), 2.91 (dd, $J = 16.6, 8.4$ Hz, 1H), 2.85 (dd, $J = 16.6, 5.3$ Hz, 1H), 2.35 (m, 4H), 1.91 – 1.80 (m, 2H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 167.90, 151.71, 128.30, 127.90, 125.51, 124.32, 116.57, 116.45, 33.63, 28.56, 20.86. HRMS(ESI+): m/z calculated for $\text{C}_{15}\text{H}_{15}\text{O}_4$ $[\text{M}+\text{H}]^+$ 259.0970; Found: 259.0972.



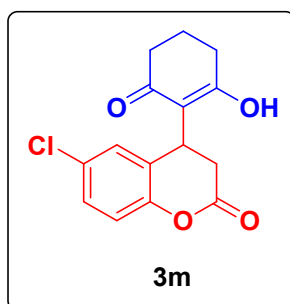
4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-6-methylchroman-2-one (3j): White solid; 82% yield; Melting Point: 176-178°C; IR (KBr) ν_{\max} (cm^{-1}): 3433, 2368, 1743, 1589, 1488, 1380, 1296, 1172, 1195, 1103, 1056, 894, 817, 709, 663; ^1H NMR (400 MHz,) δ 6.98 (dd, $J = 8.2, 2.1$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz), 6.82 (d, $J = 1.6$ Hz), 4.52 (dd, $J = 8.4, 4.9$ Hz, 1H), 2.88 (dd, $J = 16.6, 8.6$ Hz, 1H), 2.65 (dd, $J = 16.6, 4.9$ Hz, 1H), 2.34 (m, 4H), 2.20 (s, 3H) 1.83 (m, 2H). ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 168.04, 149.72, 133.16, 128.48, 128.39, 125.07, 116.66, 116.34, 33.75, 28.51, 20.86. HRMS(ESI+): m/z calculated for $\text{C}_{15}\text{H}_{14}\text{FO}_4$ $[\text{M}+\text{H}]^+$ 273.1127; Found: 273.1121.



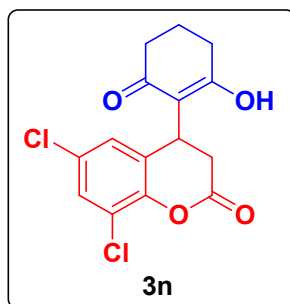
4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-6-methoxychroman-2-one (3k): White solid; 78% yield; Melting Point: 178-180°C; IR (KBr) ν_{\max} (cm^{-1}): 3440, 2947, 1735, 1585, 1365, 1248, 1145, 1157, 1084, 1019, 977, 889, 813, 794, 663, 609; ^1H NMR (500 MHz, DMSO) δ 7.06 (d, $J = 8.8$ Hz, 1H), 6.91 (dd, $J = 8.8, 3.0$ Hz, 1H), 6.66 (d, $J = 2.9$ Hz, 1H), 4.66 (dd, $J = 8.2, 5.6$ Hz, 1H), 3.81 (s, 3H), 3.00 (dd, $J = 16.6, 8.3$ Hz, 1H), 2.83 (dd, $J = 16.6, 5.5$ Hz, 1H), 2.66 – 2.64 (m, 4H), 2.00 – 1.96 (m, 2H). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) δ 168.07, 155.83, 145.67, 126.48, 117.23, 116.11, 113.20, 112.74, 55.76, 33.41, 28.80, 20.82. HRMS(ESI+): m/z calculated for $\text{C}_{15}\text{H}_{14}\text{O}_5$ $[\text{M}+\text{H}]^+$ 289.1076; Found: 289.1075.



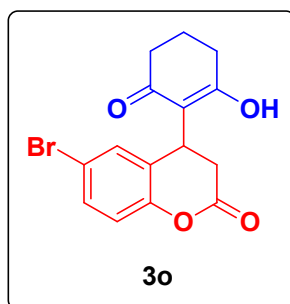
6-fluoro-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)chroman-2-one (3l): White solid; 83% yield; Melting Point: 180-182°C; IR (KBr) ν_{\max} (cm^{-1}): 3438, 3047, 1735, 1589, 1373, 1250, 1149, 1150, 1080, 1002, 972, 887, 817, 810, 663, 609; ^1H NMR (500 MHz, DMSO) δ 7.24 (d, $J = 8.5$ Hz, 1H), 7.05 – 6.99 (m, 2H), 4.55 (t, $J = 7.5$ Hz 1H), 2.99 – 2.88 (m, 1H), 2.66 (d, $J = 16.6$ Hz, 1H), 2.35 (m, 4H), 1.83 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 172.04, 155.30, 132.65, 132.55, 132.42 (d, $J_{\text{C-F}} = 5.3$ Hz), 123.28, 120.86, 37.90, 33.35, 25.52. ^{19}F NMR (500 MHz, $\text{CDCl}_3 + \text{DMSO-}d_6$) δ -115.20. HRMS(ESI+): m/z calculated for $\text{C}_{15}\text{H}_{14}\text{FO}_4$ $[\text{M}+\text{H}]^+$ 273.0876; Found: 293.0873.



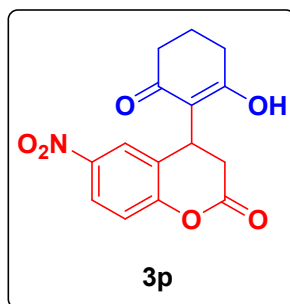
6-chloro-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)chroman-2-one (3m): White solid; 83% yield; Melting Point: 174-176°C; IR (KBr) ν_{\max} (cm^{-1}): 3456, 3047, 2345, 1743, 1589, 1481, 1411, 1373, 1249, 1211, 1149, 1080, 1002, 972, 877, 817, 794, 756, 663, 609; ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 7.43 (d, $J = 2.5$ Hz, 1H), 7.29 (dd, $J = 8.7, 2.6$ Hz, 1H), 7.12 (d, $J = 8.7$ Hz, 1H), 4.10 (dd, $J = 6.8, 3.7$ Hz, 1H), 2.61 – 2.54 (m, 2H), 2.48 – 2.31 (m, 4H), 2.03 – 1.81 (m, 2H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 197.06, 172.77, 168.00, 149.16, 128.99, 128.72, 128.39, 127.07, 118.49, 111.98, 41.91, 36.97, 28.37, 27.61, 20.61. HRMS(ESI+): m/z calculated for $\text{C}_{15}\text{H}_{14}\text{ClO}_4$ $[\text{M}+\text{H}]^+$ 293.0581; Found: 293.0581.



6,8-dichloro-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)chroman-2-one (3n): White solid; 81% yield; Melting Point: 174-176°C; IR (KBr) ν_{\max} (cm⁻¹): 3456, 2970, 1720, 1420, 1558, 1450, 1380, 1249, 1172, 1126, 1041, 918, 856, 632, 593; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.57 (s, 1H), 7.46 (s, 1H), 4.12 (s, 1H), 2.63 (s, 2H), 2.38 (m, 4H), 1.95 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 197.00, 172.73, 167.42, 145.31, 128.71, 128.61, 128.37, 128.06, 121.76, 112.39, 36.91, 28.75, 27.45, 20.56. HRMS(ESI⁺): *m/z* calculated for C₁₆H₁₇O₄ [M+H]⁺ 327.0191; Found: 327.0190.



6-bromo-4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)chroman-2-one (3o): White solid; 79% yield; Melting Point: 170-172°C; IR (KBr) ν_{\max} (cm⁻¹): 3417, 2939, 2545, 1767, 1688, 1558, 1473, 1365, 1296, 1164, 1103, 1072, 1033, 987, 948, 871, 810, 748, 702, 640; ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.36 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 4.57 (dd, *J* = 8.5, 4.7 Hz, 1H), 2.94 (dd, *J* = 16.7, 8.7 Hz, 1H), 2.66 (dd, *J* = 16.7, 4.8 Hz, 1H), 2.35 (m, 4H), 1.89 – 1.77 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.73, 167.24, 151.06, 130.69, 130.61, 128.18, 118.96, 116.23, 115.85, 33.24, 28.57, 20.82. HRMS(ESI⁺): *m/z* calculated for C₁₅H₁₄BrO₄ [M+H]⁺ 337.0075; Found: 337.0075.

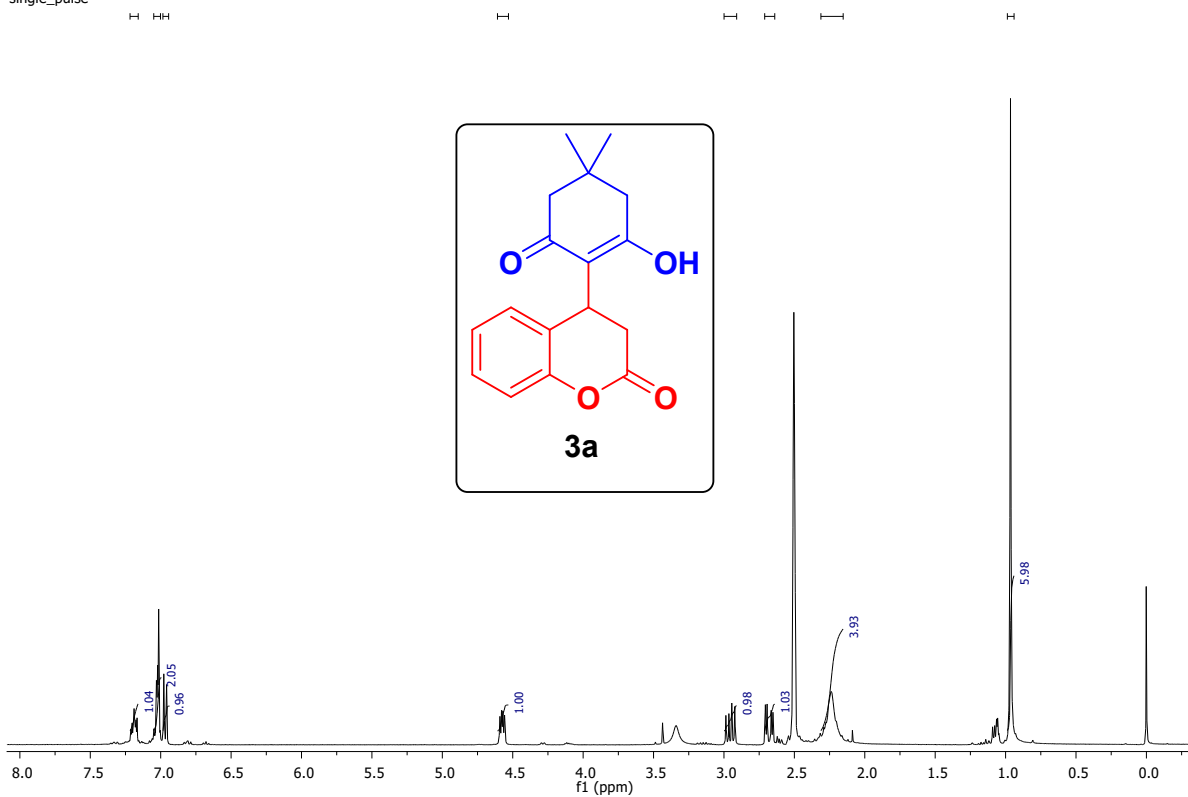


4-(2-hydroxy-6-oxocyclohex-1-en-1-yl)-6-nitrochroman-2-one (3p): White solid; 76% yield; Melting Point: 176-178°C; IR (KBr) ν_{\max} (cm⁻¹): 3425, 2345, 1704, 1643, 1519, 1380, 1342, 1226, 1134, 1002, 910, 880, 748, 663, 632; ¹H NMR (400 MHz,) δ 8.33 (s, 1H), 8.12 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 4.25 – 4.16 (m, 1H), 2.61 (m, 4H), 2.40 (s, 2H), 2.09 – 1.89 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 197.09, 172.72, 167.45, 154.96, 144.30, 126.46, 125.47, 124.35, 117.86, 112.24, 41.77, 36.92, 28.28, 27.42, 20.53. HRMS(ESI⁺): *m/z* calculated for C₁₅H₁₄NO₆ [M+H]⁺ 304.0821; Found: 304.0821

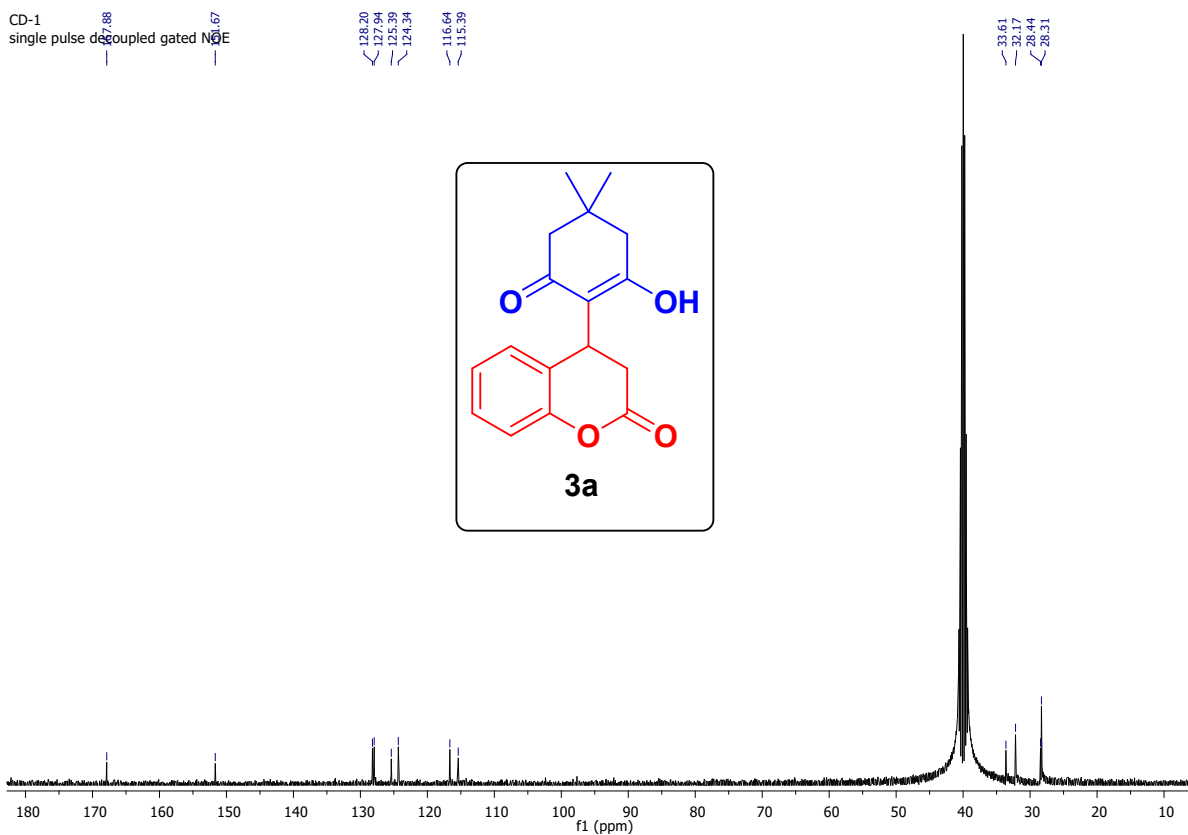
Copies of ^1H and ^{13}C NMR spectra of products(3a-p)

Copies of ^1H NMR and ^{13}C NMR spectra of Compound 3a

DC-1
single_pulse

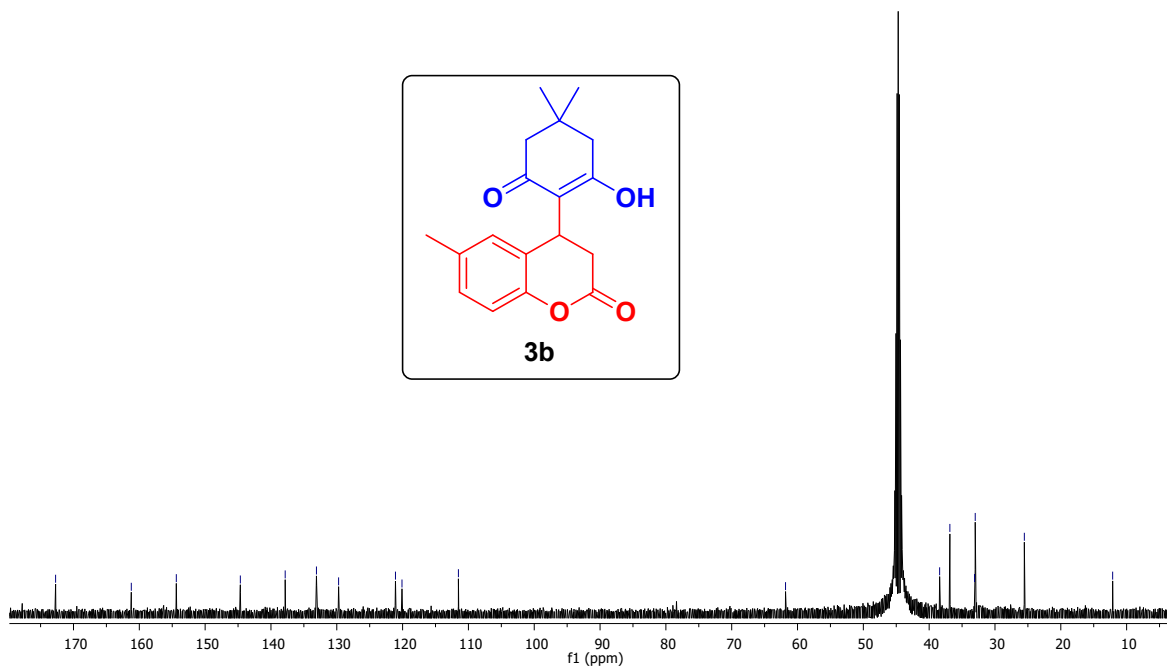
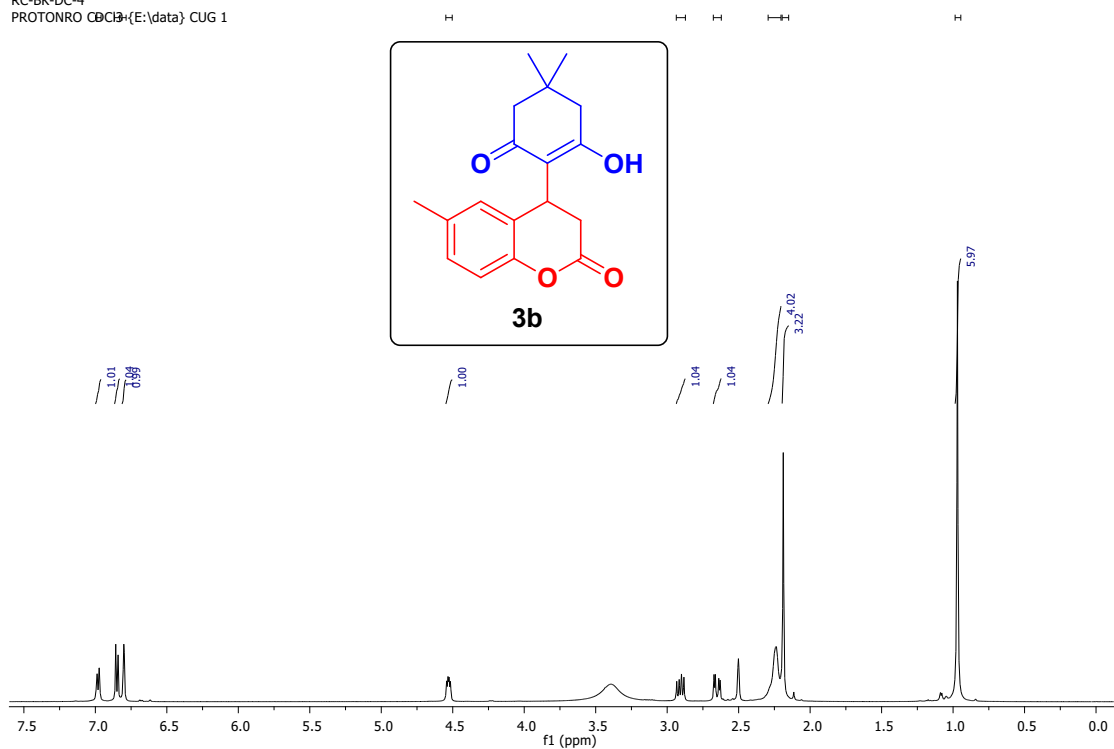


CD-1
single_pulse decoupled gated NOE

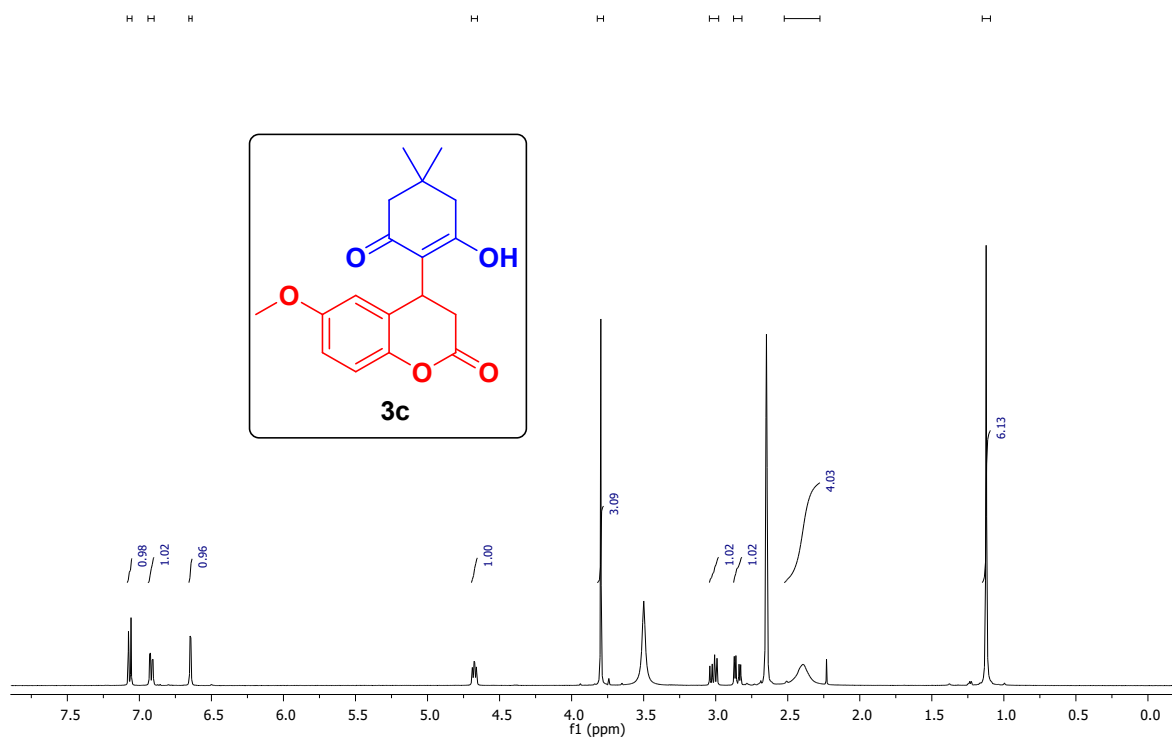


Copies of ^1H NMR and ^{13}C NMR spectra of **Compound 3b**

Bhupender
RC-BK-DC-4
PROTONRO CCl₃(E:\data) CUG 1



Copies of ¹HNMR and ¹³CNMR spectra of **Compound 3c**



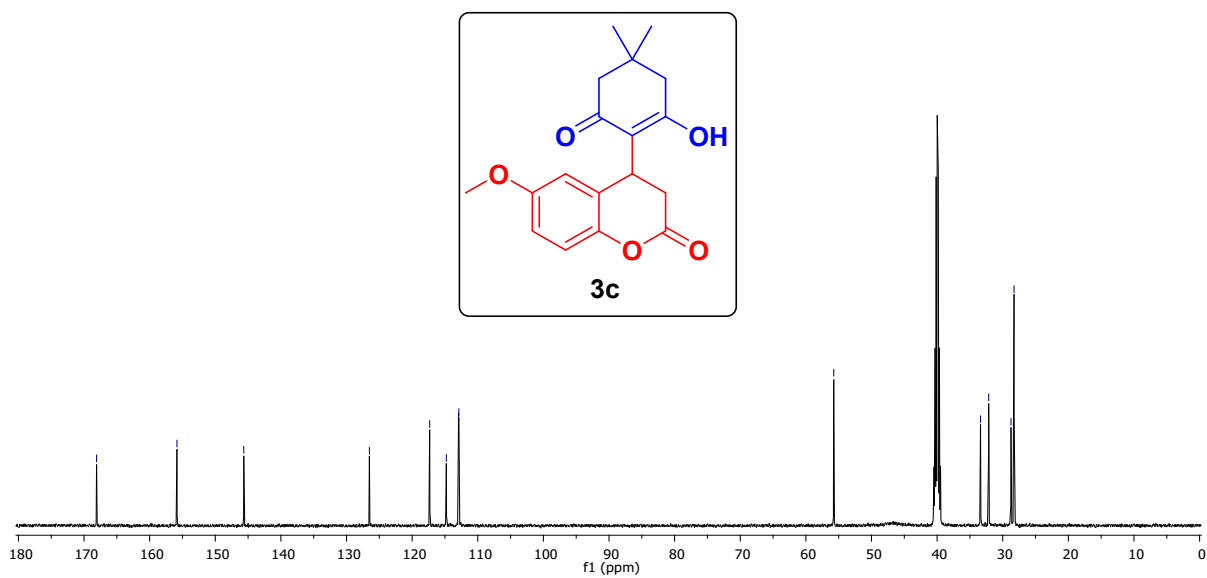
Mihir P
DC-8
C13CPD DMSO {E:\data} CUG 1

168.09
155.84
145.66

126.52
117.23
114.79
112.93
112.88

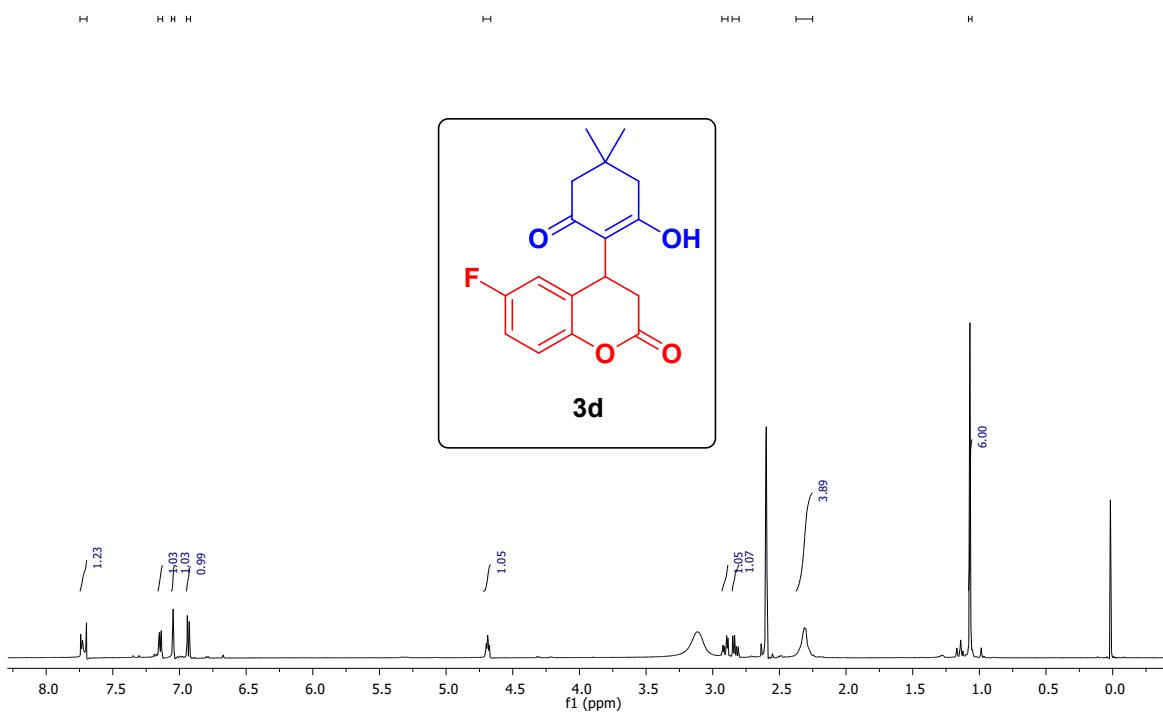
55.75

33.39
32.14
30.28

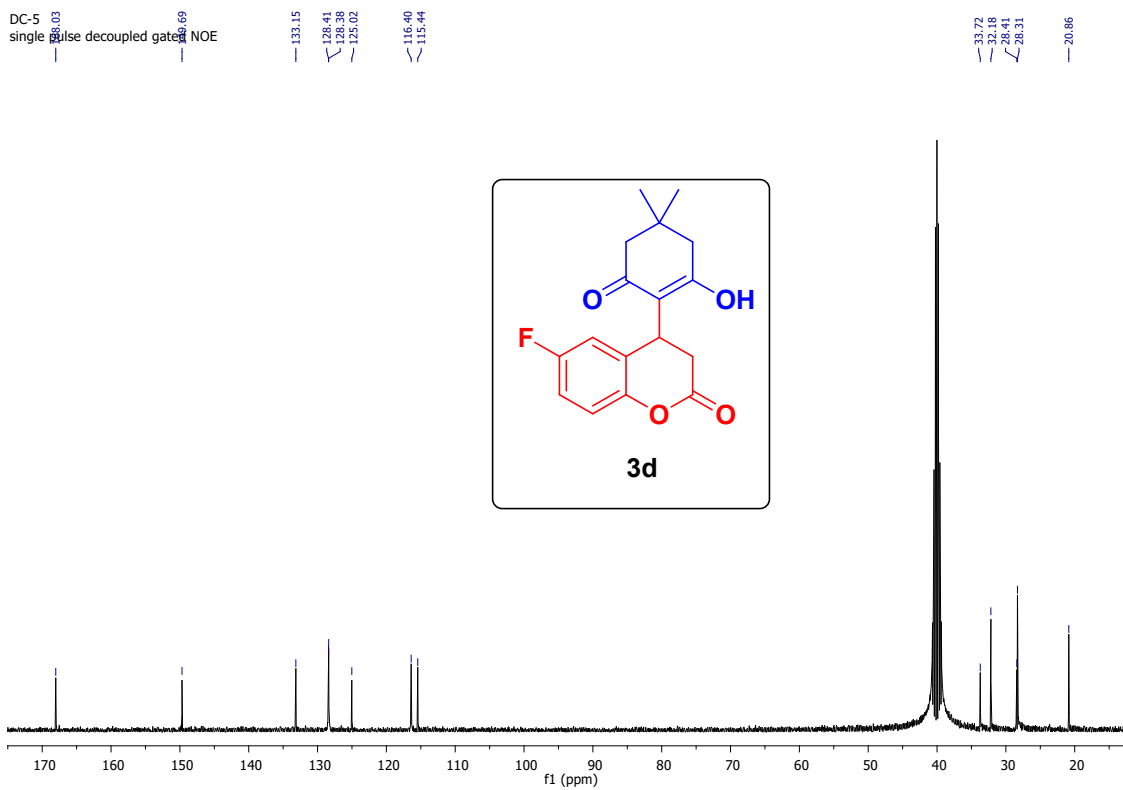


Copies of ^1H NMR and ^{13}C NMR spectra of **Compound 3d**

DC-5
single_pulse



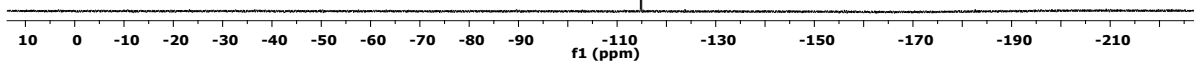
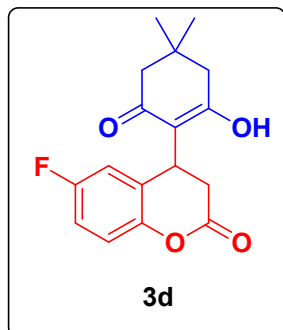
DC-5
single_pulse decoupled gated NOE



Copy of ^{19}F NMR spectra of Compound 3d

Bhupender
RC-BK-DC-05-3d
F19CPD CDCl3 {E:\data} CUG 1

-114.90



Copies of ^1H NMR and ^{13}C NMR spectra of Compound 3e

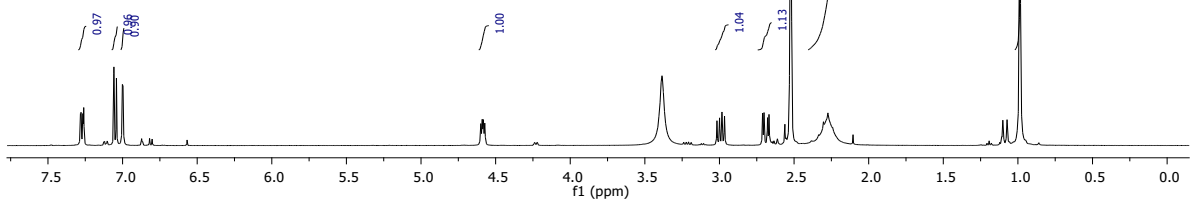
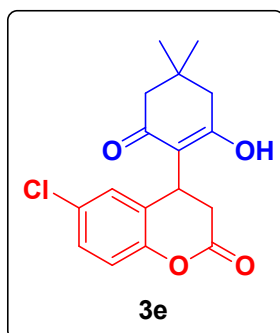
Bhupender
RC-BK-DC-3
PROTONRO DMSO {E:\data} CUG 1

H HH

H

H H H

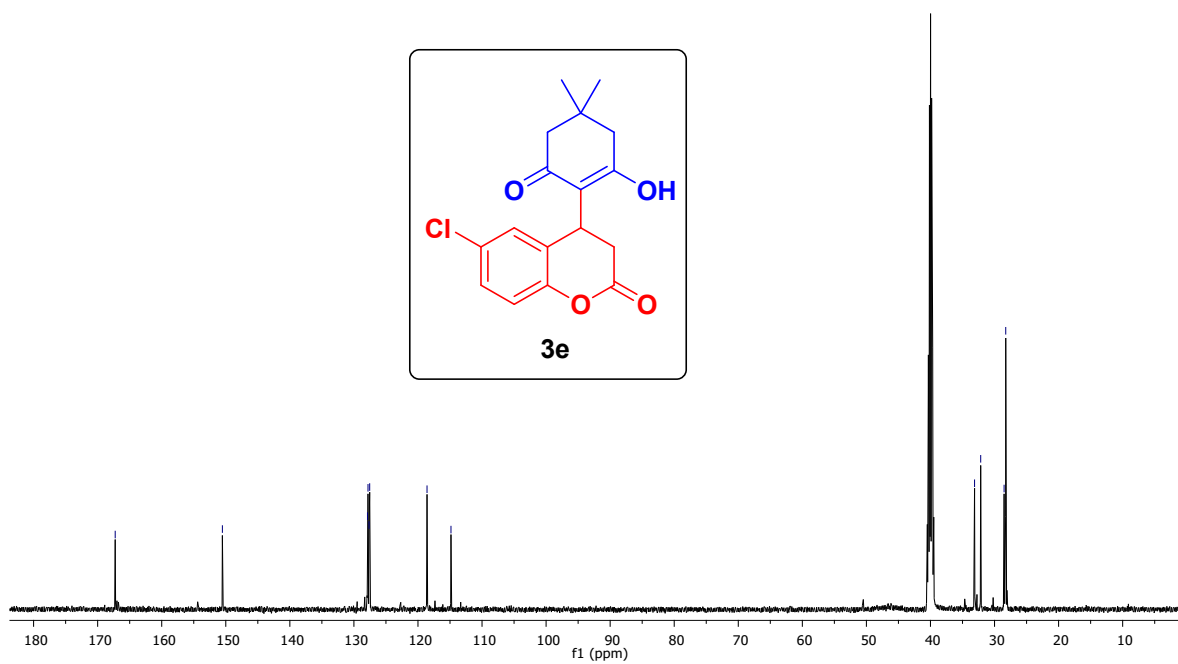
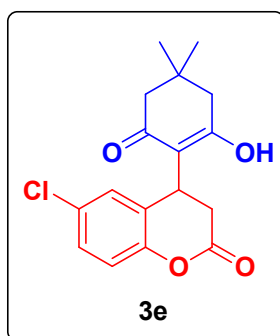
H



Bhupender
RC-BK-DC-3
C13CPD DMSO {E:\data} CUG 1

127.88
127.80
127.64
127.54
118.59
114.85

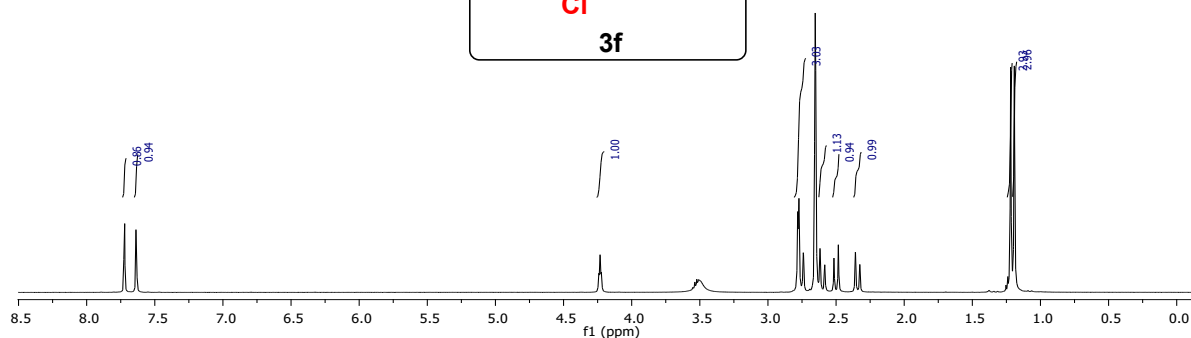
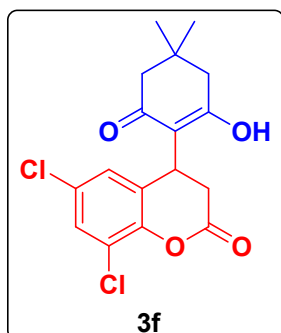
33.12
31.16
28.51
28.25



Copies of ¹HNMR and ¹³CNMR spectra of **Compound 3f**

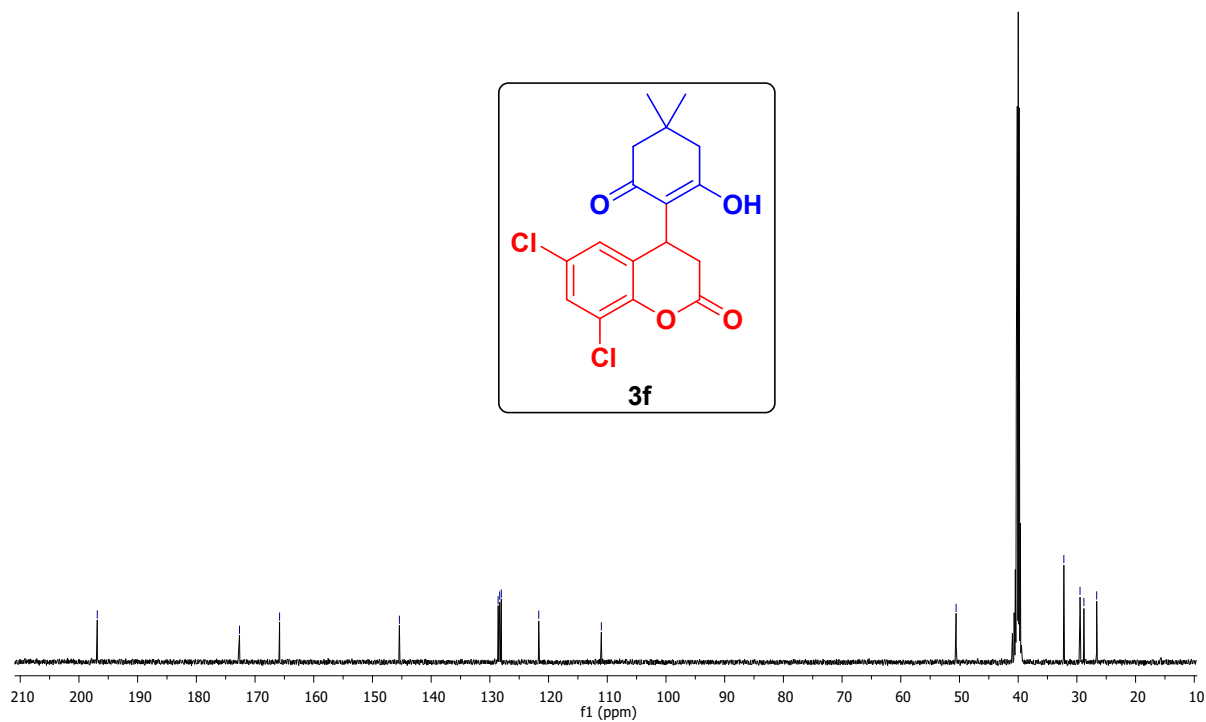
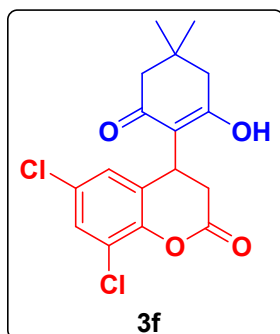
Bhupender
RC-BK-DC-7
PROTONRO DM50 {E:\data} CUG 1

H H H H H H



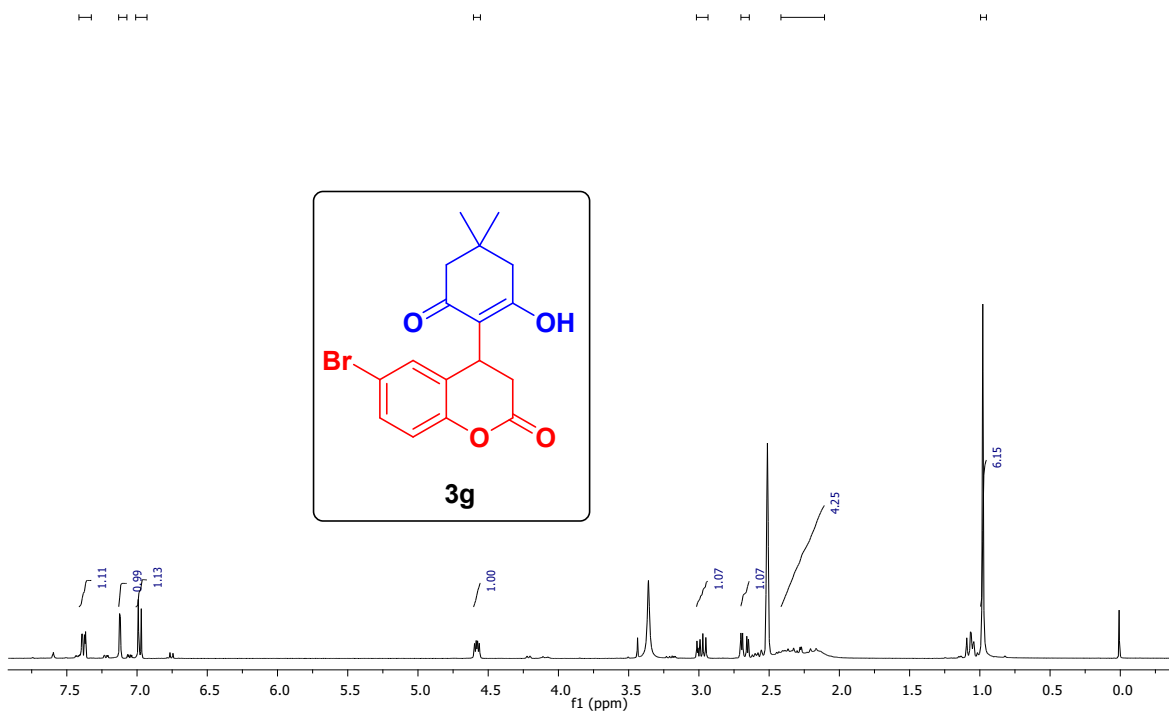
Bhupender
RC-BK-DC-7
C13CPD DM50 {E:\data} CUG 1

172.65
165.82
145.41
128.59
128.32
128.05
121.67
111.01
50.58
32.22
29.47
28.80
26.62

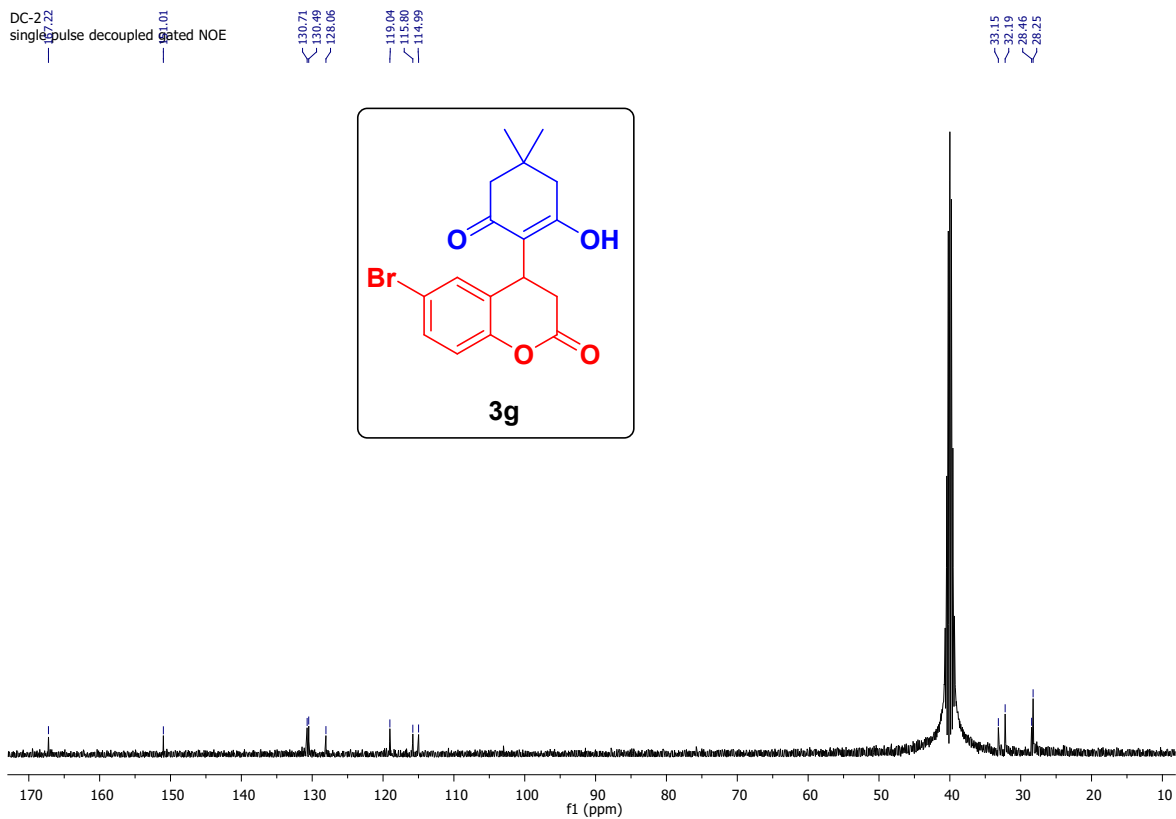


Copies of ^1H NMR and ^{13}C NMR spectra of **Compound 3g**

DC-2
single_pulse

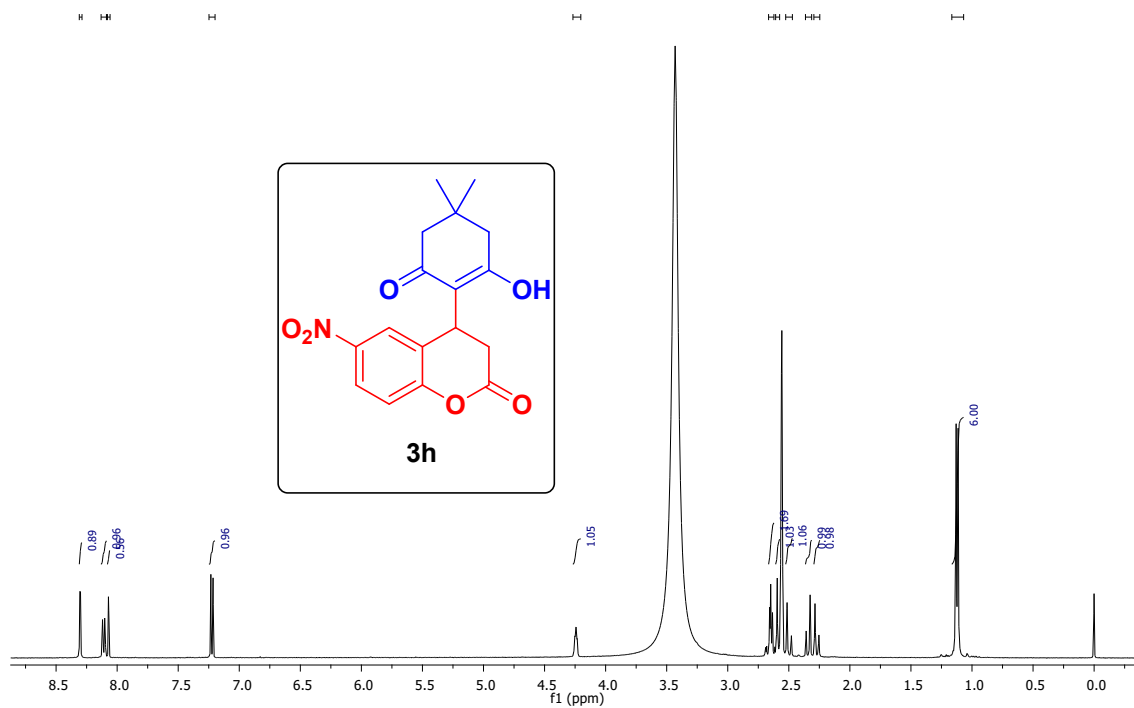


DC-2
single_pulse decoupled gated NOE



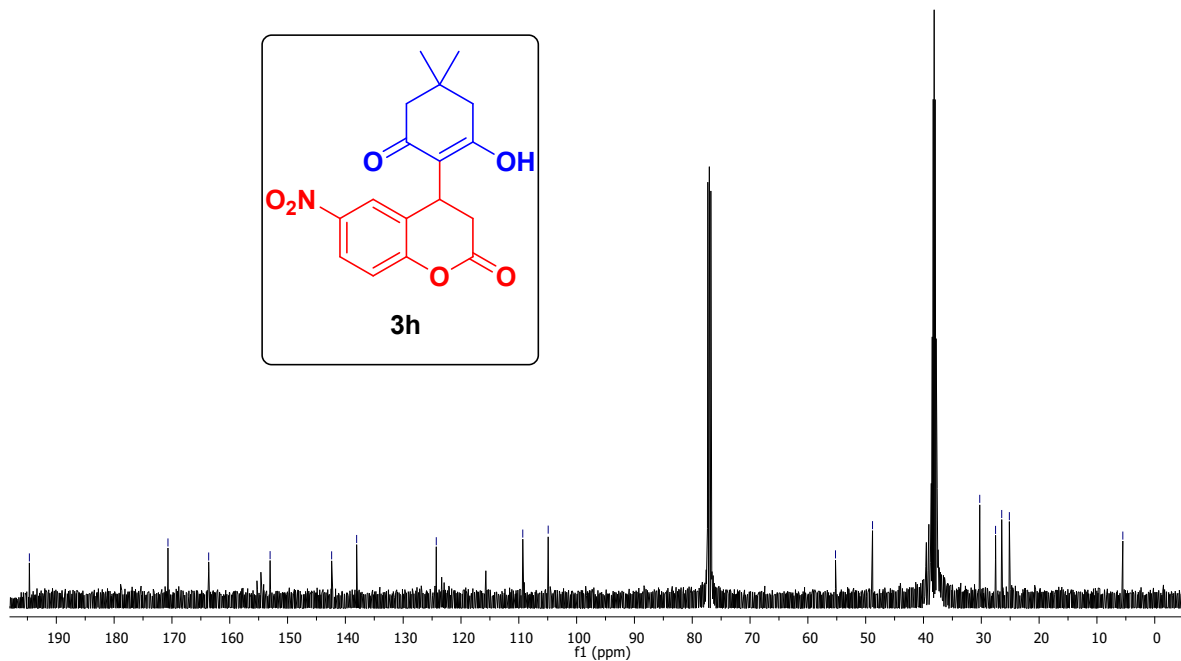
Copies of ¹HNMR and ¹³CNMR spectra of Compound 3h

Bhupender
RC-BK-DC-6
PROTONRO CDCl3 {E:\data} CUG 1



Bhupender
RC-BK-DC-6
13C_new_Dec2021 CDCl3 {E:\data} CUG 1

170.69, 163.65, 153.02, 142.38, 138.05, 124.28, 109.31, 104.92, 55.22, 48.82, 30.27, 27.53, 26.47, 25.15, 5.52



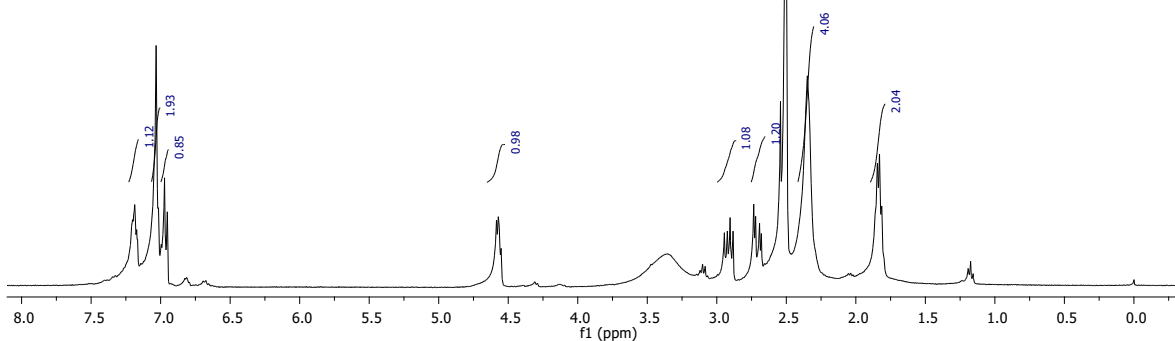
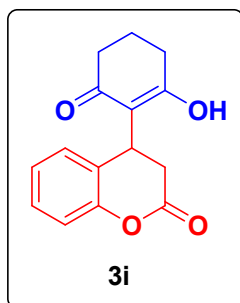
Copies of ^1H NMR and ^{13}C NMR spectra of **Compound 3i**

DC-11
single_pulse

— — —

—

— — — —



DC-11
single_pulse decoupled gated NOE

—

—

—

—

—

—

—

—

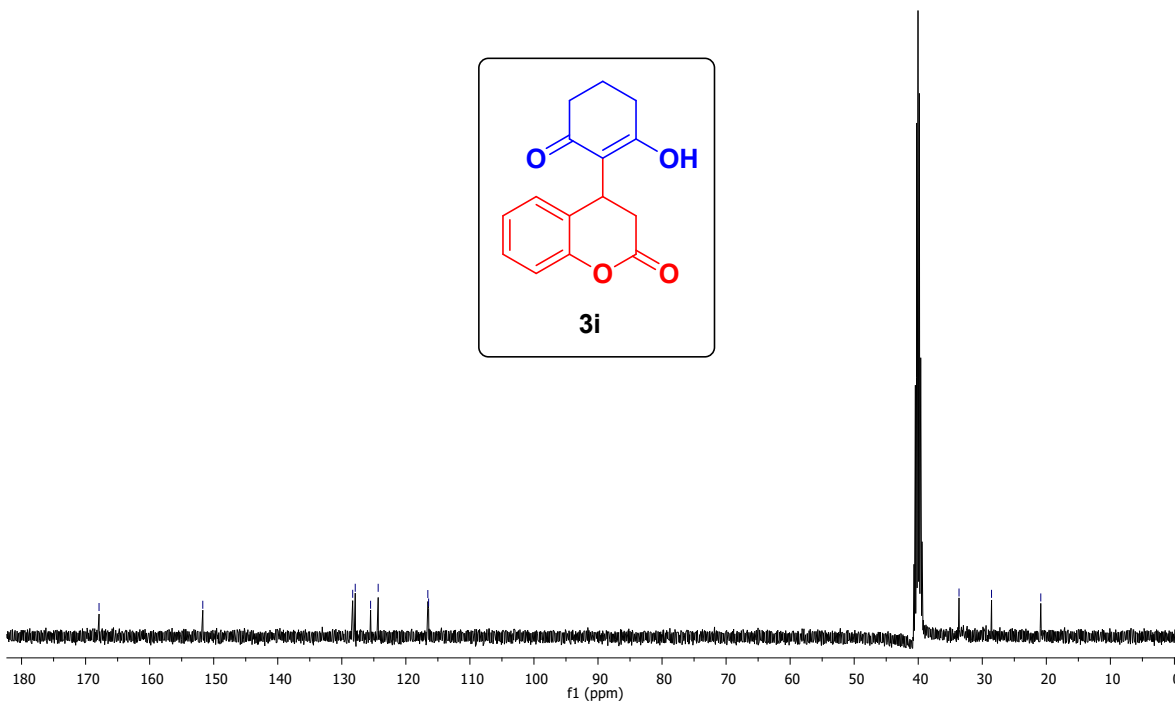
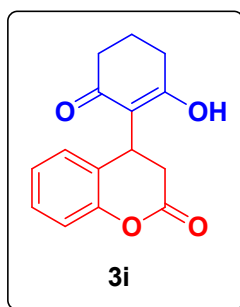
—

—

—

—

—



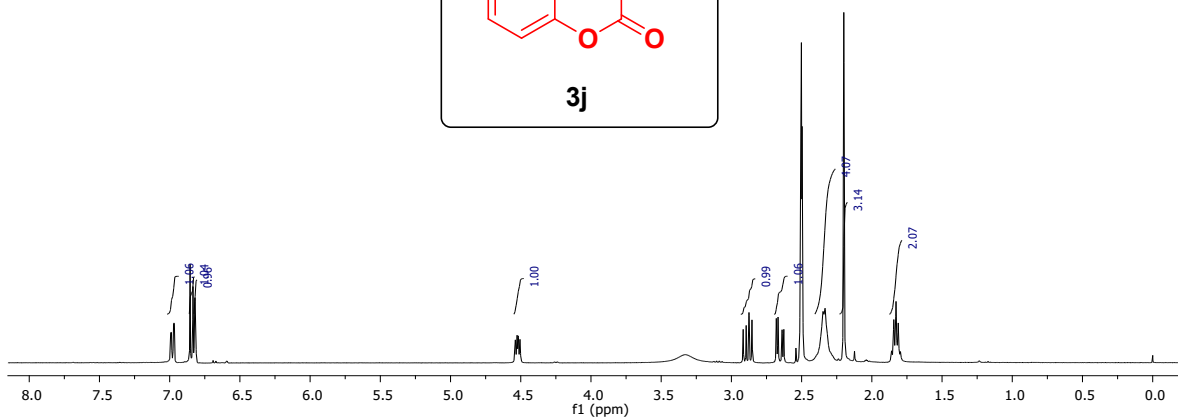
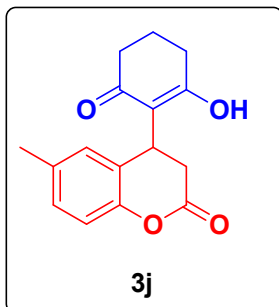
Copies of ¹HNMR and ¹³CNMR spectra of **Compound 3j**

DC-14
single_pulse

H H

H

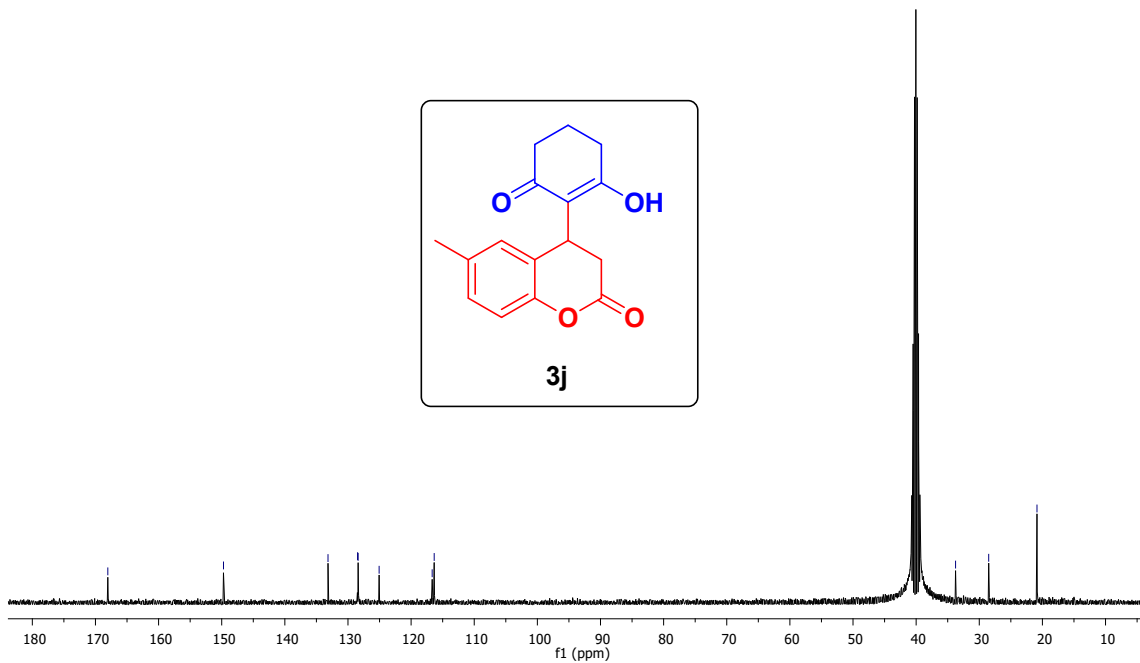
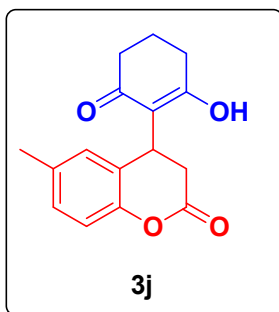
H H H H H



DC-14
single pulse decoupled gated NOE

133.16
128.48
126.39
125.07
116.66
116.34

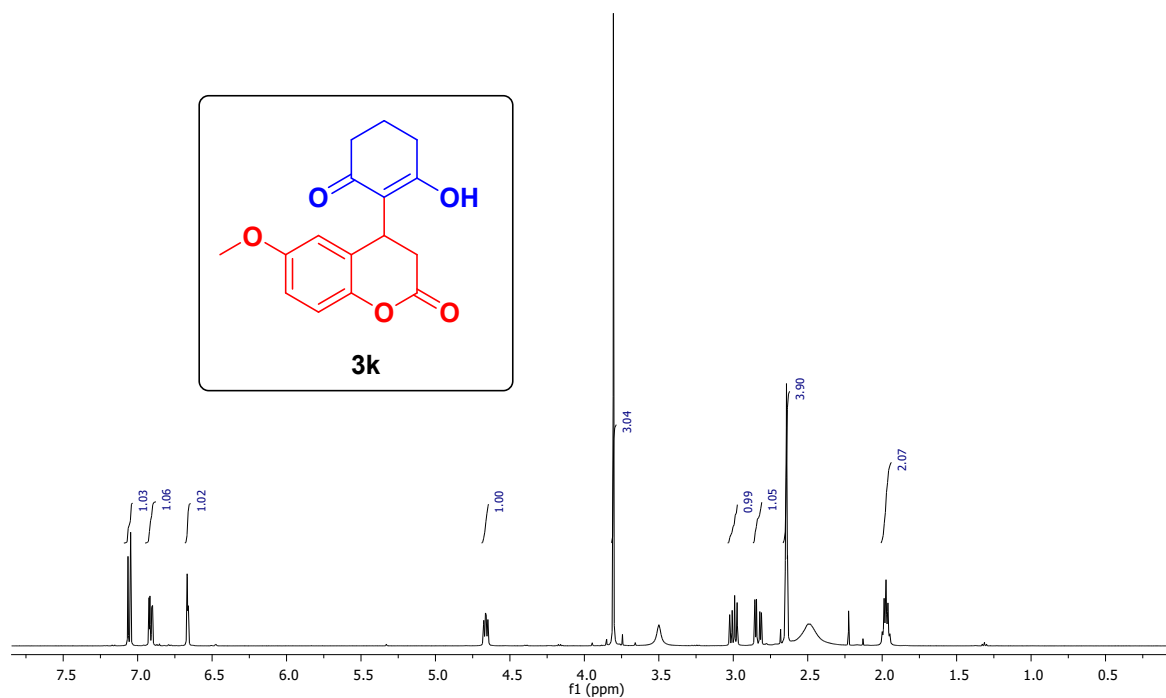
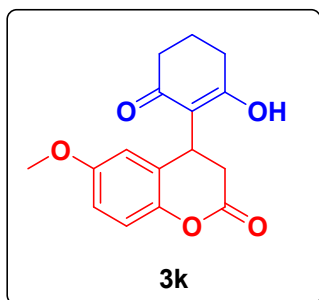
33.75
28.51
20.86



Copies of ¹H NMR and ¹³C NMR spectra of Compound 3k

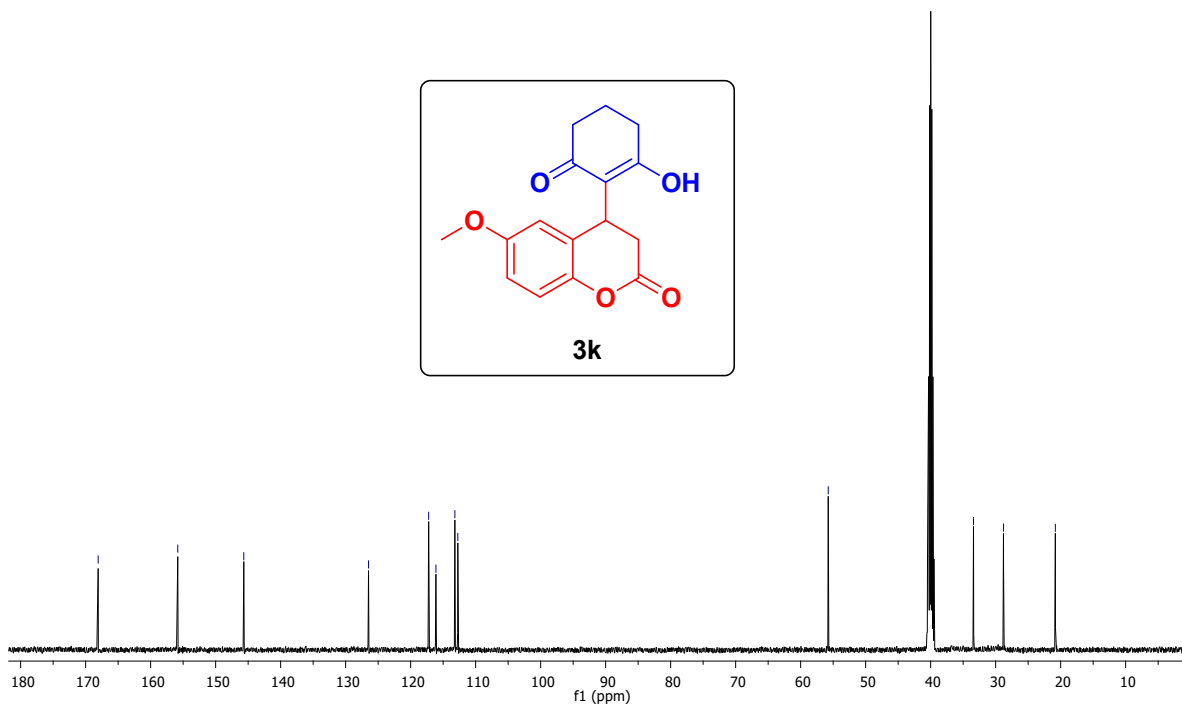
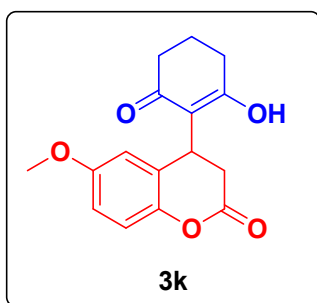
Bhupender
RC-BK-DC-18
PROTONRO DMSO-d₆ {E:\data} CUG 1

H H H H H



Bhupender
RC-BK-DC-18
C13CPD DMSO {E:\data} CUG 1

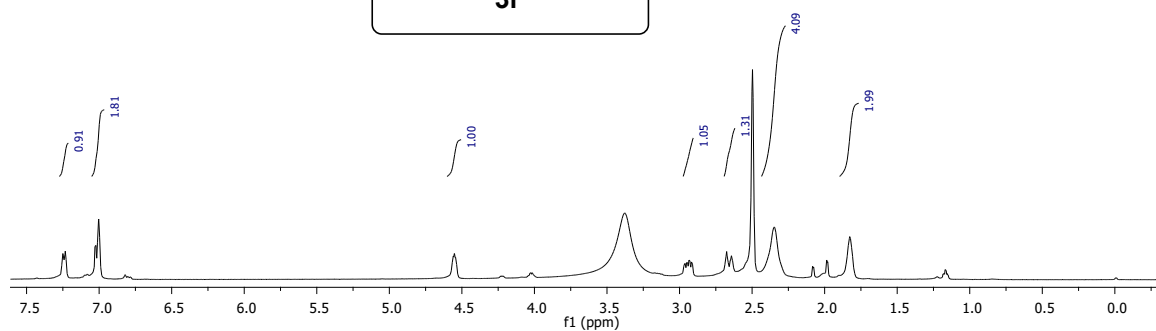
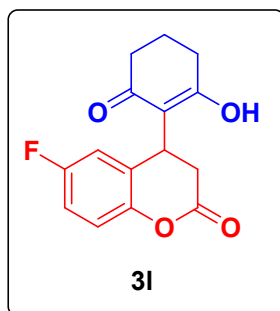
145.67 126.48 117.23 116.11 113.20 112.74 55.76 33.41 28.80 20.82



Copies of ¹HNMR and ¹³CNMR spectra of **Compound 3I**

Bhupender
RC-BK-DC-15
PROTONRO DMSO (E:\data) CUG 1

— — — — —

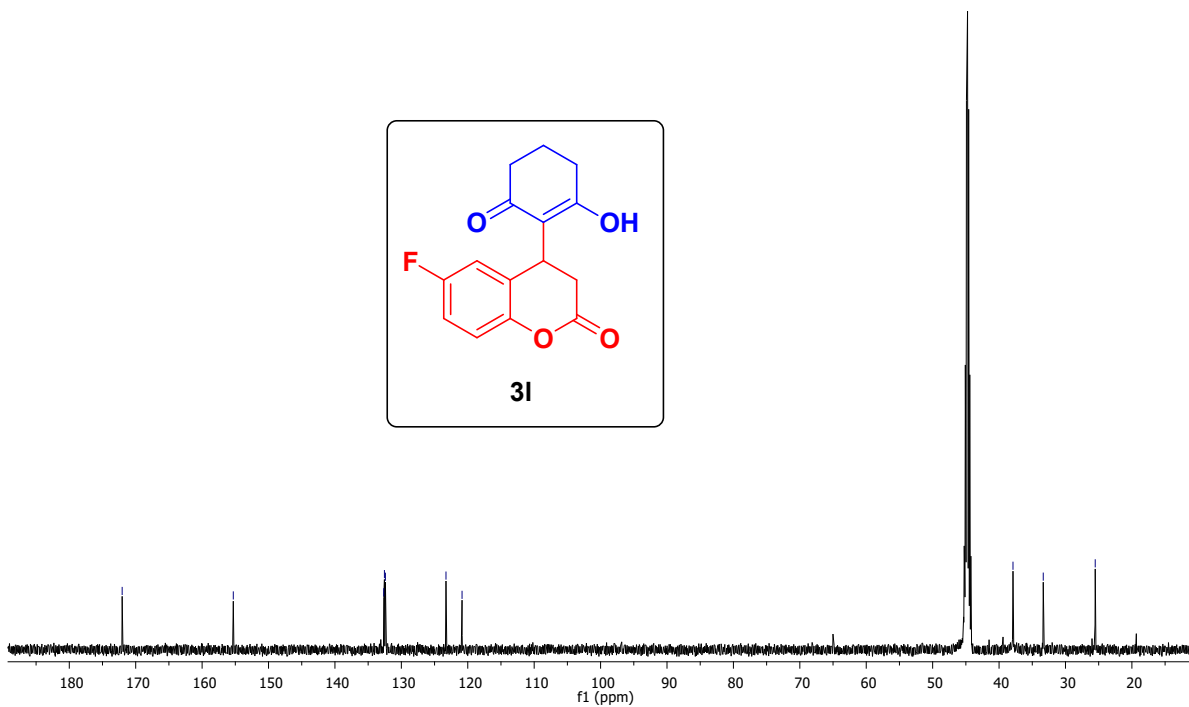
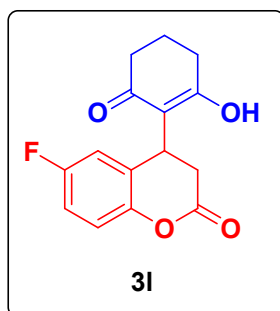


Bhupender
RC-BK-DC-15
C13CPD CDCl3 (E:\data) CUG 1

132.65
132.55
132.40

123.28
120.86

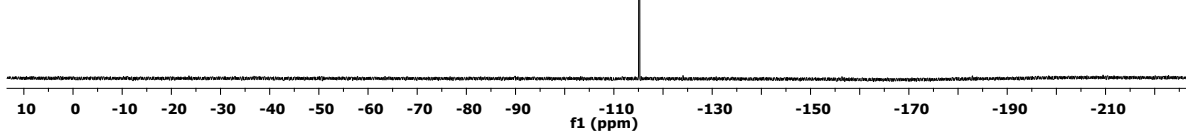
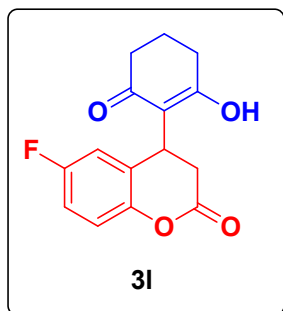
37.90
33.25
25.52



Copy of ^{19}F NMR spectra of Compound 3l

Bhupender
RC-BK-DC-15-3l
F19CPD CDCl3 (E:\data) CUG 1

-115.20



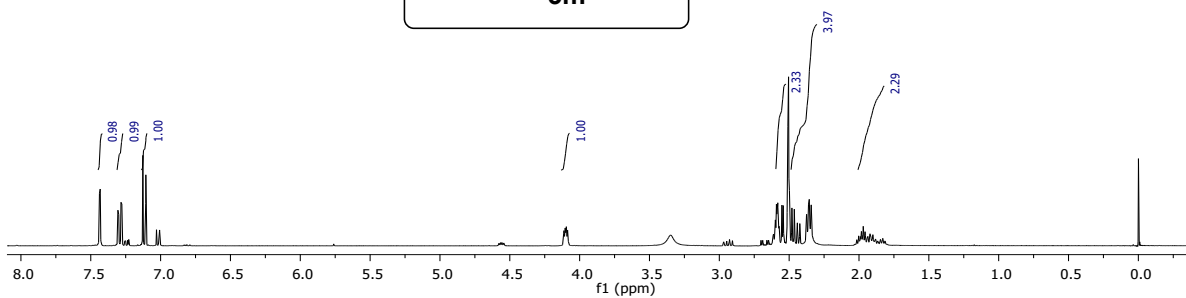
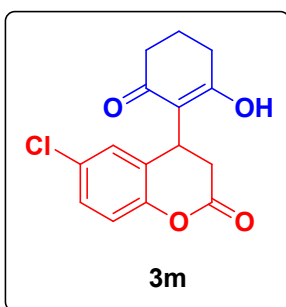
Copies of ^1H NMR and ^{13}C NMR spectra of Compound 3m

DC-13
single_pulse

H H H

H

H H H H

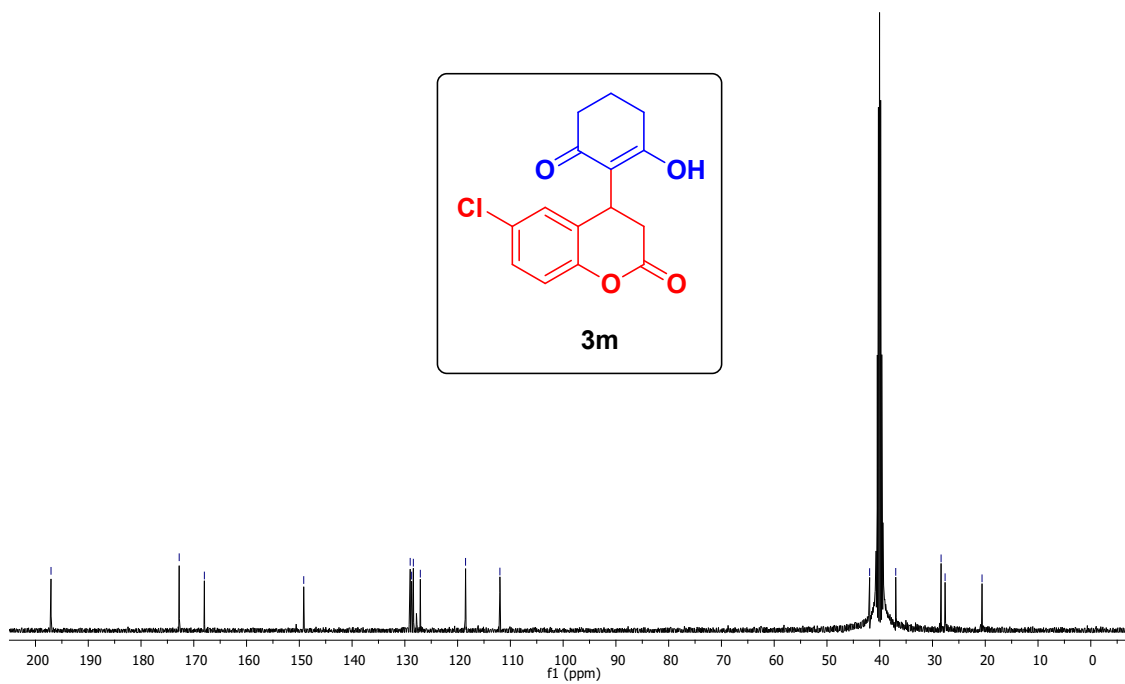
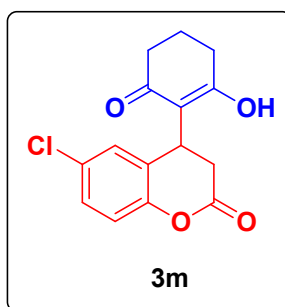


DC-13C
single pulse decoupled gated NOE

149.16

128.99
128.72
128.39
127.07
118.49
111.98

41.91
36.97
28.37
27.61
20.61



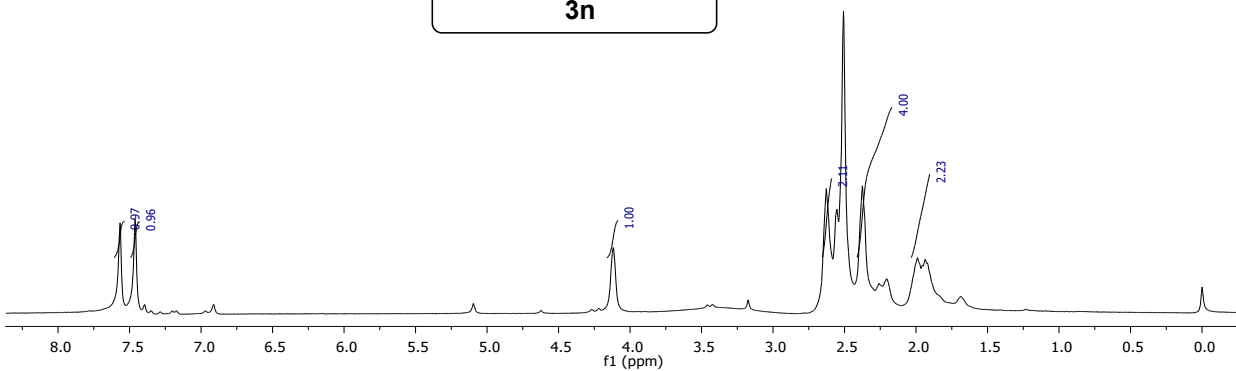
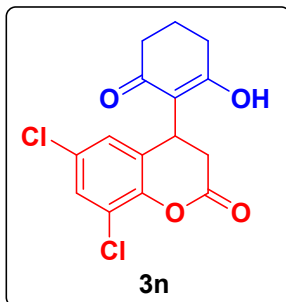
Copies of ^1H NMR and ^{13}C NMR spectra of **Compound 3n**

DC-17
single_pulse

HH

H

H H H H



DC-17
single pulse decoupled gated NGE

187.00

167.73

167.42

145.31

128.71

128.61

128.37

128.06

121.76

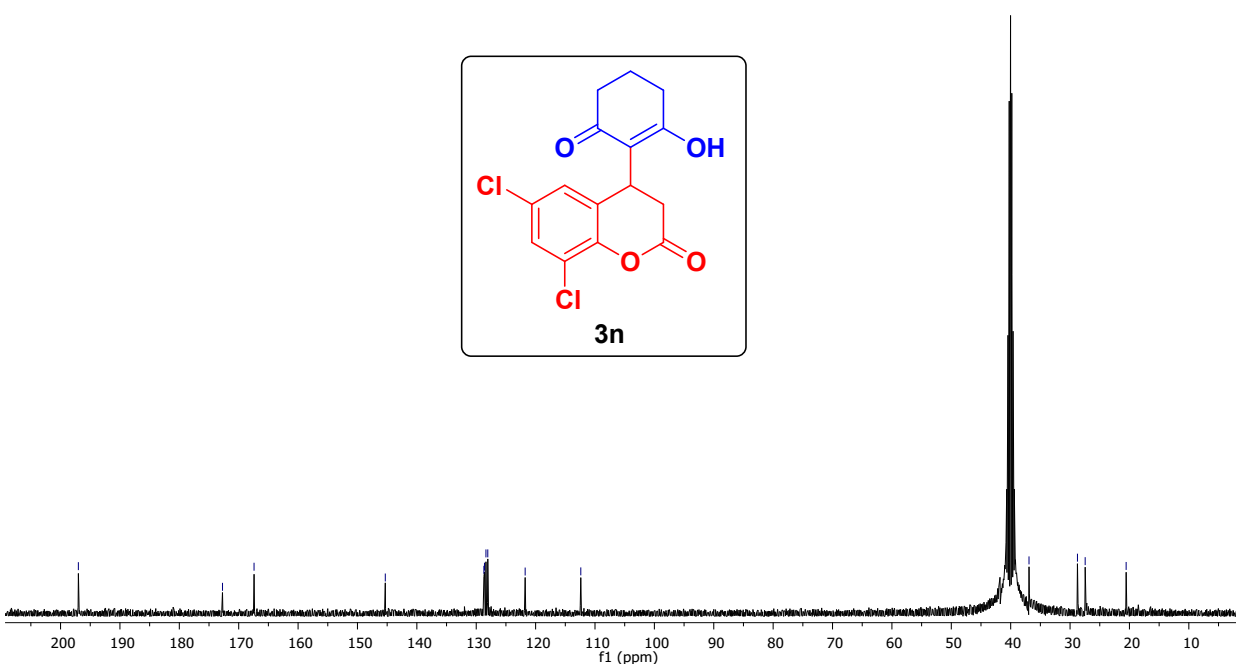
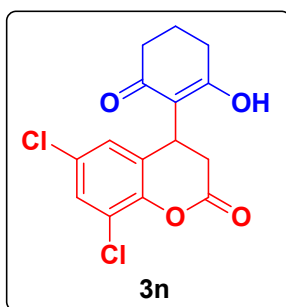
112.39

36.91

28.75

27.45

20.56



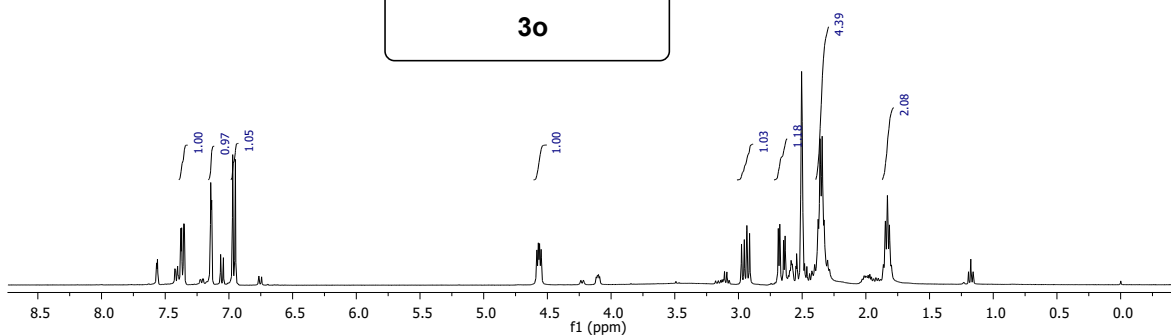
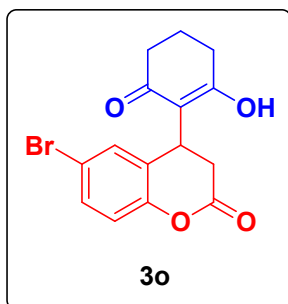
Copies of ¹HNMR and ¹³CNMR spectra of **Compound 3o**

DC-12
single_pulse

H H H

H

H H H H

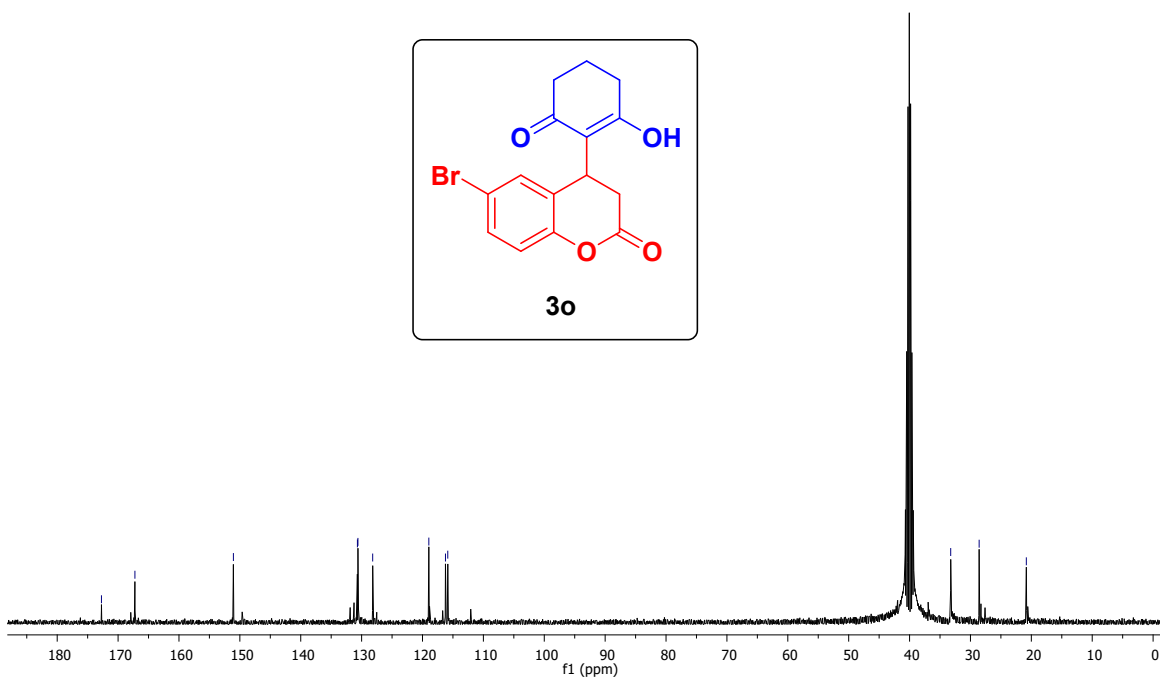
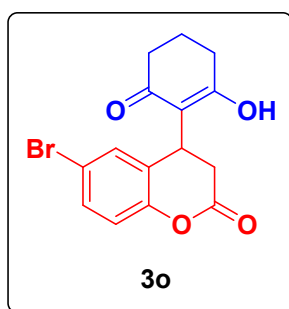


DC-12
single_pulse

decoupled gated NOE

130.69
130.61
128.18
118.96
116.23
115.85

33.24
28.57
20.82



Copies of ^1H NMR and ^{13}C NMR spectra of **Compound 3p**

DC-16
single_pulse

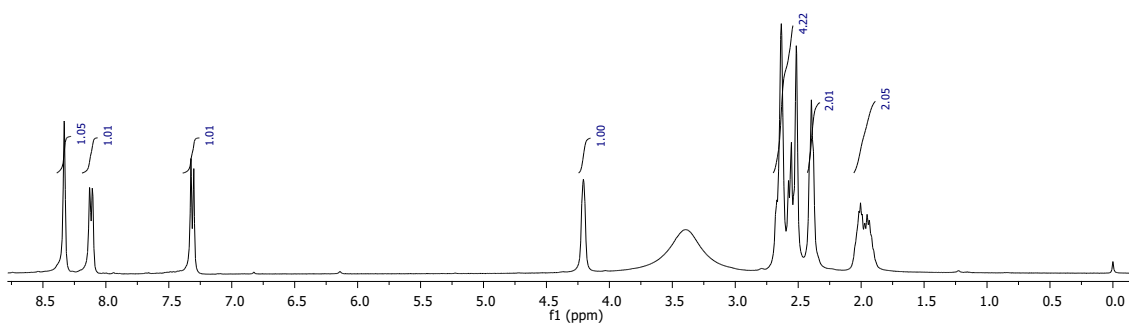
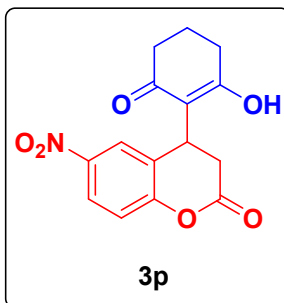
— —

—

—

— —

—



DC-16
single_pulse

— —

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

—

