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Supporting information

Visible-light synthesis of 4-substituted-chroman-2-ones and 2-substituted-chroman-4-ones using doubly decarboxylative Giese reaction

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1. General methods

NMR spectra were acquired on a Bruker Ultra Shield 700 instrument, running at 700 MHz for ^{1}H and 176 MHz for ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$: 7.26 ppm for 1H NMR, 77.16 ppm for ^{13}C NMR Mass spectra were recorded on a Bruker Maxis Impact spectrometer using electrospray (ES+) ionization (referenced to the mass of the charged species). Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates (Merck Kieselgel 60 F254) and visualized by ultraviolet irradiation. Unless otherwise noted, analytical grade solvents and commercially available reagents were used without further purification. For flash chromatography (FC) silica gel (Silica gel 60, 230-400 mesh, Fluka). Blue LED (50 W, λ = 456 nm), were purchased from commercial supplier Kessil LED photoreactor lightning. Fluorescence measurements were performed using Varian Cary Eclipse spectrofluorometer equipped with thermos stated cell holder. Coumarine-3-carboxylic acids[1] **2** and chromone-3-carboxylic acids[2] **4** were synthetized according to the literature procedure. *N*-(Acyloxy)phthalimides (NHPI esters) **1** were prepared from the corresponding starting materials following the literature procedure.[3]

Figure S1 shows the 50W 456nm photochemical reaction setup. The reaction vials in front of the 50W 456 nm bulb at approximatively 4.5 cm distance. To maintain a stable reaction temperature two fans were placed in close proximity to the reaction vials (23±2 °C).

[1] A. Song, X. Wang and K. S. Lam, *Tetrahedron Lett.* 2003, **44**, 1755.
[2] N. Ishizuka, K. Matsumura, K. Sakai, M. Fujimoto, S. Mihara and T. Yamamori, *J. Med. Chem.*, 2002, **45**, 2041.
[3] A. Fawcett, J. Pradeilles, Y. Wang, T. Mutsuga, E. L. Myers and V. K. Aggarwal, *Science*, 2017, **357**, 283.

Fig. S1. Photochemical reaction setup using 50W 456nm Kessil LED.

2. Cyclic voltammetry

The electrochemical measurements were performed using Autolab PGSTAT302N potentiostat/galvanostat (Metrohm). A three-electrode electrochemical cell was equipped with platinum plate as a working electrode, saturated calomel electrode as a reference one and platinum wire as an auxiliary electrode.

All measurements were carried out in CH_3CN with 0.1 mol/L tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte under room temperature. The solutions were degassed with argon prior to measurements. The concentration of substrates was 1 mmol/L. Cyclic voltammograms were recorded with the scan rate of 0.1 V/s.

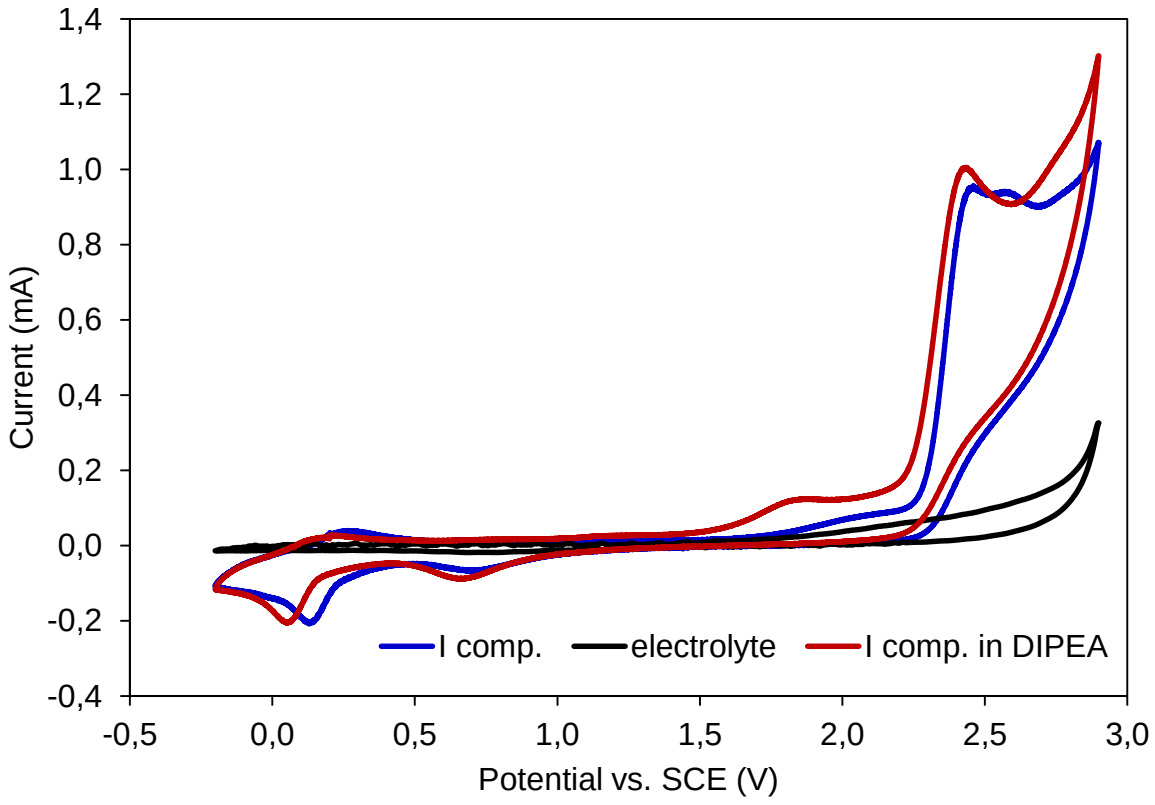


Fig. S2. Cyclic voltammograms recorded in a solution of **2a** (compound I) in the presence and without DIPEA, and in supporting electrolyte in CH_3CN at the scan rate of 0.1 V/s.

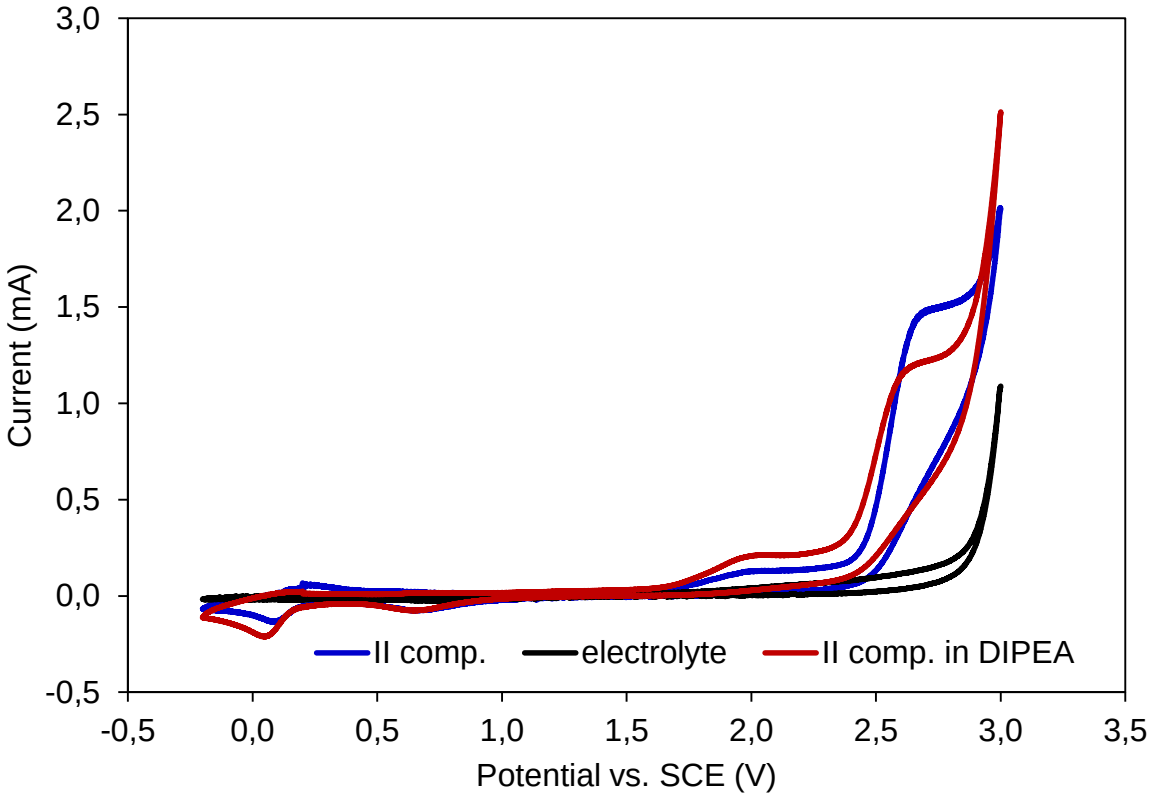


Fig. 3. Cyclic voltammograms recorded in a solution of **4a** (compound II) in the presence and without DIPEA, and in supporting electrolyte in CH_3CN at the scan rate of 0.1 V/s.

$E_{1/2}$ values determined for **2a** and **4a** vs. SCE (saturated calomel electrode)

2a coumarin-3-carboxylic acid - 2.403 V (the first peak)

2a coumarin-3-carboxylic acid in DIPEA – 2.371 V

4a chromone -3-carboxylic acid - 2.620 V

4a chromone -3-carboxylic acid in DIPEA – 2.567 V

The coumarin-3-carboxylic acid (0.2 mmol) **2a** is oxidized at Pt electrode in at least two electrode steps or in at least one electrode step in the presence of DIPEA (0.2 mmol) and in the potential range from 2.1 to 2.9 V. The value of peak current (I_p) determined from cyclic voltammograms is comparable in the presence and without DIPEA. However, the half-wave potential ($E_{1/2}$) determined from cyclic voltammograms is by about 30 mV lower in the presence of DIPEA in comparison with the solution without DIPEA.

In the case of chromone-3-carboxylic acid (0.2 mmol) **4a**, its oxidation at Pt electrode proceeds in at least one electrode step independently on the presence of DIPEA (0.2 mmol) in the potential range from 2.2 to 3.0 V. However, a slight shift in the peak potential towards lower values is observed. Simultaneously, the value of $E_{1/2}$ shifts by about 50 mV towards lower values in the presence of DIPEA. Moreover, a clear decrease in the peak current is observed in

the second compound solution with DIPEA. The comparison of these values suggests that the second compound is oxidized slightly easier in the presence of DIPEA but with the higher rate if DIPEA is not added to the solution.

3. Fluorescence Quenching

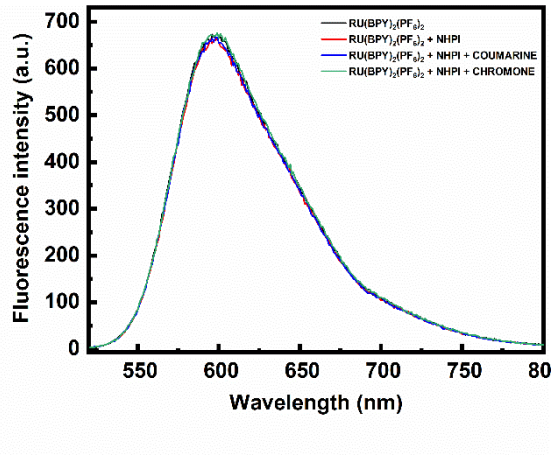


Fig. S4. Fluoresence spectra of $Ru(bpy_3)_2(PF_6)_2$ (25 μL) in CH_2Cl_2, $Ru(bpy_3)_2(PF_6)_2$ (25 μL) and NHPI (250 μL) in CH_2Cl_2, $Ru(bpy_3)_2(PF_6)_2$ (25 μL) and NHPI (250 μL) and coumarin-3-carboxylic acid (0.3 mM) in CH_2Cl_2 or $Ru(bpy_3)_2(PF_6)_2$ (25 μL) and NHPI (250 μL) and chromone-3-carboxylic acid (0.3 mM) in CH_2Cl_2 using extraction wavelength 470 nm.

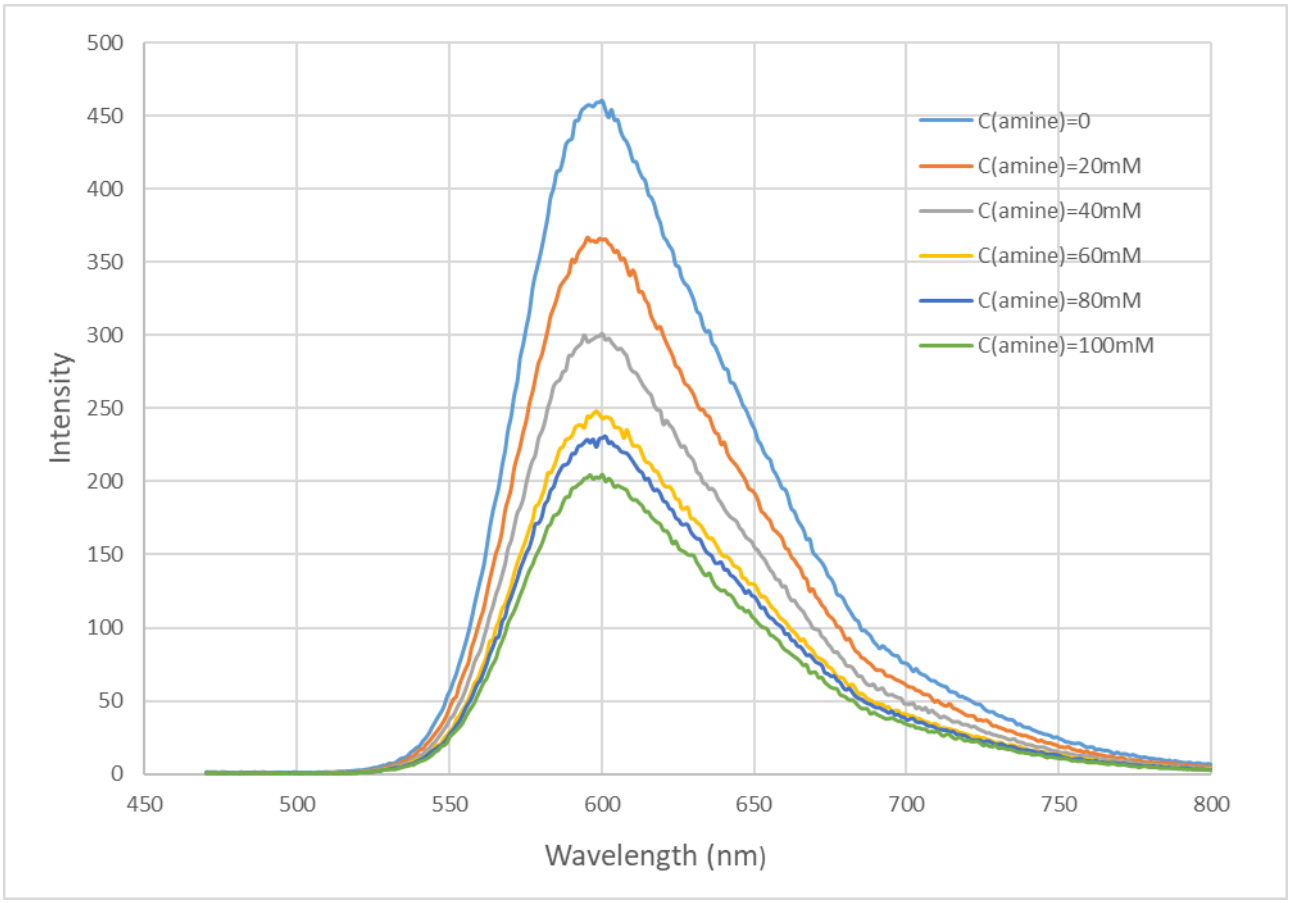


Fig. S5 Fluorescence quenching of $Ru(bpy)_3(PF_6)_3$ by DIPEA in CH_2Cl_2.

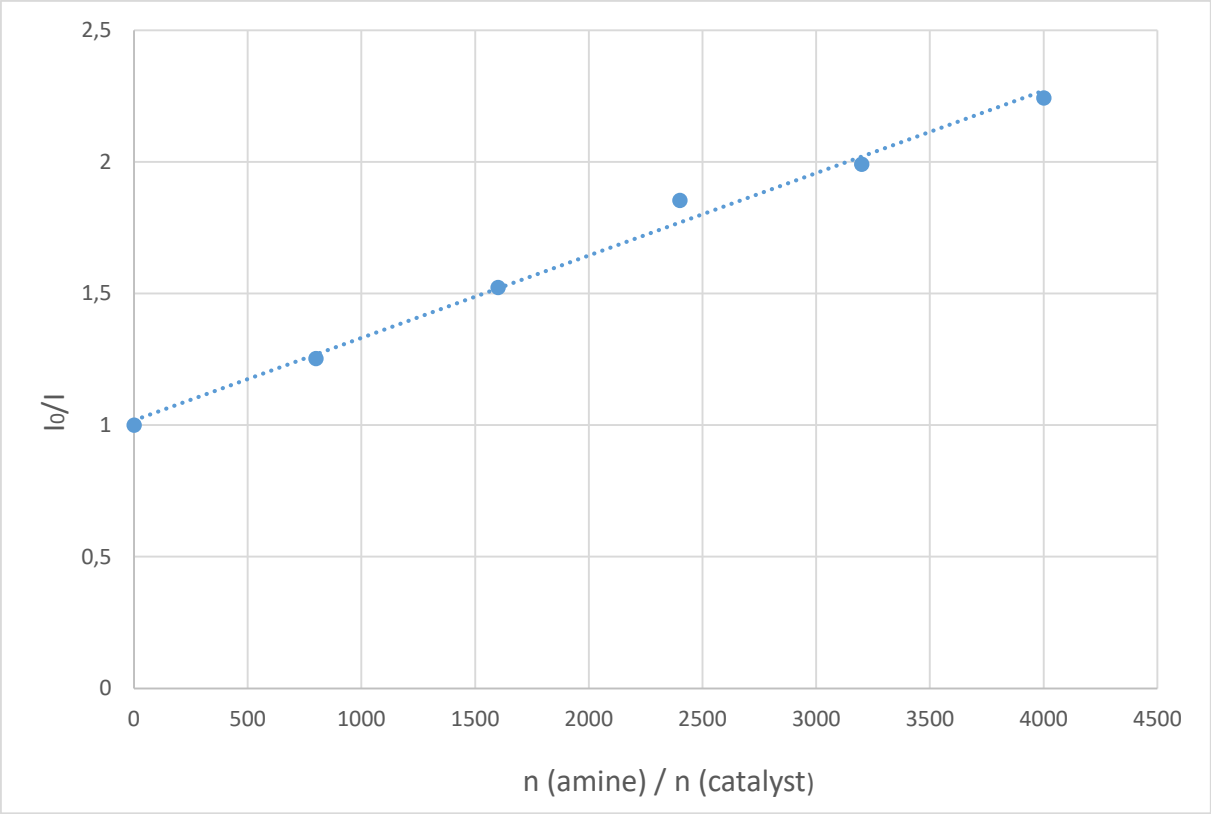


Fig. S6 Stern-Volmer plot of Fluorensence quenching of $Ru(bpy)_3(PF_6)_3$ by DIPEA.

4. General procedure for the synthesis of 4-substituted-chroman-2-ones 3aa-ia and 2-substituted-chroman-4-ones 5aa-ia

*General procedure for the synthesis of 4-substituted-chroman-2-ones **3aa-ia** and 2-substituted-chroman-4-ones **5aa-ia***. In the 10 mL Schlenk tube *N*-(acyloxy)phthalimide **1** (0.2 mmol, 1.0 equiv) and coumarin-3-carboxylic acid **2** (0.24 mmol, 1.2 equiv) or chromone-3-carboxylic acid **4** (0.24 mmol, 1.2 equiv), DIPEA (0.4 mmol, 2.0 equiv) and catalyst $Ru(bpy)_3(PF_6)_2$ (10 mol%) were dissolved in dry CH_2Cl_2 (3 mL). Reaction mixture was degassed and filled three times with argon. Subsequently, the mixture was irradiated with blue LED for 24 h. Next, the reaction was quenched with saturated solution of $NaHCO_3$ (5 mL), extracted with CH_2Cl_2 (3×10 mL) and washed with brine (5 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (*n*-hexane:ethyl acetate 95:5) to provide the desired products **3** or **5**.

4-Cyclohexylchroman-2-one **3aa**. Pure product was isolated by flash chromatography on silica gel (hexane/ethyl acetate 4:1) as yellow oil in 82% yield (37.7 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.27-7.24 (m, 1H), 7.14 (m, 1H), 7.11-7.08 (m, 1H), 7.05 (dd, *J* = 8.1, 1.2 Hz, 1H), 2.94 (dd, *J* = 15.8, 2.1 Hz, 1H), 2.76 (td, *J* = 6.8, 2.1 Hz, 1H), 2.72 (dd, *J* = 15.8, 6.8 Hz, 1H), 1.80 (ddd, *J* = 8.9, 6.9, 3.2 Hz, 1H), 1.72 (dddt, *J* = 14.6, 12.4, 4.7, 3.2 Hz, 2H), 1.65 – 1.61 (m, 1H), 1.46 (tdd, *J* = 11.6, 6.9, 3.4 Hz, 1H), 1.22 – 1.07 (m, 4H), 1.05 – 0.96 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.1, 151.8, 129.2, 128.4, 125.7, 124.1, 117.2, 41.9, 41.4, 32.5, 30.7, 29.7, 26.3, 26.3, 26.2. HRMS calculated for $C_{15}H_{19}O_2^+$ [M+H]+ m/z: 231.1380, found: 231.1382.

4-Cyclohexyl-6-methylchroman-2-one **3ab**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as pale yellow oil in 64% yield (30.6 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.06 – 7.03 (m, 1H), 6.94 – 6.92 (m, 2H), 2.94 – 2.89 (m, 1H), 2.72 – 2.66 (m, 2H), 2.33 (s, 3H), 1.81 – 1.76 (m, 1H), 1.76 – 1.69 (m, 2H), 1.65 – 1.51 (m, 1H), 1.61 – 1.57 (m, 1H), 1.48 – 1.42 (m, 1H), 1.22 – 1.06 (m, 3H), 1.04 – 0.95 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.4, 149.7, 133.6, 129.6, 128.8, 125.4, 116.9, 42.0, 41.4, 32.5, 30.8, 29.7, 26.3, 26.3, 26.2, 20.9. HRMS calculated for $C_{16}H_{21}O_2^+$ [M+H]+ m/z: 245.1536, found: 245.1533.

4-Cyclohexyl-6-methoxychroman-2-one **3ab**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as pale yellow oil in 70% yield (36.4 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.8 Hz, 1H), 6.78 (dd, *J* = 8.8, 3.0 Hz, 1H),

6.66 (d, *J* = 3.0 Hz, 1H), 3.79 (s, 3H), 2.91 (dd, *J* = 15.5, 1.7 Hz, 1H), 2.72 – 2.66 (m, 2H), 1.81 – 1.77 (m, 1H), 1.72 (dddd, *J* = 16.1, 8.2, 4.1, 2.4 Hz, 2H), 1.65 – 1.60 (m, 3H), 1.46 (ddq, *J* = 11.7, 10.0, 3.3 Hz, 1H), 1.22 – 1.05 (m, 3H), 1.05 – 0.94 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.3, 155.9, 145.8, 126.7, 117.8, 114.5, 113.1, 55.8, 41.9, 41.7, 32.4, 30.8, 29.7, 26.3, 26.3, 26.2. HRMS calculated for $C_{16}H_{21}O_3^+$ [M+H]+ m/z: 261.1485, found: 261.1489.

4-Cyclohexyl-7-methoxychroman-2-one **3ad**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as yellow oil in 71% yield (36.9 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.03 – 7.01 (m, 1H), 6.65 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.59 (d, *J* = 2.5 Hz, 1H), 3.78 (s, *J* = 3.2 Hz, 3H), 2.90 (dt, *J* = 12.4, 3.2 Hz, 1H), 2.72 – 2.67 (m, 2H), 1.79 – 1.75 (m, 1H), 1.75 – 1.67 (m, 2H), 1.64 – 1.55 (m, 2H), 1.45 – 1.38 (m, 1H), 1.19 – 1.10 (m, 2H), 1.08 (dt, *J* = 12.8, 3.4 Hz, 1H) 1.01 – 0.93 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.1, 159.7, 152.5, 129.7, 117.4, 110.2, 102.5, 55.6, 42.2, 40.6, 32.6, 30.6, 29.7, 26.3, 26.3, 26.2. HRMS calculated for $C_{16}H_{21}O_3^+$ [M+H]+ m/z: 261.1485, found: 261.1482.

4-Cyclohexyl-6-fluorochroman-2-one **3ae**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as white oil in 61% yield (30.3 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 8.7, 4.7 Hz, 1H), 6.97 – 6.94 (m, 1H), 6.85 (dd, *J* = 8.7, 3.0 Hz, 1H), 2.93 (dd, *J* = 15.7, 2.2 Hz, 1H), 2.74 (td, *J* = 6.7, 2.2 Hz, 1H), 2.69 (dd, *J* = 15.9, 6.7 Hz, 1H), 1.81 – 1.70 (m, 3H), 1.65 (ddd, *J* = 12.3, 4.8, 2.2 Hz, 1H), 1.62 – 1.57 (m, 1H), 1.50 – 1.43 (m, 1H), 1.23 – 1.06 (m, 3H), 1.00 (dqd, *J* = 15.9, 12.3, 3.4 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 168.6, 158.9 (d, *J* = 243,4 Hz), 147.8, 127.4 (d, *J* = 7.6 Hz), 118.4 (d, *J* = 8.5 Hz) 115.7 (d, *J* = 23.6 Hz), 115.0 (d, *J* = 23.5 Hz), 41.8, 41.5, 32.0, 30.7, 29.6, 26.3, 26.2, 26.2. HRMS calculated for $C_{15}H_{18}FO_2^+$ [M+H]+ m/z: 249.1285, found: 249.1288.

6-Bromo-4-cyclohexylchroman-2-one **3af**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as white oil in 51% yield (31.5 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 1H), 2.94 (dd, *J* = 16.0, 2.2 Hz, 1H), 2.74 (td, *J* = 6.7, 2.1 Hz, 1H), 2.69 (dd, *J* = 16.0, 6.7 Hz, 1H), 1.74 (dtd, *J* = 9.4, 8.1, 8.0, 4.7 Hz, 3H), 1.67 – 1.62 (m, 1H), 1.61 – 1.56 (m, 1H), 1.48 – 1.41 (m, 1H), 1.23 – 1.07 (m, 3H), 1.04 – 0.94 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 168.3, 150.9, 131.9, 131.4, 127.9, 119.0, 116.8, 41.9, 41.3, 32.0, 30.7, 29.6, 26.2, 26.2, 26.1. HRMS calculated for $C_{15}H_{18}BrO_2^+$ [M+H]+ m/z: 309.0485, found: 309.0492.

6-Chloro-4-cyclohexylchroman-2-one **3ag**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as white oil in 70% yield (37.1 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.13 (d, *J* = 2.5 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 2.94 (dd, *J* = 16.0, 2.2 Hz, 1H), 2.74 (td, *J* = 6.7, 2.2 Hz, 1H), 2.69 (dd, *J* = 16.0, 6.6 Hz, 1H), 1.74 (ddd, *J* = 14.5, 13.3, 8.6 Hz, 3H), 1.67 – 1.62 (m, 1H), 1.62 – 1.57 (m, 1H), 1.46 (tdd, *J* = 11.7, 6.6, 3.3 Hz, 1H), 1.23 – 1.07 (m, 3H), 1.04 – 0.95 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 168.3, 150.3, 129.2, 129.0, 128.4, 127.4, 118.5, 41.9, 41.4, 32.0, 30.7, 29.6, 26.2, 26.2, 26.1. HRMS calculated for $C_{15}H_{18}ClO_2^+$ [M+H]+ m/z: 265.0990, found: 265.0998.

8-Chloro-4-cyclohexylchroman-2-one **3ah**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as pale yellow oil in 38% yield (20.1 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 1H), 7.05 – 7.01 (m, 2H), 2.98 (dd, *J* = 16.0, 2.2 Hz, 1H), 2.79 – 2.75 (m, 1H), 2.72 (dd, *J* = 16.0, 6.4 Hz, 1H), 1.84 – 1.79 (m, 1H), 1.77 – 1.73 (m, 1H), 1.72 – 1.68 (m, 1H), 1.66 – 1.61 (m, 1H), 1.61 – 1.56 (m, 1H), 1.48 – 1.42 (m, 1H), 1.22 – 1.06 (m, 3H), 1.03 – 0.95 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 167.7, 147.6, 129.2, 127.7, 127.6, 124.3, 122.3, 41.8, 41.6, 32.2, 30.8, 29.8, 26.2, 26.2, 26.2. HRMS calculated for $C_{15}H_{18}ClO_2^+$ [M+H]+ m/z: 265.0990, found: 265.0991.

6,8-Dichloro-4-cyclohexylchroman-2-one **3ai**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 4:1) as white oil in 49% yield (29.3 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 2.98 (dd, *J* = 16.1, 2.2 Hz, 1H), 2.75 (td, *J* = 7.0, 2.2 Hz, 1H), 2.70 (dd, *J* = 16.2, 6.4 Hz, 1H), 1.79 (d, *J* = 16.2 Hz, 1H), 1.76 – 1.71 (m, 1H), 1.66 (d, *J* = 12.7 Hz, 1H), 1.57 (d, *J* = 12.7 Hz, 2H), 1.49 – 1.42 (m, 1H), 1.22 – 1.09 (m, 3H), 0.99 (qdd, *J* = 11.8, 9.7, 3.2 Hz, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 166.9, 146.5, 129.1, 129.0, 128.9, 127.4, 123.2, 41.9, 41.6, 31.9, 30.8, 29.7, 26.2, 26.2, 26.1. HRMS calculated for $C_{15}H_{17}Cl_2O_2^+$ [M+H]+ m/z: 300.1985, found: 300.1987.

4-Isopropylchroman-2-one **3ba**. Pure product was isolated by flash chromatography on silica gel (pentane:ethyl acetate 95:5) as pale yellow oil in 45% yield (17.1 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 1H), 7.16 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.11 (td, *J* = 7.5, 1.2 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.2 Hz, 1H), 2.93 – 2.88 (m, 1H), 2.77 – 2.75 (m, 1H), 2.75 – 2.72 (m, 1H), 1.89 – 1.82 (m, 1H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.0, 151.8, 129.1, 128.4, 125.6, 124.2, 117.2, 42.0, 32.4, 32.3, 20.3, 19.3. HRMS calculated for $C_{12}H_{15}O_2^+$ [M+H]+ m/z: 191.1067, found: 191.1071.

4-(tert-Butyl)chroman-2-one **3ca**. Pure product was isolated by flash chromatography on silica gel (pentane:ethyl acetate 95:5) as yellow oil in 60% yield (24.5 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.17 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.10 (td, *J* = 7.5, 1.2 Hz, 1H), 7.06 (dd, *J* = 8.1, 1.2 Hz, 1H), 3.04 (dd, *J* = 16.5, 1.2 Hz, 1H), 2.74 (d, *J* = 7.7 Hz, 1H), 2.68 (dd, *J* = 16.5, 7.7 Hz, 1H), 0.95 (s, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.6, 152.2, 130.9, 128.6, 123.8, 123.8, 117.3, 46.0, 35.0, 31.4, 27.5 (3 x C). HRMS calculated for $C_{13}H_{17}O_2^+$ [M+H]+ m/z: 205.1223, found: 205.1228.

4-(1-Methylcyclohexyl)chroman-2-one **3da**. Pure product was isolated by flash chromatography on silica gel (pentane:ethyl acetate 95:5) as pale yellow oil in 58% yield (28.3 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.17 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.11-7.08 (m, 1H), 7.06 (dd, *J* = 8.1, 1.2 Hz, 1H), 3.06 (dd, *J* = 16.6, 1.3 Hz, 1H), 2.81 (d, *J* = 7.4 Hz, 1H), 2.63 (dd, *J* = 16.6, 7.4 Hz, 1H), 1.59 – 1.47 (m, 4H), 1.47 – 1.30 (m, 4H), 1.30 – 1.25 (m, 1H), 1.16 (dt, *J* = 14.4, 7.6 Hz, 1H), 0.85 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.7, 152.3, 130.8, 128.4, 123.5, 123.4, 117.1, 45.7, 37.2, 35.4, 35.0, 30.3, 26.0, 21.8, 21.6, 19.6. HRMS calculated for $C_{16}H_{21}O_2^+$ [M+H]+ m/z: 245.1536, found: 245.1533.

4-(Adamantan-1-yl)chroman-2-one **3ea**. Pure product was isolated by flash chromatography on silica gel (pentane:ethyl acetate 95:5) as yellow oil in 68% yield (38.4 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H), 7.13 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.09 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (dd, *J* = 8.1, 1.2 Hz, 1H), 3.09 (dd, *J* = 16.4, 1.0 Hz, 1H), 2.59 (dd, *J* = 16.4, 7.5 Hz, 1H), 2.55 (d, *J* = 7.5 Hz, 1H), 1.98 – 1.93 (m, 3H), 1.67 – 1.62 (m, 3H), 1.57 – 1.56 (m, 2H), 1.55 – 1.54 (m, 4H), 1.54 – 1.52 (m, 2H), 1.52 (s, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 169.9, 152.3, 131.0, 128.5, 123.6, 123.0, 117.2, 46.8, 39.5 (3 x C), 36.7 (3 x C), 36.5, 29.9, 28.5 (3 x C). HRMS calculated for $C_{19}H_{23}O_2^+$ [M+H]+ m/z: 283.1693, found: 283.1687.

2-Cyclohexylchroman-4-one **5aa**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 65 % yield (29.9 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.00 – 6.96 (m, 2H), 4.20 (ddd, *J* = 12.9, 6.0, 2.9 Hz, 1H), 2.75 – 2.70 (m, *J* = 16.6, 12.9 Hz, 1H), 2.66 (dd, *J* = 16.6, 2.9 Hz, 1H), 1.82 (dd, *J* = 9.8, 3.2 Hz, 2H), 1.78 (d, *J* = 12.5 Hz, 1H), 1.76 – 1.70 (m, 2H), 1.36 – 1.27 (m, 3H), 1.24 – 1.10 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.3, 162.1, 136.0, 127.1, 121.2,

121.2, 118.0, 82.2, 42.0, 40.4, 28.4, 28.4, 26.5, 26.1, 26.1. HRMS calculated for $C_{15}H_{19}O_2^+$ [M+H]+ m/z: 231.1380, found: 231.1381.

2-Cyclohexyl-6-methylchroman-4-one **5ab**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 56% yield (27.3 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.8 Hz, 1H), 7.28 – 7.26 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.16 (ddd, *J* = 12.9, 6.1, 3.0 Hz, 1H), 2.72 – 2.67 (m, 1H), 2.63 (dd, *J* = 16.6, 3.0 Hz, 1H), 2.30 (s, 3H), 2.00 – 1.96 (m, 1H), 1.83 – 1.78 (m, 2H), 1.78 – 1.75 (m, 1H), 1.74 – 1.68 (m, 2H), 1.34 – 1.24 (m, 2H), 1.23 – 1.08 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.5, 160.1, 137.1, 130.6, 126.6, 120.8, 117.8, 82.1, 41.9, 40.5, 28.5, 28.4, 26.5, 26.1, 26.0, 20.5. HRMS calculated for $C_{16}H_{21}O_2^+$ [M+H]+ m/z: 245.1536, found: 245.1534.

2-Cyclohexyl-7-methylchroman-4-one **5ac**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 65% yield (31.7 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.76 – 7.74 (m, 1H), 6.80 (ddd, *J* = 8.0, 1.5, 0.5 Hz, 1H), 6.78 (d, *J* = 0.5 Hz, 1H), 4.17 (ddd, *J* = 12.9, 6.1, 3.0 Hz, 1H), 2.71 – 2.66 (m, 1H), 2.62 (dd, *J* = 16.6, 3.0 Hz, 1H), 2.34 (s, 3H), 2.00 – 1.96 (m, 1H), 1.83 – 1.78 (m, 2H), 1.78 – 1.73 (m, 1H), 1.73 – 1.68 (m, 2H), 1.32 – 1.24 (m, 2H), 1.23 – 1.09 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.0, 162.1, 147.5, 126.9, 122.6, 119.0, 118.0, 82.1, 41.9, 40.4, 28.4, 28.4, 26.5, 26.1, 26.0, 22.0. HRMS calculated for $C_{16}H_{21}O_2^+$ [M+H]+ m/z: 245.1536, found: 245.1536.

3-Cyclohexyl-2,3-dihydro-1H-benzo[c,f]chromen-1-one **5ad**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as pale yellow oil in 56% yield (22.1 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 9.44 (ddd, *J* = 8.6, 1.1, 0.6 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.74 (ddd, *J* = 8.0, 1.4, 0.6 Hz, 1H), 7.62 (ddd, *J* = 8.6, 6.0, 1.4 Hz, 1H), 7.41 (ddd, *J* = 8.0, 6.0, 1.1 Hz, 1H), 7.10 (d, *J* = 9.0 Hz, 1H), 4.31 (ddd, *J* = 13.5, 6.2, 3.0 Hz, 1H), 2.85 (dd, *J* = 16.2, 13.5 Hz, 1H), 2.73 (dd, *J* = 16.2, 3.0 Hz, 1H), 2.04 (d, *J* = 12.9 Hz, 1H), 1.86 – 1.76 (m, 4H), 1.76 – 1.71 (m, 1H), 1.36 – 1.24 (m, 2H), 1.24 – 1.12 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 194.2, 164.1, 137.4, 131.7, 129.6, 129.2, 128.4, 125.9, 124.8, 119.0, 112.6, 82.1, 41.8, 41.6, 28.5, 28.3, 26.5, 26.1, 26.0. HRMS calculated for $C_{19}H_{21}O_2^+$ [M+H]+ m/z: 281.1536, found: 281.1530.

2-Cyclohexyl-6-fluorochroman-4-one **5ae**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 48% yield (23.8 mg). ^{1}H NMR (700

MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.3, 3.2 Hz, 1H), 7.18 (ddd, *J* = 9.0, 7.8, 3.2 Hz, 1H), 6.95 (dd, *J* = 9.0, 4.2 Hz, 1H), 4.18 (ddd, *J* = 12.6, 6.1, 3.4 Hz, 1H), 2.71 (dd, *J* = 16.7, 12.6 Hz, 1H), 2.66 (dd, *J* = 16.7, 3.4 Hz, 1H), 1.97 (d, *J* = 12.8 Hz, 1H), 1.84 – 1.79 (m, 2H), 1.78 – 1.74 (m, 1H), 1.72 (ddd, *J* = 8.1, 6.1, 3.2 Hz, 2H), 1.32 – 1.27 (m, 2H), 1.22 – 1.10 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.3 , 158.2 , 157.0 (d, J = 241.5 Hz), 123.4 (d, J = 24.7 Hz), 121.4 (d, J = 6.4 Hz), 119.5 (d, J = 7.5 Hz), 111.8 (d, J = 23.0 Hz), 82.3 , 41.7 , 40.0 , 28.2 , 28.2 , 26.3 , 25.9 , 25.8 . HRMS calculated for $C_{15}H_{18}FO_2^+$ [M+H]+ m/z: 249.1285, found: 249.1281.

2-Cyclohexyl-7-fluorochroman-4-one **5af**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 40% yield (19.8 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.8, 6.7 Hz, 1H), 6.70 (ddd, *J* = 8.8, 8.2, 2.4 Hz, 1H), 6.65 (dd, *J* = 9.9, 2.4 Hz, 1H), 4.22 (ddd, *J* = 12.8, 6.0, 3.1 Hz, 1H), 2.71 (dd, *J* = 16.6, 12.8 Hz, 1H), 2.64 (dd, *J* = 16.6, 3.1 Hz, 1H), 1.99 – 1.94 (m, 1H), 1.84 – 1.79 (m, 2H), 1.78 – 1.69 (m, 3H), 1.33 – 1.24 (m, 2H), 1.23 – 1.09 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 191.8, 167.6 (d, *J* = 255.7 Hz), 163.7 (d, *J* = 13.7 Hz), 129.6 (d, *J* = 11.4 Hz), 118.1 (d, *J* = 2.3 Hz), 109.6 (d, *J* = 22.8 Hz), 104.7 (d, *J* = 24.2 Hz), 82.8, 41.8, 40.1, 28.3, 28.3, 26.4, 26.0, 26.0. HRMS calculated for $C_{15}H_{18}FO_2^+$ [M+H]+ m/z: 249.1285, found: 249.1282.

6-Bromo-2-cyclohexylchroman-4-one **5ag**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 39% yield (24.1 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.5 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.19 (ddd, *J* = 12.5, 6.0, 3.4 Hz, 1H), 2.71 (dd, *J* = 16.7, 12.5 Hz, 1H), 2.66 (dd, *J* = 16.7, 3.4 Hz, 1H), 1.83 – 1.80 (m, 2H), 1.75 (dd, *J* = 12.9, 10.0 Hz, 1H), 1.73 – 1.70 (m, 2H), 1.29 (ddd, *J* = 12.9, 6.0, 3.1 Hz, 2H), 1.22 – 1.10 (m, 4H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 191.9, 160.9, 138.6, 129.5, 122.5, 120.2, 113.8, 82.4, 41.8, 40.1, 28.4, 28.4, 26.4, 26.1, 26.0. HRMS calculated for $C_{15}H_{18}BrO_2^+$ [M+H]+ m/z: 309.0485, found: 309.0482.

6-Chloro-2-cyclohexyl-7-methylchroman-4-one **5ah**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 60% yield (33.5 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.80 (d, *J* = 5.2 Hz, 1H), 6.87 (d, *J* = 0.5 Hz, 1H), 4.16 (ddd, *J* = 12.5, 6.1, 3.3 Hz, 1H), 2.68 (dd, *J* = 16.7, 12.5 Hz, 1H), 2.63 (dd, *J* = 16.7, 3.3 Hz, 1H), 2.36 (s, 3H), 1.99 – 1.93 (m, 1H), 1.83 – 1.79 (m, 2H), 1.73 – 1.69 (m, 1H), 1.33 – 1.23 (m, 2H), 1.22 – 1.08 (m, 3H), 0.89 – 0.83 (m, 2H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 191.9, 160.3, 145.0,

127.4, 126.7, 120.2, 120.1, 82.4, 41.8, 40.1, 28.4 (2xC), 26.4, 26.1, 26.0, 20.9. HRMS calculated for $C_{16}H_{20}ClO_2^+$ [M+H]+ m/z: 279.1146, found: 279.1148.

6-Chloro-2-cyclohexylchroman-4-one **5ai**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 30% yield (15.9 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2.6 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 4.19 (ddd, *J* = 12.5, 5.9, 3.4 Hz, 1H), 2.73 – 2.61 (m, 2H), 1.97 (d, *J* = 13.0 Hz, 1H), 1.81 (d, *J* = 13.0 Hz, 2H), 1.78 – 1.69 (m, 2H), 1.34 – 1.24 (m, 3H), 1.23 – 1.10 (m, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 192.0, 160.5, 135.9, 126.7, 126.4, 122.0, 119.8, 82.4, 41.9, 40.1, 28.4, 28.4, 26.4, 26.1, 26.0. HRMS calculated for $C_{15}H_{18}ClO_2^+$ [M+H]+ m/z: 265.0990, found: 265.0988.

2-Isopropylchroman-4-one **5ba**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 22% yield (8.4 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48-7.45 (m, 1H), 7.01 – 6.97 (m, 2H), 4.19 (ddd, *J* = 13.0, 5.9, 3.0 Hz, 1H), 2.71 (dd, *J* = 16.6, 13.0 Hz, 1H), 2.65 (dd, *J* = 16.6, 3.0 Hz, 1H), 2.10 – 2.03 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.2, 162.1, 136.0, 127.1, 121.2, 121.2, 118.1, 82.7, 40.3, 32.3, 18.0, 18.0. HRMS calculated for $C_{12}H_{15}O_2^+$ [M+H]+ m/z: 191.1067, found: 191.1061.

2-(tert-Butyl)chroman-4-one **5ca**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 48% yield (19.6 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.47-7.45 (m, 1H), 7.00 – 6.97 (m, 2H), 4.06 (dd, *J* = 13.7, 3.0 Hz, 1H), 2.72 – 2.68 (m, 1H), 2.66 – 2.63 (m, 1H), 1.06 (d, *J* = 2.3 Hz, 9H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.7, 162.3, 136.0, 127.0, 121.2, 120.9, 118.0, 85.4, 38.6, 34.3, 25.6. HRMS calculated for $C_{13}H_{17}O_2^+$ [M+H]+ m/z: 205.1223, found: 205.1220.

2-(1-Methylcyclohexyl)chroman-4-one **5da**. Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 19% yield (9.3 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 1H), 7.48-7.45 (m, 1H), 7.00-6.96 (m, 2H), 4.15 (dd, *J* = 14.2, 2.4 Hz, 1H), 2.72 (dd, *J* = 16.5, 14.2 Hz, 1H), 2.63 (dd, *J* = 16.5, 2.4 Hz, 1H), 1.62 – 1.56 (m, 3H), 1.53 (ddd, *J* = 8.4, 7.1, 4.7 Hz, 2H), 1.51 – 1.43 (m, 3H), 1.35 – 1.30 (m, 1H), 1.27 (ddd, *J* = 15.3, 8.9, 4.7 Hz, 1H), 1.04 (s, 3H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.9,

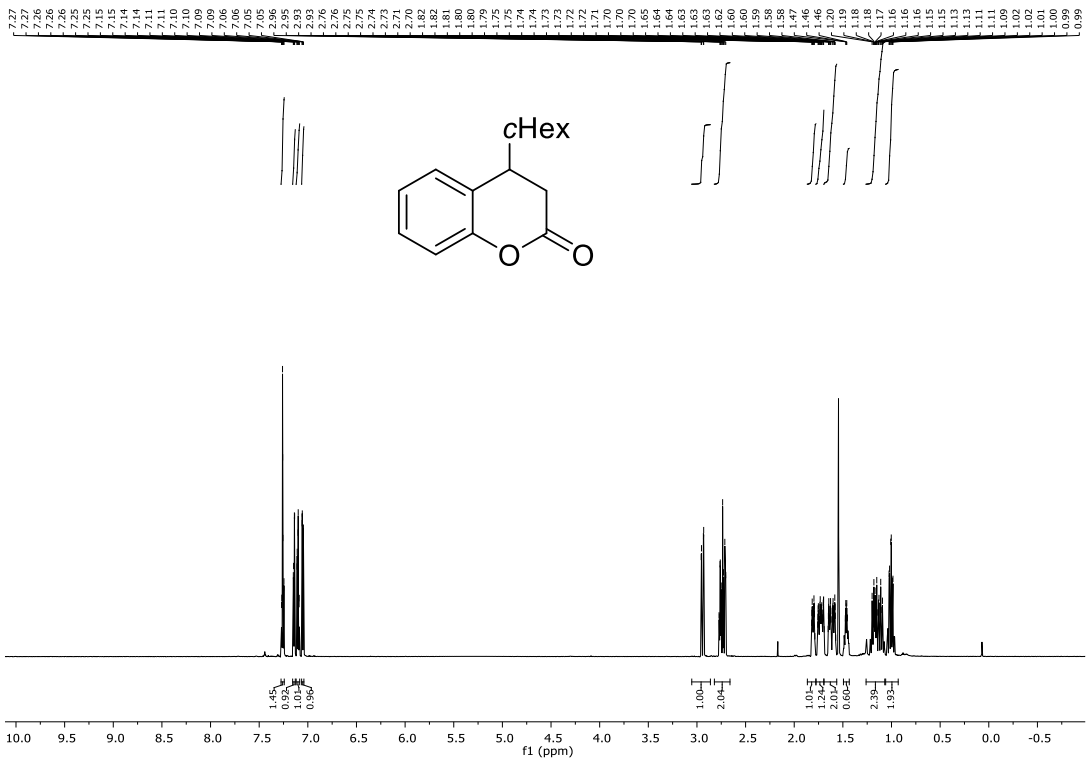
162.4, 136.0, 127.0, 121.1, 121.0, 118.0, 85.1, 37.8, 36.8, 33.8, 33.7, 26.4, 21.7, 21.6, 19.0. HRMS calculated for $C_{16}H_{21}O_2^+$ [M+H]+ m/z: 245.1536, found: 245.1533.

2-(Adamantan-1-yl)chroman-4-one **5ea.** Pure product was isolated by flash chromatography on silica gel (hexane:ethyl acetate 95:5) as yellow oil in 30% yield (16.9 mg). ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.48 – 7.44 (m, 1H), 6.98 (dd, *J* = 7.5, 6.7 Hz, 2H), 3.91 (dd, *J* = 14.2, 2.4 Hz, 1H), 2.72 (dd, *J* = 16.4, 14.2 Hz, 1H), 2.62 (dd, *J* = 16.4, 2.4 Hz, 1H), 2.06 (s, 3H), 1.77 (d, *J* = 12.1 Hz, 5H), 1.71 (d, *J* = 11.4 Hz, 3H), 1.64 (dd, *J* = 12.1, 2.1 Hz, 3H), 1.55 (s, 1H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 193.9, 162.5, 136.0, 127.0, 121.1, 118.0, 85.7, 37.9 (3 x C), 37.3, 37.2 (3 x C), 36.1, 28.4 (3 x C). HRMS calculated for $C_{19}H_{23}O_2^+$ [M+H]+ m/z: 283.1693, found: 283.1691.

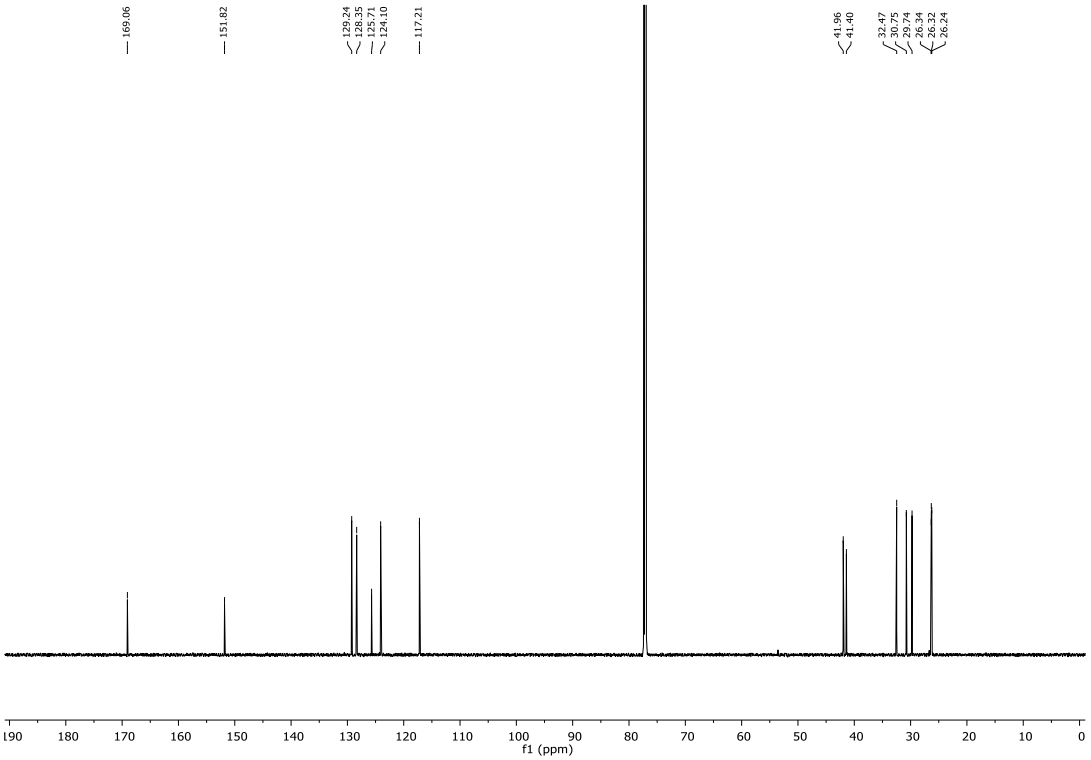
5. NMR Data

4-Cyclohexylchroman-2-one 3aa

^{1}H NMR

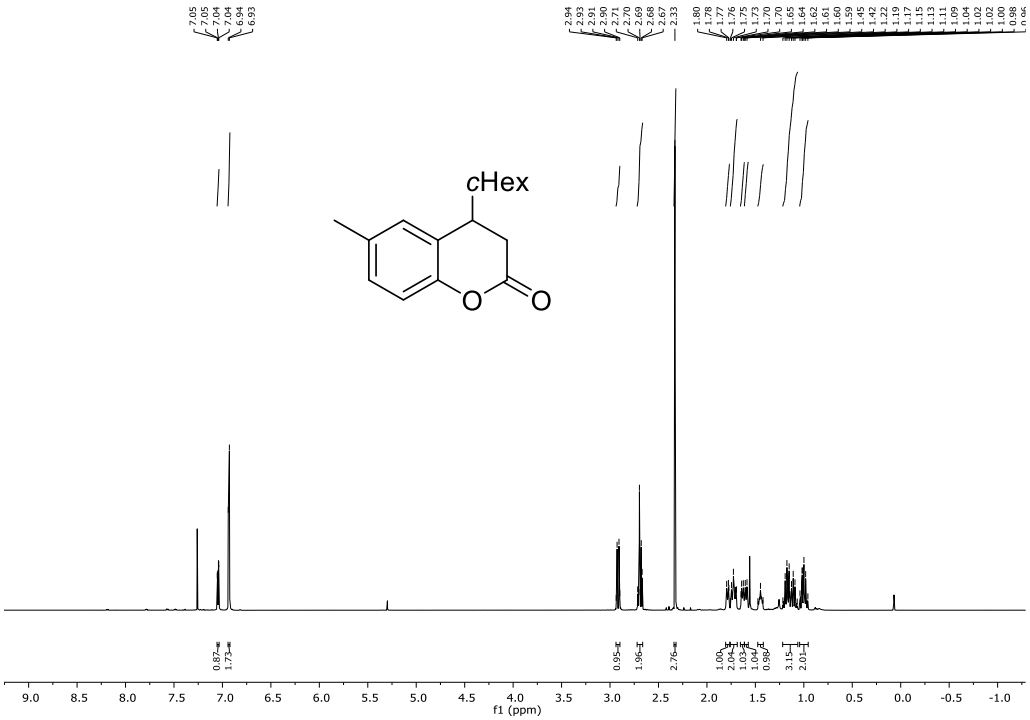


^{13}C NMR

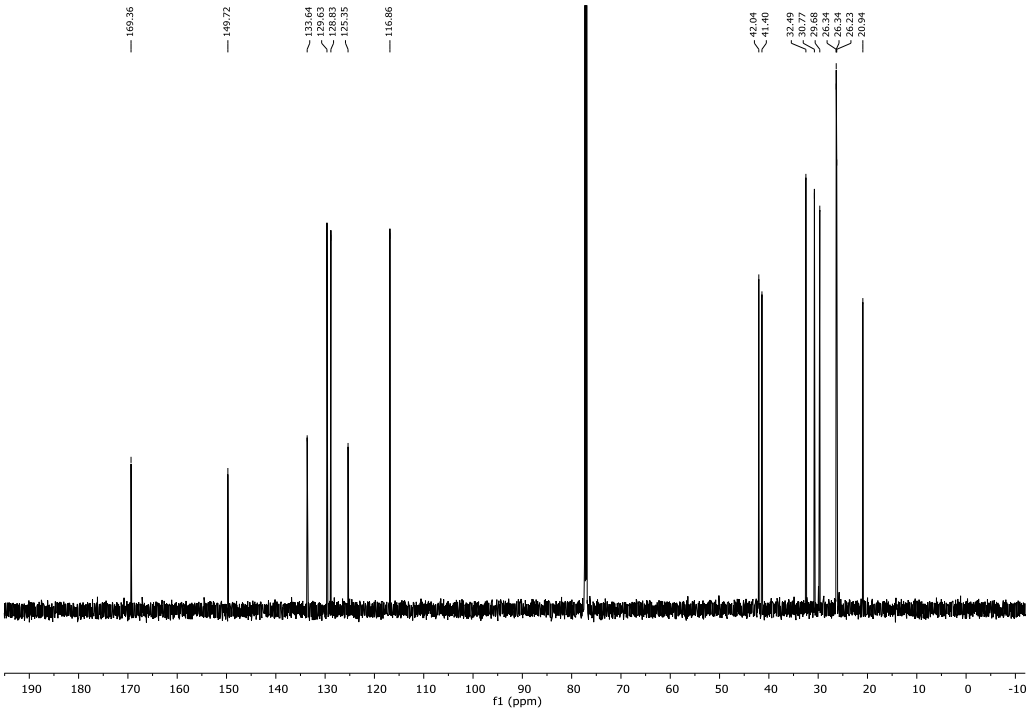


4-Cyclohexyl-6-methylchroman-2-one 3ab

^{1}H NMR

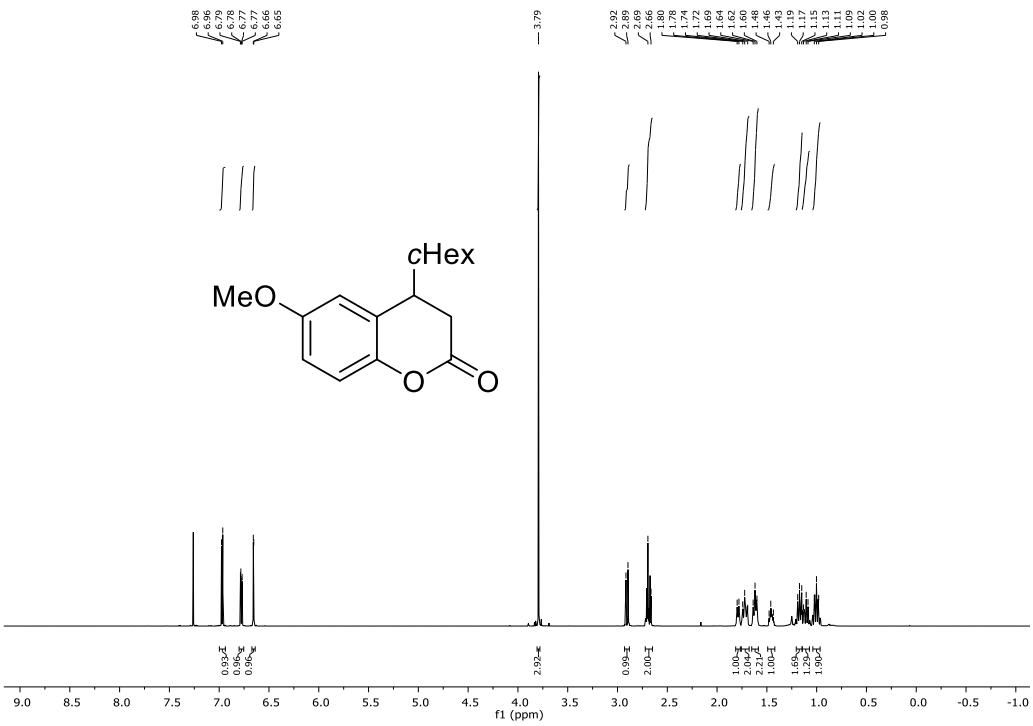


^{13}C NMR

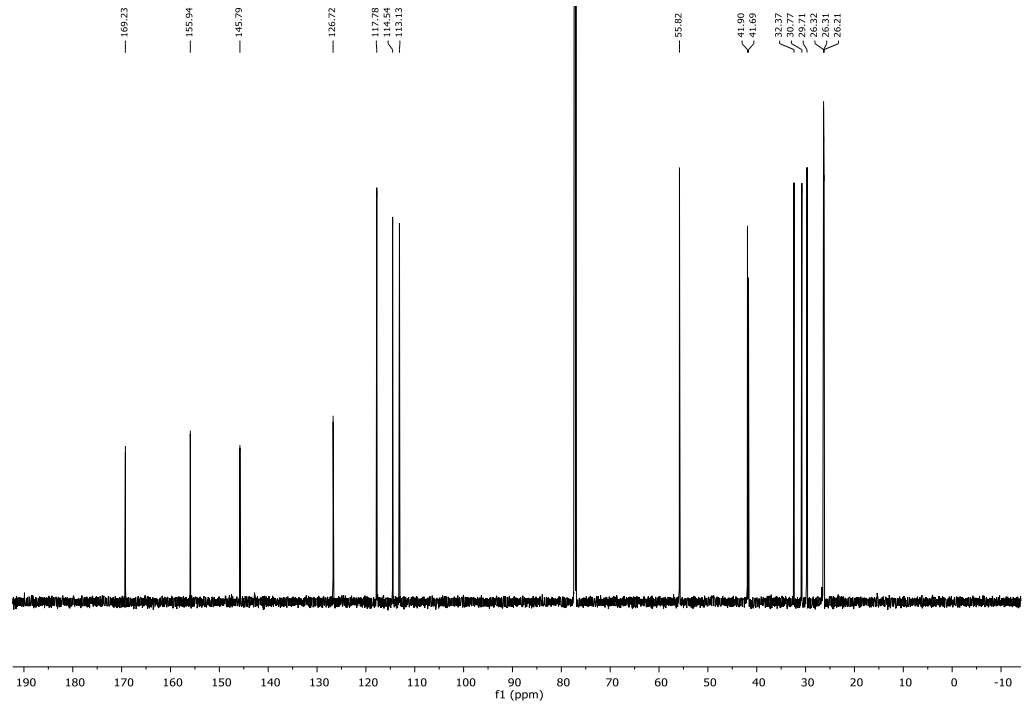


4-Cyclohexyl-6-methoxychroman-2-one 3ac

^{1}H NMR

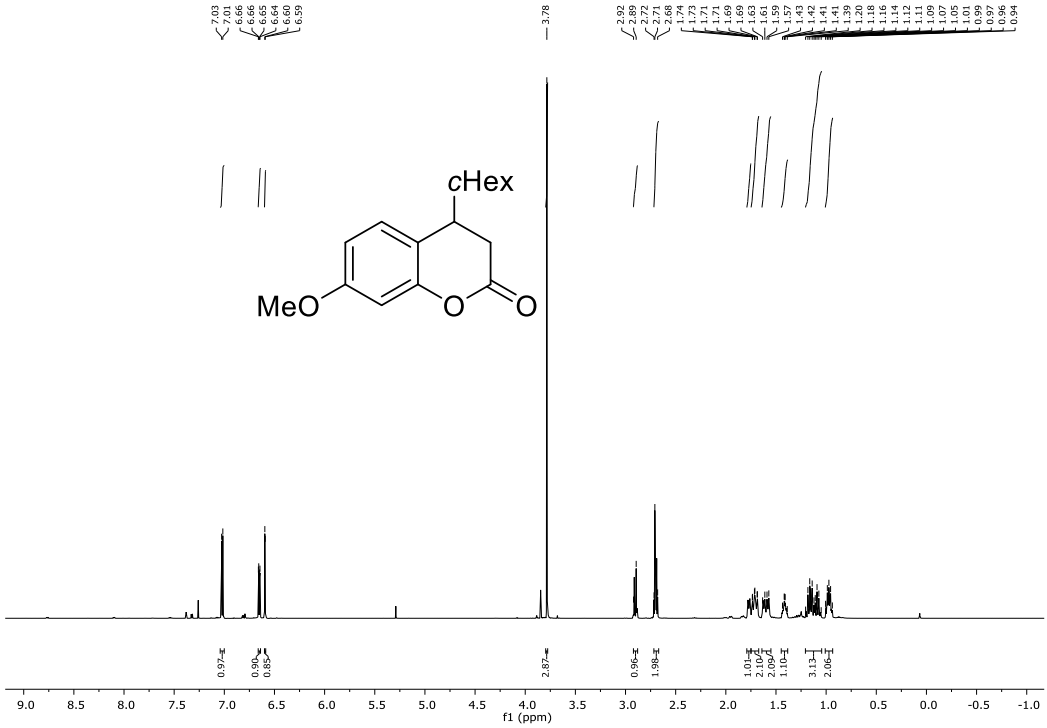


^{13}C NMR

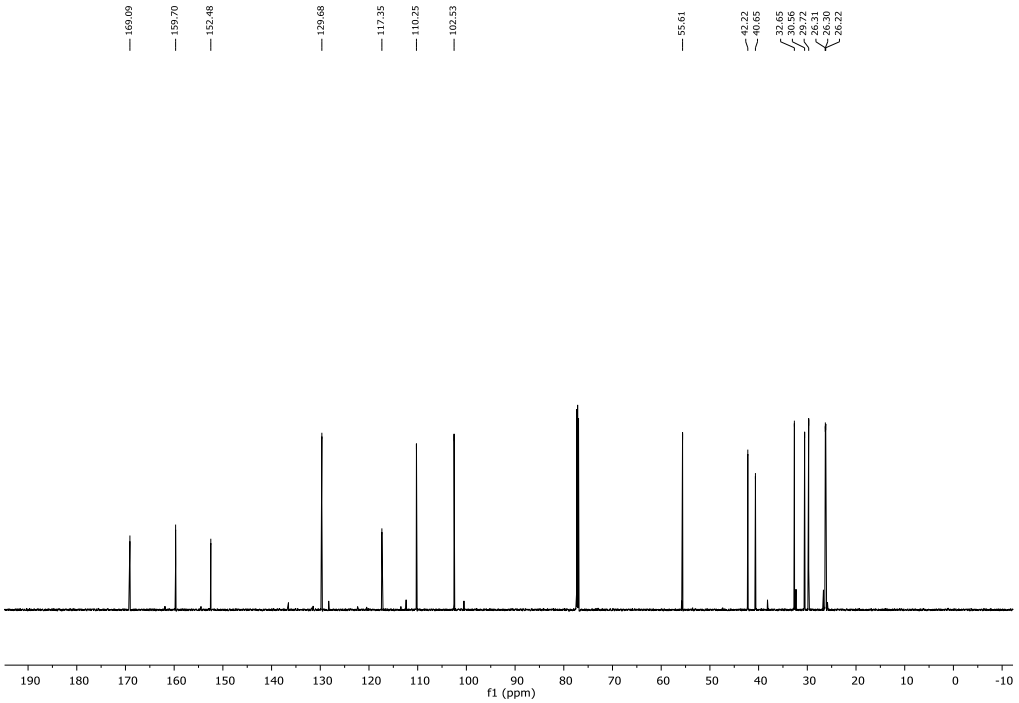


4-Cyclohexyl-7-methoxychroman-2-one 3ad

^{1}H NMR

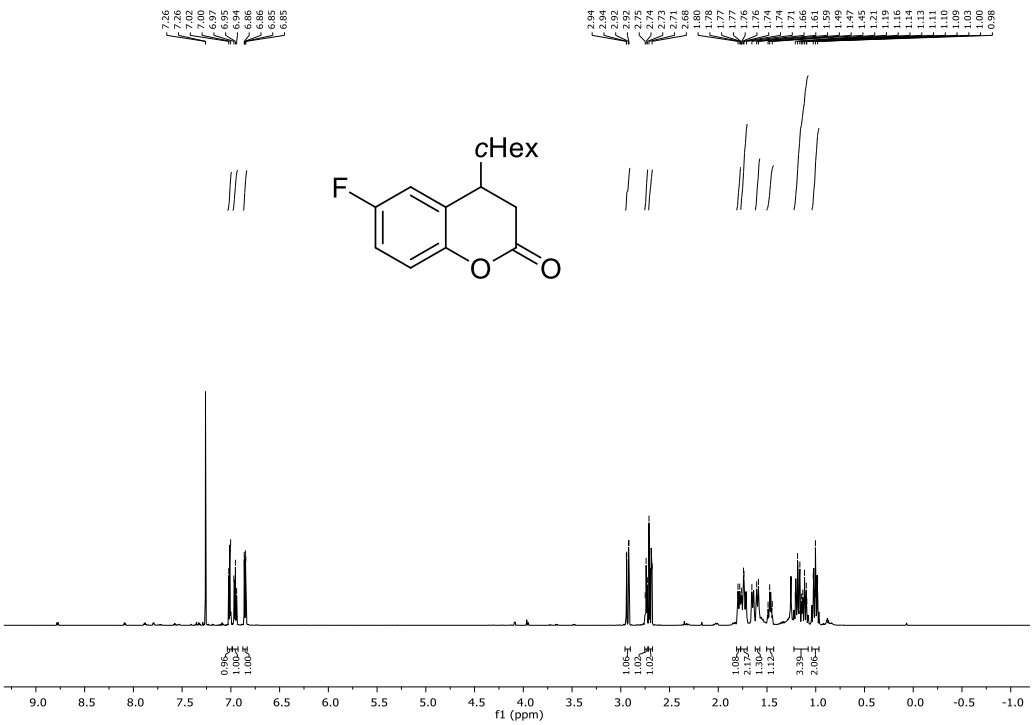


^{13}C NMR

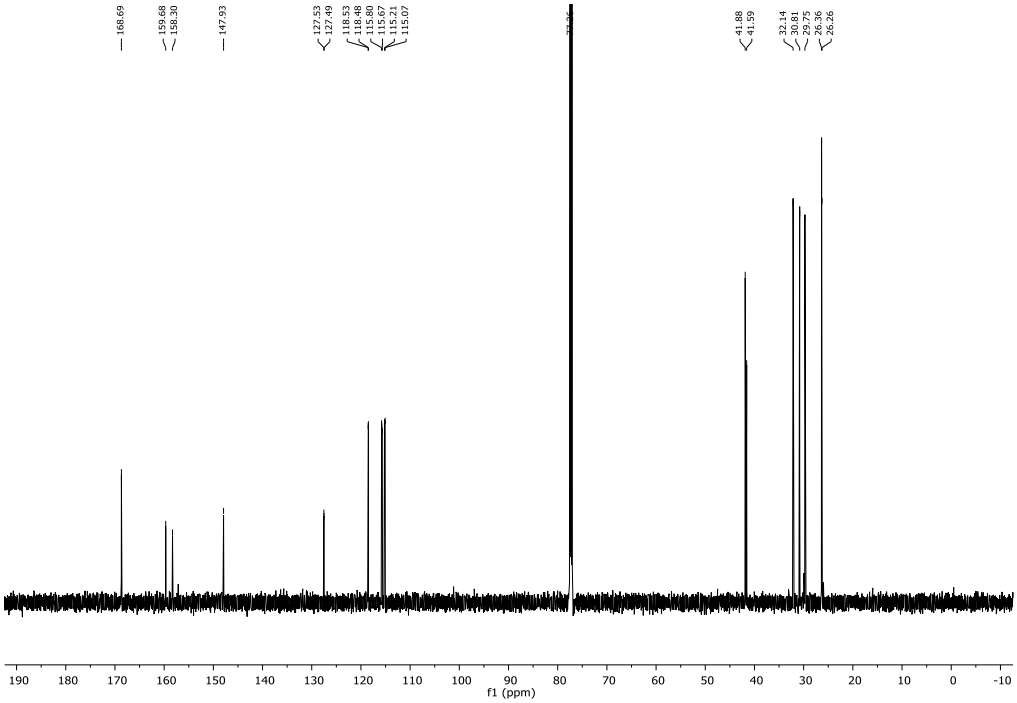


4-Cyclohexyl-6-fluorochroman-2-one 3ae

^{1}H NMR

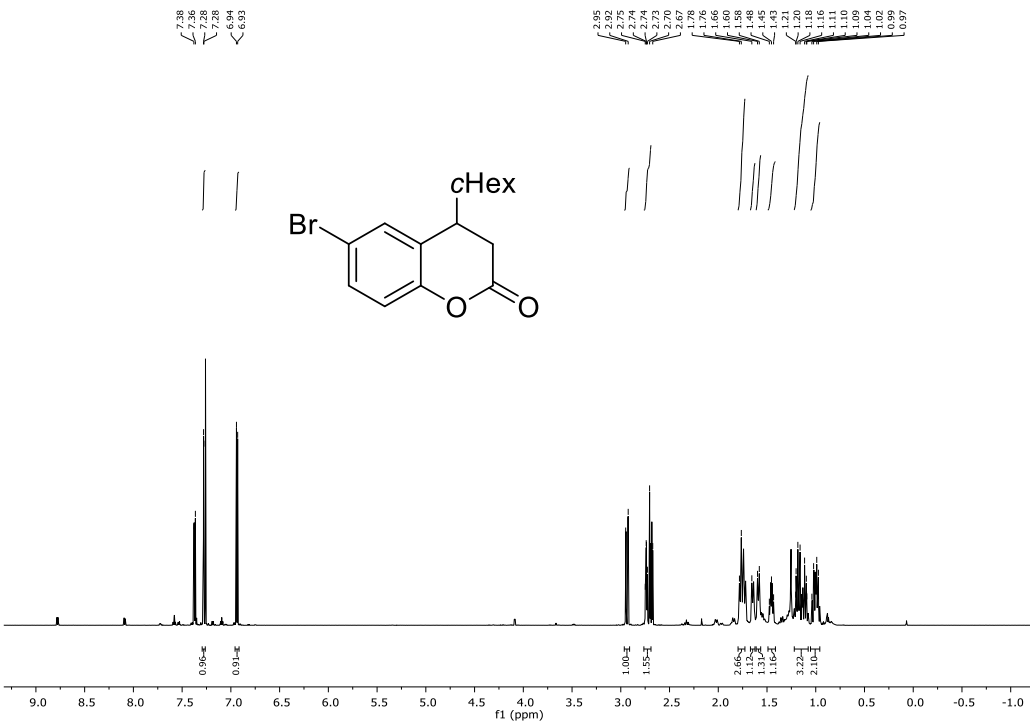


^{13}C NMR

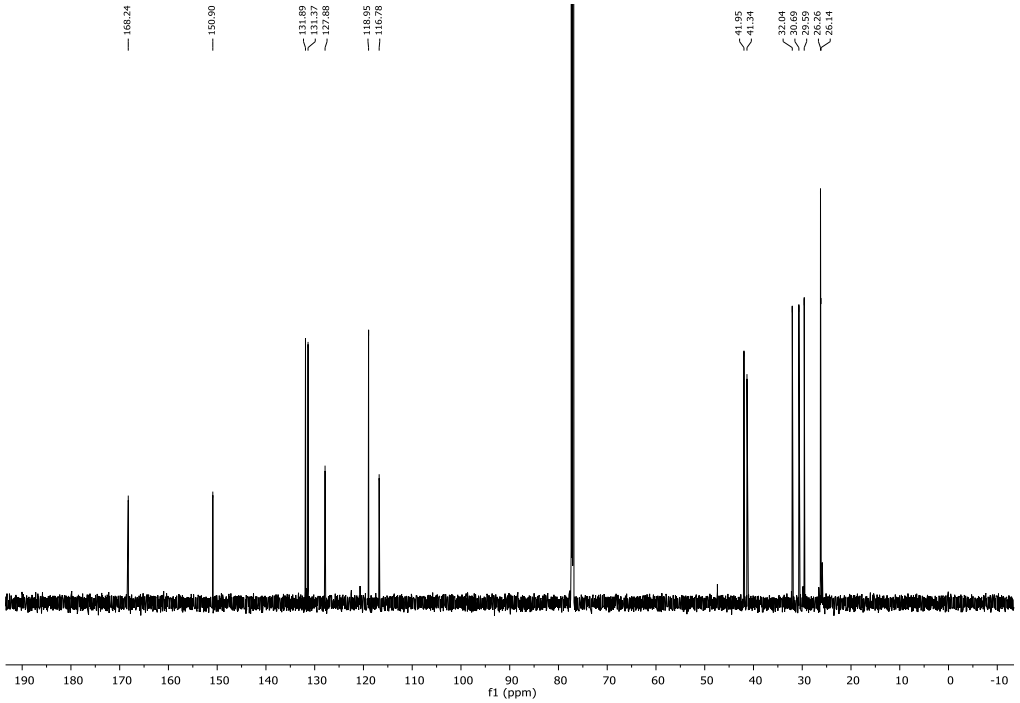


6-Bromo-4-cyclohexylchroman-2-one 3af

^{1}H NMR

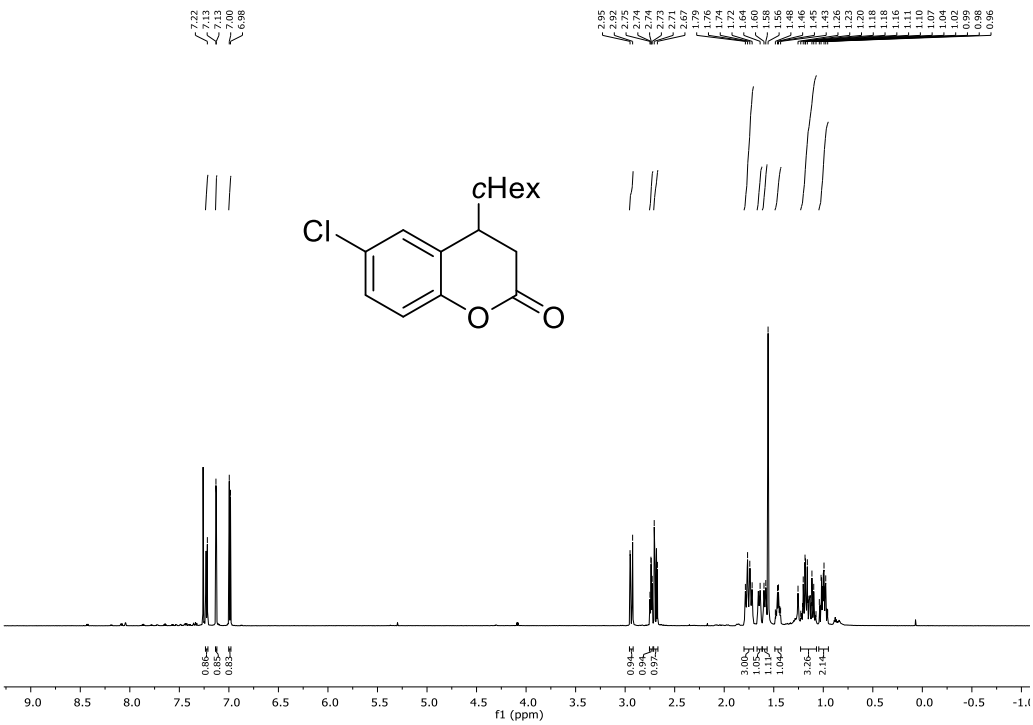


^{13}C NMR

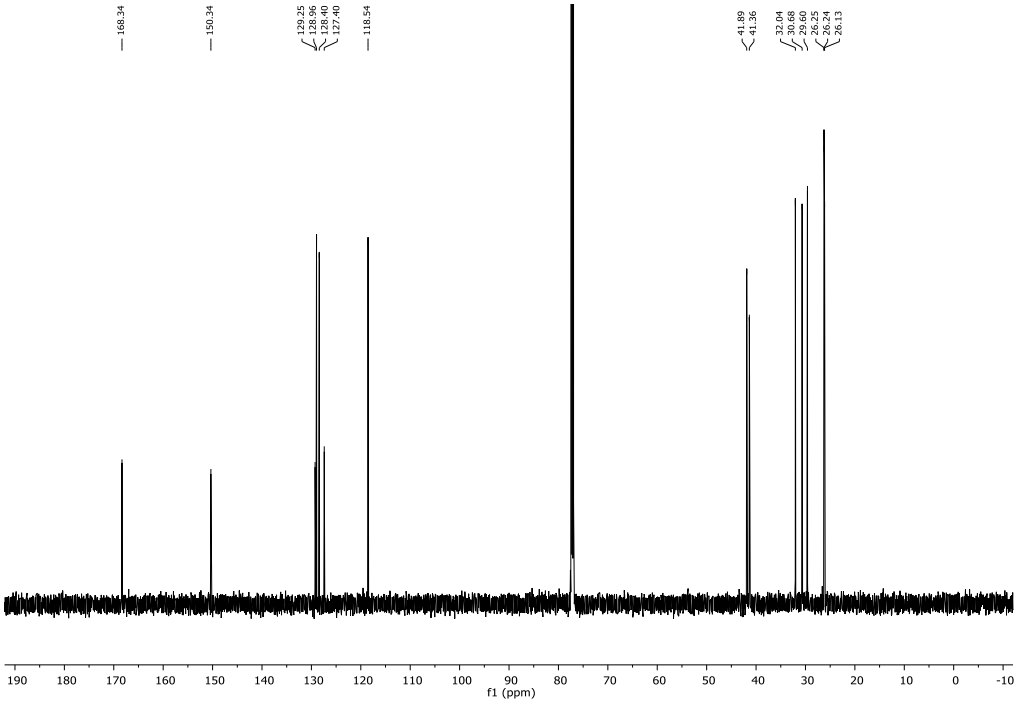


6-Chloro-4-cyclohexylchroman-2-one 3ag

^{1}H NMR

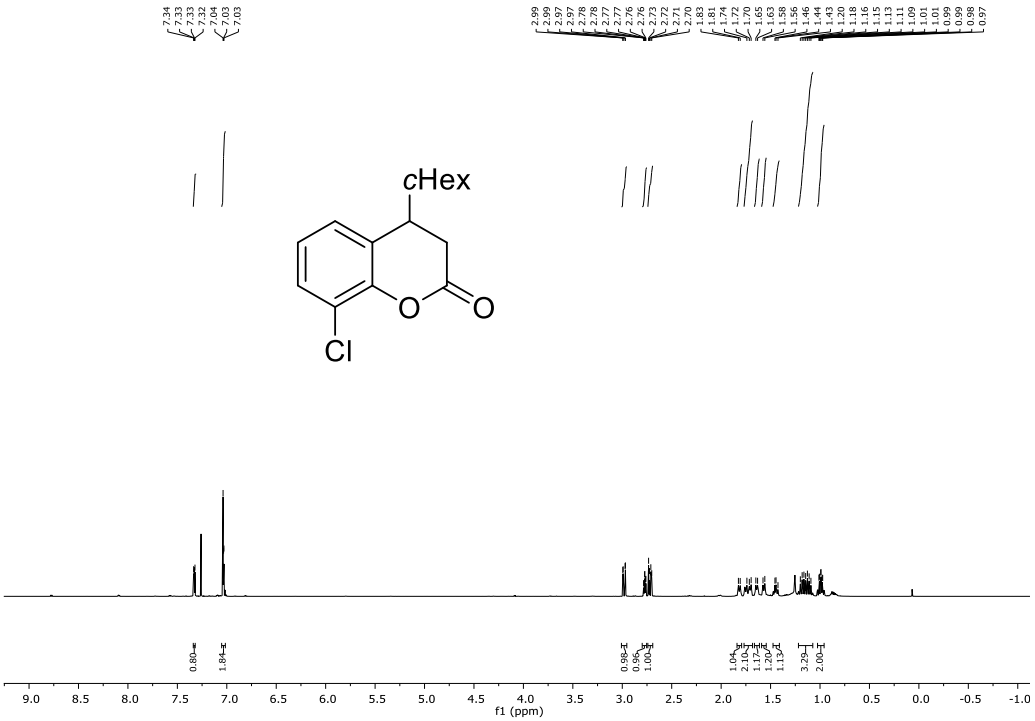


^{13}C NMR

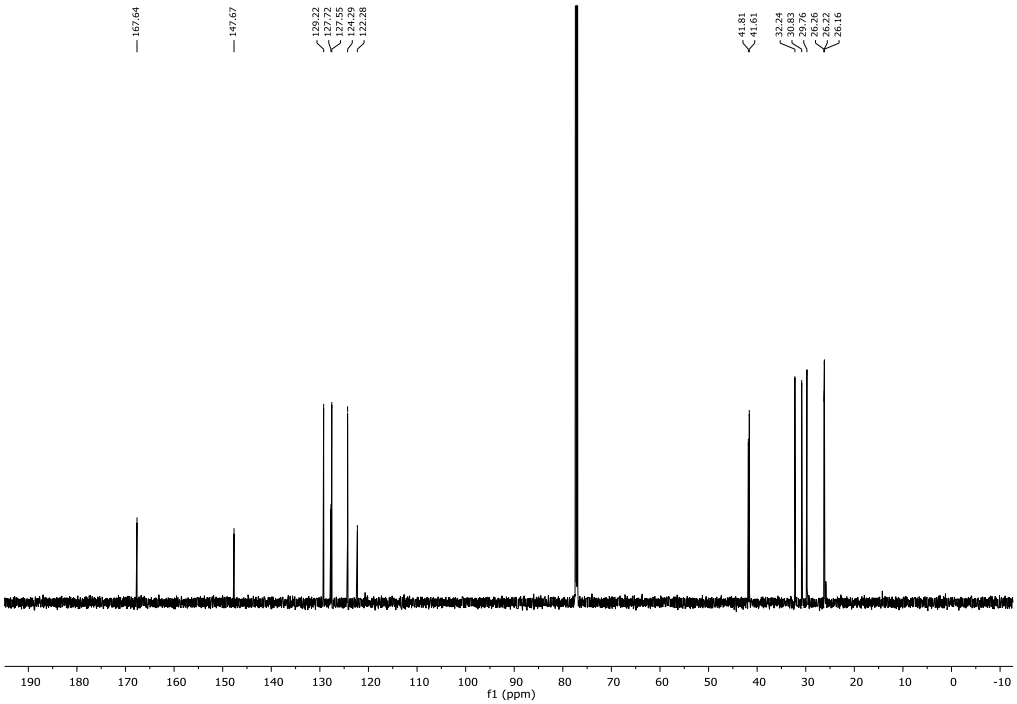


8-Chloro-4-cyclohexylchroman-2-one 3ah

^{1}H NMR

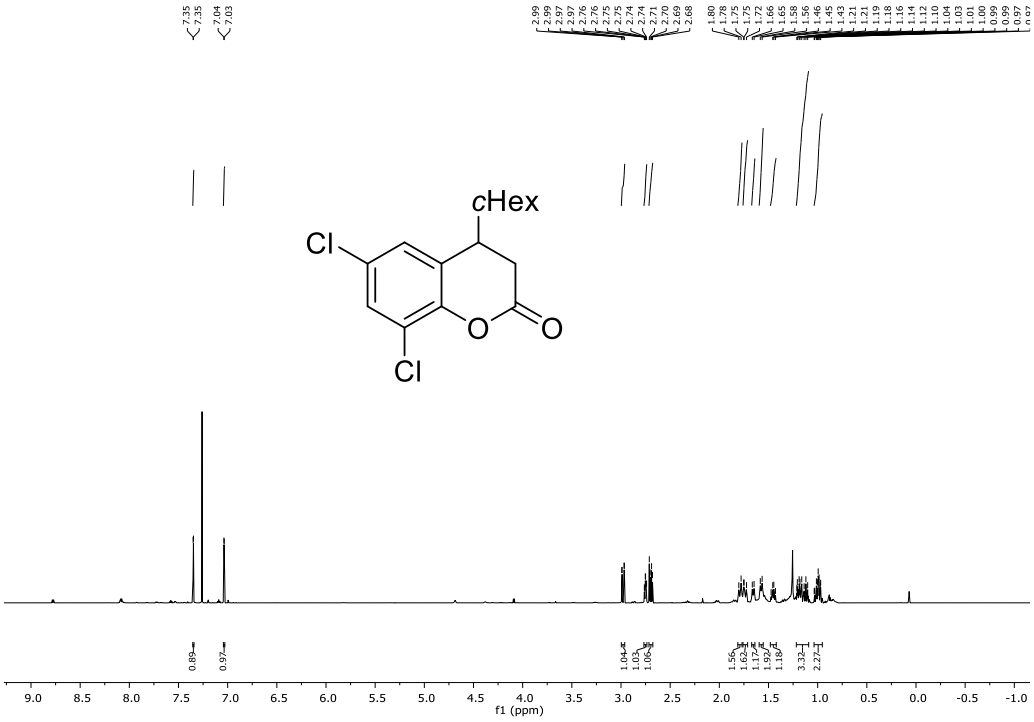


^{13}C NMR

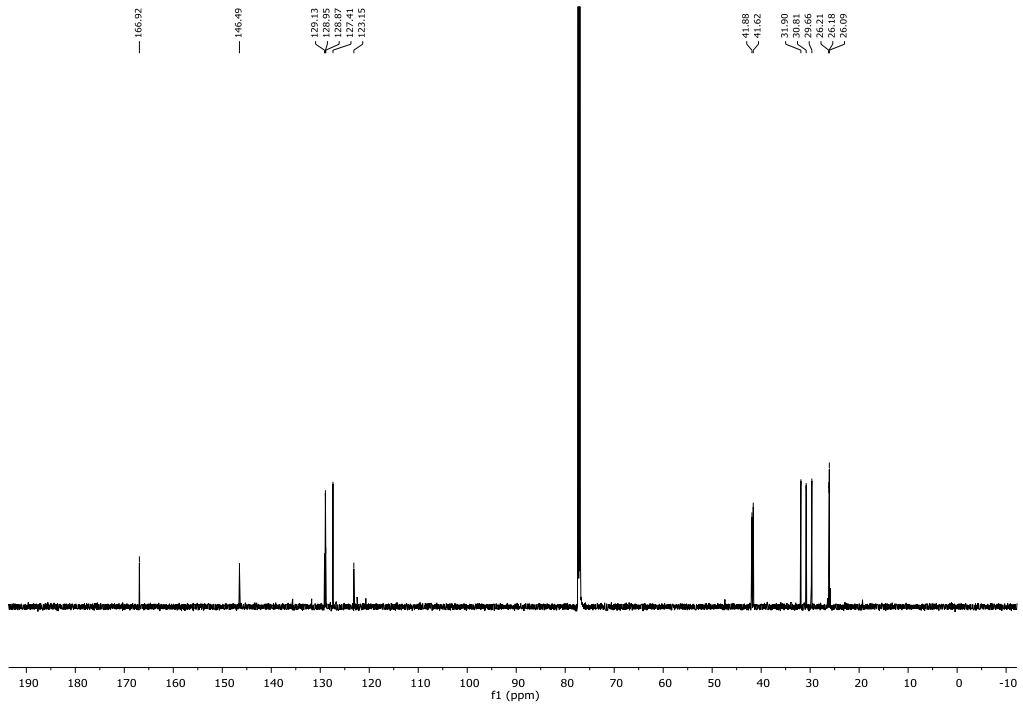


6,8-Dichloro-4-cyclohexylchroman-2-one 3ai

^{1}H NMR

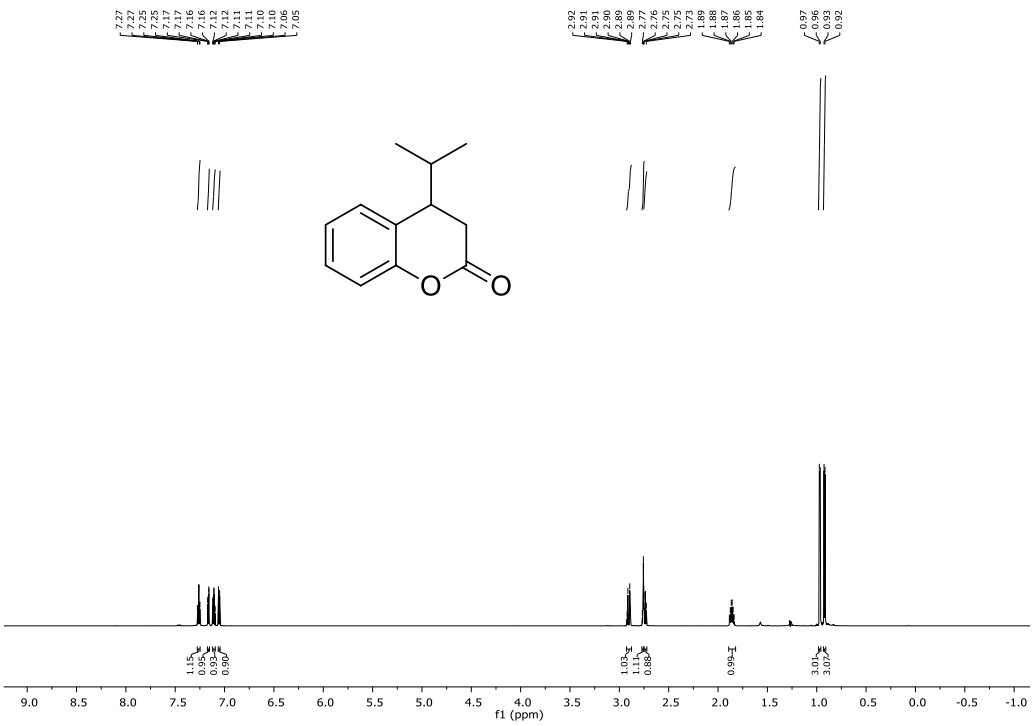


^{13}C NMR

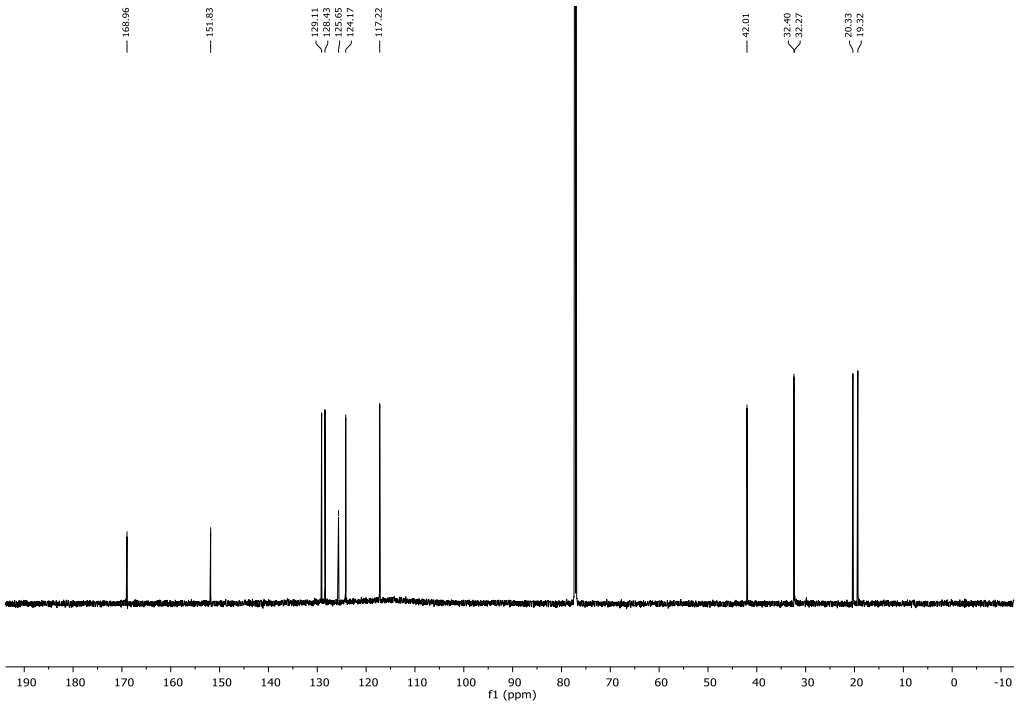


4-Isopropylchroman-2-one 3ba

^{1}H NMR

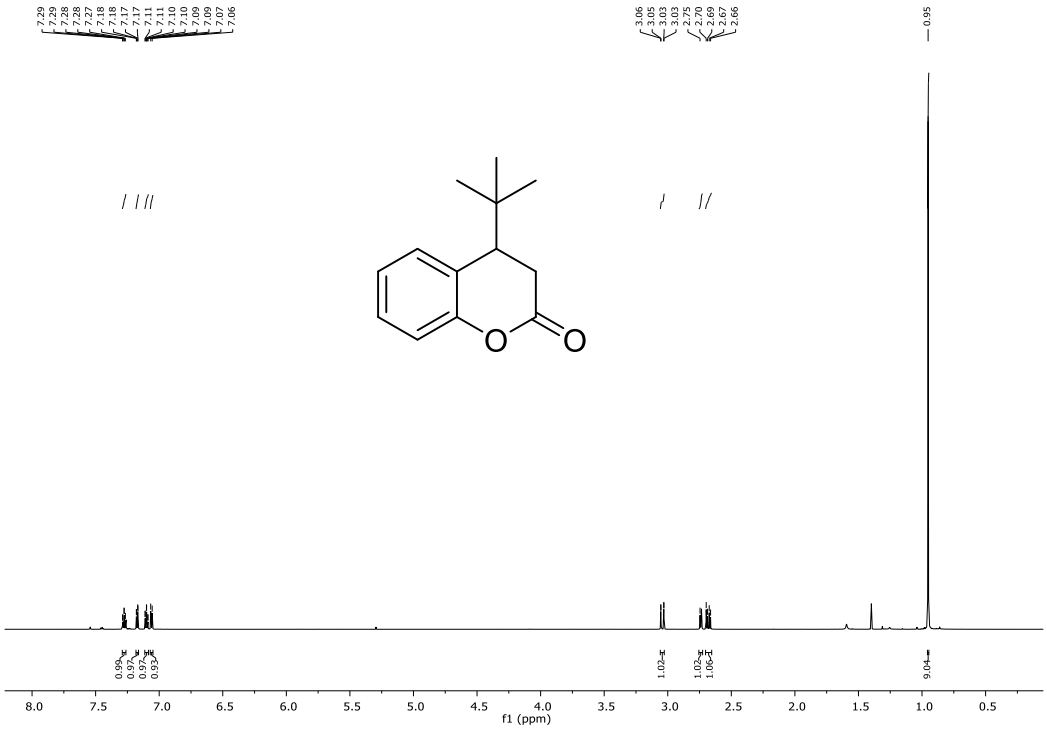


^{13}C NMR

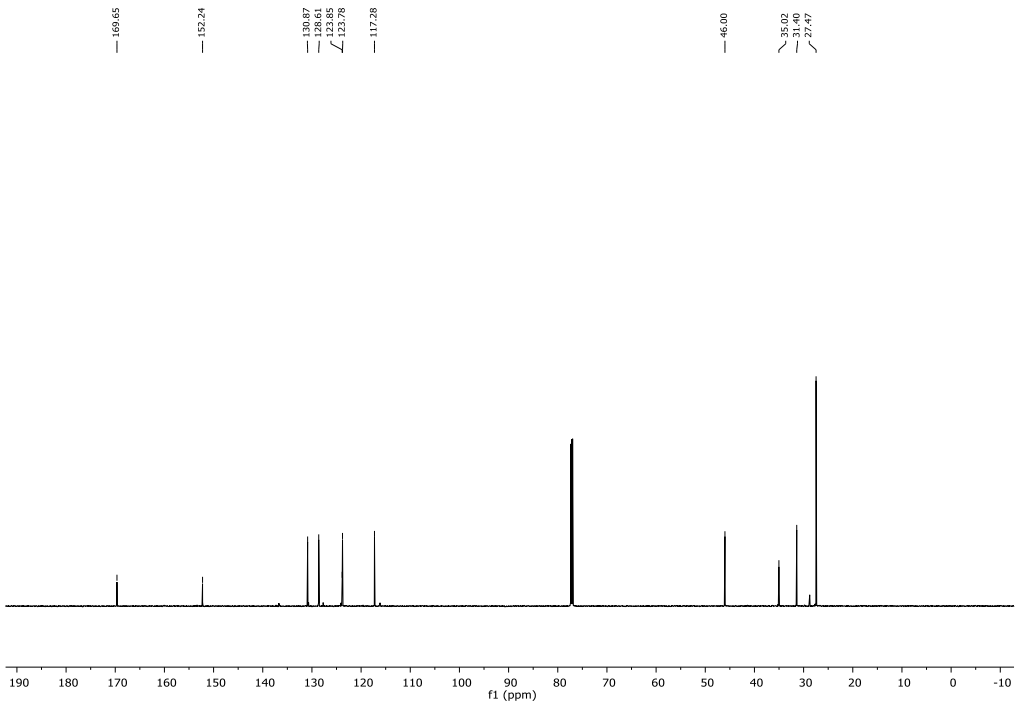


4-(*tert*-Butyl)chroman-2-one 3ca

^{1}H NMR

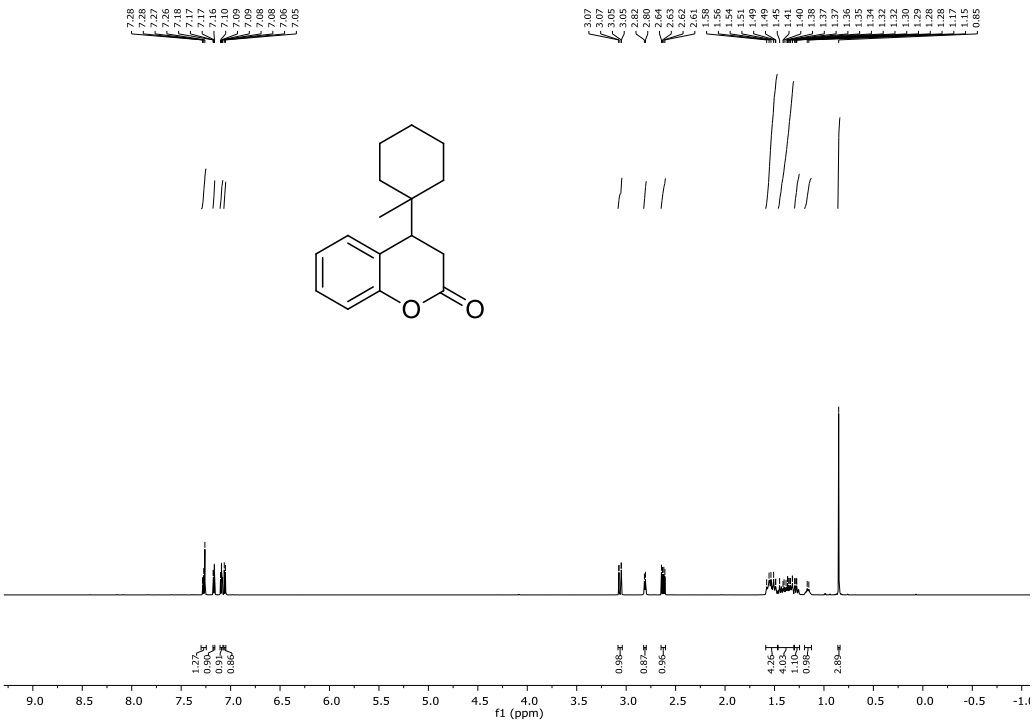


^{13}C NMR

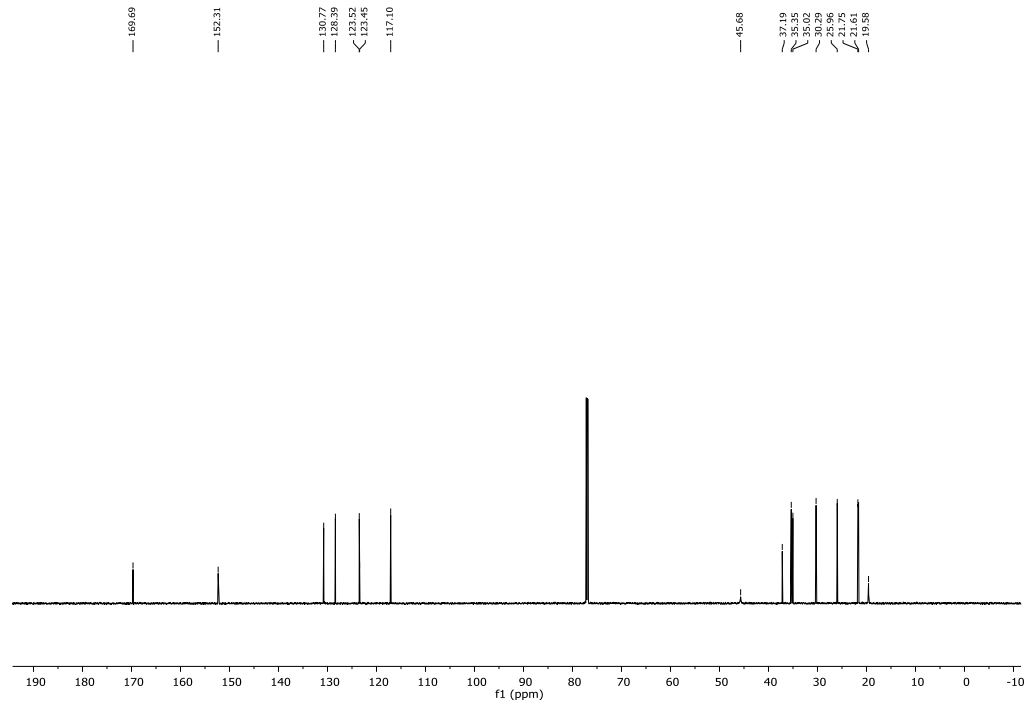


4-(1-Methylcyclohexyl)chroman-2-one 3da

^{1}H NMR

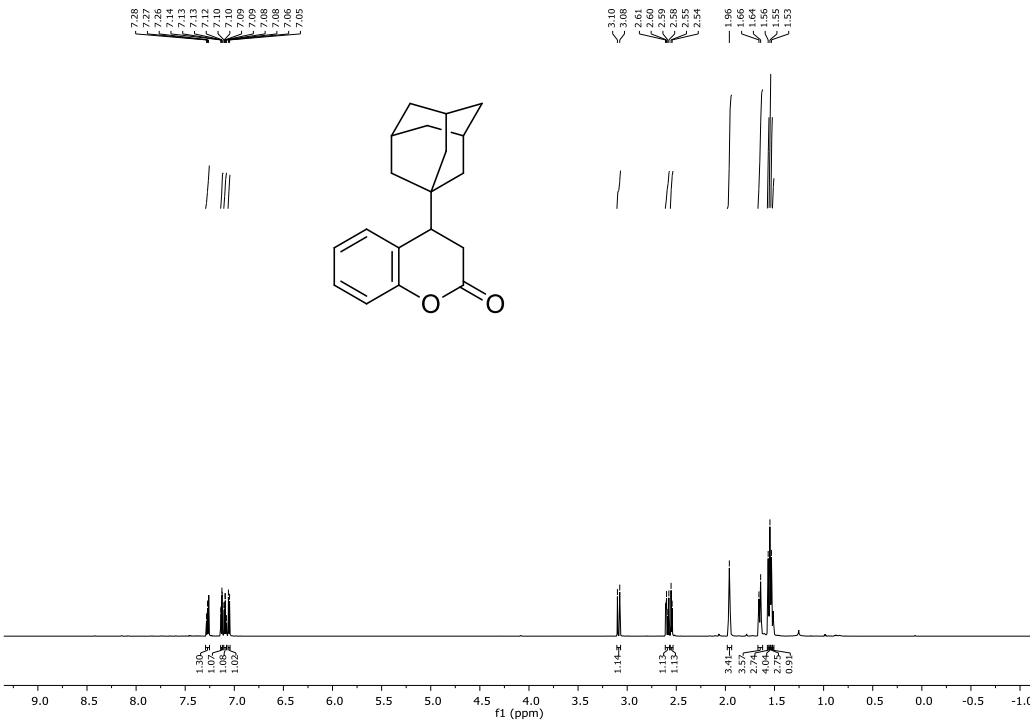


^{13}C NMR

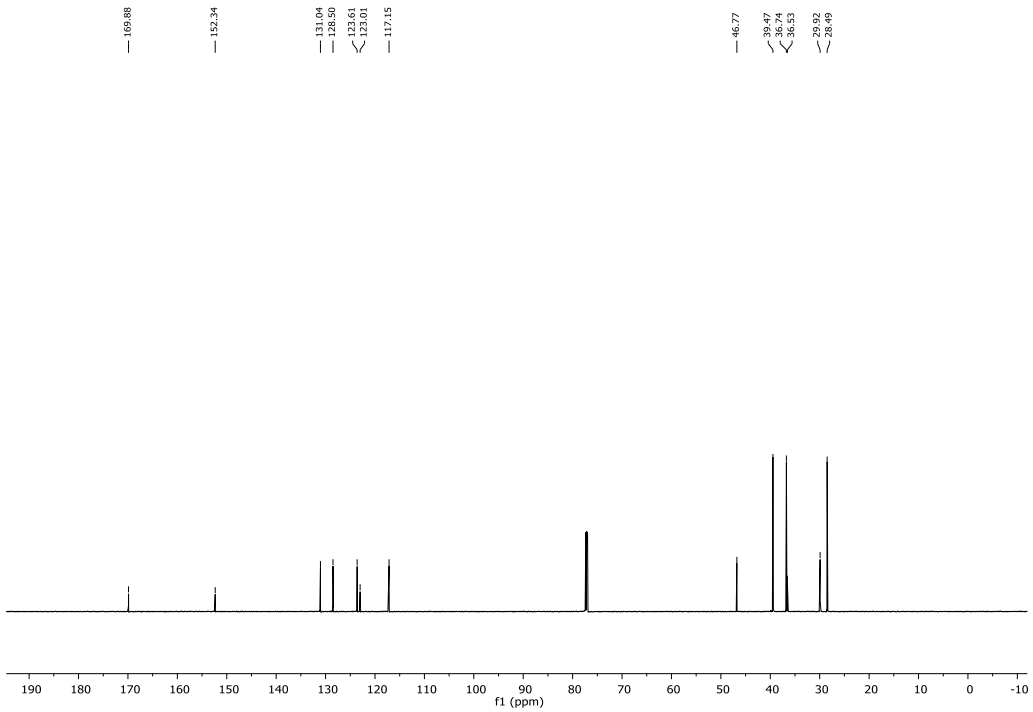


4-(Adamantan-1-yl)chroman-2-one 3ea

^{1}H NMR

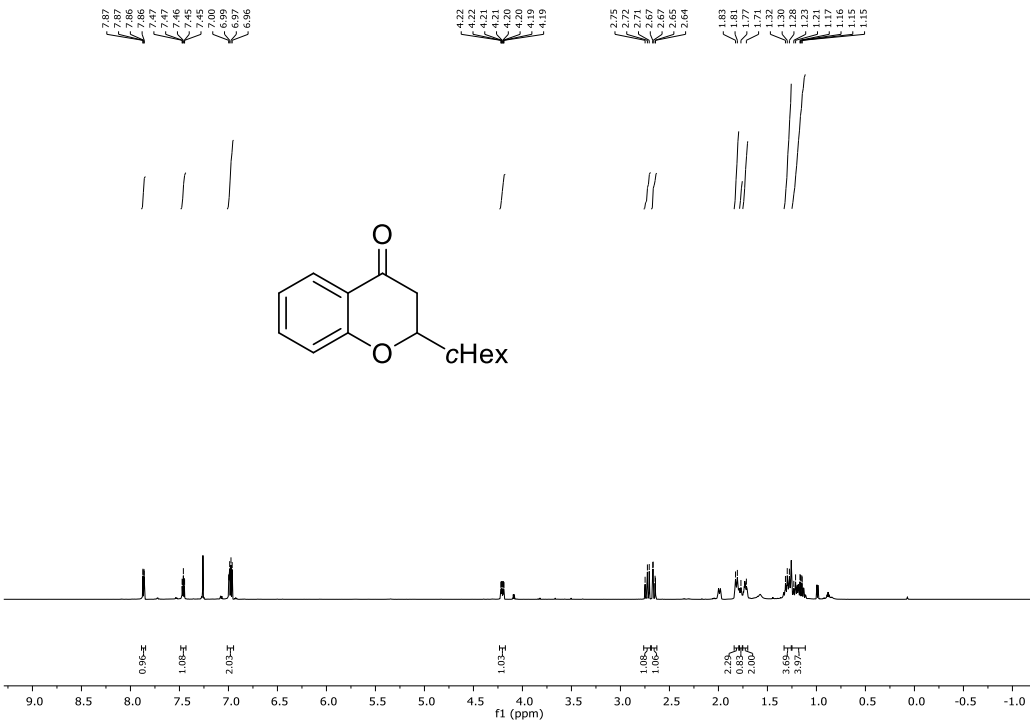


^{13}C NMR

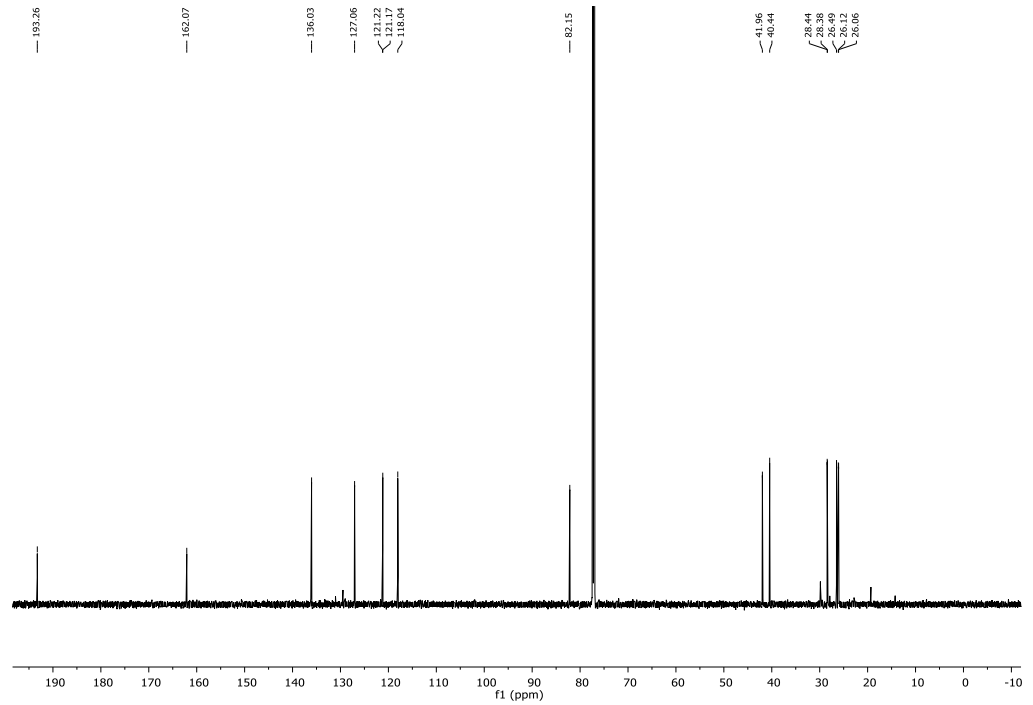


2-Cyclohexylchroman-4-one 5aa

^{1}H NMR

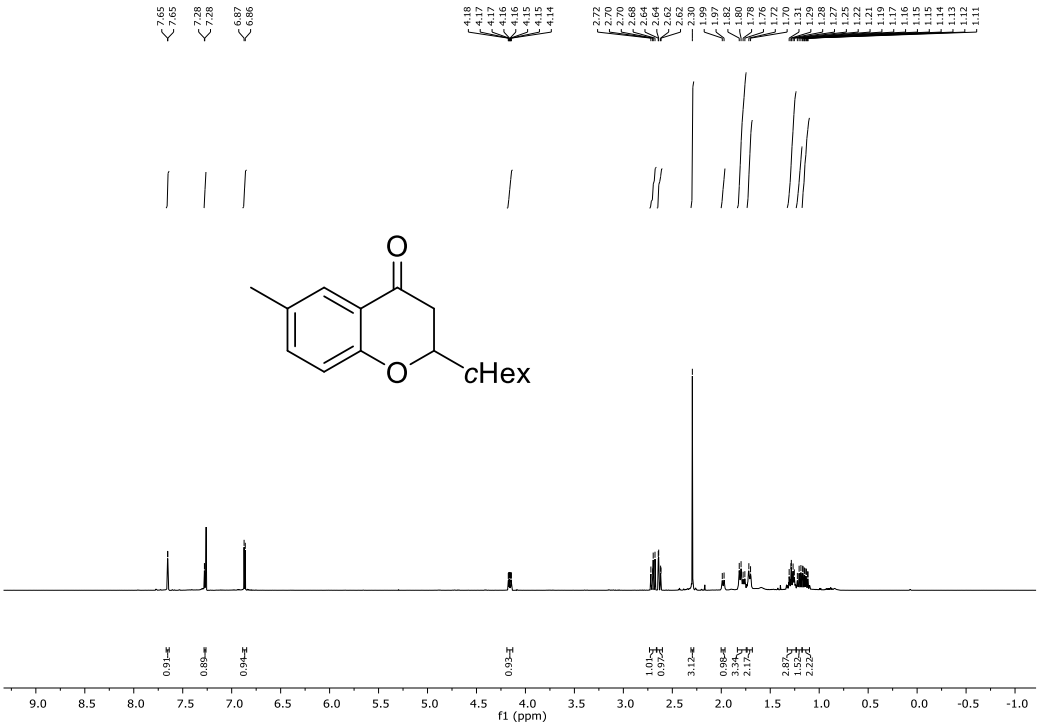


^{13}C NMR

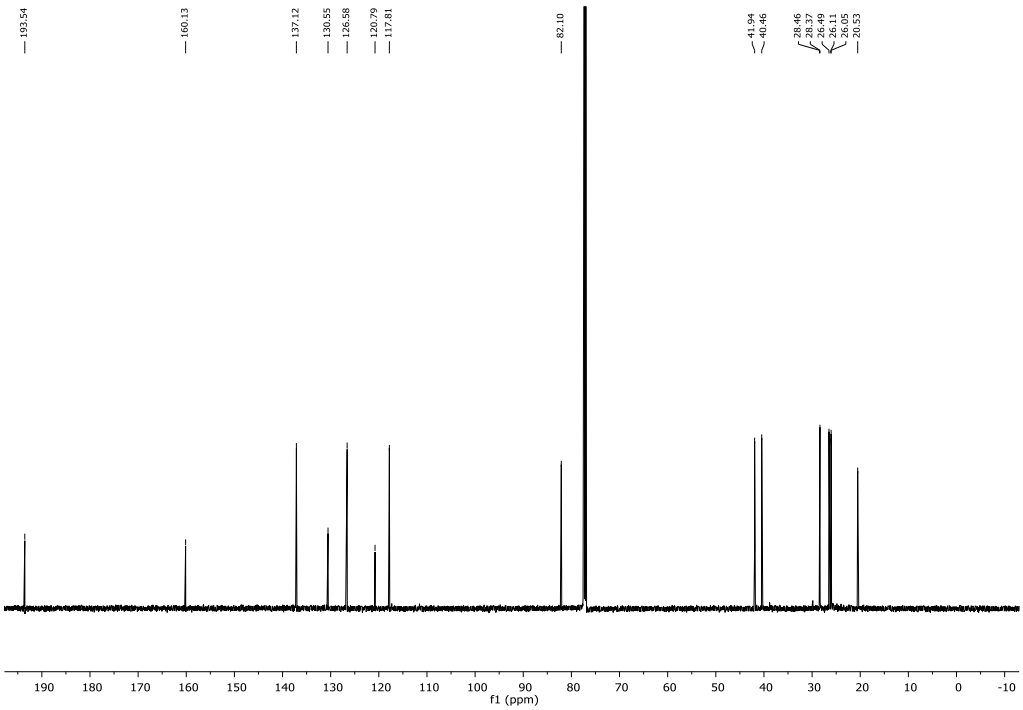


2-Cyclohexyl-6-methylchroman-4-one 5ab

^{1}H NMR

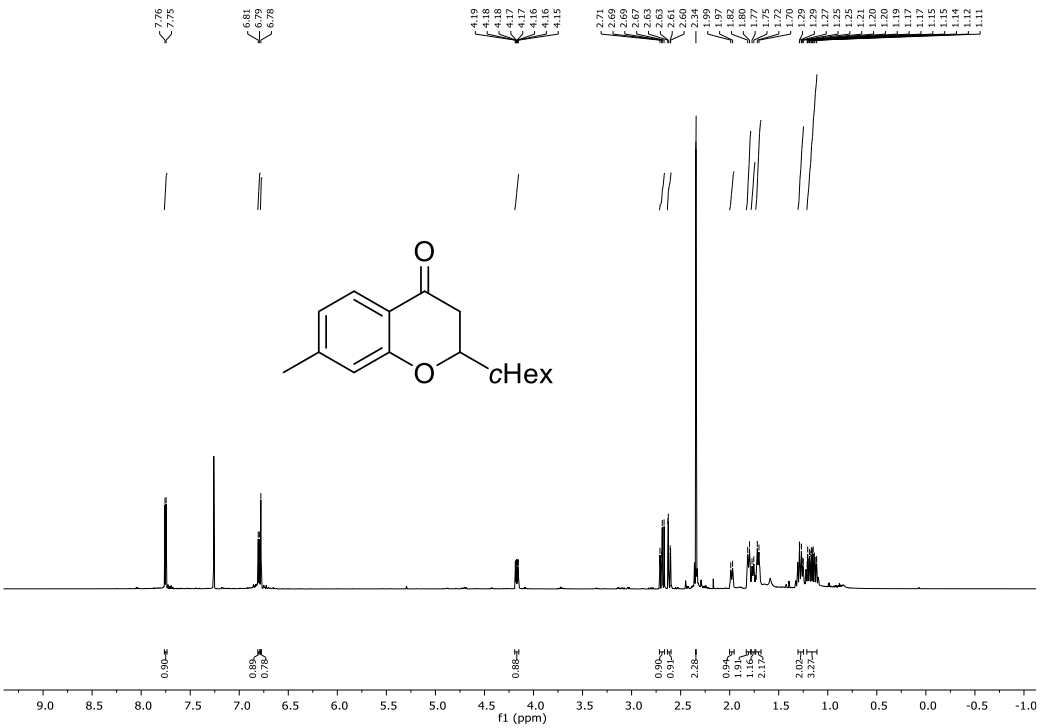


^{13}C NMR

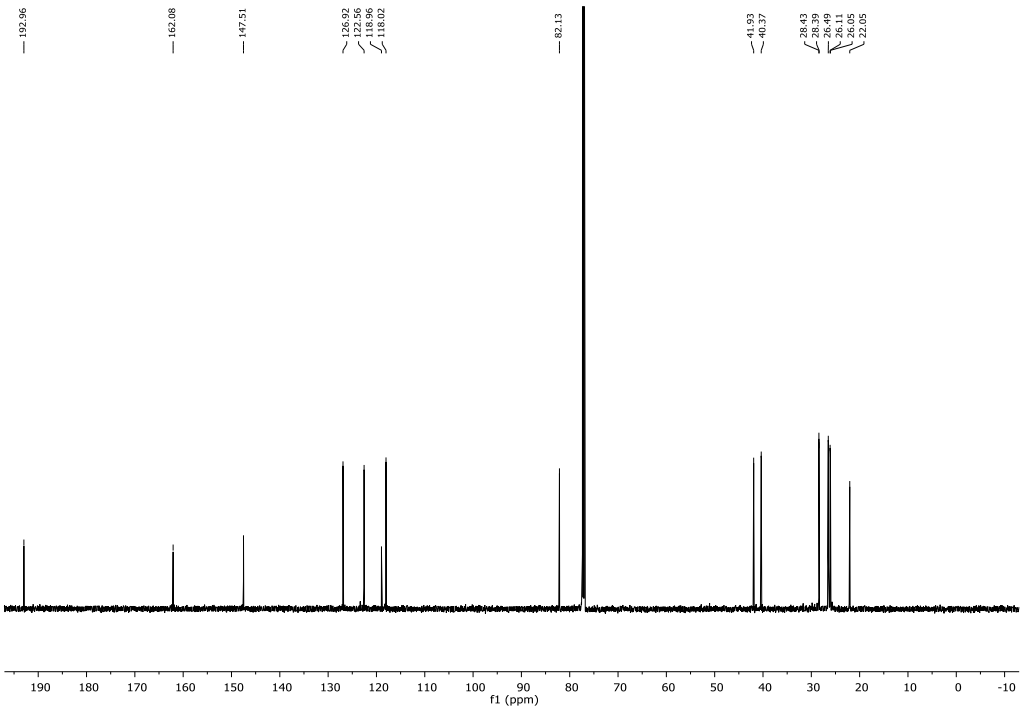


2-Cyclohexyl-7-methylchroman-4-one 5ac

^{1}H NMR

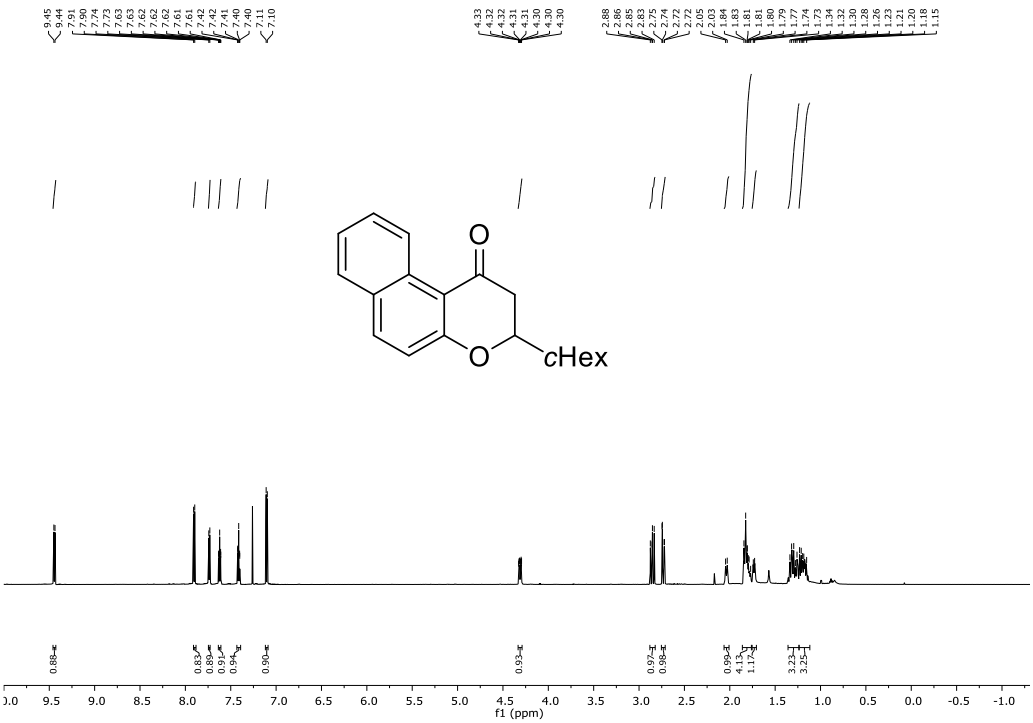


^{13}C NMR

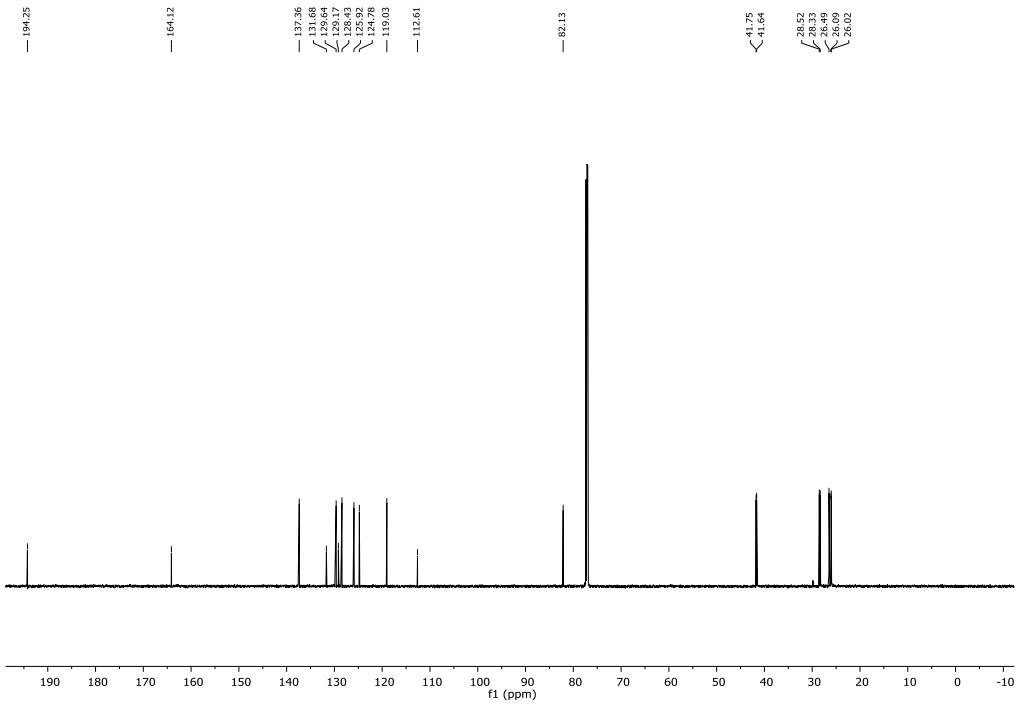


3-Cyclohexyl-2,3-dihydro-1*H*-benzo[*c,f*]chromen-1-one 5ad

^{1}H NMR

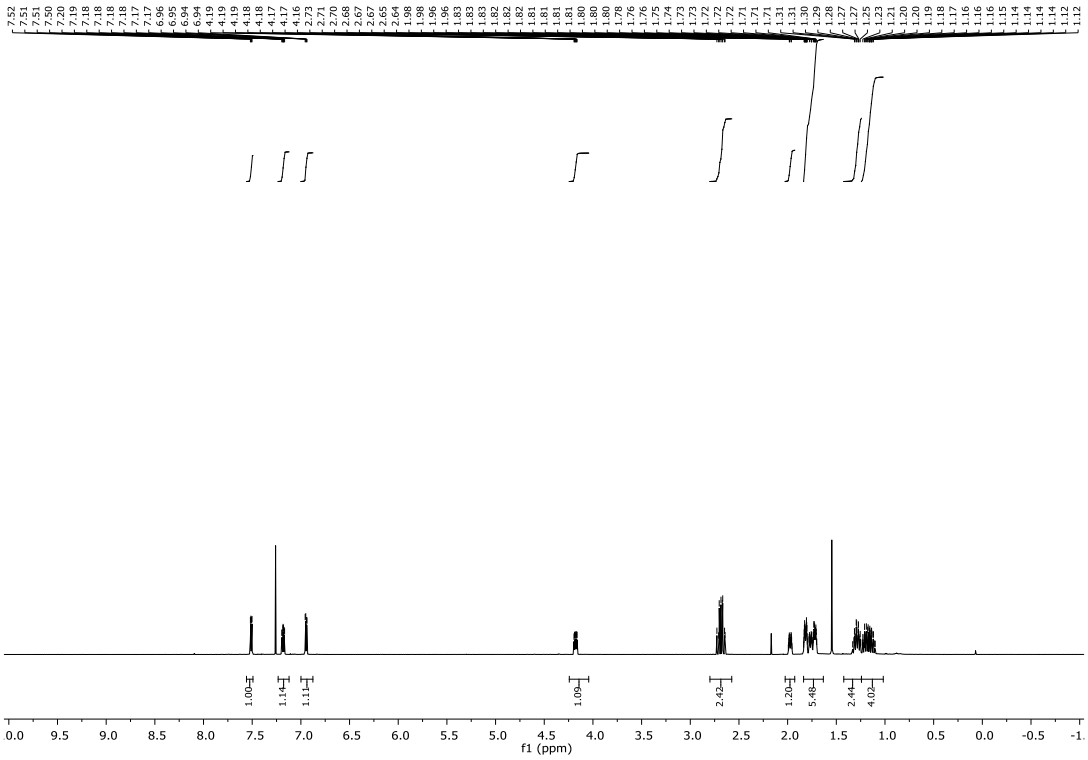


^{13}C NMR

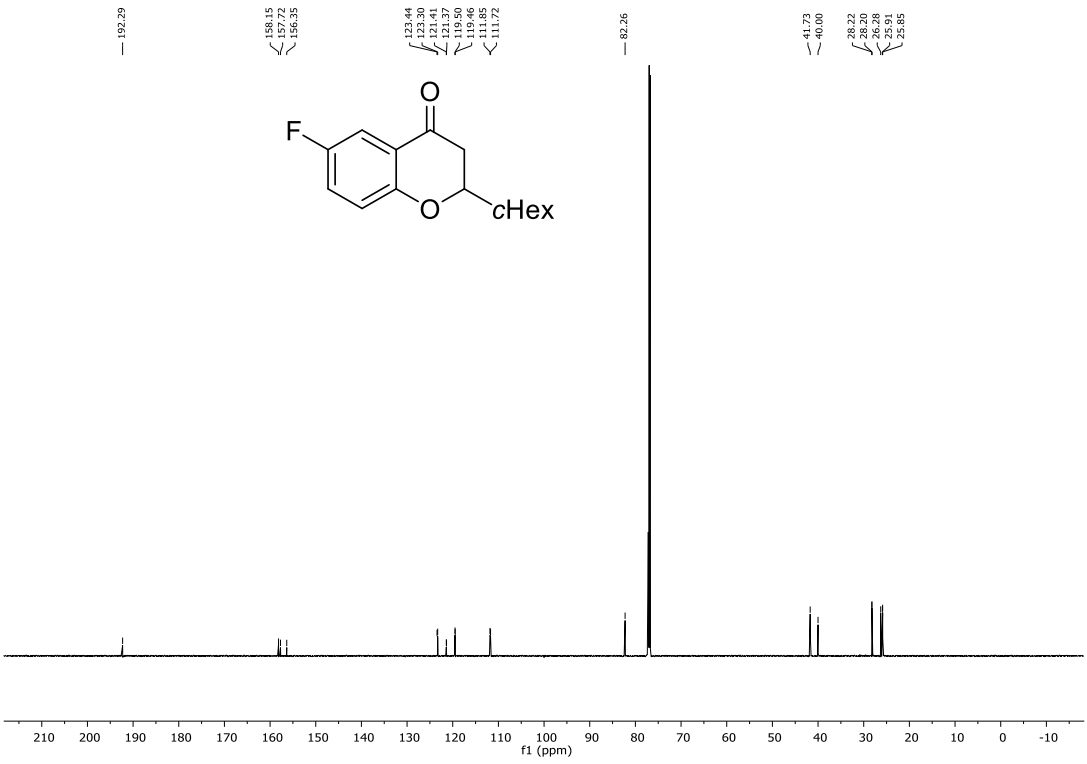


2-Cyclohexyl-6-fluorochroman-4-one 5ae

^{1}H NMR

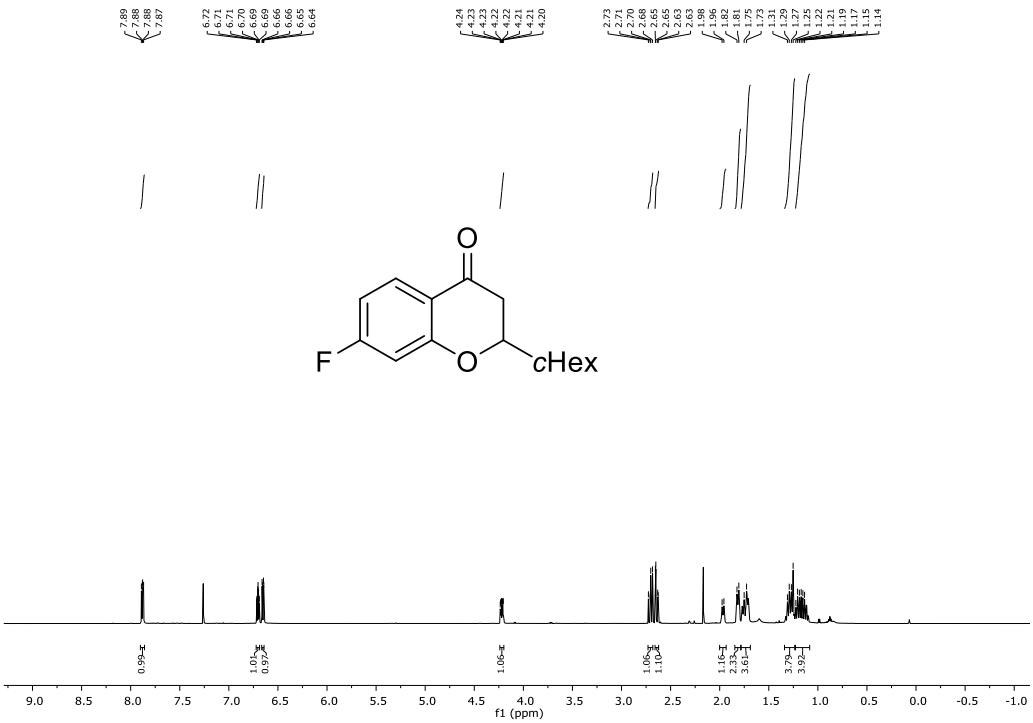


^{13}C NMR

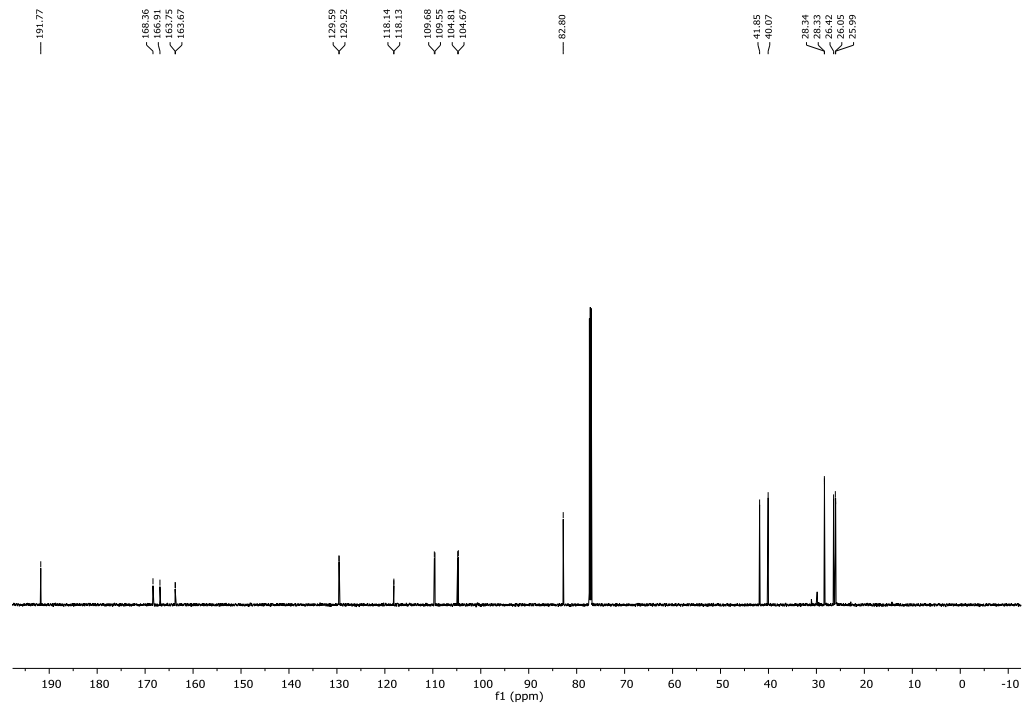


2-Cyclohexyl-7-fluorochroman-4-one 5af

^{1}H NMR

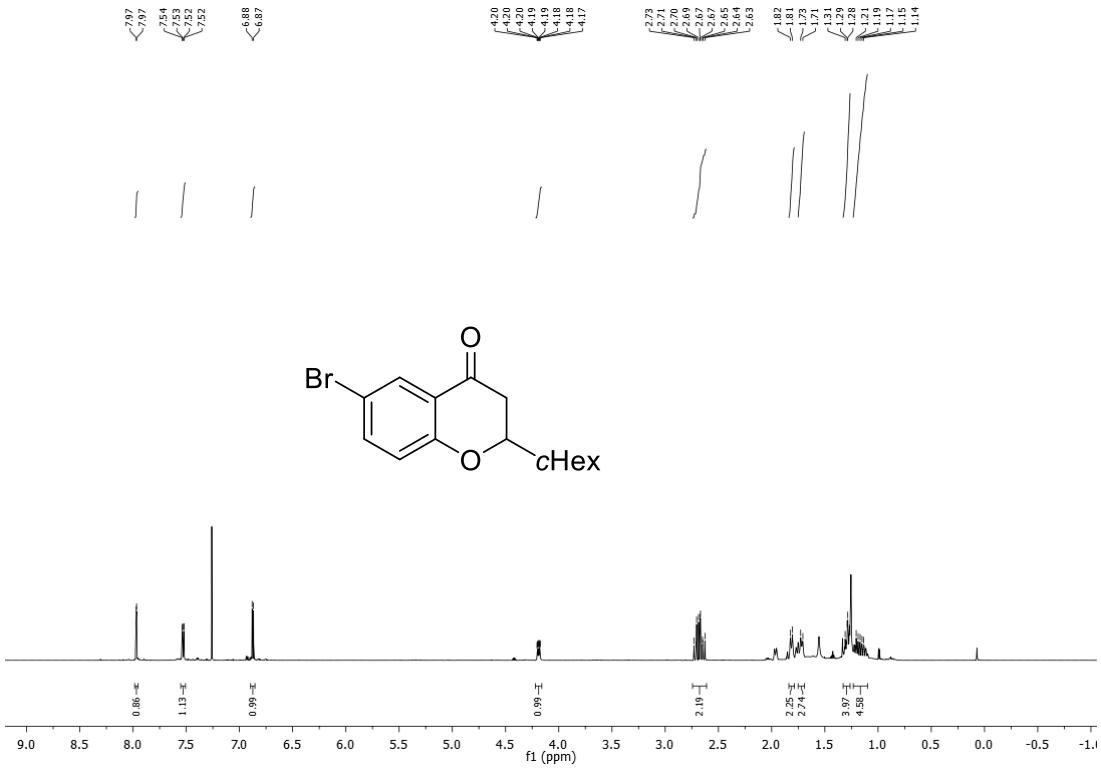


^{13}C NMR

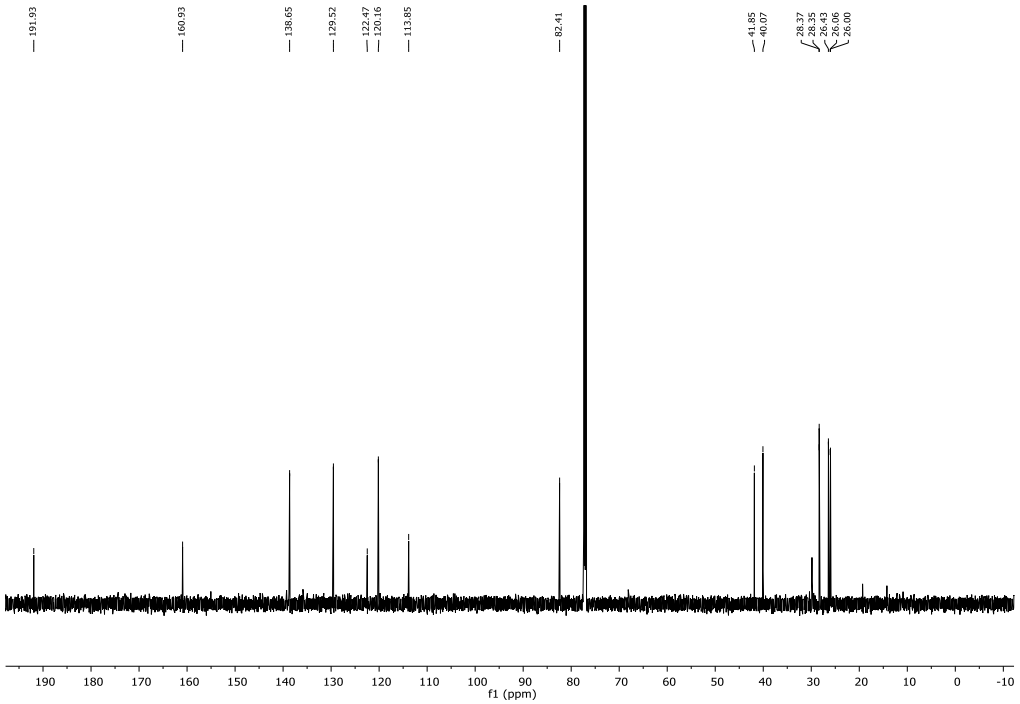


6-Bromo-2-cyclohexylchroman-4-one 5ag

^{1}H NMR

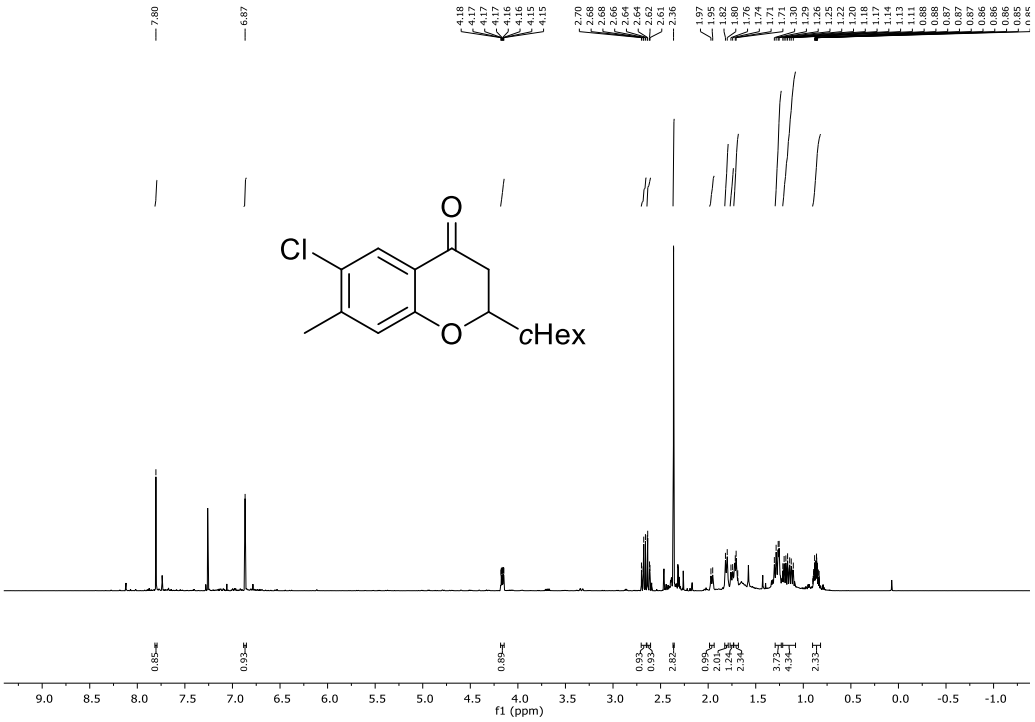


^{13}C NMR

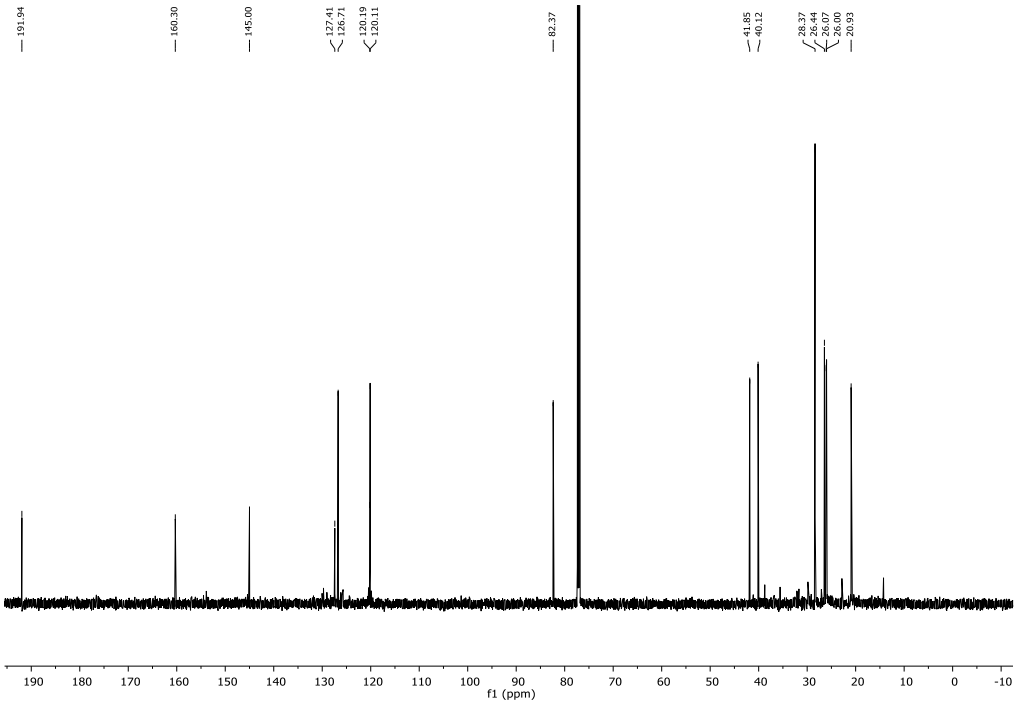


6-Chloro-2-cyclohexyl-7-methylchroman-4-one 5ah

^{1}H NMR

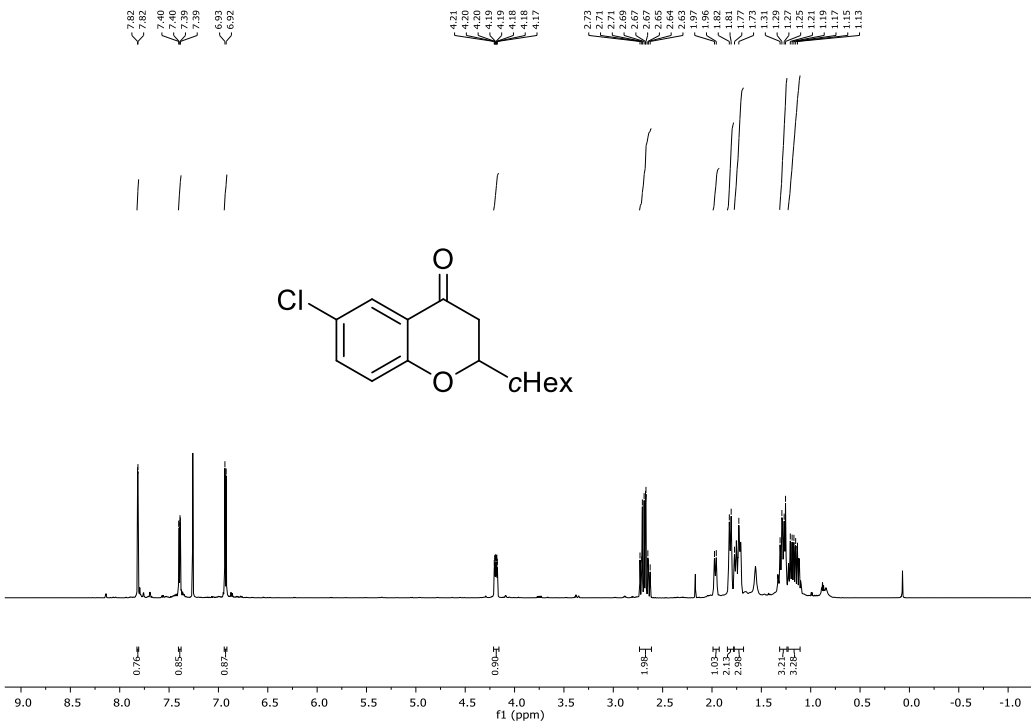


^{13}C NMR

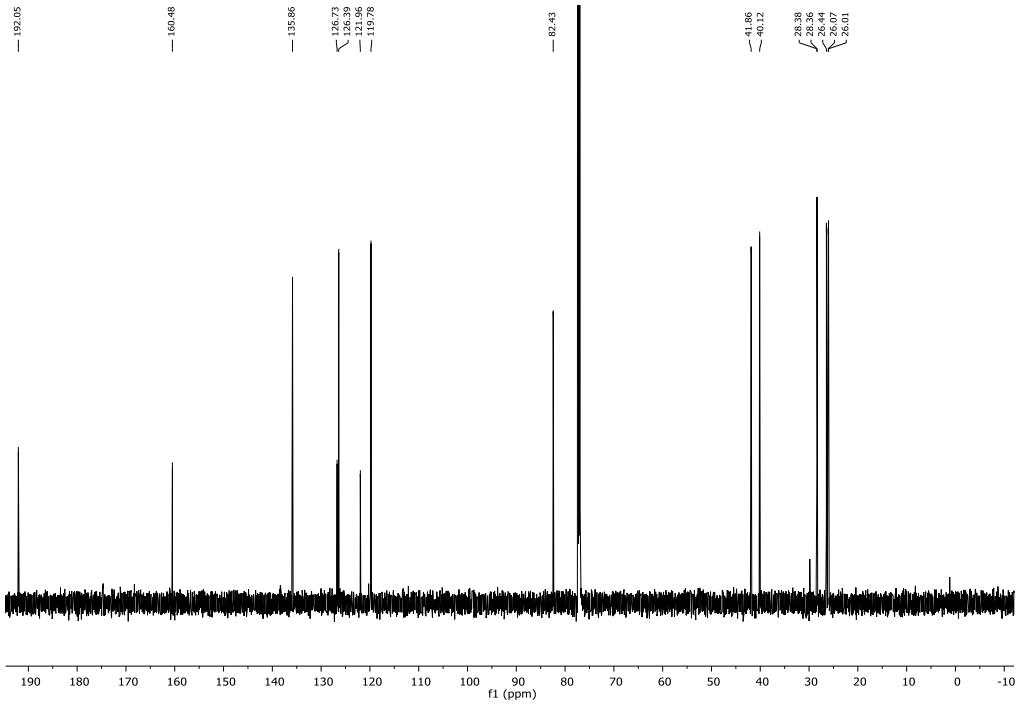


6-Chloro-2-cyclohexylchroman-4-one 5ai

^{1}H NMR

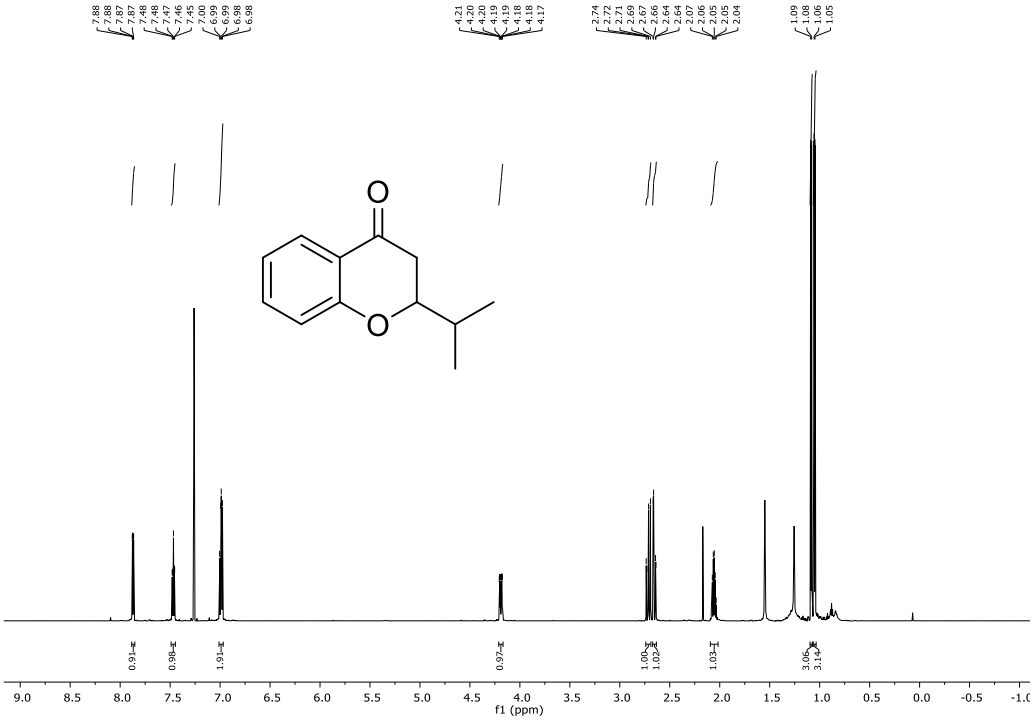


^{13}C NMR

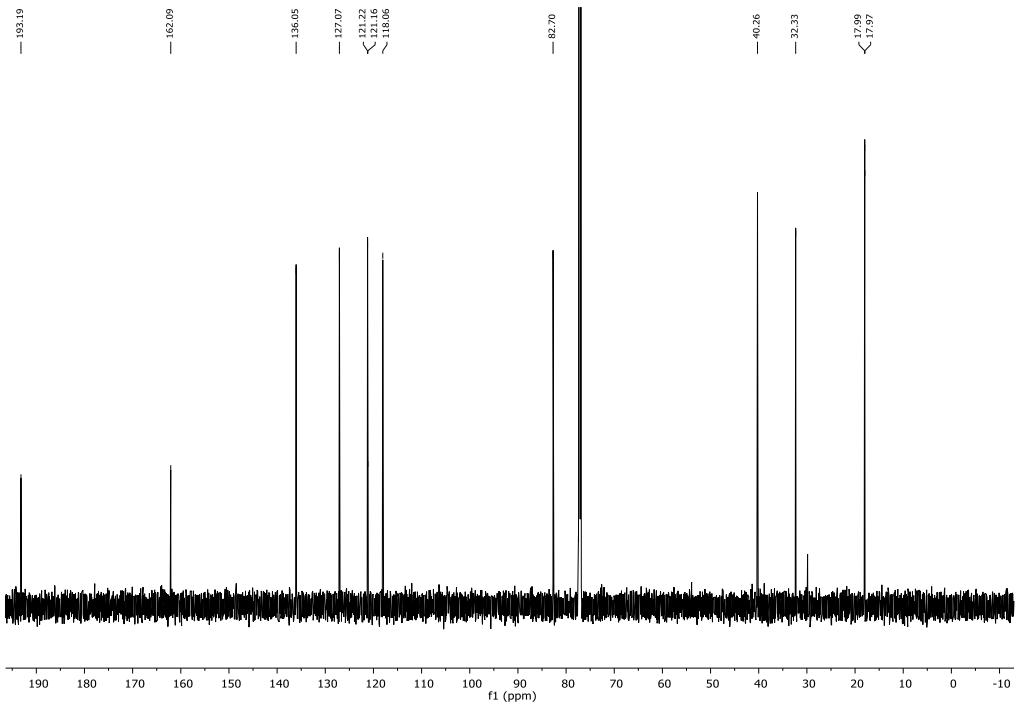


2-Isopropylchroman-4-one 5ba

^{1}H NMR



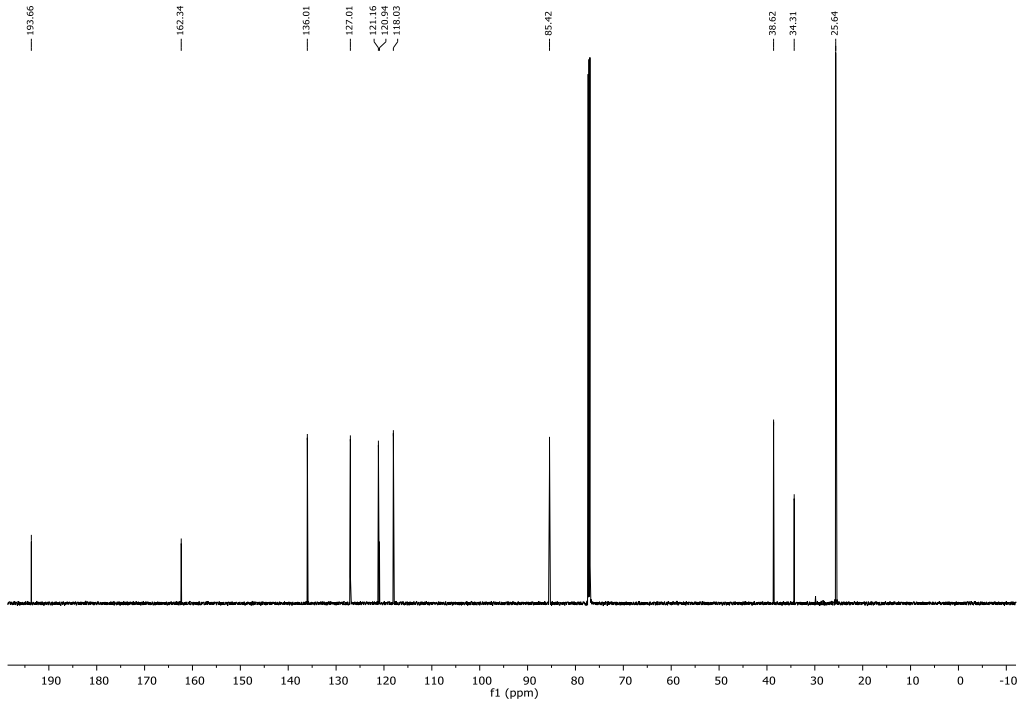
^{13}C NMR



2-(*tert*-Butyl)chroman-4-one 5ca

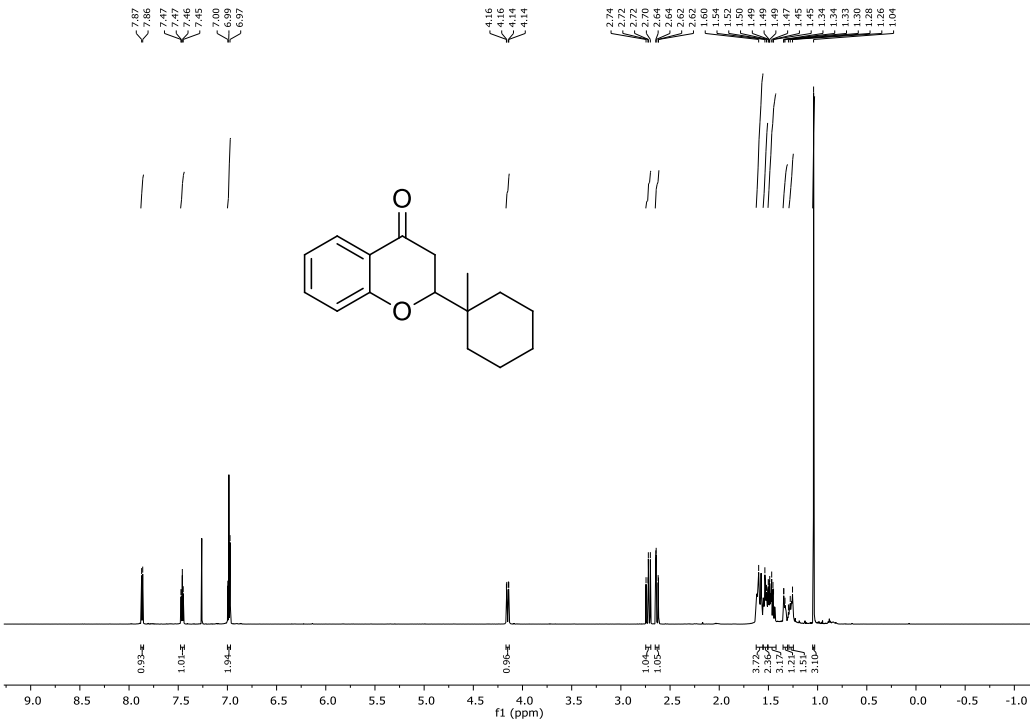
^{1}H NMR

^{13}C NMR

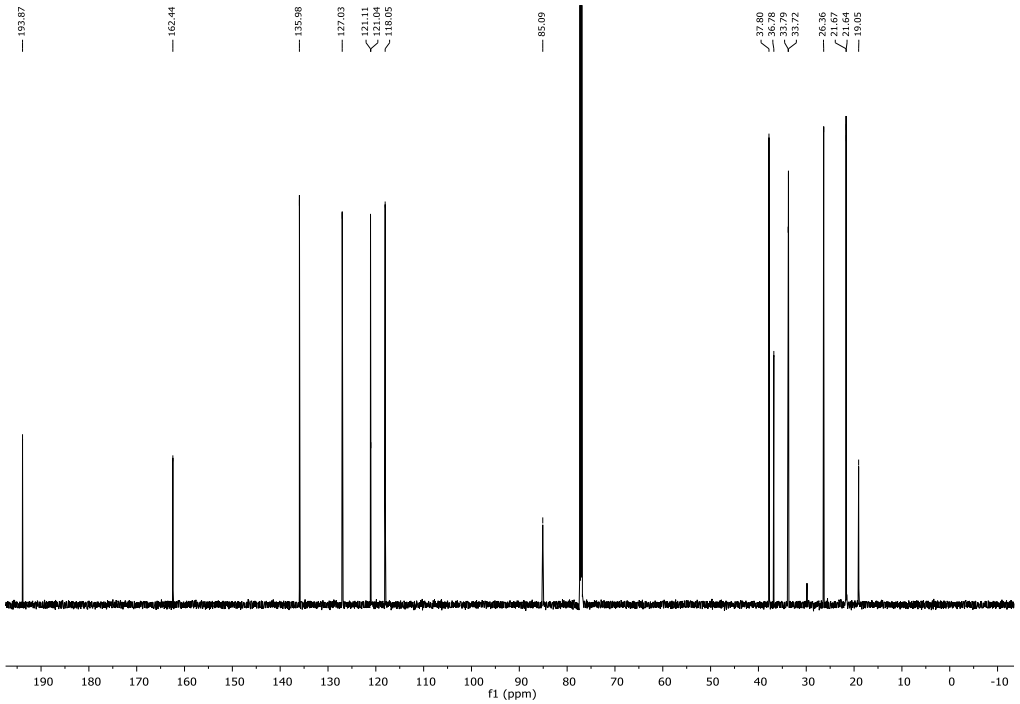


2-(1-Methylcyclohexyl)chroman-4-one 5da

^{1}H NMR

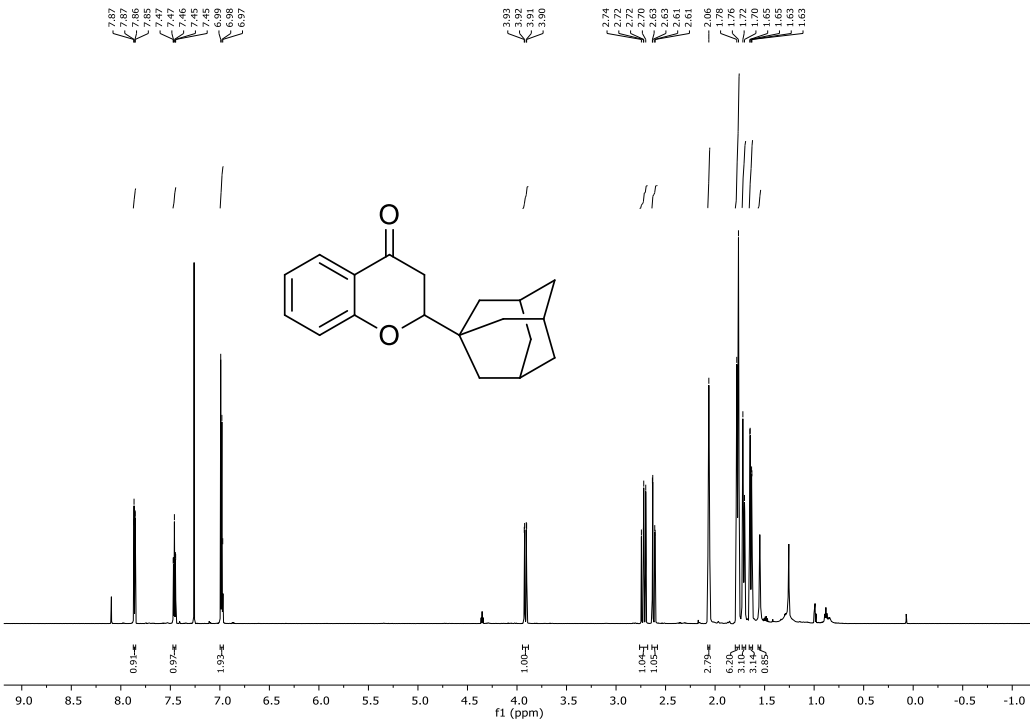


^{13}C NMR



2-(Adamantan-1-yl)chroman-4-one 5ea

^{1}H NMR



^{13}C NMR