Supporting Information

Synthesis of 2-Alkyl-chroman-4-ones *via* Cascade Alkylation-Dechlorination of 3-Chlorochromones

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1.General experimental details

General information: Unless otherwise noted, all solvents and other reagents were commercially available and used without further purification. Zn powder was activated by dilute hydrochloric acid prior to use. All reagents were weighed and handled under air at room temperature. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. NMR spectra were recorded on a Varian-MERCURY Plus-400 NMR spectrometer, a Brucker AVANCE III 500 NMR spectrometer, or a Brucker AVANCE III 600 NMR spectrometer and mass spectra (HRMS) were recorded on Micromass Ultra Q-TOF (ESI) spectrometer or Thermo DFS (EI). 3-chlorochromones, NHPI esters and compound **5'** were prepared according to the previous literatures.[1-11]

General procedure for the synthesis of 3-chlorochromones

A 100 mL round bottom flask equipped with a magnetic stirrer was charged with substituted *o*-hydroxyacetophenone (8 mmol) and 6 mL *N, N*-dimethylformamide dimethyl acetal (DMF-DMA). The mixture was heated at a reflux temperature in an open atmosphere for 1h. Then the mixture was evaporated for a crude product. Next, the crude product was dissolved with dichloromethane (15 mL) and followed by *N*-Chlorosuccinimide (8.8 mmol) in an ice bath. After 10 min, the reaction was quenched with brine (45 mL), then washed with brine for twice (45 mL× 2). The organic phase was dried with sodium sulfate and evaporated to dryness to yield a crude product, which was purified by silica gel chromatography to give the desired product.

General procedure for the synthesis of NHPI esters

To the bottle with a magnetic stirring bar were added DCC (22 mmol), DMAP (244 mg, 2mmol) and DCM (50 mL), then the acid (20 mmol, 1equiv) was added. Under stirring, NHP (3.26 g, 20 mmol) was added. After stirring for an hour, the mixture was filtrated through a short pad of silica gel, and the solid was washed by DCM. The filtrate was concentrated, and the residue was further purified by recrystallization in PE/EA or by column chromatography on silica gel using PE/EA as the eluent.

General procedure for the synthesis of compound 5'

To a stirred solution of **3a** (5.00 mmol) in $CHCl_3$ (10 mL) at -10°C was added in one portion, and as rapidly as possible, SO_2Cl_2 (1.01g, 606 µL, 7.5 mmol, tech. grade). The reaction mixture was stirred at -10°C for 1 h and then poured into brine (50 mL). The organics were separated, the aqueous layer was extracted with DCM (3 x 100 mL), the organics combined, dried over $MgSO_4$ and the volatiles removed under reduced pressure to give a pink crude reaction product, and the residue was further purified by column chromatography on silica gel using PE/EA as the eluent.

General procedure for the synthesis of 2-alkyl-chroman-4-ones

The substituted 3-chlorochromone (0.5 mmol), NHPI ester (1.0 mmol), and Zn (2.0 mmol) were added into a Schlenk tube equipped with a magnetic stirring bar, and the tube was evacuated and flushed with nitrogen for six cycles. To the tube was added DMF (3 mL) and followed by 23 µL water (1.25 mmol) the mixture was stirred vigorously for 15 hours at 20 °C. The mixture was quenched with saturated ammonium chloride solution (9 mL) and extracted with EA for 3 times (3 mL×3). The organic phase was combined and washed with brine for twice (9 mL× 2). The organic phase was concentrated, and the residue was purified by column chromatography using silica gel with PE/EA as the eluent.

General procedure for gram-scale

The substituted 3-chlorochromone (5.5 mmol), NHPI ester (11 mmol), and Zn (22 mmol) were added into a 100 mL round bottle equipped with a magnetic stirring bar, and the bottle was evacuated and flushed with nitrogen for six cycles. To the bottle was added DMF (15 mL) and followed by 250 μL water (13.8 mmol) the mixture was stirred vigorously for 15 hours at 20 ºC. The mixture was quenched with saturated ammonium chloride solution (90 mL) and extracted with EA for 4 times (30 mL×4). The organic phase was combined and washed with brine for twice (90 mL× 2). The organic phase was concentrated, and the residue was purified by column chromatography using silica gel with PE/EA as the eluent.

General procedure for the deprotection of 3ai

To the bottle with a magnetic stirring bar were added **3ai** (800 mg, 2.52 mmol), and then followed by 4M HCl in MeOH. The mixture was stirred overnight. The MeOH was removed by vacuum and 80 mL water was added. The solvent was washed with EA for 3 times, and the water phase was freeze-dried for 2 days to obtain the desired product.

2.Notes

Control experiment of adding D_2O

The reaction with D_2O has also been performed. Based on the NMR of desired product, we found that nearly half of the alpha H were deuterated. Given the existence of enol tautomerism, the deuterium might be displaced by the active hydrogen during the work-up and purification process, so that this control experiment might give some limited information (According to the results, we may tell the position where deuterium is incorporating in the product. However, the amount of deuterium incorporating in the product might not be accurately assessed through this experiment.). Followed are the NMR of D_2O Group (Fig.1) and H_2O group (Fig.2)

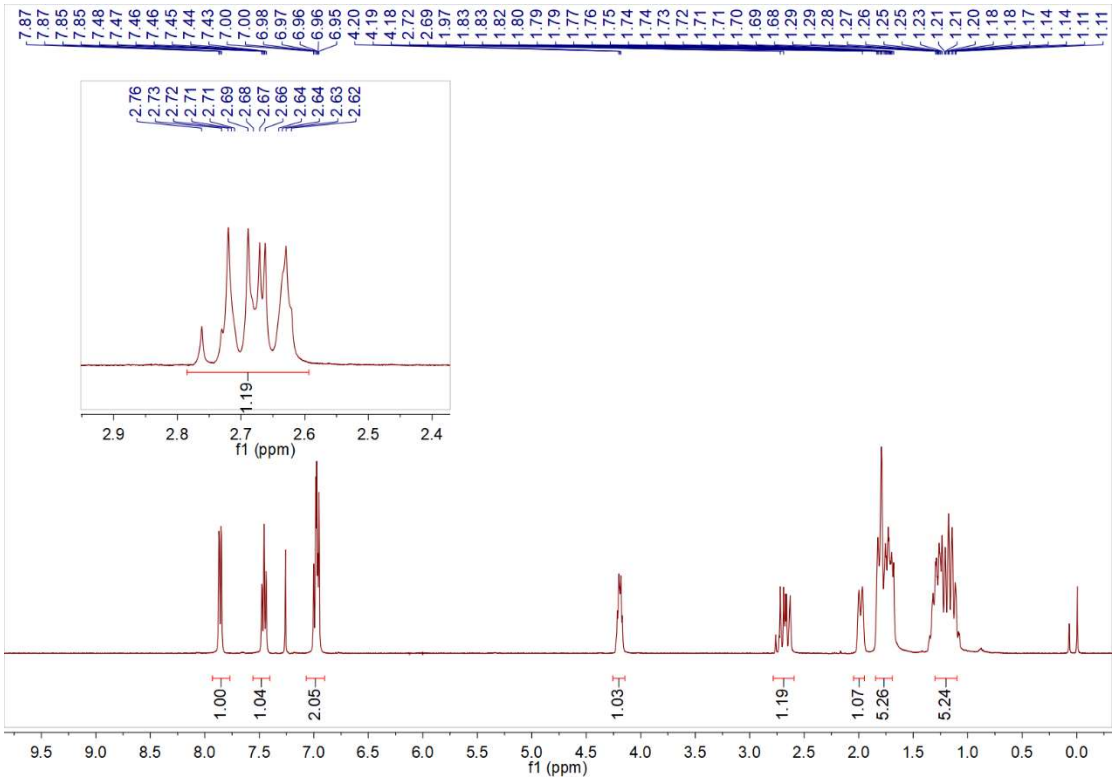


Fig.1 ^{1}H NMR spectra of compound 3a (D_2O)

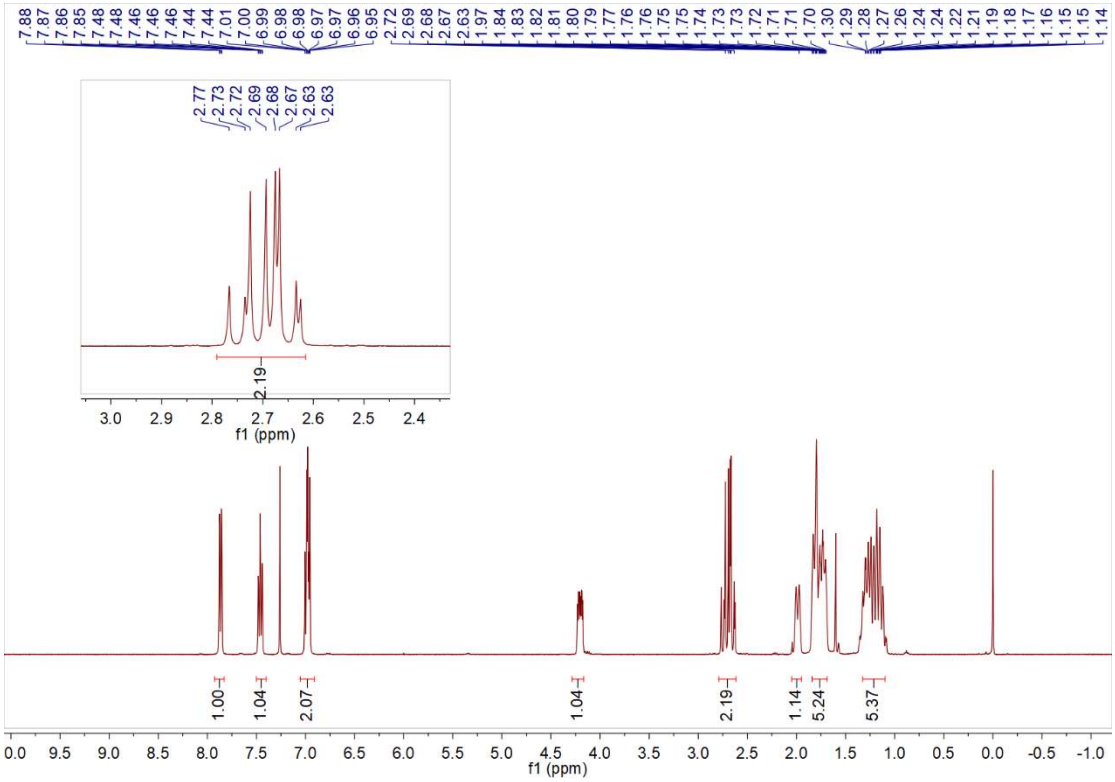


Fig.2 ^{1}H NMR spectra of compound 3a (H_2O)

The ^{1}H and ^{13}C spectra and High-resolution mass spectrometry of 3ai

Due to the existence of Boc, the rotation of 3ai was prevented, which made the spectra unsightly. Therefore, we provided the spectra of deprotected 3ai instead. Followed are the spectra and high-resolution mass spectrometry of 3ai.

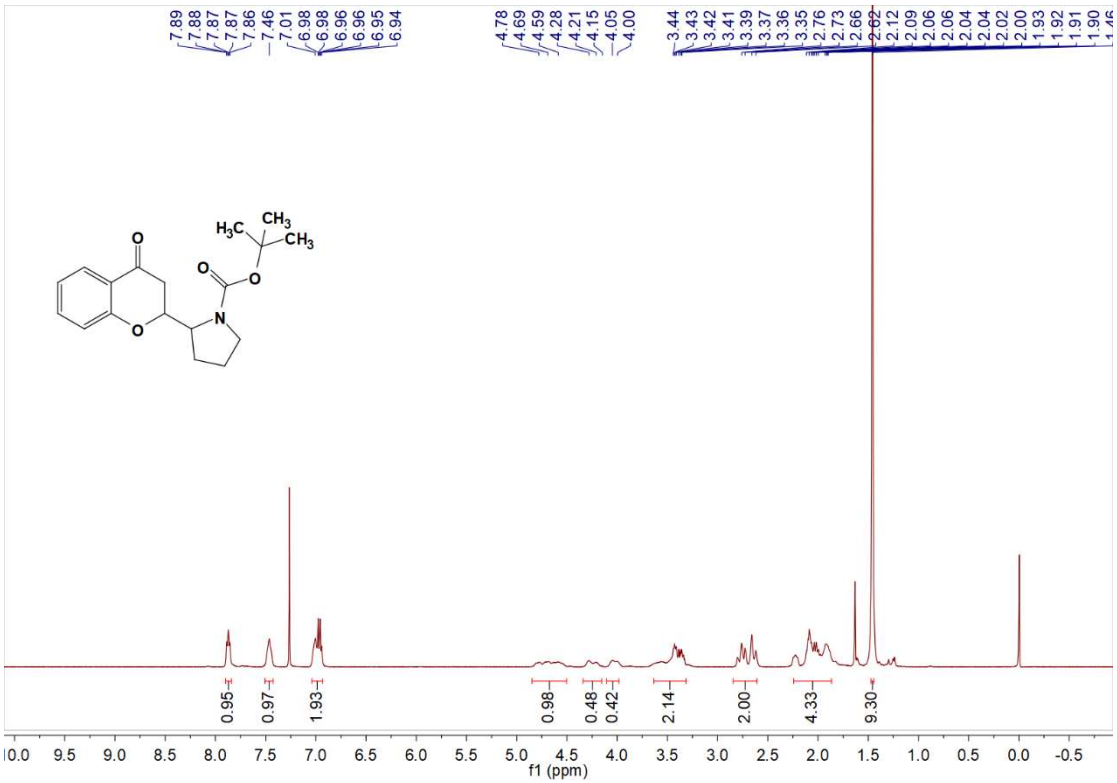


Fig. 3 ^{1}H NMR of compound 3ai

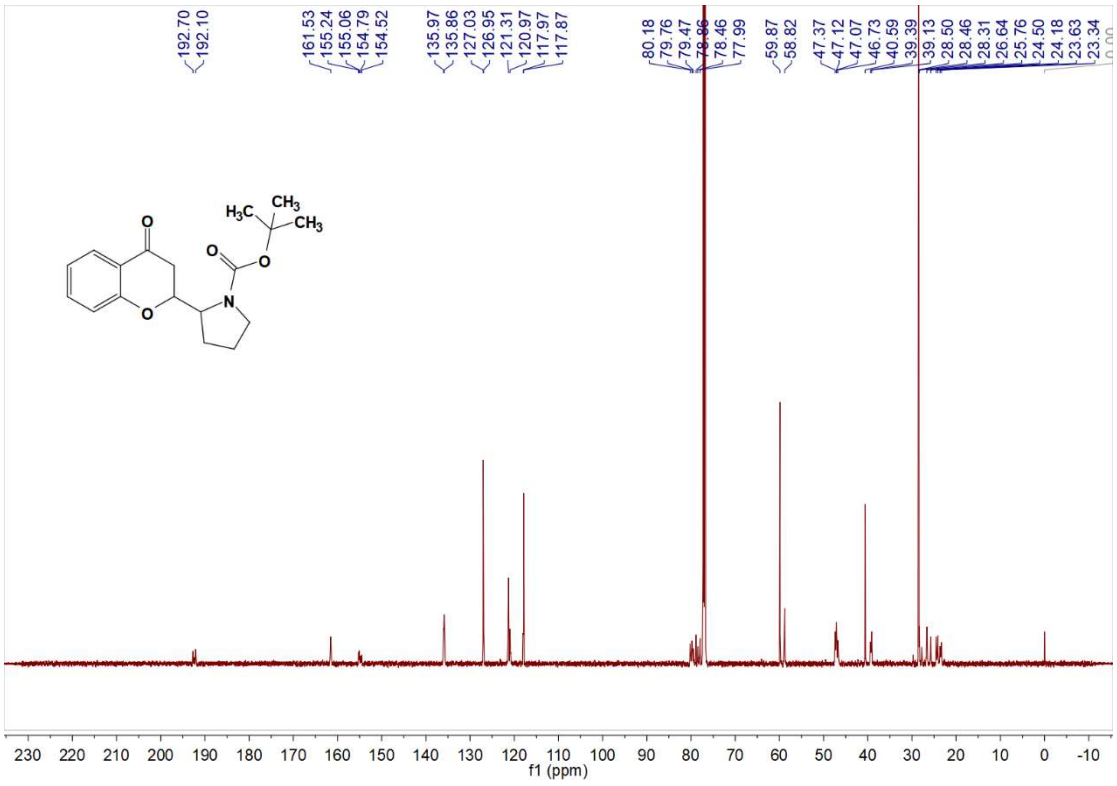


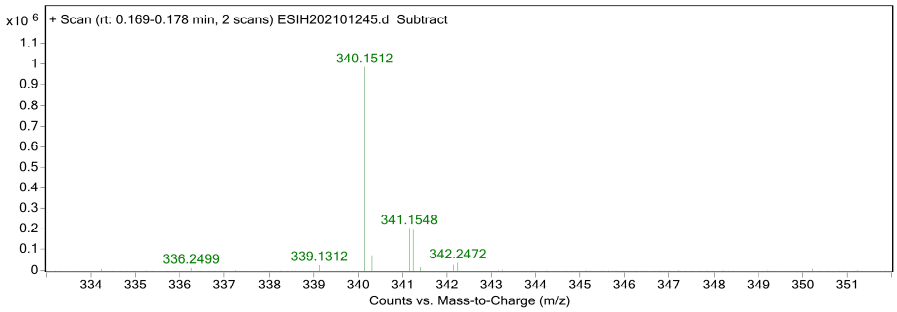
Fig. 2 ^{13}C NMR of compound 3ai

Qualitative Analysis Report

Data Filename	ESIH202101245.d	**Sample Name**	D2-D2-LSY-C32
Sample ID		**Position**	P1-D1
Instrument Name	Agilent G6520 Q-TOF	**Acq Method**	20160322_MS_ESIH_POS_1min.m
Acquired Time	3/5/2021 10:38:38	**IRM Calibration Status**	Success
DA Method	small molecular data analysis method.m	**Comment**	ESIH by ZZY

User Spectra

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
340.1512	340.1519	0.74	2.18	C18 H23 N Na O4	(M+Na)+

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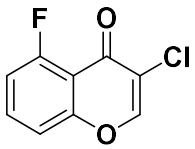
Fig. 3 High-resolution mass spectrometry of 3ai

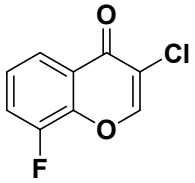
3.Characterization data of the products

3-chloro-5-fluoro-4*H*-chromen-4-one(1b)



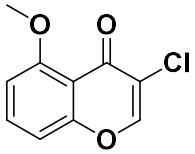
As a light yellow solid. (40%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.64 (td, *J* = 8.4, 5.5 Hz, 1H), 7.28 (dt, *J* = 8.6, 1.1 Hz, 1H), 7.13 – 7.06 (m, 1H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.17, 160.67 (d, *J* = 267.0 Hz), 157.05 (d, *J* = 3.3 Hz), 151.27, 134.39 (d, *J* = 10.7 Hz), 121.73, 114.23 (d, *J* = 4.7 Hz), 114.5 (d, *J* = 10.2 Hz), 112.71 (d, *J* = 20.5 Hz). LRMS (ESI^{+}) m/z:198.8 [M+1]$^{+}$.

3-chloro-8-fluoro-4*H*-chromen-4-one(1c)



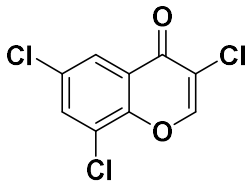
As a light yellow solid. (64%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (s, 1H), 8.05 – 7.97 (m, 1H), 7.52 – 7.44 (m, 1H), 7.43 – 7.34 (m, 1H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.51 (d, *J* = 2.8 Hz), 151.83, 151.15 (d, *J* = 254.7 Hz), 145.00 (d, *J* = 11.9 Hz), 125.77 (d, *J* = 6.5 Hz), 125.34, 121.59, 121.44 (d, *J* = 4.3 Hz), 120.07 (d, *J* = 16.6 Hz). LRMS (ESI^{+}) m/z:198.8 [M+1]$^{+}$.

3-chloro-5-methoxy-4*H*-chromen-4-one(1d)



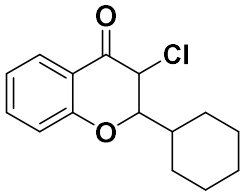
As a white solid. (47%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.55 (t, *J* = 8.4 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.34, 160.09, 158.10, 150.18, 134.32, 121.92, 114.32, 110.07, 106.94, 56.62. LRMS (ESI^{+}) m/z:210.8 [M+1]$^{+}$.

3,6,8-trichloro-4*H*-chromen-4-one(1e)



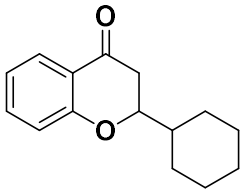
As a yellow solid. (42%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 8.14 (d, *J* = 2.6 Hz, 1H), 7.75 (t, *J* = 2.3 Hz, 1H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.77, 152.25, 150.52, 134.53, 131.82, 125.20, 124.73, 124.46, 121.62. LRMS (ESI^{+}) m/z:248.6 [M+1]$^{+}$.

3-chloro-2-cyclohexylchroman-4-one (5')



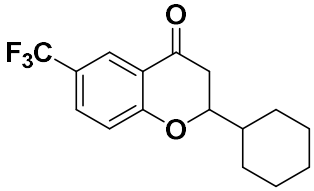
As a light yellow solid (90%, d.r ≈5:1) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 1H), 7.56 – 7.47 (m, 1H), 7.11 – 6.98 (m, 2H), 4.63 (d, *J* = 9.1 Hz, 0.85H), 4.36 (d, *J* = 1.5 Hz, 0.16H), 4.26 (dd, *J* = 9.2, 4.7 Hz, 0.81H), 4.11 – 3.97 (m, 0.13H), 2.36 (d, *J* = 12.9 Hz, 0.15H), 2.16 – 2.05 (m, 0.13H), 1.95 (tt, *J* = 11.7, 3.6 Hz, 0.88H), 1.87 – 1.59 (m, 4.71H), 1.56 – 1.16 (m, 4.58H), 1.12 – 0.81 (m, 0.39H). LRMS (ESI^{+}) m/z:264.9 $[M+1]^{+}$

2-cyclohexylchroman-4-one(3a)



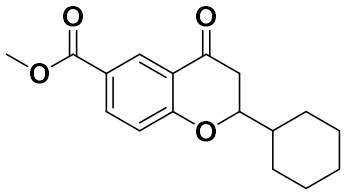
As a white solid. (78%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.2, 1.8 Hz, 1H), 7.04 – 6.91 (m, 2H), 4.20 (ddd, *J* = 12.3, 6.0, 3.4 Hz, 1H), 2.78 – 2.62 (m, 2H), 2.03 – 1.93 (m, 1H), 1.85 – 1.69 (m, 5H), 1.33 – 1.11 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.27, 162.05, 136.03, 127.04, 121.19, 121.16, 118.03, 82.13, 41.93, 40.41, 28.42, 28.35, 26.48, 26.10, 26.05. HRMS (EI) m/z: calcd for $[C_{15}H_{18}O_2]$, 230.1301; found 230.1298.

2-cyclohexyl-6-(trifluoromethyl)chroman-4-one(3b)



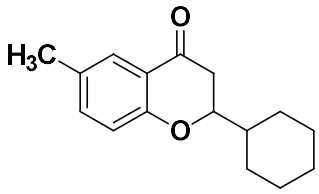
As a colorless oil. (80%) ^{1}H NMR (400 MHz, Chloroform-d) δ 8.22 – 8.09 (m, 1H), 7.68 (dd, J = 8.8, 2.4 Hz, 1H), 7.08 (d, J = 8.7 Hz, 1H), 4.27 (ddd, J = 11.0, 5.9, 4.4 Hz, 1H), 2.81 – 2.68 (m, 2H), 2.03 – 1.94 (m, 1H), 1.86 – 1.68 (m, 5H), 1.33 – 1.14 (m, 5H). ^{13}C NMR (151 MHz, Chloroform-d) δ 191.96, 163.96, 132.34 (q, J = 3.1 Hz), 124.94 (q, J = 4.0 Hz), 123.95 (q, J = 271.7 Hz), 123.71 (q, J = 33.4 Hz), 120.72, 119.01, 82.62, 41.77, 40.03, 28.29, 26.37, 26.02, 25.95. ^{19}F NMR (376 MHz, Chloroform-d) δ -62.12. HRMS (EI) m/z: calcd for $[C_{16}H_{17}O_2F_3]$, 298.1175; found 298.1170.

methyl 2-cyclohexyl-4-oxochromane-6-carboxylate(3c)



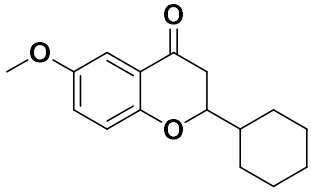
As a white solid. (80%) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.53 (d, *J* = 2.2 Hz, 1H), 8.10 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 4.25 (ddd, *J* = 12.0, 5.8, 3.8 Hz, 1H), 3.88 (s, 3H), 2.77 – 2.65 (m, 2H), 2.00 – 1.92 (m, 1H), 1.84 – 1.68 (m, 5H), 1.31 – 1.10 (m, 5H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.10, 166.16, 165.03, 136.71, 129.45, 123.35, 120.58, 118.32, 82.51, 52.19, 41.79, 40.07, 28.27, 26.35, 26.00, 25.94. HRMS (ESI^{+}) m/z: calcd for [$C_{17}H_{21}O_4$], 289.1434; found 289.1439.

2-cyclohexyl-6-methylchroman-4-one(3d)



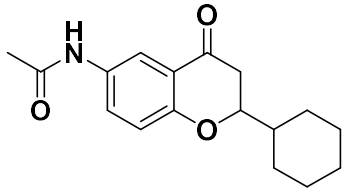
As a white solid. (71%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 2.3 Hz, 1H), 7.29 – 7.25 (m, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 4.15 (ddd, *J* = 12.2, 6.1, 3.6 Hz, 1H), 2.74 – 2.59 (m, 2H), 2.29 (s, 3H), 2.01 – 1.94 (m, 1H), 1.83 – 1.67 (m, 5H), 1.34 – 1.08 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.50, 160.11, 137.10, 130.53, 126.56, 120.77, 117.79, 82.08, 41.92, 40.44, 28.45, 28.35, 26.48, 26.10, 26.04, 20.52. HRMS (ESI^{+}) m/z: calcd for [$C_{16}H_{21}O_2$], 245.1536; found 245.1534.

2-cyclohexyl-6-methoxychroman-4-one(3e)



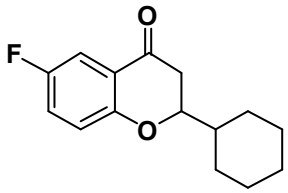
As a colorless oil. (68%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (d, *J* = 3.2 Hz, 1H), 7.07 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 1H), 4.15 (ddd, *J* = 12.4, 6.0, 3.6 Hz, 1H), 3.79 (s, 3H), 2.75 – 2.59 (m, 2H), 2.02 – 1.93 (m, 1H), 1.84 – 1.67 (m, 5H), 1.33 – 1.06 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.35, 156.83, 153.98, 125.31, 120.92, 119.32, 107.35, 82.24, 55.94, 41.93, 40.34, 28.46, 28.37, 26.48, 26.11, 26.05. HRMS (ESI^{+}) m/z: calcd for [$C_{16}H_{21}O_3$], 261.1485; found 261.1480.

N-(2-cyclohexyl-4-oxochroman-6-yl)acetamide(3f)



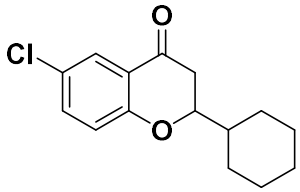
As a colorless oil. (72%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.96 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.68 (d, *J* = 2.7 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 4.15 (ddd, *J* = 12.7, 6.0, 3.1 Hz, 1H), 2.75 – 2.56 (m, 2H), 2.16 (s, 3H), 1.98 – 1.93 (m, 1H), 1.83 – 1.65 (m, 5H), 1.28 – 1.09 (m, 5H).^{13}C NMR (151 MHz, Chloroform-*d*) δ 193.35, 168.99, 158.76, 132.01, 129.55, 120.68, 118.53, 117.60, 82.13, 41.81, 40.29, 28.32, 28.30, 26.39, 26.03, 25.97, 24.35. HRMS (ESI^{+}) m/z: calcd for [$C_{17}H_{22}NO_3$], 288.1594; found 288.1597.

2-cyclohexyl-6-fluorochroman-4-one(3g)



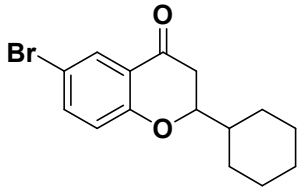
As a colorless oil. (77%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (dd, *J* = 8.3, 3.2 Hz, 1H), 7.18 (ddd, *J* = 9.0, 7.7, 3.2 Hz, 1H), 6.94 (dd, *J* = 9.1, 4.2 Hz, 1H), 4.18 (ddd, *J* = 11.7, 5.9, 4.2 Hz, 1H), 2.75 – 2.61 (m, 2H), 2.00 – 1.94 (m, 1H), 1.85 – 1.68 (m, 5H), 1.34 – 1.09 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.48, 158.30, 157.18 (d, *J* = 241.4 Hz), 123.54 (d, *J* = 24.6 Hz), 121.53 (d, *J* = 6.5 Hz), 119.65 (d, *J* = 7.3 Hz), 111.94 (d, *J* = 23.2 Hz), 82.41, 41.88, 40.15, 28.38, 28.35, 26.44, 26.07, 26.01. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -121.97 (td, *J* = 7.6, 4.2 Hz). HRMS (EI) m/z: calcd for [$C_{15}H_{17}O_2F$], 248.1207; found 248.1199.

6-chloro-2-cyclohexylchroman-4-one(3h)



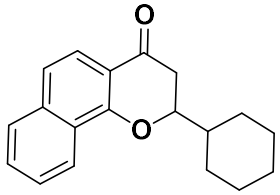
As a white solid. (72%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 2.7 Hz, 1H), 7.39 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 1H), 4.19 (ddd, *J* = 11.8, 5.9, 4.2 Hz, 1H), 2.75 – 2.62 (m, 2H), 1.99 – 1.92 (m, 1H), 1.85 – 1.68 (m, 5H), 1.35 – 1.10 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.06, 160.46, 135.85, 126.69, 126.36, 121.92, 119.77, 82.40, 41.83, 40.09, 28.35, 28.33, 26.42, 26.05, 25.99. HRMS (EI) m/z: calcd for [$C_{15}H_{17}O_2Cl$], 264.0912; found 264.0930.

6-bromo-2-cyclohexylchroman-4-one(3i)



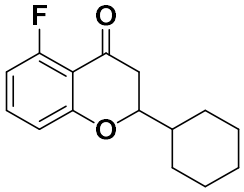
As a light yellow solid. (76%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 2.5 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 4.18 (ddd, *J* = 11.5, 5.8, 4.2 Hz, 1H), 2.75 – 2.61 (m, 2H), 1.96 (d, *J* = 12.5 Hz, 1H), 1.85 – 1.67 (m, 5H), 1.36 – 1.07 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.94, 160.89, 138.62, 129.47, 122.41, 120.14, 113.81, 82.37, 41.81, 40.02, 28.34, 28.31, 26.40, 26.04, 25.98. HRMS (EI) m/z: calcd for [$C_{15}H_{17}O_2Br$], 308.0406; found 308.0402.

2-cyclohexyl-2,3-dihydro-4H-benzo[h]chromen-4-one(3j)



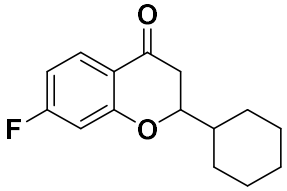
As a white solid. (75%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 – 8.29 (m, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.61 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 4.43 – 4.35 (m, 1H), 2.88 – 2.71 (m, 2H), 2.17 (d, *J* = 11.8 Hz, 1H), 1.93 – 1.81 (m, 4H), 1.81 – 1.72 (m, 1H), 1.39 – 1.20 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.77, 160.19, 137.62, 129.63, 127.97, 126.23, 125.14, 123.65, 121.91, 120.79, 115.58, 83.07, 42.10, 40.05, 28.65, 28.61, 26.48, 26.11, 26.01. HRMS (ESI^{+}) m/z: calcd for [$C_{19}H_{21}O_2$], 281.1536; found 281.1539.

2-cyclohexyl-5-fluorochroman-4-one(3k)



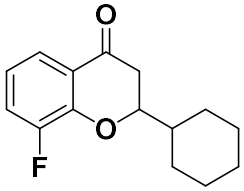
As a white solid. (74%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (td, *J* = 8.3, 6.0 Hz, 1H), 6.78 (dt, *J* = 8.4, 1.1 Hz, 1H), 6.66 (ddd, *J* = 10.5, 8.3, 1.1 Hz, 1H), 4.19 (ddd, *J* = 12.3, 6.0, 3.3 Hz, 1H), 2.77 – 2.60 (m, 2H), 2.00 – 1.93 (m, 1H), 1.84 – 1.67 (m, 5H), 1.34 – 1.07 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 190.88, 162.84, 161.80 (d, *J* = 270.2 Hz), 135.86 (d, *J* = 11.9 Hz), 113.75 (d, *J* = 4.0 Hz), 111.28 (d, *J* = 9.1 Hz), 108.61 (d, *J* = 21.1 Hz), 82.05, 41.73, 41.28, 28.35, 28.23, 26.41, 26.02, 25.96. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -111.24 (dd, *J* = 10.7, 6.0 Hz). HRMS (ESI^{+}) m/z: calcd for [$C_{15}H_{18}O_2F$], 249.1285; found 249.1289.

2-cyclohexyl-7-fluorochroman-4-one(3l)



As a colorless oil. (81%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.8, 6.7 Hz, 1H), 6.70 (td, *J* = 8.5, 2.4 Hz, 1H), 6.65 (dd, *J* = 9.9, 2.4 Hz, 1H), 4.22 (ddd, *J* = 12.3, 5.9, 3.6 Hz, 1H), 2.75 – 2.60 (m, 2H), 1.96 (dtt, *J* = 13.1, 3.4, 1.6 Hz, 1H), 1.85 – 1.67 (m, 5H), 1.36 – 1.06 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.78, 167.61 (d, *J* = 255.5 Hz), 163.69 (d, *J* = 13.8 Hz), 129.54 (d, *J* = 11.5 Hz), 118.11, 109.61 (d, *J* = 22.8 Hz), 104.74 (d, *J* = 24.2 Hz), 82.79, 41.83, 40.05, 28.33, 28.31, 26.41, 26.05, 25.98. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -100.87 (q, *J* = 7.8 Hz). HRMS (EI) m/z: calcd for [$C_{15}H_{17}O_2F$], 248.1207; found 248.1215.

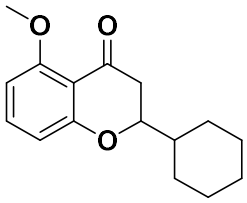
2-cyclohexyl-8-fluorochroman-4-one(3m)



As a white solid. (78%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.29 – 7.23 (m, 1H), 6.91 (td, *J* = 8.0, 4.4 Hz, 1H), 4.26 (ddd, *J* = 11.9, 6.1, 3.8 Hz, 1H), 2.82 – 2.66 (m, 2H), 2.05 – 1.98 (m, 1H), 1.86 – 1.68 (m, 5H), 1.38 – 1.09 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.17

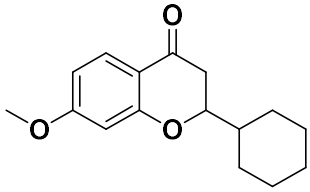
(d, *J* = 3.3 Hz), 151.94 (d, *J* = 248.8 Hz), 150.38 (d, *J* = 11.3 Hz), 123.28, 122.03 (d, *J* = 3.8 Hz), 121.80 (d, *J* = 17.6 Hz), 120.42 (d, *J* = 6.3 Hz), 83.06, 41.82, 40.39, 28.40, 28.26, 26.39, 26.02, 25.97. ^{19}F NMR (471 MHz, Chloroform-*d*) δ -135.21 (dd, *J* = 10.5, 4.6 Hz). HRMS (ESI$^+$) m/z: calcd for [$C_{15}H_{18}O_2F$], 249.1285; found 249.1288.

2-cyclohexyl-5-methoxychroman-4-one(3n)



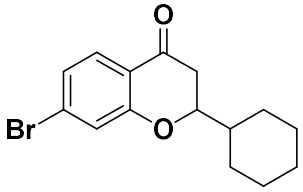
As a white solid. (58%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (t, *J* = 8.4 Hz, 1H), 6.59 – 6.53 (m, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 4.13 (ddd, *J* = 12.3, 6.3, 3.2 Hz, 1H), 3.90 (s, 3H), 2.75 – 2.57 (m, 2H), 1.97 (d, *J* = 12.8 Hz, 1H), 1.83 – 1.65 (m, 5H), 1.32 – 1.05 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.83, 163.50, 160.61, 135.69, 111.44, 110.02, 103.43, 81.37, 56.15, 41.73, 41.60, 28.34, 28.09, 26.33, 25.92, 25.86. HRMS (ESI$^+$) m/z: calcd for [$C_{16}H_{21}O_3$], 261.1485; found 261.1490.

2-cyclohexyl-7-methoxychroman-4-one(3o)



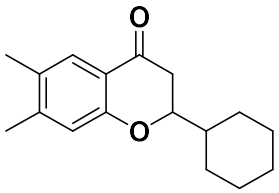
As a colorless oil. (70%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.8 Hz, 1H), 6.55 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.41 (d, *J* = 2.4 Hz, 1H), 4.19 (ddd, *J* = 12.5, 6.0, 3.3 Hz, 1H), 3.83 (s, 3H), 2.73 – 2.54 (m, 2H), 2.00 – 1.92 (m, 1H), 1.85 – 1.66 (m, 5H), 1.33 – 1.07 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.84, 166.13, 164.01, 128.72, 115.11, 109.88, 100.75, 82.52, 55.72, 41.96, 40.05, 28.46, 28.36, 26.48, 26.10, 26.04. HRMS (ESI$^+$) m/z: calcd for [$C_{16}H_{21}O_3$], 261.1485; found 261.1485.

7-bromo-2-cyclohexylchroman-4-one(3p)



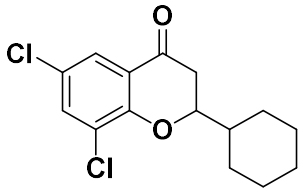
As a white solid. (75%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.18 (t, *J* = 1.5 Hz, 1H), 7.12 (dt, *J* = 8.4, 1.5 Hz, 1H), 4.20 (ddd, *J* = 11.7, 5.9, 3.8 Hz, 1H), 2.76 – 2.60 (m, 2H), 2.00 – 1.92 (m, 1H), 1.83 – 1.67 (m, 5H), 1.33 – 1.09 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.24, 162.20, 130.38, 128.25, 124.80, 121.26, 120.05, 82.62, 41.81, 40.20, 28.33, 28.29, 26.40, 26.04, 25.96. HRMS (EI) m/z: calcd for [$C_{15}H_{17}O_2Br$], 308.0406; found 308.0403.

2-cyclohexyl-6,7-dimethylchroman-4-one(3q)



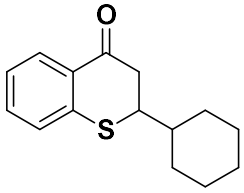
As a white solid. (73%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (s, 1H), 6.76 (s, 1H), 4.13 (ddd, *J* = 12.3, 6.0, 3.4 Hz, 1H), 2.77 – 2.56 (m, 2H), 2.25 (s, 3H), 2.20 (s, 3H), 2.04 – 1.94 (m, 1H), 1.85 – 1.65 (m, 5H), 1.38 – 1.07 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.20, 160.36, 146.46, 129.74, 126.93, 118.96, 118.48, 82.10, 41.92, 40.40, 28.45, 28.38, 26.48, 26.11, 26.04, 20.58, 18.87. HRMS (ESI^{+}) m/z: calcd for [$C_{17}H_{23}O_2$], 259.1693; found 259.1694.

6,8-dichloro-2-cyclohexylchroman-4-one(3r)



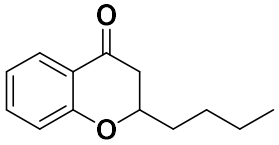
As a light yellow solid. (70%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 2.5 Hz, 1H), 7.52 (d, *J* = 2.5 Hz, 1H), 4.24 (td, *J* = 7.9, 6.5 Hz, 1H), 2.78 – 2.66 (m, 2H), 2.11 – 2.02 (m, 1H), 1.86 – 1.70 (m, 5H), 1.35 – 1.14 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.13, 156.15, 135.49, 126.31, 125.06, 124.25, 122.67, 83.21, 41.77, 40.06, 28.41, 28.40, 26.35, 25.97, 25.86. HRMS (EI) m/z: calcd for [$C_{15}H_{16}O_2Cl_2$], 298.0522; found 298.0522.

2-cyclohexylthiochroman-4-one(3s)



As a colorless oil. (35%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.41 – 7.33 (m, 1H), 7.27 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.15 (ddd, *J* = 8.1, 7.1, 1.3 Hz, 1H), 3.38 (ddd, *J* = 11.6, 6.5, 2.9 Hz, 1H), 3.03 (dd, *J* = 16.2, 2.9 Hz, 1H), 2.87 (dd, *J* = 16.2, 11.7 Hz, 1H), 1.95 – 1.83 (m, 2H), 1.82 – 1.73 (m, 2H), 1.71 – 1.57 (m, 2H), 1.31 – 1.07 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 195.45, 142.31, 133.47, 130.80, 128.96, 127.84, 124.83, 47.74, 43.87, 41.60, 30.47, 30.16, 26.30, 26.23. HRMS (EI) m/z: calcd for [$C_{15}H_{18}OS$], 246.1073; found 246.1064.

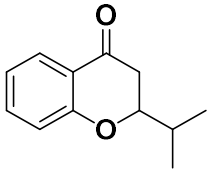
2-butylchroman-4-one(3t)



As a colorless oil. (31%)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.02 – 6.94 (m, 2H), 4.43 (qd, *J* = 7.7, 5.2 Hz, 1H), 2.70 – 2.66 (m, 2H), 1.89 (dddd, *J* = 13.8, 10.1, 7.4, 5.2 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.53 (dddd, *J* = 17.5, 7.3, 5.1, 2.0 Hz, 1H),

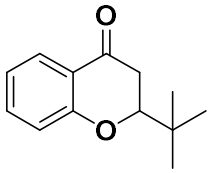
1.46 – 1.36 (m, 3H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.79, 161.83, 136.05, 127.06, 121.25, 121.16, 118.05, 78.08, 43.15, 34.79, 27.18, 22.63, 14.10. HRMS (ESI$^+$) m/z: calcd for [$C_{13}H_{17}O_2$], 205.1223; found 205.1228.

2-isopropylchroman-4-one(3u)



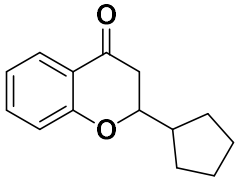
As a white solid. (65%)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 1H), 7.45 (ddd, *J* = 8.2, 7.3, 1.8 Hz, 1H), 6.98 (td, *J* = 8.4, 1.2 Hz, 2H), 4.18 (ddd, *J* = 12.7, 5.9, 3.4 Hz, 1H), 2.70 (dd, *J* = 16.6, 12.6 Hz, 1H), 2.64 (dd, *J* = 16.6, 3.4 Hz, 1H), 2.10 – 1.99 (m, 1H), 1.06 (dd, *J* = 16.9, 6.8 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.12, 162.01, 136.00, 127.00, 121.16, 121.08, 118.01, 82.63, 40.19, 32.27, 17.96, 17.93. HRMS (ESI$^+$) m/z: calcd for [$C_{12}H_{15}O_2$], 191.1067; found 191.1066.

2-(tert-butyl) chroman-4-one(3v)



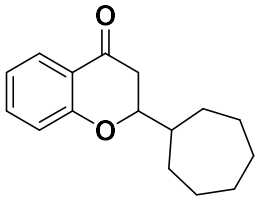
As a white solid. (91%)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.45 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.01 – 6.96 (m, 2H), 4.05 (dd, *J* = 13.0, 3.6 Hz, 1H), 2.73 – 2.59 (m, 2H), 1.06 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.58, 162.29, 135.96, 126.97, 121.12, 120.90, 117.99, 85.37, 38.57, 34.27, 25.60. HRMS (ESI$^+$) m/z: calcd for [$C_{13}H_{17}O_2$], 205.1223; found 205.1227.

2-cyclopentylchroman-4-one(3w)



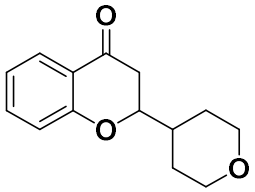
As a white solid. (55%)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.00 – 6.95 (m, 2H), 4.22 (ddd, *J* = 10.1, 7.7, 5.3 Hz, 1H), 2.74 – 2.66 (m, 2H), 2.23 (h, *J* = 8.1 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.78 (dtd, *J* = 9.0, 7.6, 4.0 Hz, 1H), 1.72 – 1.65 (m, 2H), 1.64 – 1.52 (m, 3H), 1.37 – 1.28 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.93, 161.95, 136.02, 127.00, 121.19, 121.15, 118.07, 81.83, 44.21, 42.30, 28.92, 28.53, 25.66, 25.54. HRMS (ESI$^+$) m/z: calcd for [$C_{14}H_{17}O_2$], 217.1223; found 217.1219.

2-cycloheptylchroman-4-one(3x)



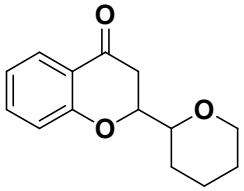
As a colorless oil. (50%)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.45 (ddd, *J* = 8.7, 7.1, 1.8 Hz, 1H), 7.00 – 6.92 (m, 2H), 4.28 (ddd, *J* = 13.4, 5.4, 2.7 Hz, 1H), 2.77 – 2.59 (m, 2H), 1.97 – 1.90 (m, 1H), 1.90 – 1.80 (m, 2H), 1.79 – 1.70 (m, 2H), 1.66 – 1.34 (m, 8H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.33, 162.12, 135.98, 127.02, 121.12, 121.10, 118.01, 82.40, 43.14, 39.99, 29.71, 29.32, 28.49, 28.48, 26.84, 26.68. HRMS (ESI^{+}) m/z: calcd for [$C_{16}H_{21}O_2$], 245.1536; found 245.1538.

2-(tetrahydro-2H-pyran-4-yl) chroman-4-one(3y)



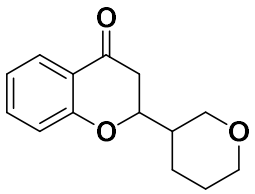
As a white solid. (66%)^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.00 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.22 (ddd, *J* = 11.2, 6.7, 4.3 Hz, 1H), 4.07 – 4.02 (m, 2H), 3.42 (tdd, *J* = 12.0, 7.8, 2.4 Hz, 2H), 2.74 – 2.66 (m, 2H), 1.98 (tdd, *J* = 10.7, 7.8, 5.3 Hz, 1H), 1.90 (ddq, *J* = 13.3, 4.1, 2.1 Hz, 1H), 1.63 – 1.50 (m, 3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.52, 161.61, 136.17, 127.05, 121.43, 121.10, 117.97, 81.19, 67.77, 67.58, 40.21, 39.35, 28.51, 28.21. HRMS (ESI^{+}) m/z: calcd for [$C_{14}H_{17}O_3$], 233.1172; found 233.1167.

2-(tetrahydro-2H-pyran-2-yl) chroman-4-one(3z)



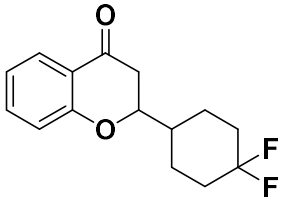
As a colorless oil. (89%, d.r ≈1:1)^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.85 (m, 1H), 7.48 – 7.43 (m, 1H), 7.05 – 6.97 (m, 2H), 4.39 – 4.31 (m, 1H), 4.12 – 4.04 (m, 1H), 3.63 (ddd, *J* = 11.3, 4.7, 2.2 Hz, 0.55H), 3.53 – 3.47 (m, 1.59H), 3.03 – 2.86 (m, 1H), 2.76 (dd, *J* = 17.0, 3.0 Hz, 0.55H), 2.60 (dd, *J* = 16.9, 2.8 Hz, 0.53H), 1.99 – 1.90 (m, 1H), 1.80 – 1.71 (m, 1H), 1.67 – 1.60 (m, 1.67H), 1.58 – 1.52 (m, 2H), 1.46 – 1.38 (m, 0.62H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.85, 192.66, 161.59, 161.49, 136.04, 136.02, 127.00, 126.93, 121.46, 121.45, 121.20, 121.10, 118.34, 118.16, 80.21, 79.76, 78.38, 78.27, 69.23, 68.90, 39.48, 38.70, 27.44, 27.11, 26.03, 25.95, 23.30, 23.14. HRMS (ESI^{+}) m/z: calcd for [$C_{14}H_{17}O_3$], 233.1172; found 233.1170.

2-(tetrahydro-2H-pyran-3-yl) chroman-4-one(3aa)



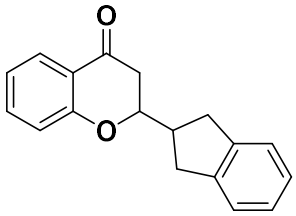
As a colorless oil. (42% d.r ≈1:1) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.06 – 6.92 (m, 2H), 4.37 – 4.24 (m, 1H), 4.23 – 4.17 (m, 0.48H), 3.97 – 3.86 (m, 1.52H), 3.50 – 3.38 (m, 2H), 2.81 – 2.58 (m, 2H), 2.12 – 1.97 (m, 1.51H), 1.91 – 1.82 (m, 0.55H), 1.71 – 1.58 (m, 2.58H), 1.46 – 1.34 (m, 0.55H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.39, 192.29, 161.67, 161.45, 136.21, 136.15, 127.12, 127.05, 121.54, 121.52, 121.13, 121.08, 118.05, 118.00, 79.09, 78.51, 69.80, 69.48, 68.62, 68.42, 40.59, 40.56, 40.17, 40.02, 25.42, 25.29, 25.18, 24.66. HRMS (ESI^{+}) m/z: calcd for [$C_{14}H_{17}O_3$], 233.1172; found 233.1172.

2-(4,4-difluorocyclohexyl) chroman-4-one(3ab)



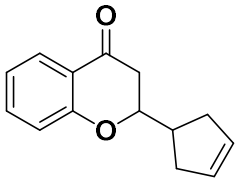
As a white solid. (52%)^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.48 (ddd, *J* = 8.7, 7.3, 1.8 Hz, 1H), 7.05 – 6.91 (m, 2H), 4.27 (ddd, *J* = 11.9, 6.1, 3.8 Hz, 1H), 2.80 – 2.63 (m, 2H), 2.27 – 2.13 (m, 2H), 2.09 (dq, *J* = 13.3, 3.4 Hz, 1H), 1.90 – 1.66 (m, 4H), 1.62 – 1.45 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.36, 161.59, 136.22, 127.10, 123.22 (dd, *J* = 242.4, 239.5 Hz), 121.54, 121.05, 117.97, 80.66 (d, *J* = 2.5 Hz), 40.08 (d, *J* = 1.6 Hz), 33.36 (dd, *J* = 25.7, 7.6 Hz), 33.20 (dd, *J* = 25.7, 7.5 Hz), 24.48 (dd, *J* = 19.1, 9.8 Hz). ^{19}F NMR (471 MHz, Chloroform-*d*) δ -91.79 (d, *J* = 236.6 Hz), -102.58 (dt, *J* = 236.3, 33.3 Hz). HRMS (ESI^{+}) m/z: calcd for [$C_{15}H_{17}O_2F_2$], 267.1191; found 267.1192.

2-(2,3-dihydro-1H-inden-2-yl) chroman-4-one (3ac)



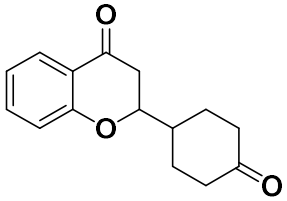
As a white solid. (35%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.84 (m, 1H), 7.54 – 7.44 (m, 1H), 7.24 (dd, *J* = 9.6, 5.0 Hz, 2H), 7.20 – 7.15 (m, 2H), 7.02 (td, *J* = 7.6, 1.3 Hz, 2H), 4.47 (q, *J* = 7.5 Hz, 1H), 3.23 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.13 – 3.02 (m, 2H), 2.96 – 2.86 (m, 2H), 2.78 – 2.74 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.48, 161.75, 142.43, 142.06, 136.16, 127.10, 126.71, 126.63, 124.69, 124.57, 121.43, 121.15, 118.07, 80.77, 43.96, 41.89, 35.51, 34.87. HRMS (EI) m/z: calcd for [$C_{18}H_{16}O_2$], 264.1145; found 264.1155.

2-(cyclopent-3-en-1-yl) chroman-4-one(3ad)



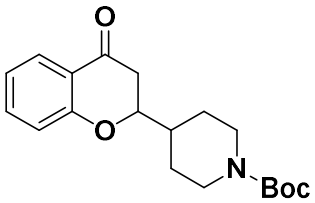
As a white solid. (38%)^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.46 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.02 – 6.96 (m, 2H), 5.75 – 5.67 (m, 2H), 4.34 (dt, *J* = 8.9, 7.2 Hz, 1H), 2.74 – 2.67 (m, 3H), 2.64 – 2.57 (m, 1H), 2.55 – 2.47 (m, 1H), 2.47 – 2.40 (m, 1H), 2.30 – 2.21 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.78, 161.90, 136.06, 129.99, 129.40, 127.05, 121.29, 121.17, 118.08, 81.09, 41.84, 41.67, 35.13, 34.61. HRMS (ESI^{+}) m/z: calcd for [$C_{14}H_{15}O_2$], 215.1067; found 215.1063.

2-(4-oxocyclohexyl) chroman-4-one(3ae)



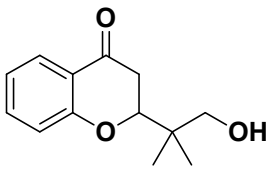
As a white solid.(50%)^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.51 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 7.04 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.37 (ddd, *J* = 12.9, 6.1, 3.0 Hz, 1H), 2.84 – 2.70 (m, 2H), 2.55 – 2.48 (m, 2H), 2.48 – 2.40 (m, 2H), 2.39 – 2.34 (m, 1H), 2.26 – 2.18 (m, 1H), 2.18 – 2.13 (m, 1H), 1.79 – 1.68 (m, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 210.77, 192.24, 161.51, 136.25, 127.09, 121.60, 120.99, 117.94, 80.48, 40.66, 40.35, 40.33, 40.16, 28.08, 27.69. HRMS (ESI^{-}) m/z: calcd for [$C_{15}H_{15}O_3$], 243.1027; found 243.1021.

tert-butyl 4-(4-oxochroman-2-yl) piperidine-1-carboxylate(3af)



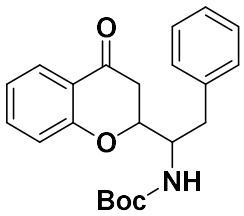
As a colorless oil. (76%)^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.00 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.0 Hz, 1H), 4.31 – 4.09 (m, 3H), 2.77 – 2.64 (m, 4H), 1.96 (d, *J* = 13.2 Hz, 1H), 1.87 (tdd, *J* = 11.9, 6.6, 3.4 Hz, 1H), 1.70 (d, *J* = 13.4 Hz, 1H), 1.46 (s, 9H), 1.36 (dtd, *J* = 16.9, 12.5, 11.2, 4.3 Hz, 2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 192.53, 161.64, 154.86, 136.20, 127.08, 121.47, 121.09, 117.98, 81.06, 79.69, 40.46, 40.37, 28.59, 27.58, 27.50. HRMS (ESI^{+}) m/z: calcd for [$C_{19}H_{25}O_4NNa$], 354.1676; found 354.1685.

2-(1-hydroxy-2-methylpropan-2-yl) chroman-4-one(3ag)



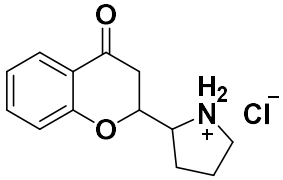
As a colorless oil. (51%) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.5, 5.0, 1.7 Hz, 1H), 7.04 – 6.95 (m, 2H), 4.39 (dd, *J* = 14.2, 2.6 Hz, 1H), 3.71 (dd, *J* = 10.8, 4.6 Hz, 1H), 3.55 (dd, *J* = 11.6, 3.5 Hz, 1H), 2.84 – 2.62 (m, 2H), 1.94 – 1.86 (m, 1H), 1.07 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.14, 161.79, 136.09, 127.16, 121.57, 121.04, 117.95, 82.74, 69.63, 38.87, 38.43, 21.14, 19.45. HRMS (ESI^{+}) m/z: calcd for [$C_{13}H_{17}O_3$], 221.1172; found 221.1166.

tert-butyl (1-(4-oxochroman-2-yl)-2-phenylethyl) carbamate(3ah)



As a white solid. (93%, d.r ≈1:0.9) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 7.8, 1.8 Hz, 0.44H), 7.86 (dd, *J* = 7.9, 1.7 Hz, 0.52H), 7.53 – 7.49 (m, 1H), 7.32 – 7.26 (m, 2H), 7.26 – 7.17 (m, 3H), 7.08 – 7.01 (m, 2H), 4.93 (d, *J* = 10.0 Hz, 0.41H), 4.62 (d, *J* = 9.7 Hz, 0.42H), 4.42 – 4.34 (m, 1H), 4.22 (s, 0.41H), 4.05 (dtd, *J* = 9.8, 7.9, 1.7 Hz, 0.46H), 3.14 – 2.98 (m, 2H), 2.94 (dd, *J* = 17.0, 14.2 Hz, 0.54H), 2.84 – 2.70 (m, 1H), 2.50 (dd, *J* = 17.0, 2.6 Hz, 0.5H), 1.42 (s, 4H), 1.37 (s, 5H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.35, 191.82, 161.22, 161.08, 155.58, 155.30, 137.44, 137.00, 136.21, 136.14, 129.62, 129.47, 128.80, 128.76, 127.27, 127.22, 126.85, 121.87, 121.84, 121.24, 121.16, 117.99, 117.77, 80.03, 78.84, 54.43, 53.84, 40.47, 40.23, 38.47, 36.17, 28.46, 28.40. HRMS (ESI^{+}) m/z: calcd for [$C_{22}H_{25}O_4NNa$], 390.1676; found 390.1669.

2-(4-oxochroman-2-yl)pyrrolidin-1-ium chloride (deprotection of 3ai)



As a pink solid. (d.r ≈1:1)^{1}H NMR (500 MHz, Methanol-d_4) δ 7.94 – 7.80 (m, 1H), 7.64 – 7.54 (m, 1H), 7.19 – 7.07 (m, 2H), 4.99 – 4.91 (m, 0.52H), 4.79 – 4.67 (m, 0.55H), 4.06 – 3.92 (m, 1H), 3.49 – 3.38 (m, 2H), 2.99 – 2.75 (m, 2H), 2.33 – 2.05 (m, 4H), 2.00 – 1.83 (m, 1H).^{13}C NMR (126 MHz, Methanol-d_4) δ 192.09, 191.80, 161.99, 161.71, 137.70, 137.63, 127.86, 123.46, 123.40, 122.18, 122.10, 119.23, 119.15, 78.38, 76.85, 63.92, 62.87, 47.52, 46.86, 41.17, 40.48, 27.42, 25.25, 25.11, 24.88. HRMS (ESI^{+}) m/z: calcd for [$C_{13}H_{16}O_2N$], 218.1176; found 218.1181.

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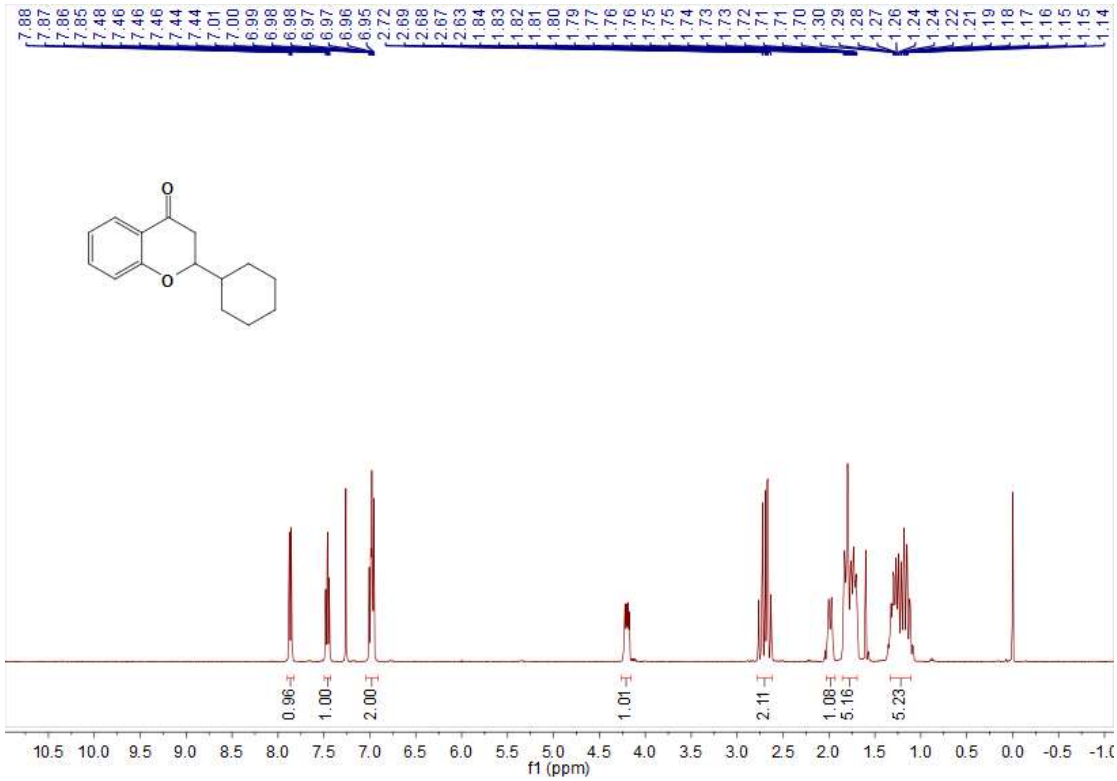
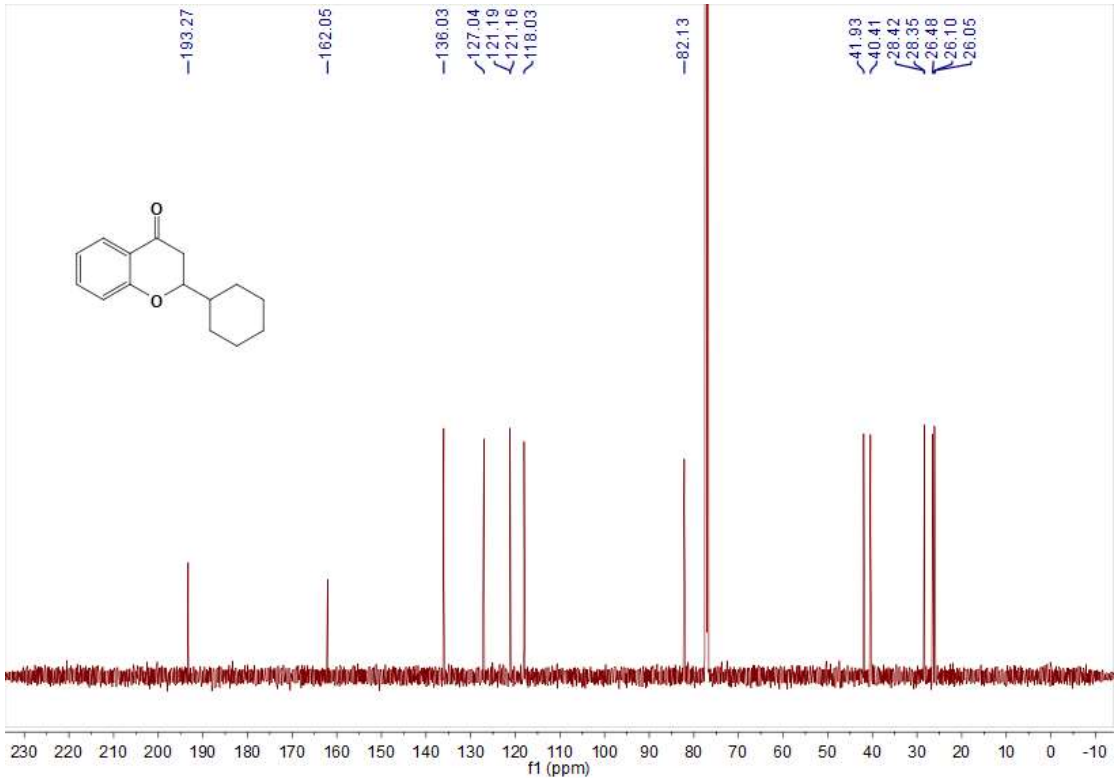
Copies of ^{1}H and ^{13}C NMR Spectra

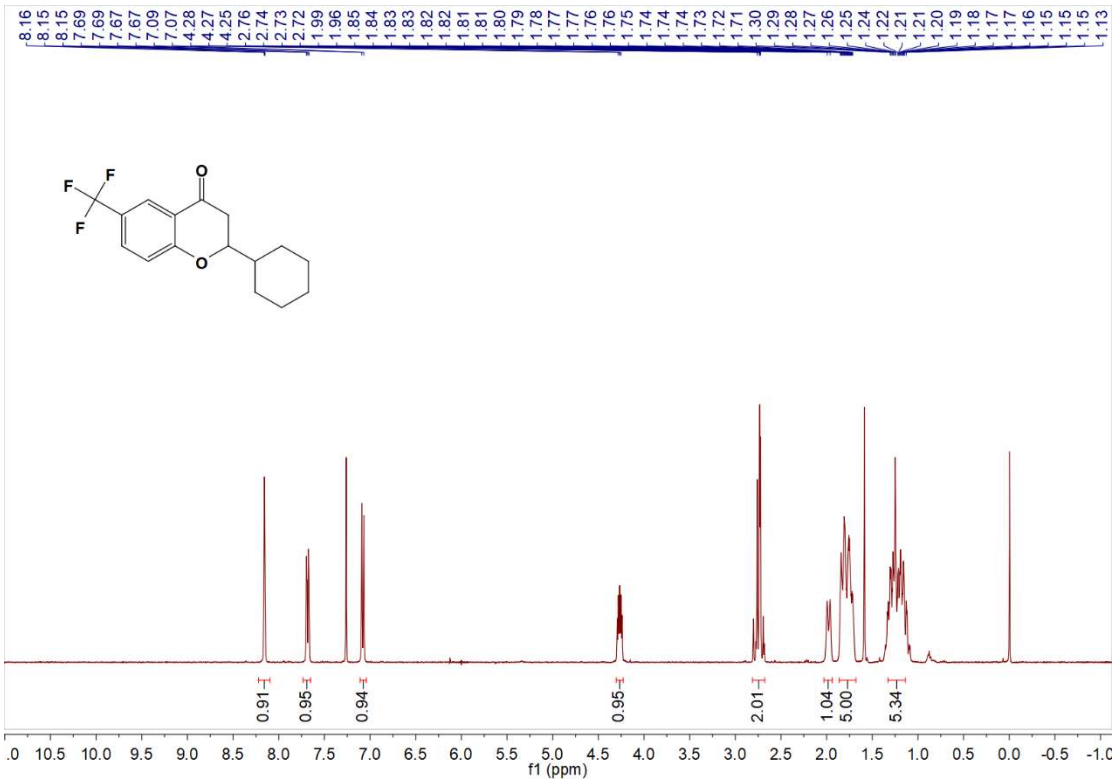
^{1}H NMR of compound 3a



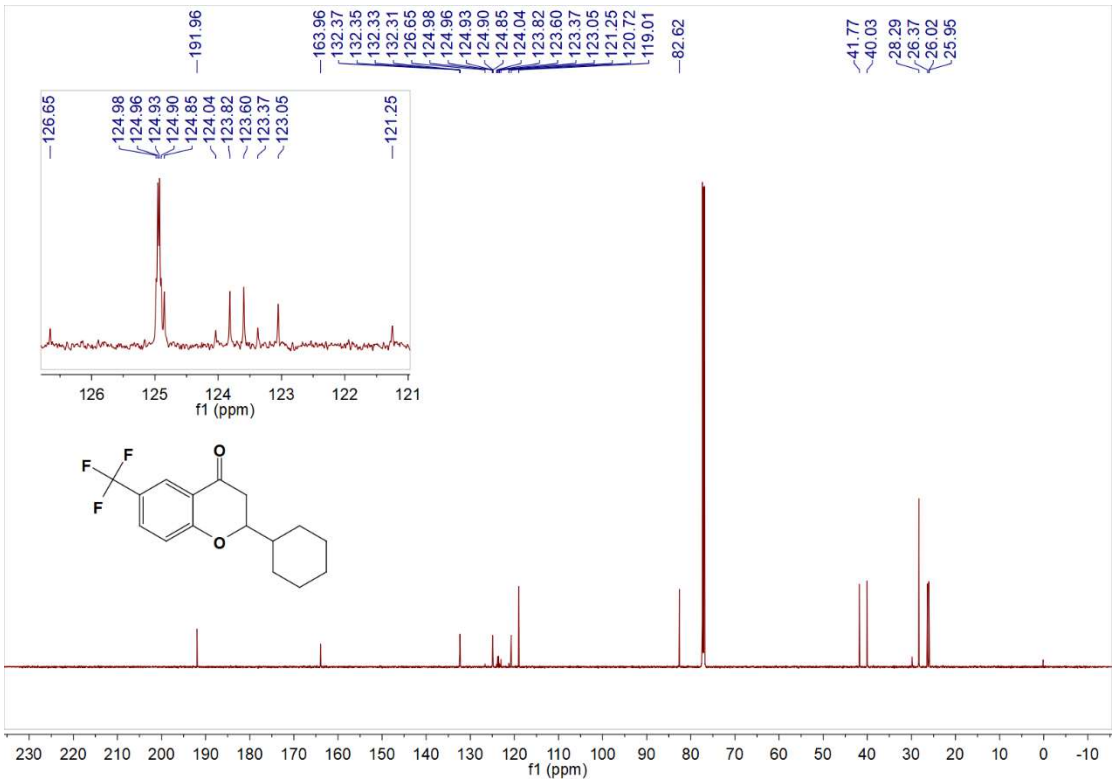
^{13}C NMR of compound 3a



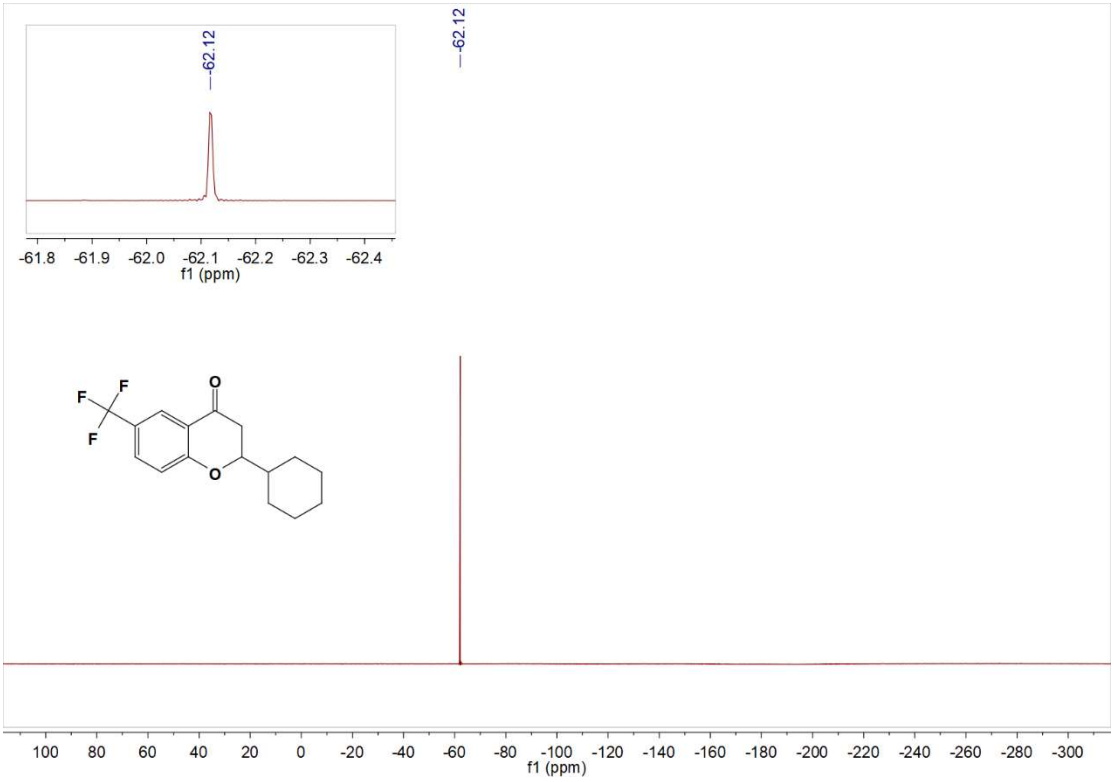
^{1}H NMR of compound 3b



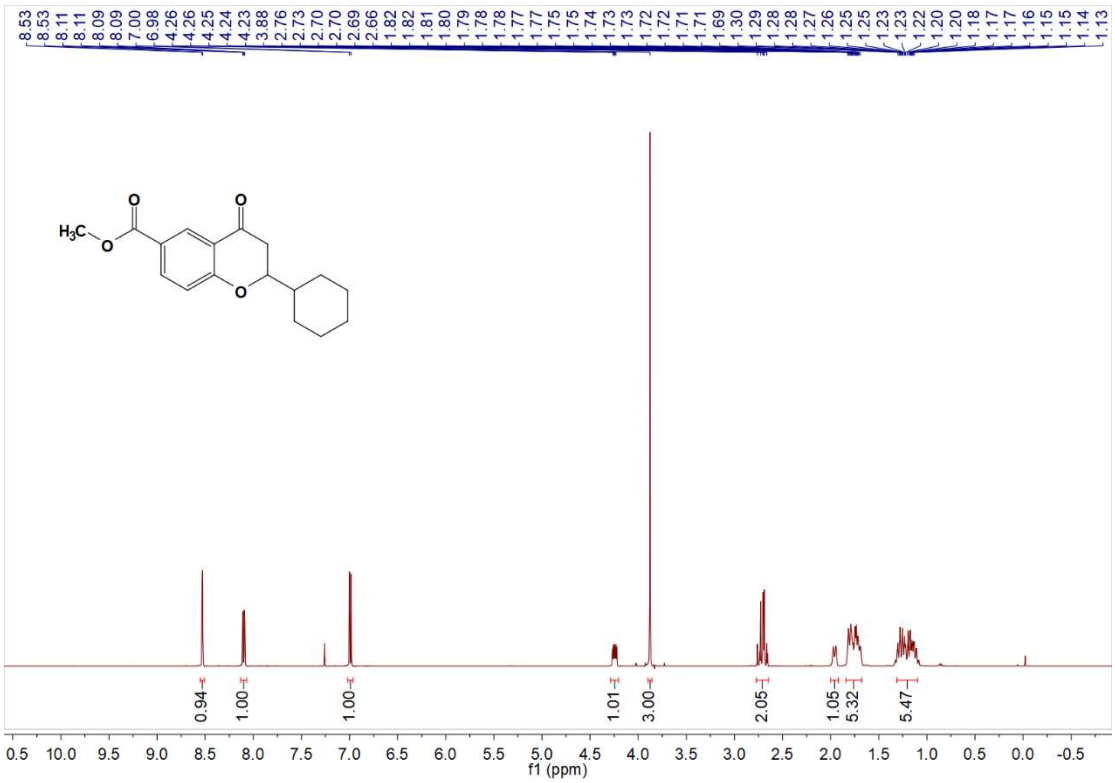
^{13}C NMR of compound 3b



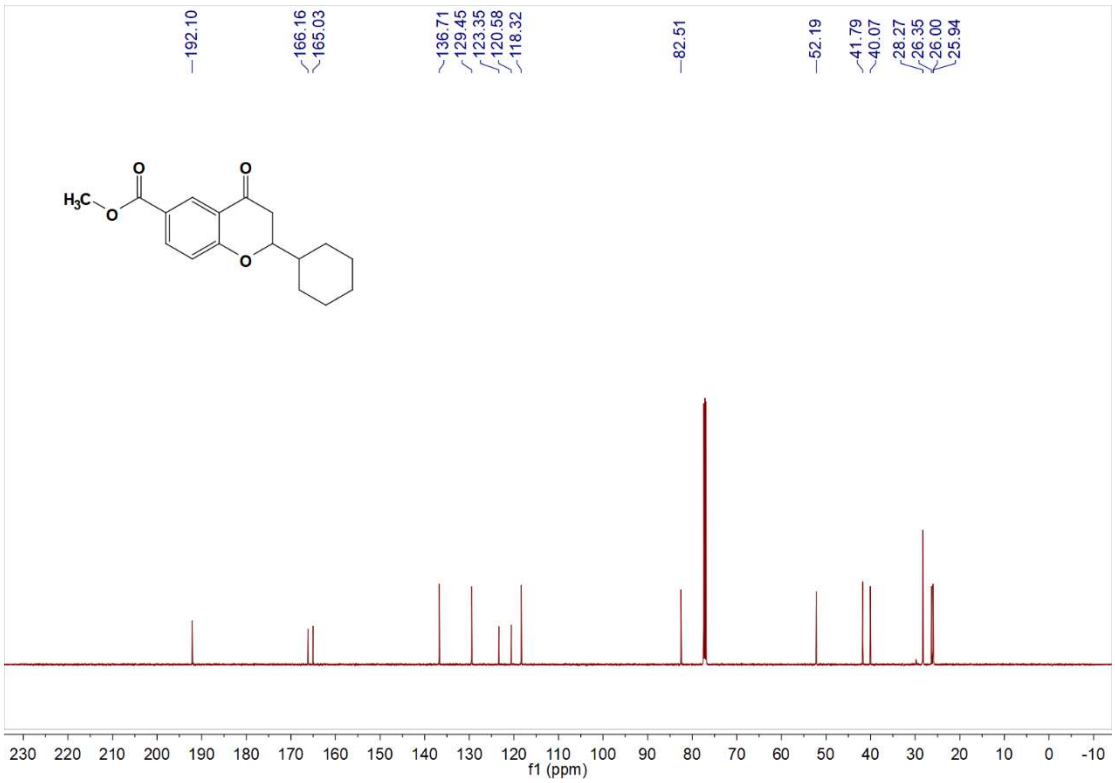
^{19}F NMR of compound 3b



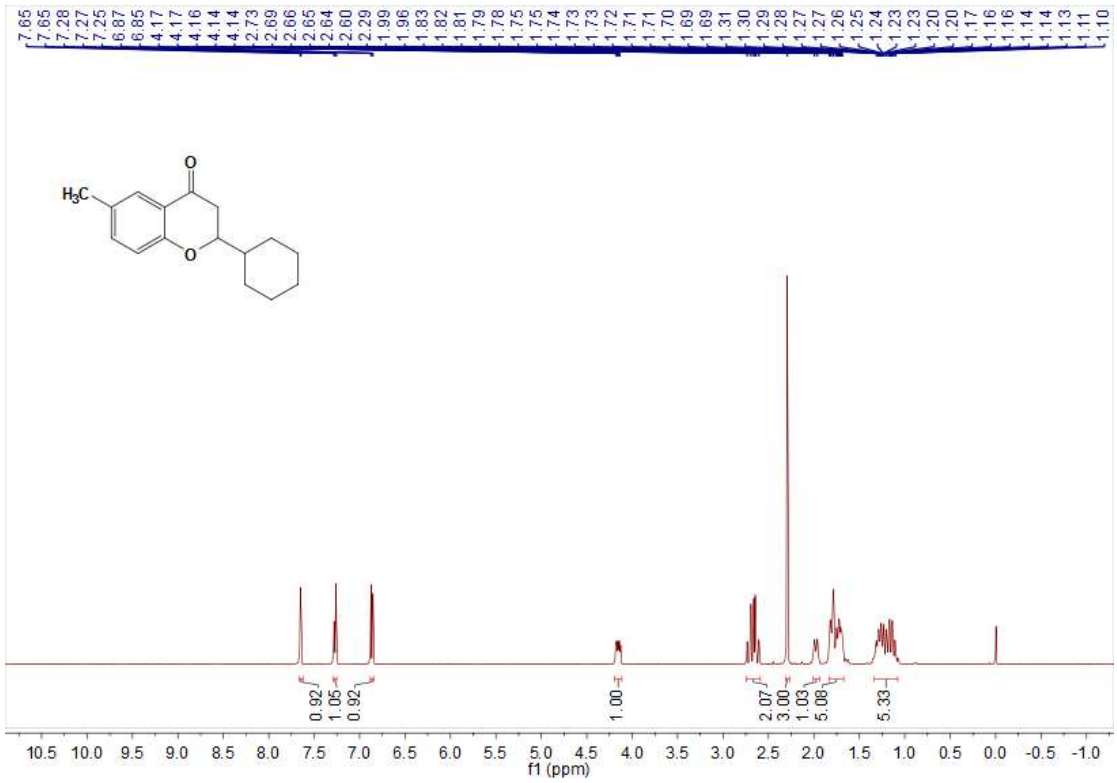
^{1}H NMR of compound 3c



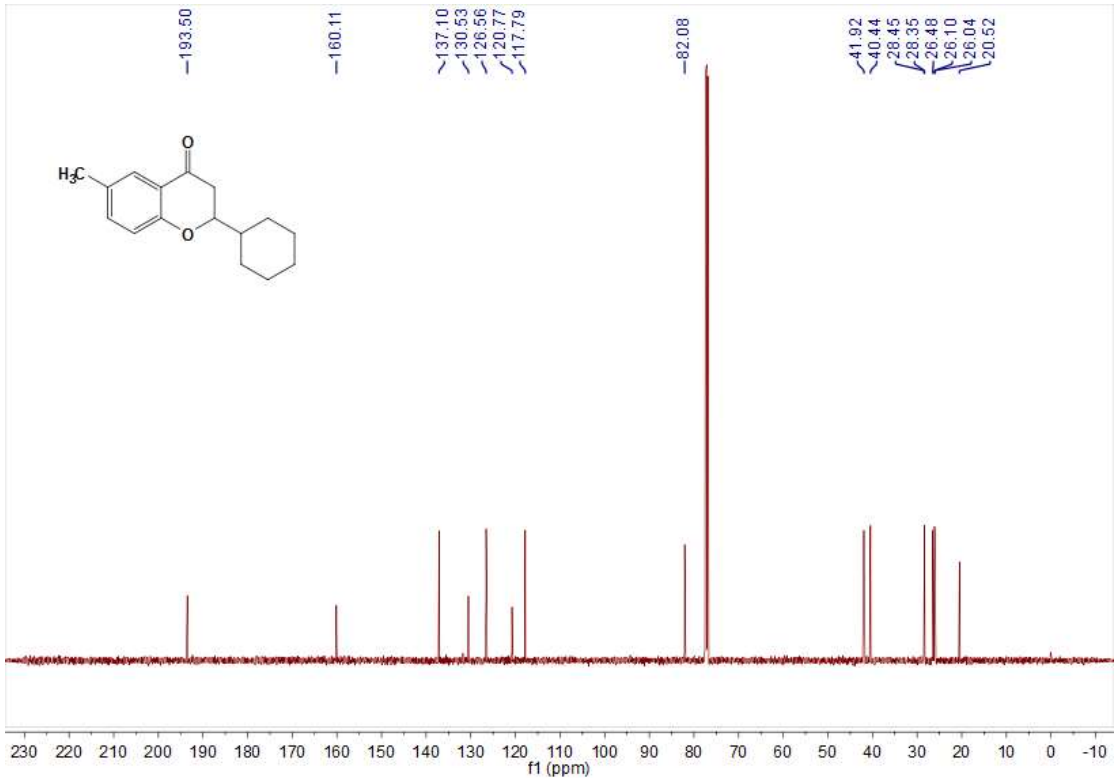
^{13}C NMR of compound 3c



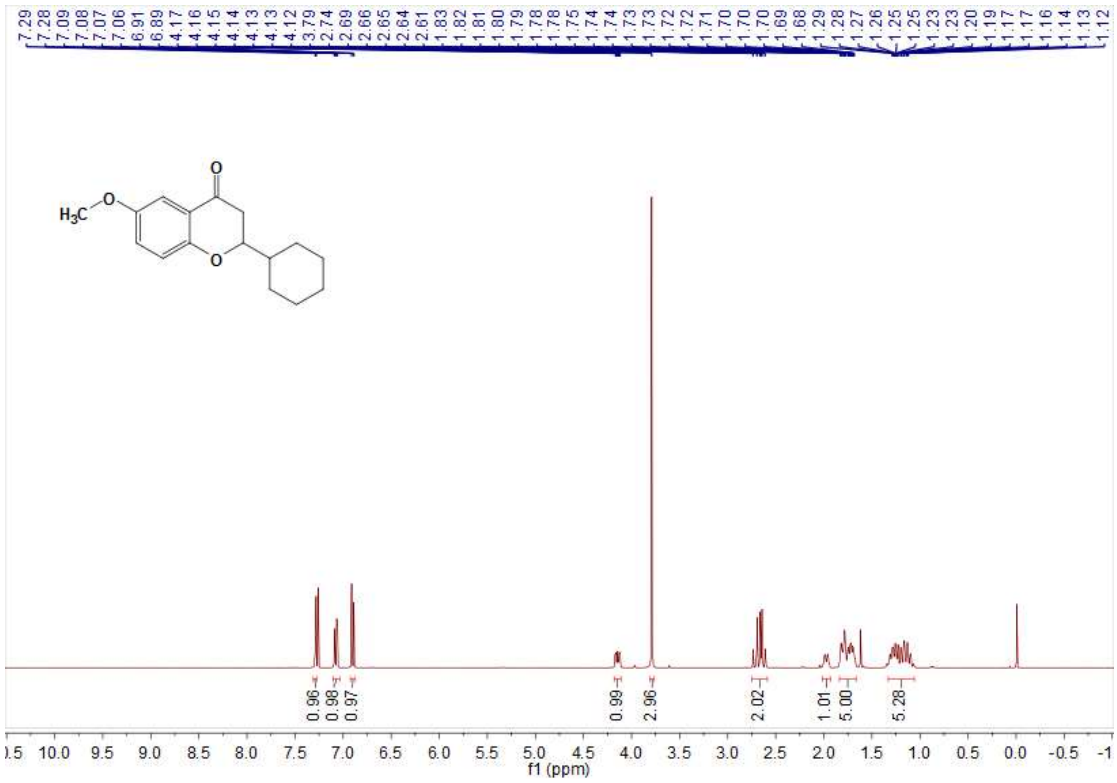
^{1}H NMR of compound 3d



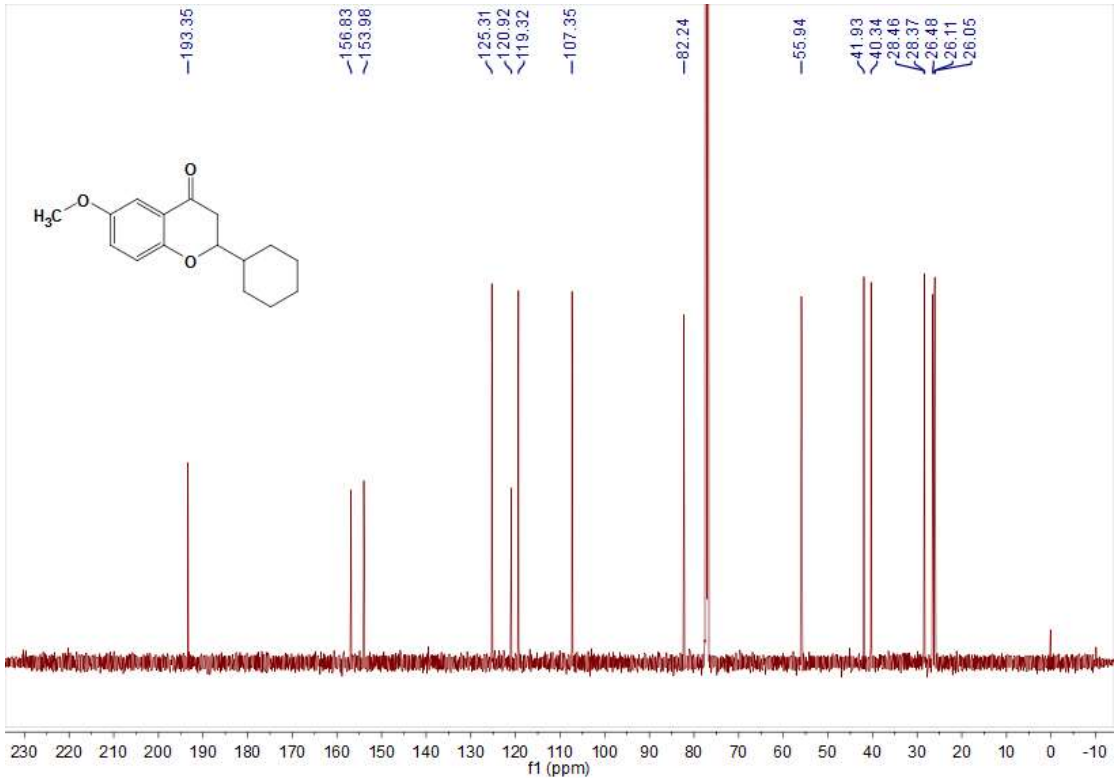
^{13}C NMR of compound 3d



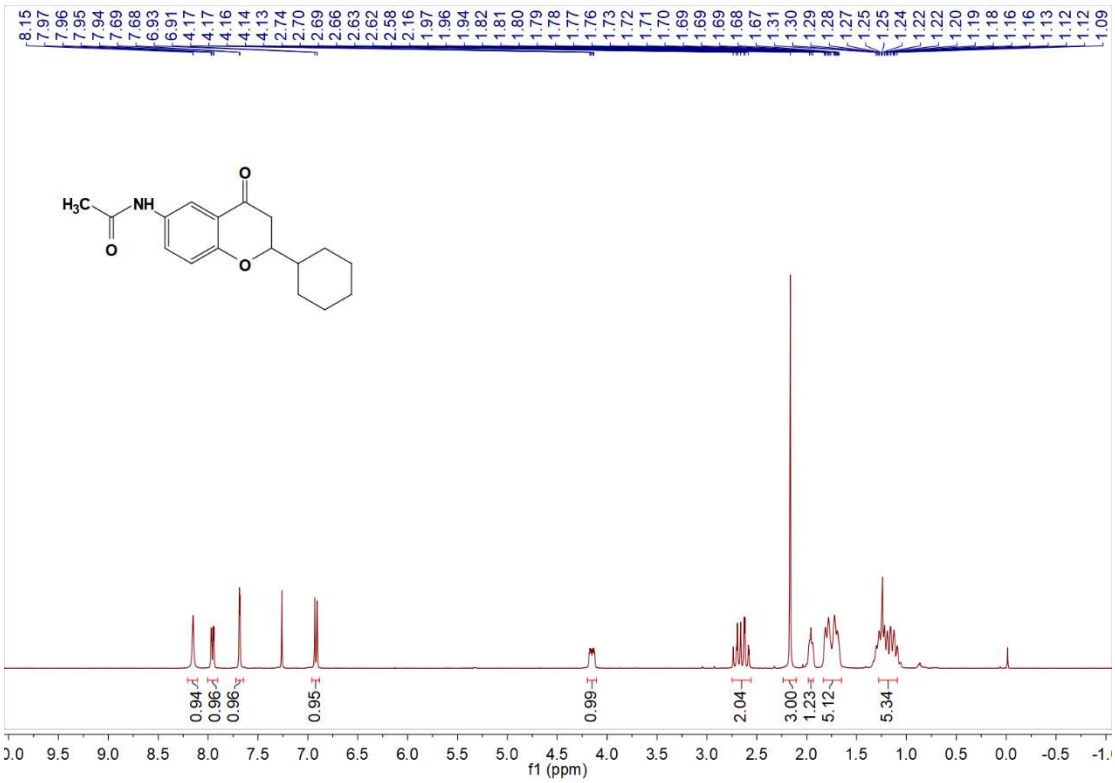
^{1}H NMR of compound 3e



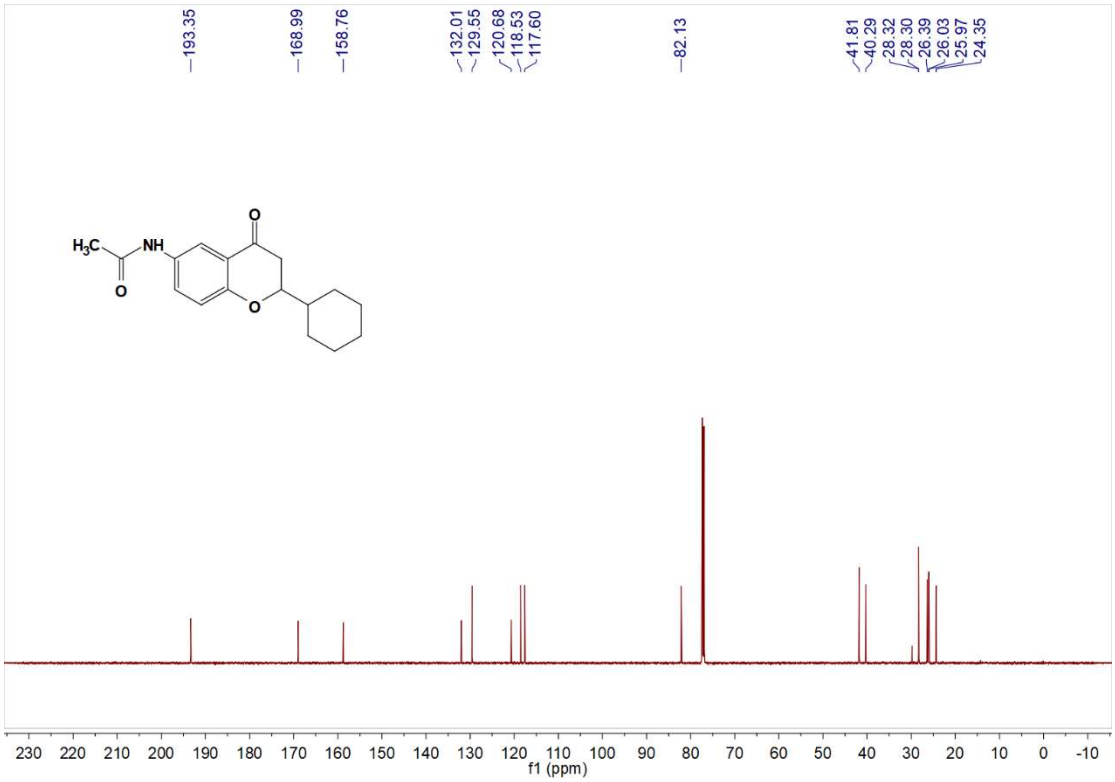
^{13}C NMR of compound 3e



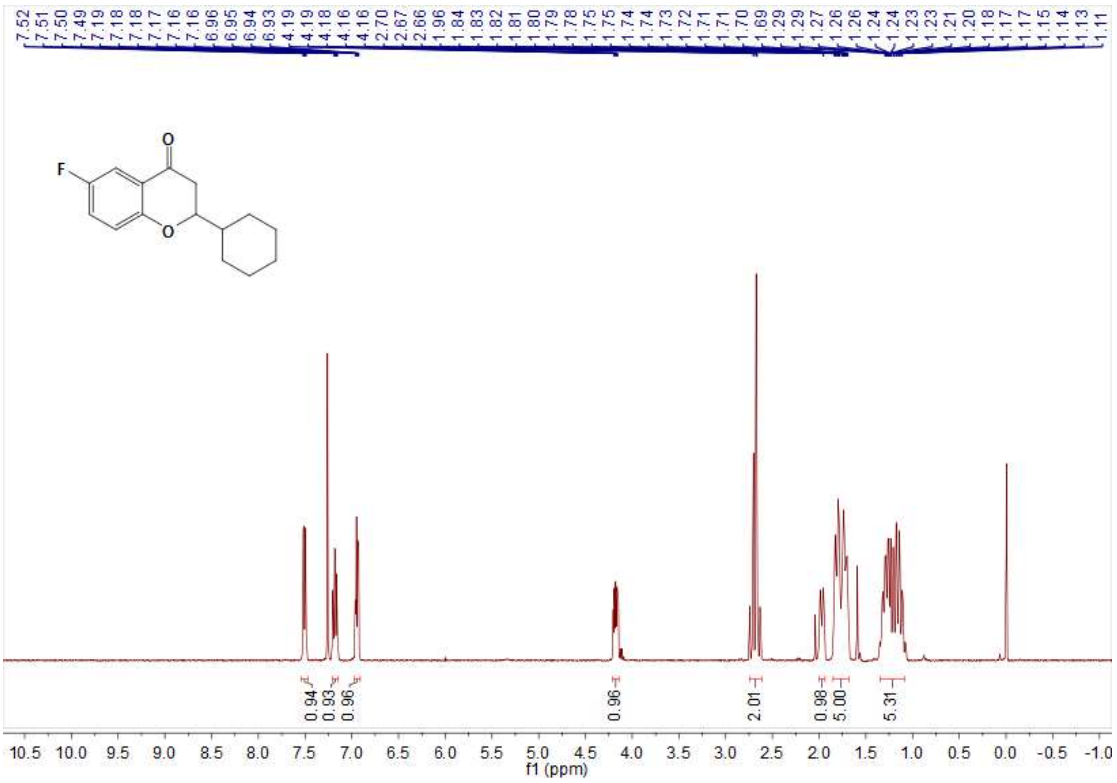
^{1}H NMR of compound 3f



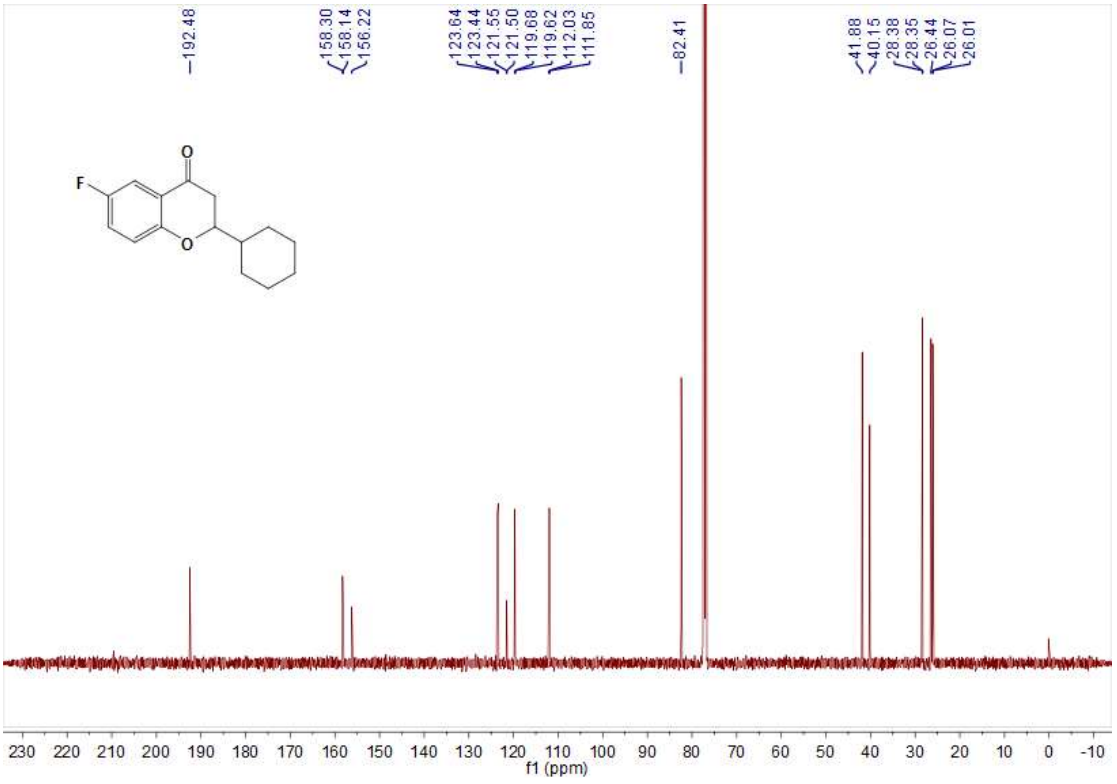
^{13}C NMR of compound 3f



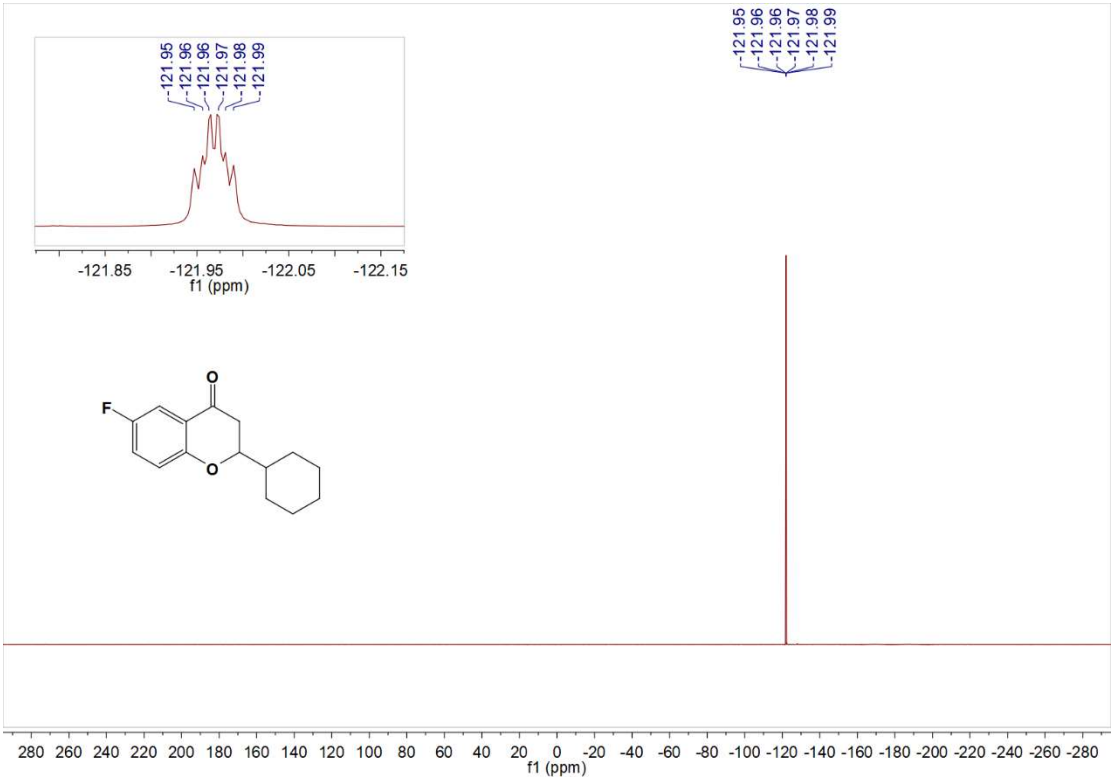
^{1}H NMR of compound 3g



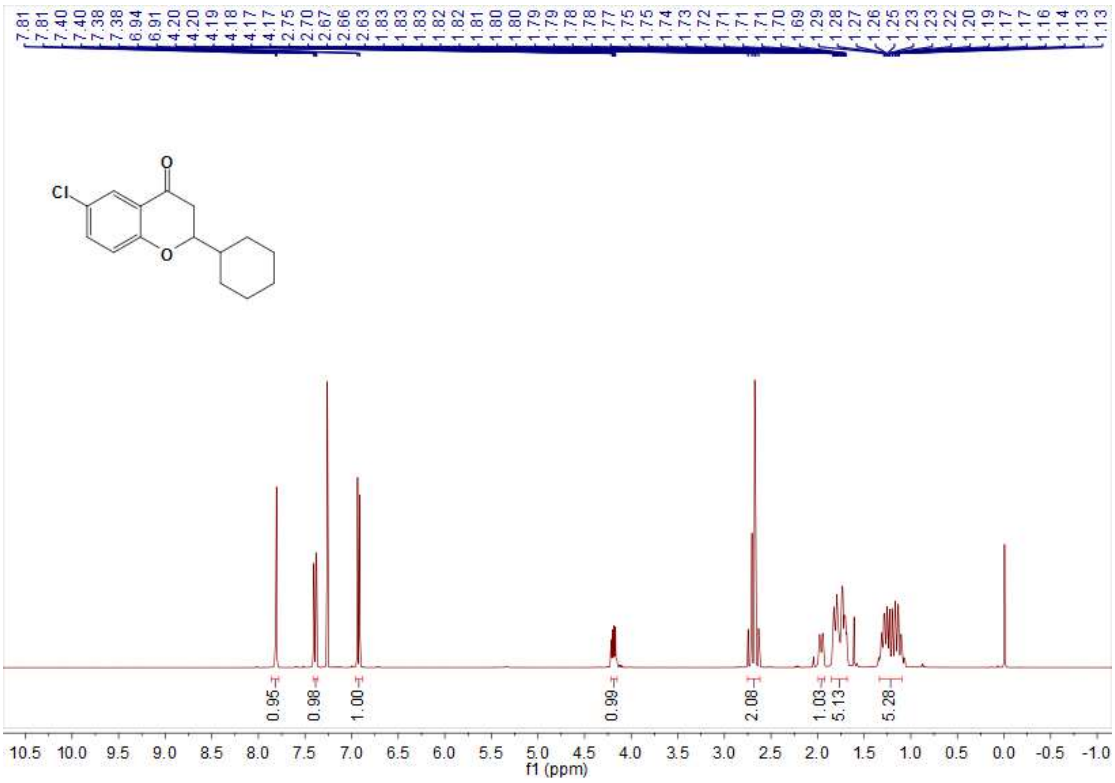
^{13}C NMR of compound 3g



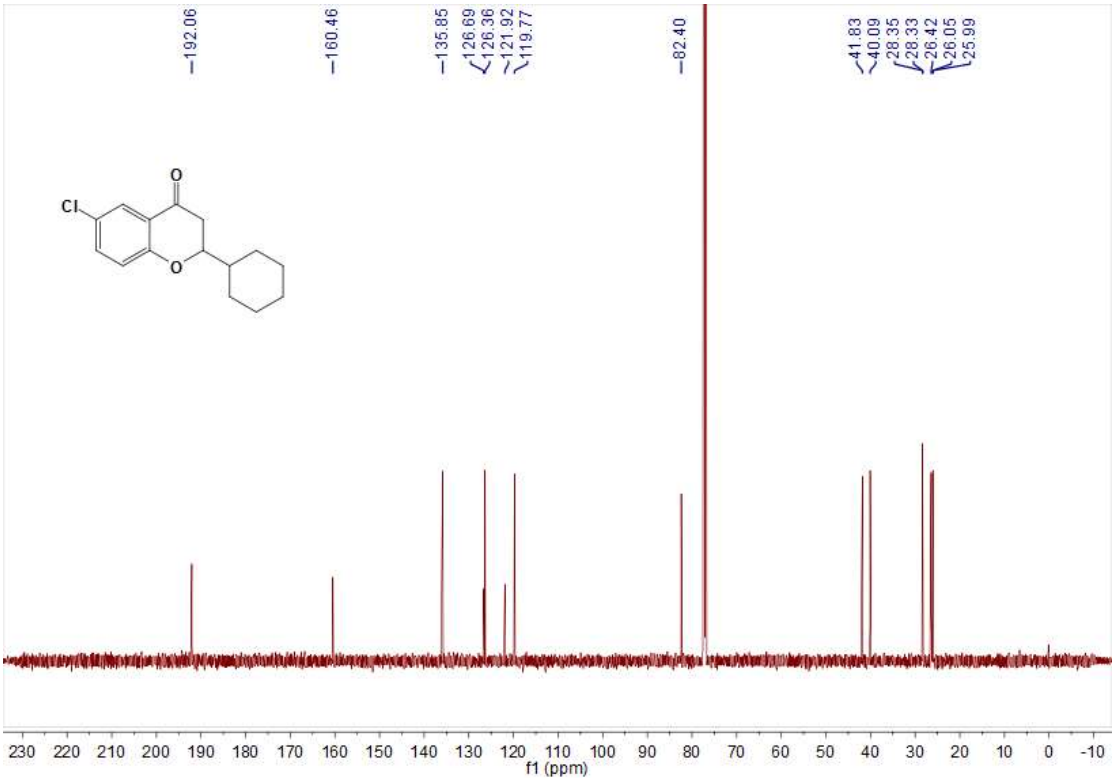
^{19}C NMR of compound 3g



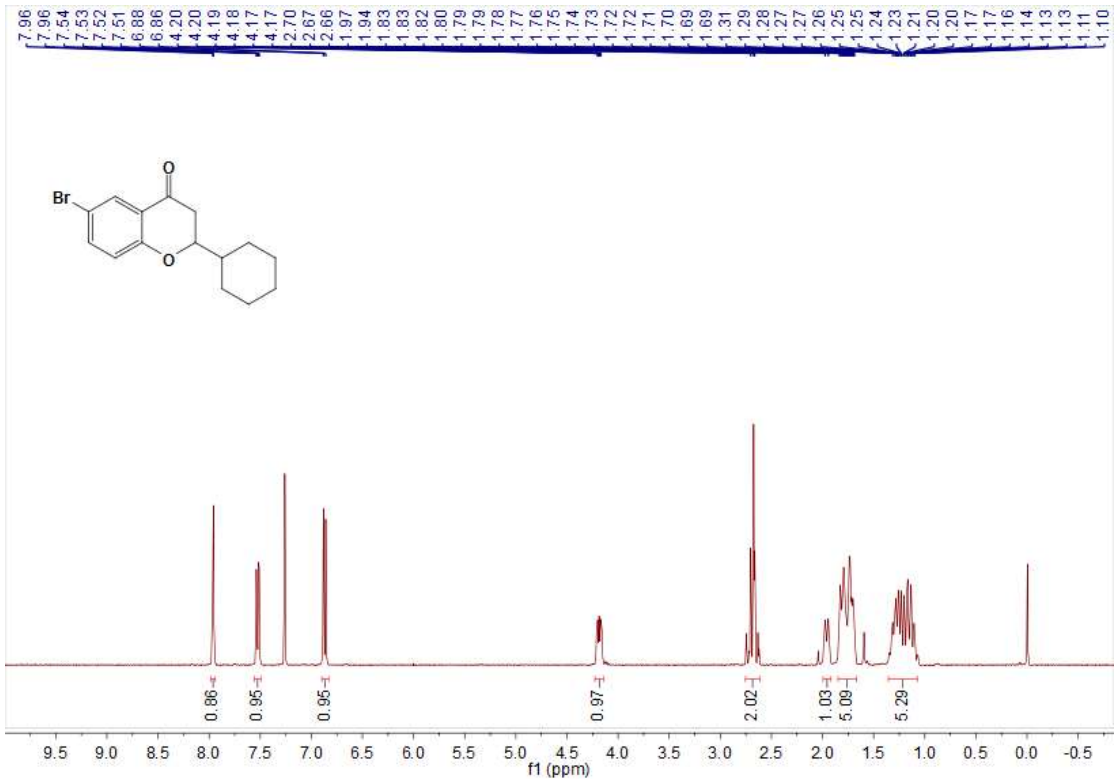
^{1}H NMR of compound 3h



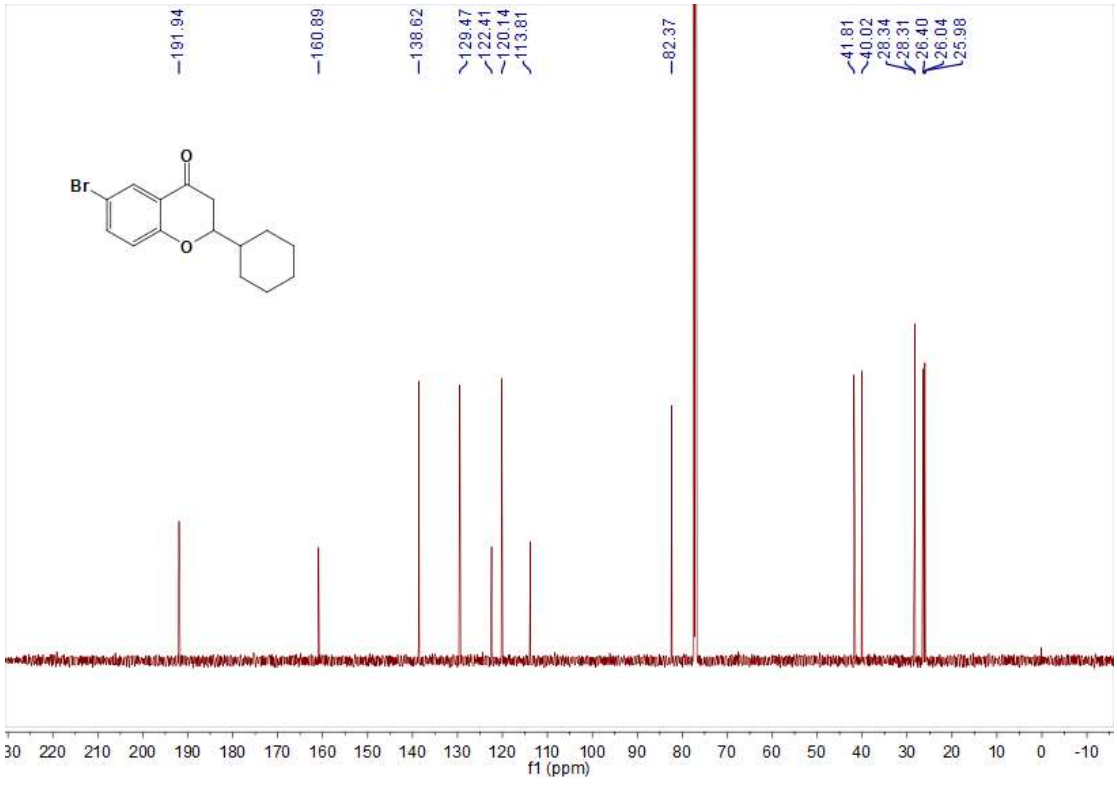
^{13}C NMR of compound 3h



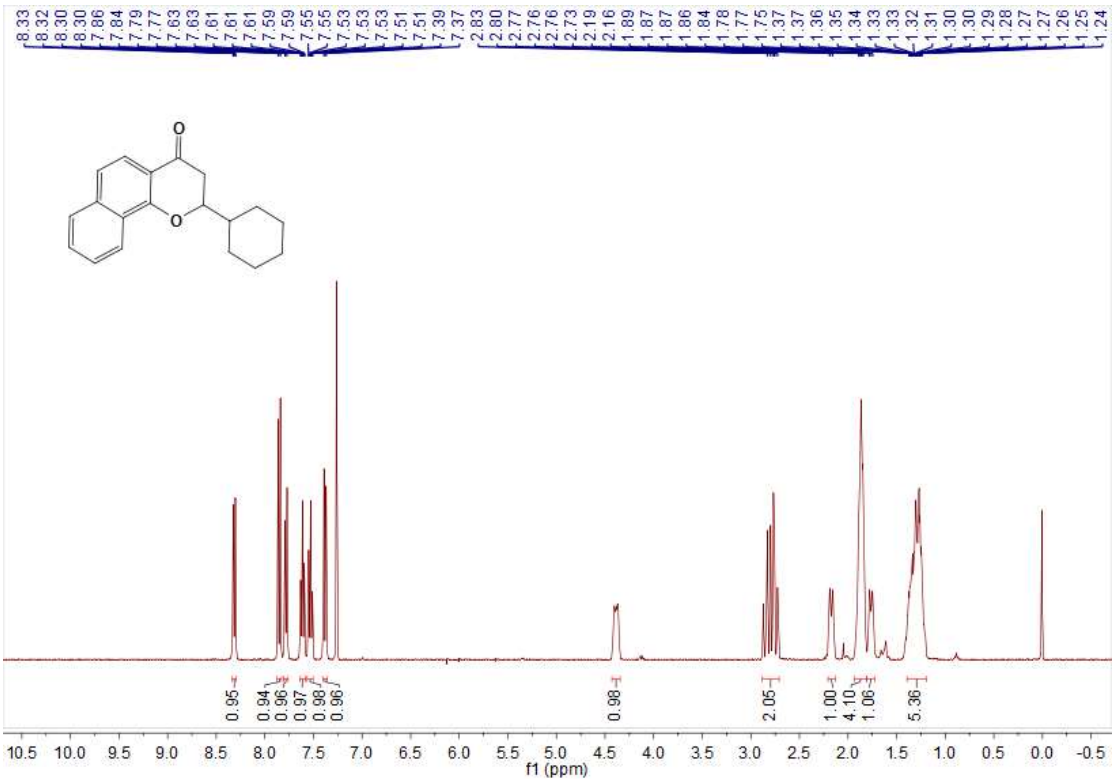
^{1}H NMR of compound 3i



^{13}C NMR of compound 3i



^{1}H NMR of compound 3j



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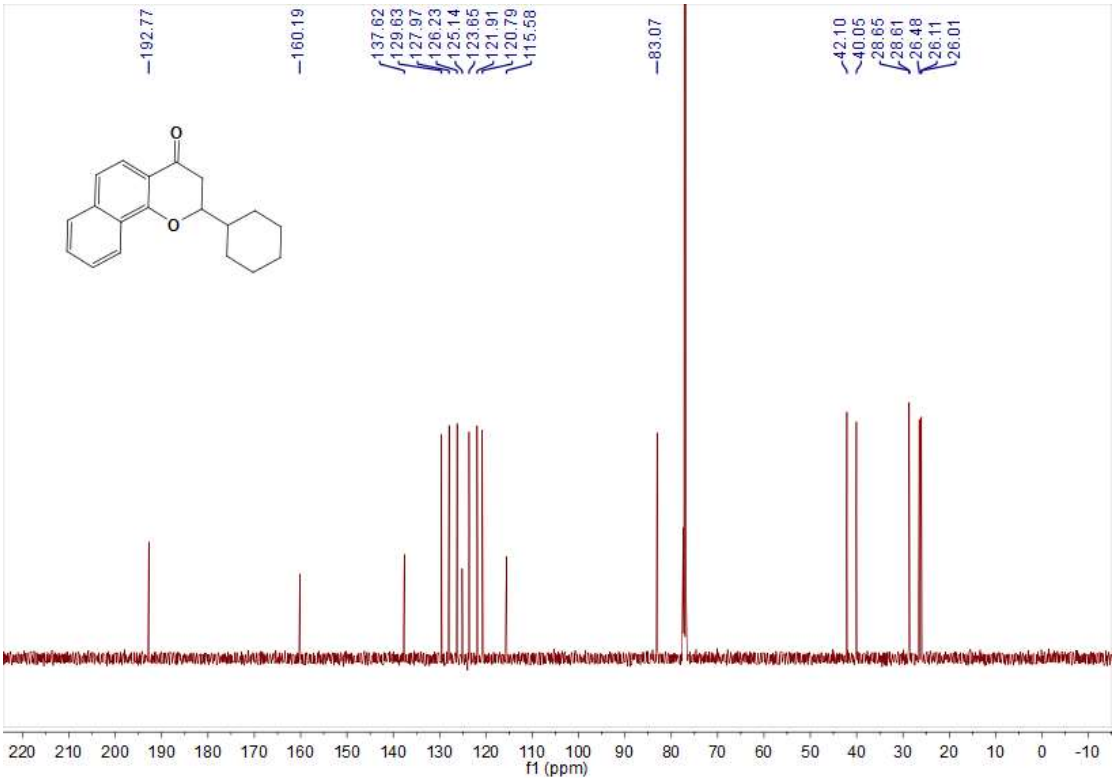
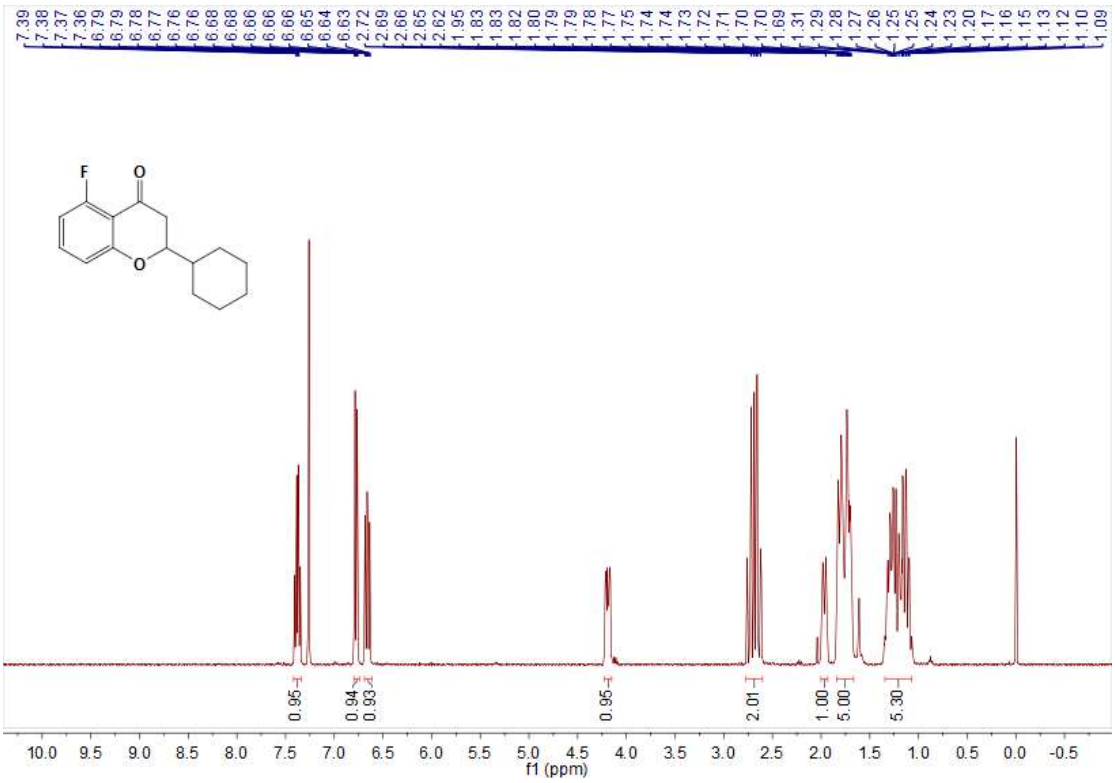
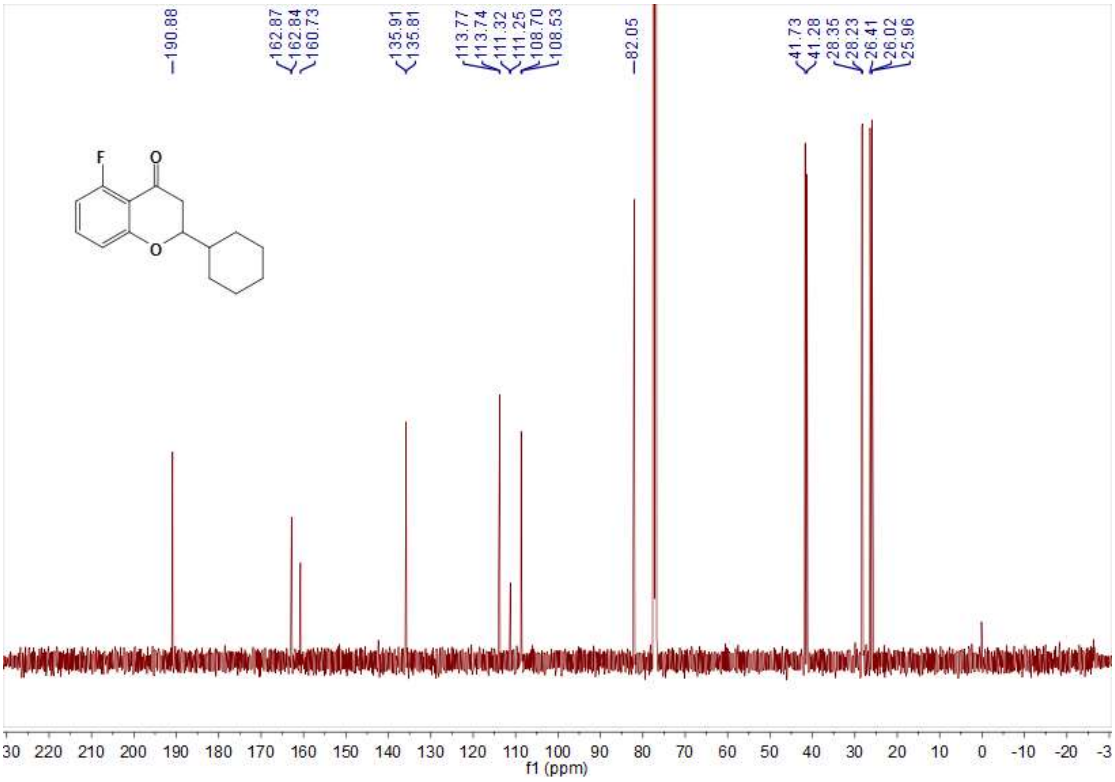


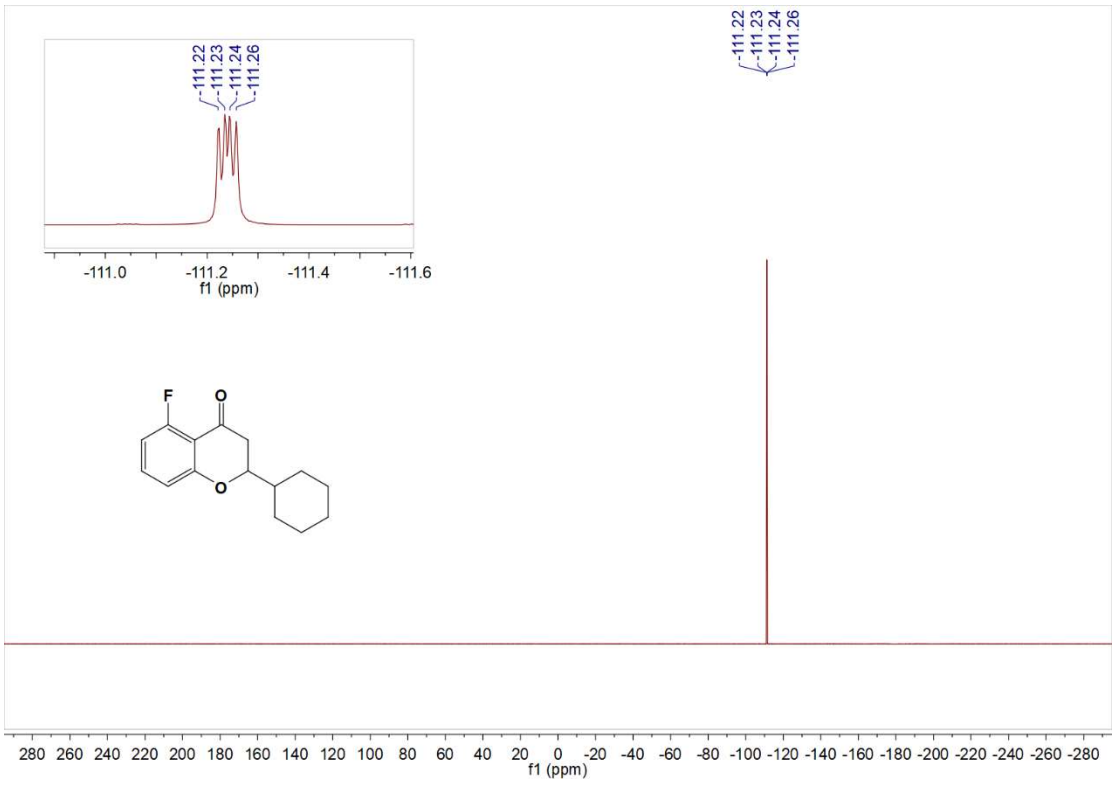
^{1}H NMR of compound 3k



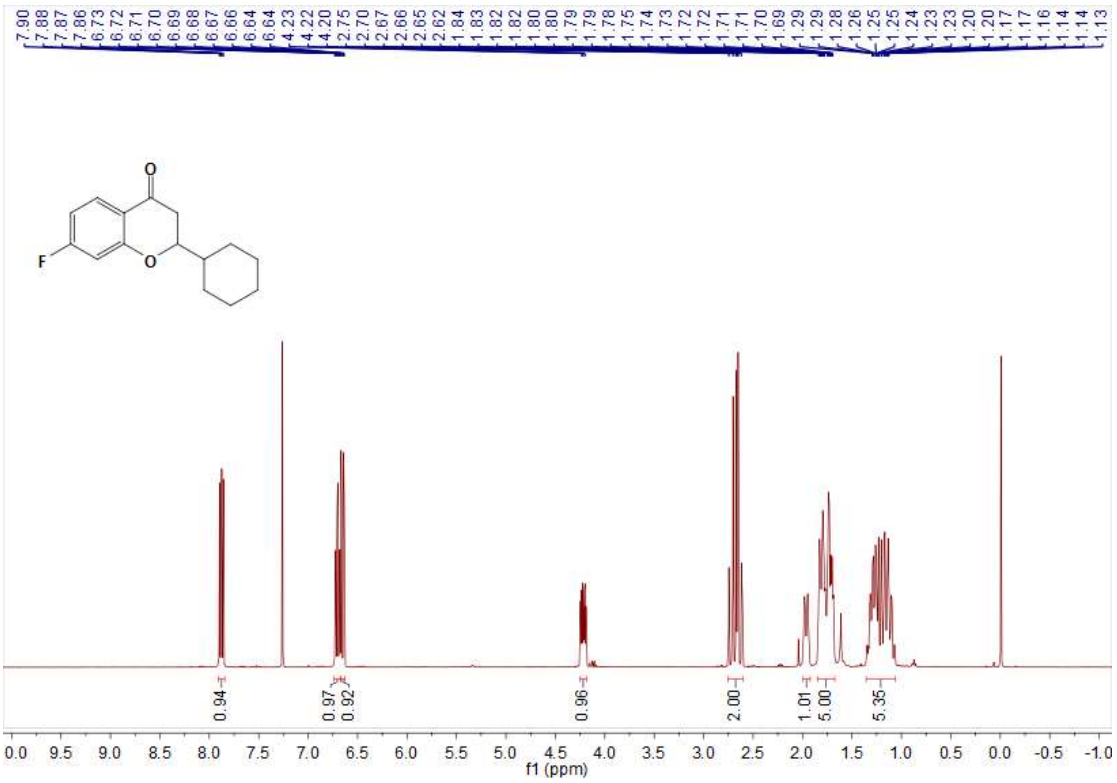
^{13}C NMR of compound 3k



^{19}F NMR of compound 3k



^{1}H NMR of compound 3l



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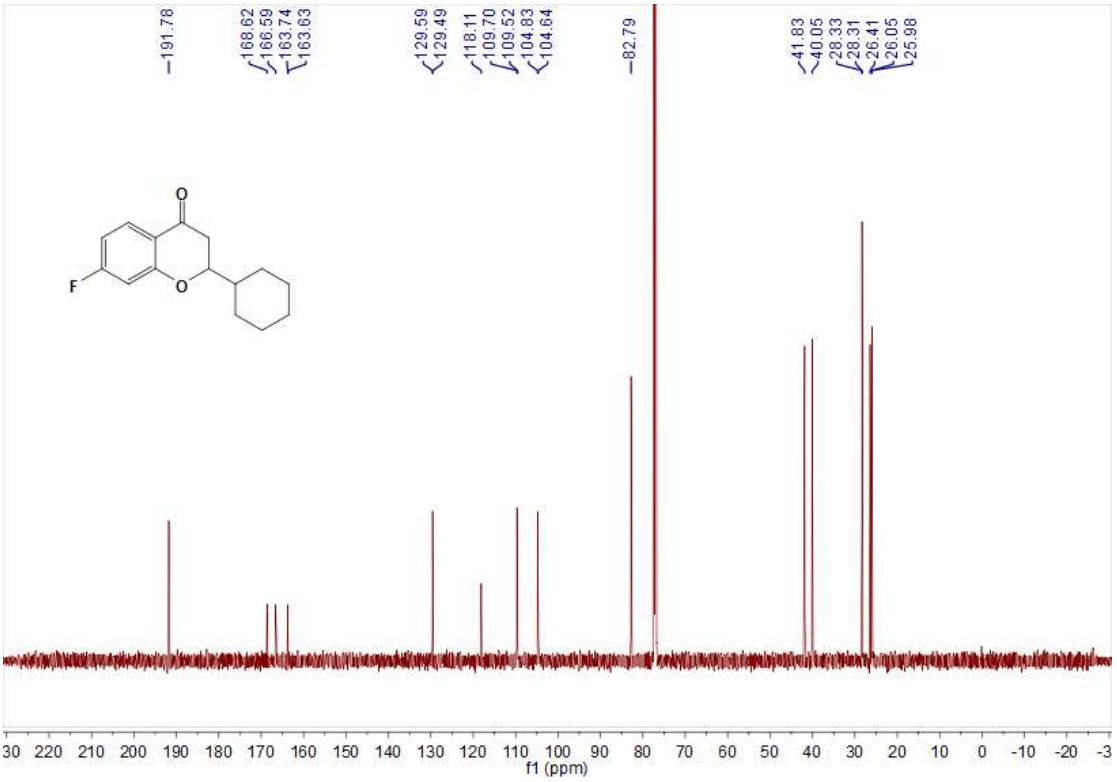

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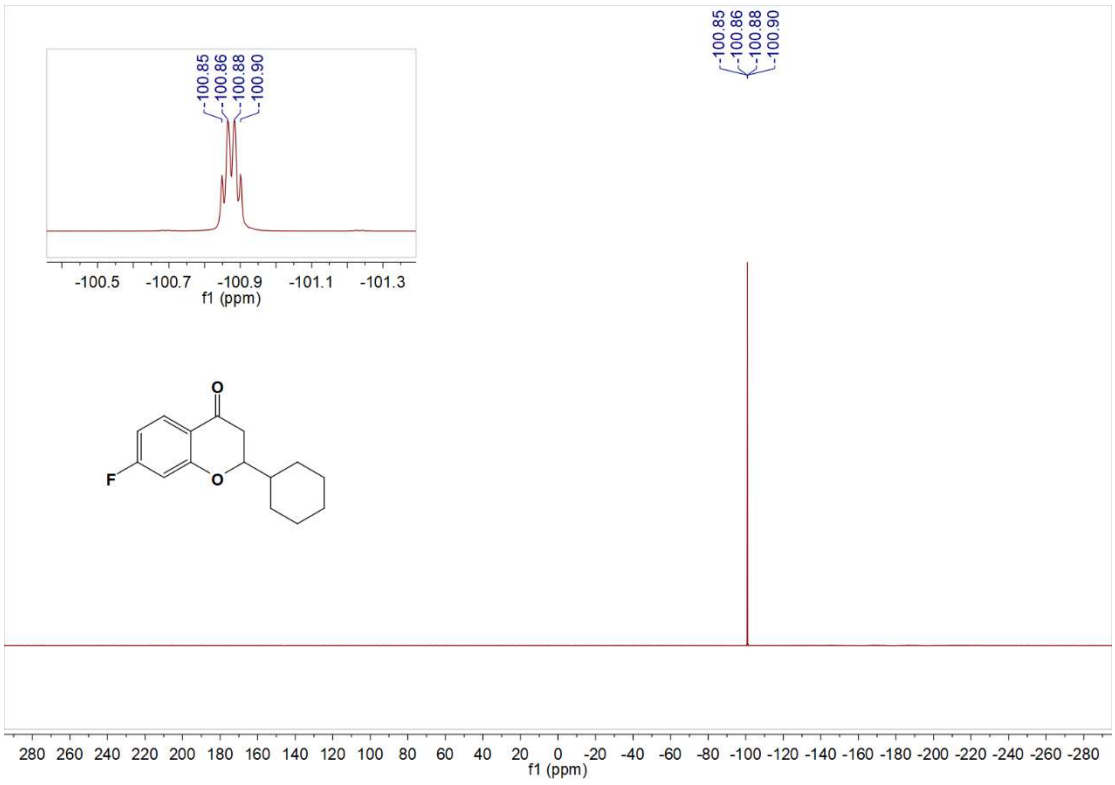
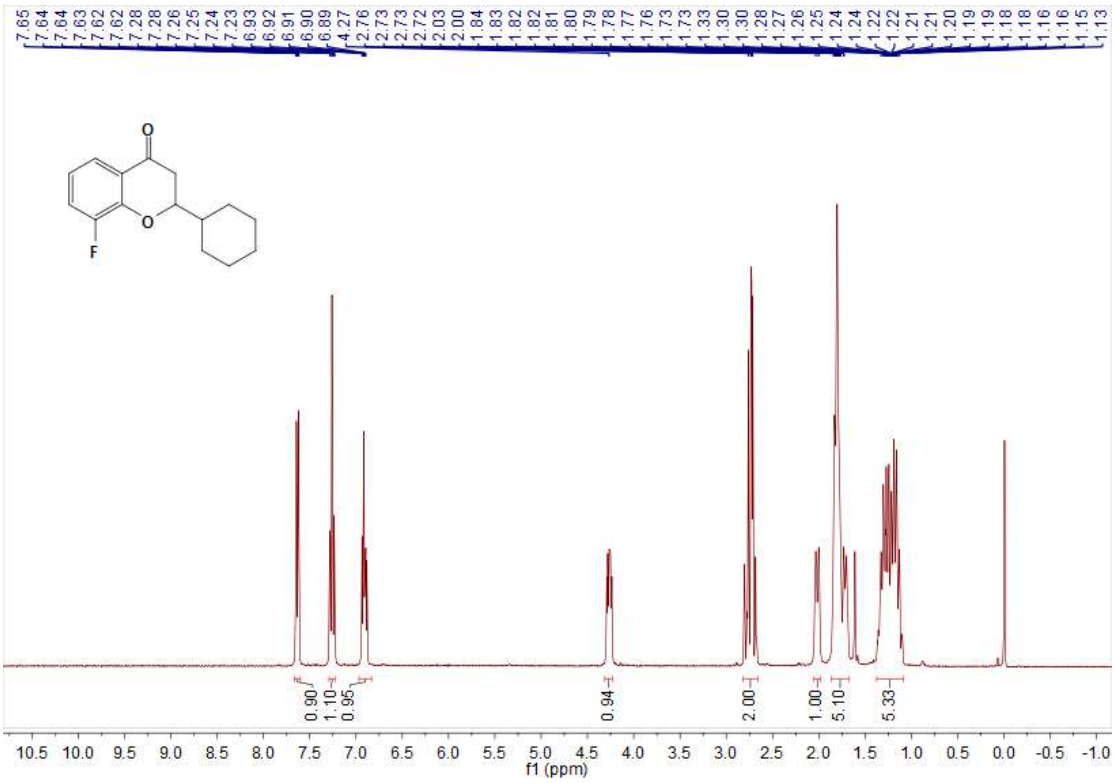
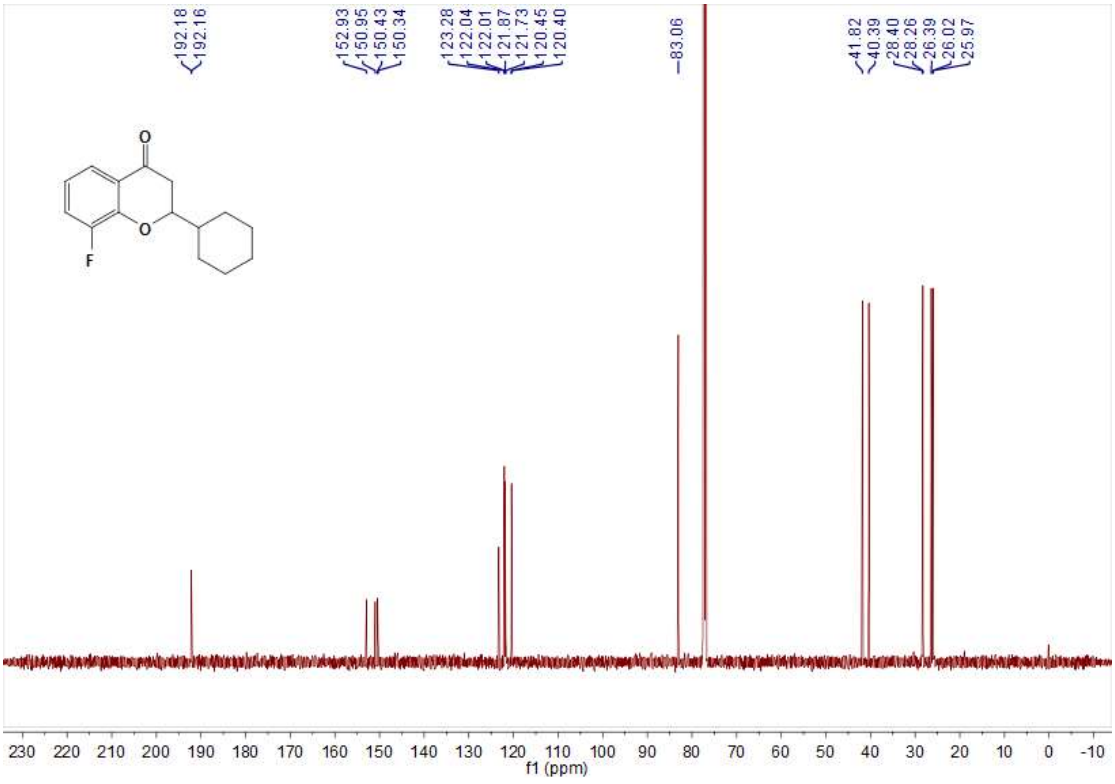


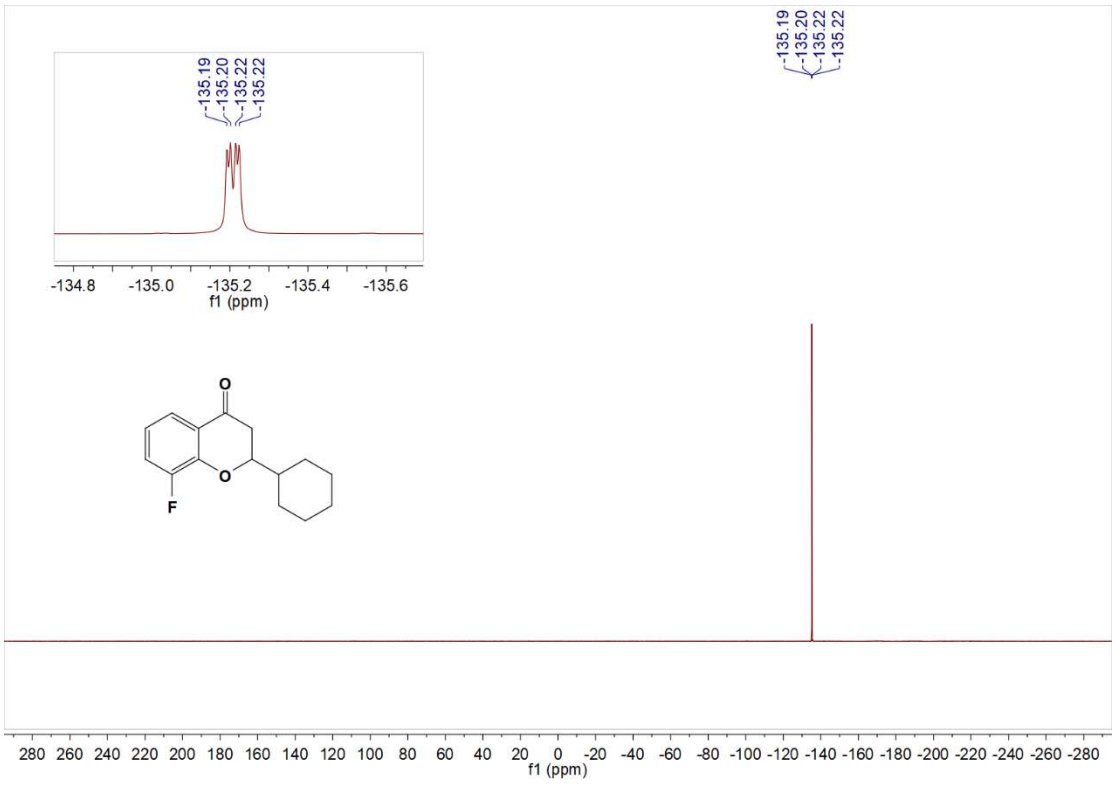
^{1}H NMR of compound 3m



^{13}C NMR of compound 3m



^{19}F NMR of compound 3m



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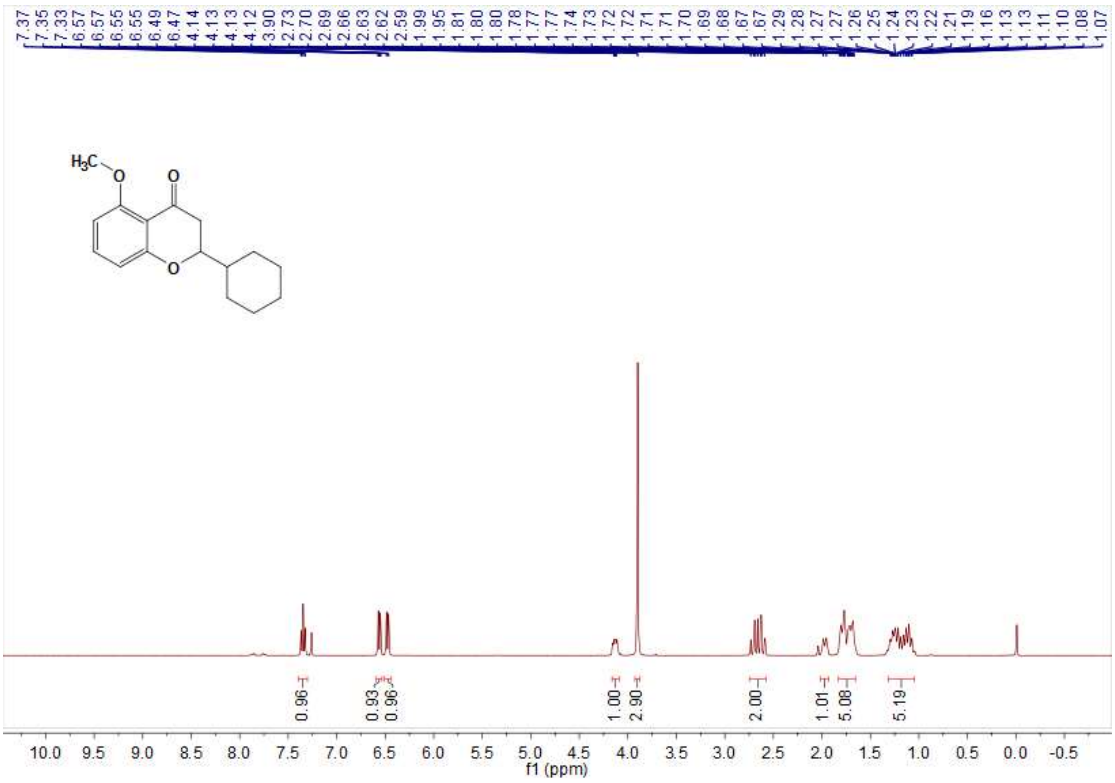

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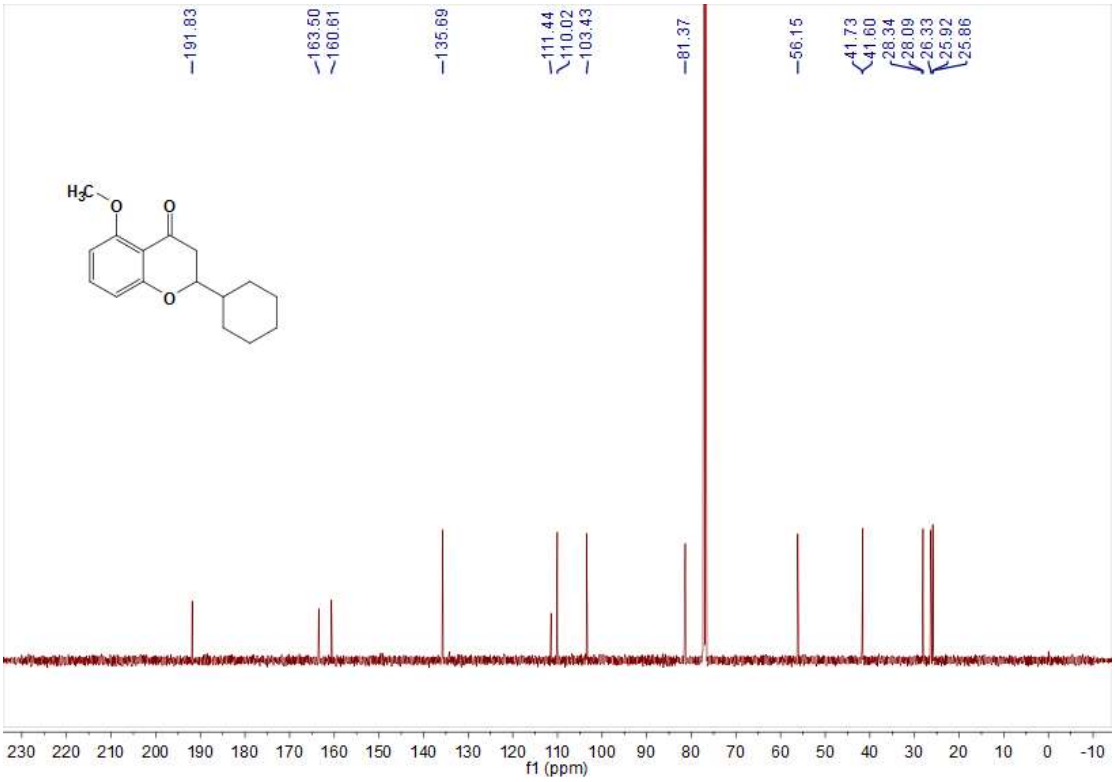
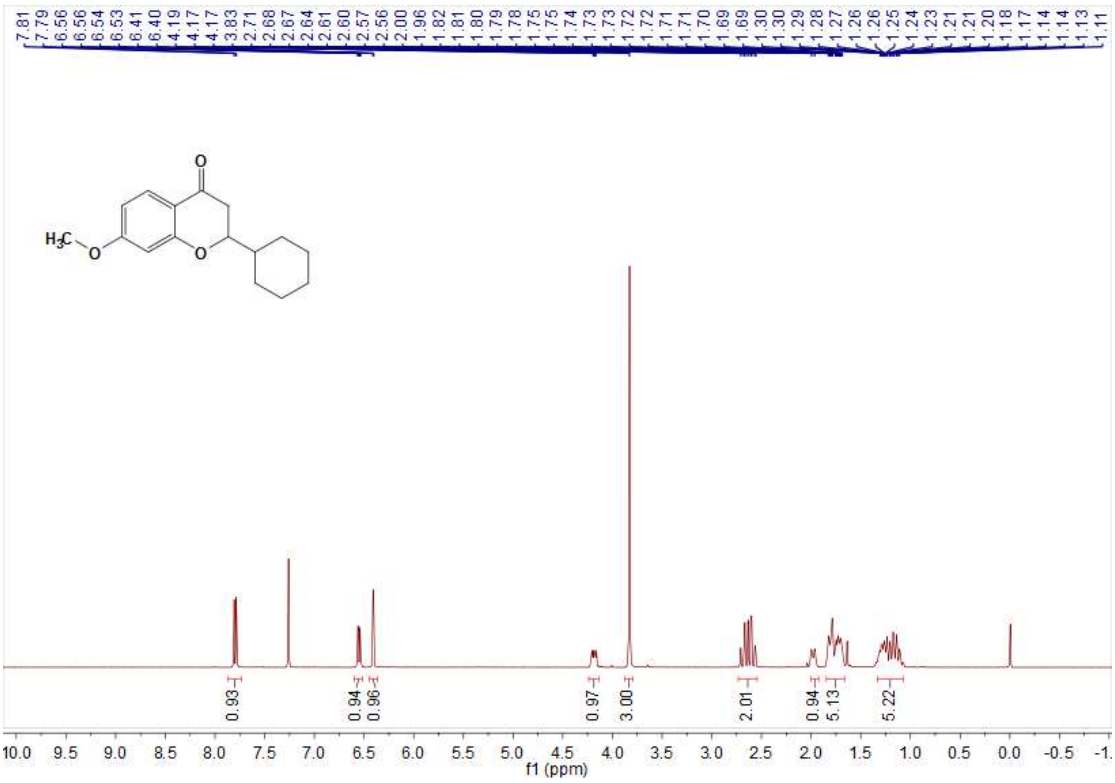


^{1}H NMR of compound 3o



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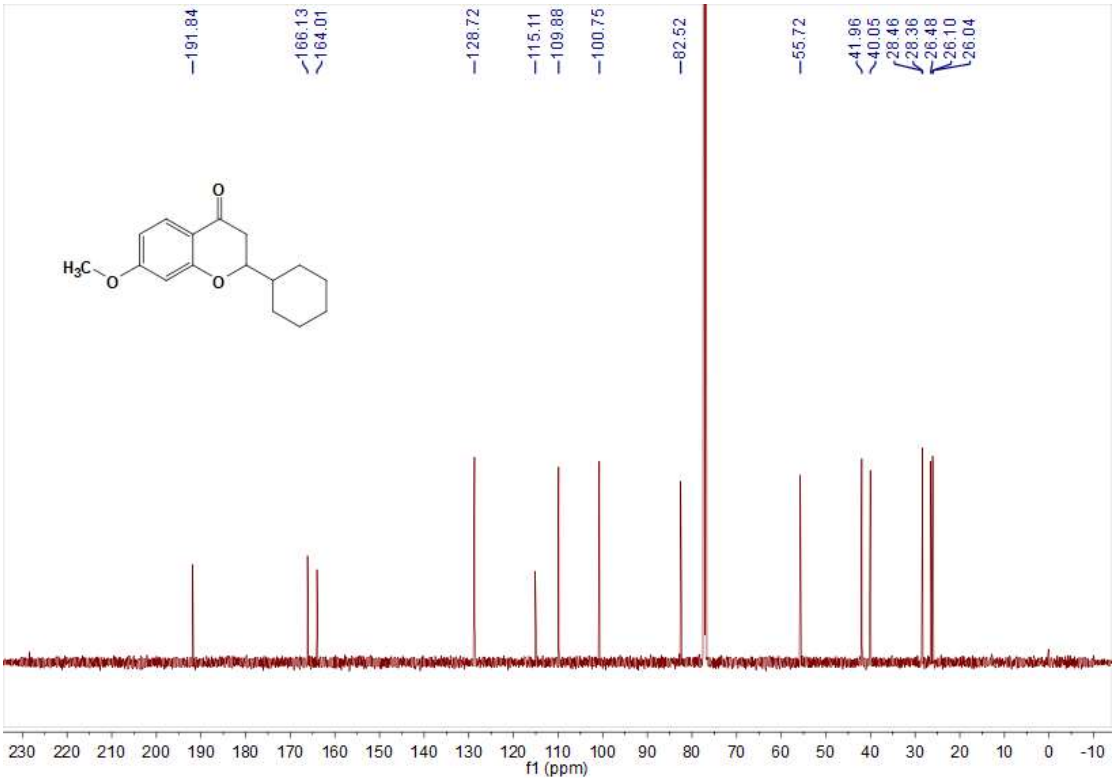
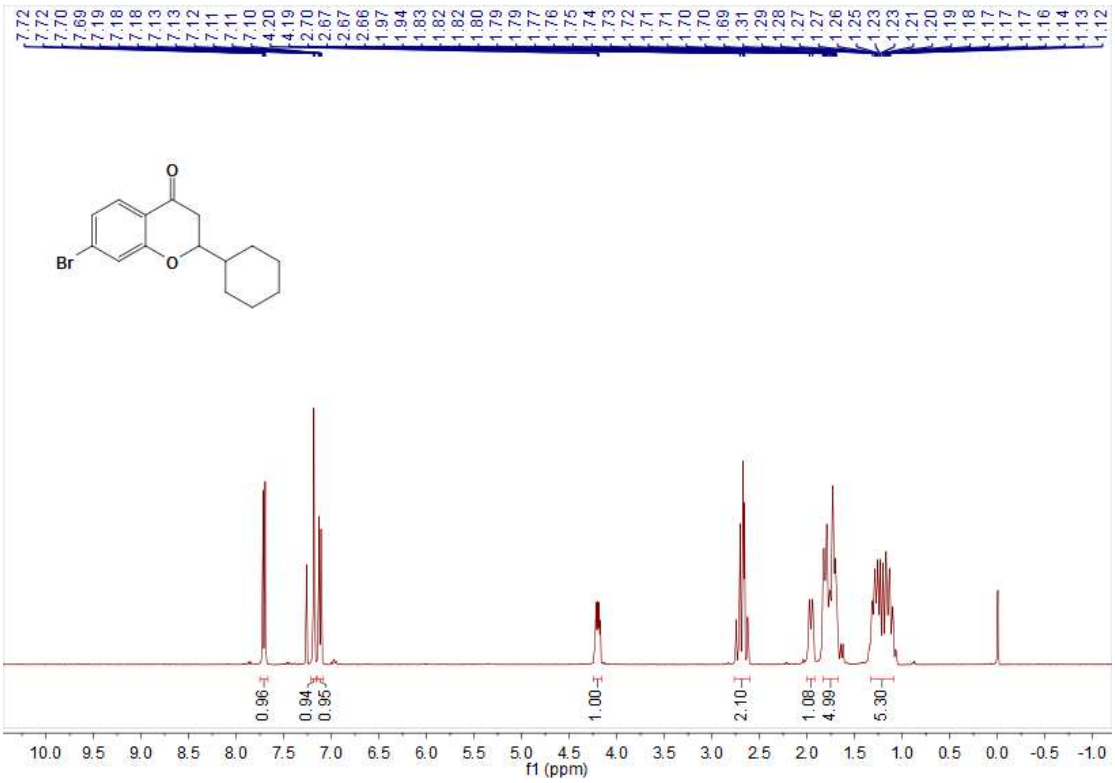
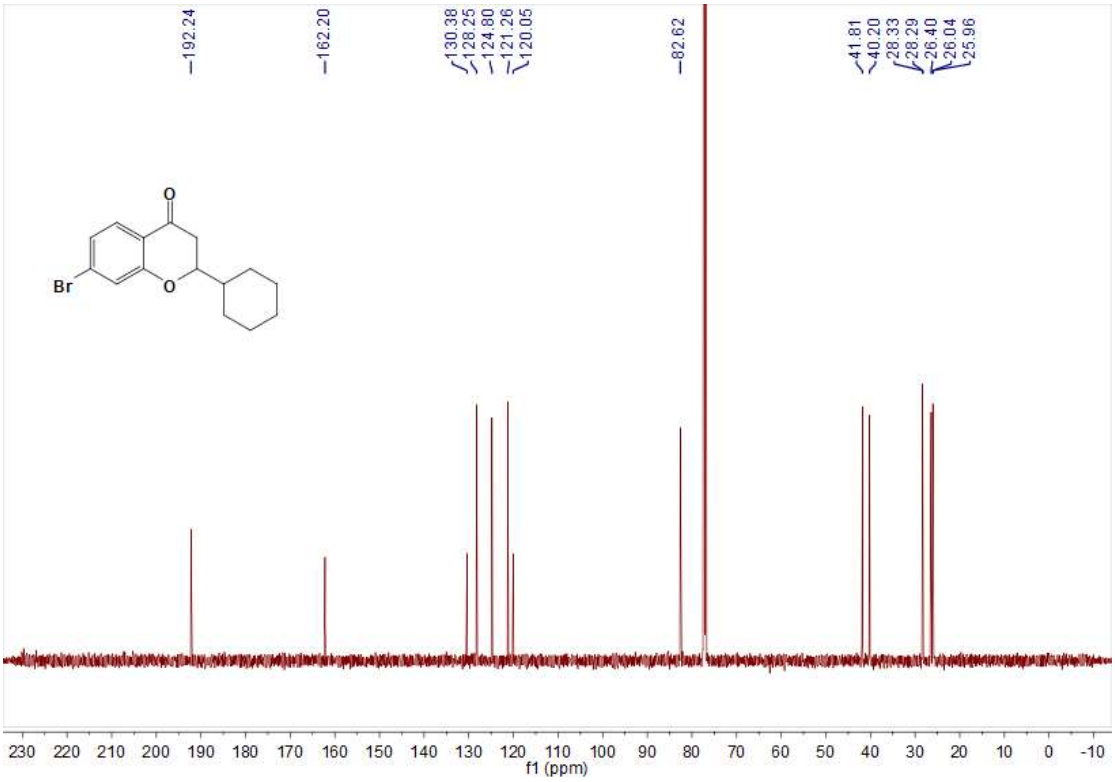


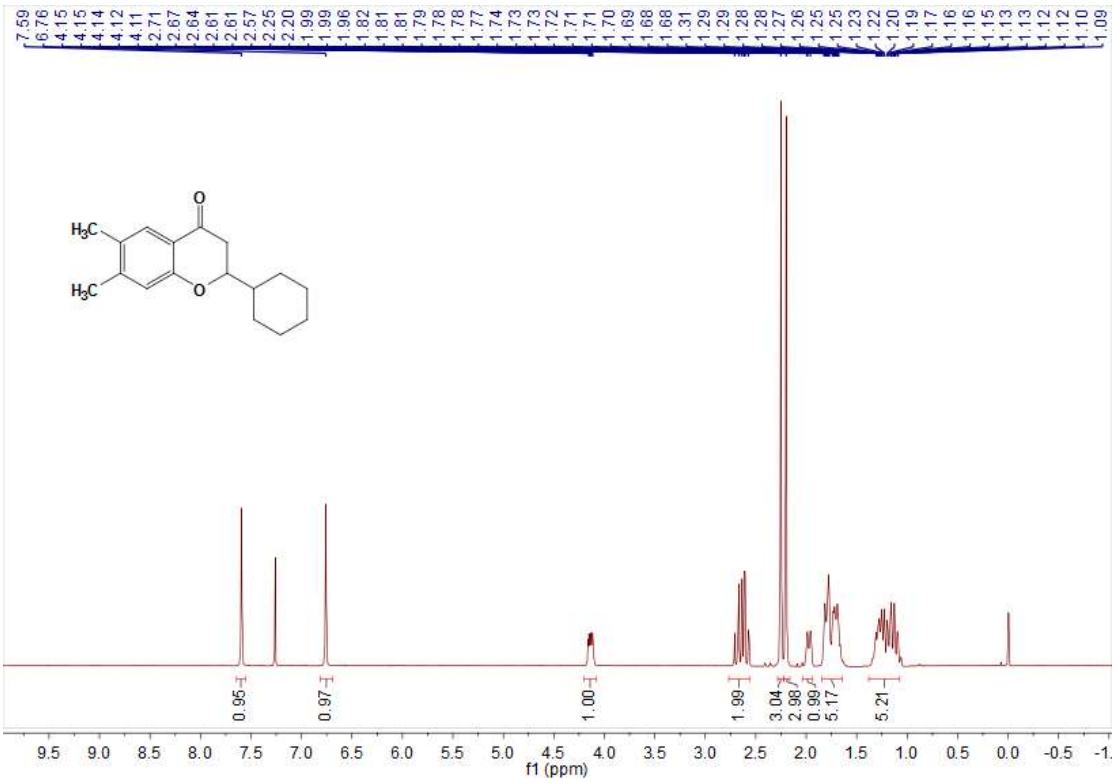
^{1}H NMR of compound 3p



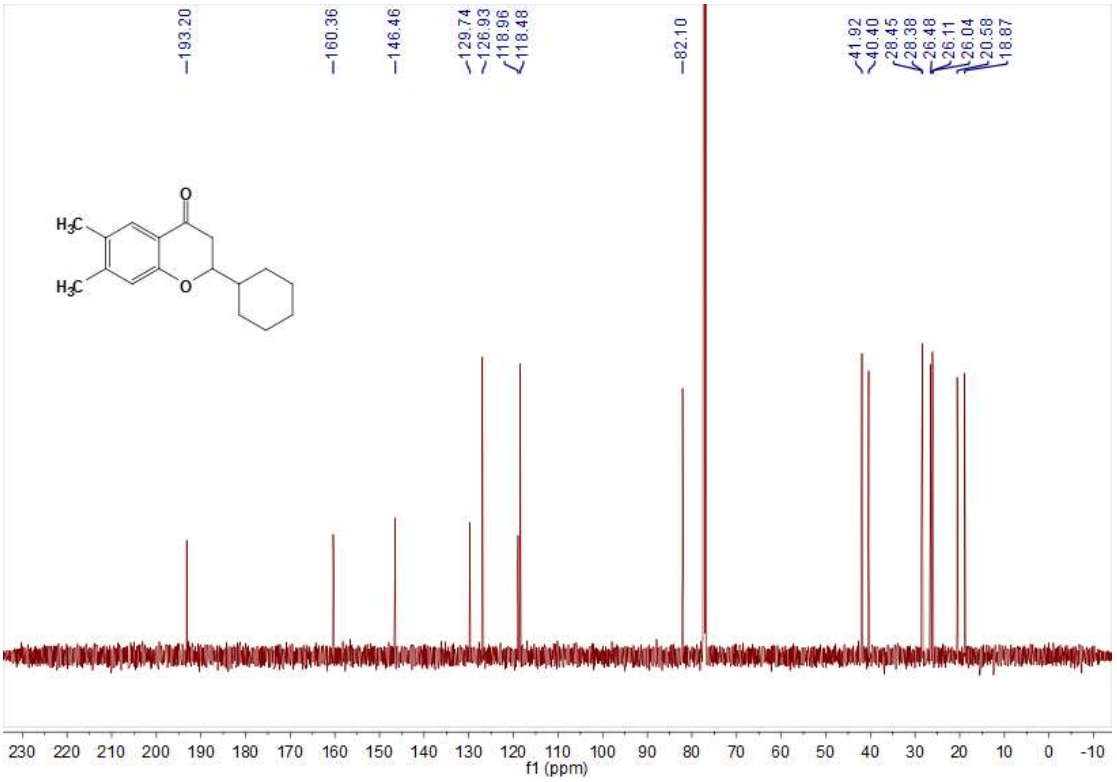
^{13}C NMR of compound 3p



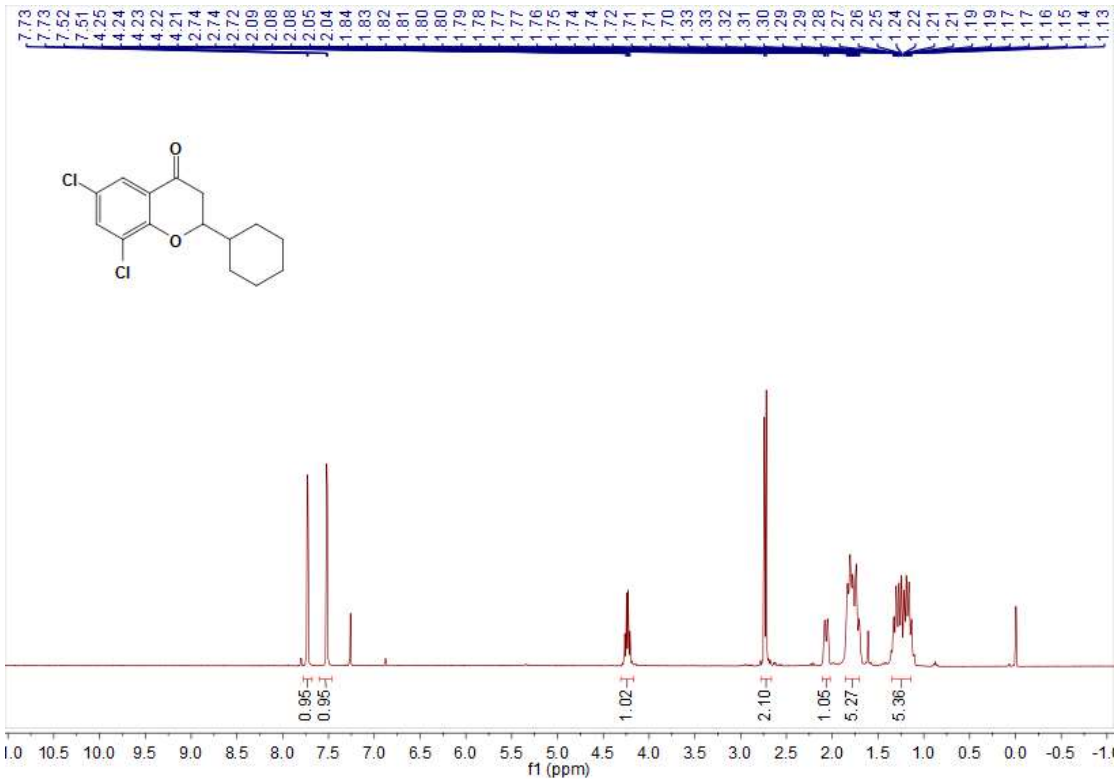
^{1}H NMR of compound 3q



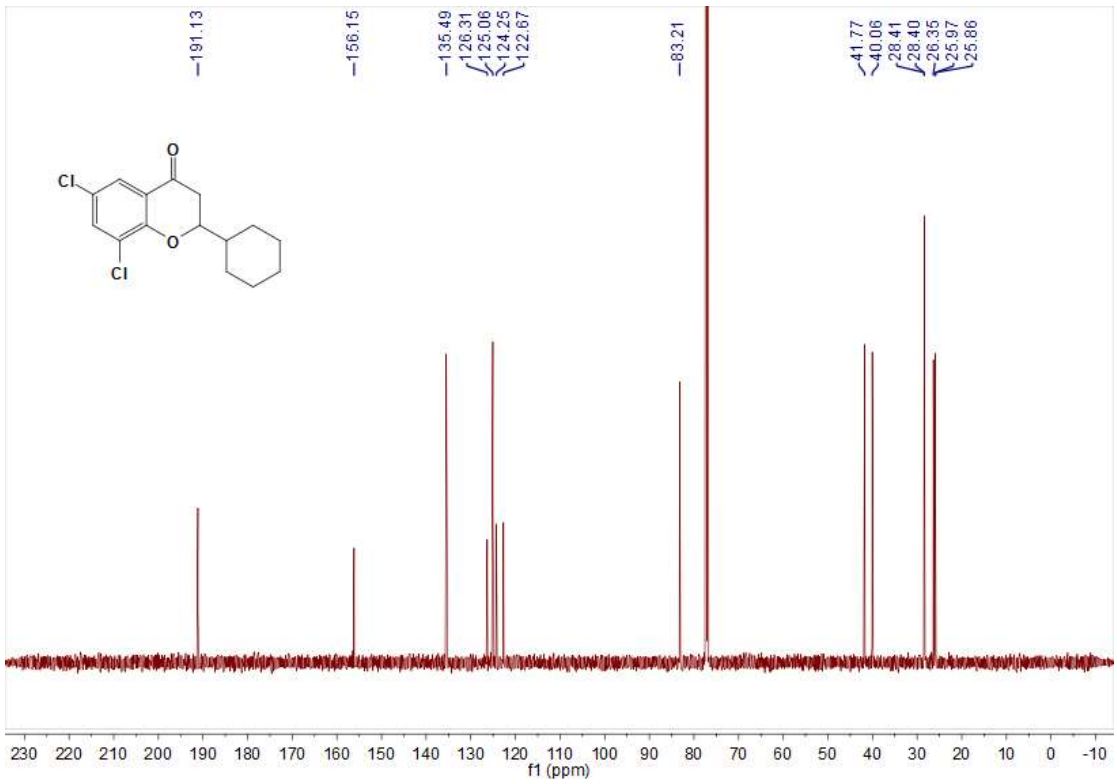
^{13}C NMR of compound 3q



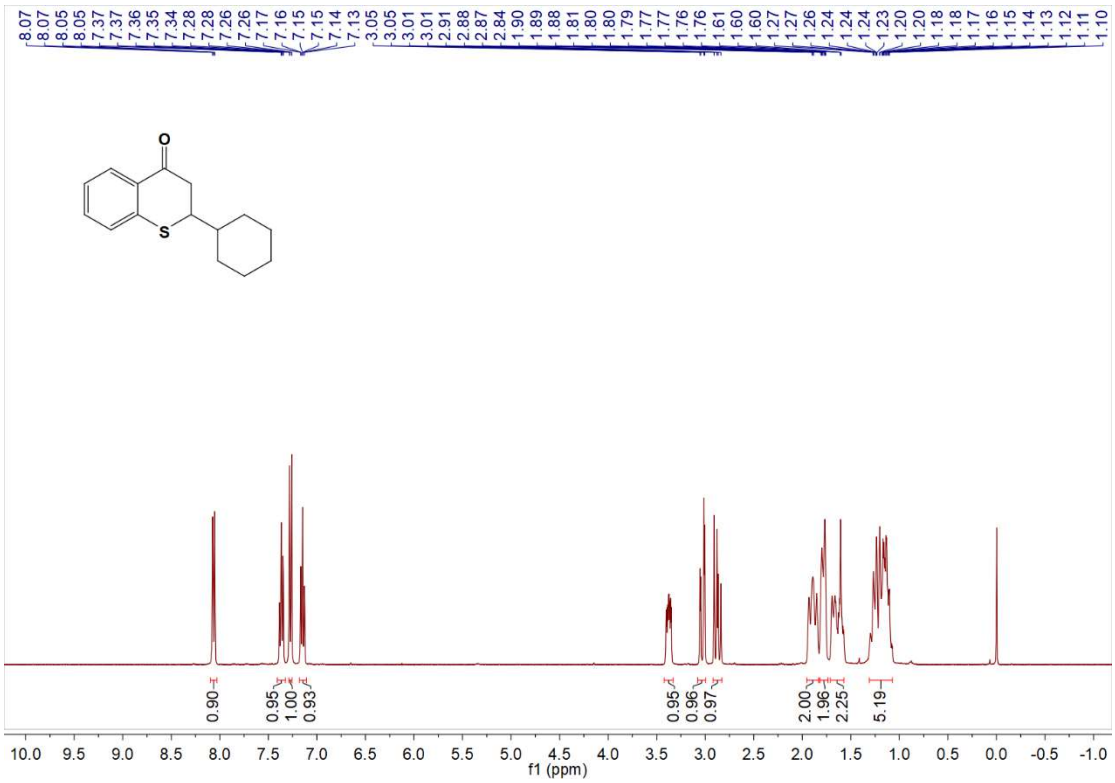
^{1}H NMR of compound 3r



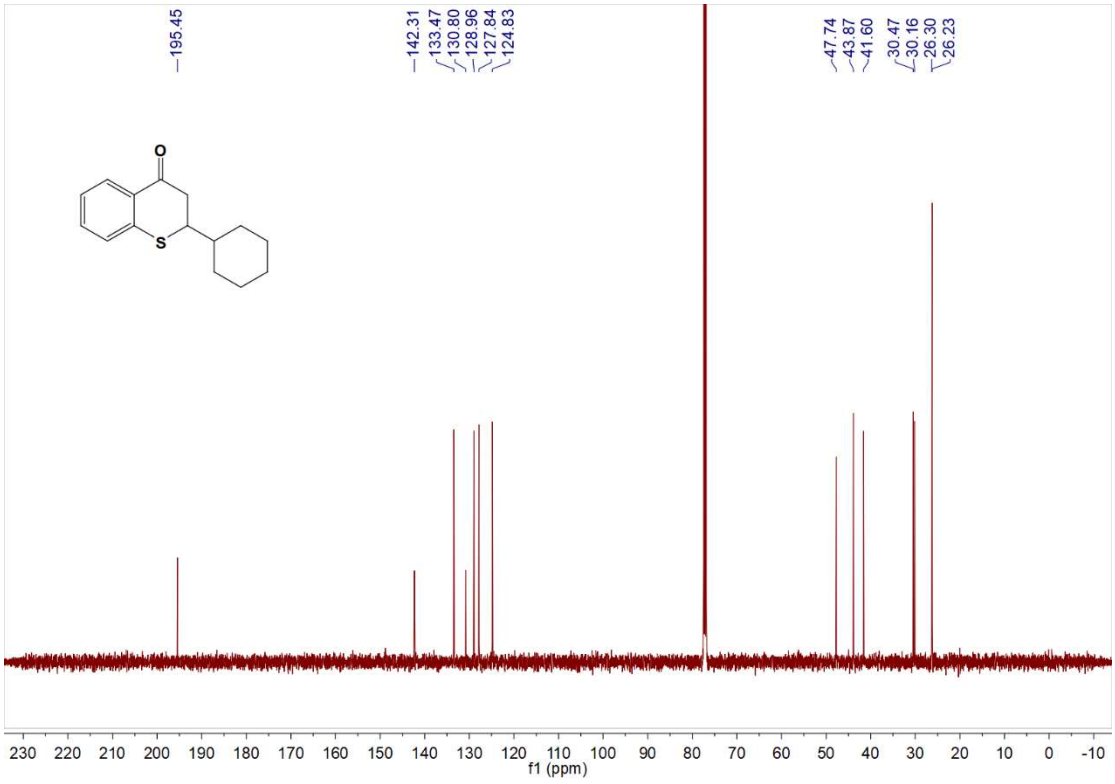
^{13}C NMR of compound 3r



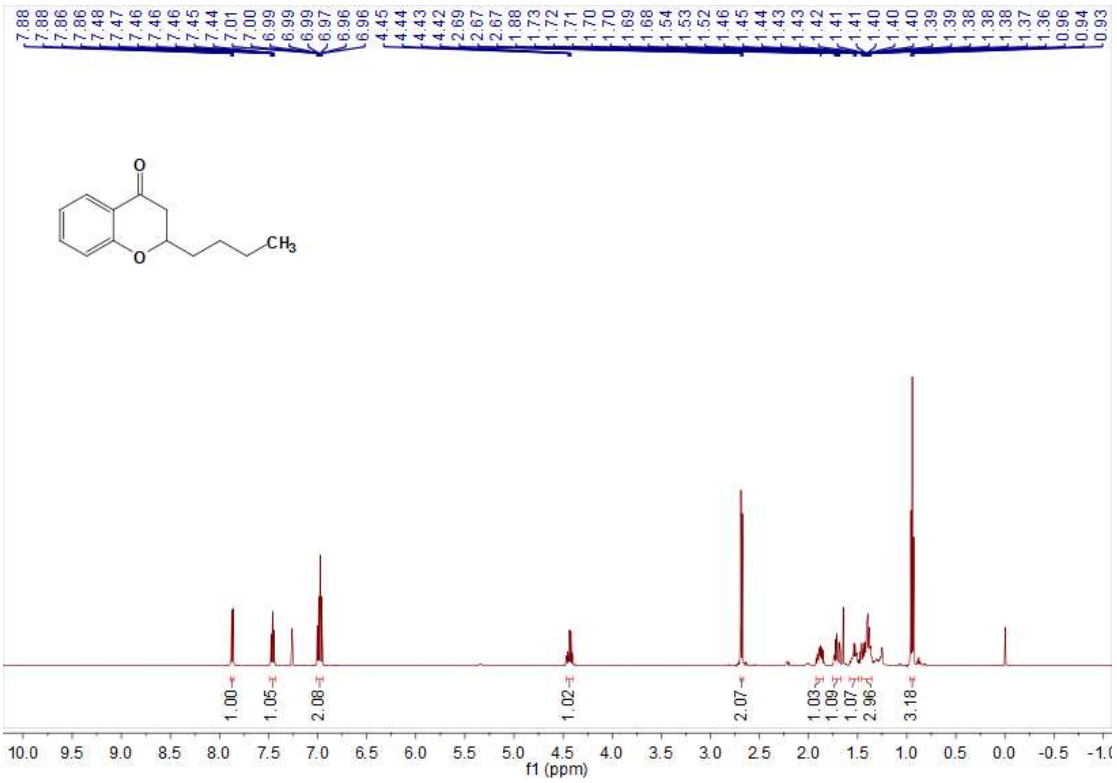
^{1}H NMR of compound 3s



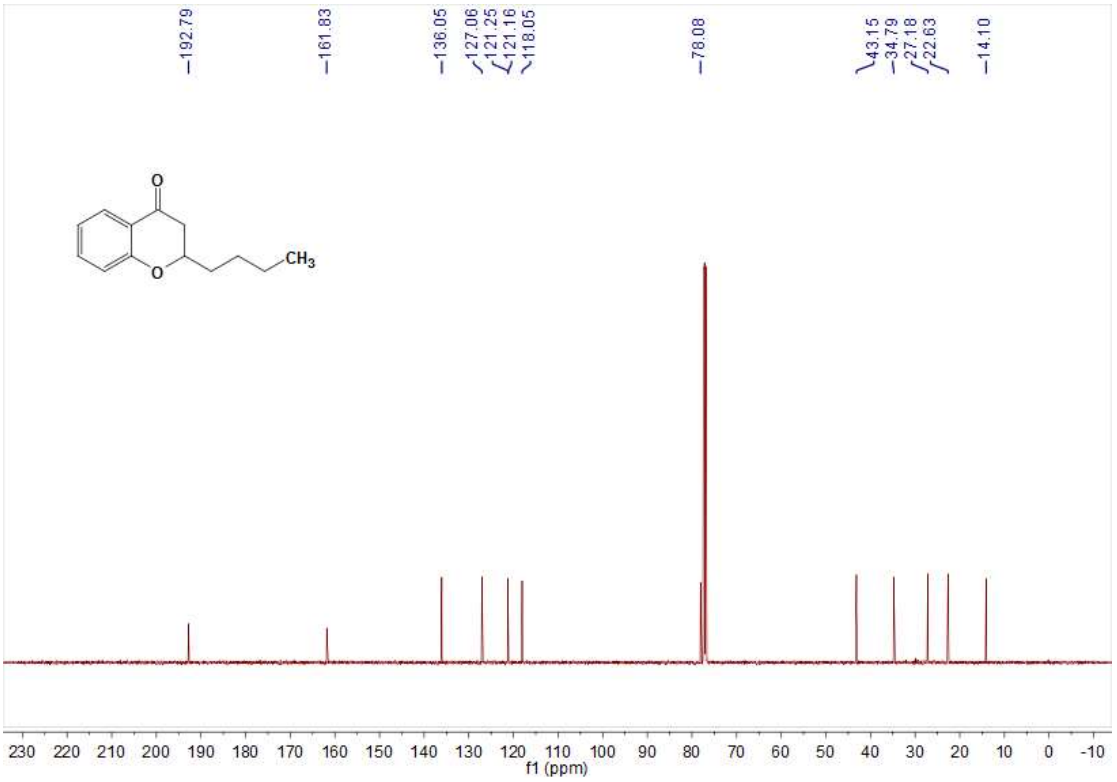
^{13}C NMR of compound 3s



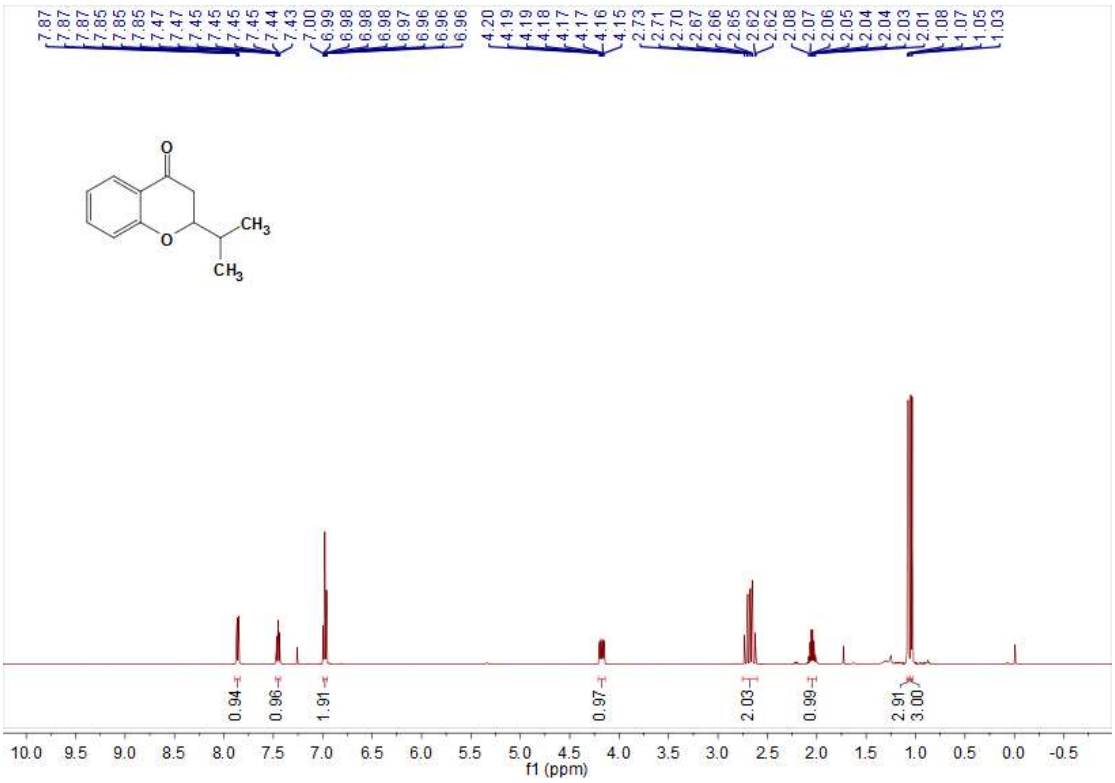
^{1}H NMR of compound 3t



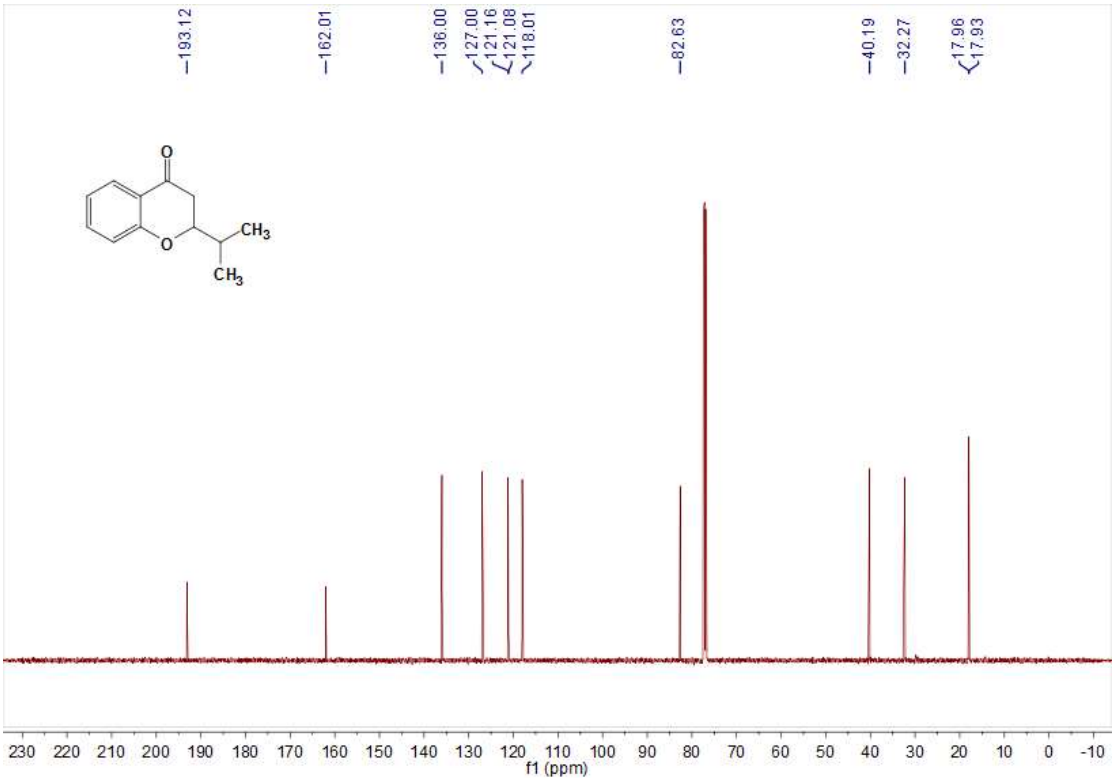
^{13}C NMR of compound 3t



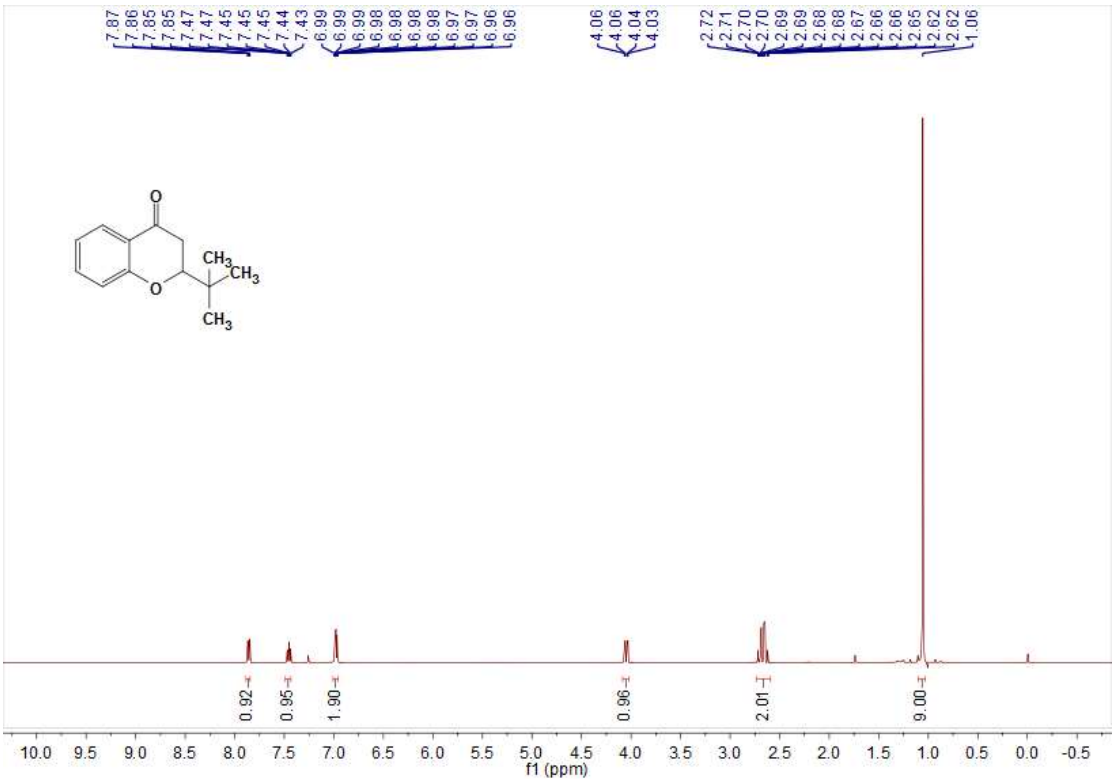
^{1}H NMR of compound 3u



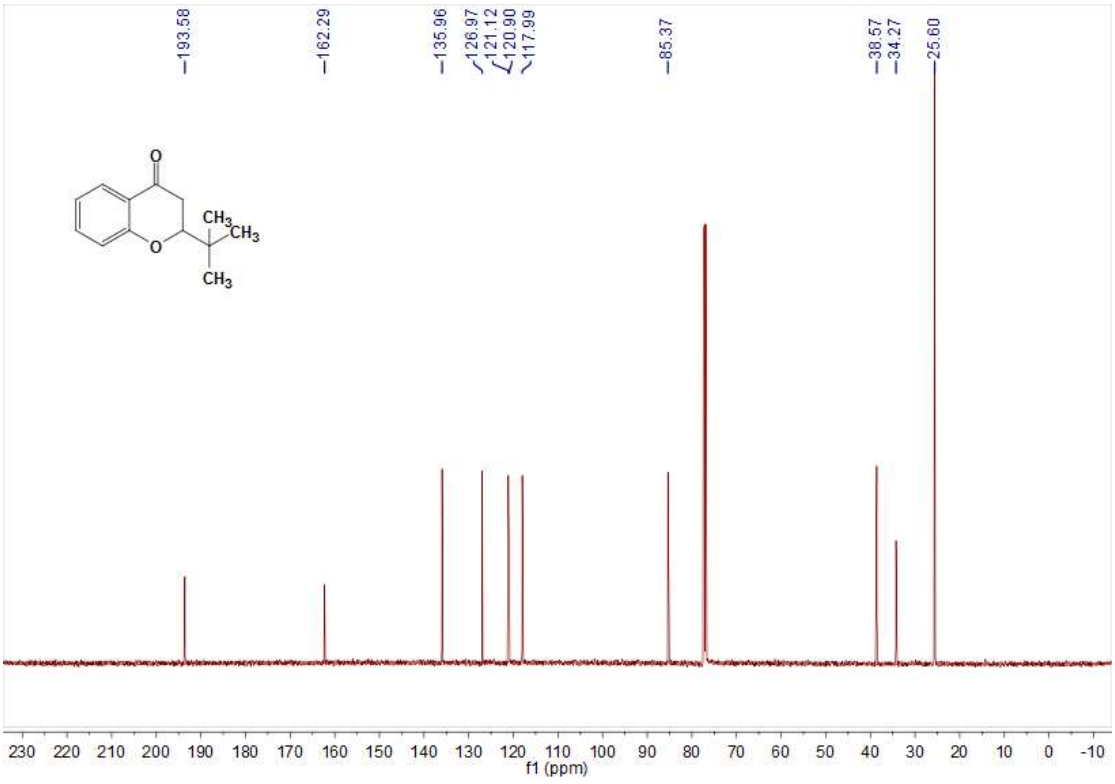
^{13}C NMR of compound 3u



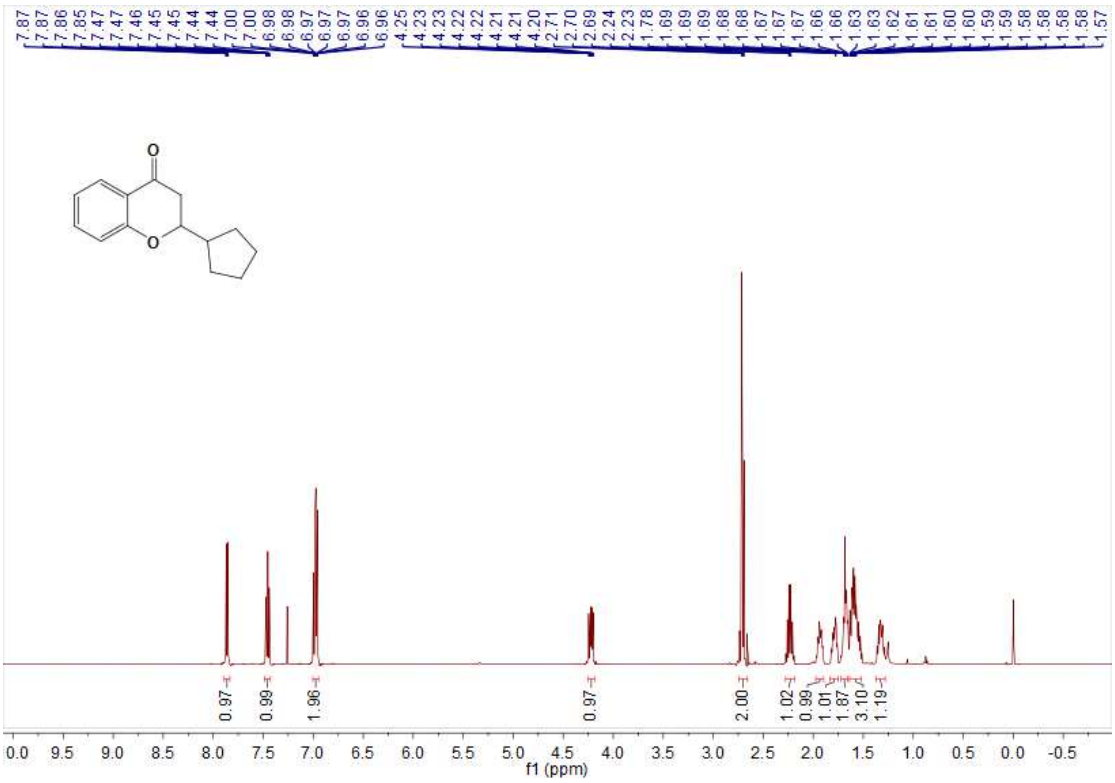
^{1}H NMR of compound 3v



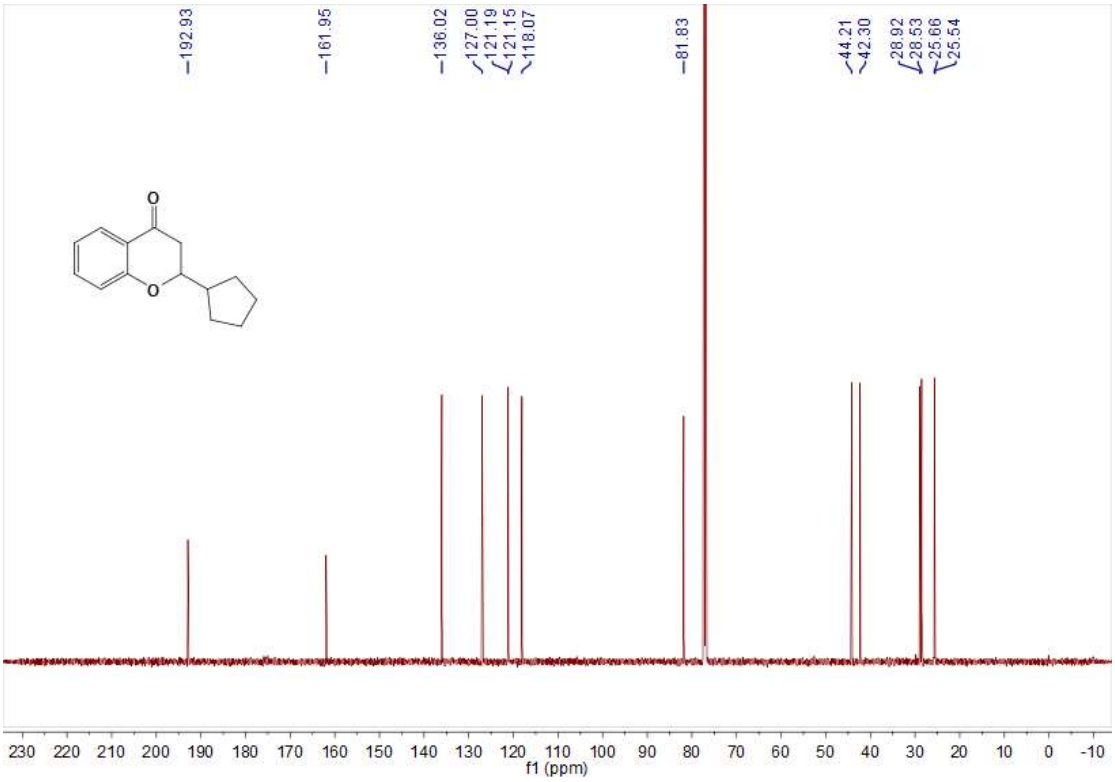
^{13}C NMR of compound 3v



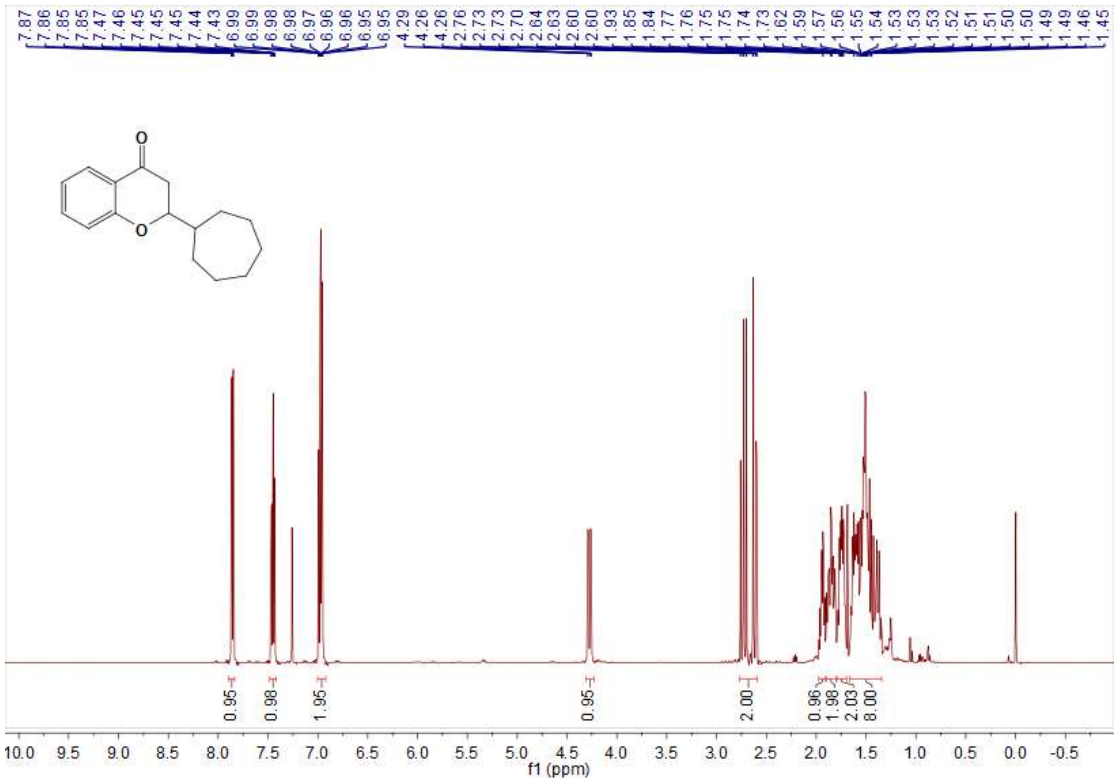
^{1}H NMR of compound 3w



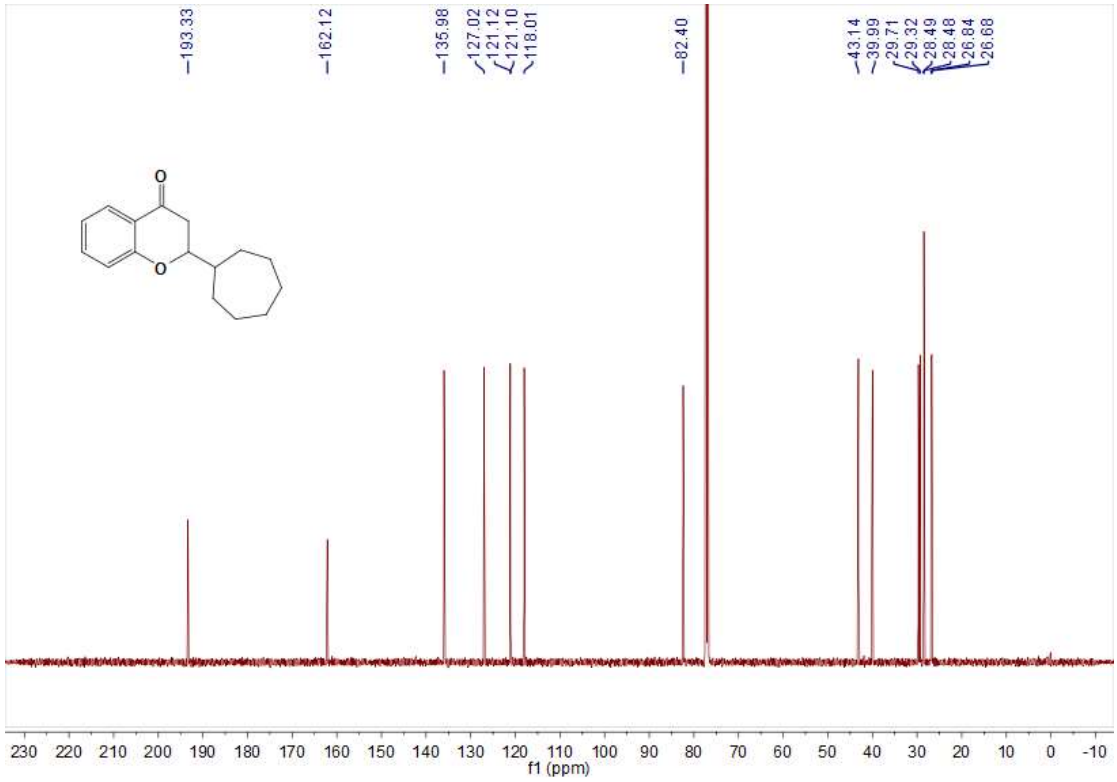
^{13}C NMR of compound 3w



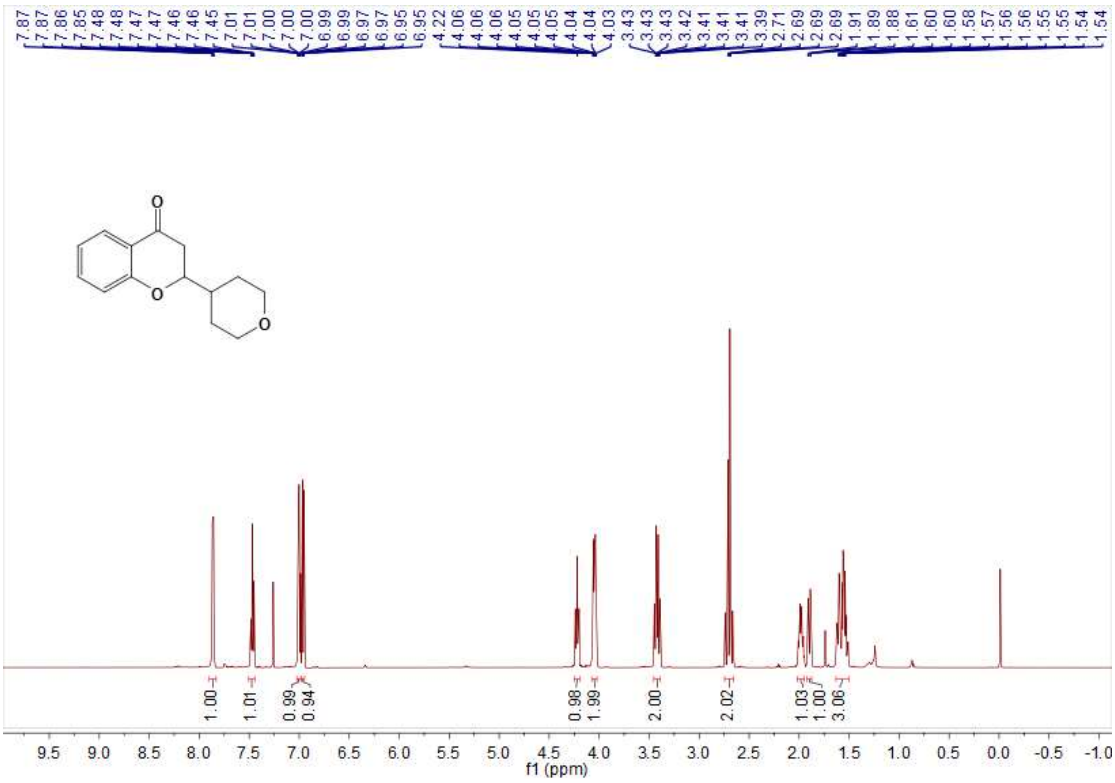
^{1}H NMR of compound 3x



^{13}C NMR of compound 3x



^{1}H NMR of compound 3y



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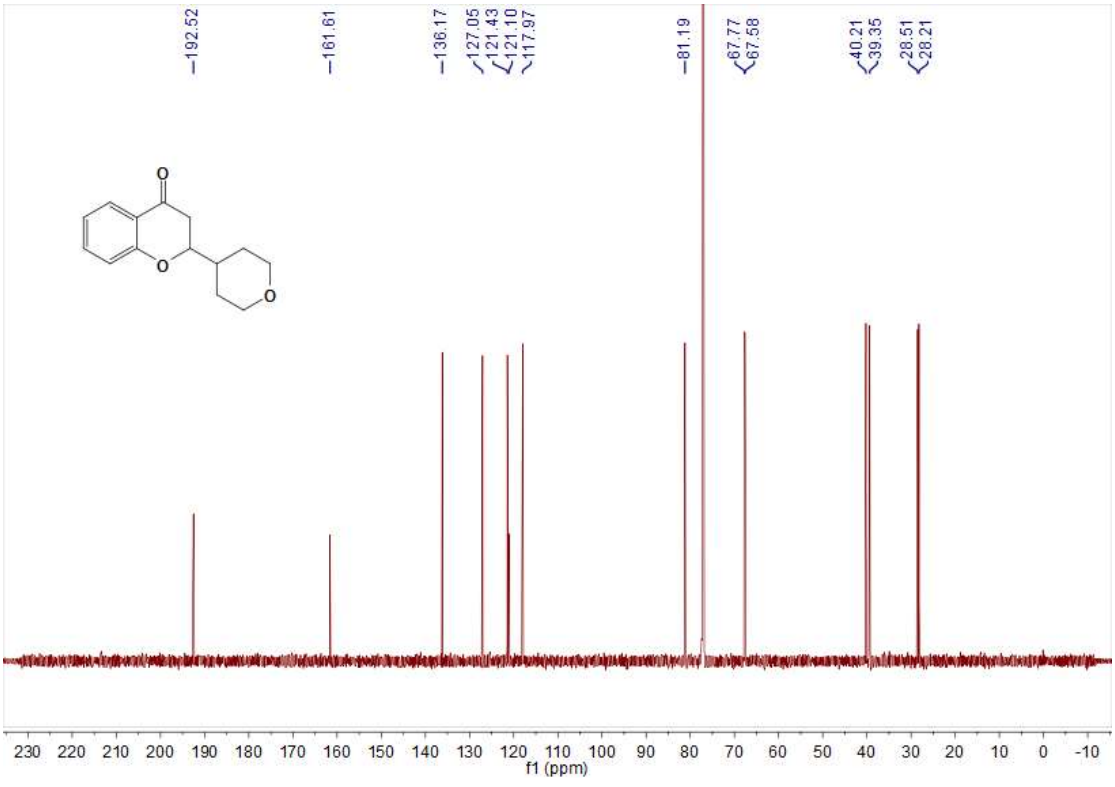
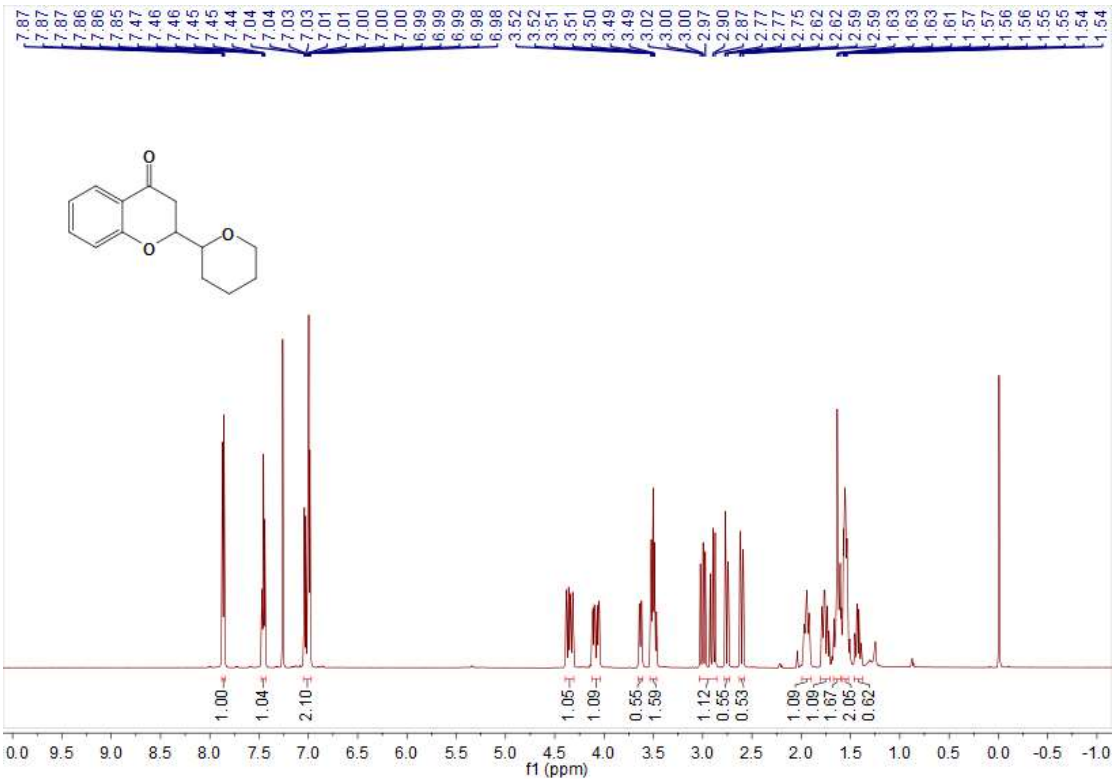
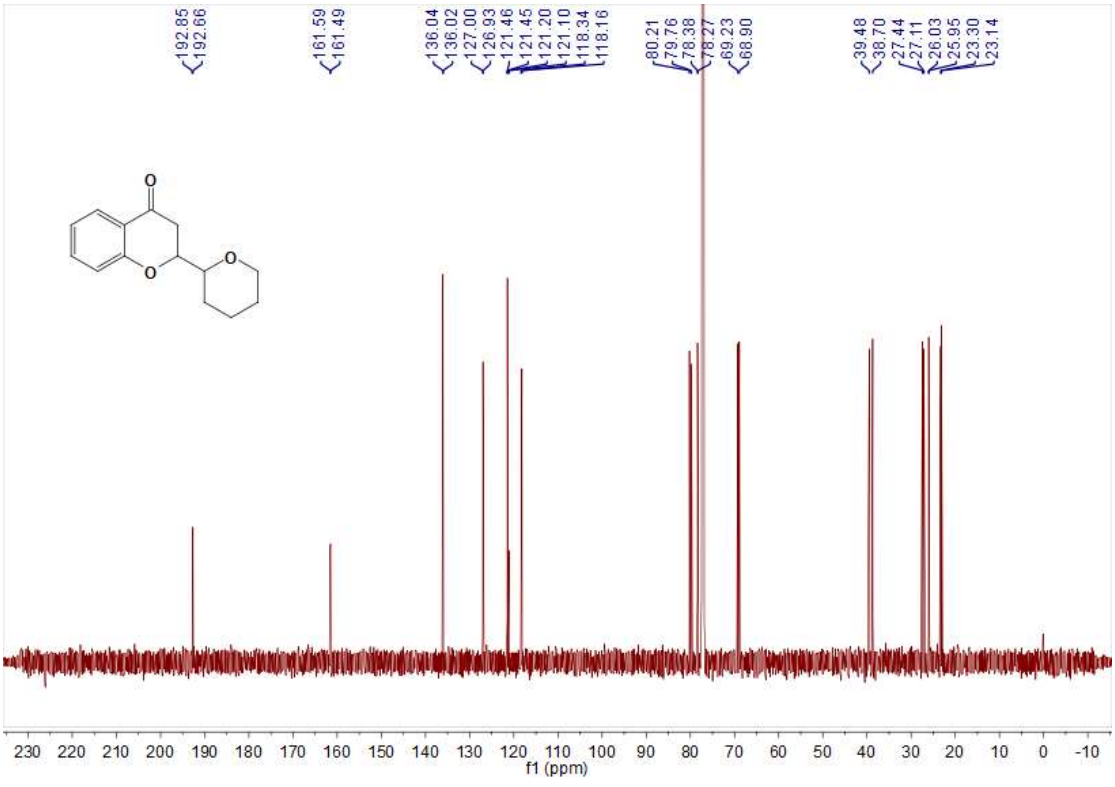


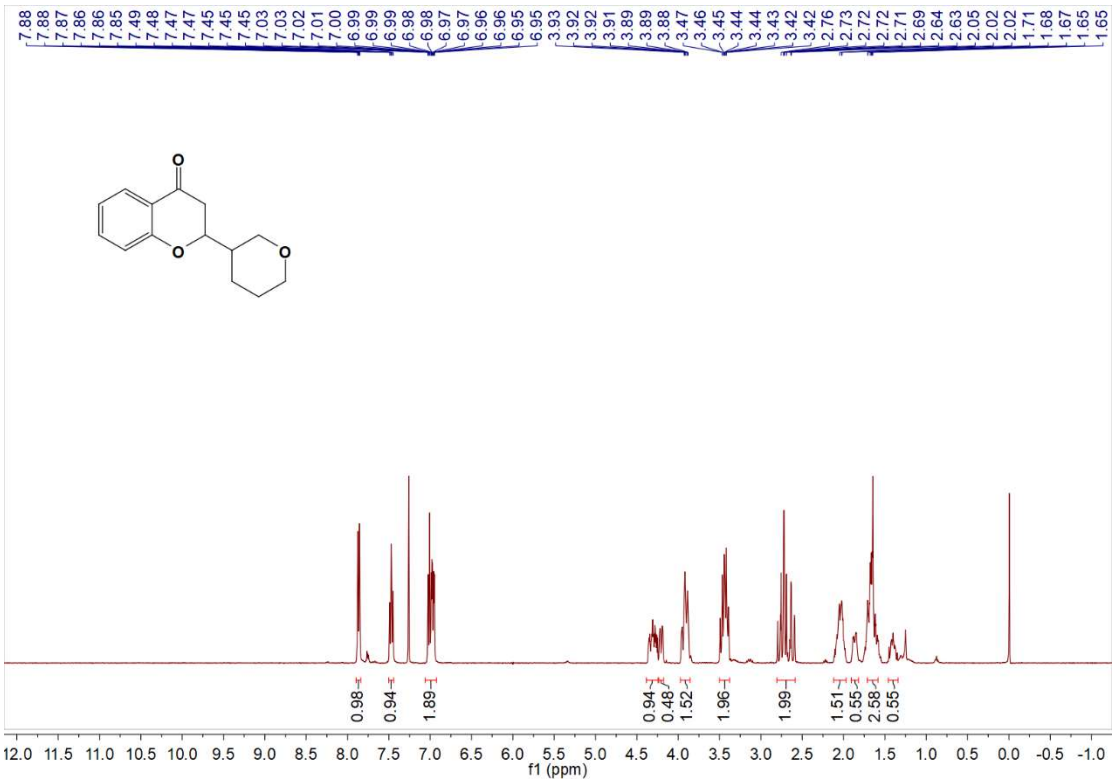
^{1}H NMR of compound 3z



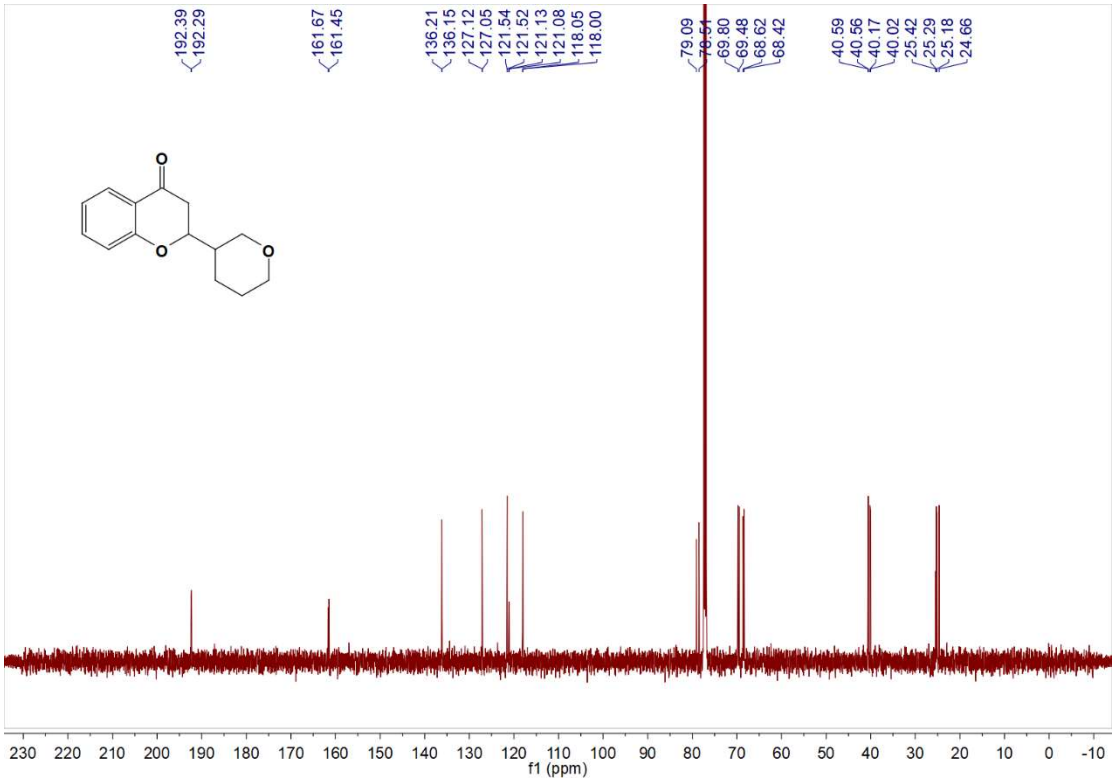
^{13}C NMR of compound 3z



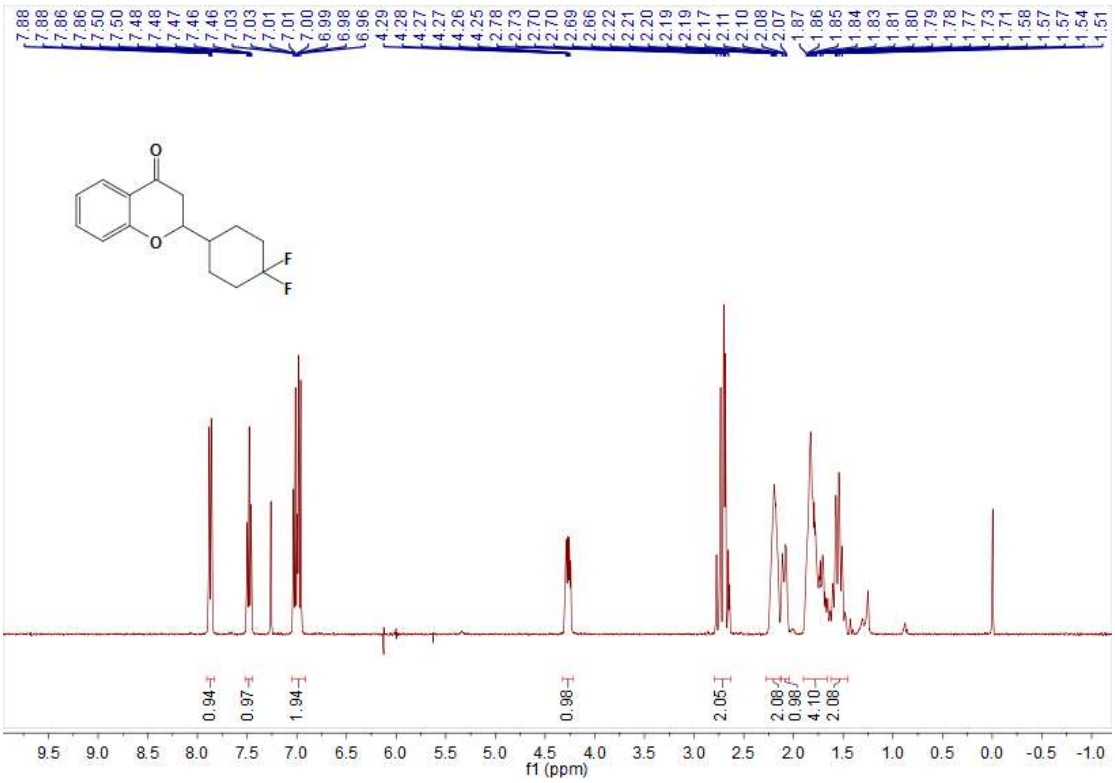
^{1}H NMR of compound 3aa



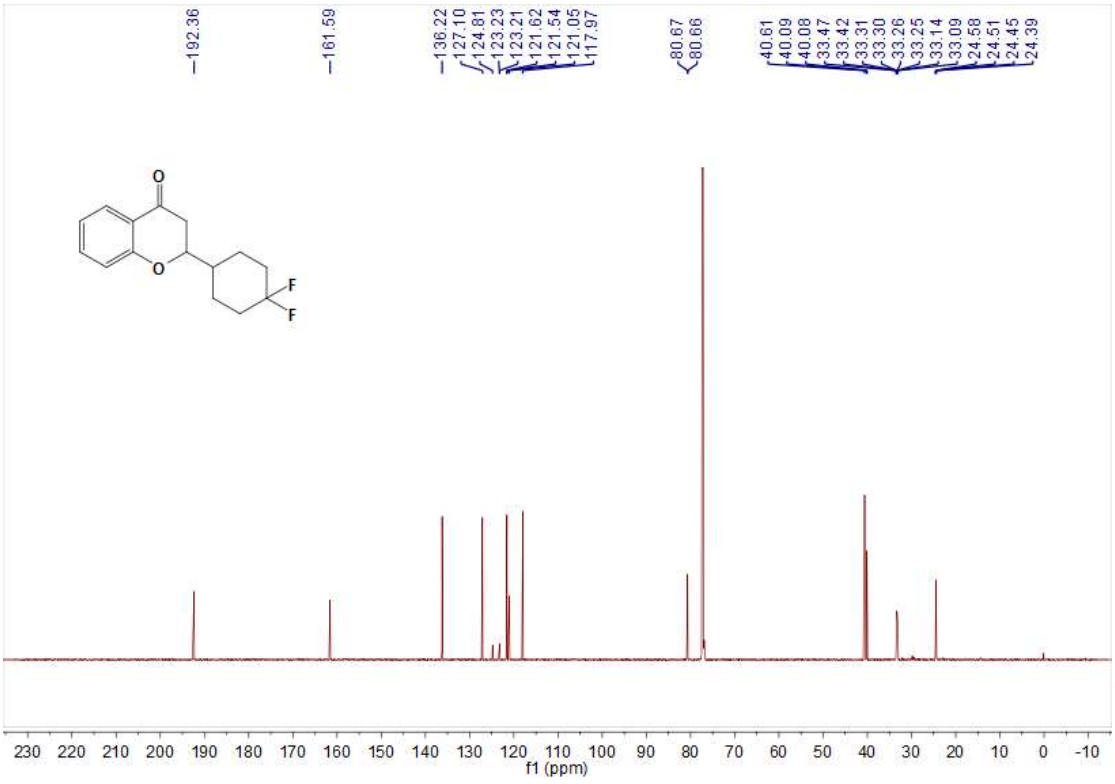
^{13}C NMR of compound 3aa



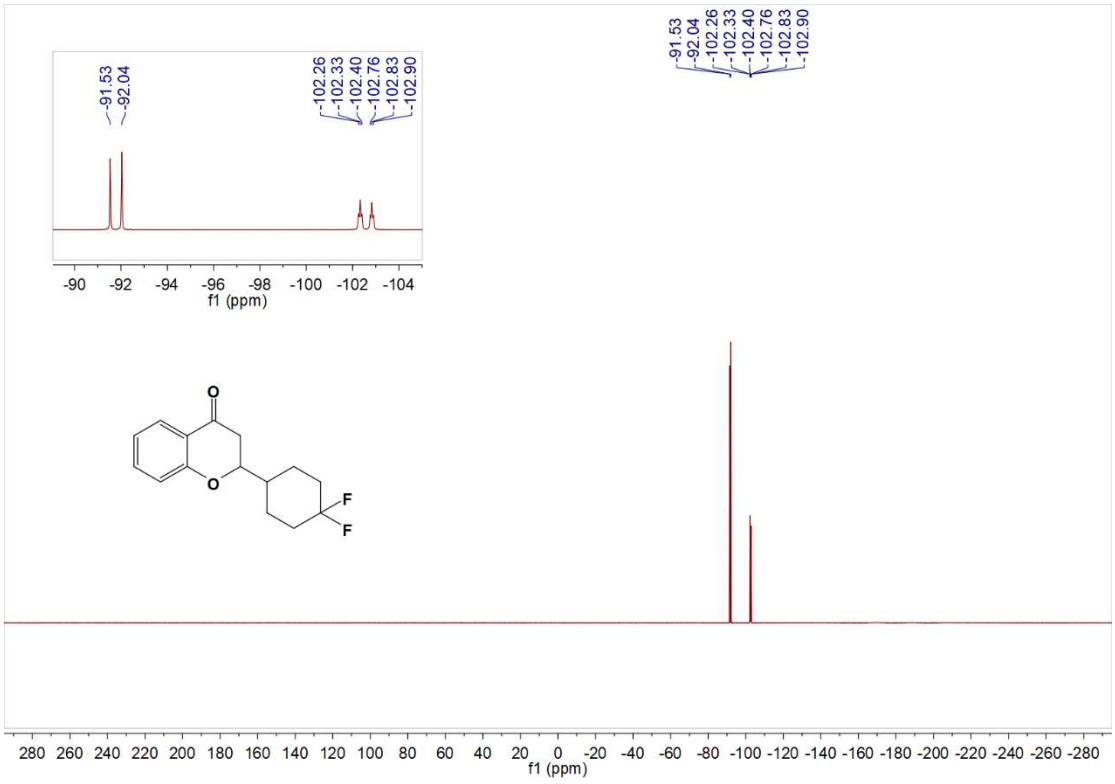
^{1}H NMR of compound 3ab



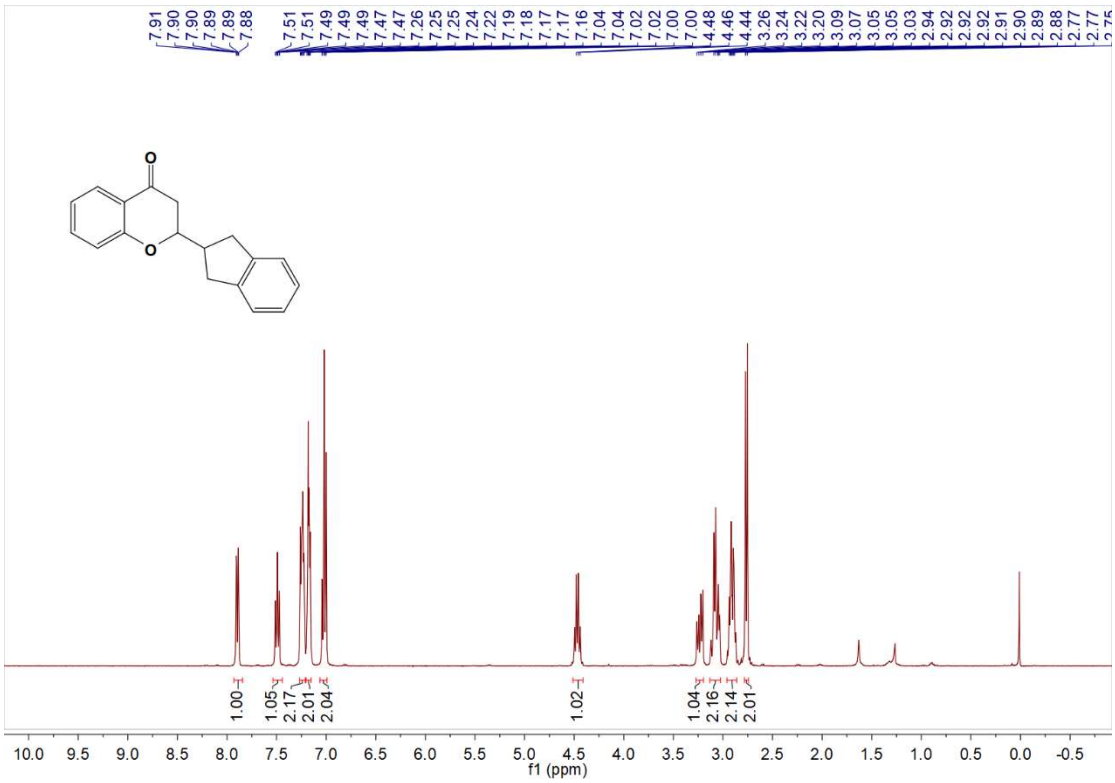
^{13}C NMR of compound 3ab



^{19}F NMR of compound 3ab



^{1}H NMR of compound 3ac



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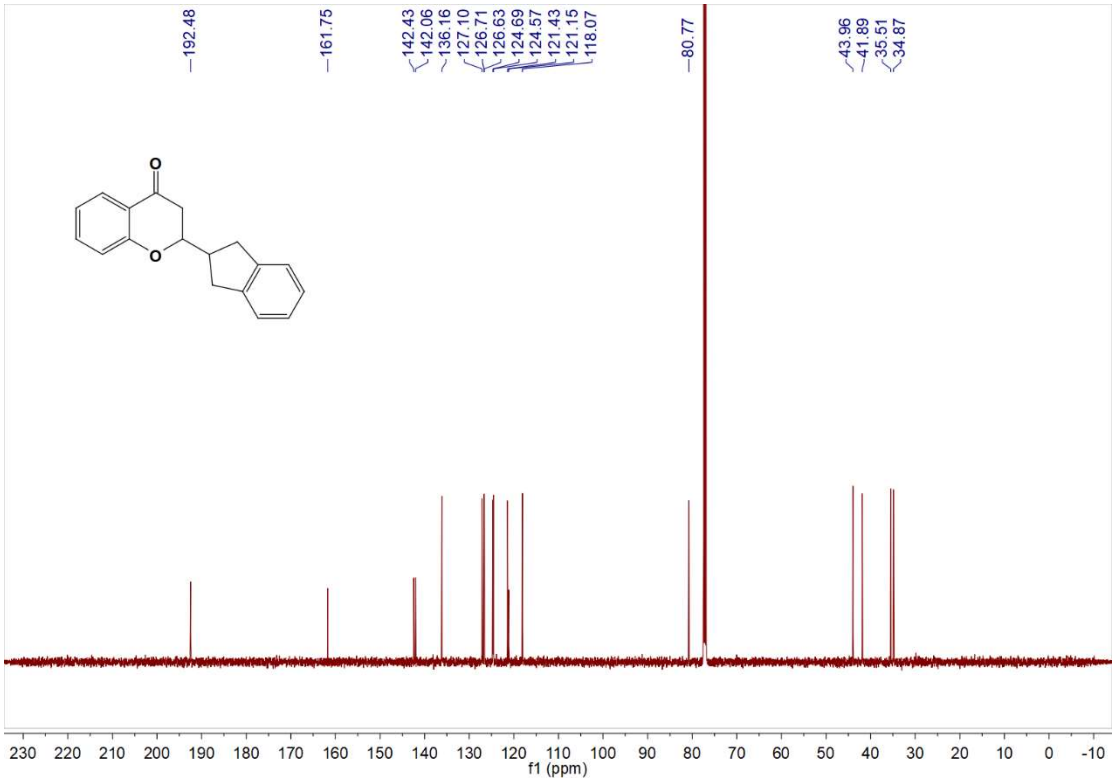
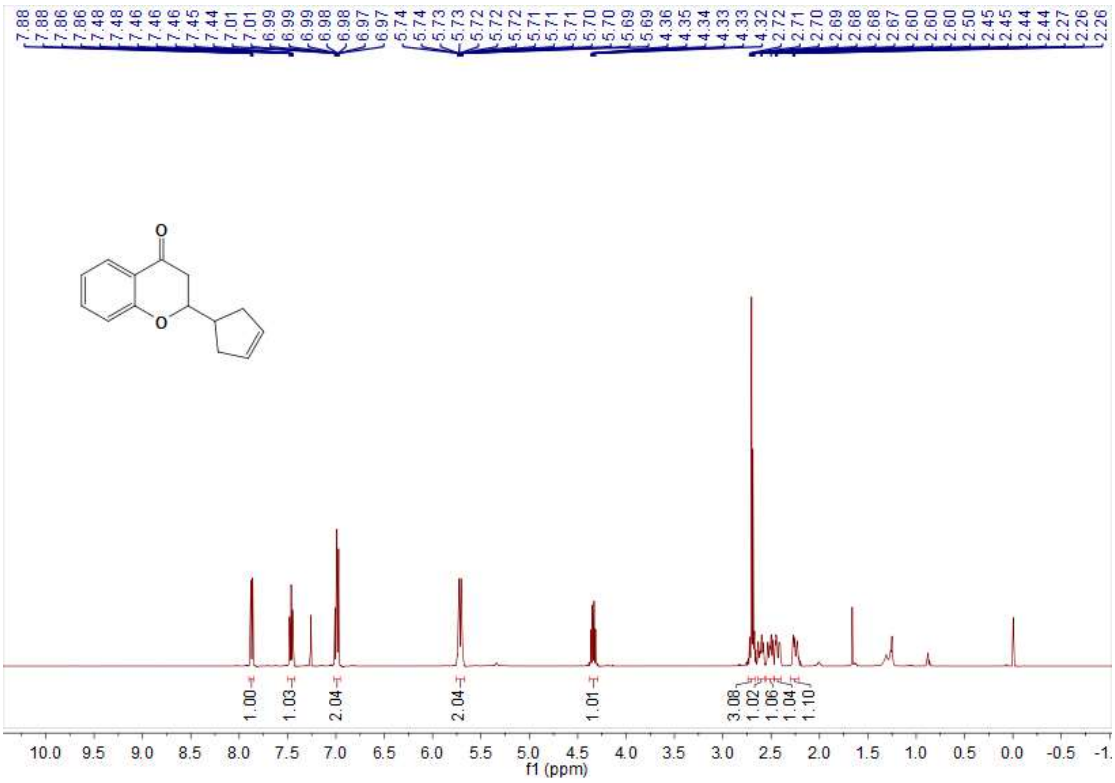
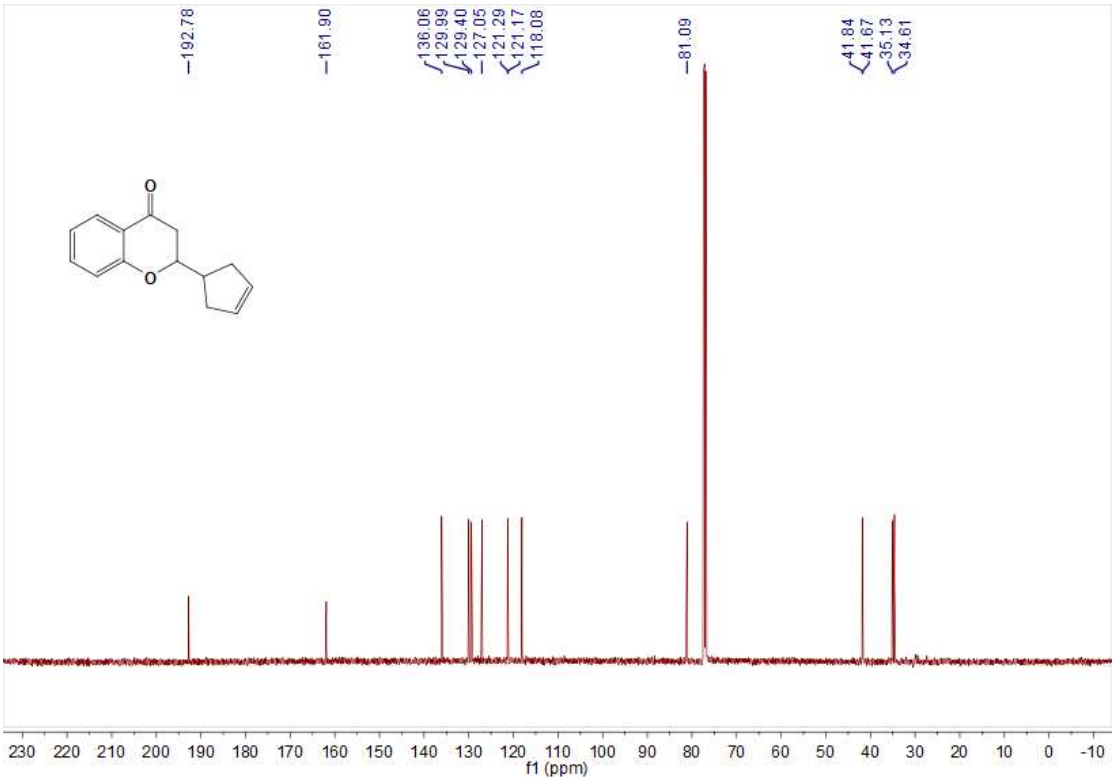


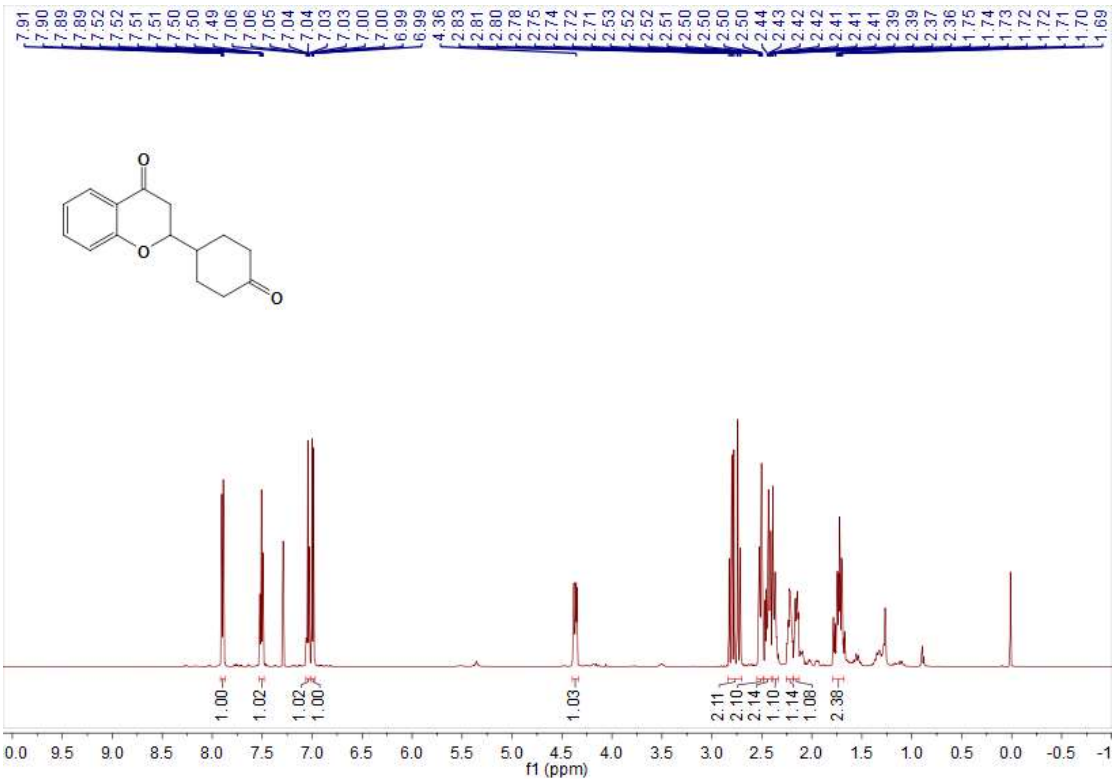
^{1}H NMR of compound 3ad



^{13}C NMR of compound 3ad



^{1}H NMR of compound 3ae



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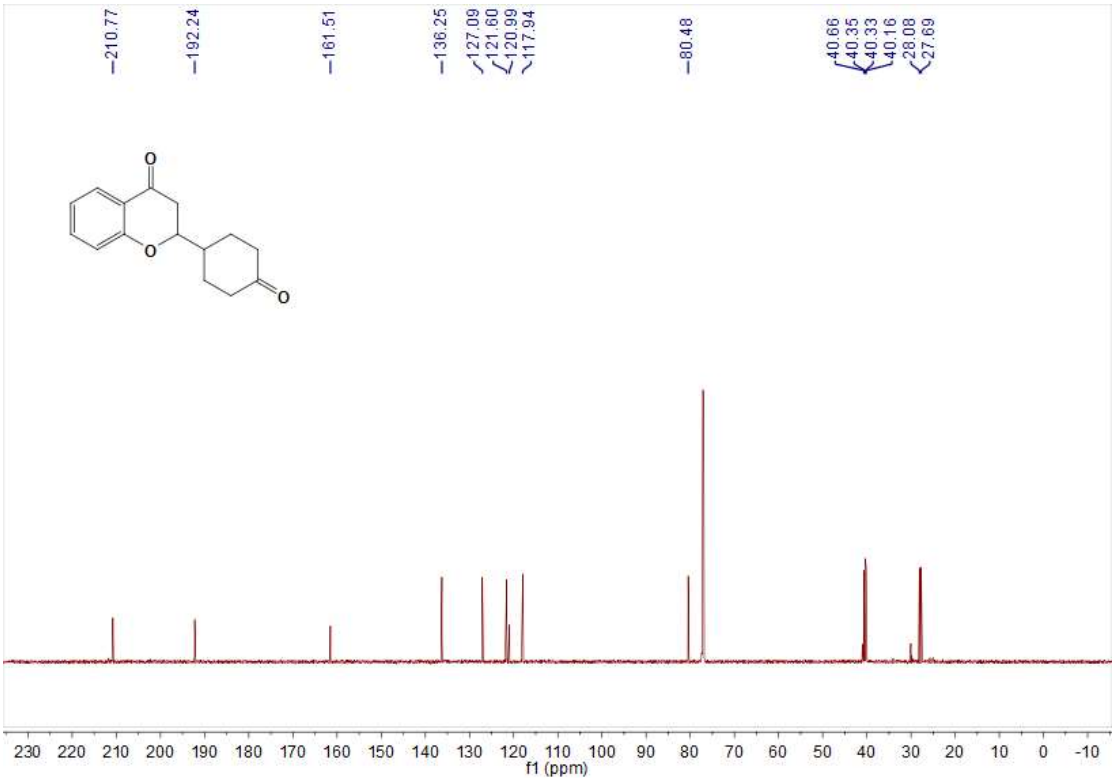
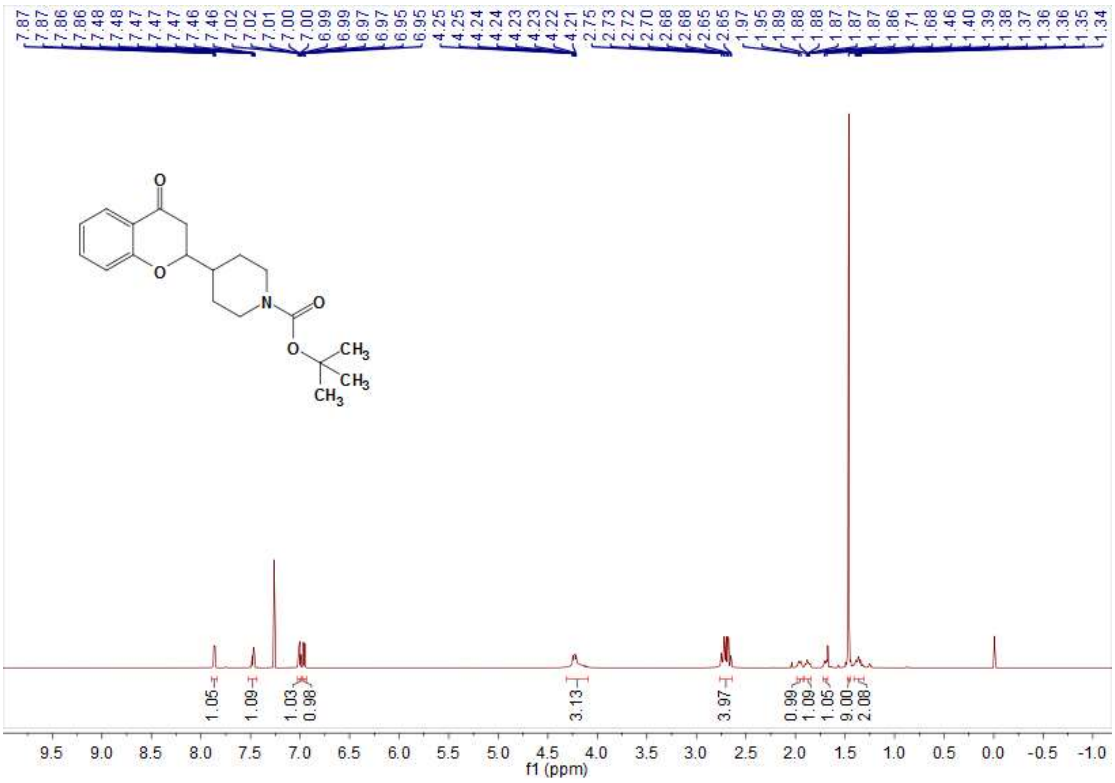
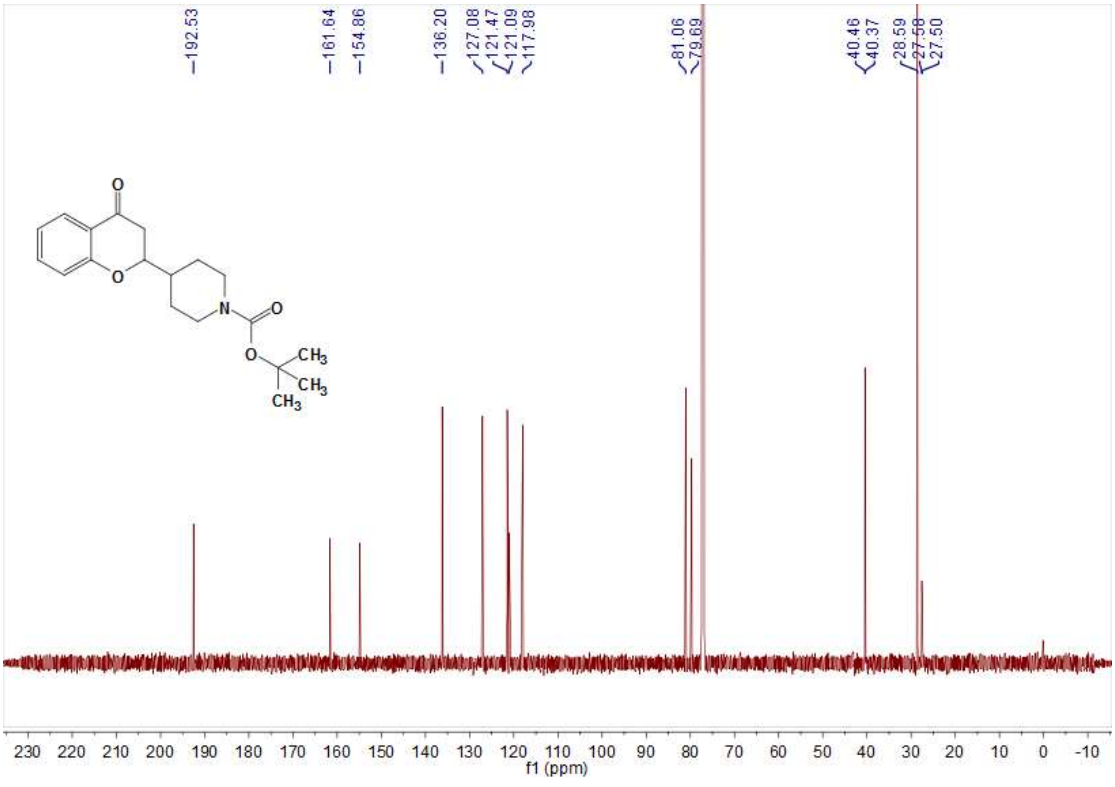


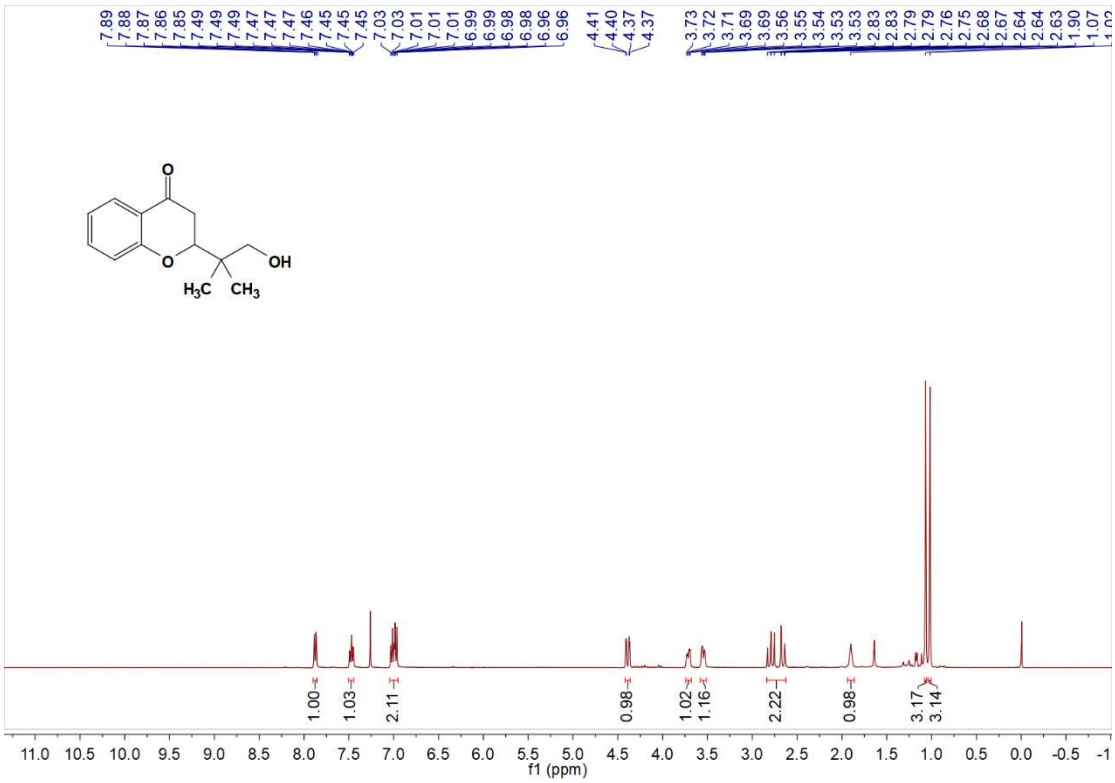
^{1}H NMR of compound 3af



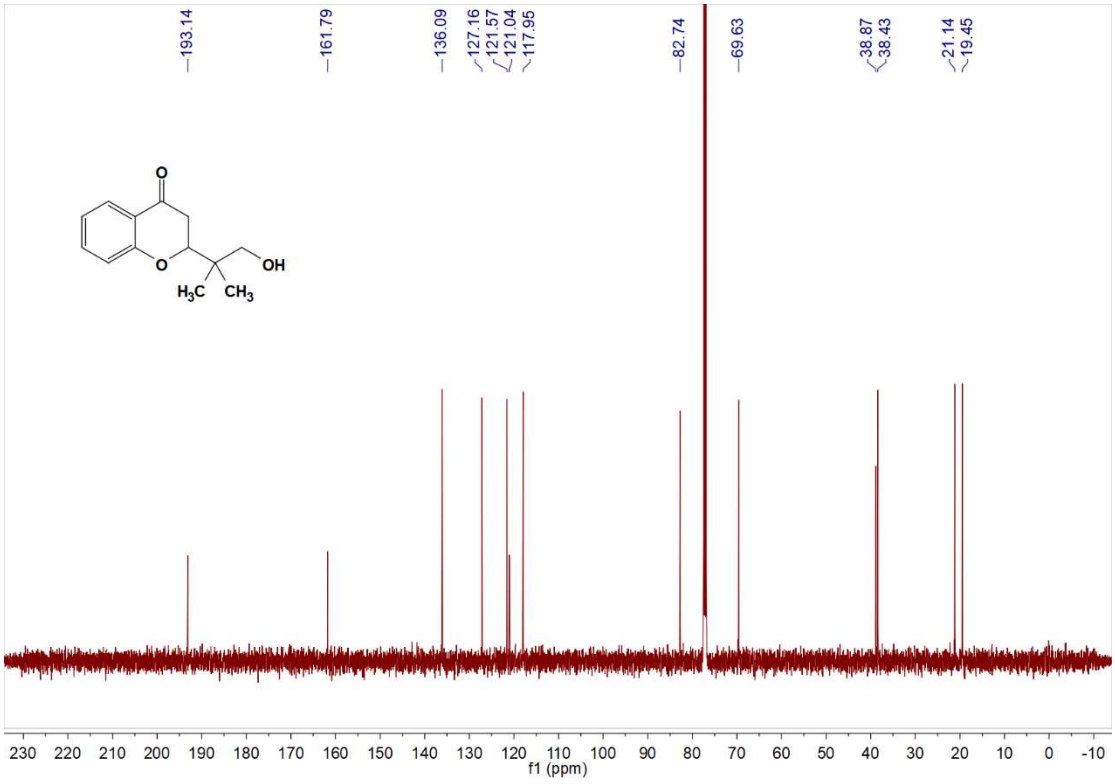
^{13}C NMR of compound 3af



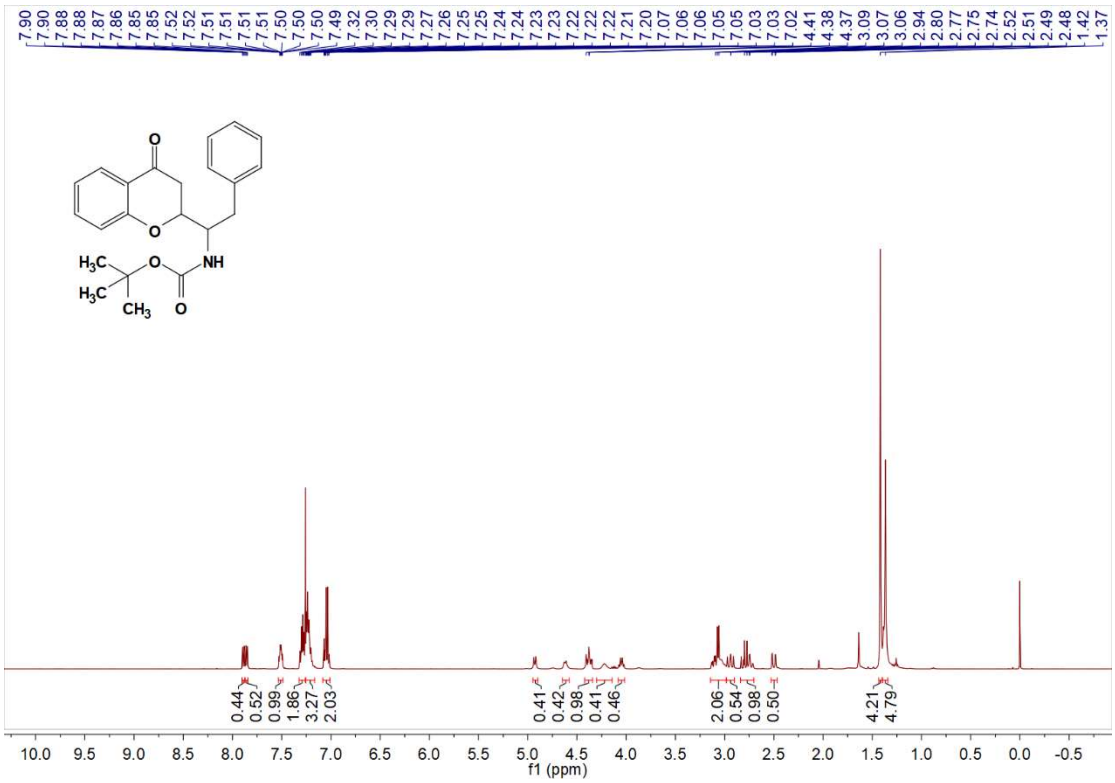
^{1}H NMR of compound 3ag



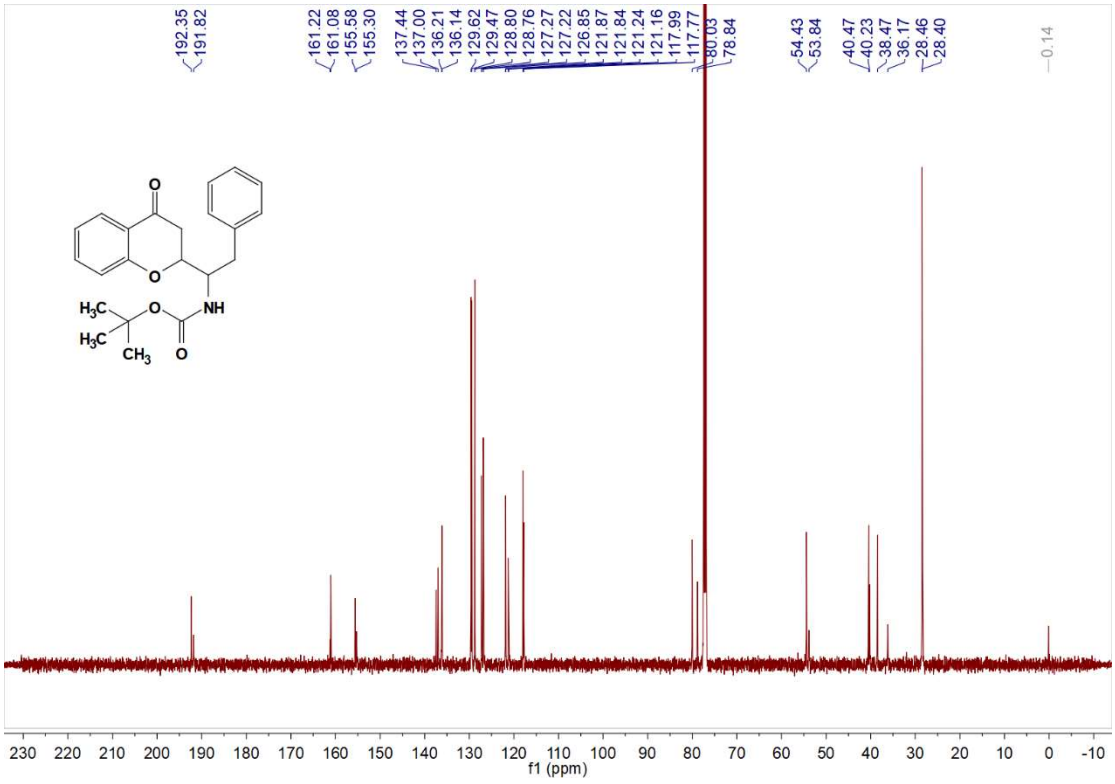
^{13}C NMR of compound 3ag



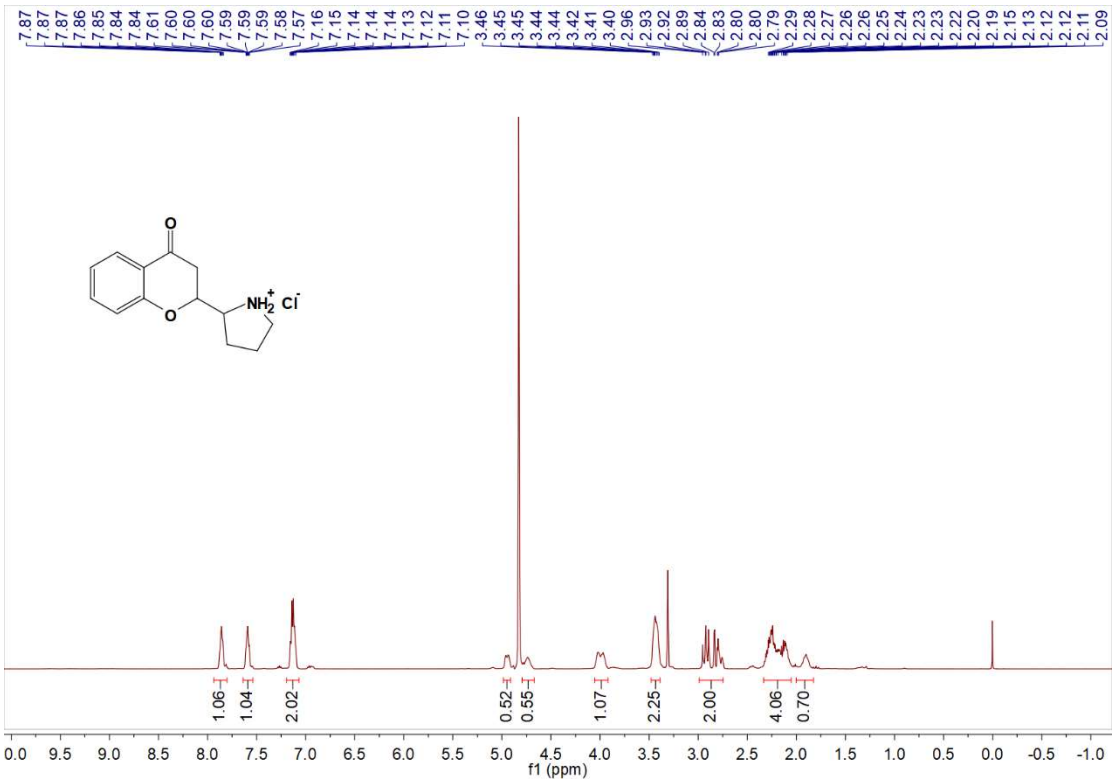
^{1}H NMR of compound 3ah



^{13}C NMR of compound 3ah



^{1}H NMR of compound De-Boc of 3ai



^{13}C NMR of compound De-Boc of 3ai