Supplymentary Information

Silver-catalyzed decarboxylative cascade radical cyclization of *tert*-carboxylic acids and *o*-(allyloxy)arylaldehydes towards chroman-4-one derivatives

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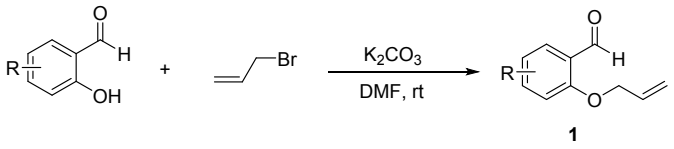
1. General information

All reagents were purchased and used without further purification. All reactions were monitored by thin layer chromatography (TLC), and column chromatography was carried out on 300–400 mesh of silica gel purchased from Qing Dao Hai Yang Chemical Industry Co. ^{1}H, ^{13}C and ^{19}F spectra were record on a Bruker Avance 400 MHz spectrometer operating at 400.1 MHz, 100.6 MHz and 376.4 MHz, respectively. All NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 3 °C). Proton chemical shifts δ were given in ppm relative to tetramethylsilane (0.00 ppm) in $CDCl_3$. High resolution mass spectra (HRMS) were obtained with a Waters Micromass Q-Tof Micro instrument using the ESI technique.

2. Experimental procedures

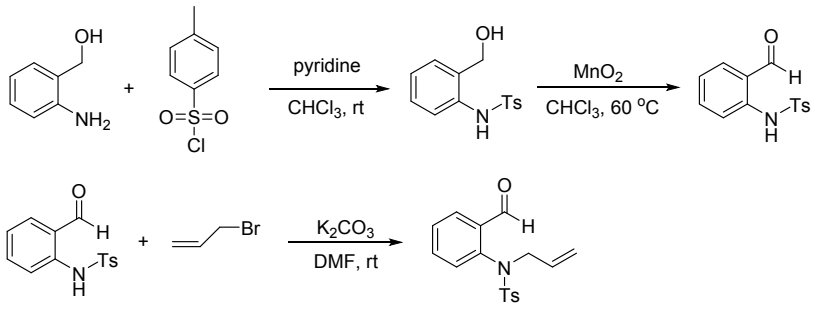
General experimental procedures for the synthesis of *o*-(allyloxy)arylaldehydes (1a-m)[1]:



1

o-(allyloxy)arylaldehyde **1** was prepared according the reported procedures. In a 50 mL round-bottomed flask with a stir bar, salicylaldehyde derivative (5 mmol, 1.0 eq.) was dissolved in 15 mL DMF and kept stirring at room temperature. To this stirring solution was added potassium carbonate (6 mmol, 1.2 eq.) followed by the dropwise addition of allyl bromide (6 mmol, 1.2 eq.). The reaction mixture was then stirred for 15 h at room temperature. Water (50 mL) was then added and the mixture was extracted with dichloromethane (3 × 25 mL). The combined organic extracts were washed with brine (50 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was then purified by flash column chromatography to afford the *o*-(allyloxy)benzaldehyde derivatives.

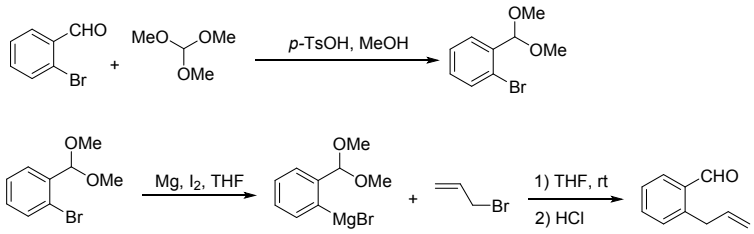
General experimental procedures for the synthesis of N-allyl-N-(2-formylphenyl)-4-methylbenzenesulfonamide[1a]:



N-containing substrate, N-allyl-N-(2-formylphenyl)-4-methylbenzenesulfonamide, was prepared according to the report. In a 100 mL round-bottom flask, 2-aminobenzyl alcohol (1.232 g, 10 mmol, 1.0 eq.) and pyridine (949 mg, 12 mmol, 1.2 eq.) were dissolved in 35 mL $CHCl_3$ and *p*-

toluenesulfonyl chloride (2.100 g, 11 mmol, 1.1 eq.) dissolved in 36 mL $CHCl_3$ was added slowly to the previous solution. The mixture reactant was stirred at room temperature for 24 h and then the solution was evaporated under reduced pressure. The remaining crude product N-(2-(hydroxymethyl)phenyl)-4-methylbenzenesulfonamide was directly used for the next step reaction without purification. 25 mL $CHCl_3$ was added to the remaining dry solid, after dissolving activated MnO_2 (4.350 g, 50 mmol, 5 eq.) was added. The mixture was stirred at 60 °C for 6 h. After completion of oxidation, the mixture was cooled to room temperature and filtered. The filtrate was evaporated under reduced pressure and the crude product was purified by silica gel chromatography (petroleum ether: ethyl acetate = 8:1 to 5:1) to give 1.730 g product N-(2-formylphenyl)-4-methylbenzenesulfonamide in 63% isolated yield. Next, N-(2-formylphenyl)-4-methylbenzenesulfonamide (1.730 g, 6.3 mmol, 1 eq.) was dissolved in 10 mL DMF and kept stirring at room temperature. To this stirring solution was added potassium carbonate (952 mg, 6.9 mmol, 1.1 eq.) followed by the dropwise addition of allyl bromide (835 mg, 6.9 mmol, 1.1 eq.). The reaction mixture was stirred for 24 h at room temperature. Water (50 mL) was then added and the mixture was extracted with DCM (3 × 25 mL). The combined organic extracts were washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was then purified by silica gel chromatography (petroleum ether: ethyl acetate = 8:1) to give 1.240 g desired product **1n** in 57% isolated yield.

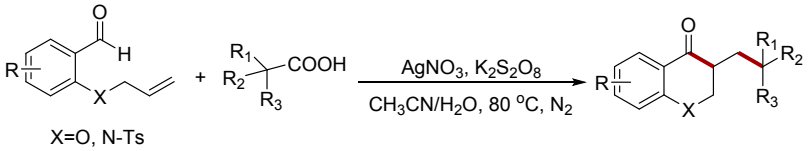
General experimental procedures for the preparation of 2-allylbenzaldehyde[2]:



In a 50 mL flask with a stir-bar was charged with 2-bromobenzaldehyde (10 mmol, 1.850 g) and *p*-TsOH (1 mmol, 180 mg). 20 mL methanol and trimethyl orthoformate (25 mmol, 2.650 g) were added and the mixture was heated to 70 °C for 8 h. Aqueous $NaHCO_3$ solution (1.5 mmol) was added and most of the THF was evaporated. The solution was extracted with dichloromethane (15 mL × 3). The combined solution was dried by anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting mixture was passed through a short silica gel to give 1-bromo-2-(dimethoxymethyl)benzene (2.195 g, 95%).

In a dry 100 mL flask with a stir-bar was charged with magnesium (0.277 g, 11.4 mmol) and a grain of iodine under N_2 atmosphere. 1-bromo-2-(dimethoxymethyl)benzene (2.195 g, 9.5 mmol) was dissolved in 25 mL dry THF and about 8 mL mixed solution was added to the above flask. The mixture was heated and stirred until the color of solution faded. Another 17 mL mixted solution was added dropwise at the reflux temperature. After 2 h the reaction was cooled to room temperature and allyl bromide (12.4 mmol, 1.500 g) was added. The reaction was stirred at room temperature for 4 h and quenched with 2M aq. HCl (10 mL). The resulting solution was extracted with ethyl acetate (15 mL × 3) and dried by anhydrous Na_2SO_4. The combined organic phases were concentrated under reduced pressure. The crude product was then purified by flash column chromatography on silica to afford the pure product as yellow oil (943 mg, 68%).

General experimental procedures for the synthesis of products 3:



A mixture of **1** (0.5 mmol), carboxylic acid **2** (2.0 mmol or 1.0 mmol), $AgNO_3$ (20 mol%) and $K_2S_2O_8$ (3 eq.) in a mixed solvent of MeCN (2.0 mL) and water (2.0 mL) was evacuated and backfilled with nitrogen gas 3 times. After the reaction mixture was stirred at 80 °C for 12 h, 15 mL ethyl acetate and 20 mL water were added. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (15 mL × 2). The combined organic layer was washed with brine (20 mL × 2), dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography to give corresponding product **3**.

Procedure for gram scale reaction

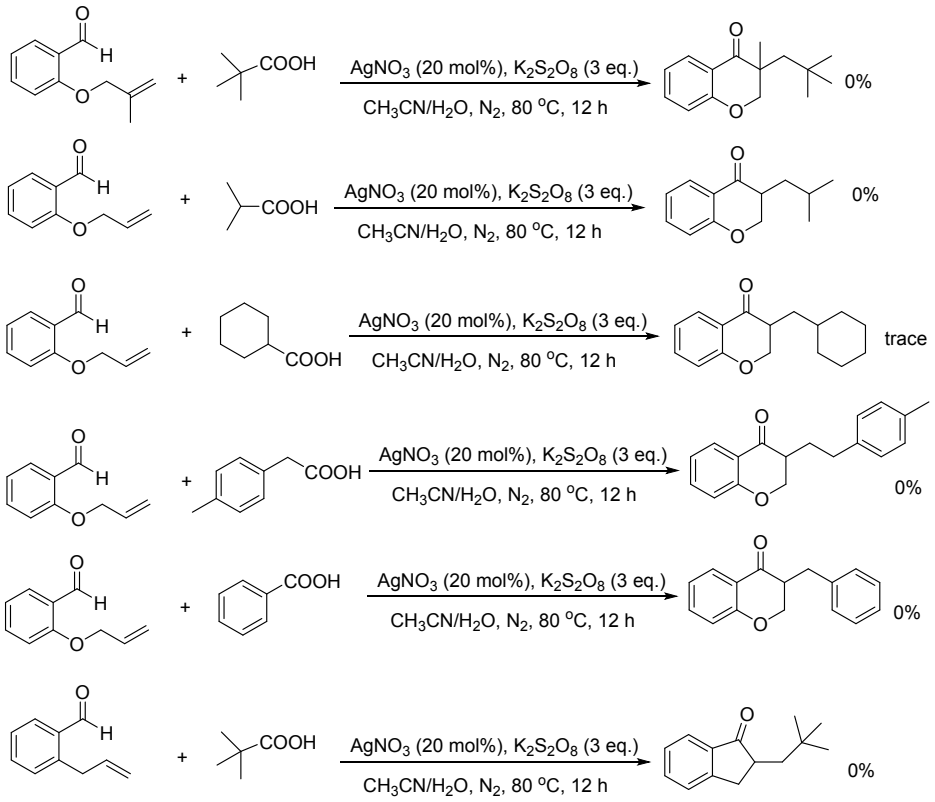
A mixture of **1a** (10 mmol), carboxylic acid **2a** (40 mmol), $AgNO_3$ (20 mol%) and $K_2S_2O_8$ (3 eq.) in a mixed solvent of MeCN (20 mL) and water (20 mL) was evacuated and backfilled with nitrogen gas 3 times. After the reaction mixture was stirred at 80 °C for 12 h, 100 mL ethyl acetate and 80 mL water were added. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (80 mL × 2). The combined organic layer was washed with brine (80 mL × 2), dried over anhydrous Na_2SO_4. After filtration, the solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography to give corresponding product **3a** (1.113 g, 51%).

Reference

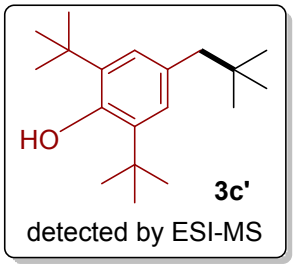
1. (a) Hirano, K.; Biju, A. T.; Piel, I.; Glorius, F. *J. Am. Chem. Soc.* **2009,** 131, 14190-14191; (b) Zhao, J.; Li, P.; Li, X.; Xia, C.; Li, F. *Chem. Commun.* **2016,** 52, 3661-3664.

2. (a) Lu, D.; Wan, Y.; Kong, L.; Zhu, G. *Org. Lett.* **2017,** 19, 2929-2932; (b) Andersen, T. L.; Donslund, A. S.; Neumann, K. T.; Skrydstrup, T. *Angew. Chem. Int. Ed.* **2017,** 57, 800-804.

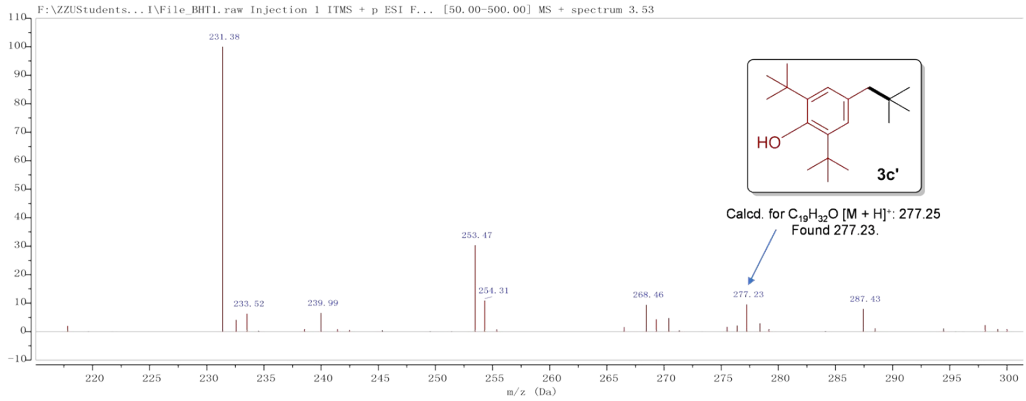
3. More investigations of the scope of the substrates



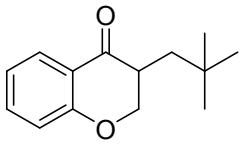
4. Characterization of compounds



Calcd. for $C_{19}H_{32}O$ $[M + H]^+$: 277.25, Found 277.23.

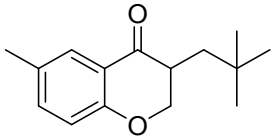


3-neopentylchroman-4-one (**3a**)



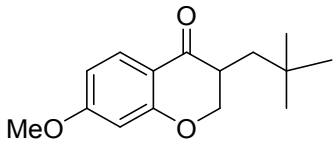
Yellow solid (81 mg, 74% yield). M. p. 54-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (s, 9H), 1.05 (dd, J = 14,4, 5.6 Hz, 1H), 2.06 (dd, J = 14.4, 4 Hz, 1H), 2.69-2.75 (m, 1H), 4.18 (t, J = 11.2 Hz, 1H), 4.50 (dd, J = 11.2 Hz, 5.2 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 7.00 (t, J = 8.0 Hz, 1H), 7.46 (td, J = 8.4, 1.6 Hz, 1H), 7.90 (dd, J = 8.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.6, 38.2, 42.7, 71.8, 117.5, 120.7, 121.1, 127.5, 135.4, 161.1, 194.5. HRMS Calcd. for $C_{14}H_{18}O_2$ $[M + H]^+$: 219.1380, Found 219.1379.

6-methyl-3-neopentylchroman-4-one (**3b**)



Yellow oil (73 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (s, 9H), 1.05 (dd, J = 14.4, 5.6 Hz, 1H), 2.04 (dd, J = 14.4, 4 Hz, 1H), 2.30 (s, 3H), 2.67-2.72 (m, 1H), 4.15 (t, J = 10.8 Hz, 1H), 4.46 (dd, J = 11.2, 4.8 Hz, 1H), 6.85 (d, J = 8.4 Hz, 1H), 7.26 (dd, J = 8.4, 2.4 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 20.4, 29.4, 30.7, 38.3, 42.8, 71.9, 117.3, 120.3, 127.1, 130.6, 136.6, 159.4, 195.0. HRMS Calcd. for $C_{14}H_{20}O_2$ $[M + H]^+$: 233.1536, Found 233.1534.

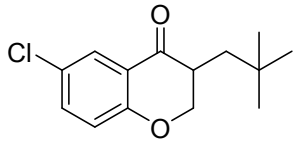
7-methoxy-3-neopentylchroman-4-one (**3c)**



Yellow solid (53 mg, 43% yield). M. p. 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (s, 9H), 1.04 (dd, J = 14.4, 6.0 Hz, 1H), 2.04 (dd, J = 14.4, 3.6 Hz, 1H), 2.62-2.68 (m, 1H), 3.83 (s, 3H), 4.16 (t, J = 10.8 Hz, 1H), 4.48 (dd, J = 11.2, 4.8 Hz, 1H), 6.39 (d, 2.4 Hz, 1H), 6.57 (dd, J = 8.8,

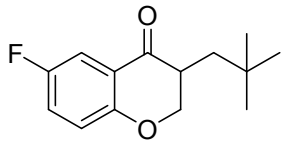
2.4 Hz, 1H), 7.83 (d, J = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.7, 38.3, 42.4, 55.6, 72.2, 100.4, 109.7, 114.6, 129.2, 163.3, 165.6, 193.5. HRMS Calcd. for $C_{15}H_{20}O_3$ $[M + H]^+$: 249.1485, Found 249.1485.

chloro-3-neopentylchroman-4-one (**3d**)



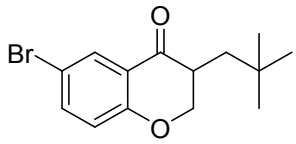
Yellow solid (90 mg, 71% yield). M. p. 43-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (s, 9H), 1.04 (dd, J = 14.4, 5.6 Hz, 1H), 2.04 (dd, J = 14.4, 3.6 Hz, 1H), 2.67-2.73 (m, 1H), 4.17 (t, J = 11.2 Hz, 1H), 4.49 (dd, J = 11.6, 5.2 Hz, 1H), 6.91 (d, J = 8.8 Hz, 1H), 7.38 (dd, J = 8.8, 2.8 Hz, 1H), 7.83 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.7, 38.2, 42.5, 72.0, 119.3, 121.5, 126.7, 126.8, 135.4, 159.8, 193.6. HRMS Calcd. for $C_{14}H_{17}ClO_2$ $[M + H]^+$: 253.0990, Found 253.0988.

6-fluoro-3-neopentylchroman-4-one (**3e**)



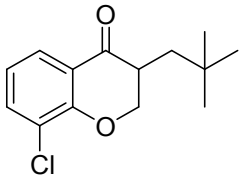
Yellow solid (68 mg, 58% yield). M. p. 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (s, 9H), 1.05 (dd, J = 14.4, 5.6 Hz, 1H), 2.04 (dd, J = 14.4, 3.6 Hz, 1H), 2.67-2.73 (m, 1H), 4.16 (t, 11.2 Hz, 1H), 4.48 (dd, J = 11.2, 4.8 Hz, 1H), 6.93 (dd, J = 9.2, 4.4 Hz, 1H), 7.15-7.20 (m, 1H), 7.53 (dd, J = 8.4, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 29.7, 38.2, 42.6, 72.0, 112.3, 112.5, 119.1, 119.2, 121.1, 121.2, 122.9, 123.2, 155.9, 157.7, 158.3, 194.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ: -121.7. HRMS Calcd. for $C_{14}H_{17}FO_2$ $[M + H]^+$: 237.1285, Found 237.1287.

6-bromo-3-neopentylchroman-4-one (**3f**)



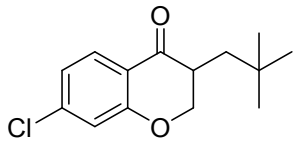
Yellow solid (99 mg, 67% yield). M. p. 52-54 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (s, 9H), 1.04 (dd, J = 14.0, 5.6 Hz, 1H), 2.03 (dd, 14.4, 3.6 Hz, 1H), 2.67-2.73 (m, 1H), 4.16 (t, J = 11.2 Hz, 1H), 4.49 (dd, J = 11.2, 4.8 Hz, 1H), 6.85 (d, J = 8.8 Hz, 1H), 7.51 (dd, J = 8.8, 2.8 Hz, 1H), 7.97 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.7, 38.2, 42.5, 71.9, 113.8, 119.7, 122.0, 129.9, 138.1, 160.3, 193.4. HRMS Calcd. for $C_{14}H_{17}BrO_2$ $[M + H]^+$: 297.0485, Found 297.0488.

8-chloro-3-neopentylchroman-4-one (**3g**)



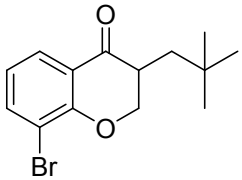
Yellow solid (88 mg, 70% yield). M. p. 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (s, 9H), 1.04 (dd, J = 14.4, 5.6 Hz, 1H), 2.04 (dd, J = 14.4, 4.0 Hz, 1H), 2.67-2.73 (m, 1H), 4.18 (t, J = 11.2 Hz, 1H), 4.50 (dd, J = 11.6, 5.2 Hz, 1H), 6.97-6.99 (m, 2H), 7.81 (dd, J = 7.2, 2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.7, 38.2, 42.6, 72.2, 117.7, 119.3, 122.0, 128.7, 141.3, 161.8, 193.7. HRMS Calcd. for $C_{14}H_{17}ClO_2$ $[M + H]^+$: 253.0990, Found 253.0992.

7-chloro-3-neopentylchroman-4-one (**3h**)



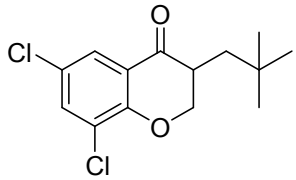
Yellow oil (78 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (s, 9H), 1.06 (dd, J = 14.4, 5.6 Hz, 1H), 2.07 (dd, J = 14.4, 3.6 Hz, 1H), 2.73-2.79 (m, 1H), 4.26 (t, J = 11.2 Hz, 1H), 4.64 (dd, J = 11.2, 5.2 Hz, 1H), 6.96 (t, 8 Hz, 1H), 7.54 (dd, J = 7.6, 1.2 Hz, 1H), 7.81 (dd, J = 7.6, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.7, 38.1, 42.4, 72.4, 121.3, 122.0, 122.3, 126.1, 135.6, 156.9, 193.8. HRMS Calcd. for $C_{14}H_{17}ClO_2$ $[M + H]^+$: 253.0990, Found 253.0094.

8-bromo-3-neopentylchroman-4-one (**3i**)



Yellow oil (96 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.97 (s, 9H), 1.05 (dd, J = 14.4, 5.6 Hz, 1H), 2.08 (dd, J = 14.4, 3.6 Hz, 1H), 2.72-2.79 (m, 1H), 4.26 (t, J = 11.2 Hz, 1H), 4.65 (dd, J = 11.2, 5.2 Hz, 1H), 6.9 (t, J = 8 Hz, 1H), 7.71 (dd, J = 8, 1.6 Hz, 1H), 7.85 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.6, 38.1, 42.3, 72.4, 111.2, 122.0, 122.02, 126.9, 138.7, 157.7, 193.8. HRMS Calcd. for $C_{14}H_{17}BrO_2$ $[M + H]^+$: 297.0485, Found 297.0484.

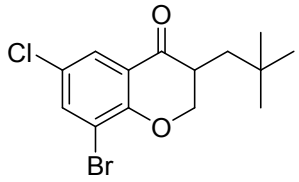
6,8-dichloro-3-neopentylchroman-4-one (**3j**)



Yellow solid (82 mg, 57% yield). M. p. 60-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (s, 9H), 1.05 (dd, J = 14.4, 5.6 Hz, 1H), 2.05 (dd, J = 14.4, 3.6 Hz, 1H), 2.72-2.78 (m, 1H), 4.25 (t, J = 11.2 Hz, 1H), 4.64 (dd, J = 11.2, 5.2 Hz, 1H), 7.52 (d, J = 2.8 Hz, 1H), 7.76 (d, J = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.3, 30.7, 38.0, 42.3, 72.5, 122.3, 123.4, 125.6, 126.4, 135.1,

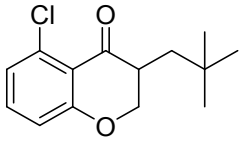
155.6, 192.7. HRMS Calcd. for $C_{14}H_{16}Cl_2O_2$ $[M + H]^+$: 287.0600, Found 287.0600.

8-bromo-6-chloro-3-neopentylchroman-4-one (**3k)**



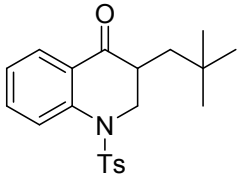
Yellow solid (84 mg, 58% yield). M. p. 81-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.96 (s, 9H), 1.05 (dd, J = 14.4, 5.6 Hz, 1H), 2.05 (dd, J = 14.4, 3.6 Hz, 1H), 2.71-2.78 (m, 1H), 4.25 (t, 11.2 Hz, 1H), 4.64 (dd, J = 11.6 Hz, 5.2Hz, 1H), 7.69 (d, J = 2.4 Hz, 1H), 7.80 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.3, 30.7, 38.0, 42.2, 72.5, 112.0, 122.1, 126.3, 126.9, 138.0, 156.4, 192.7. HRMS Calcd. for $C_{14}H_{16}BrClO_2$ $[M + H]^+$: 331.0095, Found 331.0097.

5-chloro-3-neopentylchroman-4-one (**3k**)



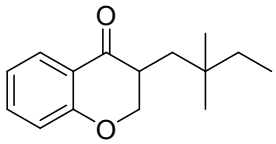
Yellow oil (44 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.95 (s, 9H), 1.09 (dd, J = 14.4, 5.6 Hz, 1H), 2.05 (dd, J = 14.4, 4.8 Hz, 1H), 2.70-2.76 (m, 1H), 4.20 (t, J = 11.2 Hz, 1H), 4.49 (dd, J = 11.2, 4.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.4, 30.6, 38.7, 43.6, 71.6, 116.6, 118.1, 124.4, 134.3, 134.4, 162.6, 193.1. HRMS Calcd. for $C_{14}H_{17}ClO_2$ $[M + H]^+$: 253.0990, Found 253.0994.

3-neopentyl-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one (**3l**)



Yellow oil (83 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89-0.94 (m, 9H + 1H), 2.02 (dd, J = 14, 2.8 Hz, 1H), 2.25-2.33 (m, 1H), 2.38 (s, 3H), 3.64 (t, J = 14 Hz, 1H), 4.51 (dd, J = 14, 5.2 Hz, 1H), 7.21-7.25 (m, 2H + 1H), 7.54 (td, J = 7.8, 2.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.86 (dd, J = 8.4, 0.4 Hz, 1H), 7.97 (dd, J = 8.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.5, 29.4, 30.7, 40.3, 42.5, 52.3, 123.2, 124.9, 125.1, 126.9, 128.2, 130.0, 134.3, 136.9, 144.2, 144.5, 195.7. HRMS Calcd. for $C_{21}H_{25}NO_3S$ $[M + H]^+$: 372.1628, Found 372.1630.

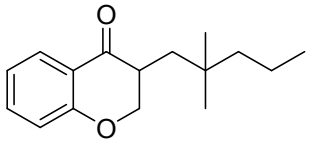
3-(2,2-dimethylbutyl)chroman-4-one (**3m**)



Yellow oil (74 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.85 (t, J = 7.6 Hz, 3H), 0.90 (s,

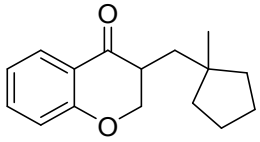
9H), 1.05 (dd, *J* = 14.8, 6 Hz, 1H), 1.25-1.35(m, 2H), 2.06 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.68-2.74 (m, 1H), 4.17 (t, *J* = 11.2 Hz, 1H), 4.49 (dd, *J* = 11.2, 5.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 7.45 (m, 1H), 7.89 (dd, *J* = 8.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 8.4, 26.50, 26.55, 33.1, 34.3, 36.0, 42.4, 71.9, 117.5, 120.8, 121.2, 127.5, 135.5, 161.4, 194.8. HRMS Calcd. for $C_{15}H_{20}O_2$ $[M + H]^+$: 233.1536, Found 233.1538.

3-(2,2-dimethylpentyl)chroman-4-one (**3n**)



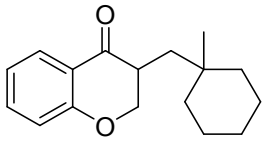
Yellow oil (64 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.87-0.91 (m, 3H+6H), 1.05 (dd, *J* = 14.4, 6 Hz, 1H), 1.18-1.30 (m, 2H+2H), 2.06 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.69-2.75 (m, 1H), 4.17 (t, *J* = 11.2 Hz, 1H), 4.49 (dd, *J* = 11.2, 4.8 Hz, 1H), 6.94 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.98-7.02 (m, 1H), 7.43-7.47 (m, 1H), 7.89 (dd, *J* = 8.0, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 14.9, 17.2, 27.0, 27.1, 36.2, 36.4, 42.4, 44.6, 72.0, 117.5, 120.8, 121.2, 127.5, 135.5, 161.4, 194.8. HRMS Calcd. for $C_{16}H_{22}O_2$ $[M + H]^+$: 247.1693, Found 247.1695.

3-((1-methylcyclopentyl)methyl)chroman-4-one (**3o**)



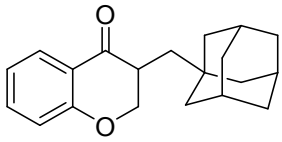
Yellow oil (43 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 1.01 (s, 3H), 1.21 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.37-1.43 (m, 4H), 1.63-1.67 (m, 4H), 2.15 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.71-2.77 (m, 1H), 4.21 (t, *J* = 11.2 Hz, 1H), 4.52 (dd, *J* = 11.2, 4.8 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 7.02 (m, 1H), 7.43-7.48 (m, 1H), 7.89 (dd, 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 24.1, 24.4, 25.9, 36.8, 39.4, 39.8, 42.2, 43.6, 71.8, 117.5, 120.7, 121.2, 127.5, 135.6, 161.4, 195.0. HRMS Calcd. for $C_{16}H_{20}O_2$ $[M + H]^+$: 245.1536, found 245.1539.

3-((1-methylcyclohexyl)methyl)chroman-4-one (**3p**)



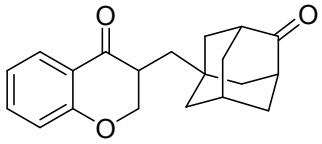
Yellow oil (69 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.93 (s, 3H,), 1.06 (dd, *J* = 14.4, 5.2 Hz, 1H), 1.25-1.33 (m, 6H), 1.40-1.51 (m, 4H), 2.09 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.71-2.77 (m, 1H), 4.18 (t, *J* = 11.2 Hz, 1H), 4.49 (dd, *J* = 11.2, 5.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 7.43-7.48 (m, 1H), 7.88 (dd, *J* = 8.0, 2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 21.9, 22.0, 26.3, 33.0, 37.5, 37.9, 41.9, 72.1, 117.5, 120.8, 121.2, 127.5, 135.5, 161.4, 194.9. HRMS Calcd. for $C_{17}H_{22}O_2$ $[M + H]^+$: 259.1693, Found 259.1697.

3-(adamantan-1-ylmethyl)chroman-4-one (**3q**)



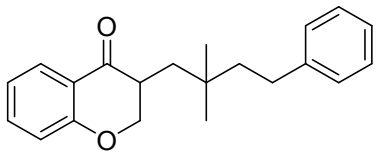
White solid (86 mg, 58% yield). M. p. 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.90 (dd, J = 14.4, 5.6 Hz, 1H), 1.53 (s, 6H), 1.63 (d, J = 11.6 Hz, 3H), 1.70 (d, J = 11.6 Hz, 3H), 1.91 (dd, J = 14.4, 3.6 Hz, 1H), 1.97 (s, 3H), 2.77-2.81 (m, 1H), 4.14 (t, J = 11.2 Hz, 1H), 4.45 (dd, J = 11.2, 4.8 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.4 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.5, 32.4, 36.9, 38.8, 40.8, 42.3, 72.1, 117.5, 120.8, 121.1, 127.5, 135.5, 161.4, 194.9. HRMS Calcd. for $C_{20}H_{24}O_2$ $[M + H]^+$: 297.1849, Found 297.1850.

3-(4-oxoadamantan-1-ylmethyl)chroman-4-one (**3r**)



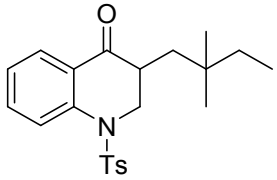
Yellow solid (64 mg, 41%). M. p. 57-59 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (dd, J = 14.4, 5.2 Hz, 1H), 1.80 (s, 2H), 1.86 (s, 4H), 1.99 (s, 4H), 2.05 (dd, J = 14.8, 4.4 Hz, 1H), 2.16-2.17 (m, 1H), 2.57 (s, 2H), 2.74-2.80 (m, 1H), 4.17 (t, J = 11.2 Hz, 1H), 4.45 (dd, J = 11.2, 4.8 Hz, 1H), 6.96 (d, J = 8.4 Hz, 1H), 7.01-7.05 (m, 1H), 7.46-7.50 (m, 1H), 7.88 (dd, J = 8.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.7, 32.5, 37.1, 38.6, 40.9, 41.0, 43.2, 43.3, 46.25, 46.28, 71.8, 117.6, 120.6, 121.3, 127.5, 135.7, 161.3, 194.3, 217.9. HRMS Calcd. for $C_{20}H_{22}O_3$ $[M + H]^+$: 311.1642, Found 311.1646.

3-(2,2-dimethyl-4-phenylbutyl)chroman-4-one (**3s**)



Yellow oil (80 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.02 (d, J = 2.4 Hz, 6H), 1.12 (dd, J = 14.4, 5.6 Hz, 1H), 1.49-1.63 (m, 2H), 2.17 (dd, J = 14.4, 3.6 Hz, 1H), 2.53-2.68 (m, 2H), 2.72-2.79 (m, 1H), 4.19 (t, J = 11.2 Hz, 1H), 4.50 (dd, J = 11.6, 5.2 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 7.01 (m, 1H), 7.14-7.19 (m, 3H), 7.25-7.29 (m, 2H), 7.46 (m, 1H), 7.91 (dd, J = 8.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.0, 30.7, 33.3, 36.4, 42.4, 44.4, 71.9, 117.6, 120.7, 121.3, 125.6, 127.5, 128.3, 128.3, 135.6, 143.0, 161.4, 194.7. HRMS Calcd. for $C_{21}H_{24}O_2$ $[M + H]^+$: 309.1849, Found 309.1850.

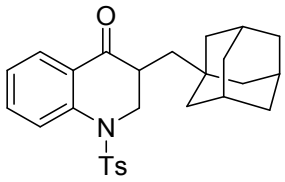
3-(2,2-dimethylbutyl)-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one (**3t**)



Yellow oil (92 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.81-0.84 (m, 3H + 6H), 0.90 (dd, J =

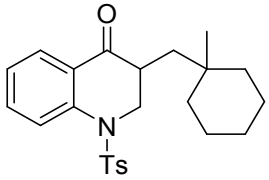
14.4, 6.0 Hz, 1H), 1.16-1.22 (m, 2H), 2.02 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.25-2.33 (m , 1H), 2.38 (s, 3H), 3.64 (t, *J* = 14.0 Hz, 1H), 4.49 (dd, *J* = 14.0 Hz, 1H), 7.21-7.25 (m, 2H + 1H), 7.51-7.55 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 8.4, 21.5, 26.4, 26.5, 33.1, 34.3, 38.2, 42.1, 52.4, 123.2, 124.9, 125.1, 126.9, 128.2, 130.0, 134.3, 136.9, 142.2, 144.5, 195.8. HRMS Calcd. for $C_{22}H_{27}NO_3S$ $[M + H]^+$: 386.1784, Found 386.1788.

3-(adamantan-1-ylmethyl)-1-tosyl-2,3-dihydroquinolin-4(1*H*)-one (**3u**)



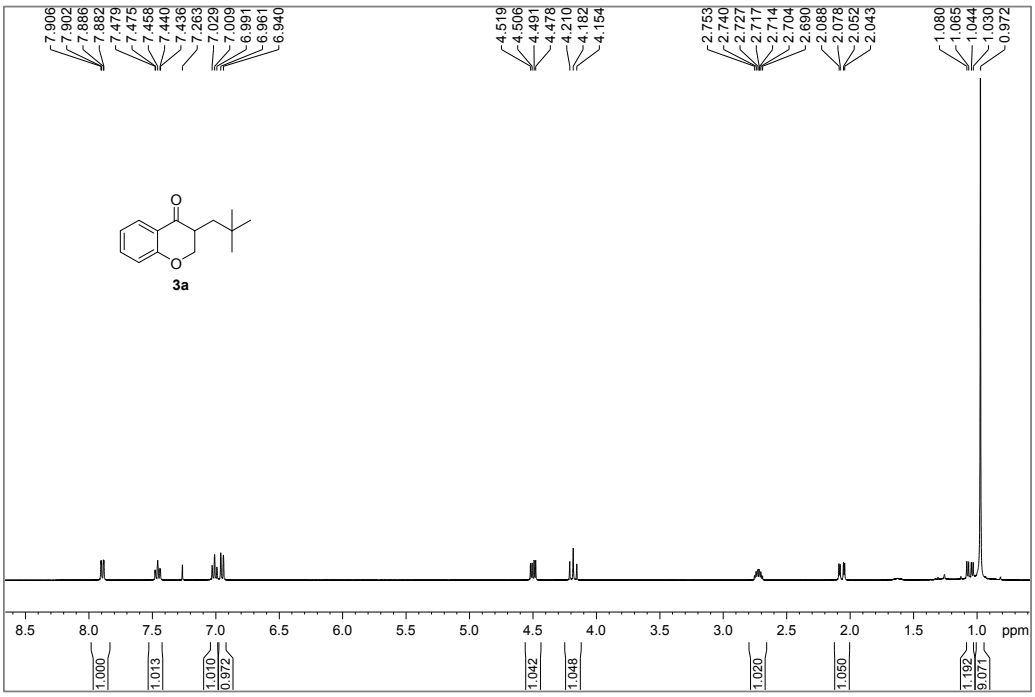
Yellow oil (58 mg, 26%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.74 (dd, *J* = 14.4, 5.6 Hz, 1H), 1.39 (q, 6H), 1.60 (d, *J* = 11.6 Hz, 3H), 1.72 (d, *J* = 12 Hz, 3H), 1.85 (dd, *J* = 14.4, 3.2 Hz, 1H), 1.96 (s, 3H), 2.24-2.31 (m, 1H), 2.38 (s, 3H), 3.62 (t, *J* = 14.0 Hz, 1H), 4.43 (dd, 14.0, 5.2 Hz, 1H), 7.22-7.26 (m, 2H + 1H), 7.52-7.56 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 7.6, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 21.5, 28.5, 32.4, 36.9, 40.3, 41.0, 42.2, 52.5, 123.5, 124.9, 125.2, 127.0, 128.2, 130.0, 134.3, 137.1, 142.3, 144.5, 196.0. HRMS Calcd. for $C_{27}H_{31}NO_3S$ $[M + H]^+$: 450.2097, Found 450.2100.

3-((1-methylcyclohexyl)methyl)-1-tosyl-2,3-dihydroquinolin-4(1*H)*-one (**3v**)

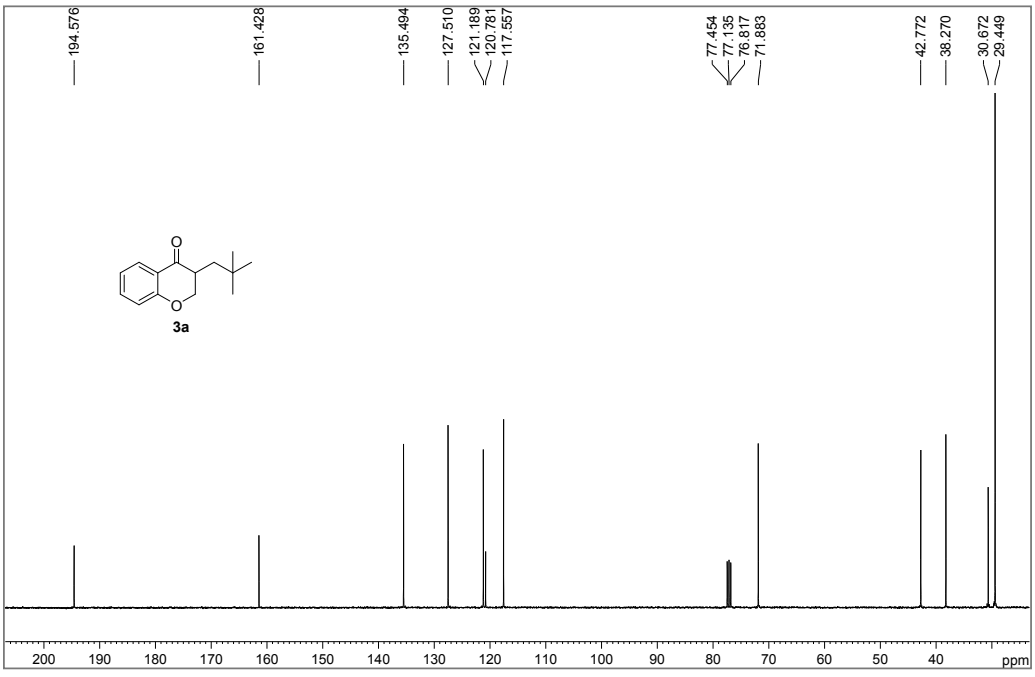


Yellow oil (84 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 0.84 (s, 3H), 0.91 (dd, *J* = 14.4, 6.0 Hz, 1H), 1.16-1.46 (m, 10H), 2.06 (dd, *J* = 14.4, 2.8 Hz, 1H), 2.26-2.33 (m, 1H), 2.38 (s, 3H), 3.64 (t, *J* = 13.6 Hz, 1H), 4.48 (dd, *J* = 14.0, 5.2 Hz, 1H), 7.21-7.24 (m, 2H + 1H), 7.51-7.56 (m, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 21.5, 21.93, 21.99, 26.3, 33.0, 37.4, 37.9, 41.6, 52.5, 123.2, 124.9, 125.1, 126.9, 128.2, 130.0, 134.3, 136.9, 142.2, 144.5, 195.9. HRMS Calcd. for $C_{24}H_{29}NO_3S$ $[M + H]^+$: 412.1941, Found 412.1944.

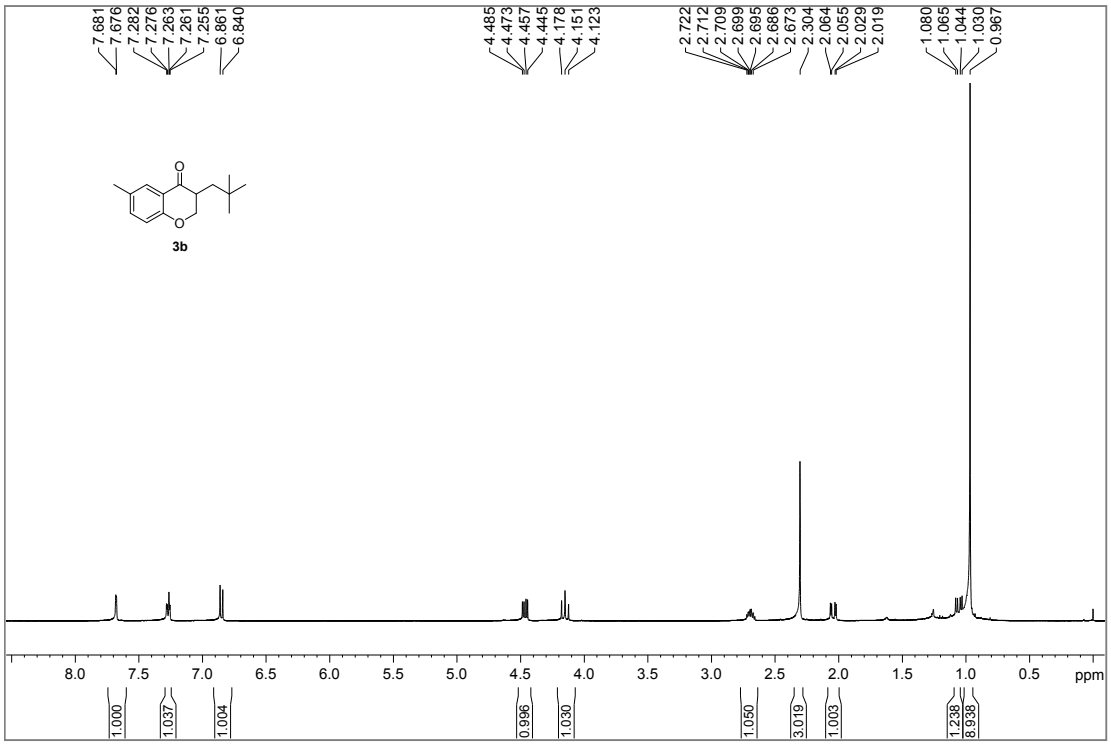
5. ^{1}H NMR and ^{13}C NMR copies of the products



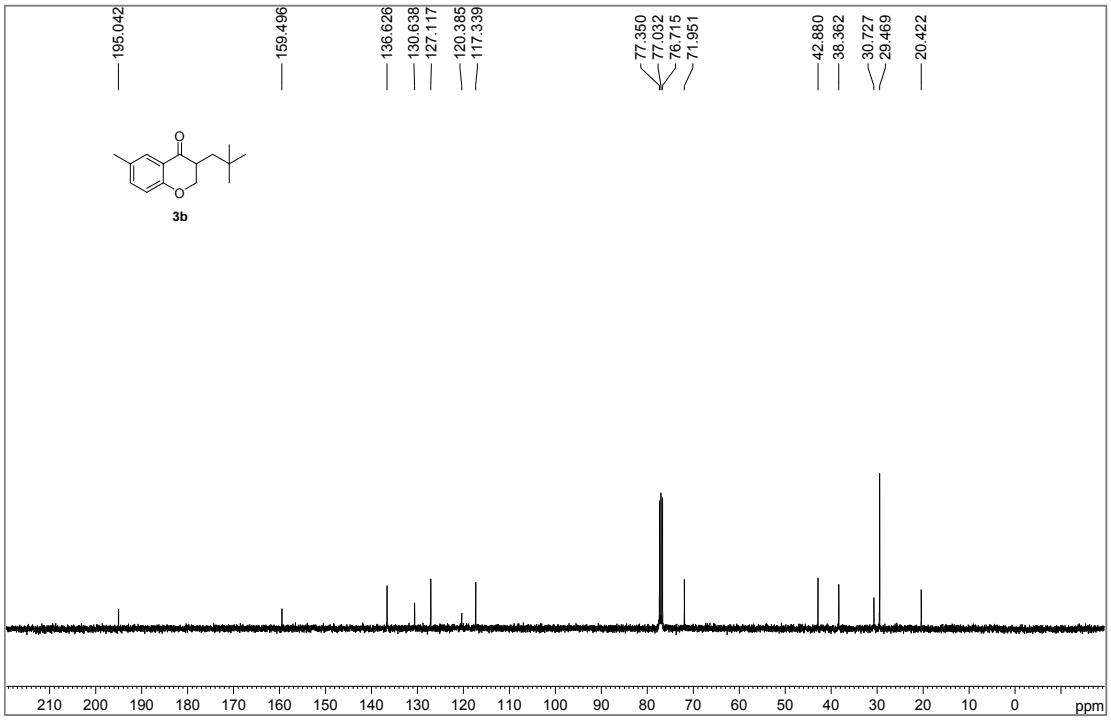
^{1}H NMR spectrum of compound **3a**



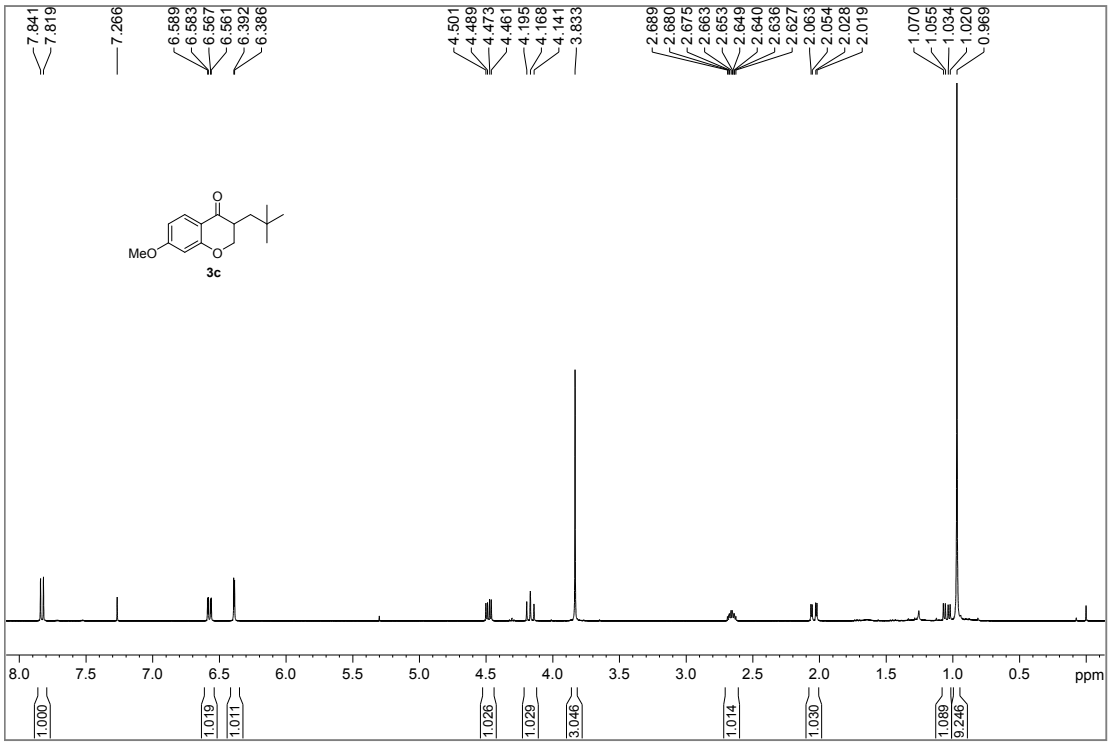
^{13}C NMR spectrum of compound **3a**



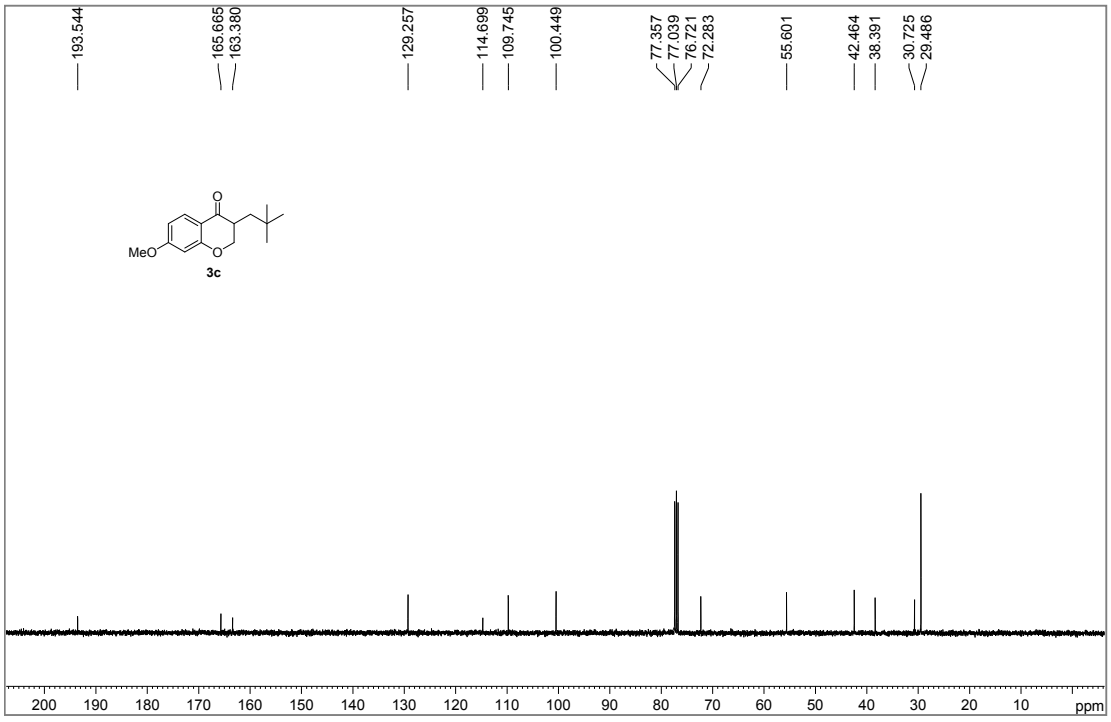
^{1}H NMR spectrum of compound **3b**



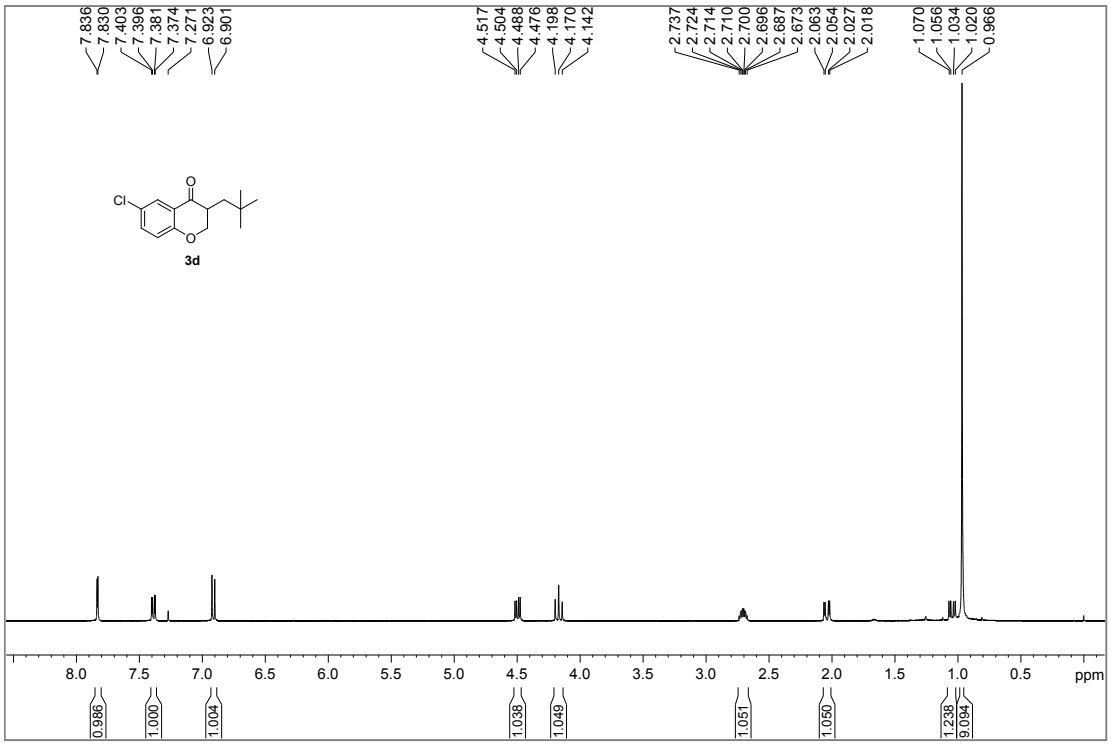
^{13}C NMR spectrum of compound **3b**



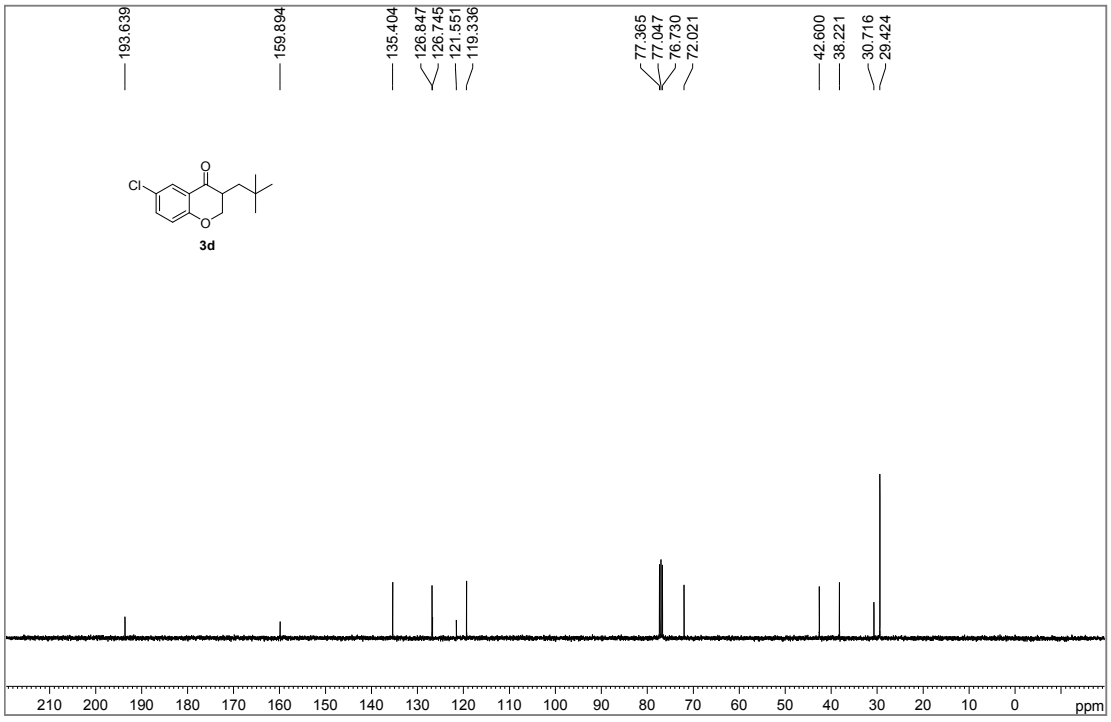
^{1}H NMR spectrum of compound **3c**



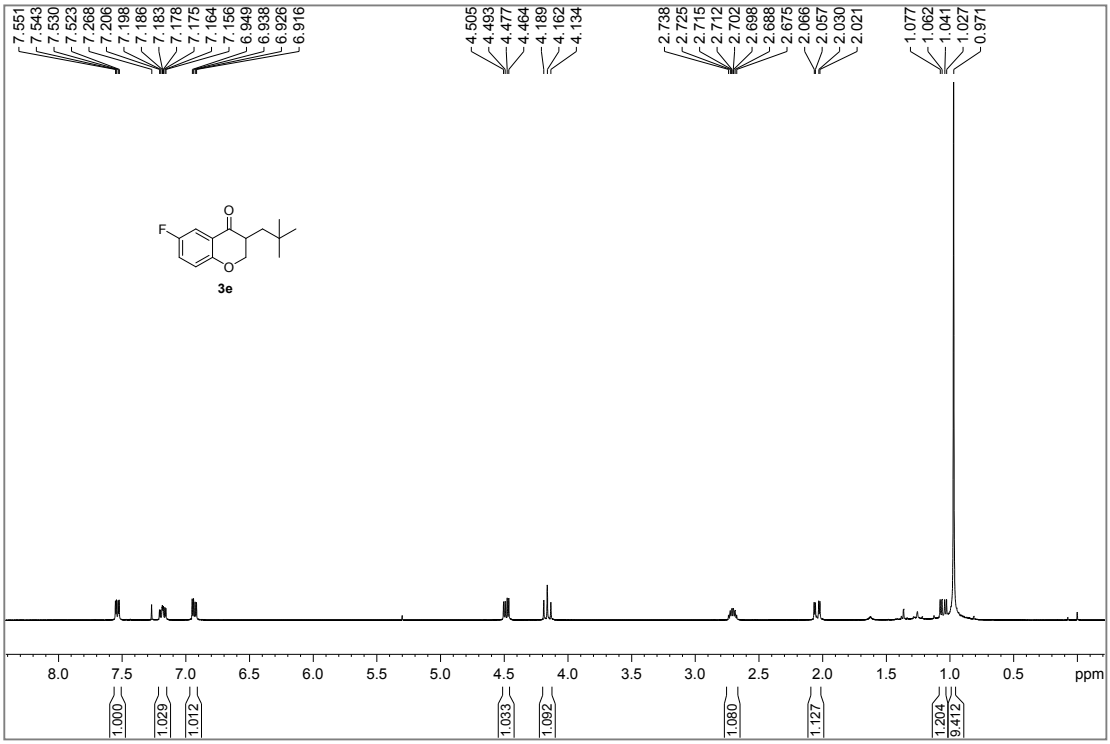
^{13}C NMR spectrum of compound **3c**



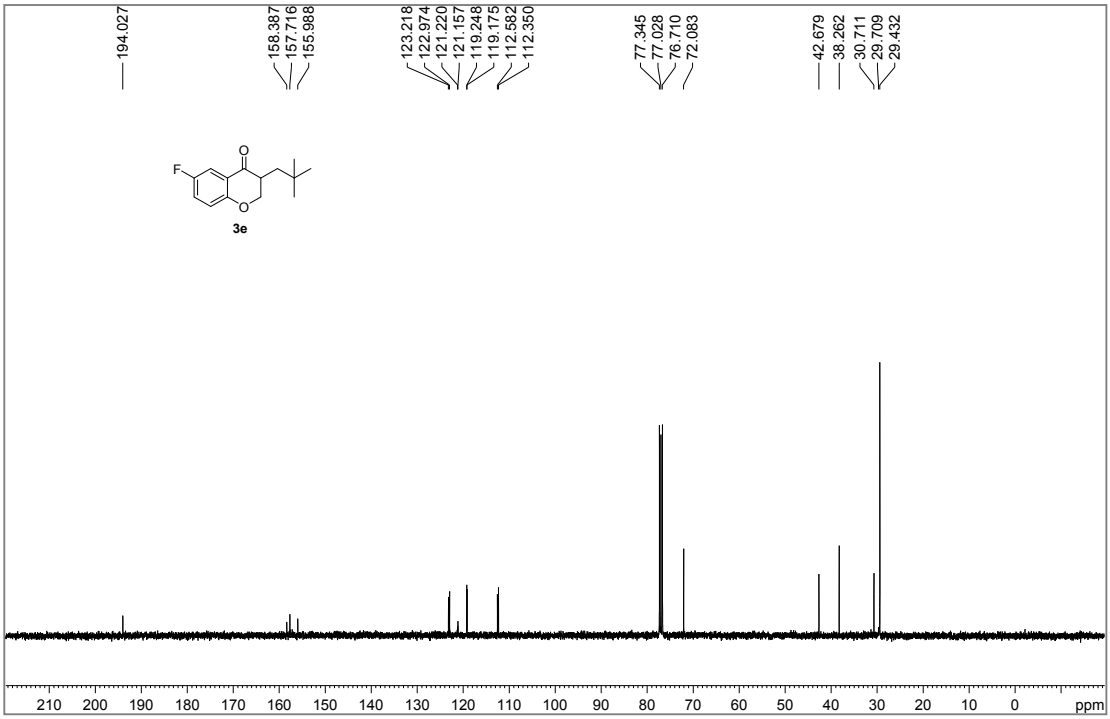
^{1}H NMR spectrum of compound **3d**



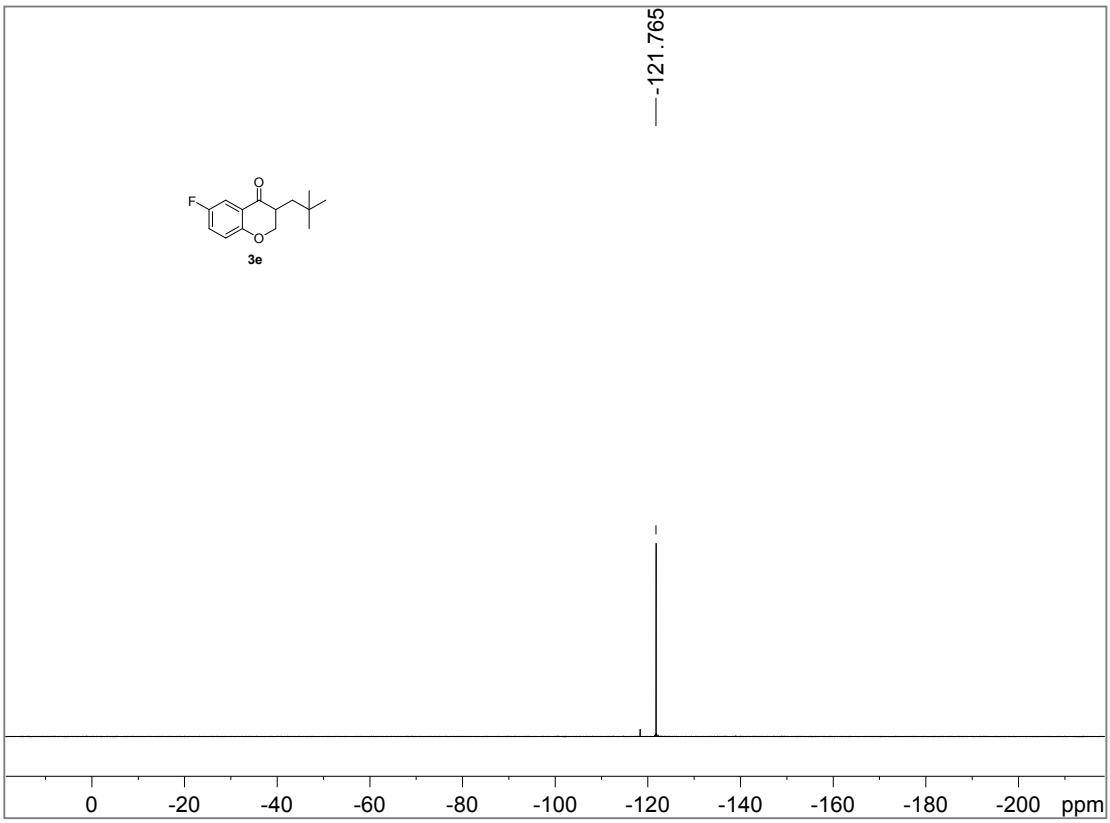
^{13}C NMR spectrum of compound **3d**



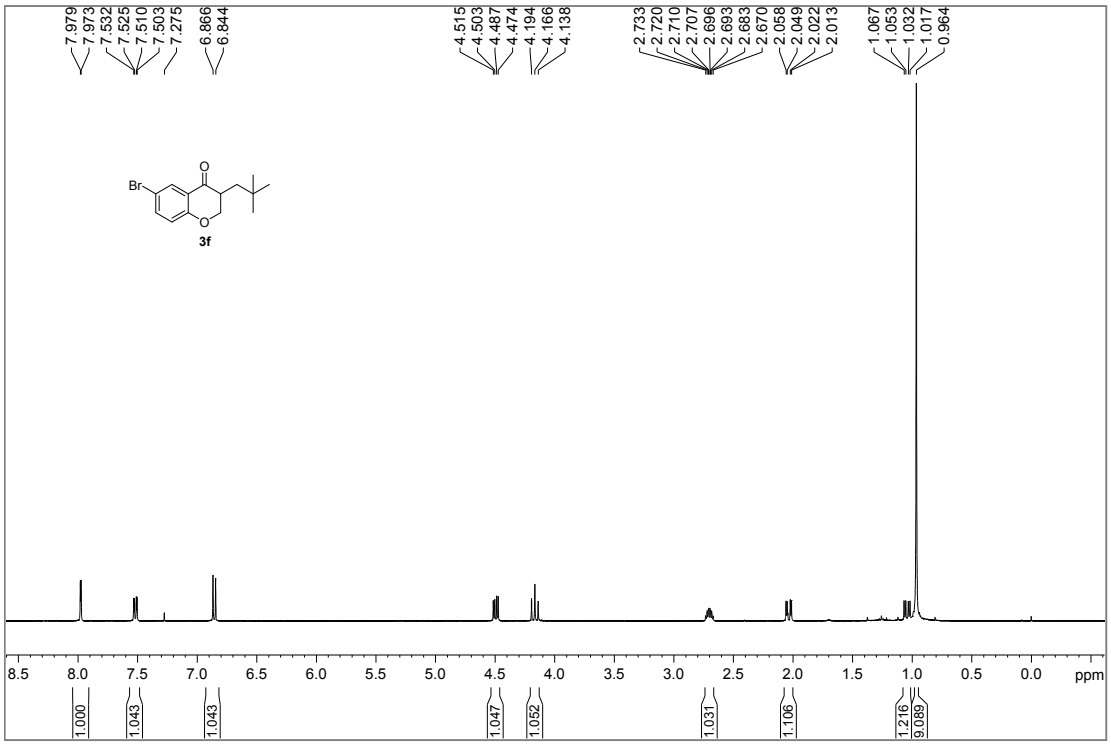
^{1}H NMR spectrum of compound **3e**



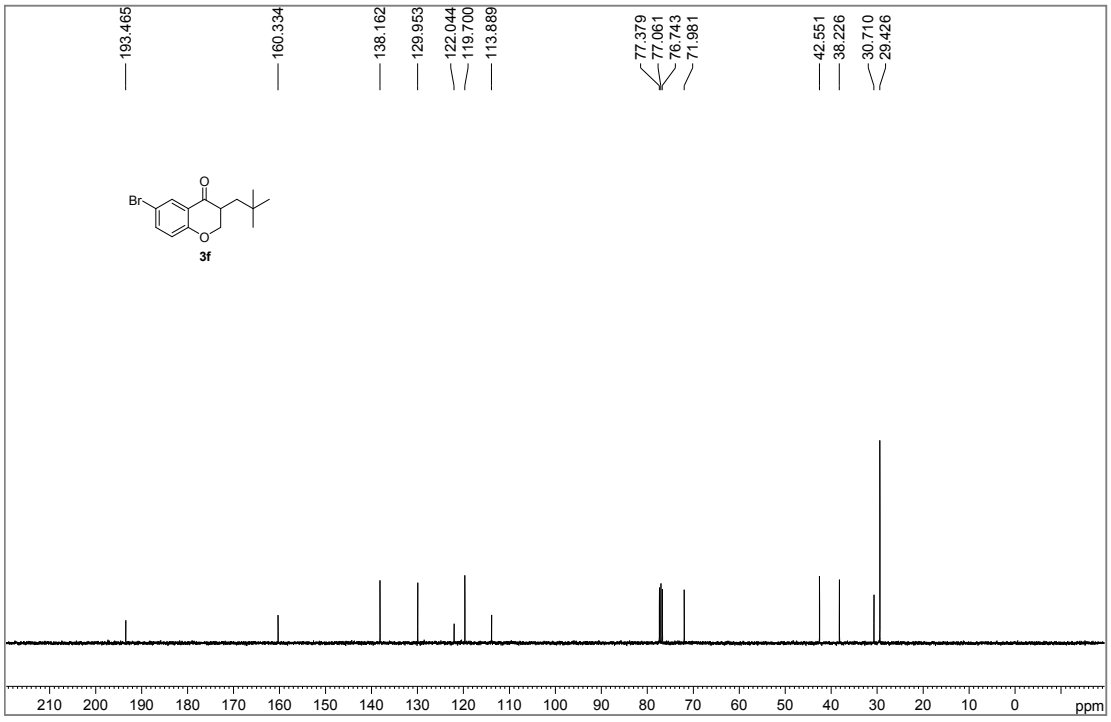
^{13}C NMR spectrum of compound **3e**



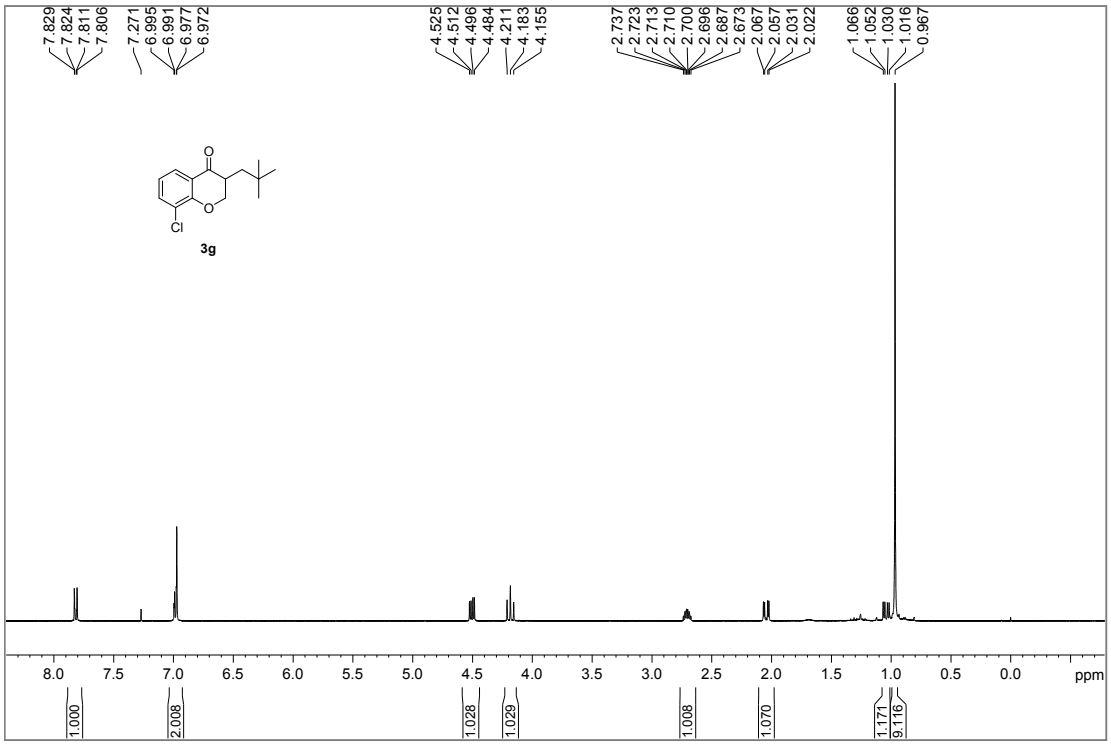
^{19}F NMR spectrum of compound **3e**



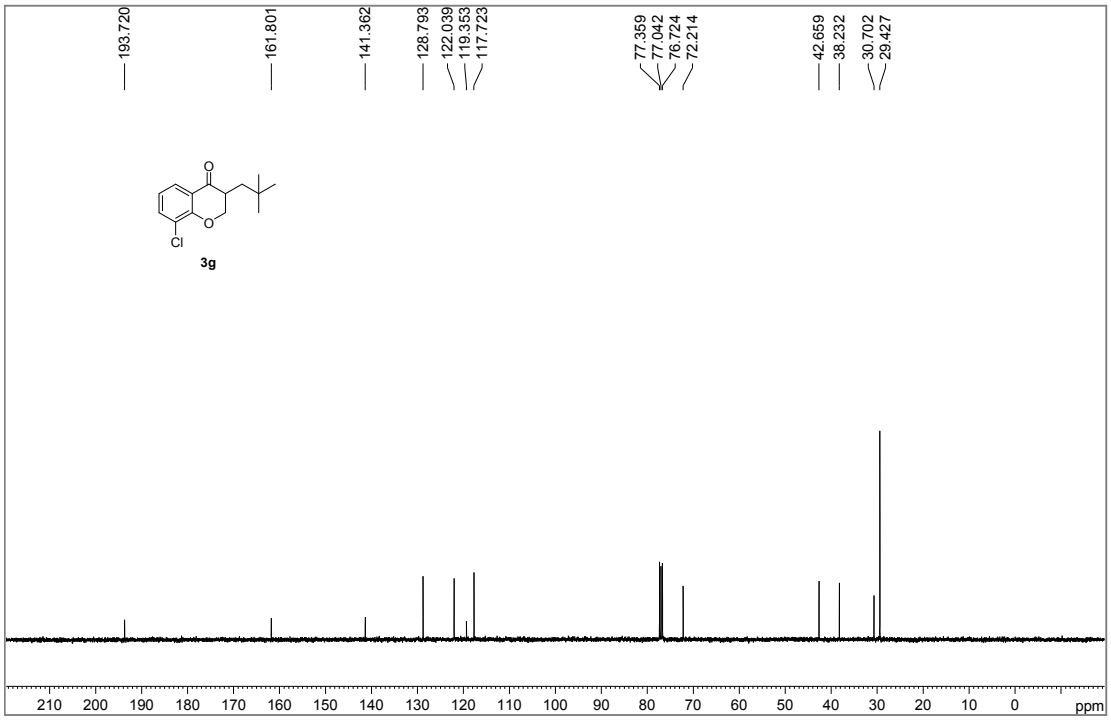
^{1}H NMR spectrum of compound **3f**



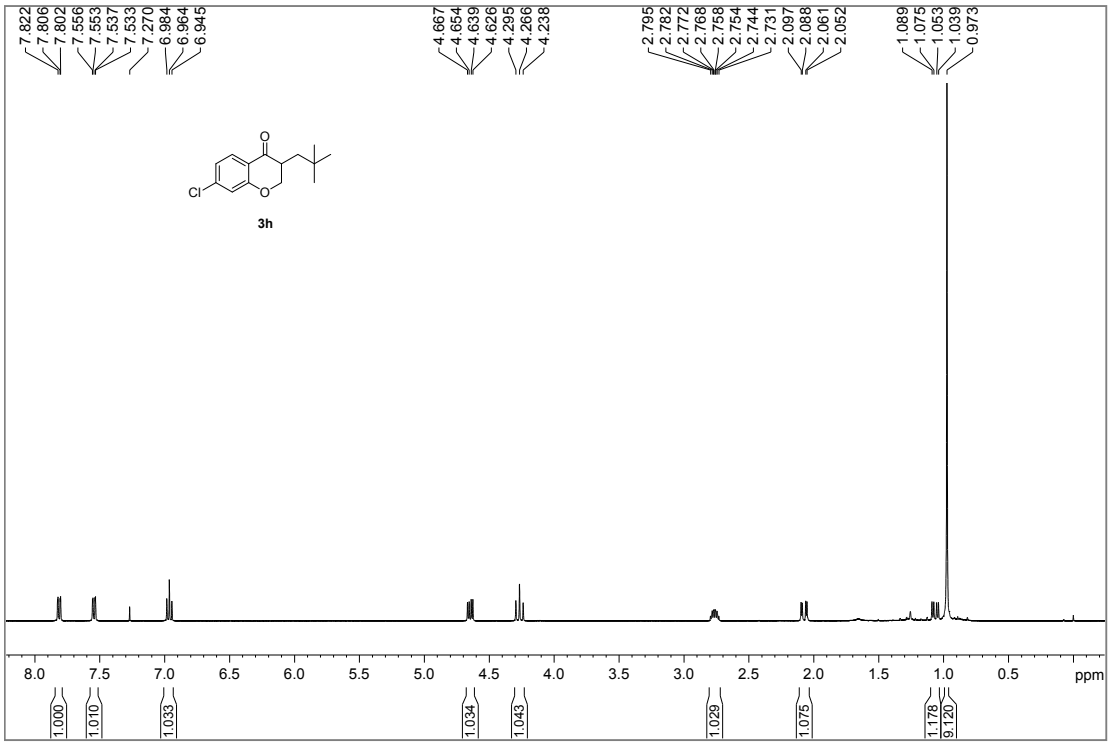
^{13}C NMR spectrum of compound **3f**



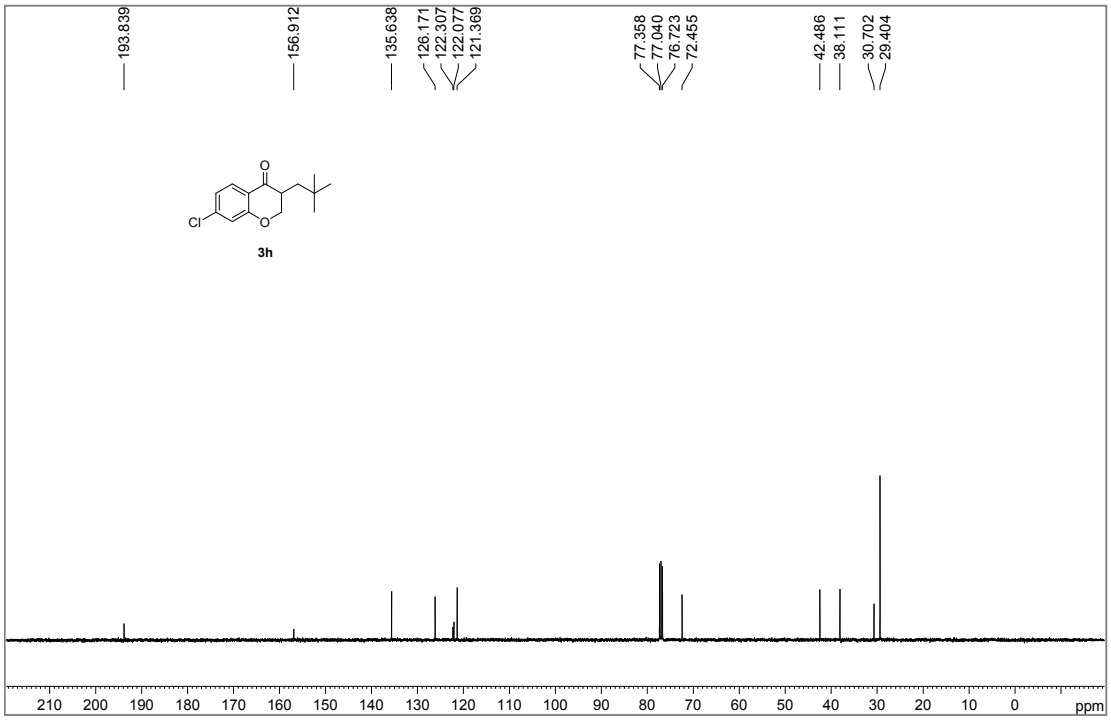
^{1}H NMR spectrum of compound **3g**



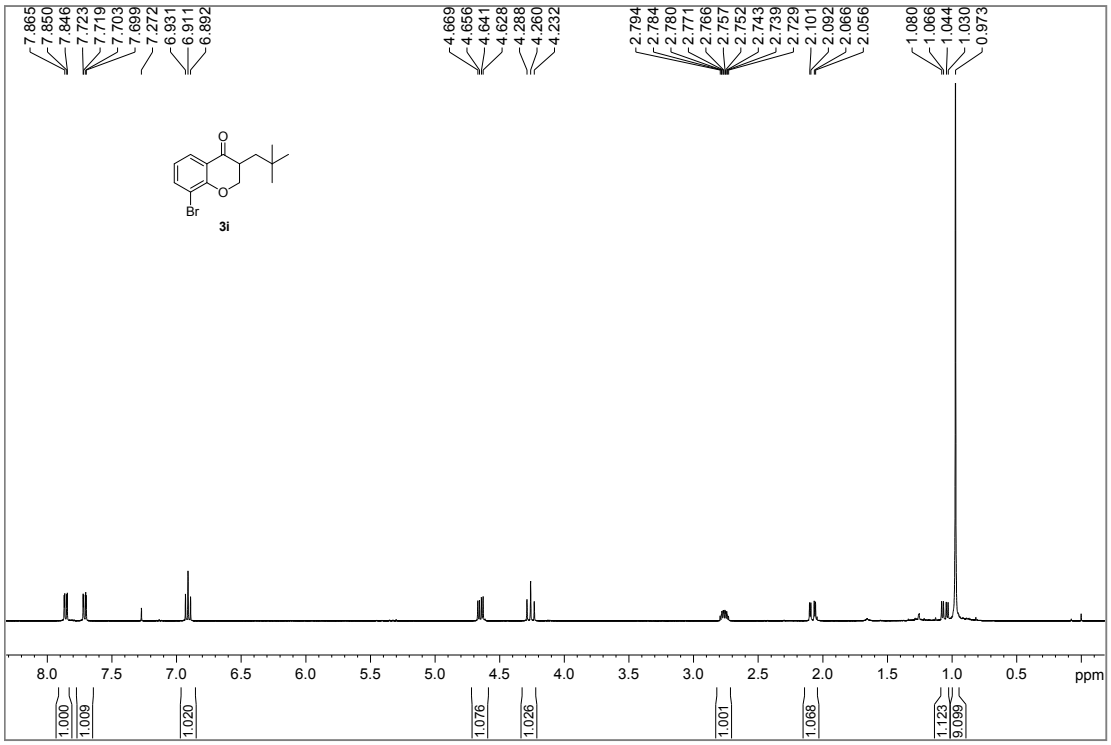
^{13}C NMR spectrum of compound **3g**



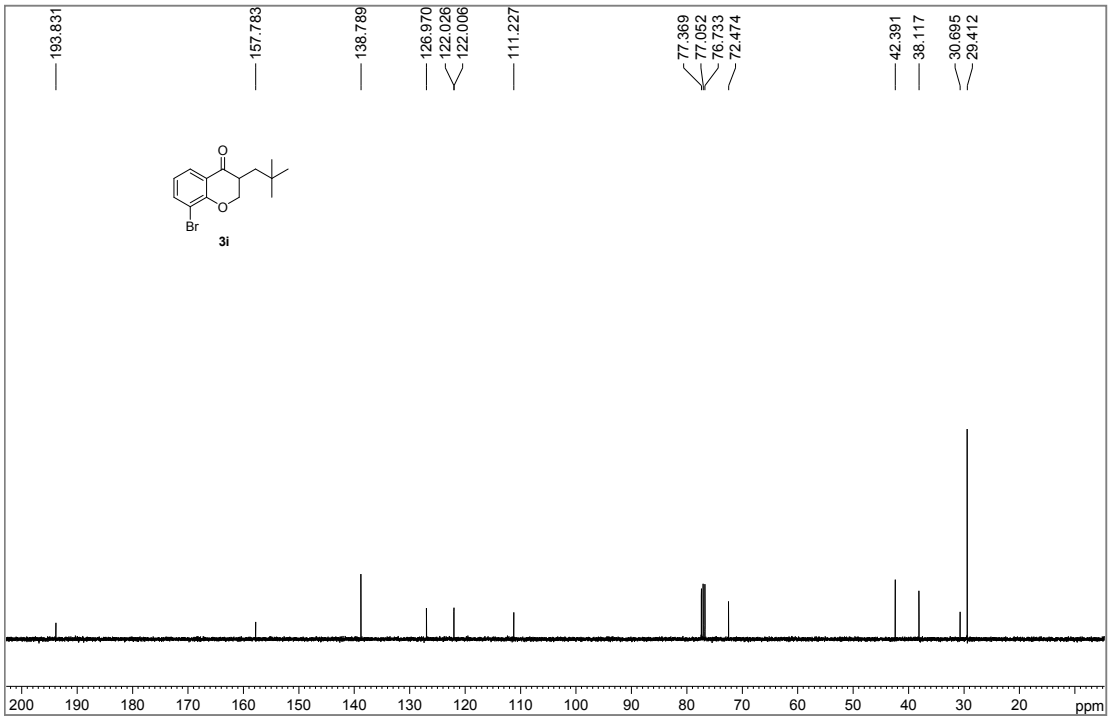
^{1}H NMR spectrum of compound **3h**



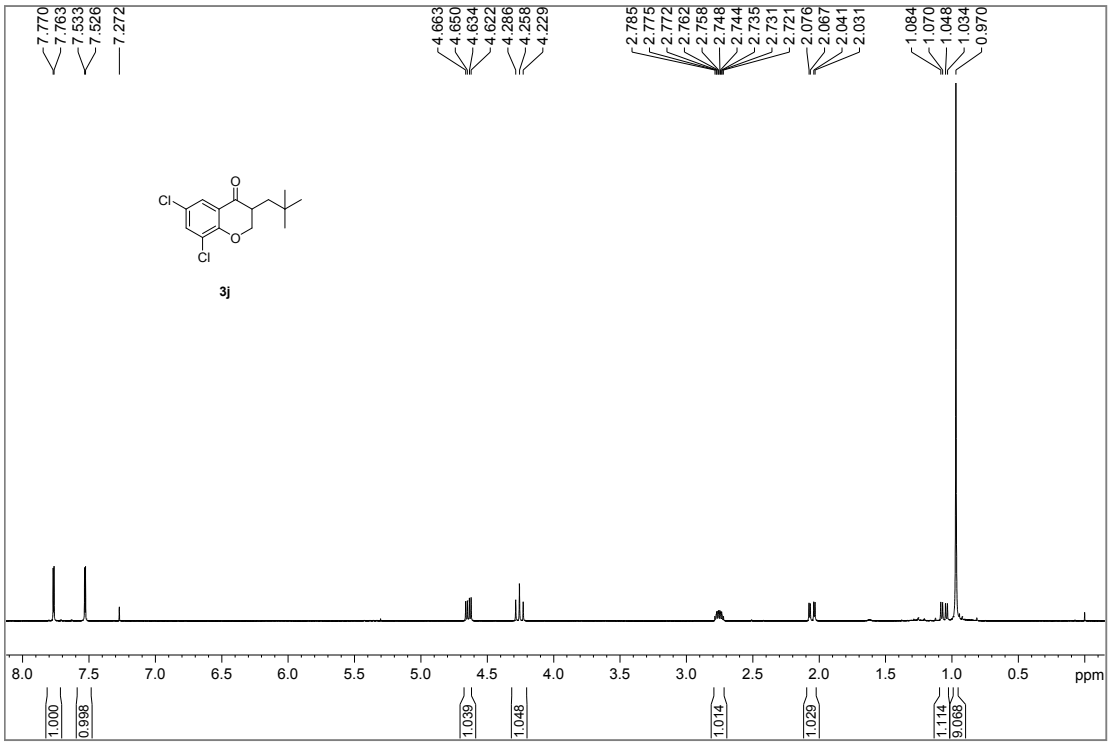
^{13}C NMR spectrum of compound **3h**



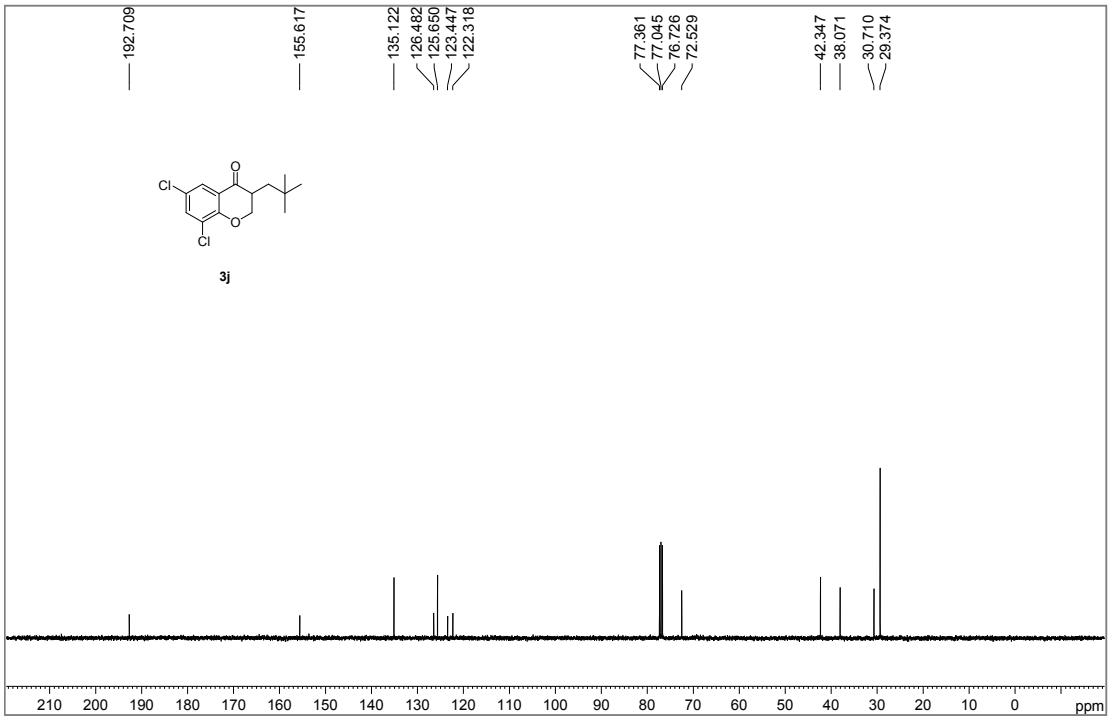
^{1}H NMR spectrum of compound **3i**



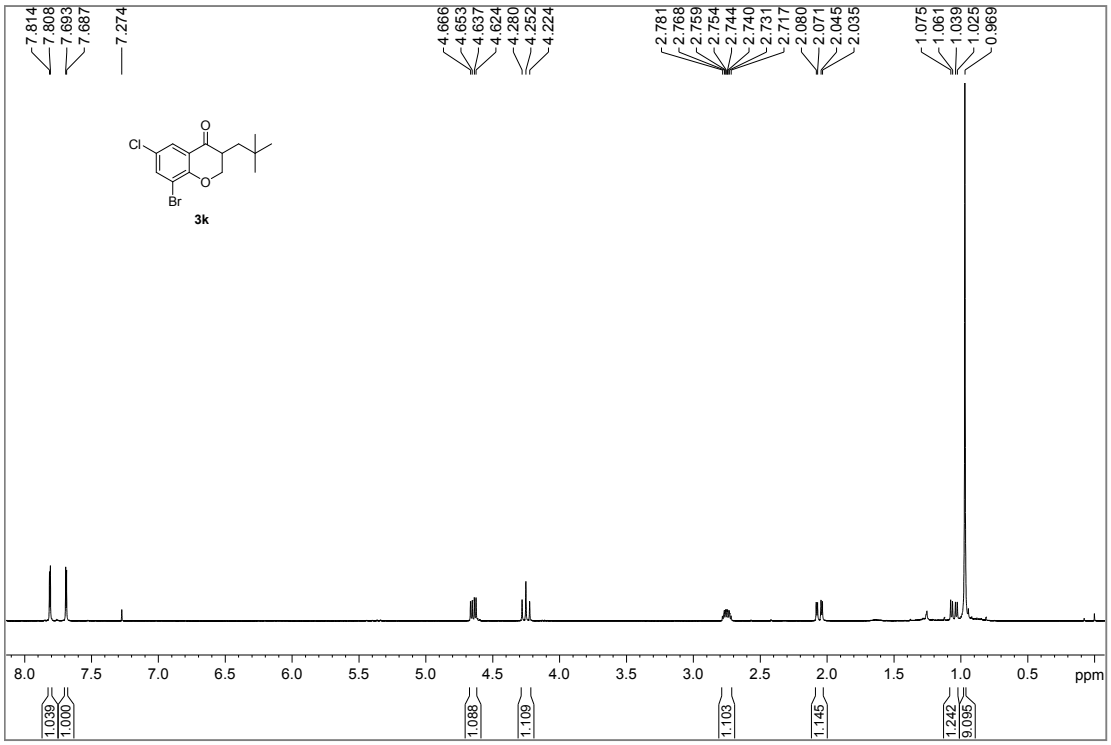
^{13}C NMR spectrum of compound **3i**



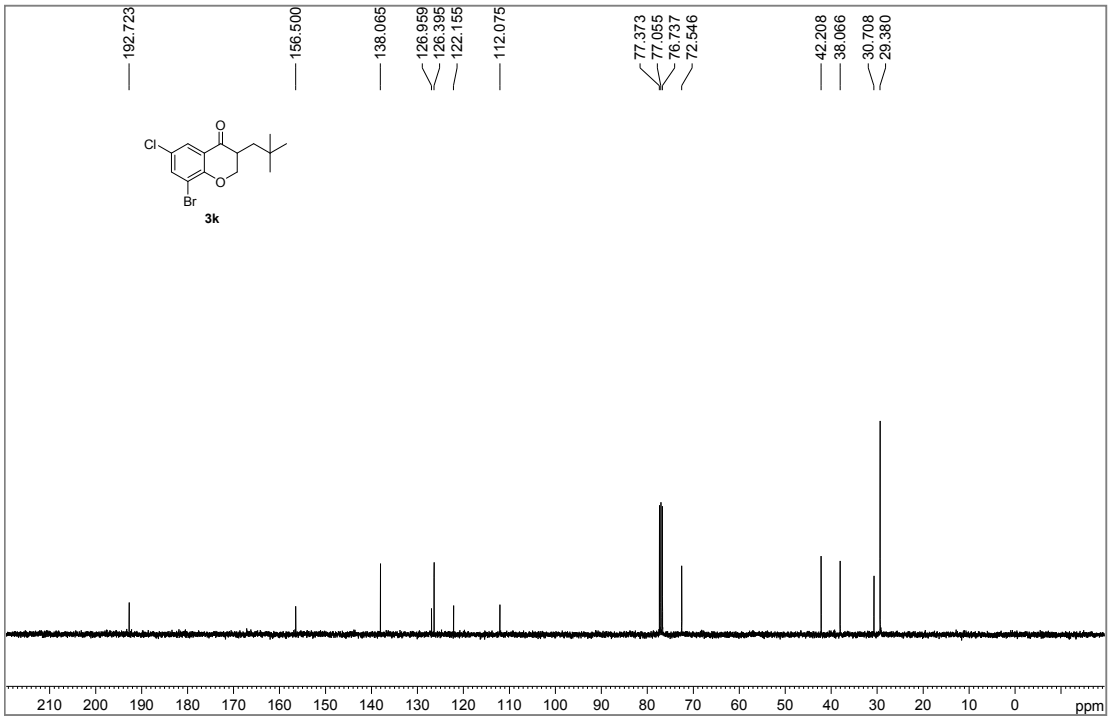
^{1}H NMR spectrum of compound **3j**



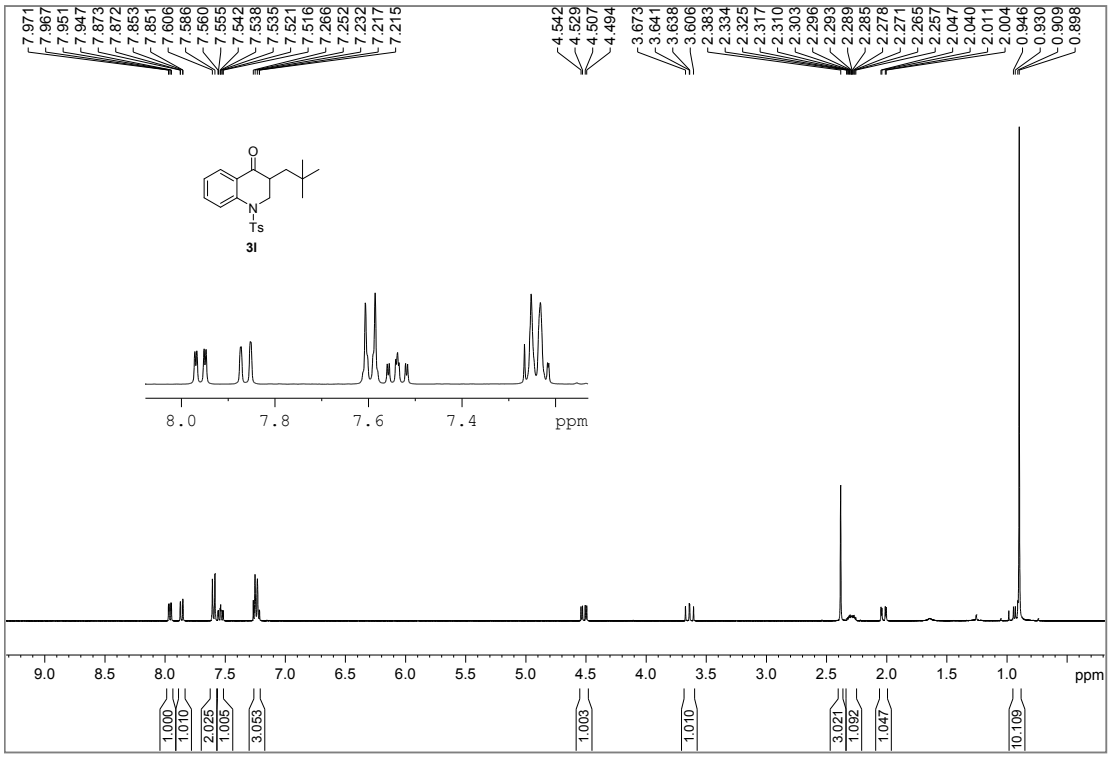
^{13}C NMR spectrum of compound **3j**



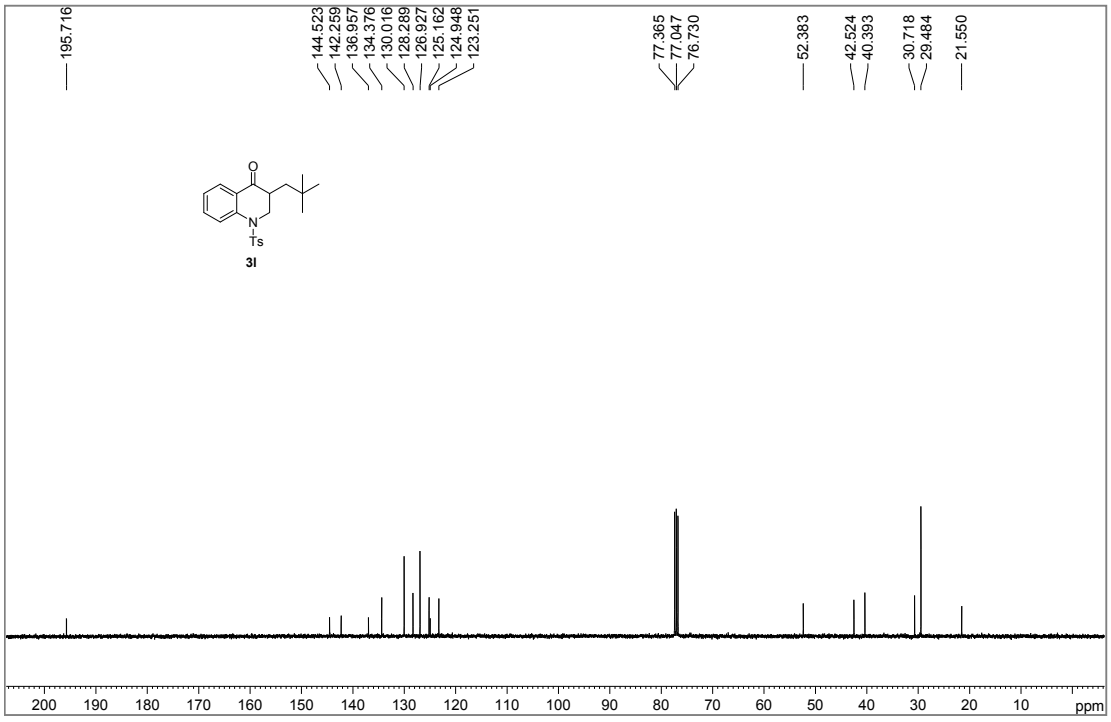
^{1}H NMR spectrum of compound **3k**



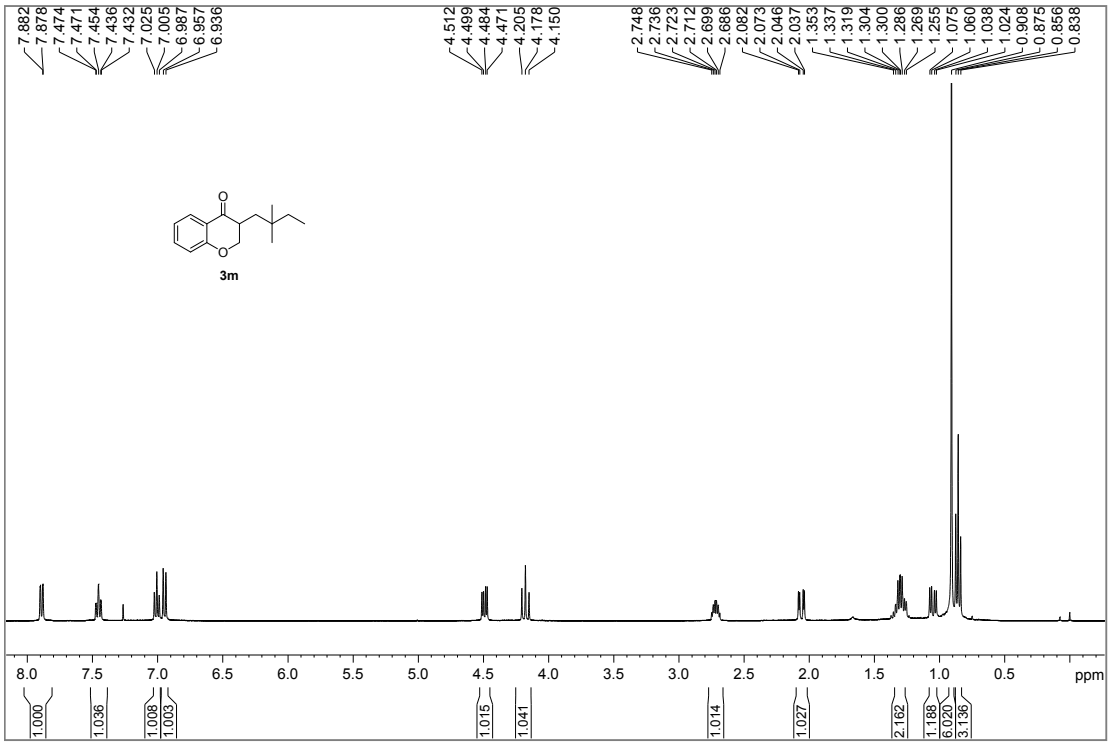
^{13}C NMR spectrum of compound **3k**



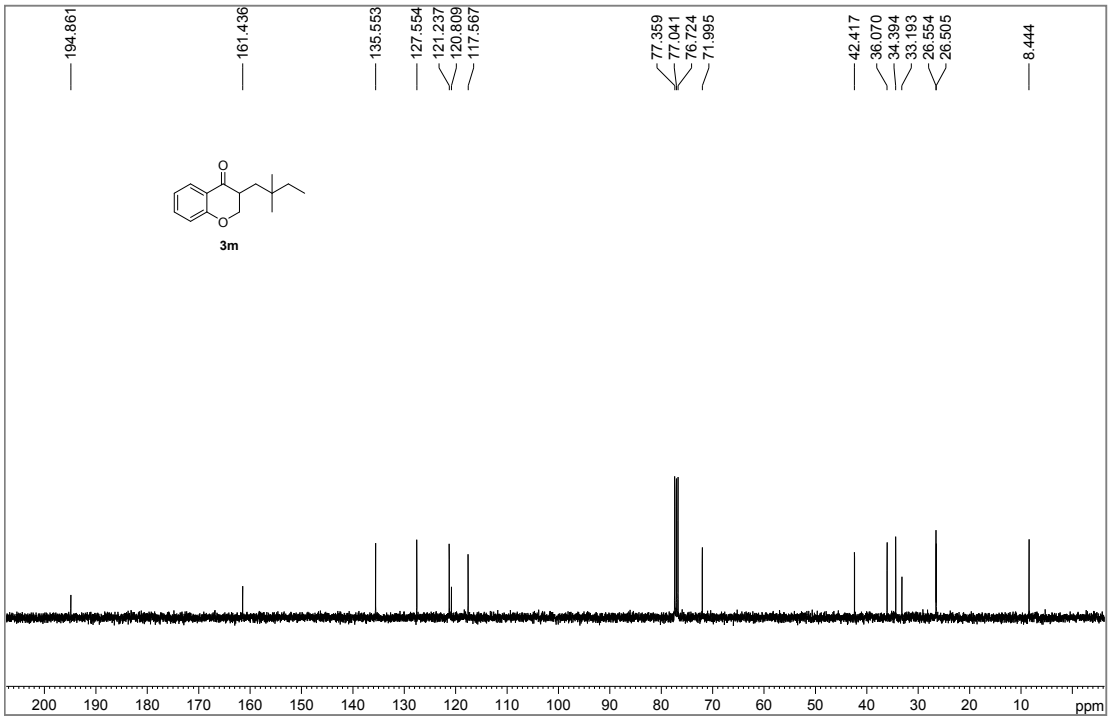
^{1}H NMR spectrum of compound **3l**



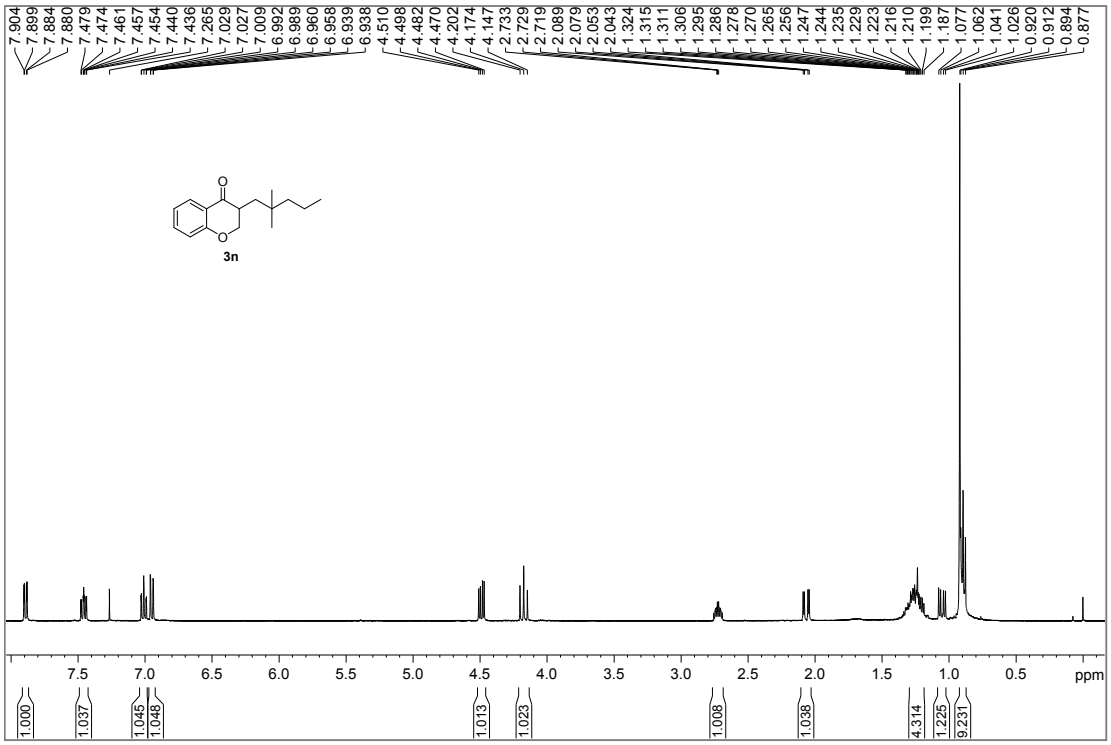
^{13}C NMR spectrum of compound **3l**



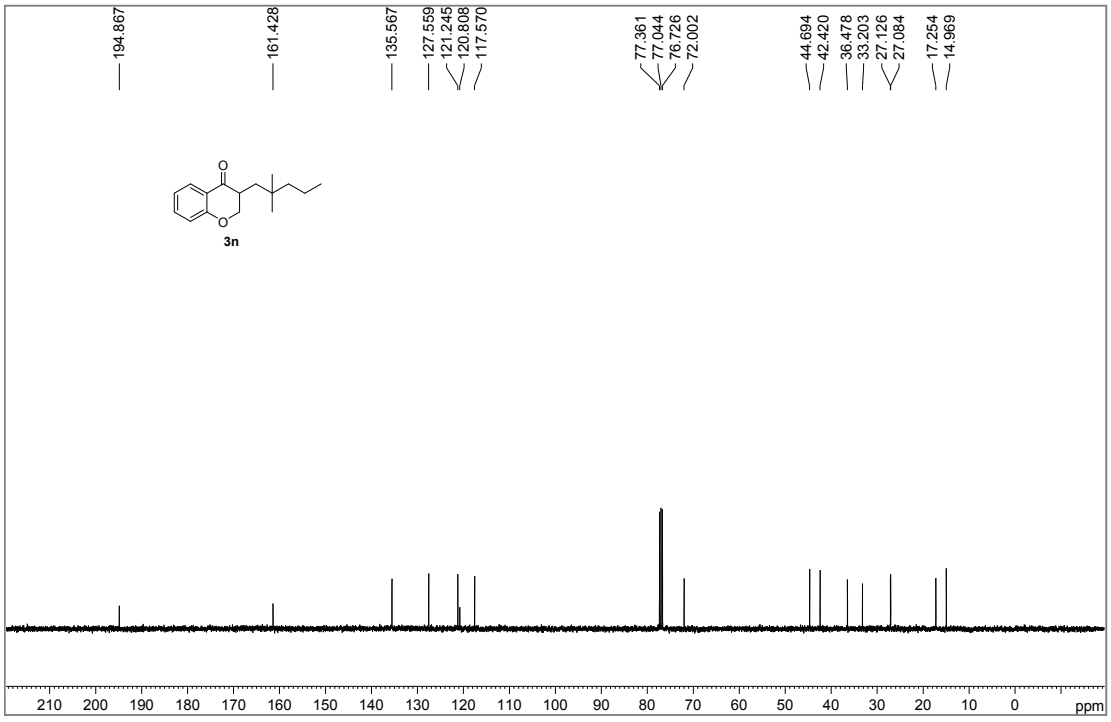
^{1}H NMR spectrum of compound **3m**



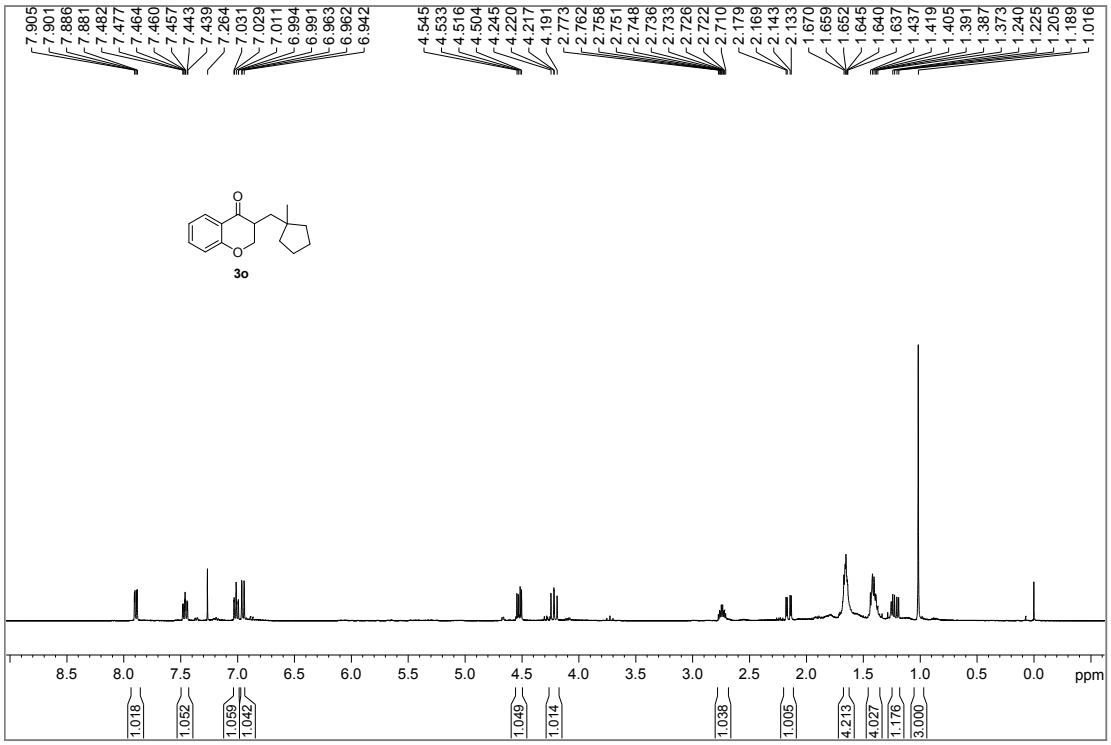
^{13}C NMR spectrum of compound **3m**



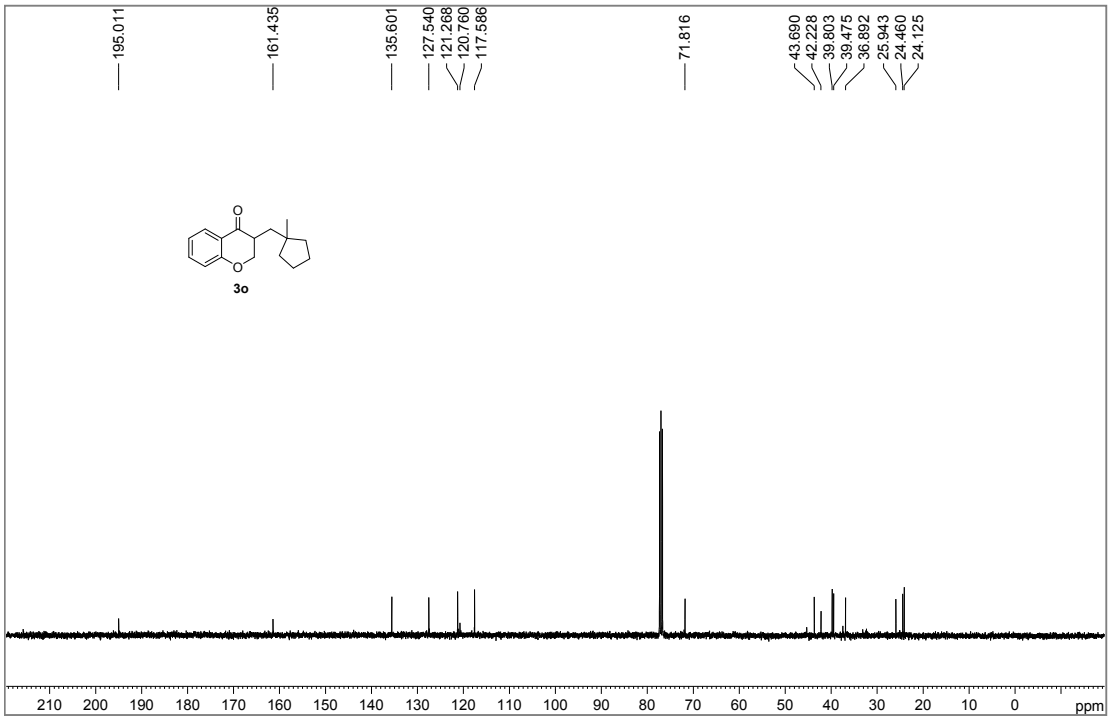
^{1}H NMR spectrum of compound **3n**



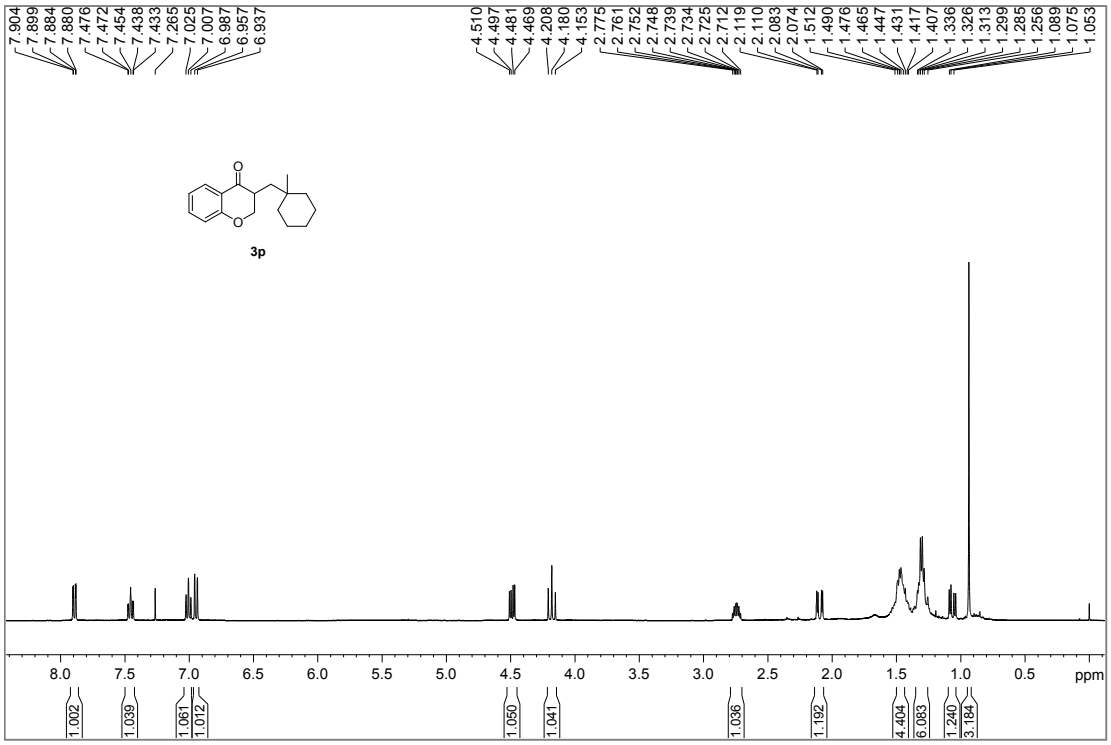
^{13}C NMR spectrum of compound **3n**



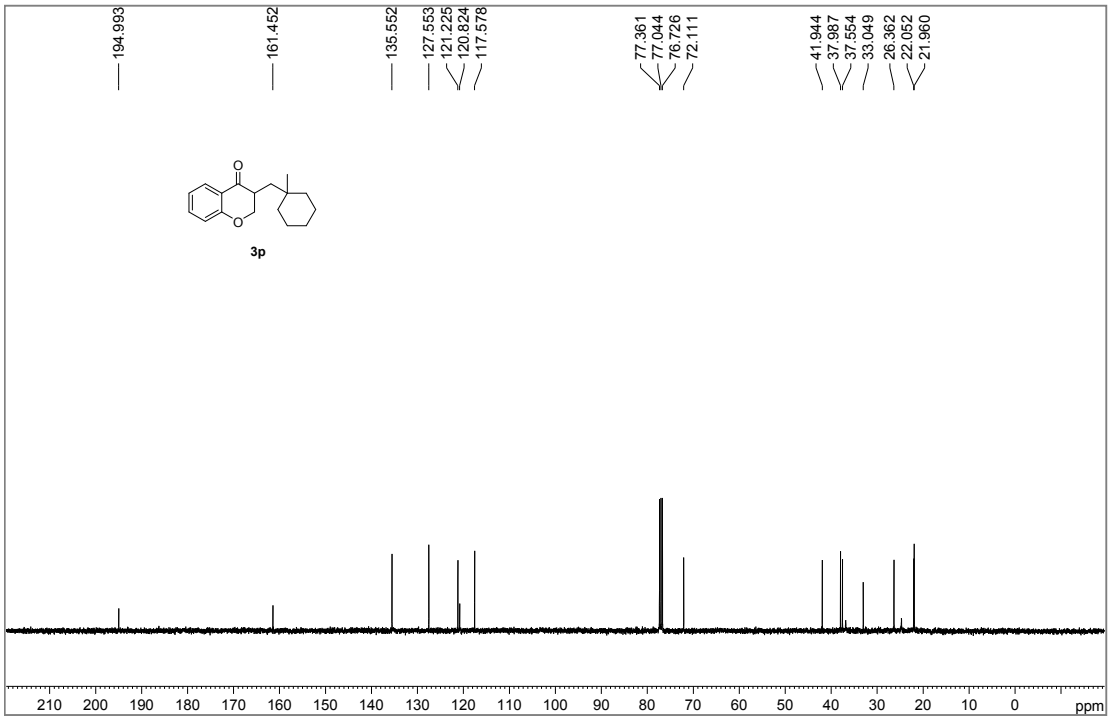
^{1}H NMR spectrum of compound **3o**



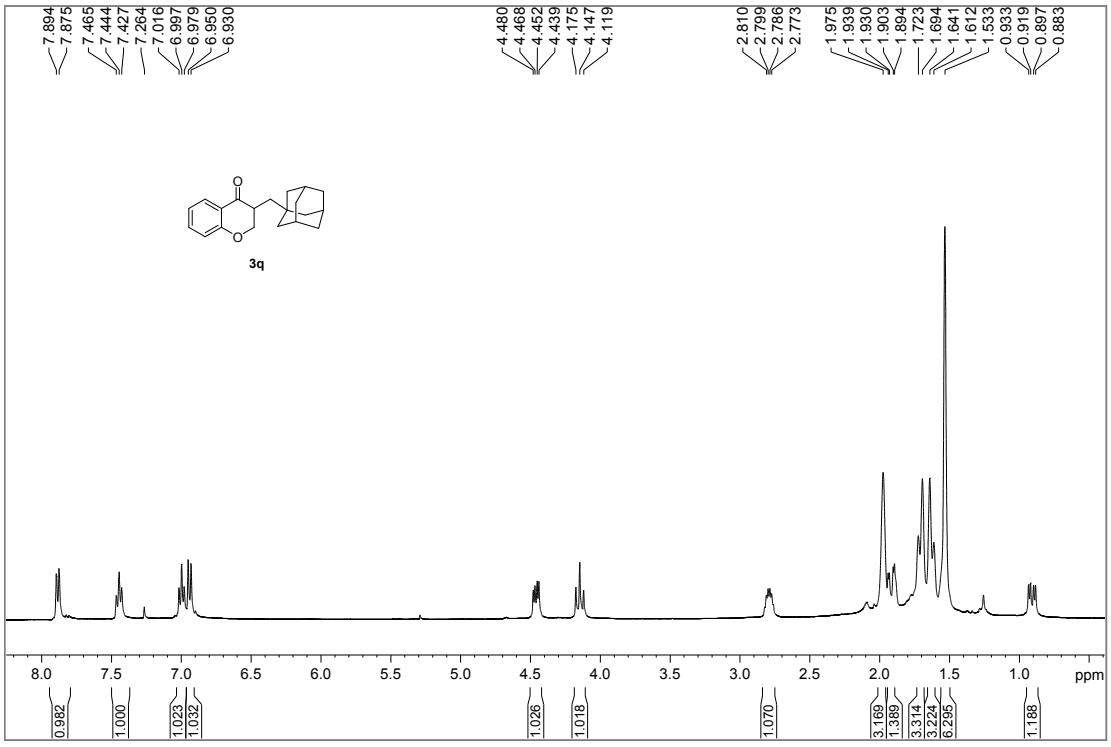
^{13}C NMR spectrum of compound **3o**



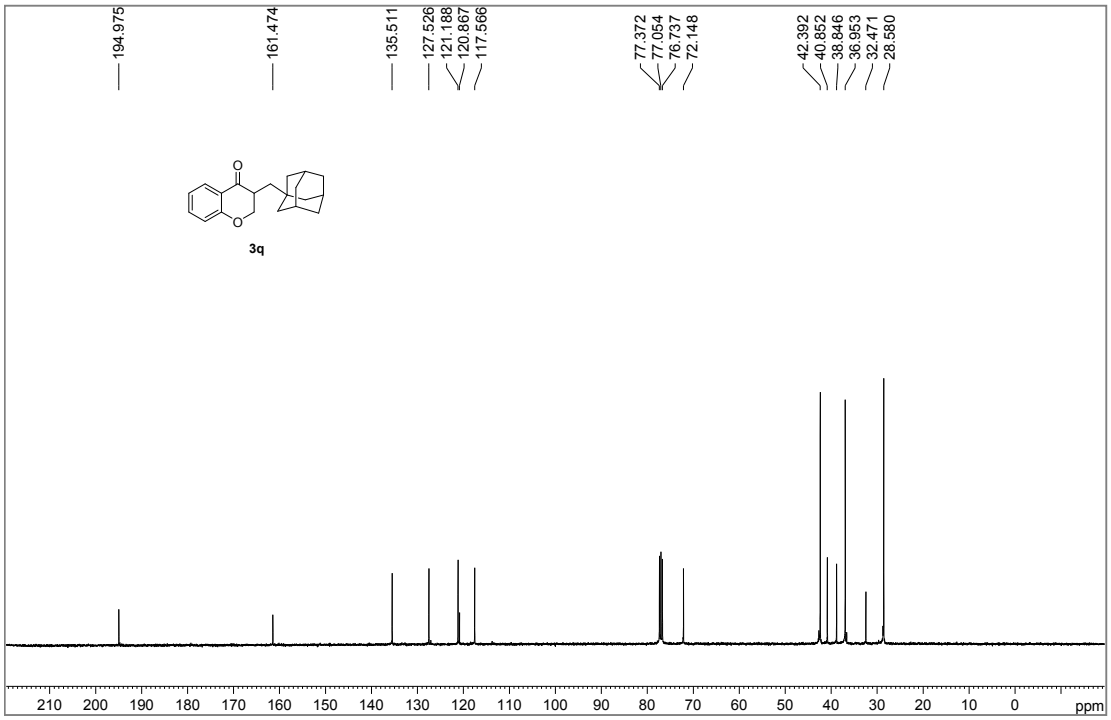
^{1}H NMR spectrum of compound **3p**



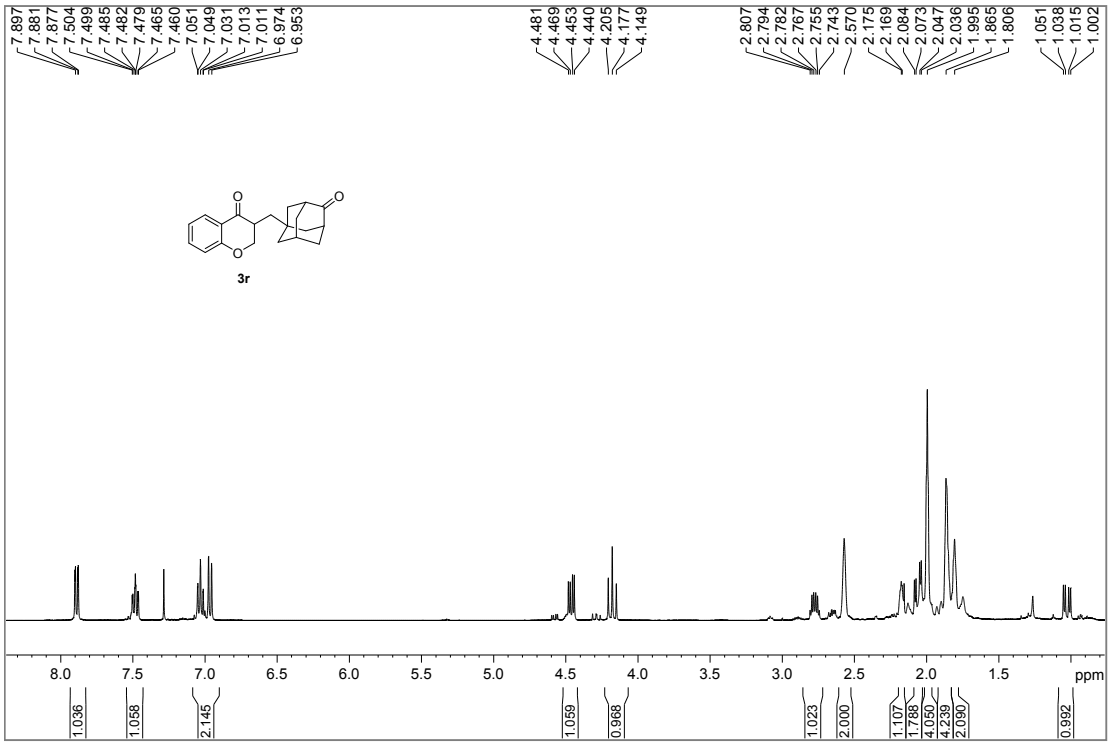
^{13}C NMR spectrum of compound **3p**



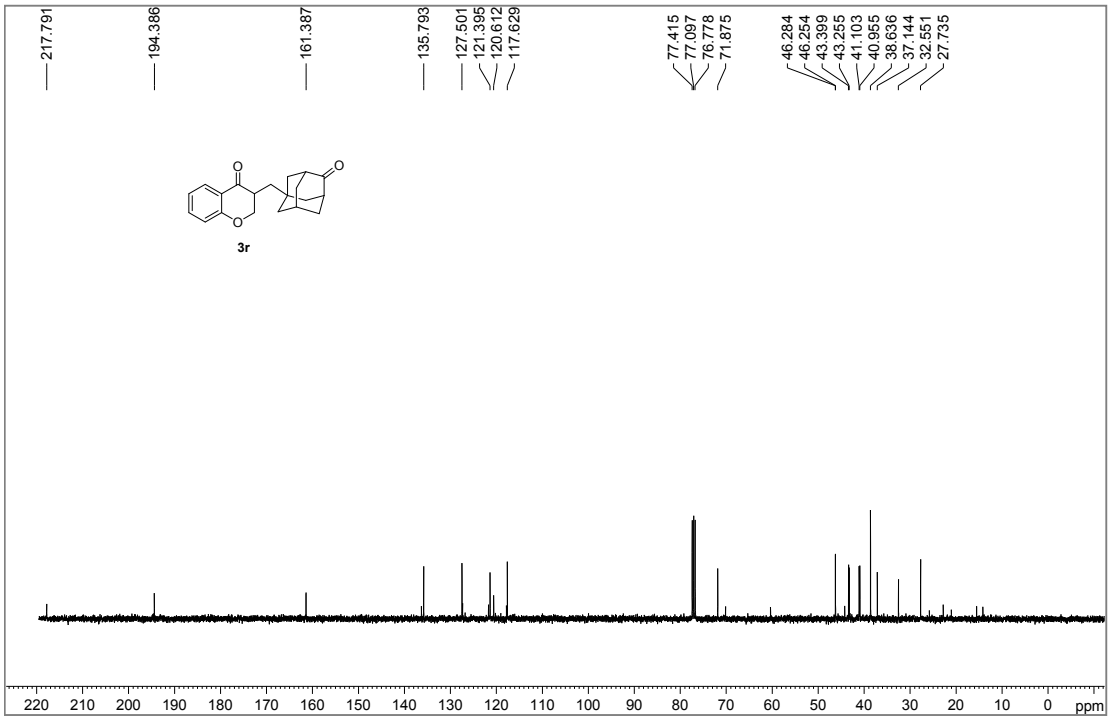
^{1}H NMR spectrum of compound **3q**



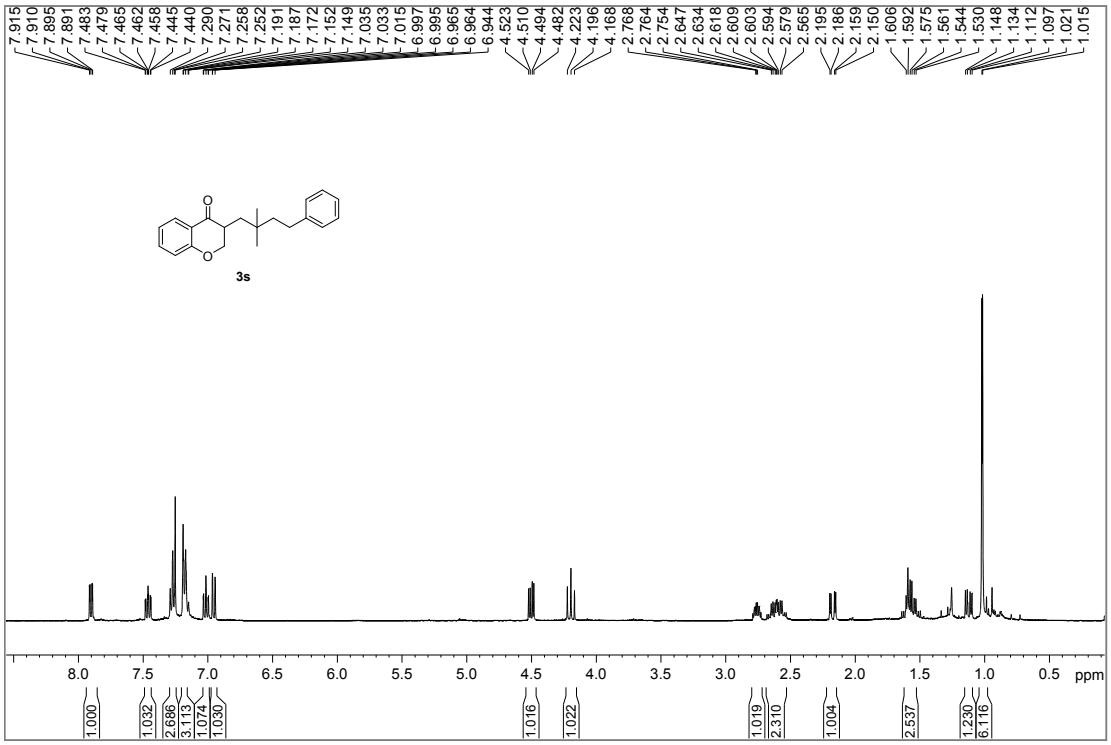
^{13}C NMR spectrum of compound **3q**



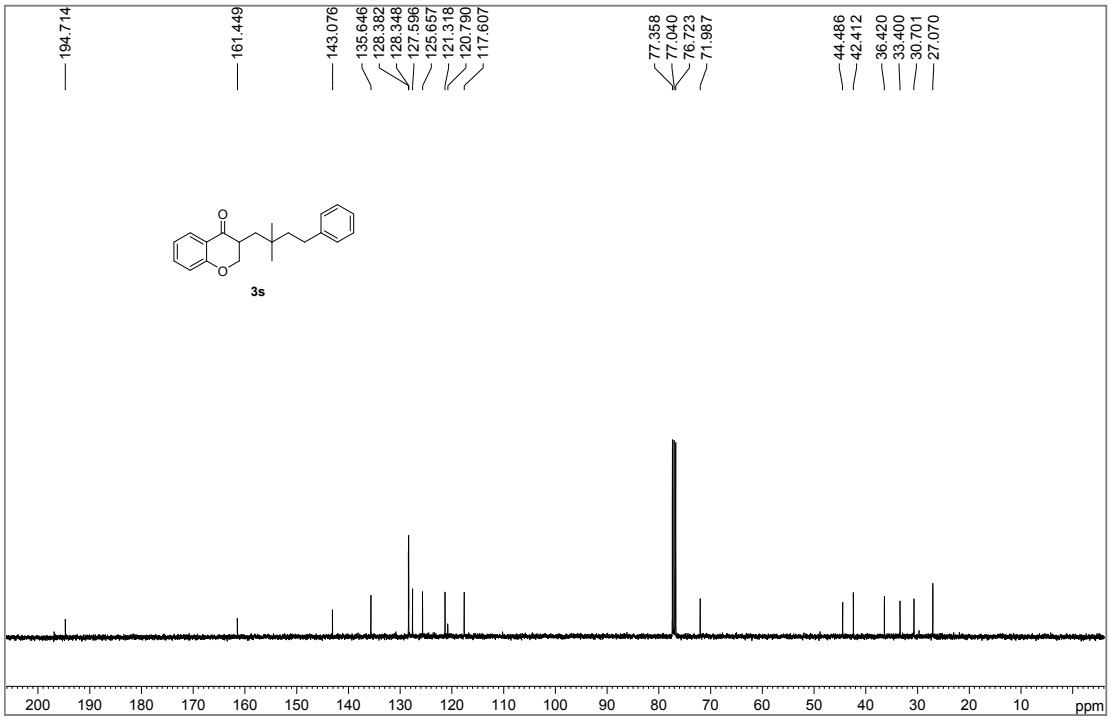
^{1}H NMR spectrum of compound **3r**



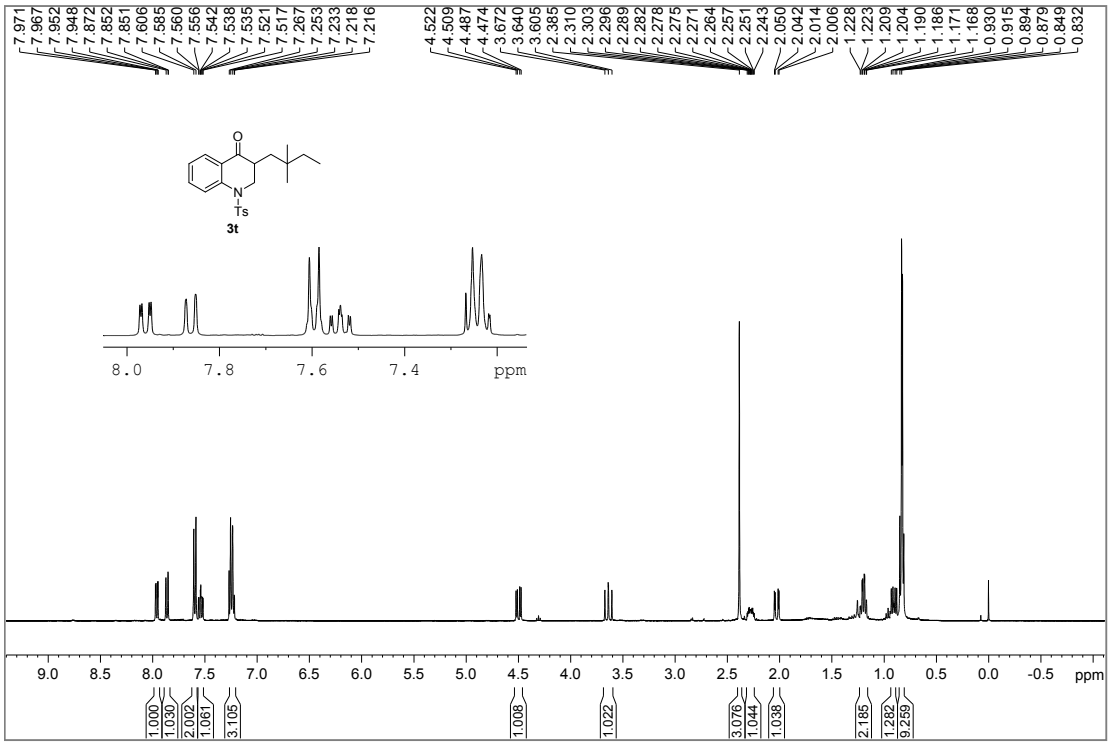
^{13}C NMR spectrum of compound **3r**



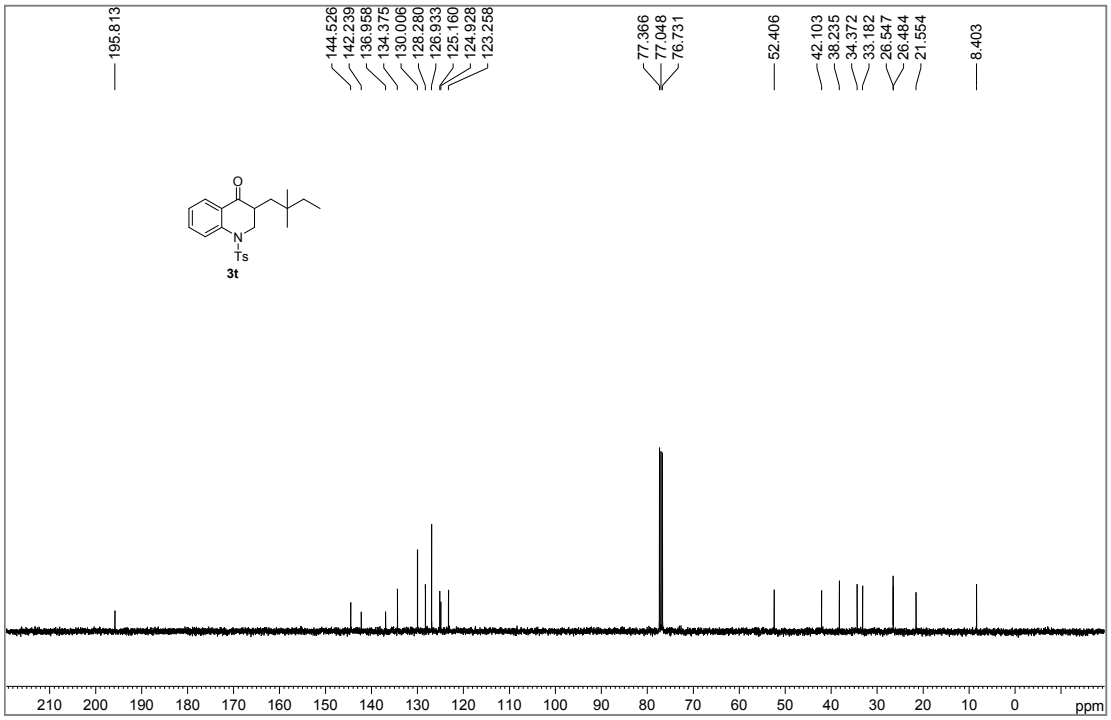
^{1}H NMR spectrum of compound **3s**



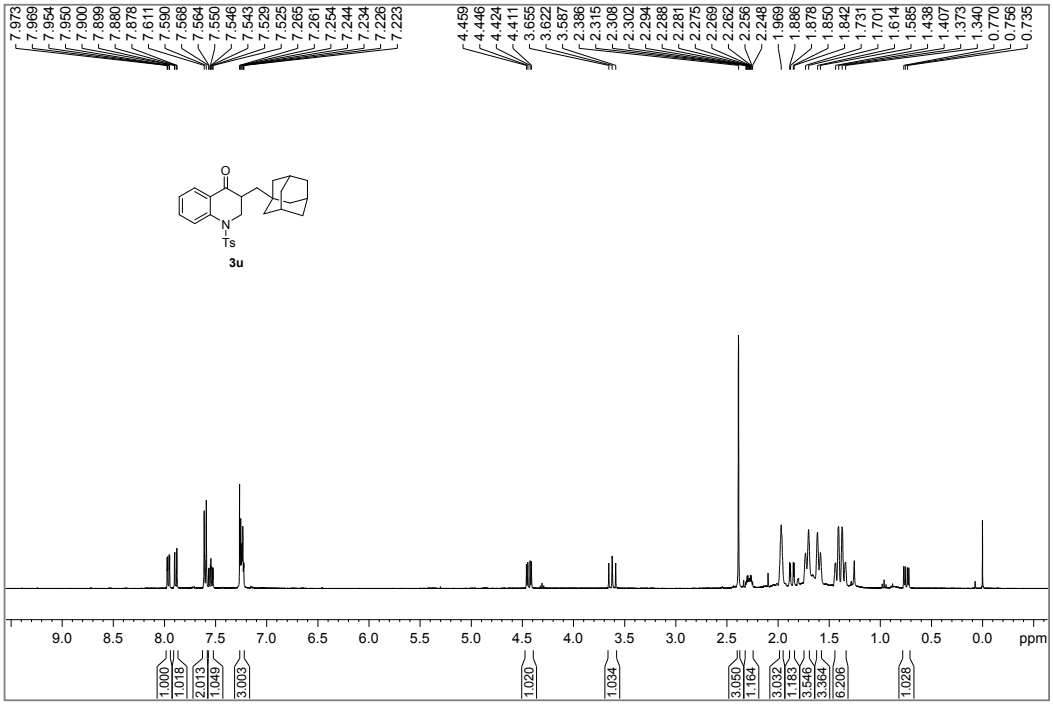
^{13}C NMR spectrum of compound **3s**



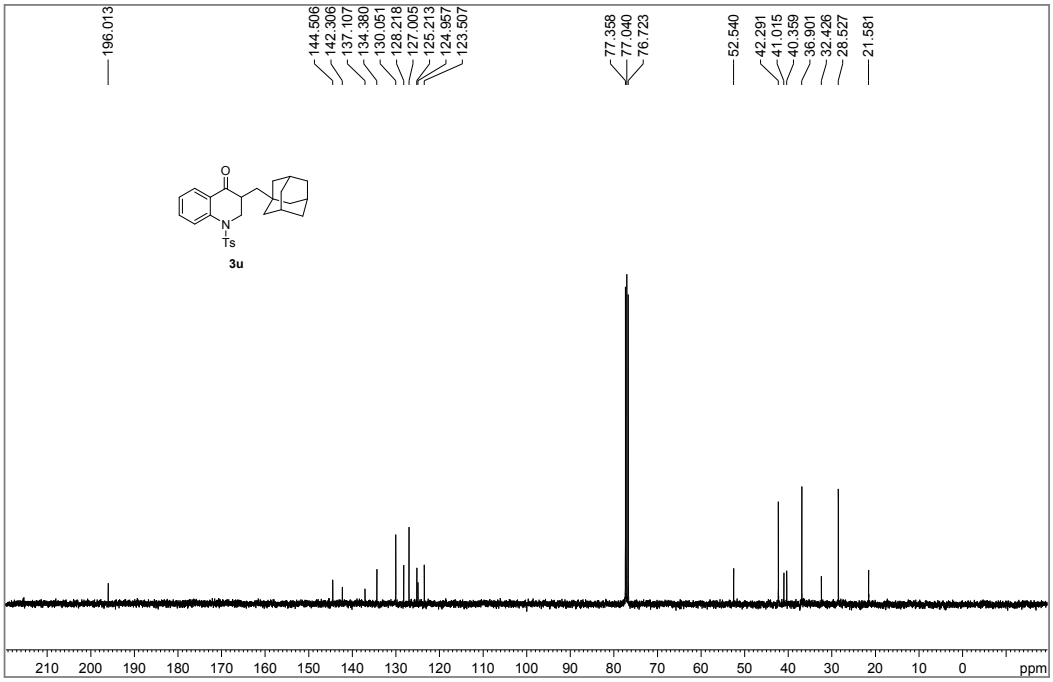
^{1}H NMR spectrum of compound **3t**



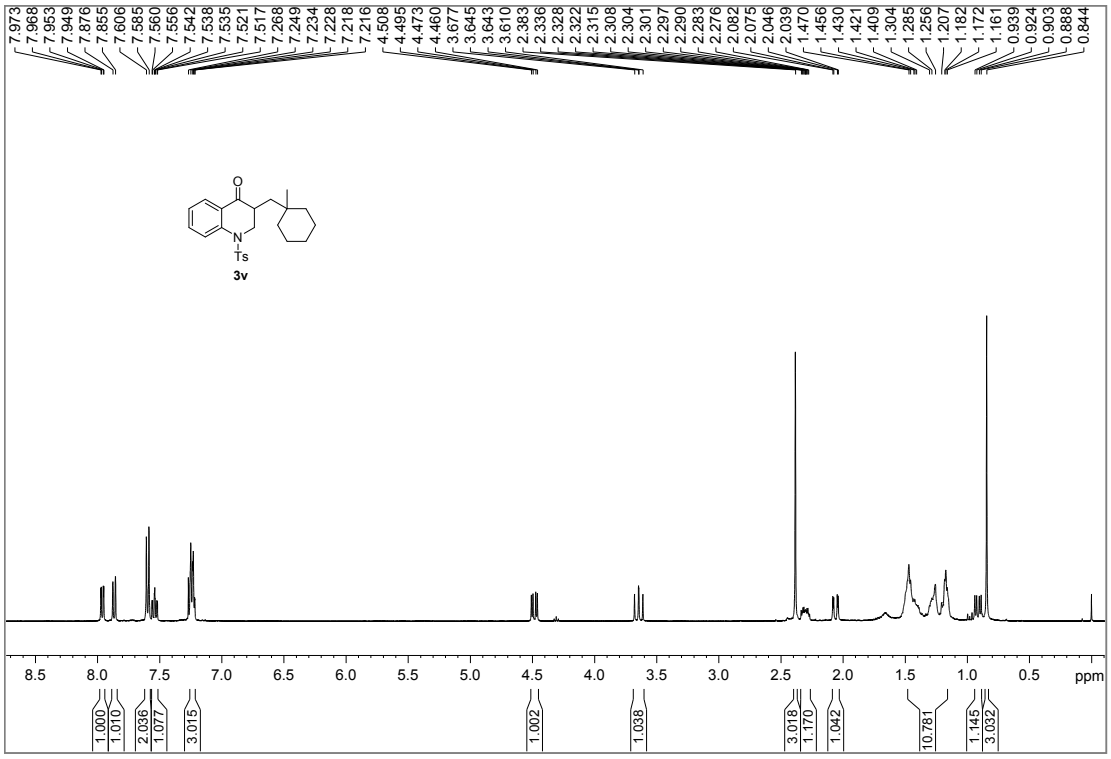
^{13}C NMR spectrum of compound **3t**



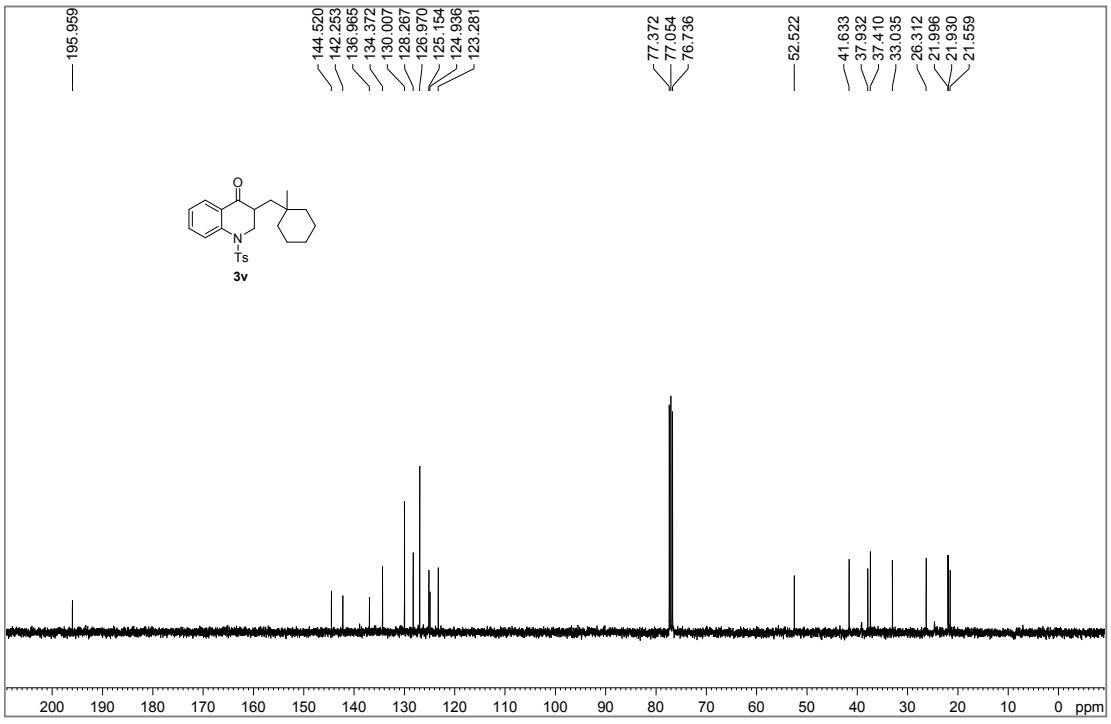
^{1}H NMR spectrum of compound **3u**



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



^{1}H NMR spectrum of compound **3v**



^{13}C NMR spectrum of compound **3v**