Supporting Information

DTBP-promoted site-selective α-alkoxyl C-H functionalization of alkyl esters: synthesis of 2-alkyl ester substituted chromanones

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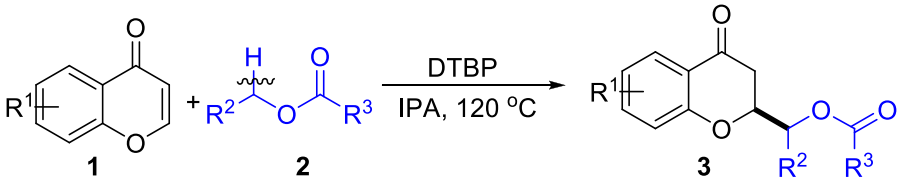
General experimental details

General Information:

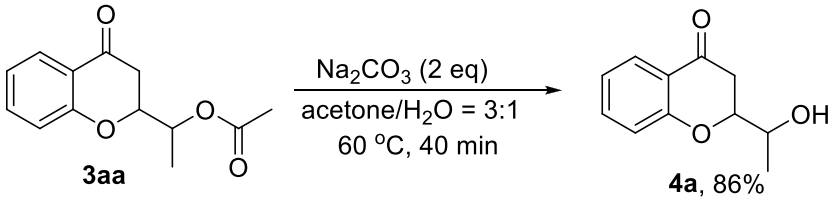
All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer. Chemical shifts (δ) are given in parts per million (ppm), and were referenced to $CDCl_3$ (7.26 or 77.0 ppm) as the internal standard. HRMS were recorded on a TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive or negative ion mode.

Experimental procedure:



Under N_2, the mixture of **1** (0.2 mmol), **2** (1 mL), DTBP (1.2 mmol, 6 eq) and isopropanol (1 mmol, 5 eq) were added into the tube and sealed. The reaction mixture was vigorously stirred at 120 °C for 12 h. Then, solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the products **3**.

Experiment procedure for the Hydrolysis



A 10 mL reaction tube equipped with a magnetic stir bar was charged with 1-(4-oxochroman-2-yl)ethyl acetate (**3aa**, 0.2 mmol, 47 mg), sodium carbonate (Na_2CO_3, 42 mg, 0.4 mmol), H_2O (0.5 mL) and acetone (2 mL). The reaction mixture was stirred at 60 ℃ for 40 min. After completion (checked by TLC), the mixture was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography to afford 2-(1-hydroxyethyl)chroman-4-one **4a**. Yield: 33.0 mg, 86%. Colorless oil.

1. Mechanism Studies

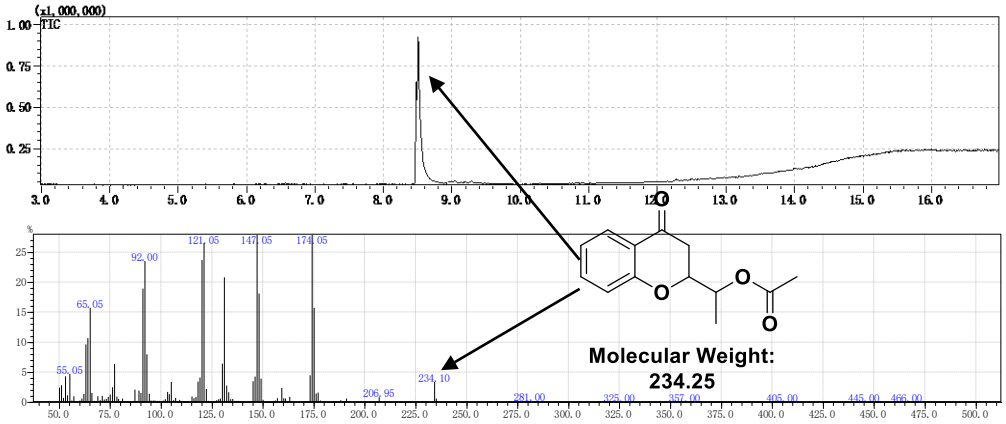
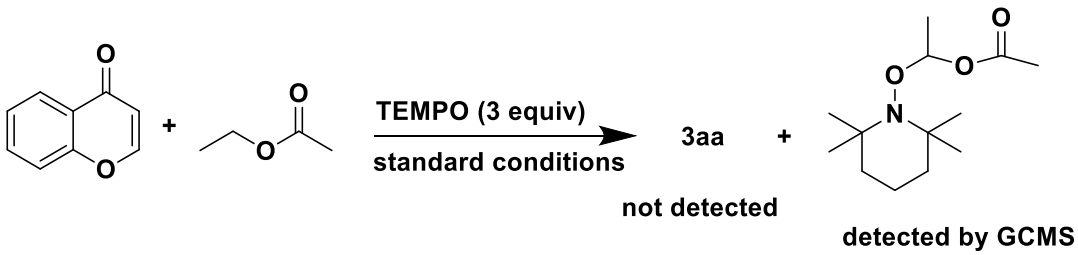
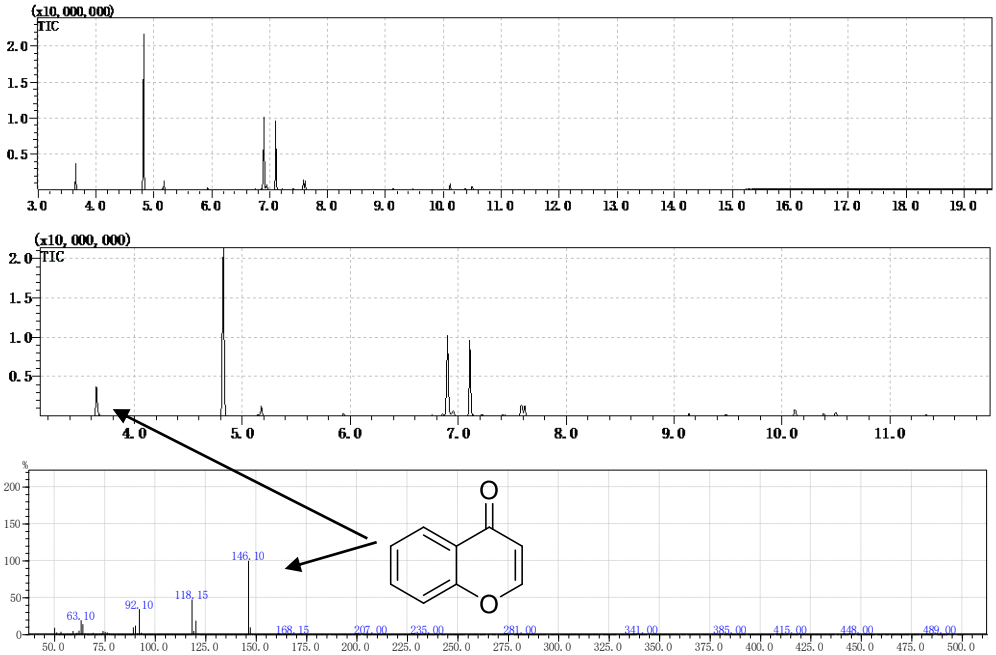


Figure S1 GC-MS spectra of the product **3aa**

Standard Procedure + TEMPO (3.0 equiv)





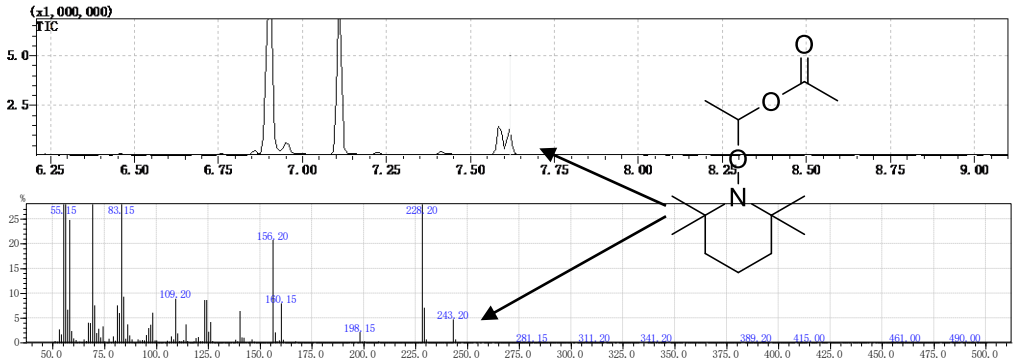
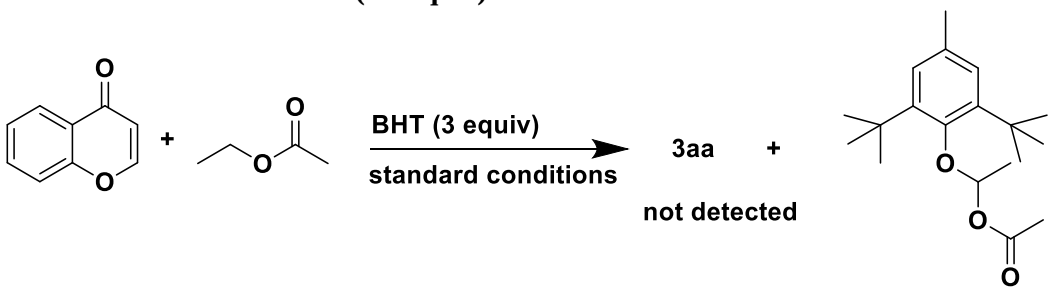
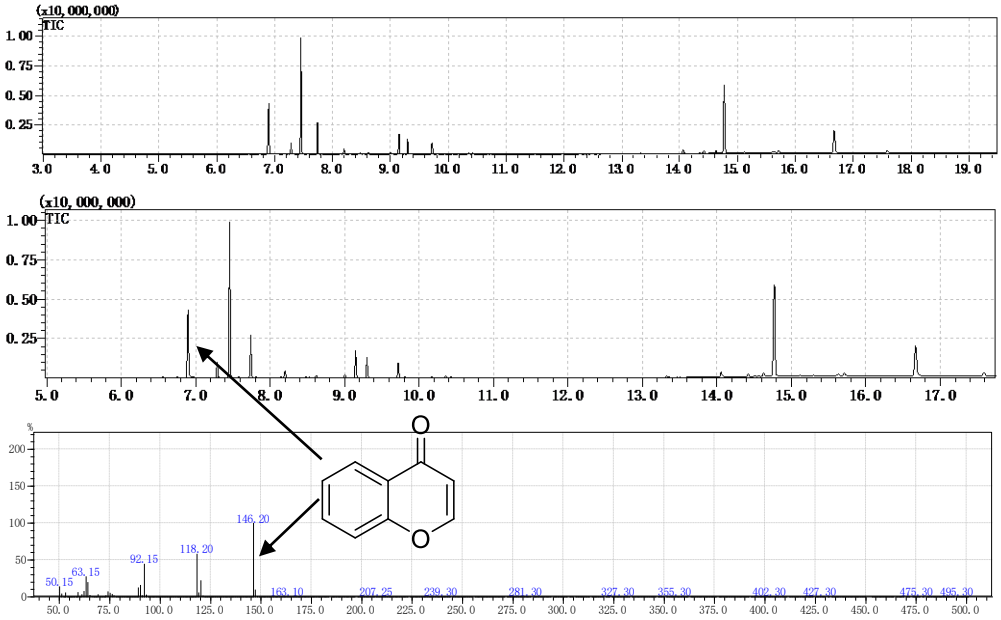


Figure S2 GC-MS spectra of the free radical capture results

Standard Procedure + BHT (3.0 equiv)



detected by GCMS



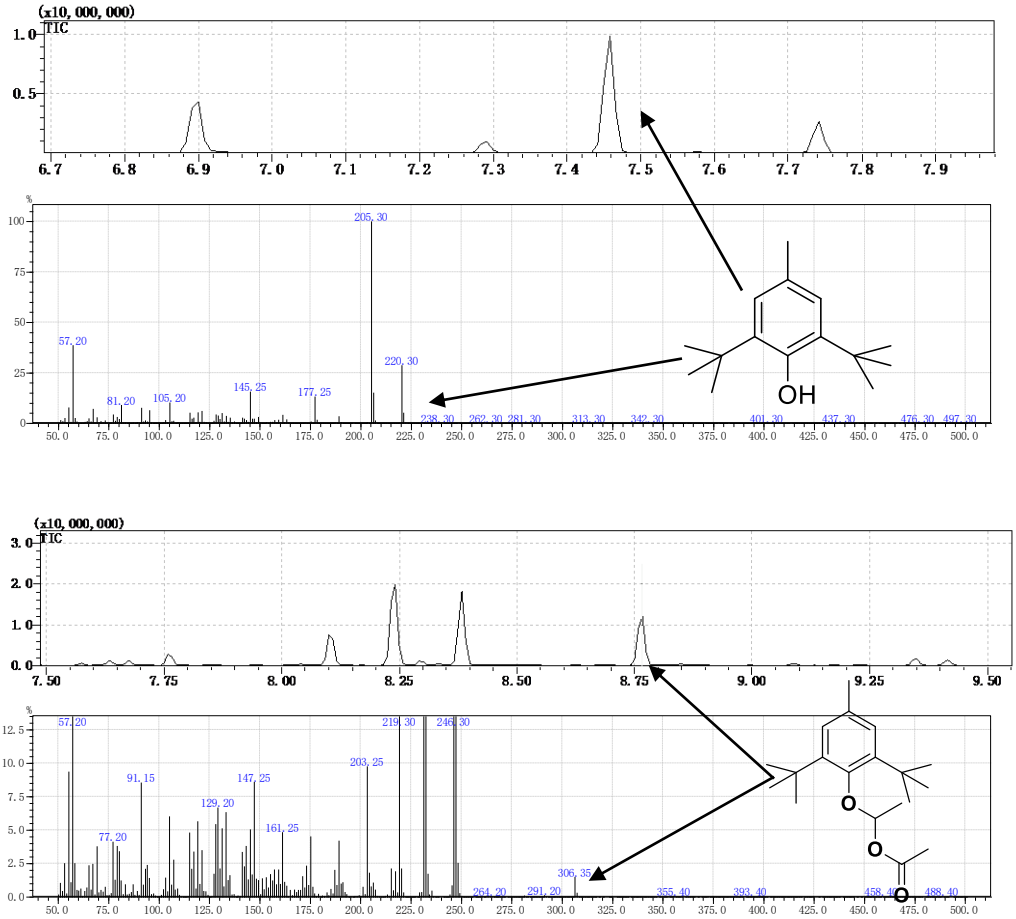
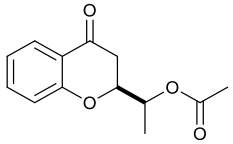


Figure S3 GC-MS spectra of the free radical capture results

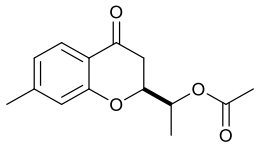
3. Characterization data of the products

1-(4-Oxochroman-2-yl)ethyl acetate (3aa)



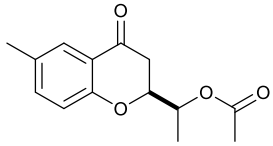
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3aa** as a yellow oil (33.2 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.50-7.46 (m, 1H), 7.04-6.99 (m, 2H), 5.26-5.16 (m, 1H), 4.50-4.43 (m, 1H), 2.87-2.77 (m, 1H), 2.75-2.62 (m, 1H), 2.09 (s, 1.5H), 2.07 (s, 1.5H), 1.40 (d, *J* = 6.6 Hz, 1.5H), 1.36 (d, *J* = 6.5 Hz, 1.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 191.5, 170.1, 170.1, 161.1, 161.0, 136.1, 136.1, 126.9, 126.9, 121.6, 120.9, 120.8, 117.9, 78.9, 78.4, 70.7, 70.3, 39.0, 38.3, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{14}NaO_4^+$ [M+Na$^+$]: 257.0784, found 257.0781.

1-(7-Methyl-4-oxochroman-2-yl)ethyl acetate (3ba)



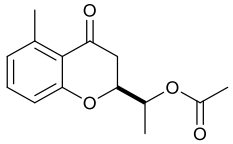
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.3) give **3ba** as a yellow oil (43.6 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.9 Hz, 1H), 6.88-6.76 (m, 2H), 5.26-5.10 (m, 1H), 4.47-4.33 (m, 1H), 2.82-2.56 (m, 2H), 2.34 (s, 3H), 2.09 (s, 1.5H), 2.07 (s, 1.5H), 1.38 (d, *J* = 6.6 Hz, 1.5H), 1.34 (d, *J* = 6.6 Hz, 1.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 191.2, 170.2, 170.1, 161.1, 161.0, 147.7, 147.6, 126.7, 126.7, 122.9, 122.9, 118.6, 118.5, 117.9, 78.8, 78.4, 70.7, 70.3, 38.9, 38.2, 21.9, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_4^+$[M+Na$^+$]: 271.0941, found 271.0935.

1-(6-Methyl-4-oxochroman-2-yl)ethyl acetate (3ca)



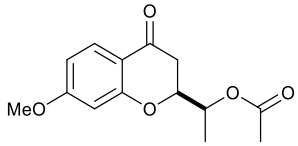
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.3) give **3ca** as a yellow oil (40.2 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.29 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 5.25-5.11 (m, 1H), 4.50-4.35 (m, 1H), 2.85-2.53 (m, 2H), 2.30 (s, 3H), 2.09 (s, 1.5H), 2.08 (s, 1.5H), 1.39 (d, *J* = 6.5 Hz, 1.5H), 1.35 (d, *J* = 6.5 Hz, 1.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 191.8, 170.2, 170.1, 159.1, 159.1, 137.2, 137.1, 131.0, 126.4, 126.4, 120.4, 120.4, 117.7, 78.9, 78.4, 70.7, 70.3, 39.0, 38.4, 21.1, 21.0, 20.4, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_4^+$[M+Na$^+$]: 271.0941, found 271.0936.

1-(5-Methyl-4-oxochroman-2-yl)ethyl acetate (3da)



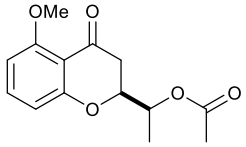
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3da** as a yellow oil (31.2 mg, 63% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 7.0 Hz, 1H), 7.34 (d, *J* = 7.1 Hz, 1H), 6.91 (t, 7.6 Hz, 1H), 5.30-5.20 (m, 1H), 4.47-4.38 (m, 1H), 2.85-2.60 (m, 2H), 2.24 (s, 3H), 2.10 (s, 1.55H), 2.07 (s, 1.44H), 1.39 (t, *J* = 5.7 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.9, 191.9, 170.2, 170.1, 159.2, 159.2, 136.9, 127.2, 127.1, 124.4, 121.0, 120.5, 78.7, 78.5, 70.7, 70.3, 38.9, 38.4, 21.0, 21.0, 15.8, 15.6, 15.5, 15.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_4^+$[M+Na^+]: 271.0941, found 271.0936.

1-(7-Methoxy-4-oxochroman-2-yl)ethyl acetate (3ea)



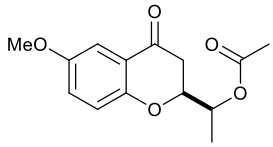
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.3) give **3ea** as a yellow oil (37.0 mg, 70% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 1H), 6.59-6.55 (m, 1H), 6.44-6.42 (m, 1H), 5.25-5.13 (m, 1H), 4.48-4.39 (m, 1H), 3.82 (d, *J* = 1.4 Hz, 3H), 2.82-2.69 (m, 1H), 2.67-2.52 (m, 1H), 2.09 (s, 1.45H), 2.07 (s, 1.55H), 1.38 (d, *J* = 6.5 Hz, 1.45H), 1.34 (d, *J* = 6.5 Hz, 1.55H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.2, 190.1, 170.2, 170.1, 166.1, 166.1, 163.1, 163.0, 128. 6, 114.7, 114.7, 110.2, 110.2, 100.8, 100.7, 79.3, 78.8, 70.6, 70.3, 55.6, 38.6, 37.9, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_5^+$ [M+Na^+]: 287.0890, found 287.0886.

1-(5-Methoxy-4-oxochroman-2-yl)ethyl acetate (3fa)



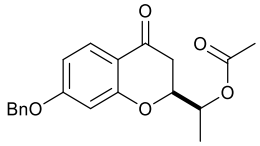
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3fa** as a yellow oil (40.7 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 5.21-5.13 (m, 1H), 4.42-4.35 (m, 1H), 3.90 (s, 3H), 2.84-2.73 (m, 1H), 2.68-2.56 (m, 1H), 2.09 (s, 1.39H), 2.07 (s, 1.61H), 1.36 (d, *J* = 6.6 Hz, 1.4H), 1.33 (*J* = 6.5 Hz, 1.6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3, 170.2, 170.1, 162.7, 162.6, 160.5, 136.0, 135.9, 111.2, 110.0, 104.0, 78.3, 77.9, 70.5, 70.1, 56.1, 40.3, 39.7, 21.1, 21.0, 15.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_5^+$ [M+Na^+]: 287.0890, found 287.0886.

1-(6-Methoxy-4-oxochroman-2-yl)ethyl acetate (3ga)



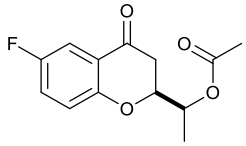
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.3) give **3ga** as a yellow oil (32.7 mg, 62% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, *J* = 3.1 Hz, 1H), 7.11-7.06 (m, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 5.22-5.16 (m, 1H), 4.45-4.36 (m, 1H), 3.78 (s, 3H), 2.82-2.69 (m, 1H), 2.67-2.52 (m, 1H), 2.09 (s, 1.45H), 2.07 (s, 1.55H), 1.38 (d, *J* = 6.5 Hz, 1.45H), 1.34 (d, *J* = 6.5 Hz, 1.55H). ^{13}C NMR (75 MHz, $CDCl_{3)}$ δ 191.7, 191.6, 170.2, 170.1, 155.8, 155.7, 154.2, 125.3, 125.2, 120.7, 120.7, 119.2, 107.2, 107.2, 79.0, 78.5, 70.7, 70.2, 55.7, 38.9, 38.3, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_5^+$ [M+Na^+]: 287.0890, found 287.0888.

1-(7-(Benzyloxy)-4-oxochroman-2-yl)ethyl acetate (3ha)



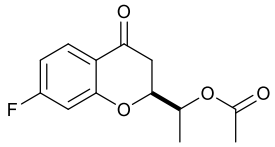
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1, R_f = 0.33) give **3ha** as a yellow oil (53.0 mg, 78% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.8 Hz, 1H), 7.44-7.32 (m, 5H), 6.69-6.63 (m, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 5.26-5.14 (m, 1H), 5.08 (d, *J* = 1.0 Hz, 2H), 4.50-4.38 (m, 1H), 2.84-2.50 (m, 2H), 2.10 (s, 1.5H), 2.08 (s, 1.5H), 1.39 (d, *J* = 6.6 Hz, 1.5H), 1.35 (d, *J* = 6.5 Hz, 1.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.2, 190.11, 170.2, 170.1, 165.1, 163.0, 162.9, 135.7, 130.2, 128.6, 128.61, 128.3, 127.4, 114.9, 114.8, 110.7, 110.7, 101.3, 101.6, 79.2, 78.7, 70.6, 70.2, 38.6, 37.8, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{20}H_{20}NaO_5^+$ [M+Na^+]: 363.1203, found 363.1200.

1-(6-Fluoro-4-oxochroman-2-yl)ethyl acetate (3ia)



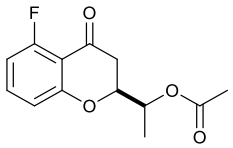
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3ia** as a yellow oil (33.8 mg, 67%yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 8.2, 3.2 Hz, 1H), 7.20 (td, *J* = 8.3, 7.7, 4.6 Hz, 1H), 6.99 (dd, *J* = 9.1, 4.2 Hz, 1H), 5.26-5.14 (m, 1H), 4.50-4.39 (m, 1H), 2.84-2.63 (m, 2H), 2.09 (s, 1.53H), 2.08 (s, 1.47H), 1.39 (d, *J* = 6.6 Hz, 1.53H), 1.35 (d, *J* = 6.6 Hz, 1.47H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 190.8, 190.8, 190.8, 170.2, 170.10, 157.2 (d, J_{C-F} = 240.8 Hz), 157.3, 157.3, 157.2, 157.2, 123.8 (d, J_{C-F} = 3.0 Hz), 123.45 (d, J_{C-F} = 3.0 Hz), 121.3, 121.3, 121.2, 121.2, 119.7, 119.6, 111.9 (d, J_{C-F} = 23.2 Hz), 111.8 (d, J_{C-F} = 22.5 Hz), 79.1, 78.6, 70.5, 70.2, 38.7, 38.0, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}FNaO_4^+$ [M+Na^+]: 275.0690, found 275.0687.

1-(7-Fluoro-4-oxochroman-2-yl)ethyl acetate (3ja)



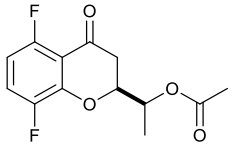
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3ja** as a yellow oil (37.8 mg, 75%yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 8.8, 6.6 Hz, 1H), 6.76-6.65 (m, 2H), 5.25-5.13 (m, 1H), 4.51-4.43 (m, 1H), 2.83-2.74 (m, 1H), 2.72-2.59 (m, 1H), 2.07 (s, 1.55H), 2.06 (s, 1.45H), 1.38 (d, *J* = 6.5 Hz, 1.56H), 1.34 (d, *J* = 6.6 Hz, 1.44H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.0, 189.9, 167.4 (d, J_{C-F} = 255.0 Hz), 162.7, 162.7, 162.6, 162.5, 129.44 (d, J_{C-F} = 3.7 Hz), 129.3 (d, J_{C-F} = 3.7 Hz), 117.8, 117.7, 117.7, 110.0 (d, J_{C-F} = 22.5 Hz), 104.7 (d, J_{C-F} = 24.7 Hz), 79.5, 79.0, 70.4, 70.1, 38.6, 37.9, 21.0, 20.9, 15.5, 15.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}FNaO_4^+$ [M+Na^+]: 275.0690, found 275.0685.

1-(5-Fluoro-4-oxochroman-2-yl)ethyl acetate (3ka)



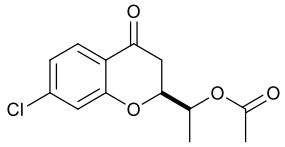
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.65) give **3ka** as a yellow oil (25.7 mg, 51% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44-7.36 (m, 1H), 6.81 (dt, *J* = 8.4, 1.1 Hz, 1H), 6.69 (dd, *J* = 10.5, 8.3 Hz, 1H), 5.25-5.13 (m, 1H), 4.50-4.40 (m, 1H), 2.88-2.60 (m, 2H), 2.08 (s, 1.55H), 2.07 (s, 1.45H), 1.38 (d, *J* = 6.5 Hz, 1.56H), 1.34 (d, *J* = 6.5 Hz, 1.44H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 189.1, 170.1, 170.0, 161.5 (d, J_{C-F} = 264.0 Hz), 161.5 (d, J_{C-F} = 264.0 Hz), 161.9, 161.8, 161.8, 161.7, 159.7, 159.7, 136.0 (d, J_{C-F} = 3.0 Hz), 135.9 (d, J_{C-F} = 3.0 Hz), 113.7, 113.6, 111.1, 111.1, 110.9, 110.9, 109.1 (d, J_{C-F} = 21.0 Hz), 78.8, 78.4, 70.4, 70.1, 21.1, 21.0, 15.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}FNaO_4^+$ [M+Na^+]: 275.0690, found 275.0685.

1-(5,8-Difluoro-4-oxochroman-2-yl)ethyl acetate (3la)



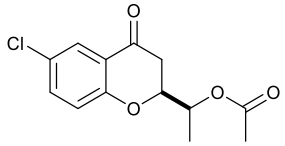
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3la** as a yellow oil (21.6 mg, 40% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.30 (m, 1H), 7.11-7.04 (m, 1H), 5.26-5.20 (m, 1H), 4.56-4.45 (m, 1H), 2.87-2.76 (m, 2H), 2.08 (s, *J* = 1.55H), 2.07 (s, 1.45H), 1.41 (d, *J* = 6.6 Hz, 1.55H), 1.37 (d, *J* = 6.5 Hz, 1.45H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 170.1, 167.0, 155.7 (d, J_{C-F} = 252.7 Hz), 155.3 (d, J_{C-F} = 297.0 Hz), 122.6, 122.5, 111.3, 111.3, 111.0, 111.0, 110.9, 110.6, 107.4, 107.3, 107.2, 107.1, 107.0, 106.9, 79.9, 79.4, 70.5, 70.0, 39.0, 38.4, 21.0, 20.9, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}F_2NaO_4^+$ [M+Na^+]: 293.0596, found 293.0599.

1-(7-Chloro-4-oxochroman-2-yl)ethyl acetate (3ma)



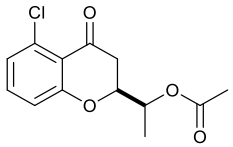
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3ma** as a yellow oil (47.7 mg, 89% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.9 Hz, 1H), 7.03-6.97 (m, 2H), 5.25-5.13 (m, 1H), 4.51-4.42 (m, 1H), 2.86-2.74 (m, 1H), 2.73-2.61 (m, 1H), 2.08 (s, 1.6H), 2.06 (s, 1.4H), 1.38 (d, *J* = 6.5 Hz, 1.6H), 1.34 (d, *J* = 6.6 Hz, 1.4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.4, 190.3, 170.1, 170.0, 161.3, 161.3, 141.9, 141.9, 128.1, 128.0, 122.4, 119.4, 119.4, 118.1, 118.1, 79.3, 78.9, 70.4, 70.1, 38.8, 38.0, 21.03,21.0, 15.6, 15.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}ClNaO_4^+$ [M+Na^+]: 291.0395, found 291.0389.

1-(6-Chloro-4-oxochroman-2-yl)ethyl acetate (3na)



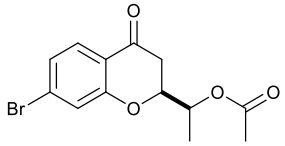
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.4) give **3na** as a yellow oil (32.7 mg, 61% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 2.7 Hz, 1H), 7.44-7.40 (m, 1H), 6.96 (d, *J* =8.8 Hz, 1H), 5.27-5.14 (m, 1H), 4.50-4.41 (m, 1H), 2.94-2.62 (m, 2H), 2.09 (s, 1.44H), 2.07 (s, 1.56H),1.39 (d, *J* = 6.5 Hz, 1.45H), 1.35 (d, *J* = 6.5 Hz, 1.55H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.4, 190.3, 170.1, 170.1, 159.5, 159.4, 135.9, 135.9, 127.2, 126.2, 126.2, 121.6, 121.6, 119.7, 79.2, 78.7, 70.5, 70.2, 38.7, 38.0, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}ClNaO_4^+$ [M+Na^+]: 291.0395, found 291.0391.

1-(5-Chloro-4-oxochroman-2-yl)ethyl acetate (3oa)



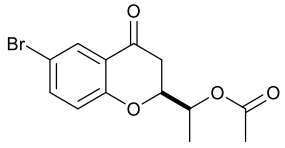
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1, R_f = 0.4) give **3oa** as a yellow oil (22.5 mg, 42% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.29 (m, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 5..25-5.13 (m, 1H), 4.49-4.40 (m, 1H), 2.92-2.64 (m, 2H), 2.08 (s, 1.6H), 2.06 (s, 1.4H), 1.37 (d, *J* = 6.6 Hz, 1.6H), 1.34 (d, *J* = 6.5 Hz, 1.4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 170.1, 170.0, 162.5, 162.4, 134.7, 134.7, 134.2, 134.2, 124.8, 118.2, 118.1, 117.0, 78.5, 78.0, 70.4, 70.1, 40.0, 39.3, 21.0, 21.0, 15.5, 15.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}ClNaO_4^+$ [M+Na^+]: 291.0395, found 291.0389.

1-(7-Bromo-4-oxochroman-2-yl)ethyl acetate (3pa)



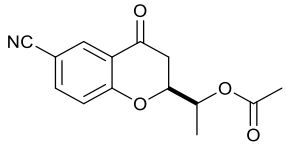
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3pa** as a yellow oil (45.1 mg, 72% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.26-7.14 (m, 2H), 5.25-5.13 (m, 1H), 4.51-4.41 (m, 1H), 2.86-2.61 (m, 2H), 2.08 (s, 1.58H), 2.07 (s, 1.42H), 1.38 (d, *J* = 6.5 Hz, 1.58H), 1.34 (d, *J* = 6.6 Hz, 1.42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.6, 190.5, 170.1, 170.0, 161.2, 161.1, 130.5, 130.4, 128.1, 128.0, 125.2, 121.2, 121.1, 119.8, 119.7, 79.3, 78.8, 70.4, 70.2, 38.8, 38.1, 21.0, 21.0, 15.6, 15.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}BrNaO_4^+$ [M+Na^+]: 334.9889, found 334.9883.

1-(6-Bromo-4-oxochroman-2-yl)ethyl acetate (3qa)



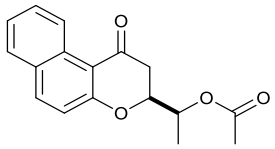
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3qa** as a yellow oil (32.4 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 2.5 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.0 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 5.27-5.14 (m, 1H), 4.52-4.39 (m, 1H), 2.89-2.63 (m, 2H), 2.09 (s, 1.6H), 2.08 (s, 1.4H), 1.39 (d, *J* = 6.5 Hz, 1.6H), 1.35 (d, *J* = 6.5 Hz, 1.4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.2, 190.2, 170.1, 170.03, 159.9, 159.8, 138.7, 138.7, 129.3, 129.3, 122.1, 122.0, 120.0, 114.3, 79.1, 78.6, 70.5, 70.1, 38.6, 37.9, 21.1, 21.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{13}BrNaO_4^+$ [M+Na^+]: 334.9889, found 334.9884.

1-(6-Cyano-4-oxochroman-2-yl)ethyl acetate (3ra)



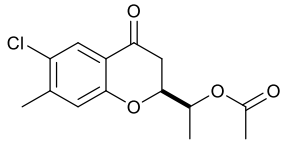
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3ra** as a yellow oil (32.6 mg, 63% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19-8.18 (m, 1H), 7.73-7.69 (m, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 5.35-5.15 (m, 1H), 4.60-4.47 (m, 1H), 2.90-2.72 (m, 2H), 2.07 (s, 1.6H), 2.06 (s, 1.4H), 1.41 (d, *J* = 6.6 Hz, 1.6H), 1.36 (d, *J* = 6.6 Hz, 1.4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.2, 167.0, 169.9, 163.5, 163.4, 138.4, 138.4, 132.1, 132.0, 121.2, 121.1, 119.6, 119.5, 117.9, 117.8, 105.6, 105.6, 79.6, 79.1, 70.3, 70.1, 38.6, 37.7, 21.0, 20.9, 15.6, 15.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{13}NNaO_4^+$ [M+Na^+]: 282.0737, found 282.0736.

1-(1-Oxo-2,3-dihydro-1H-benzo[f]chromen-3-yl)ethyl acetate (3sa)



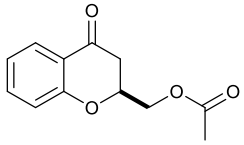
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1, R_f = 0.3) give **3sa** as a yellow oil (40.9 mg, 72% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.43 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 5.32 – 5.21 (m, 1H), 4.62-4.52 (m, 1H), 3.00-2.68 (m, 2H), 2.12 (s, 1.58H), 2.10 (s, 1.42H), 1.43 (d, *J* = 6.6 Hz, 1.58H), 1.40 (d, *J* = 6.5 Hz, 1.42H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.6, 170.3, 170.2, 163.2, 163.1, 137.5, 137.5, 131.3, 129.7, 129.2, 128.3, 125.8, 125.8, 124.9, 118.6, 112.5, 78.9, 78.5, 70.5, 70.1, 40.1, 39.5, 21.1, 21.1, 15.6, 15.6. HRMS (ESI) *m/z* calcd for $C_{17}H_{16}NaO_4^+$ [M+Na^+]: 307.0941, found 307.0933.

1-(6-Chloro-7-methyl-4-oxochroman-2-yl)ethyl acetate (3ta)



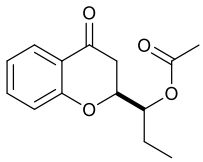
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3ta** as a yellow oil (35.0 mg, 62% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80 (s, 1H), 6.90 (s, 1H), 5.24-5.15 (m, 1H), 4.47-4.36 (m, 1H), 2.81-2.59 (m, 2H), 2.38-2.35 (s, 3H), 2.09 (s, 1.6H), 2.07 (s, 1.4H), 1.38 (d, *J* = 6.5 Hz, 1.6H), 1.34 (d, *J* = 6.6 Hz, 1.4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3, 190.5, 170.2, 170.1, 159.3, 159.2, 145.2, 145.2, 127.8, 126.5, 126.5, 120.0, 119.8, 119.8, 79.1, 78.6, 70.5, 70.2, 38.7, 38.0, 21.1, 21.0, 20.8, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{15}ClNaO_4^+$ [M+Na^+]: 305.0551, found 305.0550.

(4-Oxochroman-2-yl)methyl acetate (3ab)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.43) give **3ab** as a yellow oil (29.0 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 7.9, 7.8 Hz, 1H), 7.52-7.47 (m, 1H), 7.06-7.00 (m, 2H), 4.72-4.66 (m, 1H), 4.39-4.37 (m, 2H), 2.89-2.67 (m, 2H), 2.13 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.1, 170.6, 160.9, 136.2, 126.9, 121.7, 120.8, 117.9, 75.3, 65.0, 39.3, 20.7. HRMS (ESI) *m/z* calcd for $C_{12}H_{12}NaO_4^+$ [M+Na^+]: 243.0628, found 243.0628.

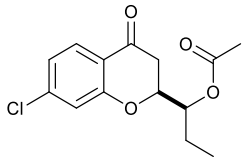
1-(4-Oxochroman-2-yl)propyl acetate (3ac)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3ac** as a yellow oil (31.7 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.51-7.45 (m, 1H), 7.05-6.98 (m, 2H), 5.24-5.19 (m, 0.51H), 5.09-5.05 (m, 0.49H), 4.58-4.48 (m, 1H), 2.89-2.61 (m, 2H), 2.11 (s, 1.48H), 2.09 (s,

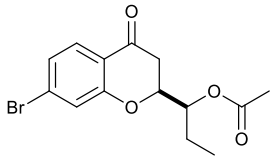
1.51H), 1.88-1.73 (m, 2H), 1.00-0.95 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 191.6, 170.5, 170.3, 161.1, 161.0, 136.1, 136.0, 126.8, 121.5, 121.5, 120.9, 120.8, 117.9, 117.9, 77.8, 74.9, 74.9, 39.2, 38.3, 23.1, 22.9, 20.9, 20.8, 9.7, 9.6. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_4^+$ [M+Na$^+$]: 271.0941, found 271.0938.

1-(7-Chloro-4-oxochroman-2-yl)propyl acetate (3mc)



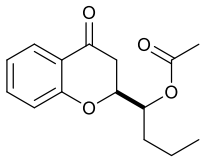
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3mc** as a yellow oil (29.3 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.03-6.99 (m, 2H), 5.22-5.17 (m, 0.49H), 5.08-5.03 (m, 0.51H), 4.58-4.49 (m, 1H), 2.84-2.62 (m, 2H), 2.10, 2.08 (s, 3H), 1.83-1.70 (m, 2H), 0.97 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 170.4, 170.3, 161.4, 161.3, 142.0, 141.9, 128.1, 128.1, 122.4, 119.4, 119.4, 118.1, 118.1, 78.3, 77.6, 74.8, 74.7, 39.0, 38.0, 23.1, 23.0, 20.9, 20.8, 9.7, 9.6. HRMS (ESI) *m/z* calcd for $C_{14}H_{15}ClNaO_4^+$ [M+Na$^+$]: 305.0551, found 305.0549.

1-(7-Bromo-4-oxochroman-2-yl)propyl acetate (3pc)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3pc** as a yellow oil (31.3 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.21 (s, 1H), 7.16 (dt, *J* = 8.4, 1.6 Hz, 1H), 5.22-5.17 (m, 0.49H), 5.07-5.03 (m, 0.51H), 4.58-4.48 (m, 1H), 2.84-2.62 (m, 2H), 2.10 (s, 1.54H), 2.08 (s, 1.46H), 1.82-1.70 (m, 2H), 0.97 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 170.4, 170.3, 161.3, 130.5, 130.4, 128.1, 128.0, 125.2, 121.2, 121.1, 119.8, 119.7, 78.3, 77.6, 74.8, 74.7, 39.0, 38.1, 23.1, 23.0, 20.9, 20.8, 9.7, 9.6. HRMS (ESI) *m/z* calcd for $C_{14}H_{15}BrNaO_4^+$ [M+Na$^+$]: 349.0046, found 349.0043.

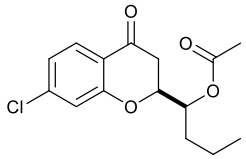
1-(4-Oxochroman-2-yl)butyl acetate (3ad)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.65) give **3ad** as a yellow oil (27.8 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.50-7.45 (m, 1H), 7.04-6.98 (m, 2H), 5.32-5.27 (m, 0.48H), 5.17-5.13 (m, 0.52H), 4.55-4.46 (m, 1H), 2.89-2.61 (m, 2H), 2.8 (d, 3H), 1.78-1.67 (m, 2H), 1.46-1.33 (m, 2H), 0.98-0.94 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.73, 191.71, 170.5, 170.4, 161.1, 161.0, 136.1, 136.0, 126.9, 121.6, 121.5, 120.9, 120.8, 118.0, 117.9,

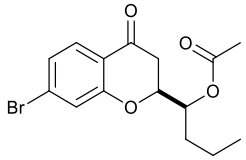
78.2, 73.5, 73.4, 39.2, 38.2, 32.1, 31.9, 29.7, 20.9, 20.8, 18.6, 18.5, 13.8, 13.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{18}NaO_4^+$ [M+Na^+]: 285.1097, found 285.1093.

1-(7-Chloro-4-oxochroman-2-yl)butyl acetate (3md)



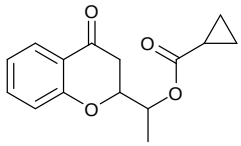
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3md** as a yellow oil (24.9 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 2.6 Hz, 1H), 7.43-7.39 (m, 1H), 6.96 (d, *J* = 8.8, 3.2 Hz, 1H), 5.31-5.26 (m, 0.51H), 5.17-51.2 (m, 0.49H), 4.54-4.45 (m, 1H), 2.85-2.63 (m, 2H), 2.08 (d, 3H), 1.77-1.60 (m, 2H), 1.44-1.33 (m, 2H), 0.98-0.93 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 170.4, 170.2, 161.4, 161.3, 141.9, 141.9, 128.1, 128.1, 122.4, 119.5, 119.4, 118.1, 118.1, 78.7, 78.0, 73.3, 39.0, 38.0, 32.0, 31.9, 20.9, 20.8, 18.5, 13.9, 13.8. HRMS (ESI) *m/z* calcd for $C_{15}H_{17}ClNaO_4^+$ [M+Na^+]: 319.0708, found 319.0707.

1-(7-Bromo-4-oxochroman-2-yl)butyl acetate (3pd)



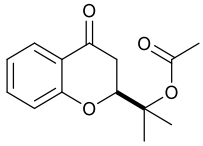
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3pd** as a yellow oil (23.8 mg, 35% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 1.2 Hz, 1H), 7.18-7.15 (m, 1H), 5.30-5.26 (m, 0.54H), 5.16-5.12 (m, 0.45H), 4.56-4.47 (m, 1H), 2.88-2.59 (m, 2H), 2.08 (d, 3H), 1.79-1.61 (m, 2H), 1.48-1.31 (m, 2H), 0.98-0.94 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 170.4, 170.3, 161.3, 161.2, 130.5, 130.4, 128.1, 128.0, 125.2, 121.2, 121.1, 119.8, 119.7, 78.7, 77.9, 73.3, 39.0, 38.0, 32.0, 31.9, 20.9, 20.8, 18.5, 14.2, 13.9, 13.8. HRMS (ESI) *m/z* calcd $C_{15}H_{17}BrNaO_4^+$ [M+Na^+]: 363.0202, found 363.0200.

1-(4-oxochroman-2-yl)ethyl cyclopropanecarboxylate (3ae)



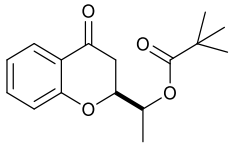
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3ae** as a yellow oil (35.9 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (d, *J* = 7.8, 1.8 Hz, 1H), 7.51-7.46 (m, 1H), 7.05-6.99 (m, 2H), 5.26-5.17 (m, 1H), 4.50-4.43 (m, 1H), 2.87-2.62 (m, 2H),1.66-1.58 (m, 1H), 1.40 (d, *J* = 6.6 Hz, 1.55H), 1.36 (d, *J* = 6.5 Hz, 1.45H), 1.03-0.98 (m, 2H), 0.91-0.85 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 191.6, 174.1, 174.0, 161.12, 161.08, 136.12, 136.08, 126.9, 126.8, 121.6, 121.5, 120.9, 120.8, 117.9, 79.0, 78.5, 70.6, 70.1, 38.9, 38.4, 15.6, 15.6, 12.96, 12.90, 8.8, 8.7, 8.6. HRMS (ESI) *m/z* calcd for $C_{15}H_{16}NaO_4^+$ [M+Na^+]: 283.0941, found 283.0945.

2-(4-Oxochroman-2-yl)propan-2-yl acetate (3ag)



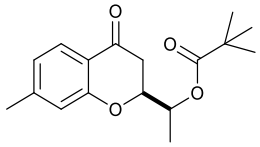
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.5) give **3ag** as a yellow oil (23.3 mg, 47% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 7.8, 6.0 Hz, 1H), 7.51-7.47 (m, 1H), 7.05-6.99 (m, 2H), 4.58 (dd, *J* = 13.1, 9.9 Hz, 1H), 2.86-2.71 (m, 2H), 2.01 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.2, 170.0, 161.2, 136.0, 126.9, 121.5, 120.9, 117.8, 81.5, 81.3, 37.8, 22.6, 22.2, 21.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{16}NaO_4^+$ [M+Na^+]: 271.0941, found 271.0942.

1-(4-Oxochroman-2-yl)ethyl pivalate (3af)



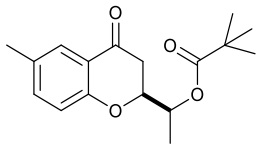
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3af** as a yellow oil (44.2 mg, 80% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.51-7.44 (m, 1H), 7.04-6.96 (m, 2H), 5.23-5.15 (m, 1H), 4.51-4.41 (m, 1H), 2.88-2.61 (m, 2H), 1.37 (d, *J* = 6.5 Hz, 1.59H), 1.34 (d, *J* = 6.5 Hz, 1.39H), 1.20 (s, 4.74H), 1.19 (s, 4.18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 191.6, 177.6, 177.5, 161.1, 136.1, 136.1, 126.9, 121.5, 120.9, 120.8, 117.9, 79.0, 78.6, 70.4, 70.0, 38.9, 38.9, 38.8, 38.3, 27.1, 27.0, 15.7, 15.4. HRMS (ESI) *m/z* calcd for $C_{16}H_{20}NaO_4^+$ [M+Na^+]: 299.1254, found 299.1255.

1-(7-Methyl-4-oxochroman-2-yl)ethyl pivalate (3bf)



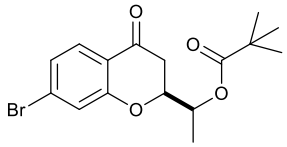
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3bf** as a yellow oil (44.7 mg, 77% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0Hz, 1H), 6.85-6.78 (m, 2H), 5.22-5.15 (m, 1H), 4.48-4.38 (m, 1H), 2.81-2.57 (m, 2H), 2.35 (s, 3H), 1.36 (d, *J* = 6.5Hz, 1.5H), 1.33 (d, *J* = 6.5Hz, 1.5H), 1.21 (s, 4.5H), 1.19 (s, 4.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 191.3, 177.6, 177.5, 161.2, 147.7, 147.7, 126.8, 122.9, 118.6, 118.6, 117.9, 79.0, 78.6, 70.4, 70.0, 38.9, 38.3, 27.1, 27.0, 21.9, 21.9, 15.7, 15.4. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NaO_4^+$ [M+Na^+]: 313.1410, found 313.1404.

1-(6-Methyl-4-oxochroman-2-yl)ethyl pivalate (3cf)



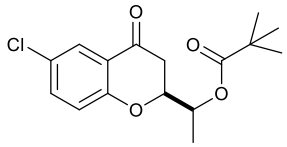
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3cf** as a yellow oil (41.8 mg, 72% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.31-7.27 (m, 1H), 6.88 (dd, *J* = 8.4, 2.2 Hz, 1H), 5.21-5.15 (m, 1H), 4.47-4.37 (m, 1H), 2.85-2.56 (m, 2H), 2.30 (s, 3H), 1.35 (t, *J* = 6.9 Hz, 3H), 1.21 (d, 4.5H), 1.19 (s, 4.5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 191.9, 177.6, 177.5, 159.2, 137.2, 137.2, 131.0, 126.4, 120.5, 120.4, 117.7, 79.0, 78.6, 70.4, 69.9, 39.0, 38.9, 38.4, 27.1, 27.0, 20.4, 15.7, 15.4. HRMS (ESI) *m/z* calcd for $C_{17}H_{22}NaO_4^+$ [M+Na^+]: 313.1410, found 313.1404.

1-(7-Bromo-4-oxochroman-2-yl)ethyl pivalate (3pf)



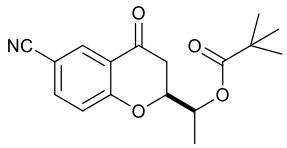
Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3pf** as a yellow oil (52.5 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 1H), 7.20-7.16 (m, 2H), 5.21-5.11 (m, 1H), 4.51-4.43 (m, 1H), 2.84-2.62 (m, 2H), 1.36 (d, *J* = 6.5 Hz, 1.5H), 1.32(d, *J* = 6.5 Hz, 1.5H), 1.19 (s, 4.5H), 1.18(s, 4.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 190.6, 177.5, 177.4, 161.3, 130.5, 130.4, 128.1, 125.2, 125.2, 121.1, 119.7, 119.7, 79.5, 79.0, 70.1, 69.8, 38.8, 38.8, 38.1, 27.0, 27.0, 15.6, 15.4. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}BrNaO_4^+$ [M+Na^+]: 377.0359, found 377.0352.

1-(6-Chloro-4-oxochroman-2-yl)ethyl pivalate (3nf)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.6) give **3nf** as a yellow oil (38.4 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 2.6 Hz, 1H), 7.41 (dt, *J* = 8.9, 2.5 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.24-5.12 (m, 1H), 4.47-4.40 (m, 1H), 2.81-2.67 (m, 2H), 1.36 (d, *J* = 6.5Hz, 1.5H), 1.33 (d, *J* = 6.5Hz, 1.5H), 1.20 (s, 4.5H), 1.18 (s, 4.5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 177.6, 159.5, 135.9, 135.9, 127.1, 126.2, 121.6, 119.6, 79.3, 78.8, 70.2, 69.8, 38.8, 38.6, 38.0, 27.0, 27.0, 15.7, 15.4. HRMS (ESI) *m/z* calcd for $C_{16}H_{19}ClNaO_4^+$ [M+Na^+]: 333.0864, found 333.0861.

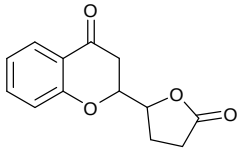
1-(6-Cyano-4-oxochroman-2-yl)ethyl pivalate (3rf)



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 5:1, R_f = 0.4) give **3rf** as a yellow oil (39.1 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 1H), 7.72-7.68 (m, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 5.26-5.16 (m, 1H), 4.59-4.52 (m, 1H), 2.84-2.73 (m, 2H), 1.37 (d, *J* = 6.5 Hz, 1.47H), 1.33 (d, *J* = 6.5 Hz, 1.53H), 1.17 (s,

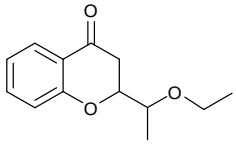
4.59H), 1.16 (s, 4.41H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 189.3, 177.5, 177.4, 163.5, 138.4, 138.4, 132.1, 132.1, 121.1, 121.1, 119.5, 117.8, 105.5, 105.5, 79.7, 79.2, 70.0, 69.7, 38.9, 38.8, 38.5, 37.7, 27.0, 15.6, 15.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}NNaO_4^+$ [M+Na^+]: 324.1206, found 324.1206.

2-(5-oxotetrahydrofuran-2-yl)chroman-4-one (3ah)



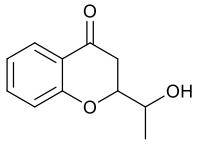
Flash column chromatography on silica gel (petroleum ether/ethyl acetate 5/1) gave **3ah** as a yellow liquid (16.2 mg, 35%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.52-7.48 (m, 1H), 7.07-7.03 (m, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 4.71-4.67 (m, 1H), 4.54-4.49 (m, 1H), 3.14-3.07 (m, 1H), 2.85-2.76 (m, 1H), 2.69-2.56 (m, 2H), 2.49-2.39 (m, *2*H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.1, 176.5, 160.6, 136.3, 127.1, 122.0, 120.7, 117.9, 79.5, 78.5, 39.4, 28.1, 23.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{12}NaO_4^+$ [M+Na^+]: 255.0628, found 255.0631.

2-(1-ethoxyethyl)chroman-4-one (3ak)[1]



Flash column chromatography on silica gel (petroleum ether/ethyl acetate 3/1) gave **3ak** as a yellow liquid (30.8 mg, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.84 (m, 1H), 7.48-7.43 (m, 1H), 7.01-6.97 (m, 2H), 4.45-4.39 (m, 0.46H), 4.35-4.30 (m, 0.54H), 3.75-3.63 (m, 2H), 3.59-3.49 (m, 1H), 2.97-2.75 (m, 1.54H), 2.64-2.60 (m, 0.47H), 1.32 (d, *J* = 6.4 Hz, 1.4H), 1.27 (d, *J* = 6.3 Hz, 1.64H), 1.22-1.17 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.8, 192.6, 161.4, 161.3, 135.9, 135.8, 126.8, 126.7, 121.23, 121.21, 121.0, 118.0, 117.9, 80.6, 79.7, 75.9, 75.5, 65.3, 65.2, 38.9, 38.4, 16.2, 15.5, 15.4, 15.3.

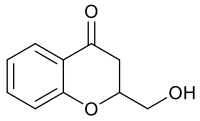
2-(1-Hydroxyethyl)chroman-4-one (4a)[1]



Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1, R_f = 0.6) give **4** as a colorless oil (24.8 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$): 7.89-7.86 (m, 1H), 7.51-7.45 (m, 1H), 7.05-7.00 (m, 2H), 4.39-4.19 (m, 1.5H), 4.01-3.94 (m, 0.5H), 2.98-2.82 (m, 1H), 2.69-2.63 (m, 1H), 2.27 (d, *J* = 15.9 Hz, 1H), 1.33 (d, *J* = 6.5 Hz, 1.42H), 1.27 (d, *J* = 6.6 Hz, 1.58H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 161.2, 160.8, 136.1, 136.0, 127.0, 126.9, 121.7, 121.5, 120.9, 117.8, 81.5, 81.2, 69.2, 68.4, 39.6, 36.9, 18.4, 17.6.

[1] R. Chen, J.-T. Yu and J. Cheng, *Org. Biomol. Chem.* 2018, **16**, 1823.

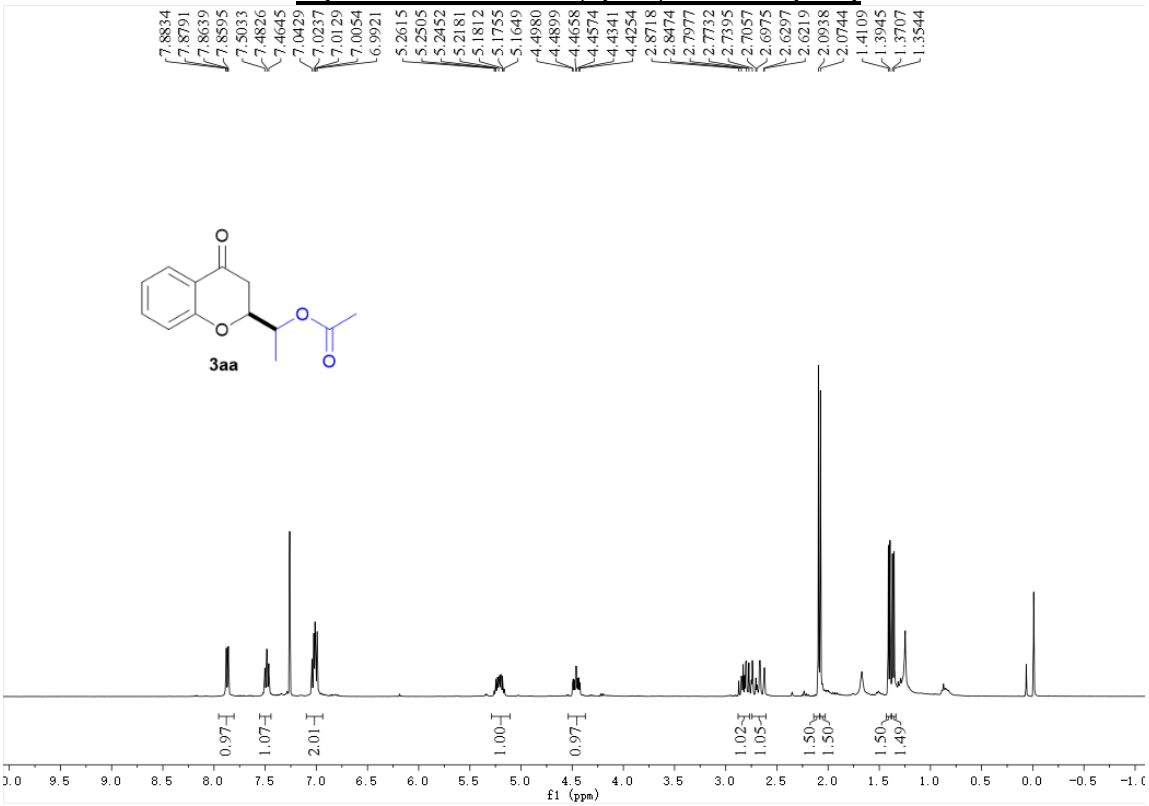
2-(Hydroxymethyl)chroman-4-one (4b)[1]

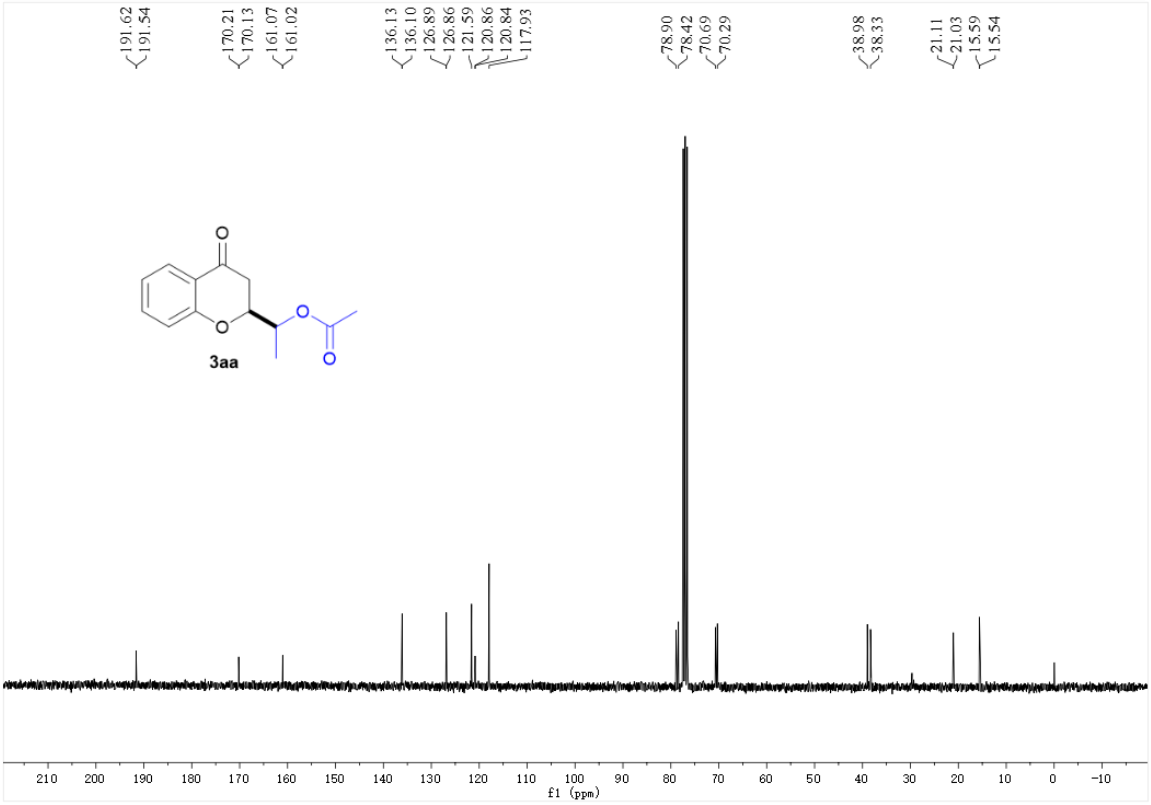


Flash column chromatography on a silica gel (petroleum ether : ethyl acetate, 3:1, R_f = 0.6) give **5** as a yellow oil (24.0 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$): 7.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.50-7.46 (m, 1H), 7.04-6.98 (m, 2H), 4.61-4.54 (m, 1H), 4.01-3.97 (m, 1H), 3.87-3.82 (m, 1H), 2.97-2.90 (m, 1H), 2.65-2.60 (m, 1H), 2.35-2.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 161.0, 136.1, 127.0, 121.6, 120.8, 117.8, 78.1, 64.5, 39.0.

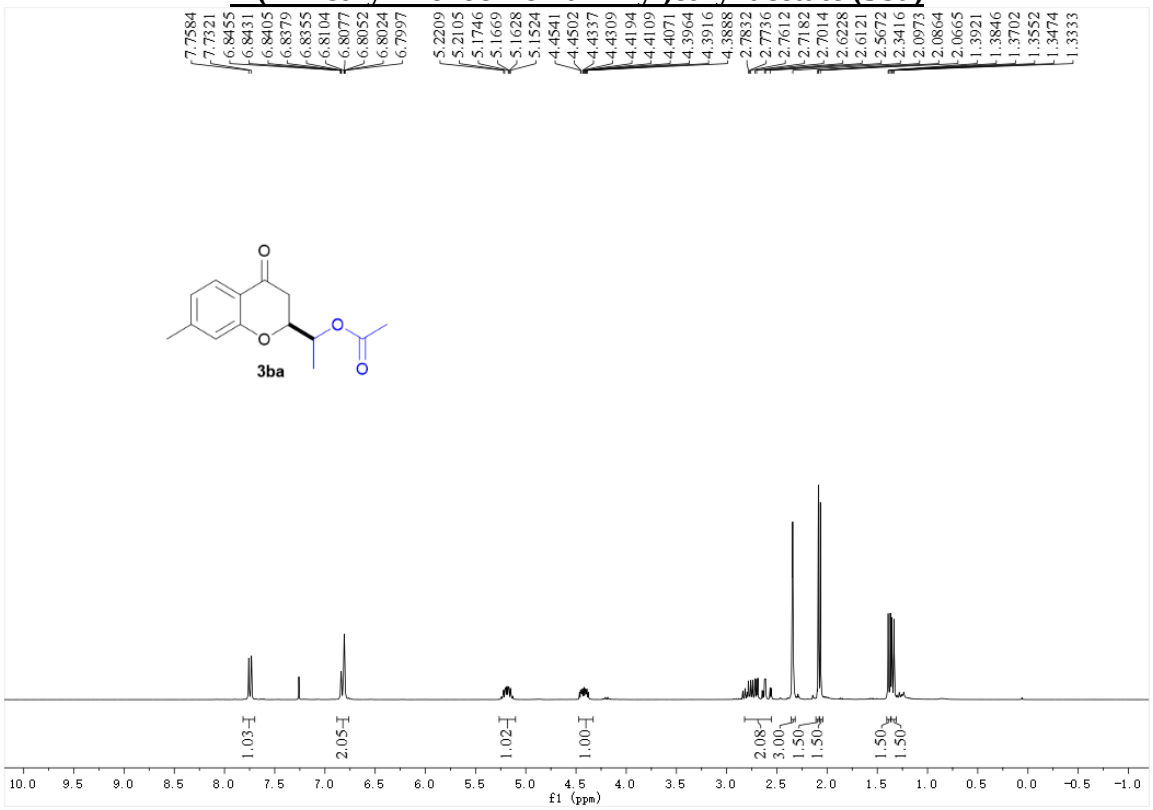
4. Copies of ^{1}H NMR and ^{13} C NMR spectra of the products

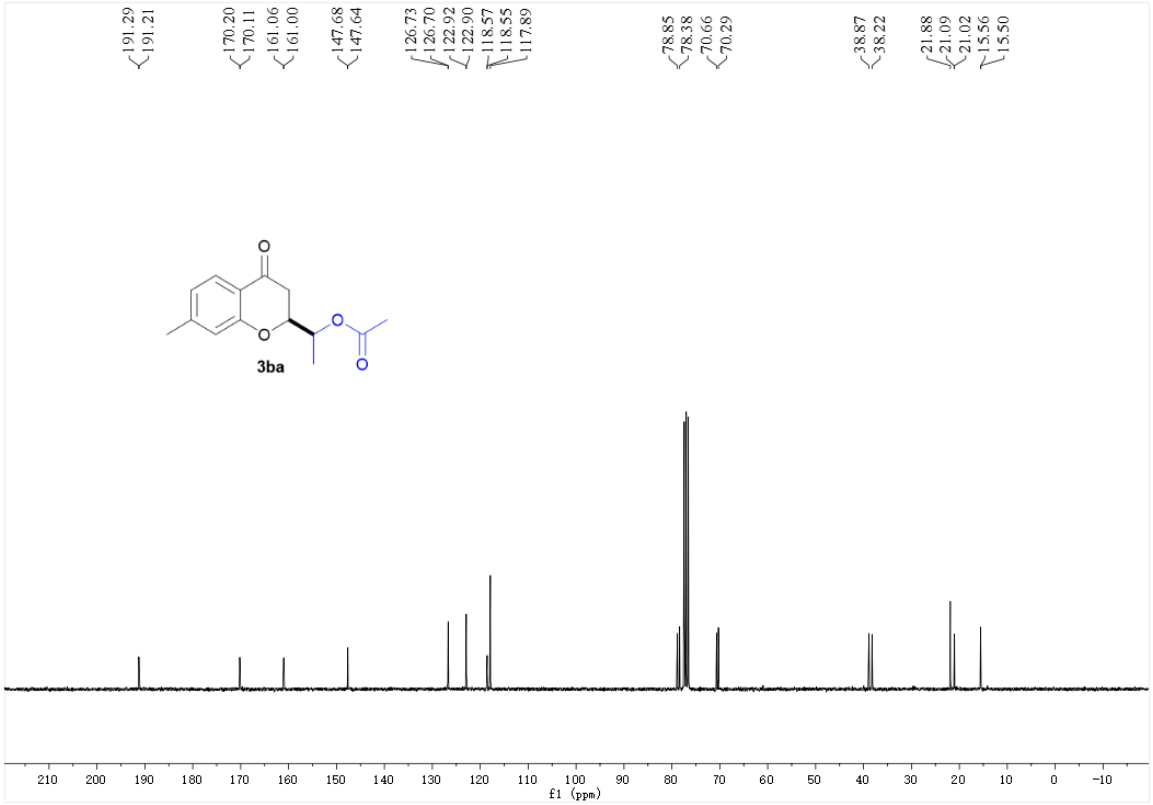
1-(4-Oxochroman-2-yl)ethyl acetate (3aa)



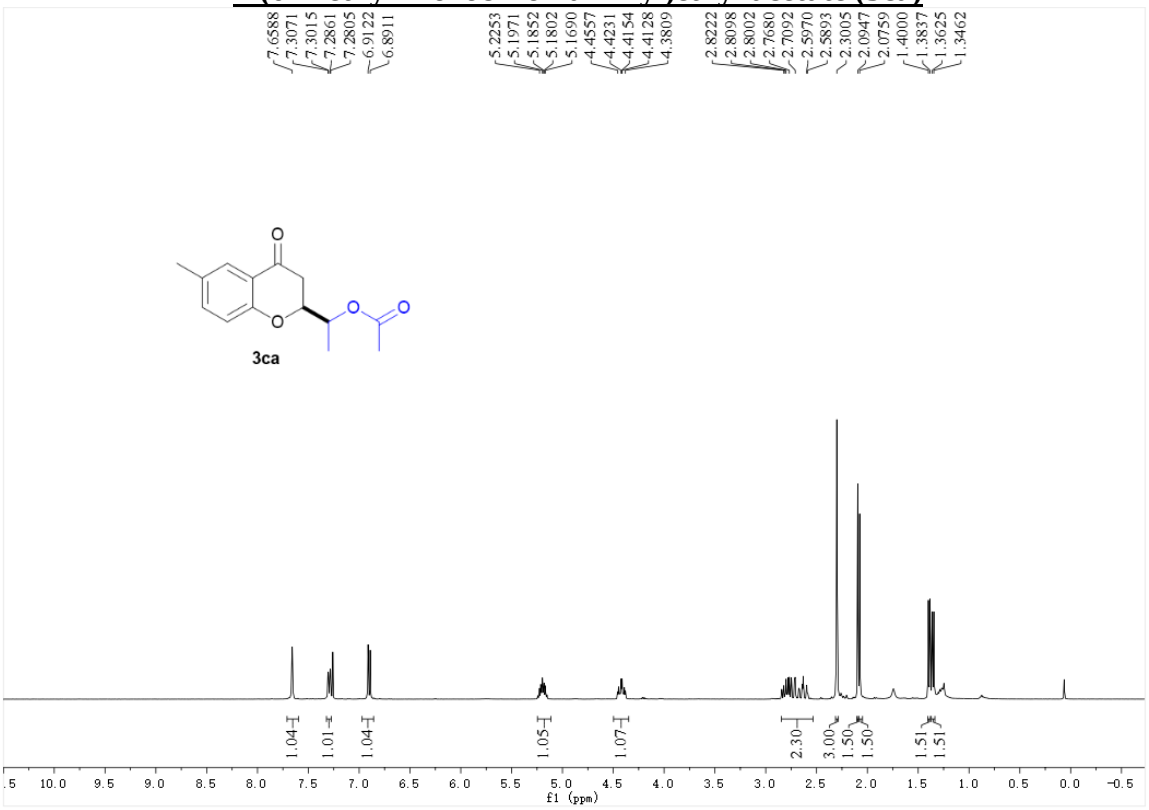


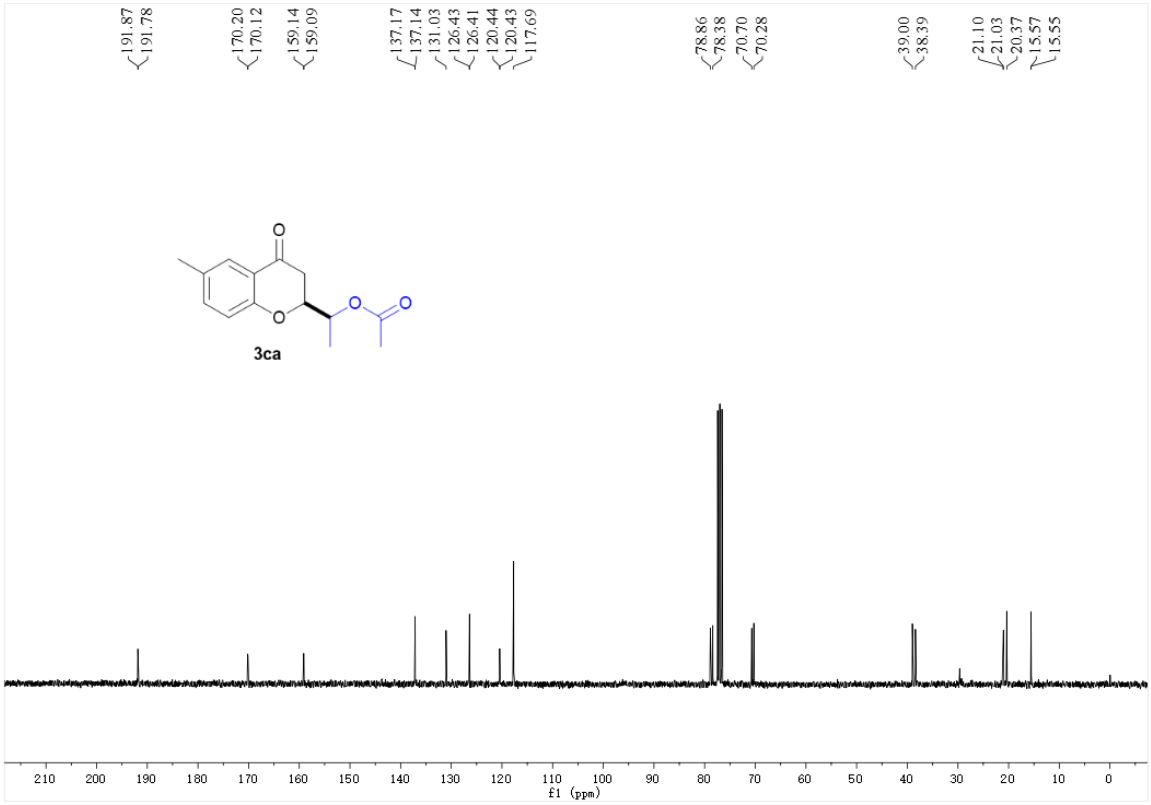
1-(7-Methyl-4-oxochroman-2-yl)ethyl acetate (3ba)



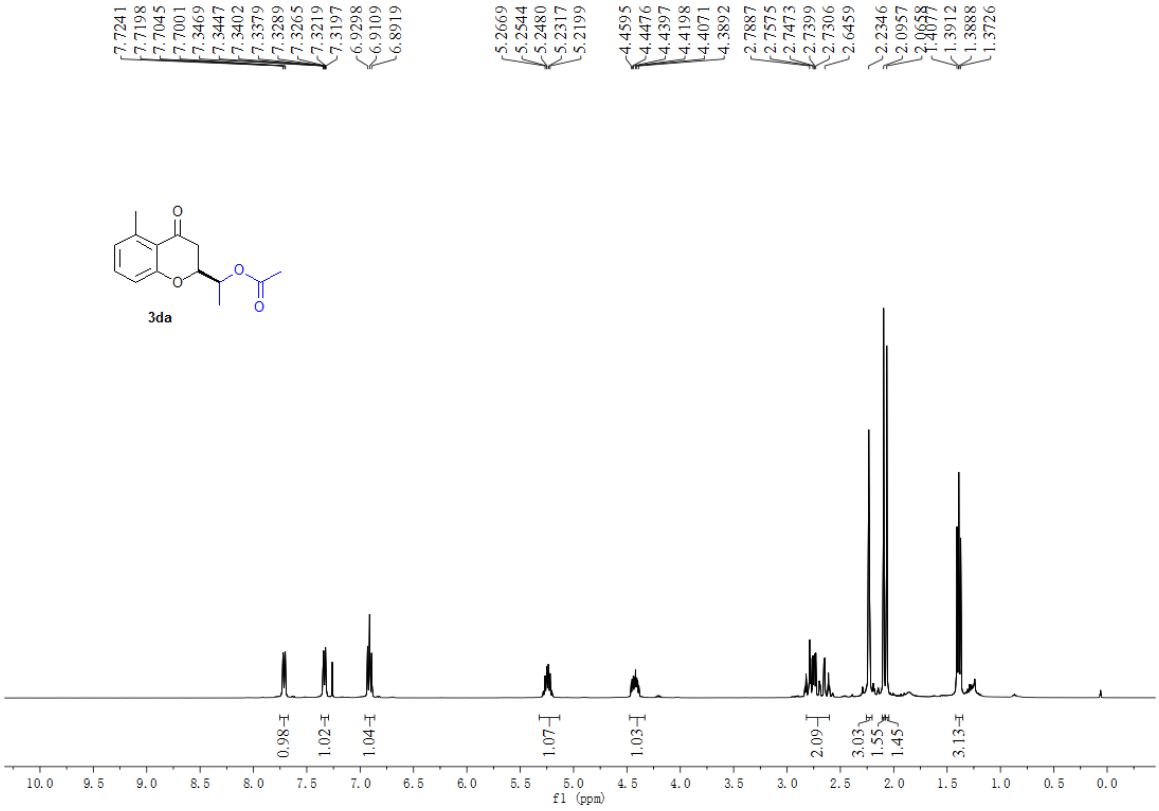


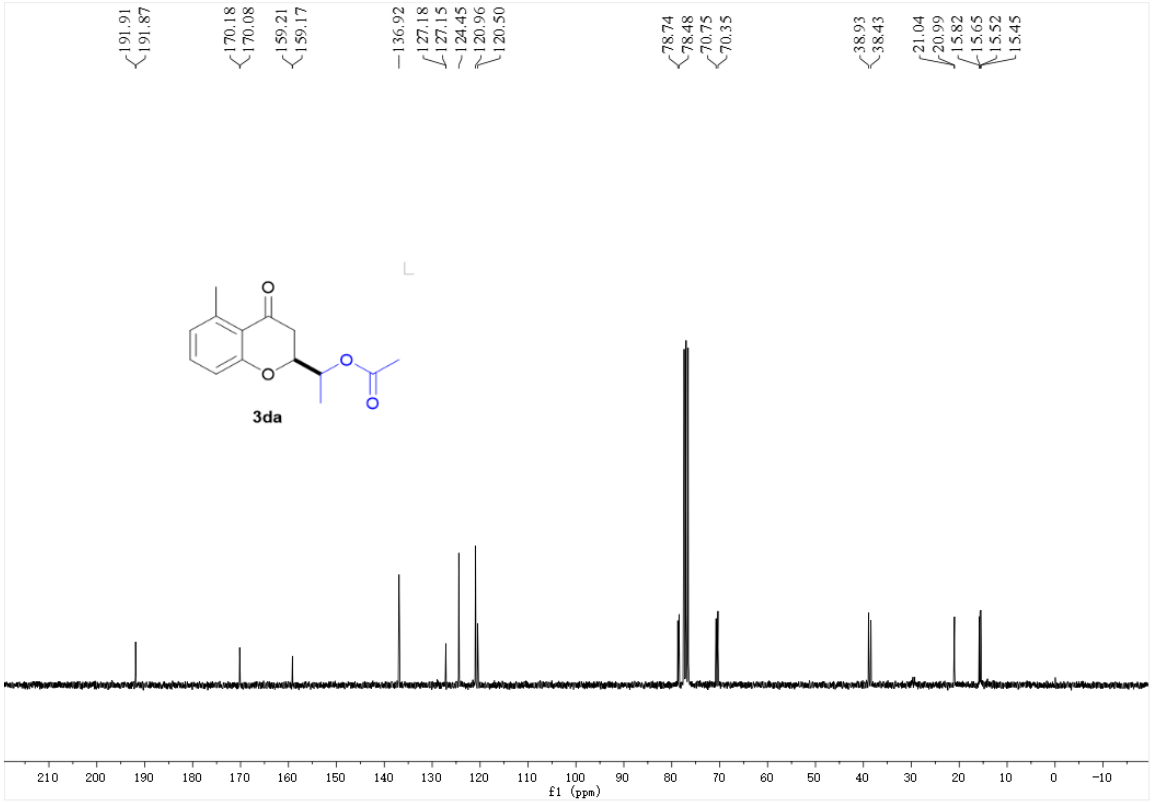
1-(6-Methyl-4-oxochroman-2-yl)ethyl acetate (3ca)



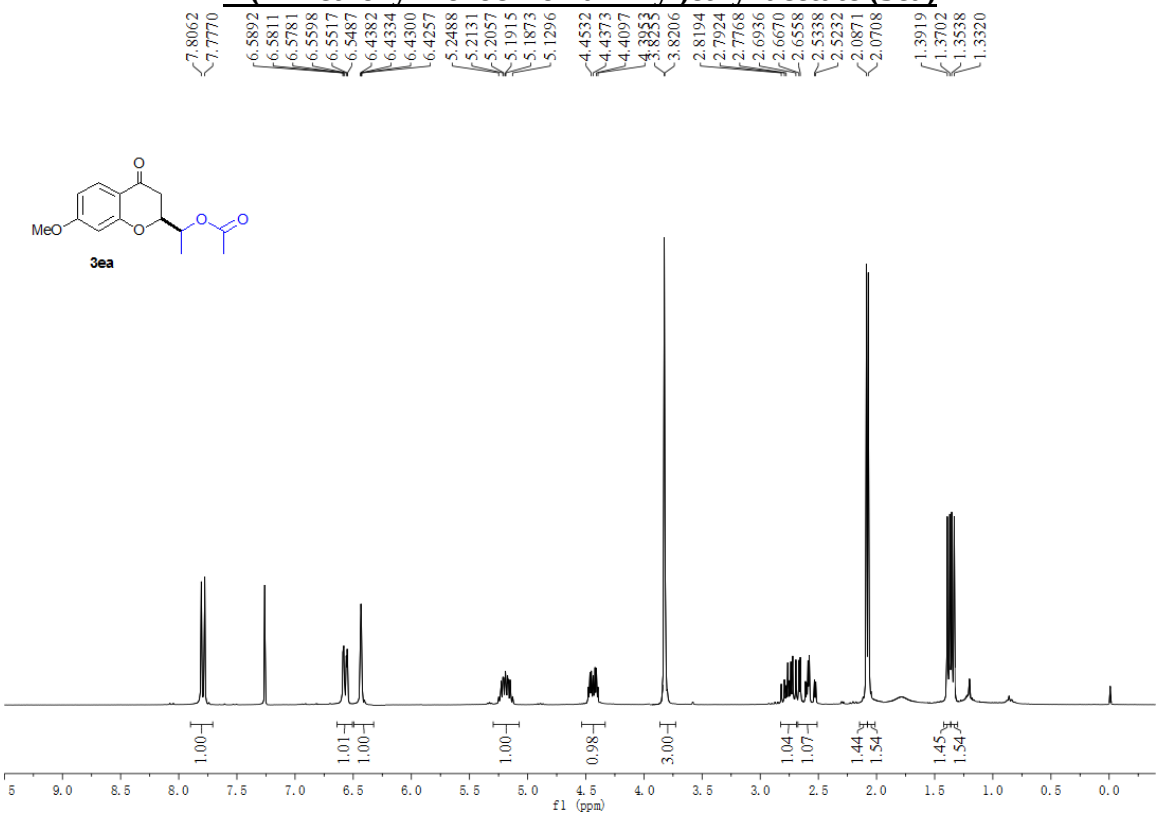


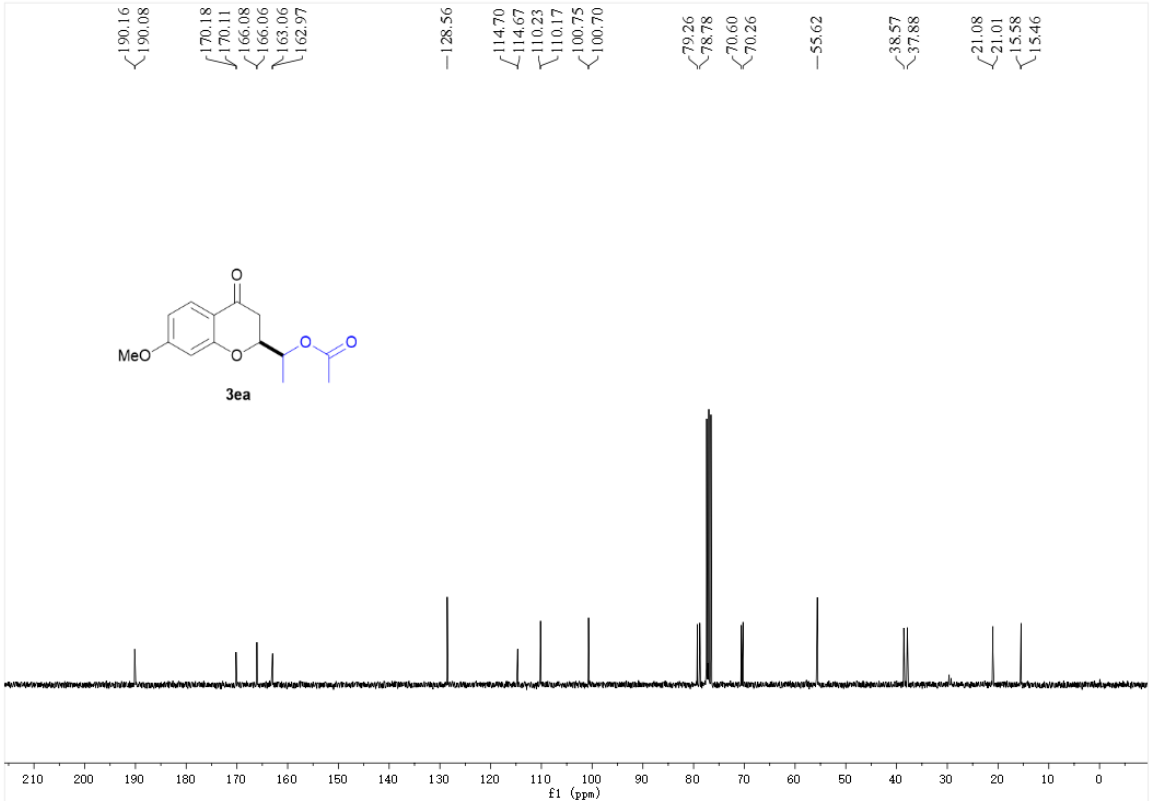
1-(5-Methyl-4-oxochroman-2-yl)ethyl acetate (3da)



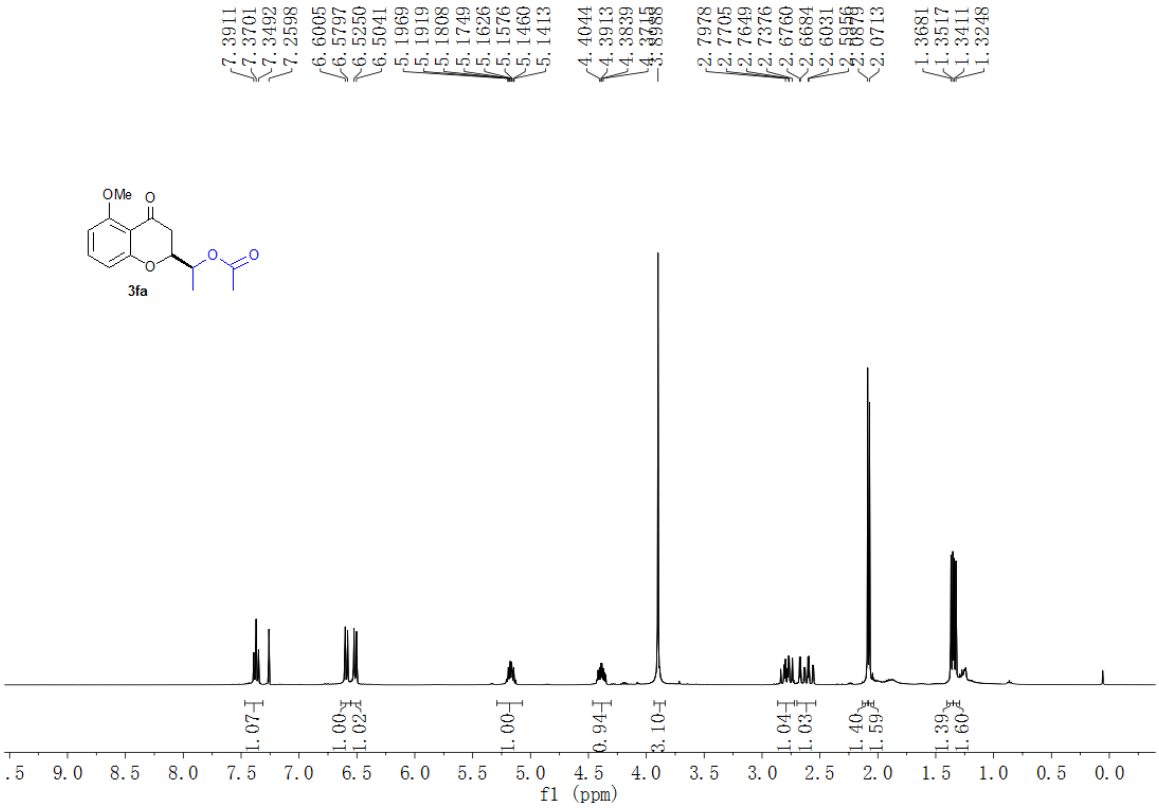


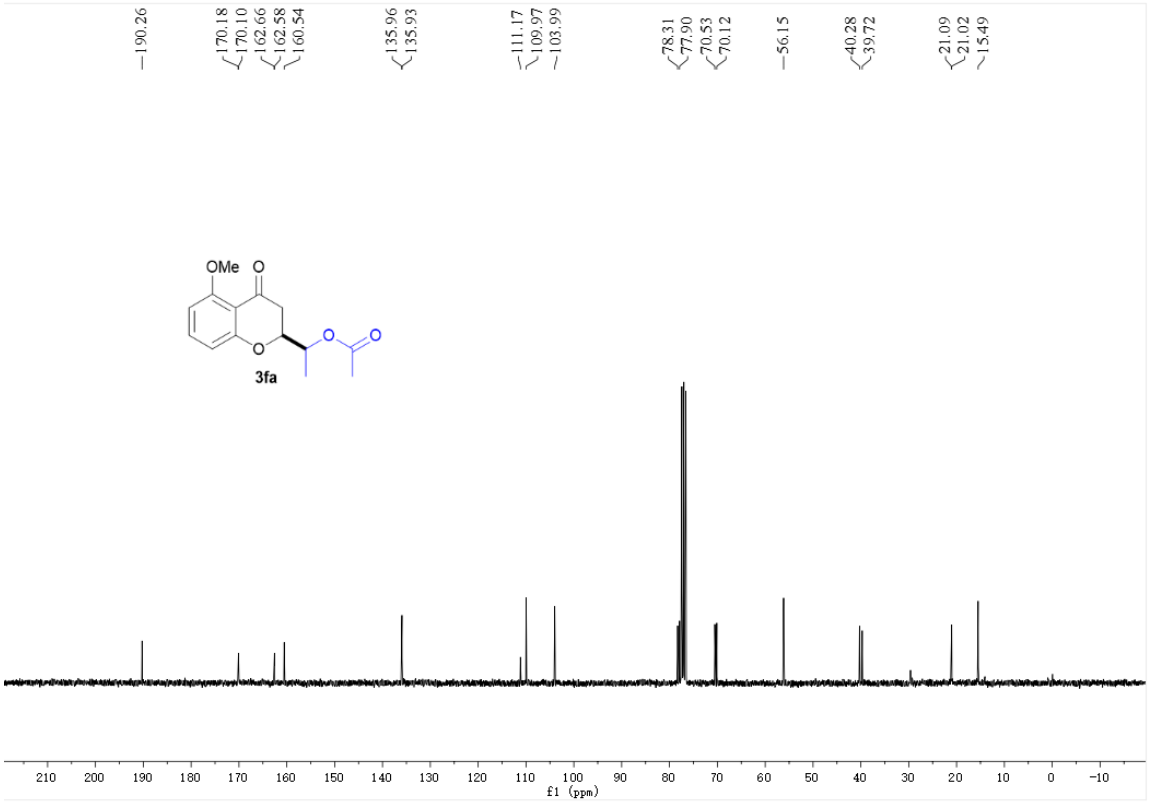
1-(7-Methoxy-4-oxochroman-2-yl)ethyl acetate (3ea)



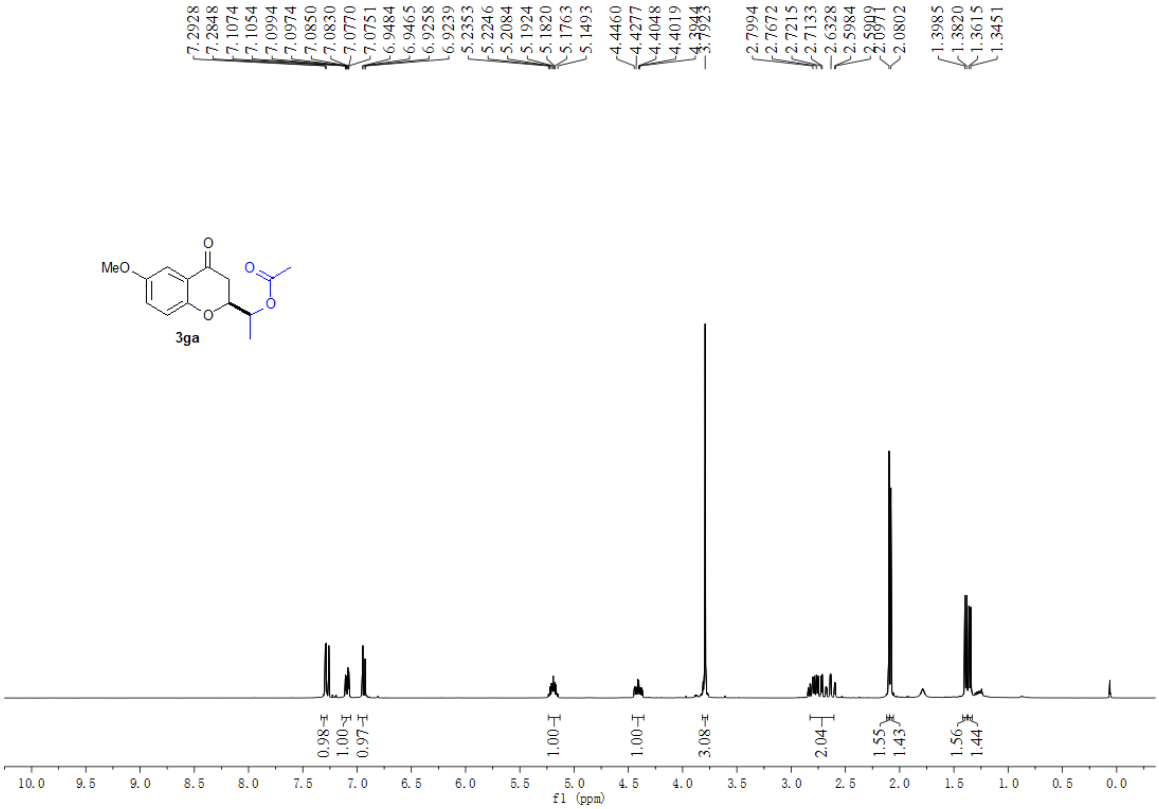


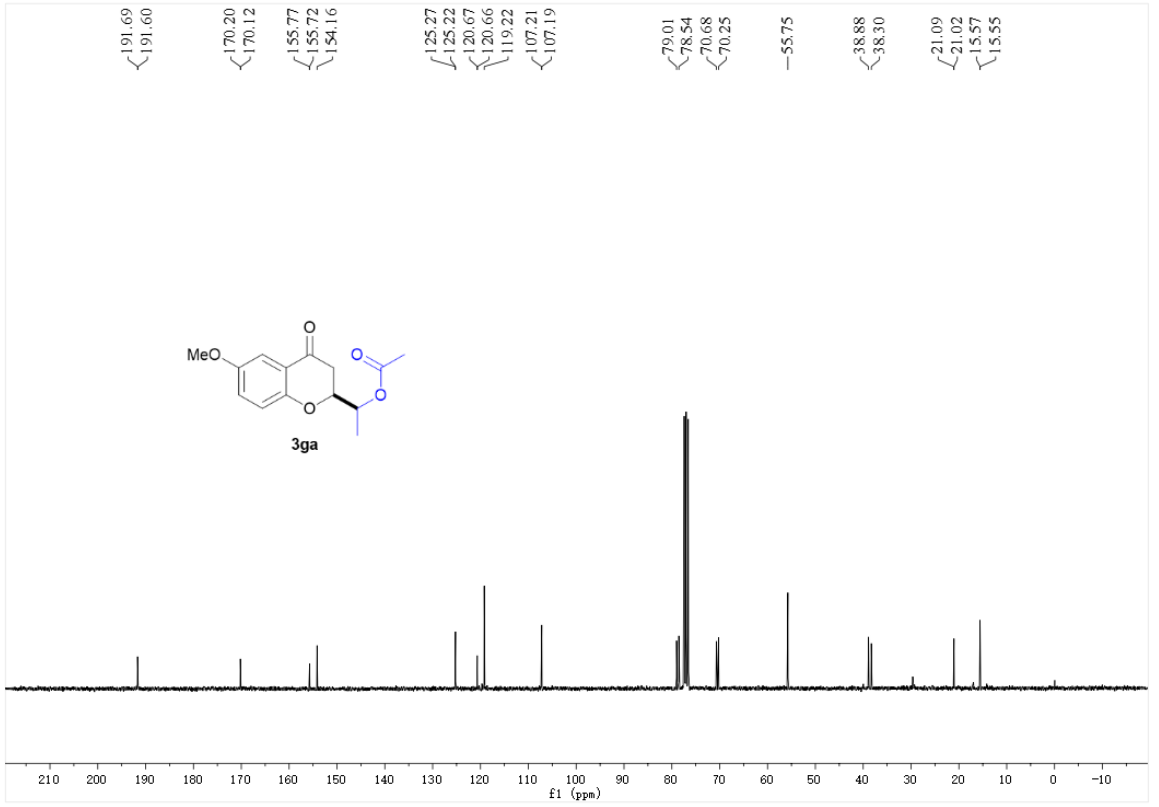
1-(5-Methoxy-4-oxochroman-2-yl)ethyl acetate (3fa)



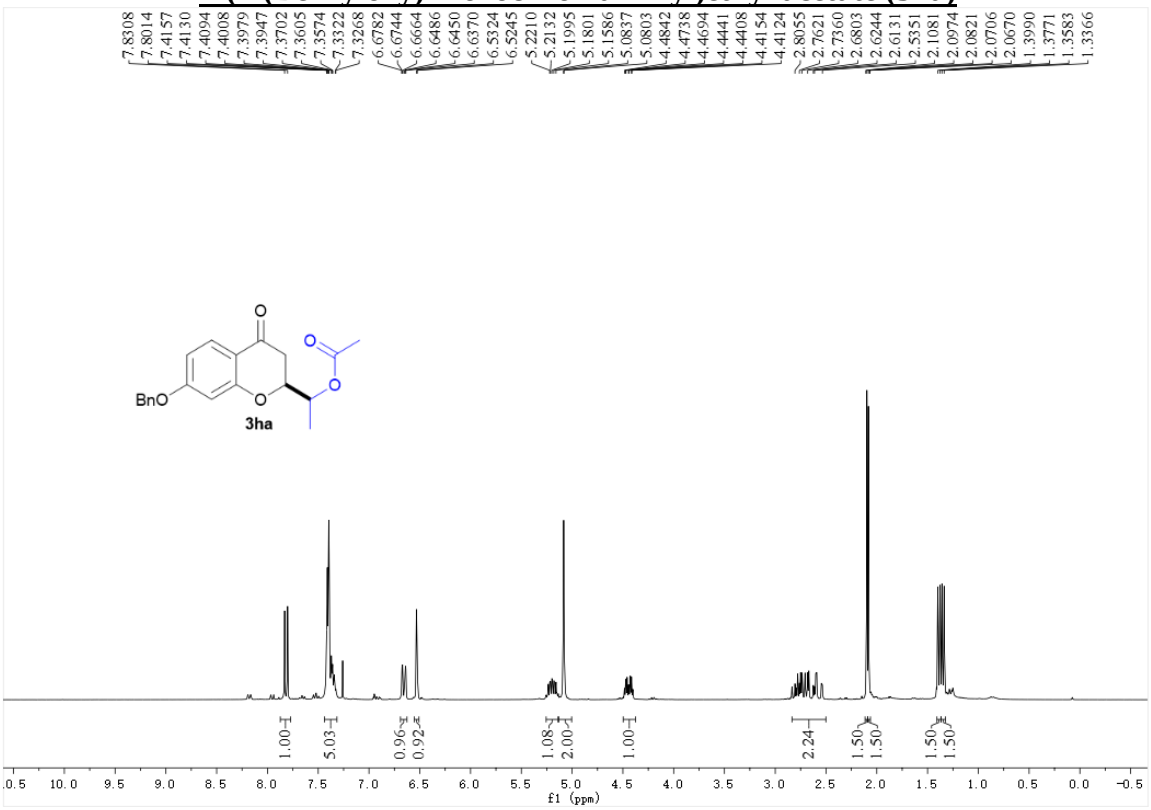


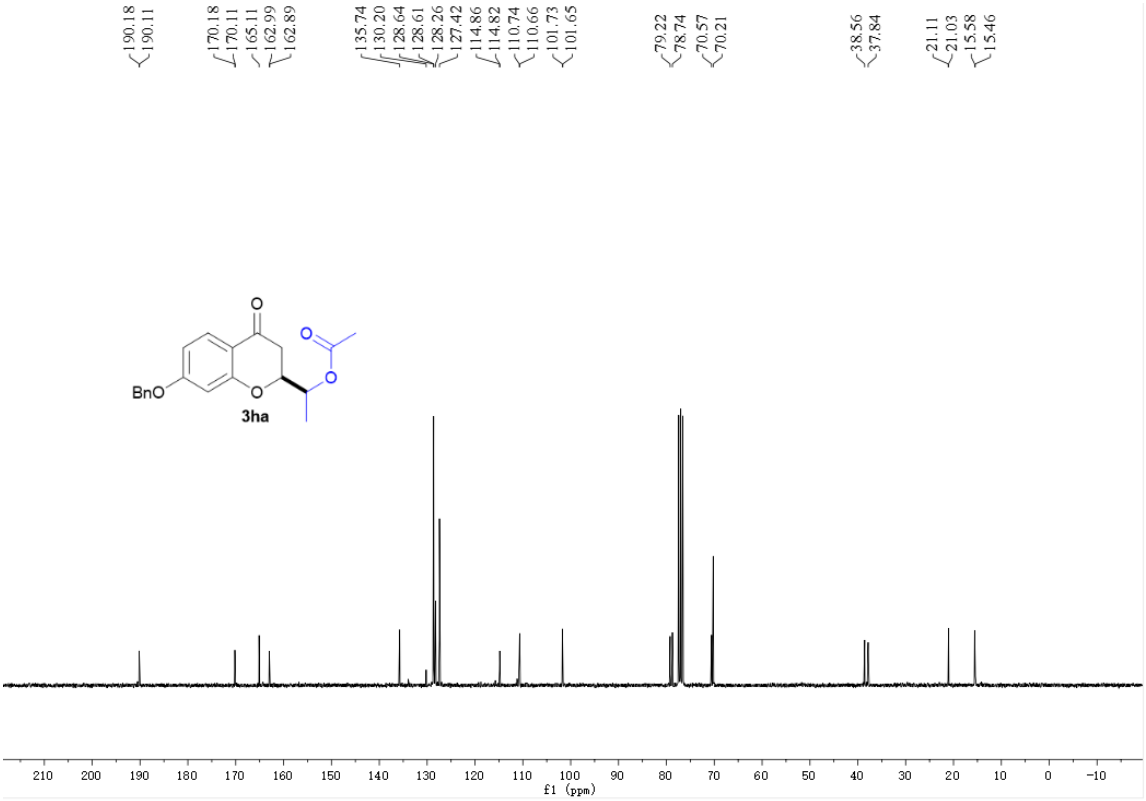
1-(6-Methoxy-4-oxochroman-2-yl)ethyl acetate (3ga)



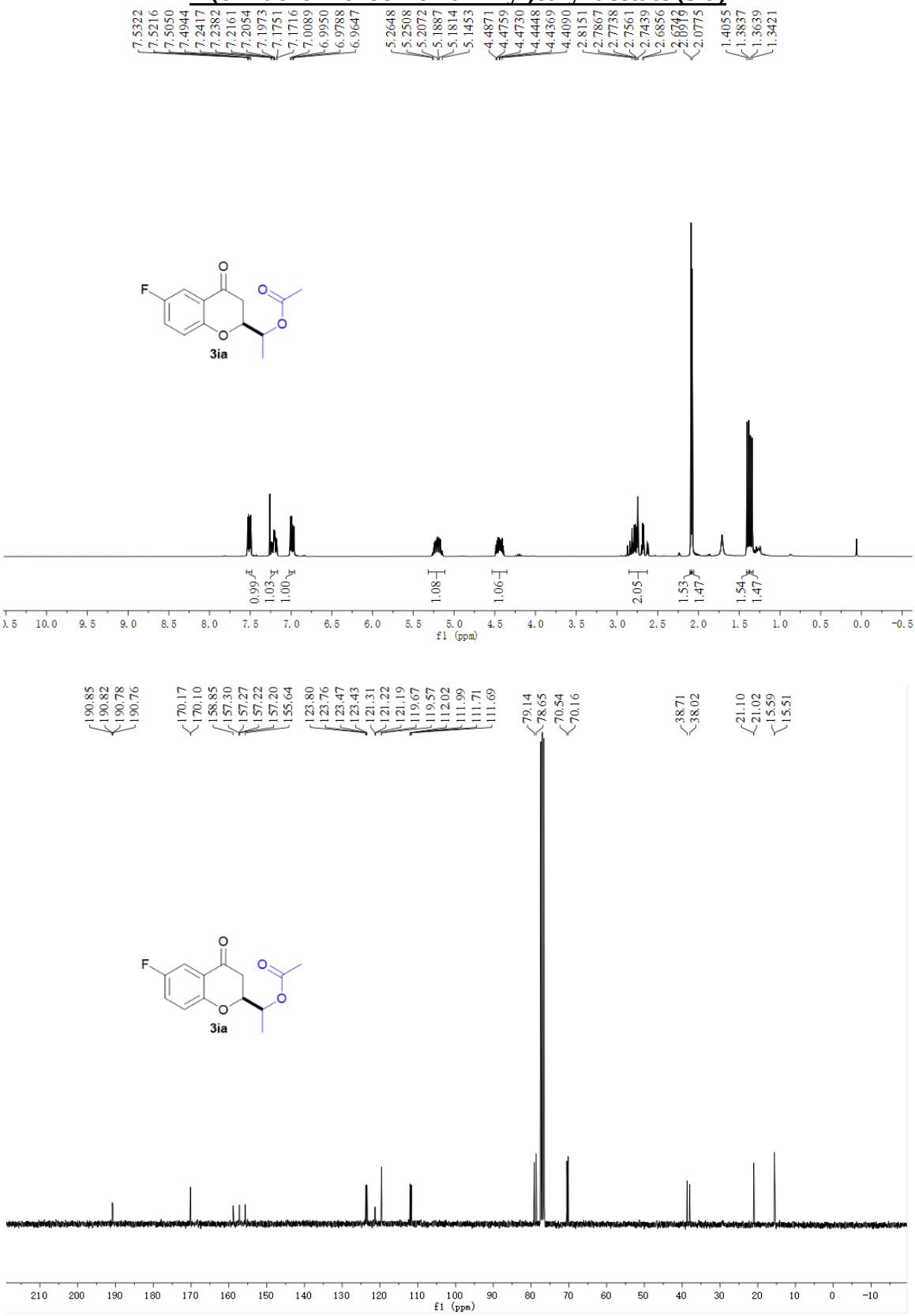


1-(7-(Benzyloxy)-4-oxochroman-2-yl)ethyl acetate (3ha)

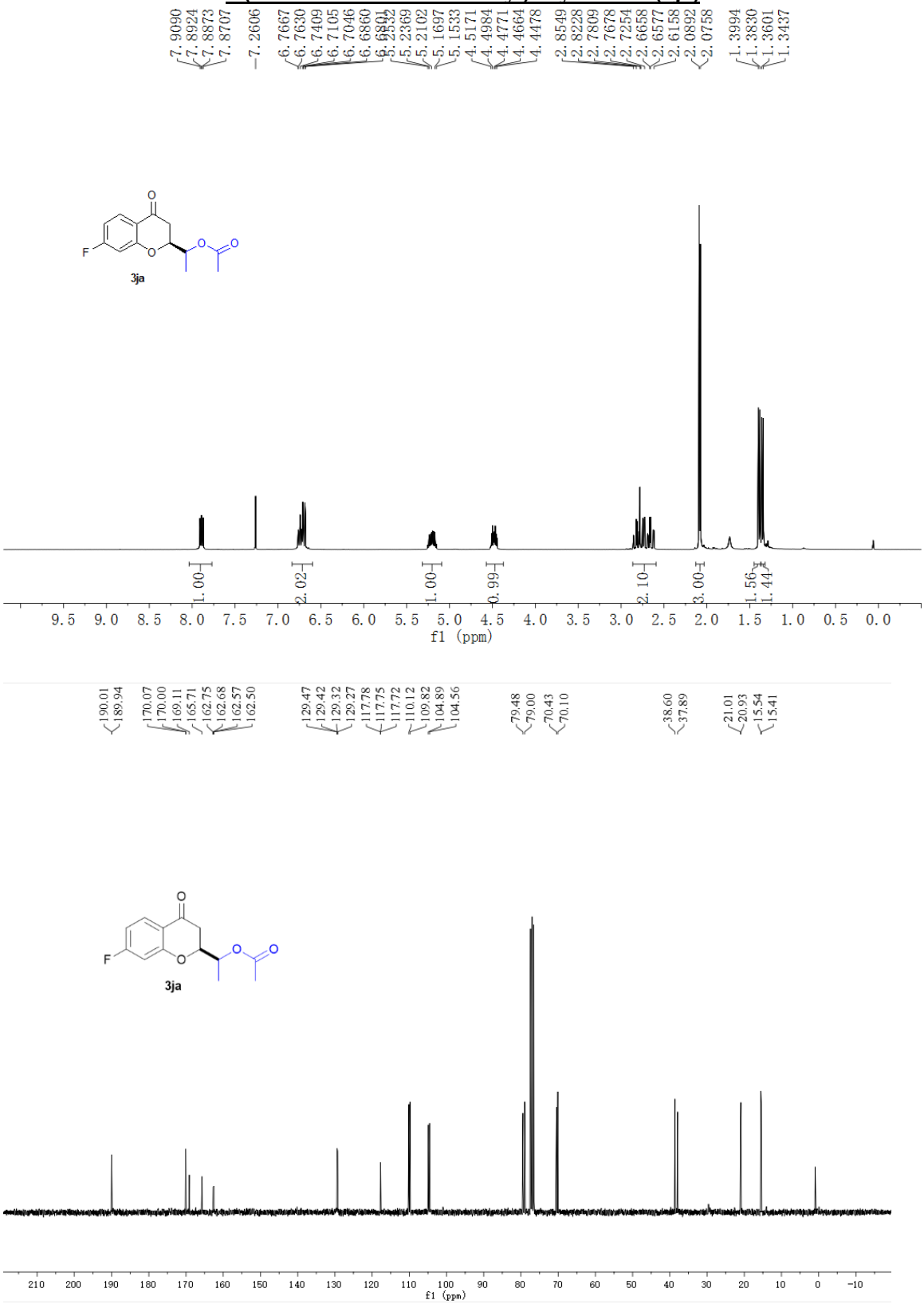




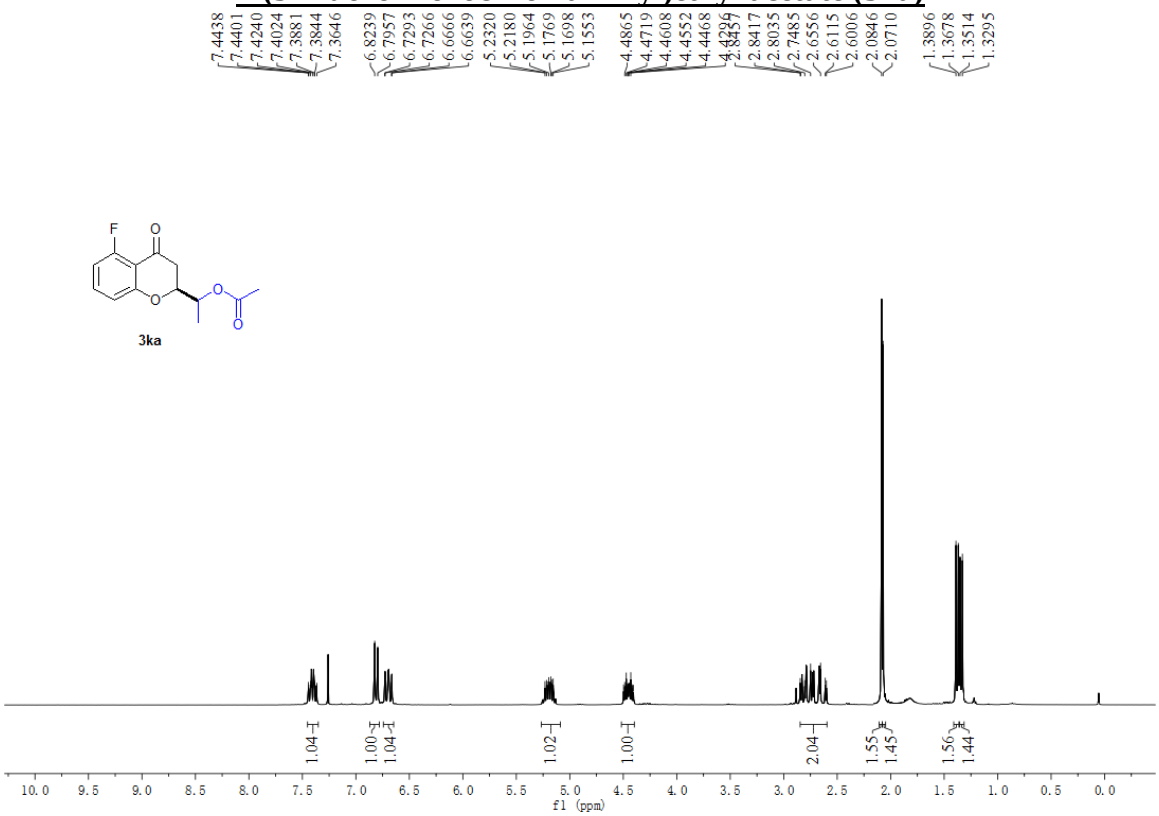
1-(6-Fluoro-4-oxochroman-2-yl)ethyl acetate (3ia)

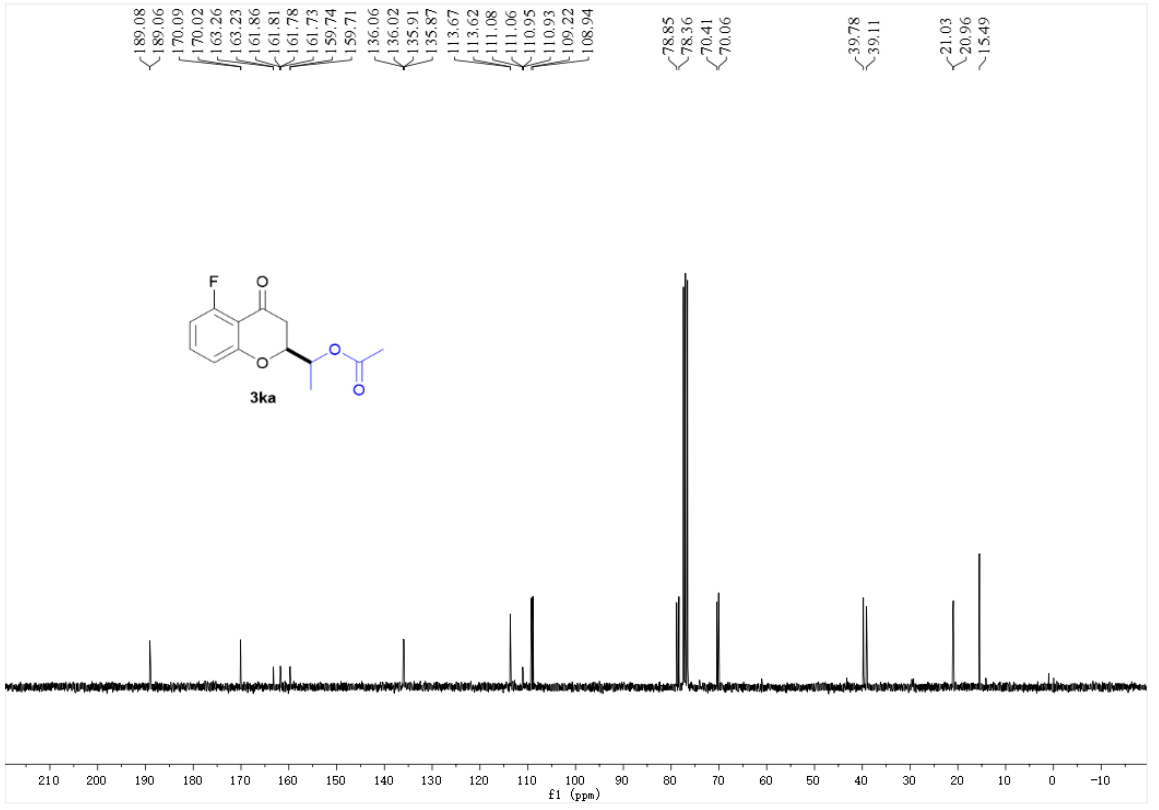


1-(7-Fluoro-4-oxochroman-2-yl)ethyl acetate (3ja)

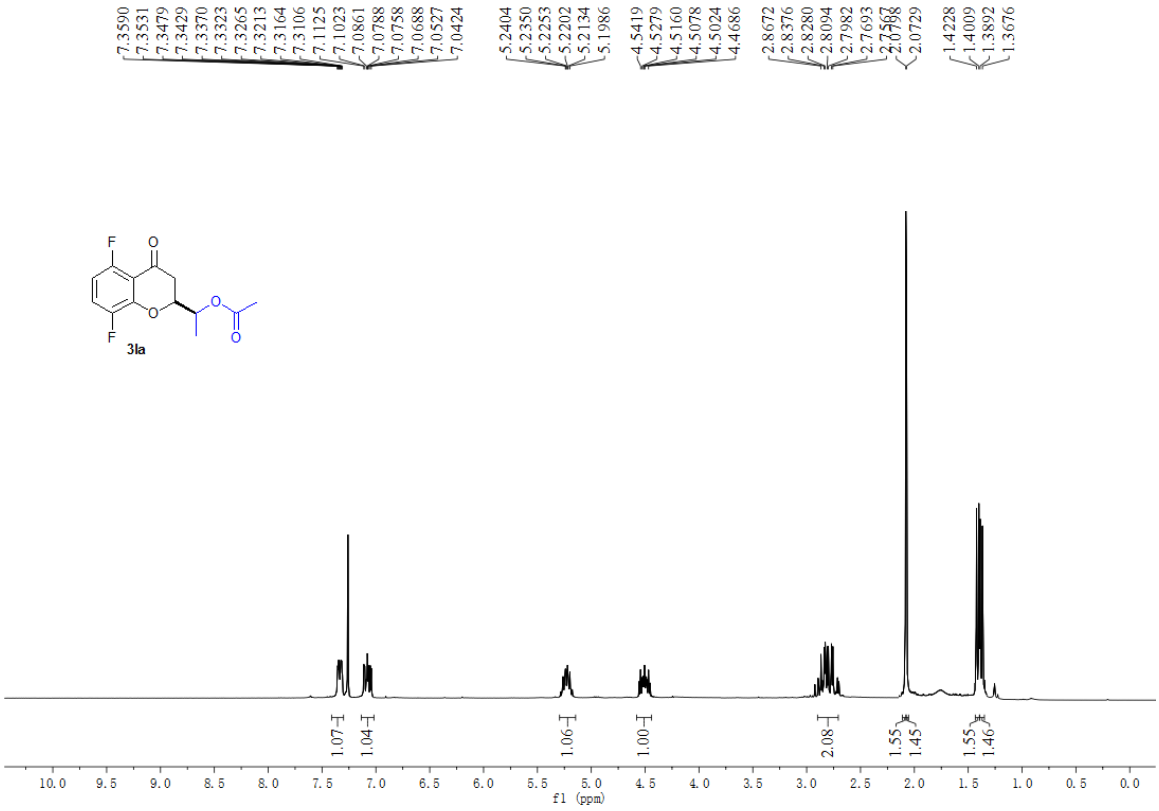


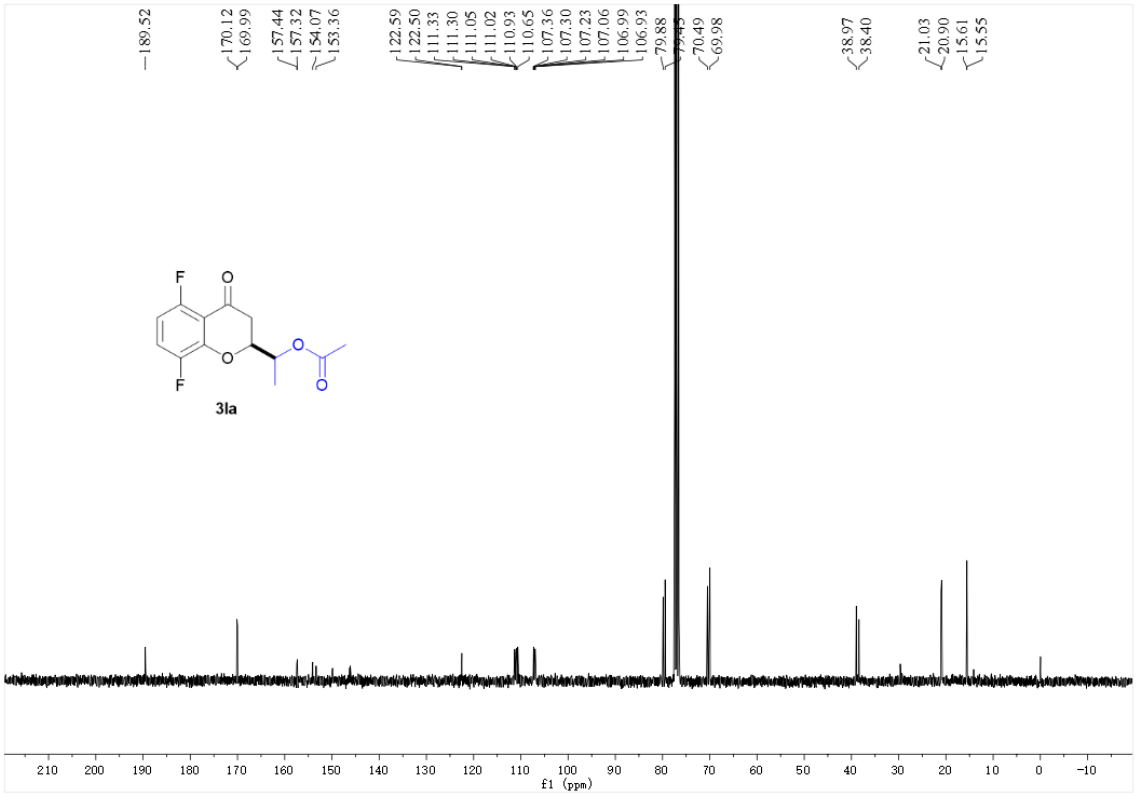
1-(5-Fluoro-4-oxochroman-2-yl)ethyl acetate (3ka)



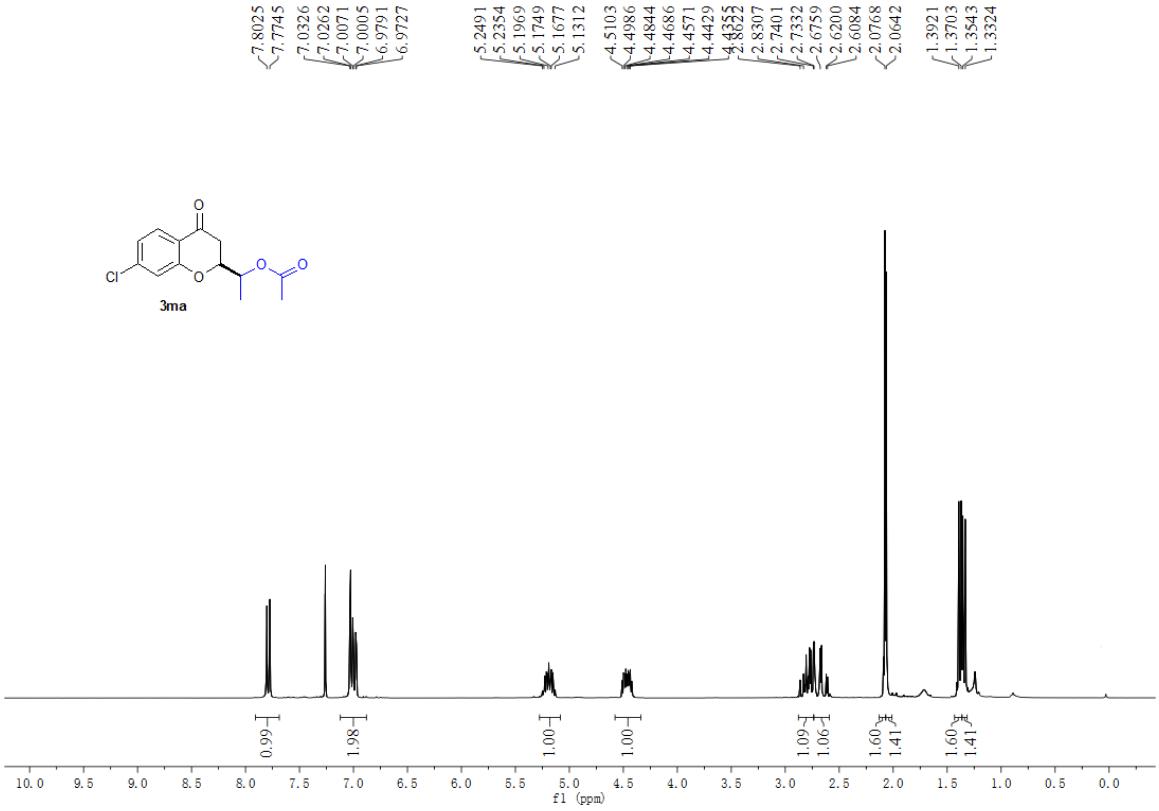


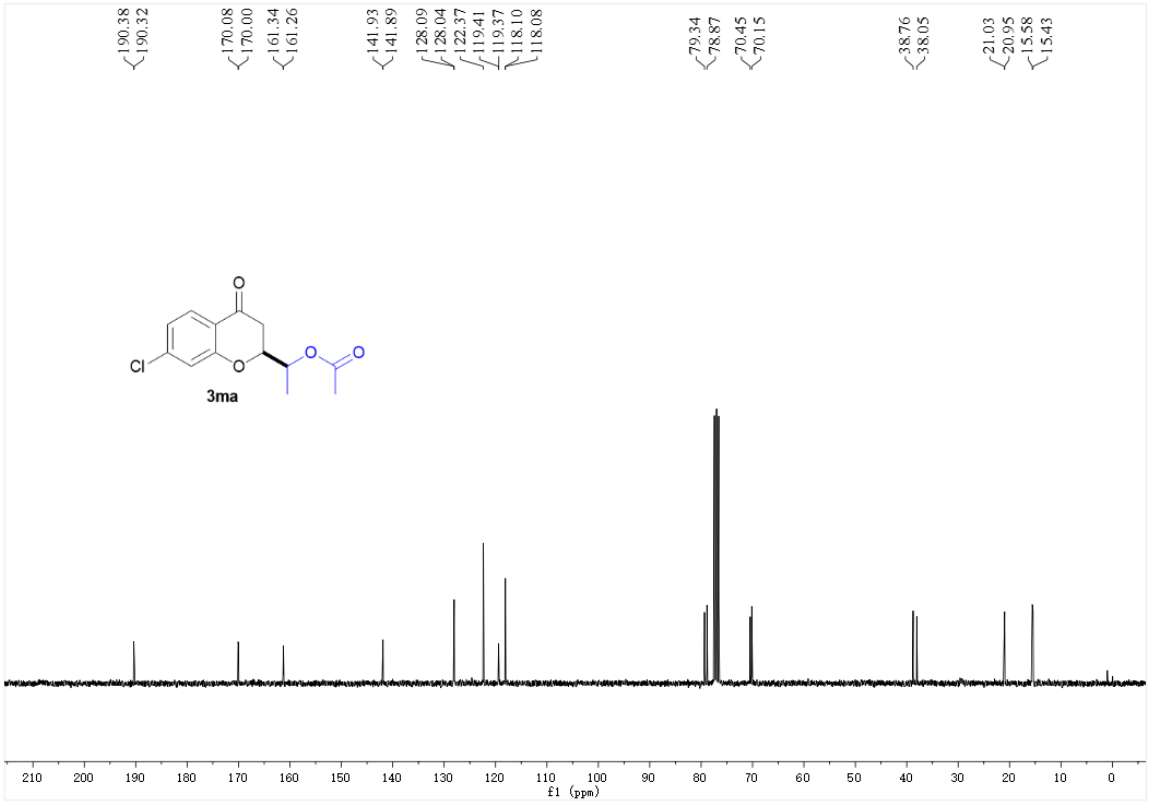
1-(5,8-Difluoro-4-oxochroman-2-yl)ethyl acetate (3la)



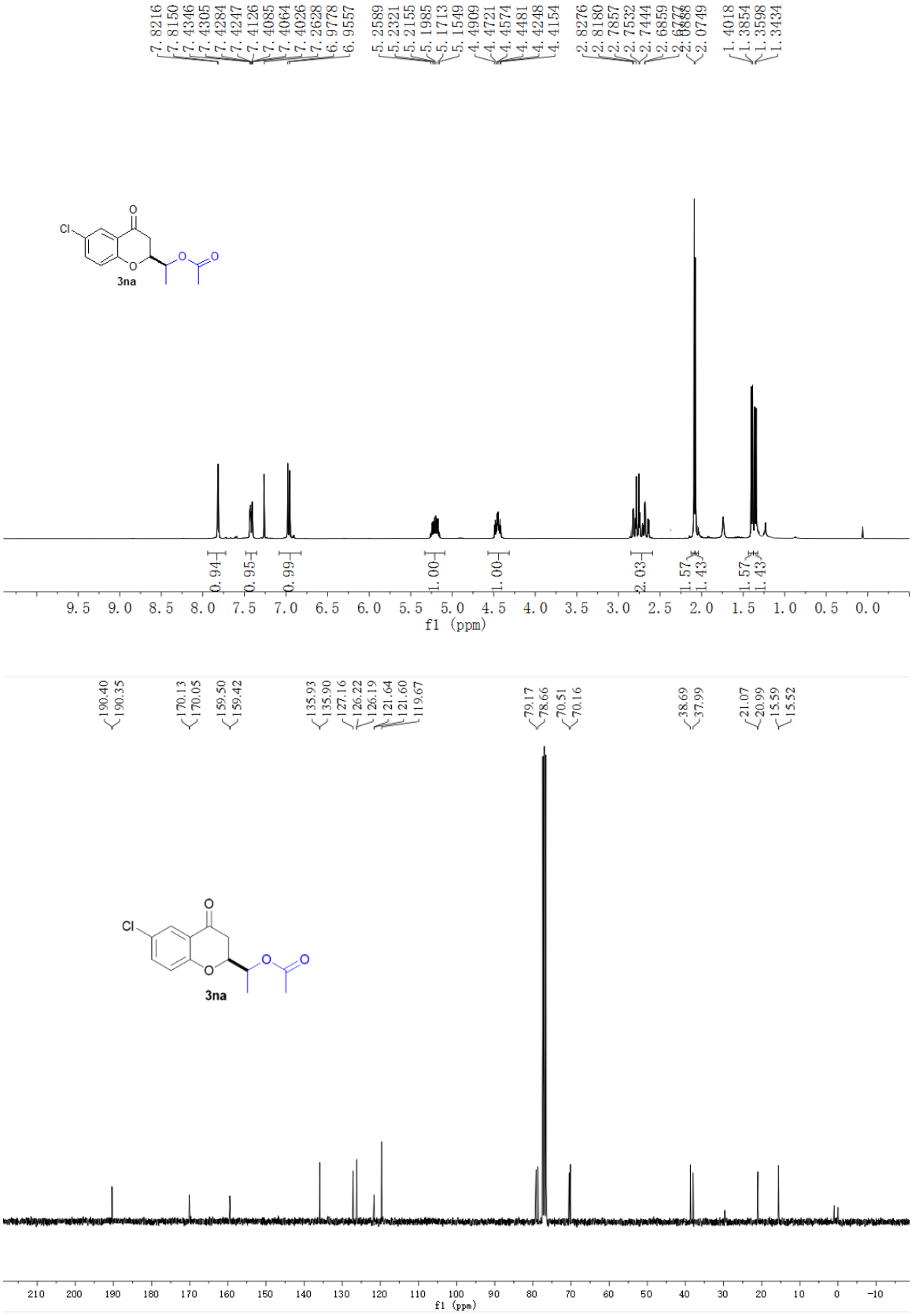


1-(7-Chloro-4-oxochroman-2-yl)ethyl acetate (3ma)

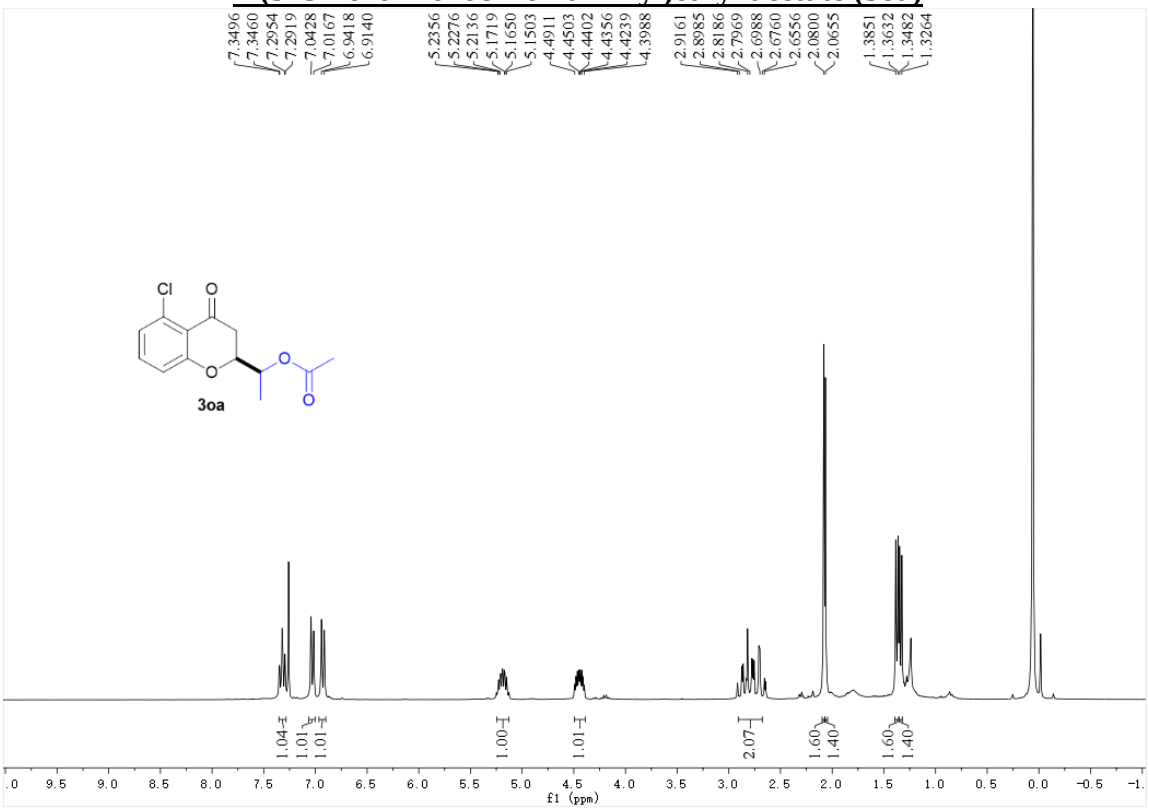


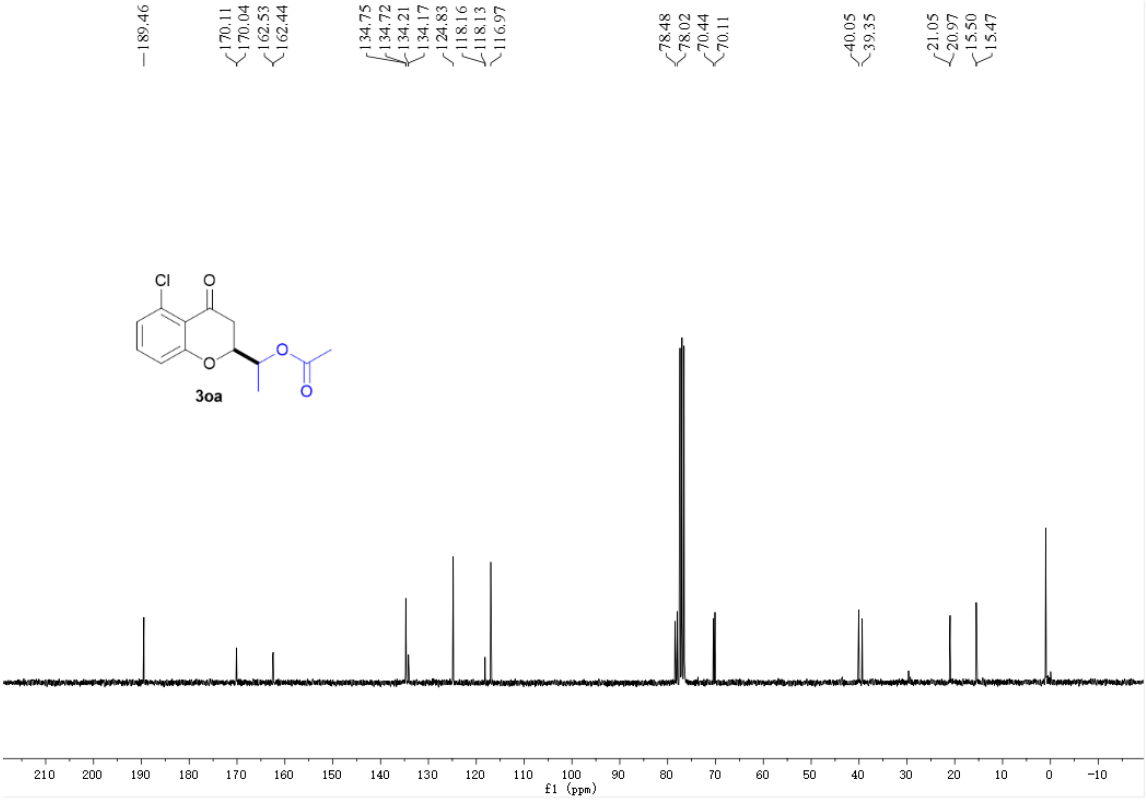


1-(6-Chloro-4-oxochroman-2-yl)ethyl acetate (3na)

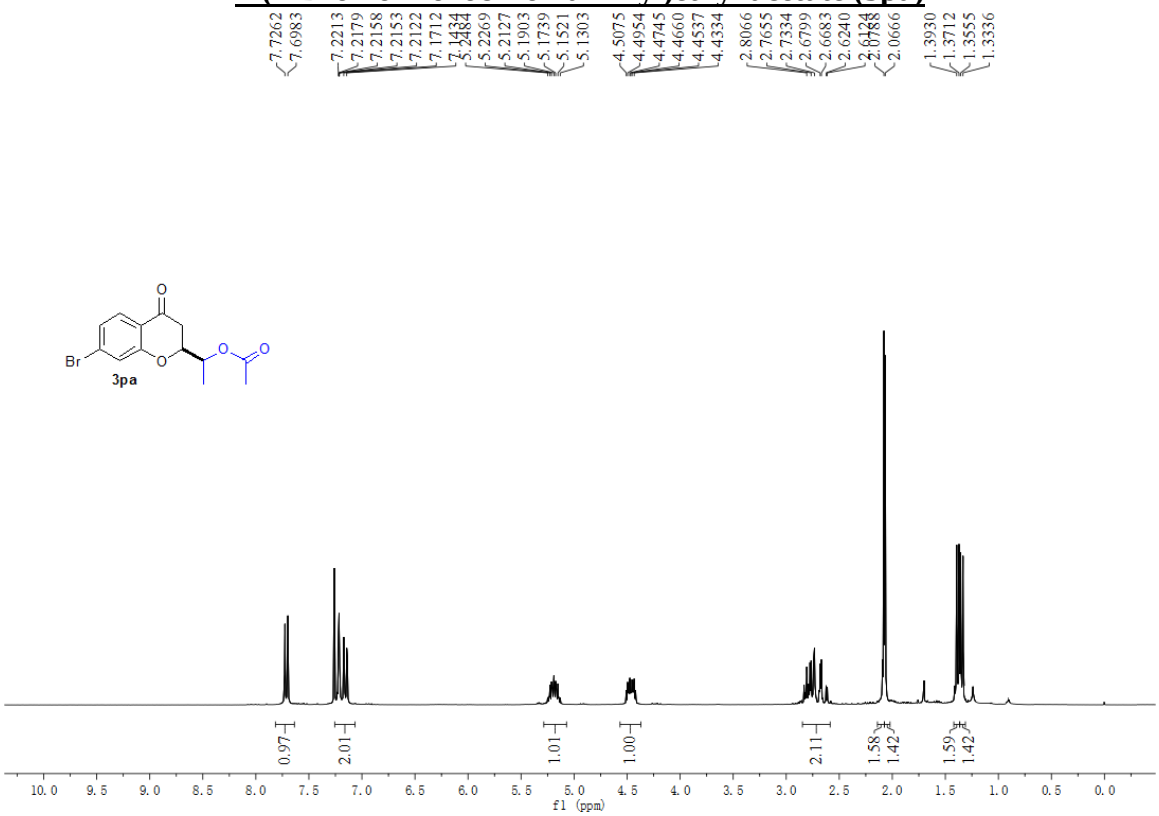


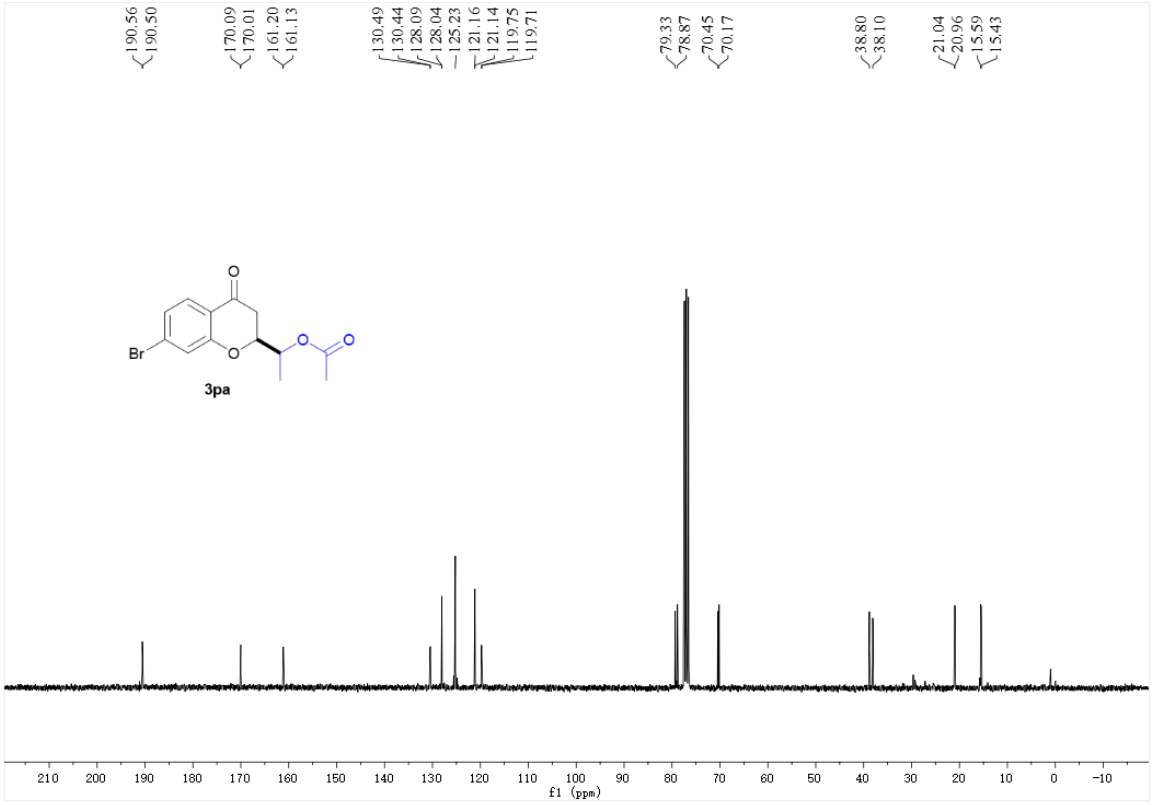
1-(5-Chloro-4-oxochroman-2-yl)ethyl acetate (3oa)



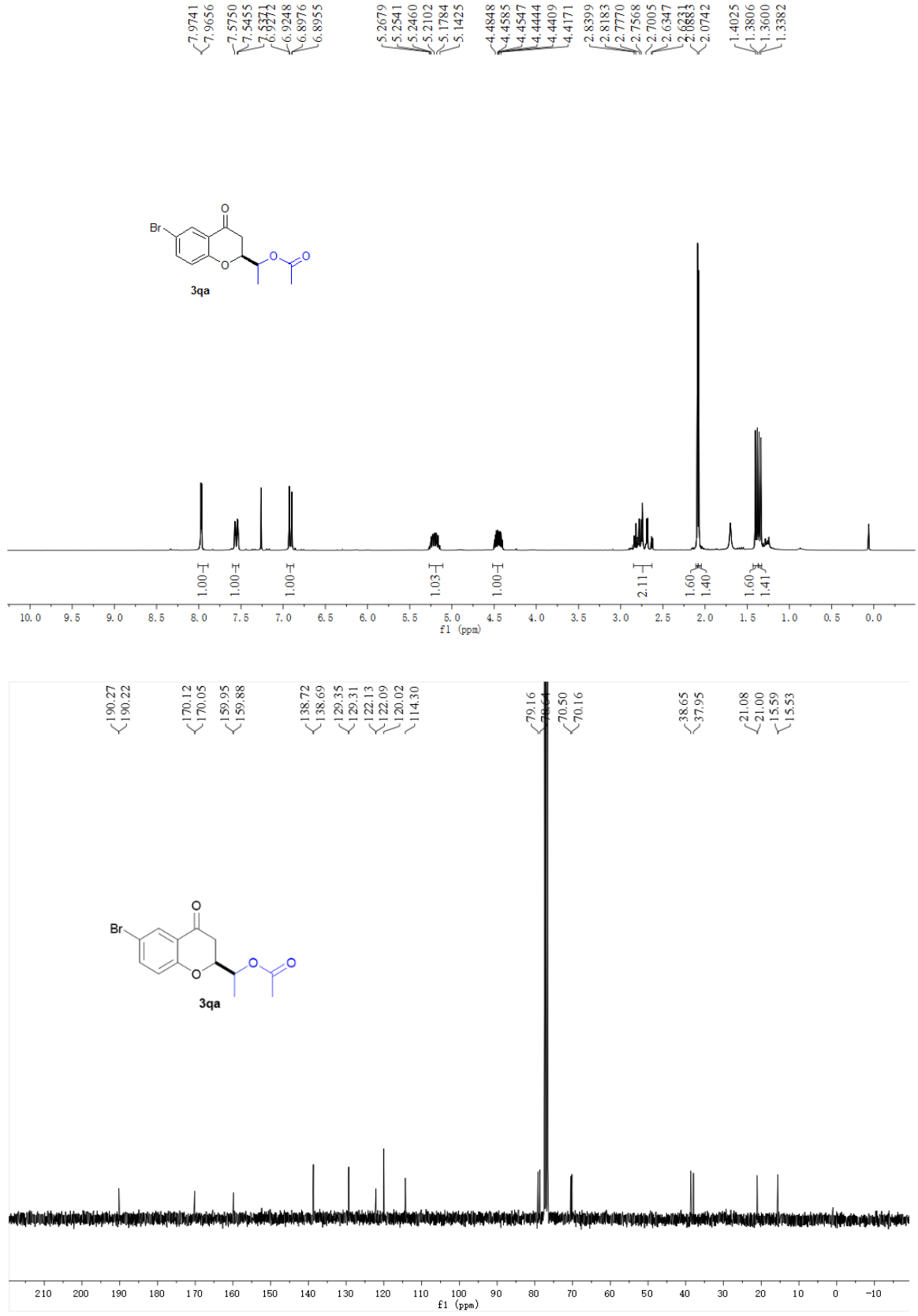


1-(7-Bromo-4-oxochroman-2-yl)ethyl acetate (3pa)

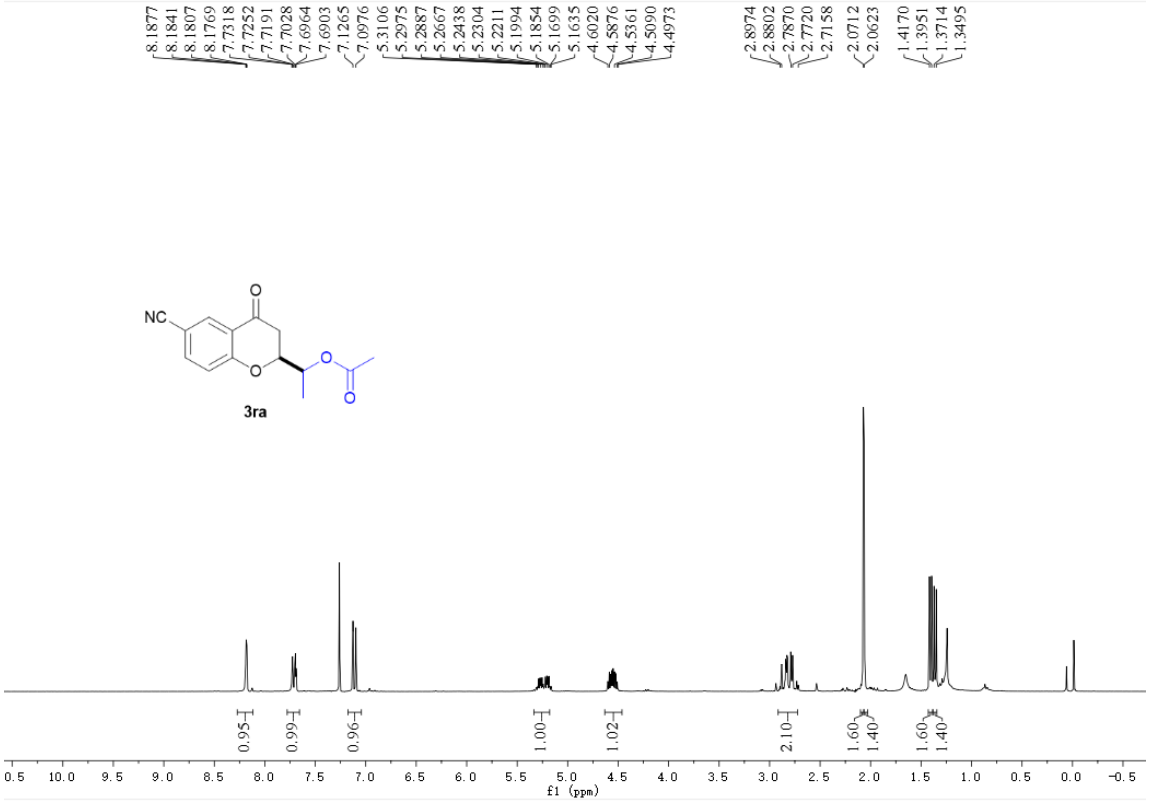


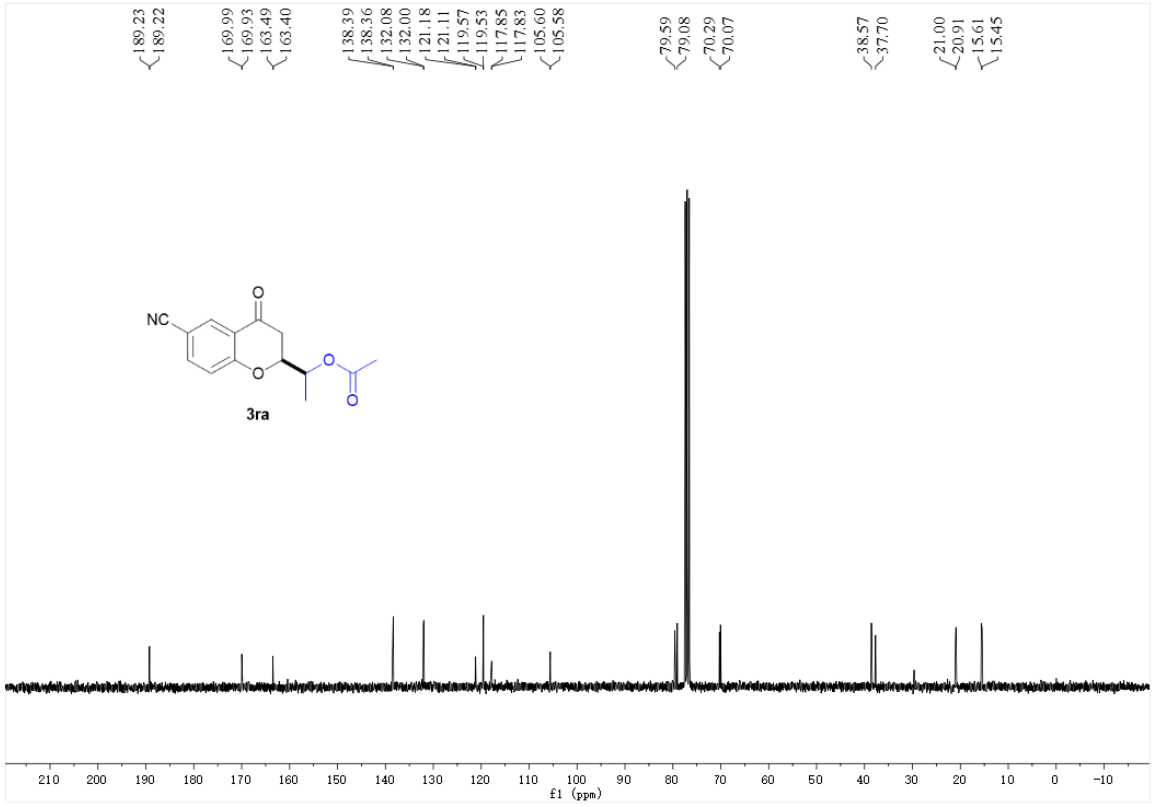


1-(6-Bromo-4-oxochroman-2-yl)ethyl acetate (3qa)

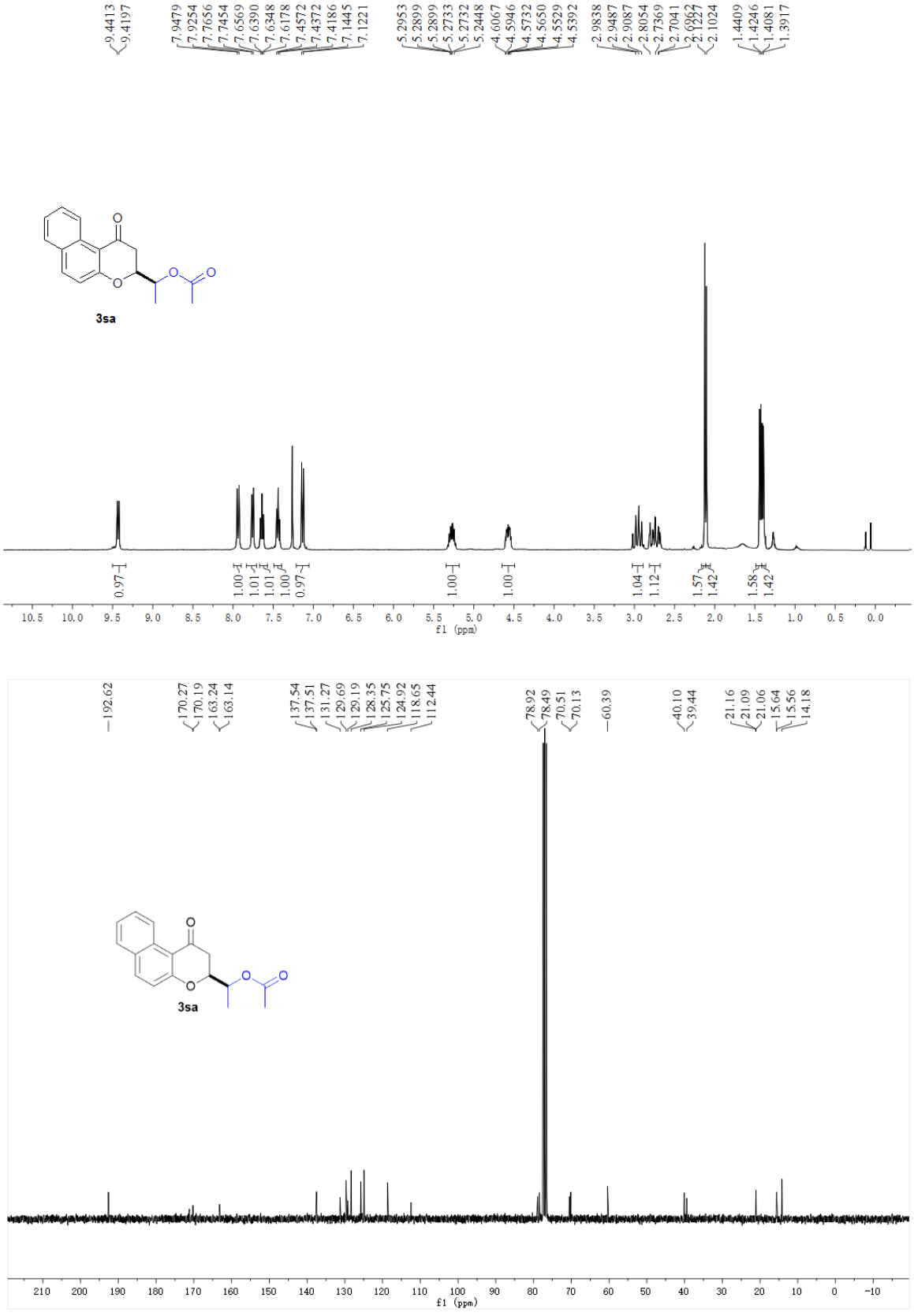


1-(6-Cyano-4-oxochroman-2-yl)ethyl acetate (3ra)

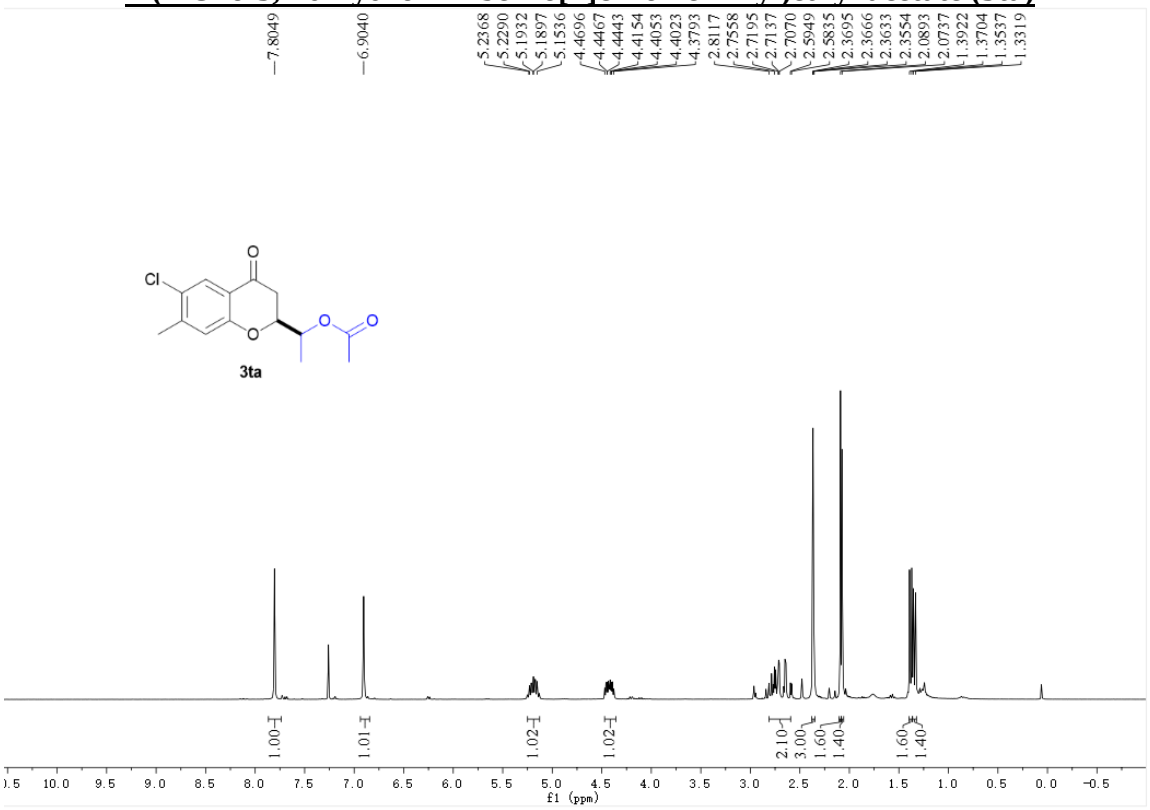


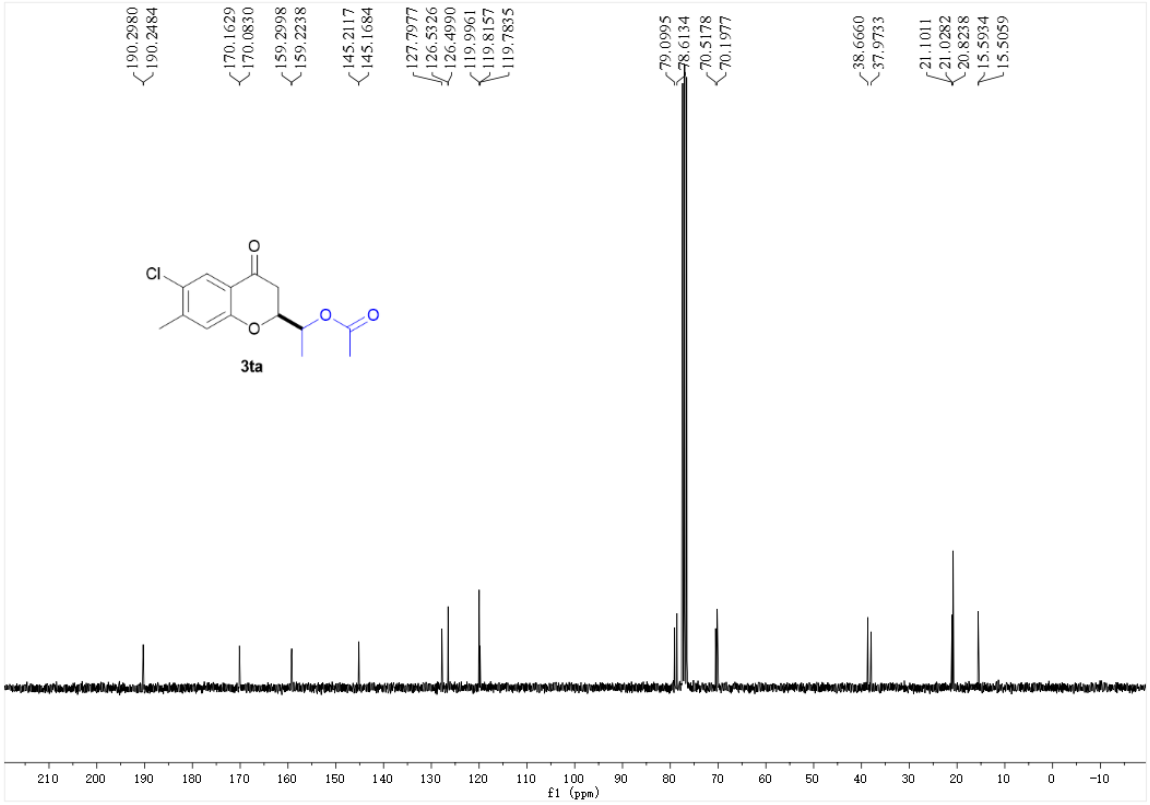


1-(1-Oxo-2,3-dihydro-1H-benzo[f]chromen-3-yl)ethyl acetate (3sa)

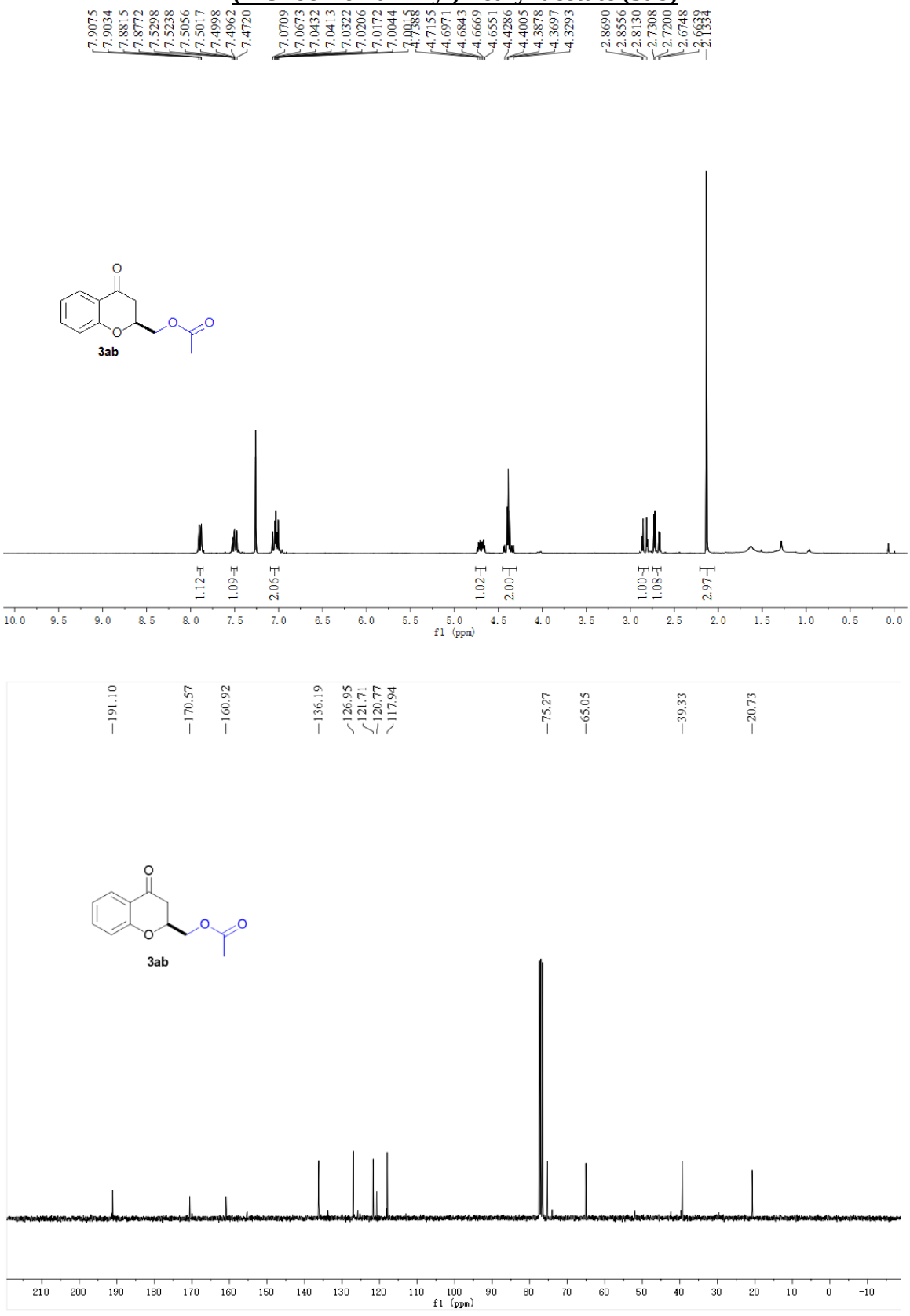


1-(4-Oxo-3,4-dihydro-2H-benzo[h]chromen-2-yl)ethyl acetate (3ta)

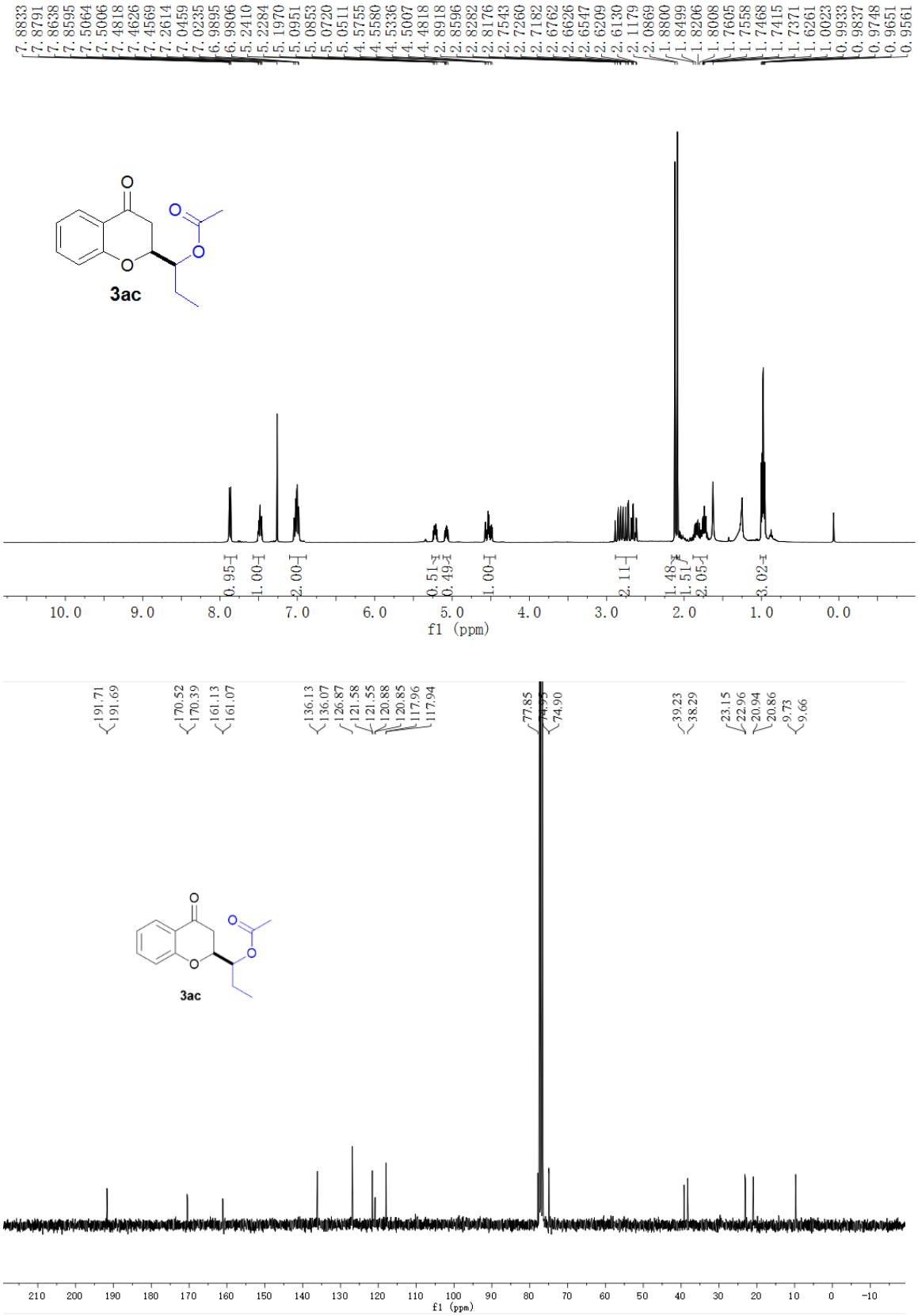




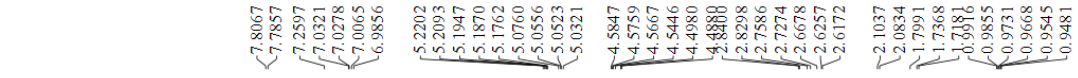
(4-Oxochroman-2-yl)methyl acetate (3ab)

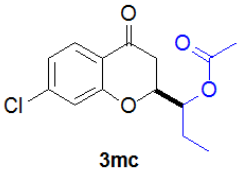


1-(4-Oxochroman-2-yl)propyl acetate (3ac)

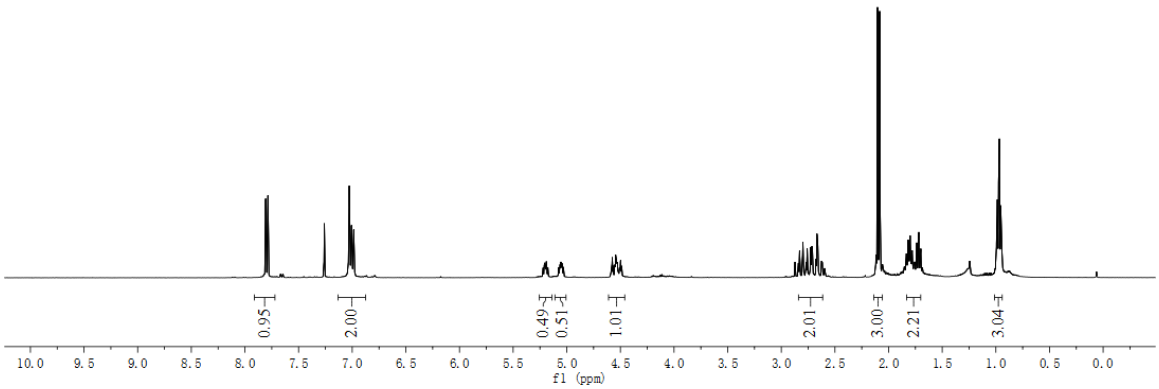


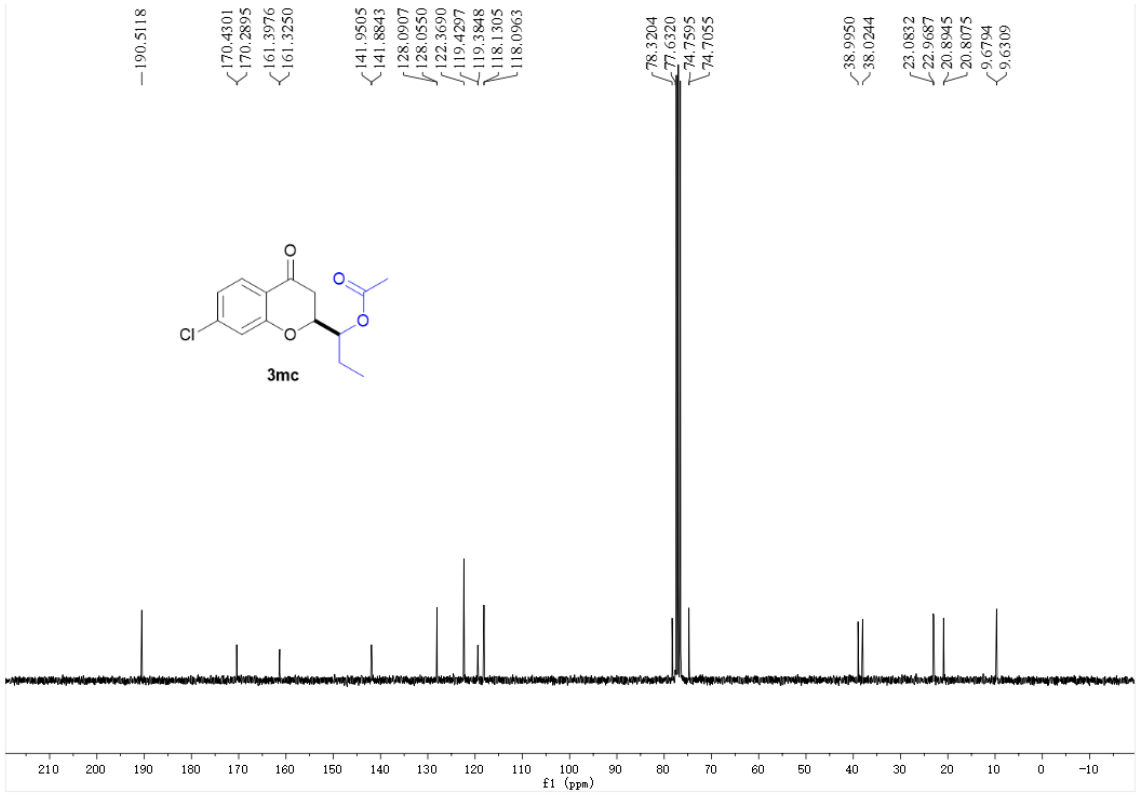
1-(7-Chloro-4-oxochroman-2-yl)propyl acetate (3mc)



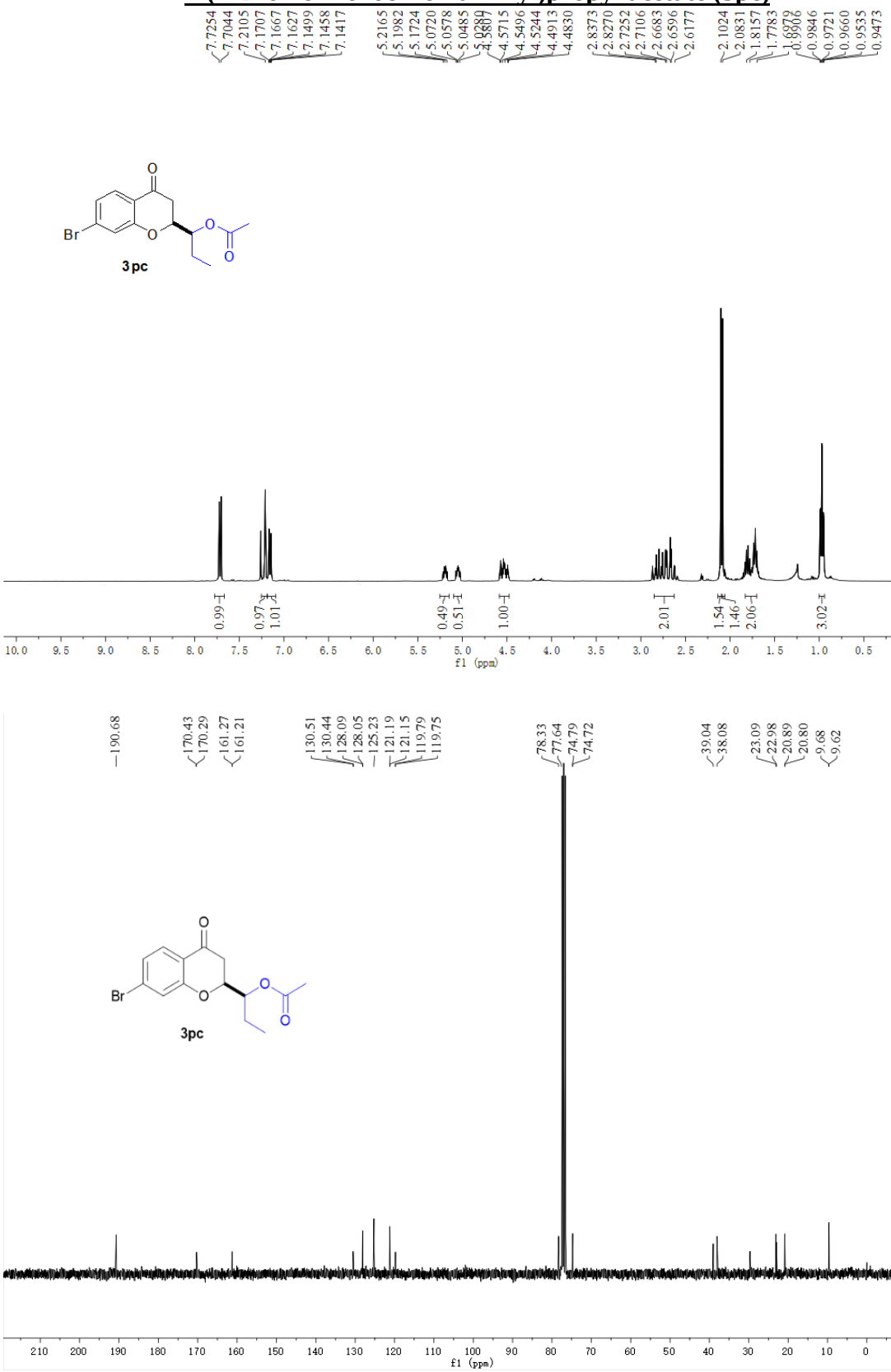


3mc

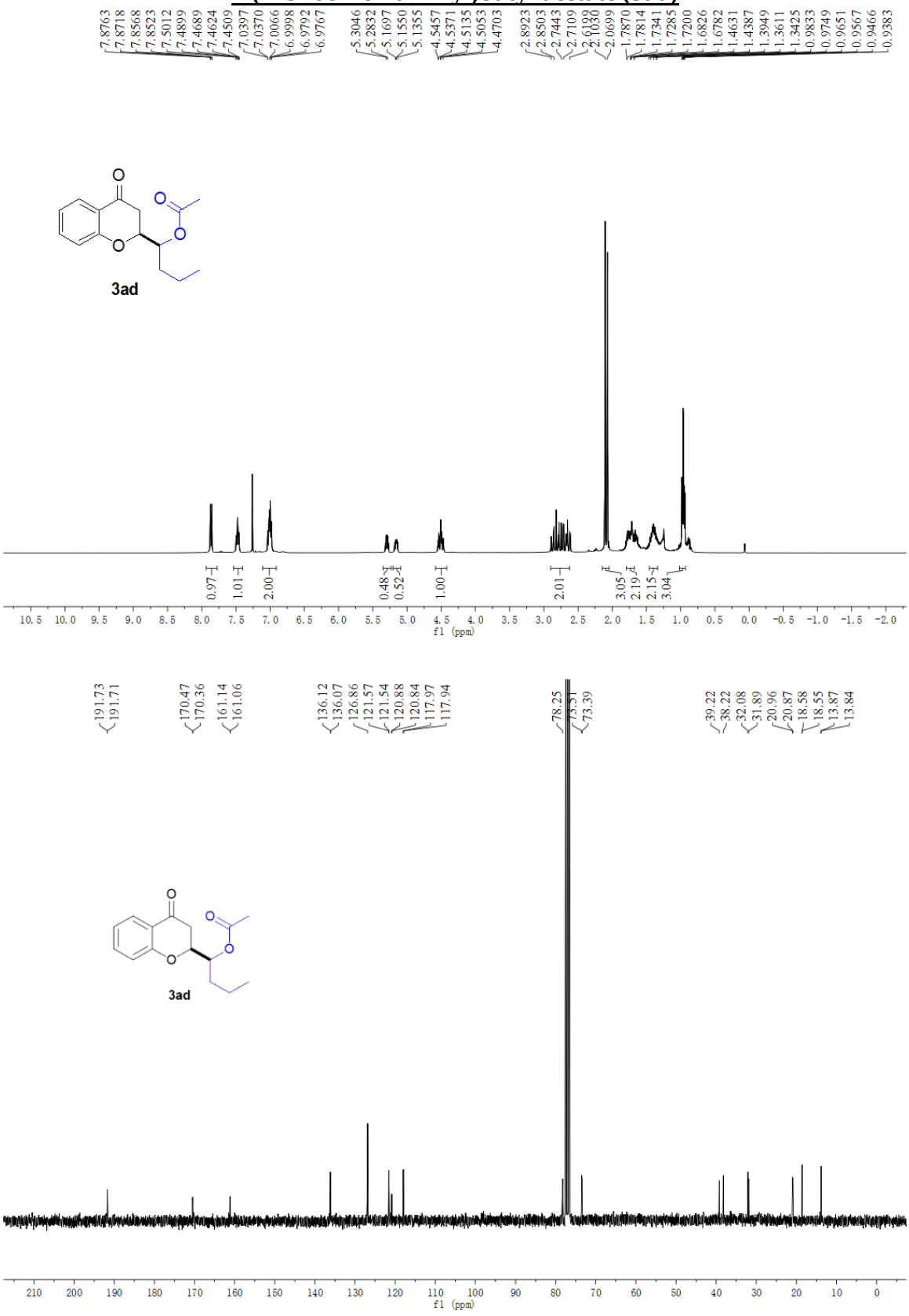




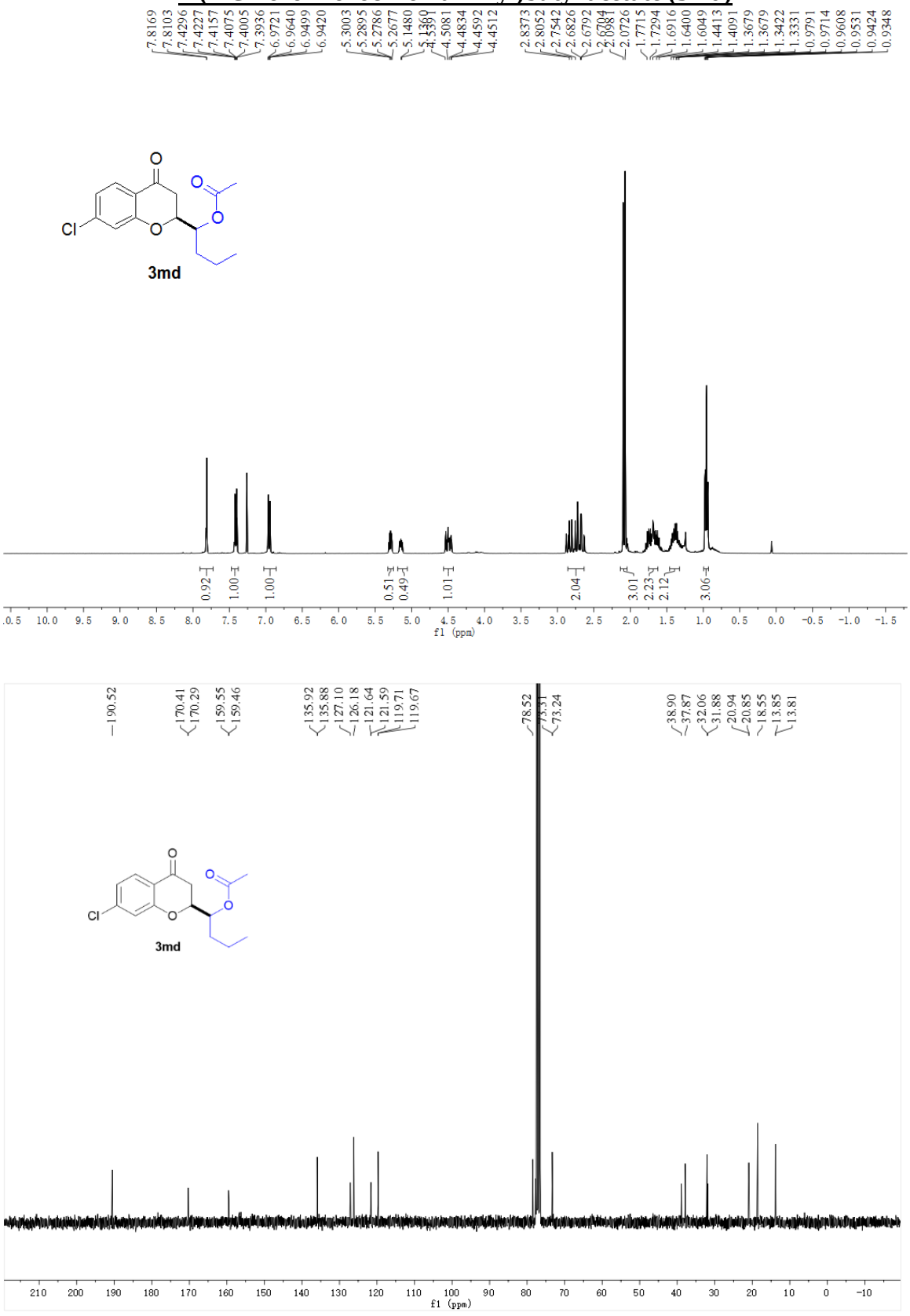
1-(7-Bromo-4-oxochroman-2-yl)propyl acetate (3pc)



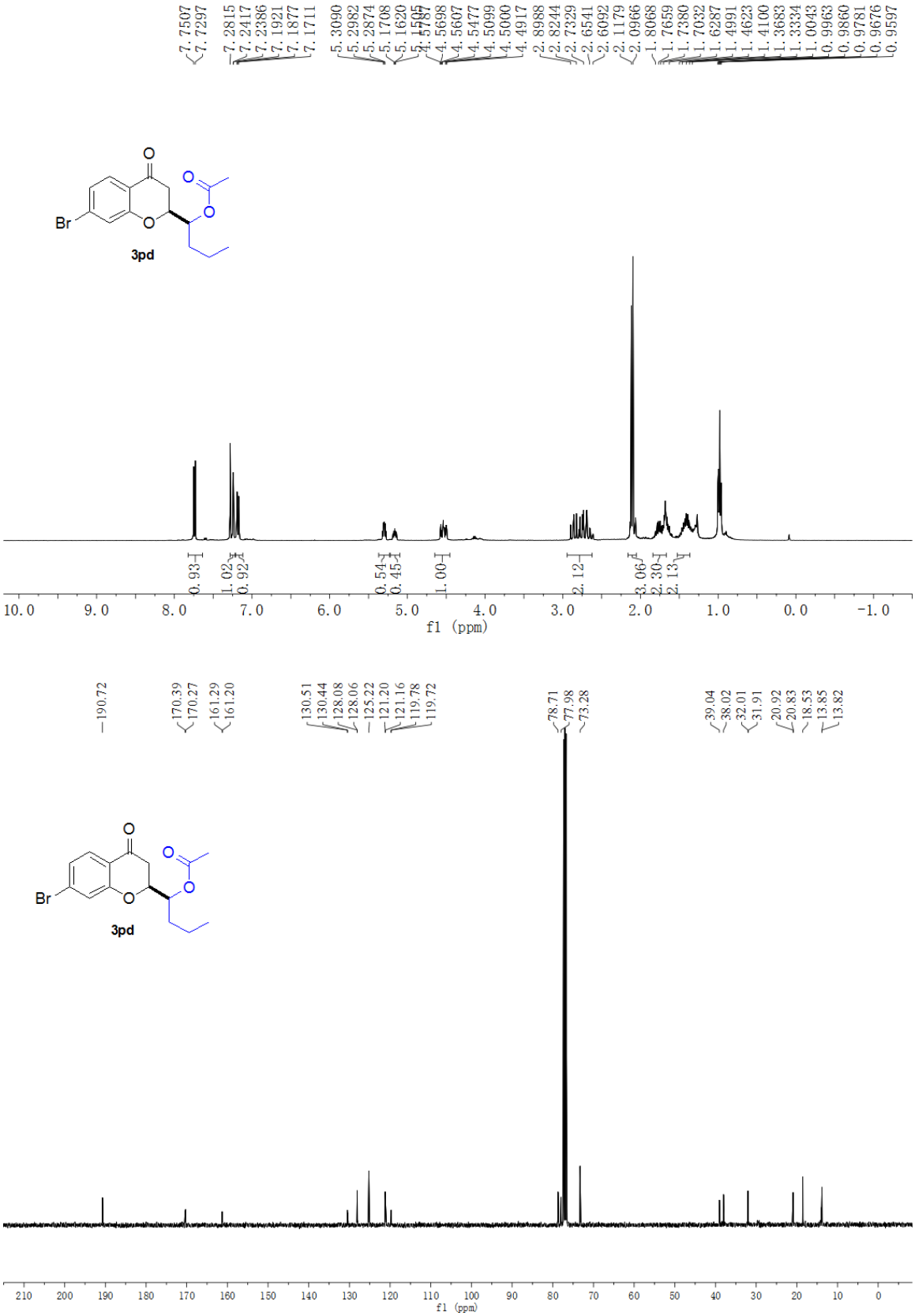
1-(4-Oxochroman-2-yl)butyl acetate (3ad)



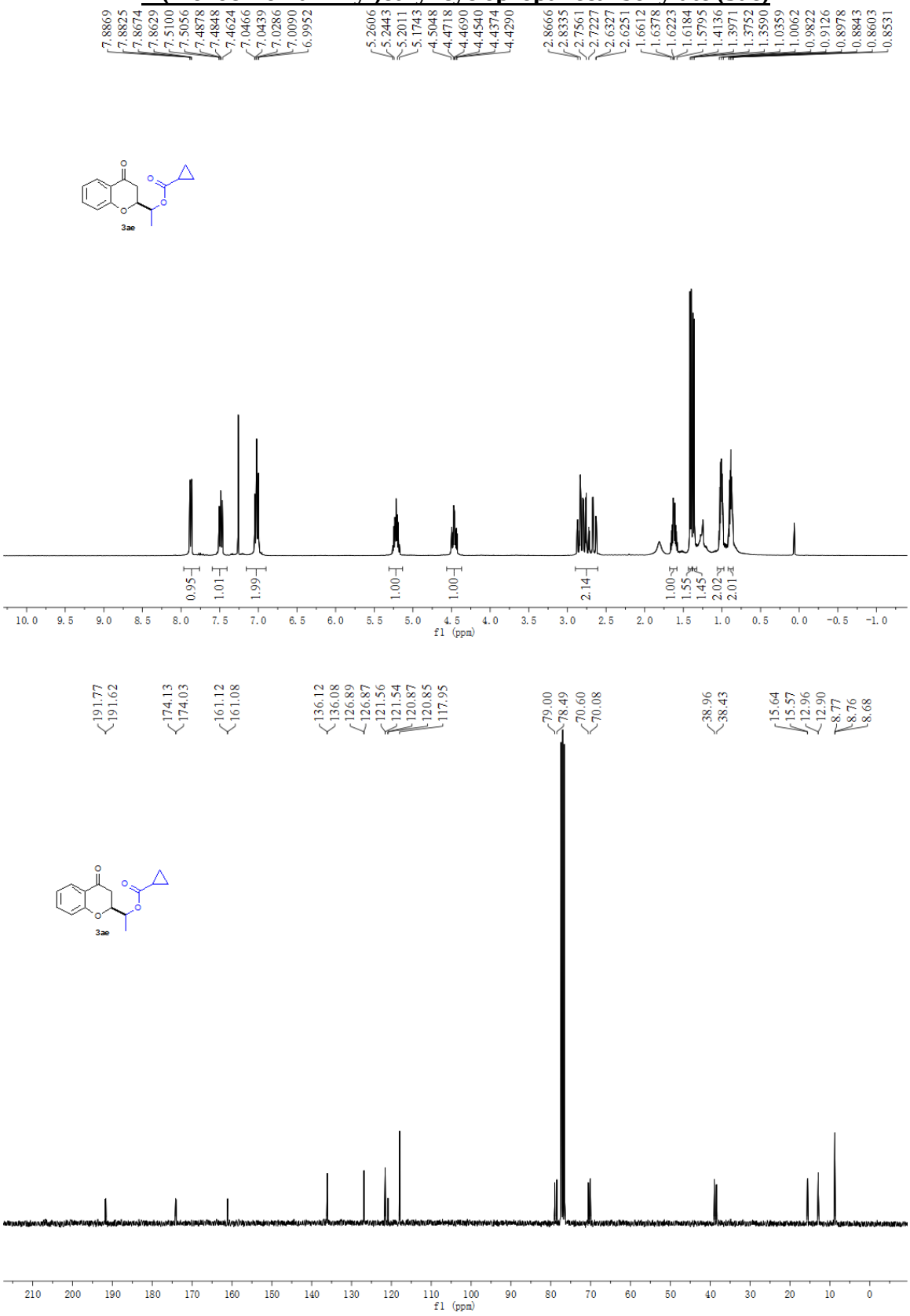
1-(7-Chloro-4-oxochroman-2-yl)butyl acetate (3md)



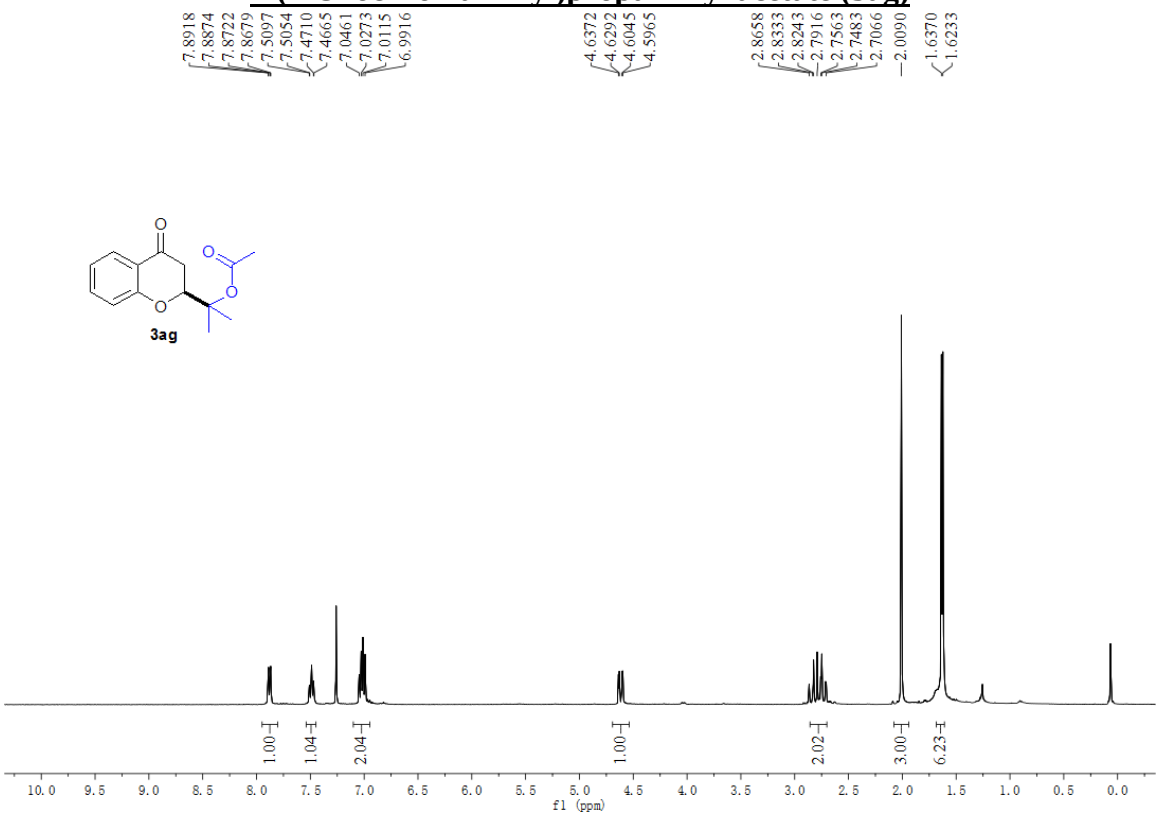
1-(7-Bromo-4-oxochroman-2-yl)butyl acetate (3pd)

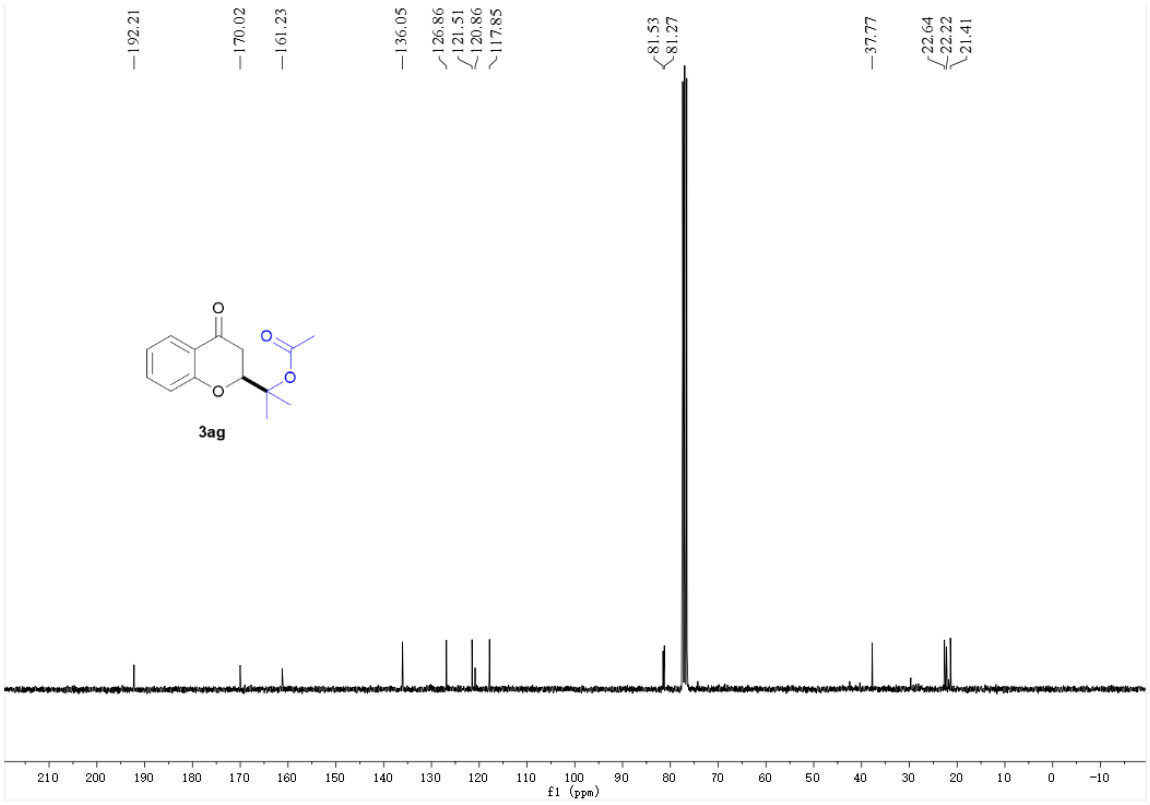


1-(4-oxochroman-2-yl)ethyl cyclopropanecarboxylate (3ae)

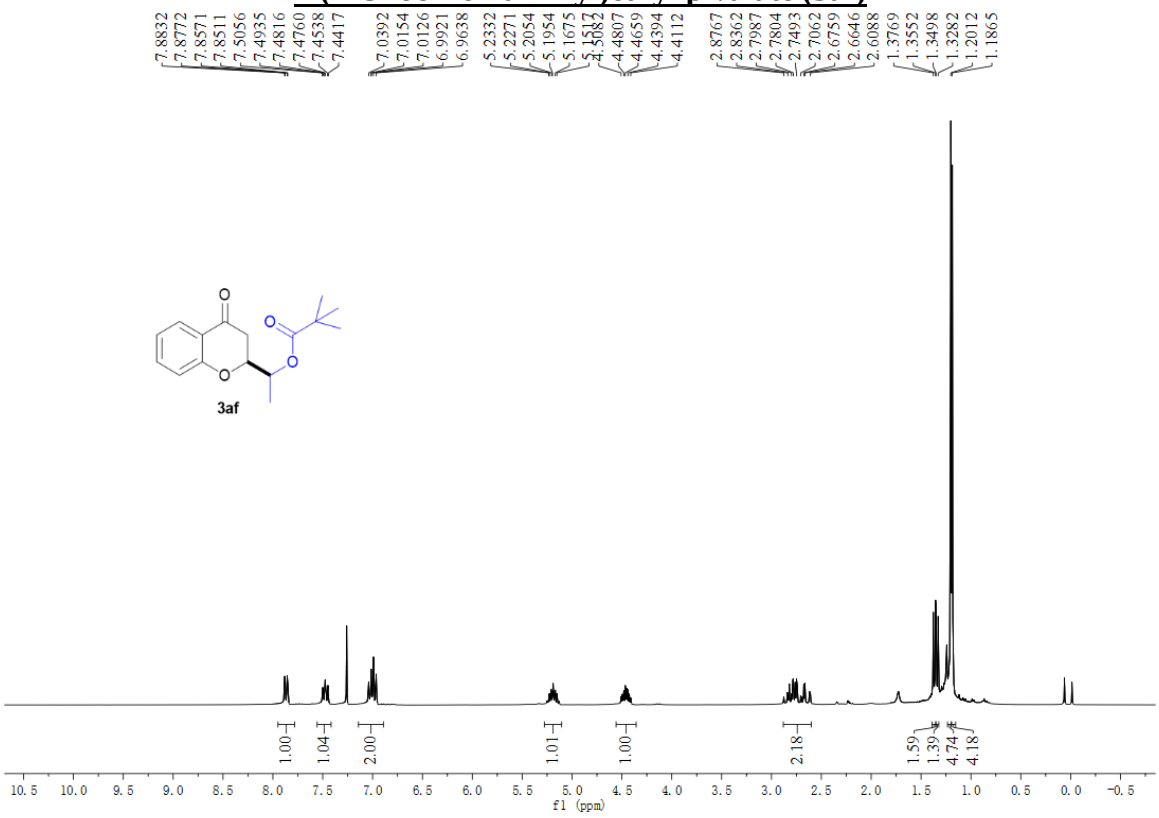


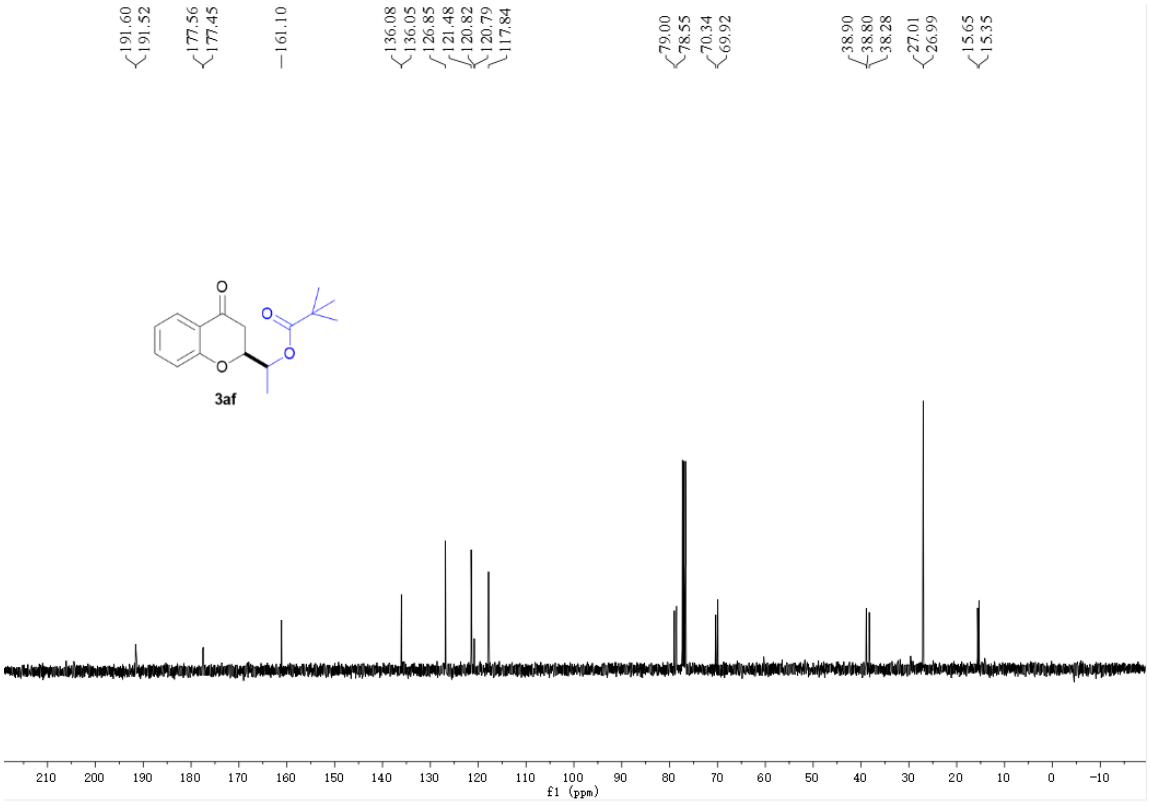
2-(4-Oxochroman-2-yl)propan-2-yl acetate (3ag)



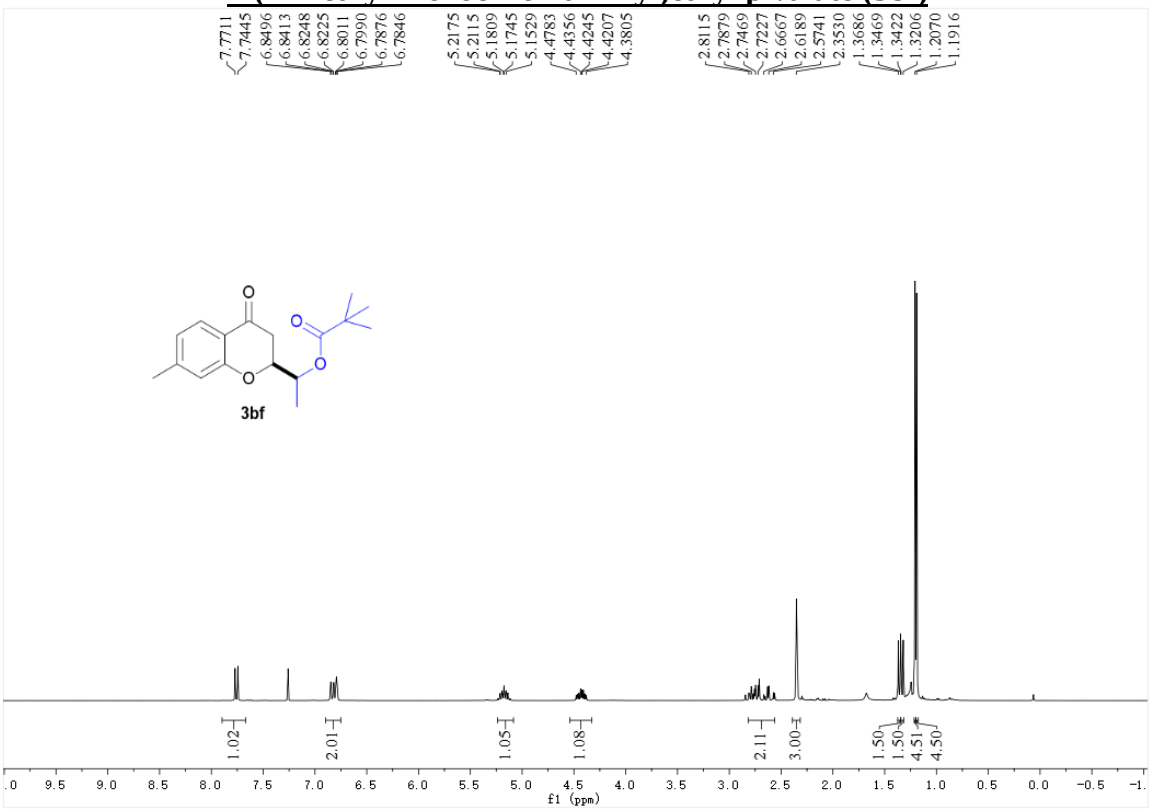


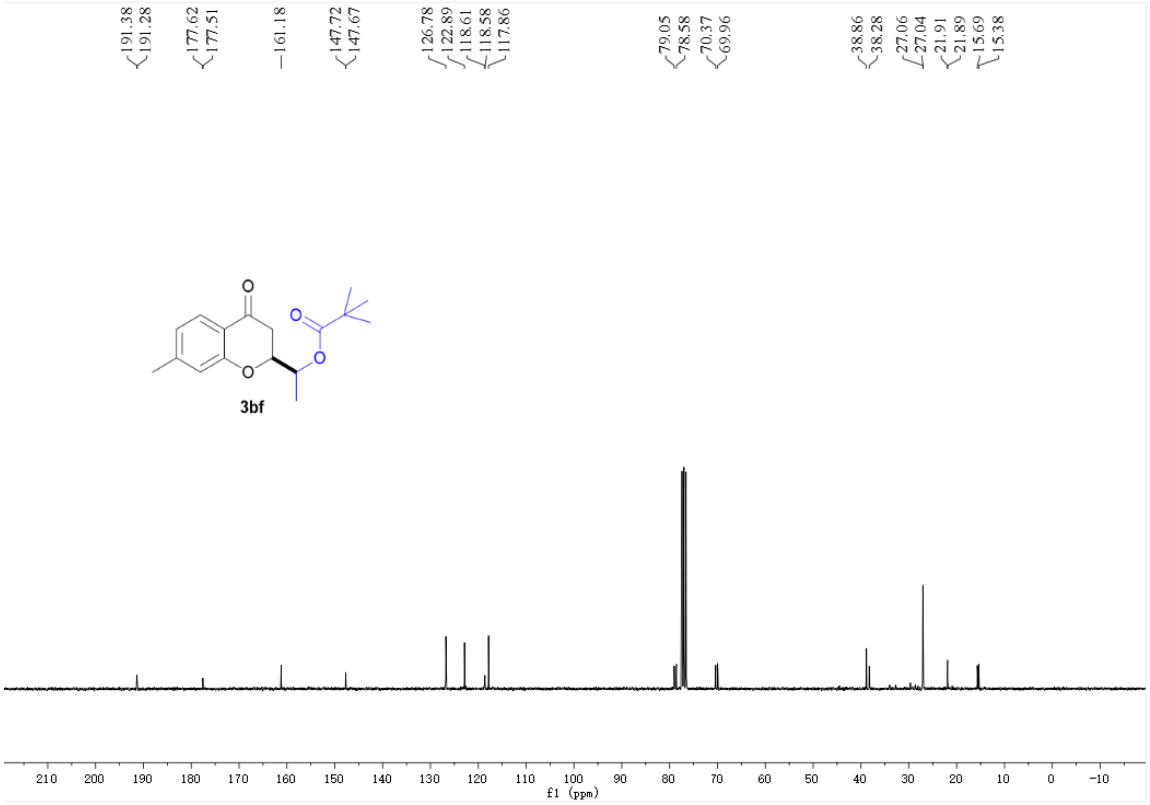
1-(4-Oxochroman-2-yl)ethyl pivalate (3af)



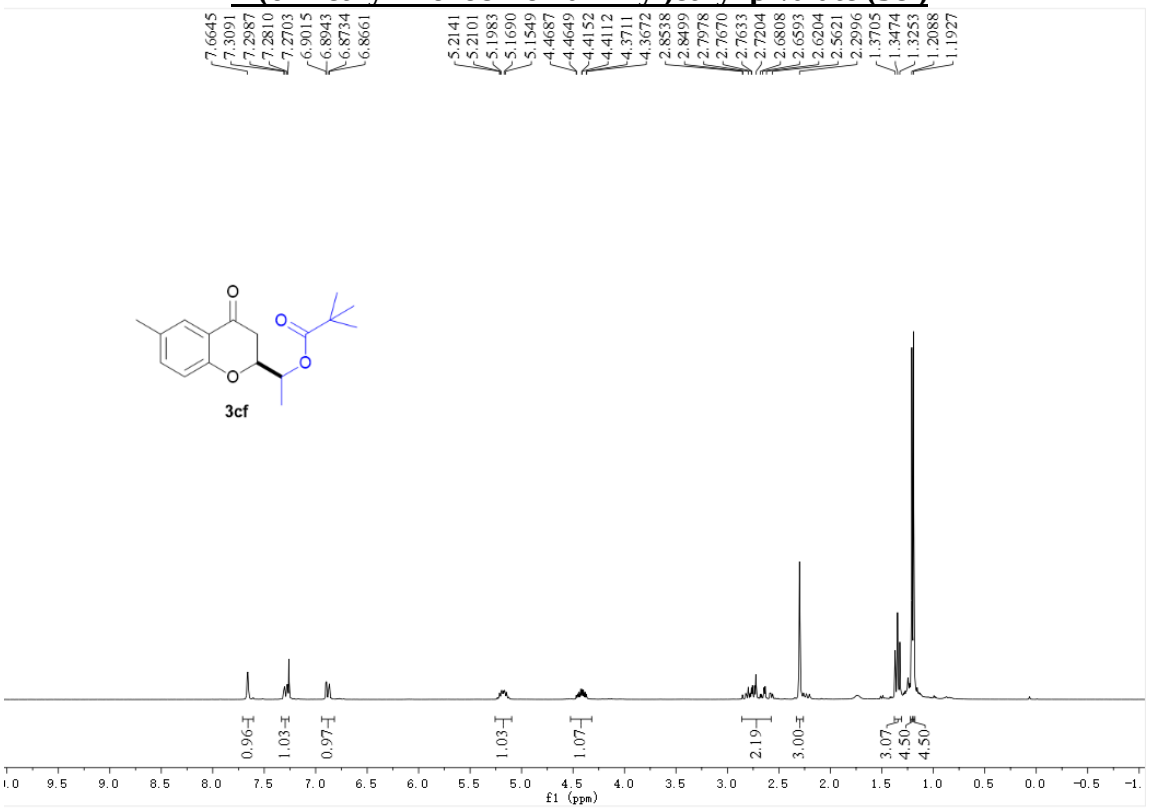


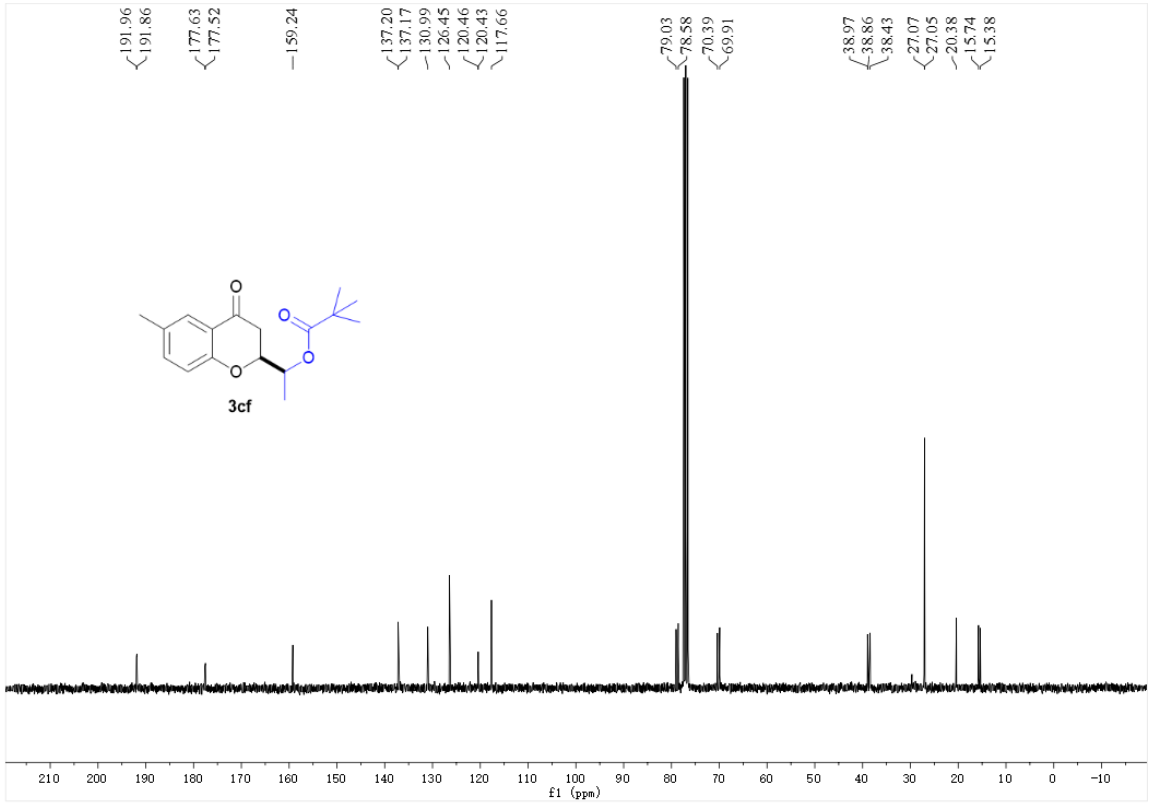
1-(7-Methyl-4-oxochroman-2-yl)ethyl pivalate (3bf)



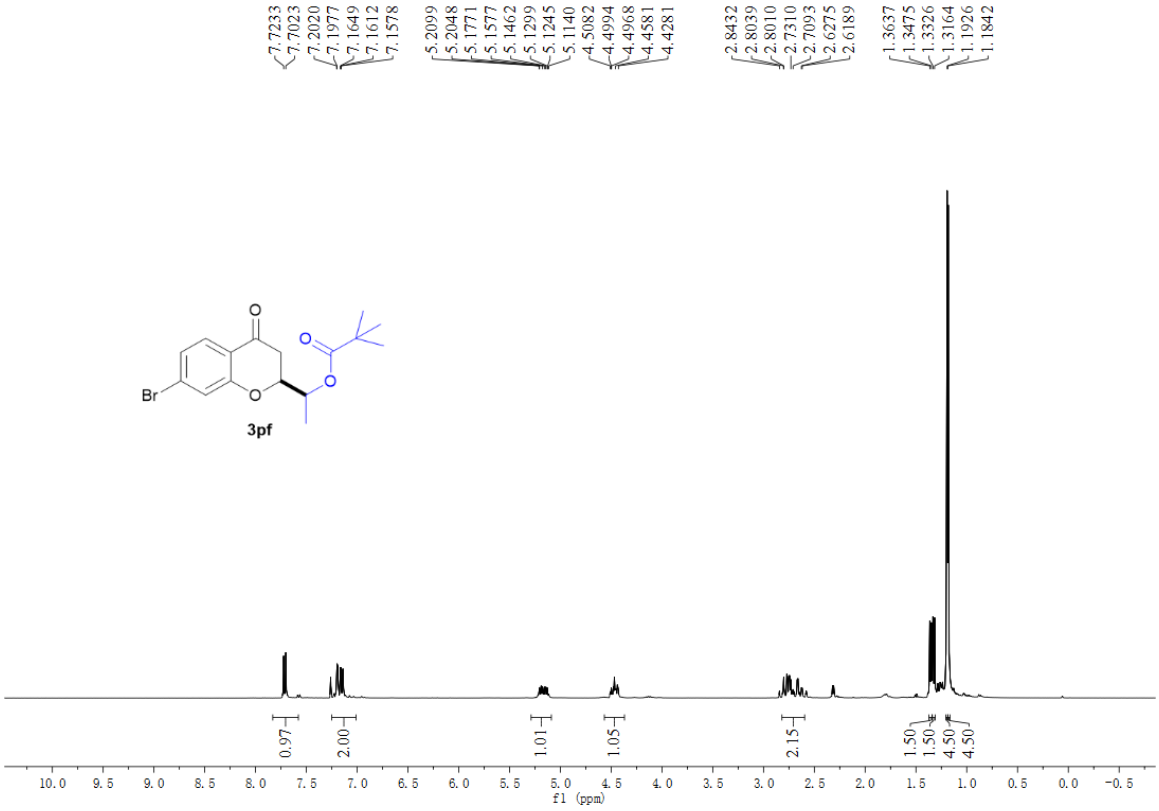


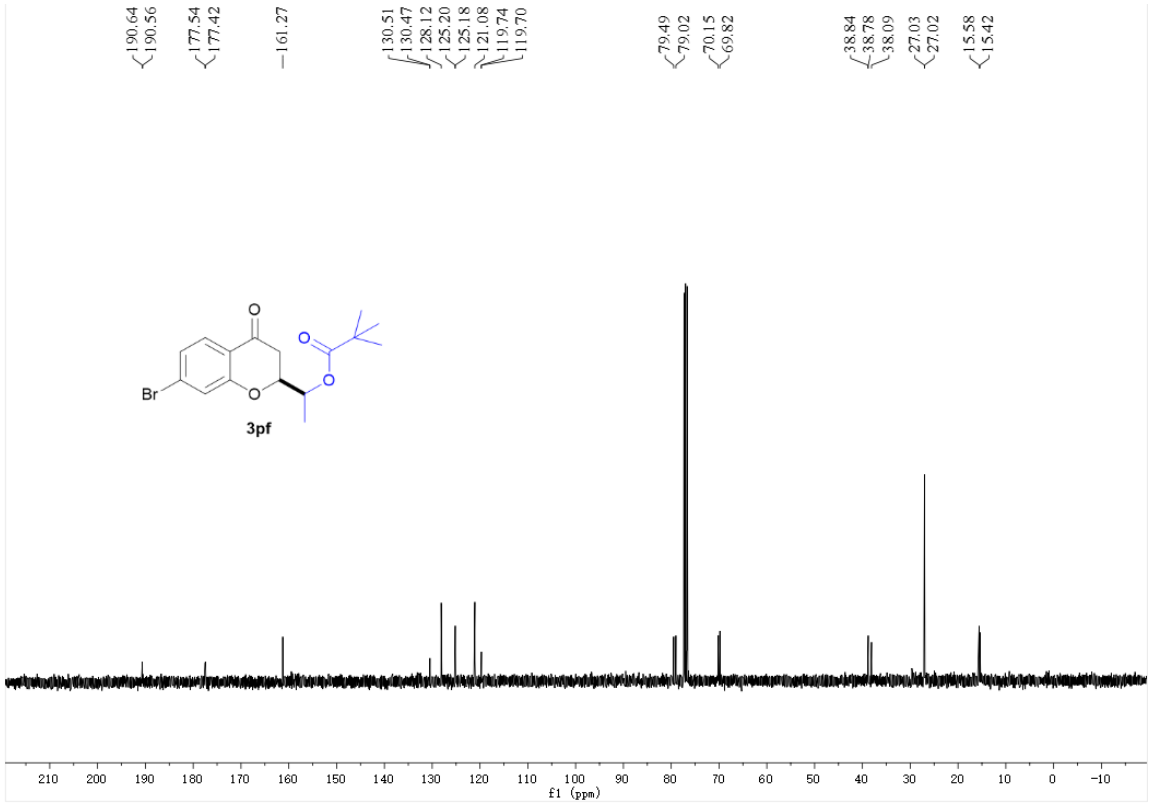
1-(6-Methyl-4-oxochroman-2-yl)ethyl pivalate (3cf)



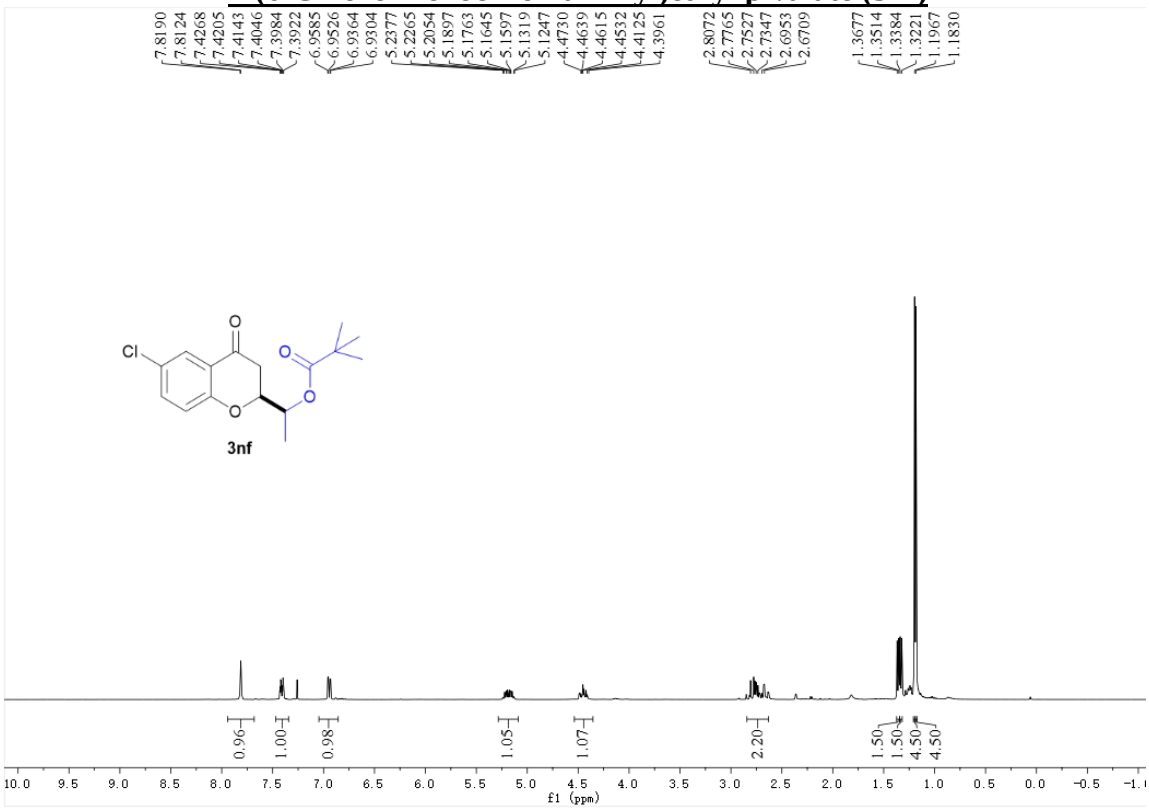


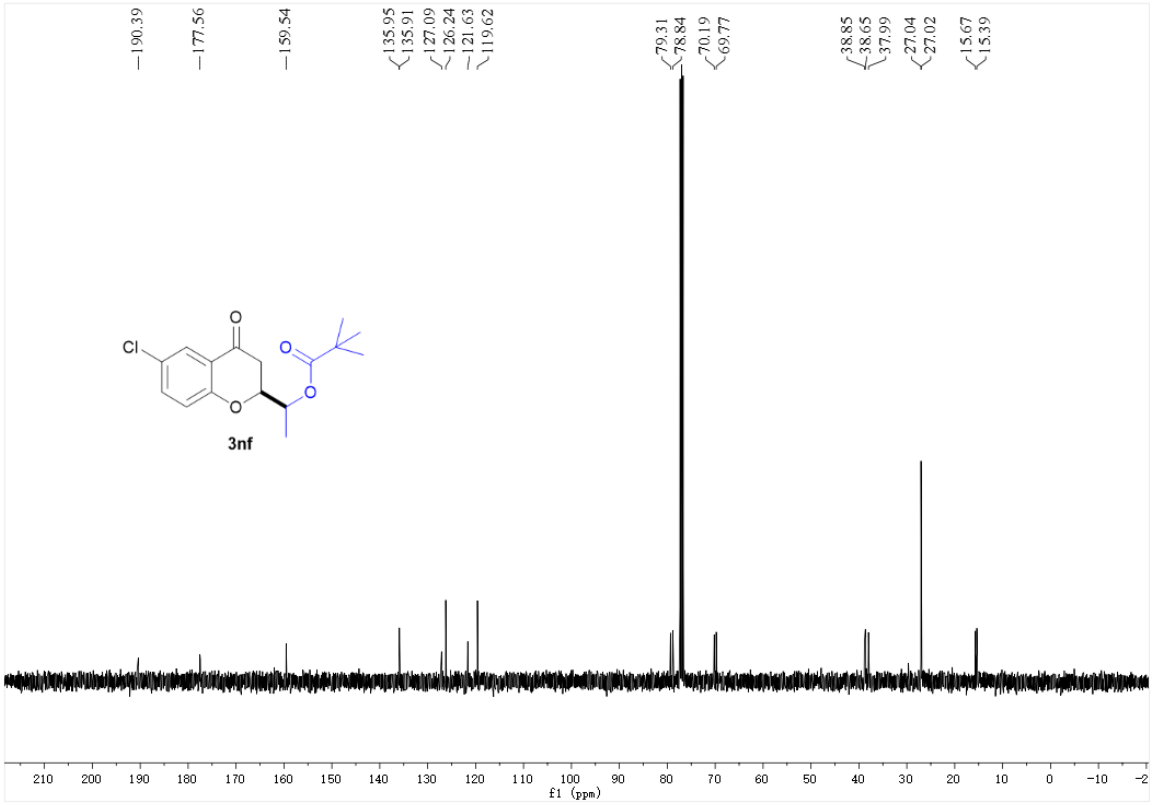
1-(7-Bromo-4-oxochroman-2-yl)ethyl pivalate (3pf)



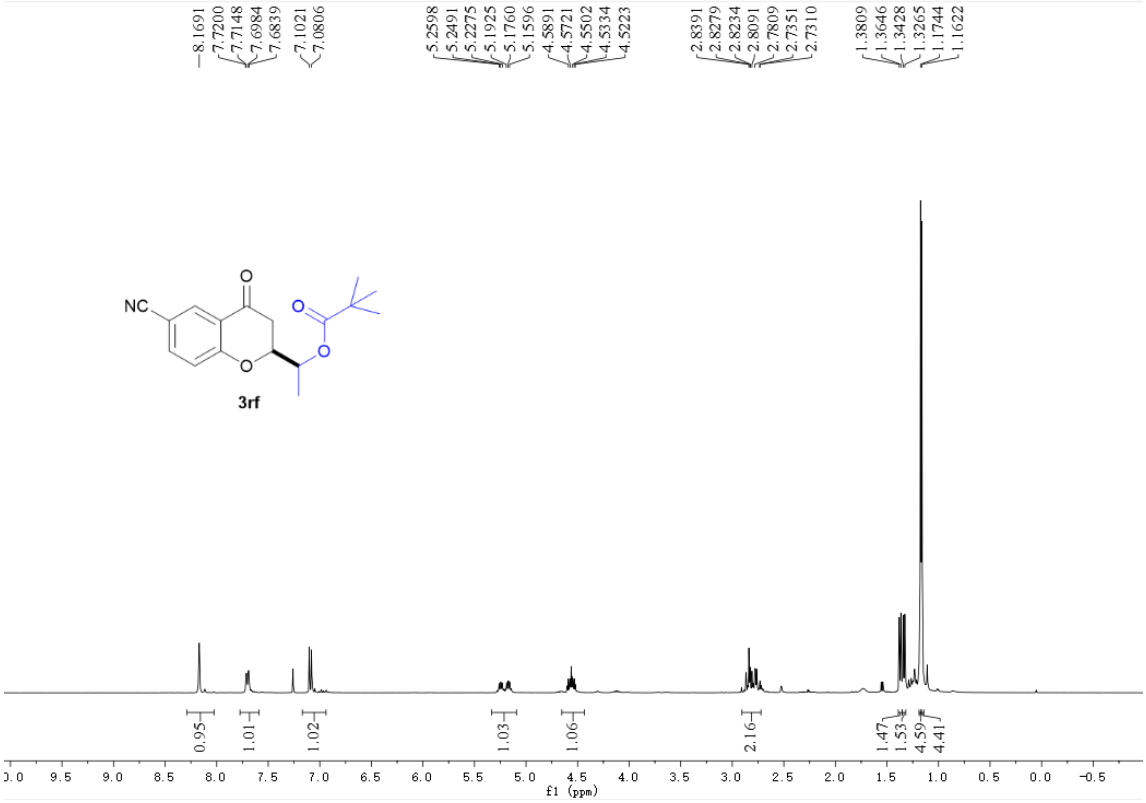


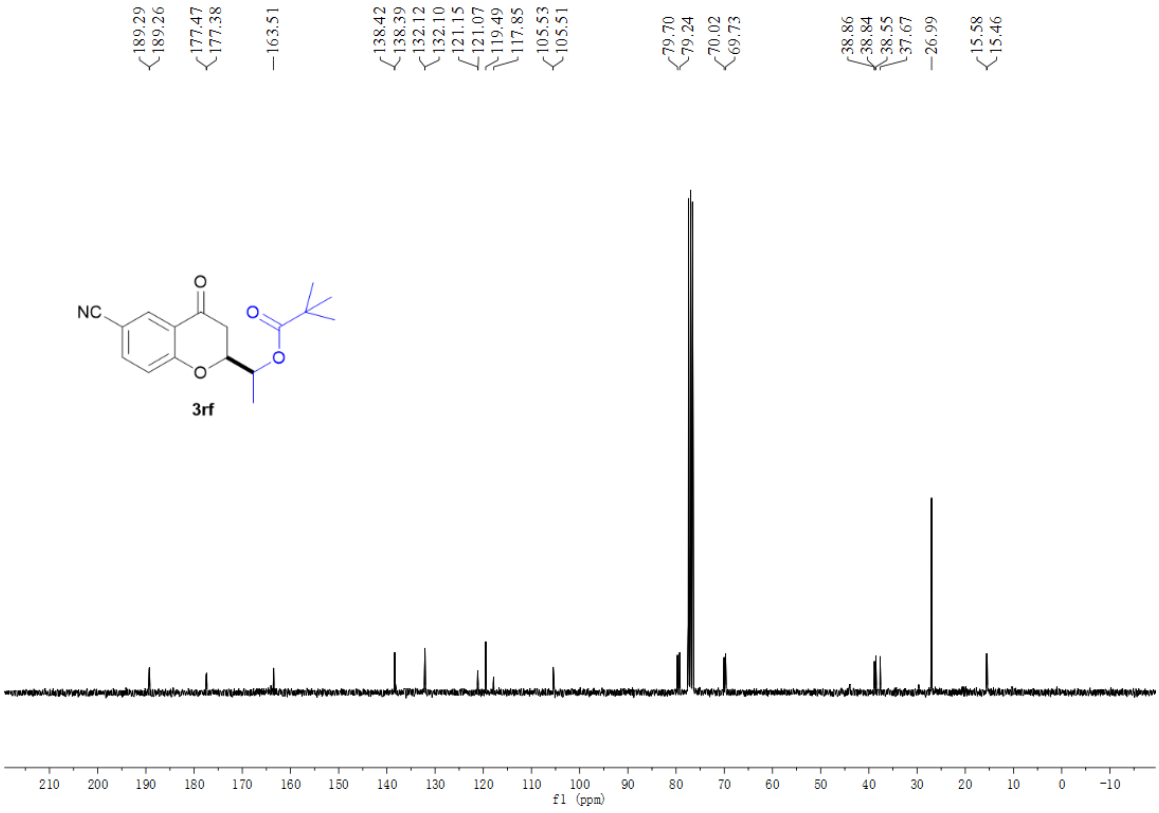
1-(6-Chloro-4-oxochroman-2-yl)ethyl pivalate (3nf)



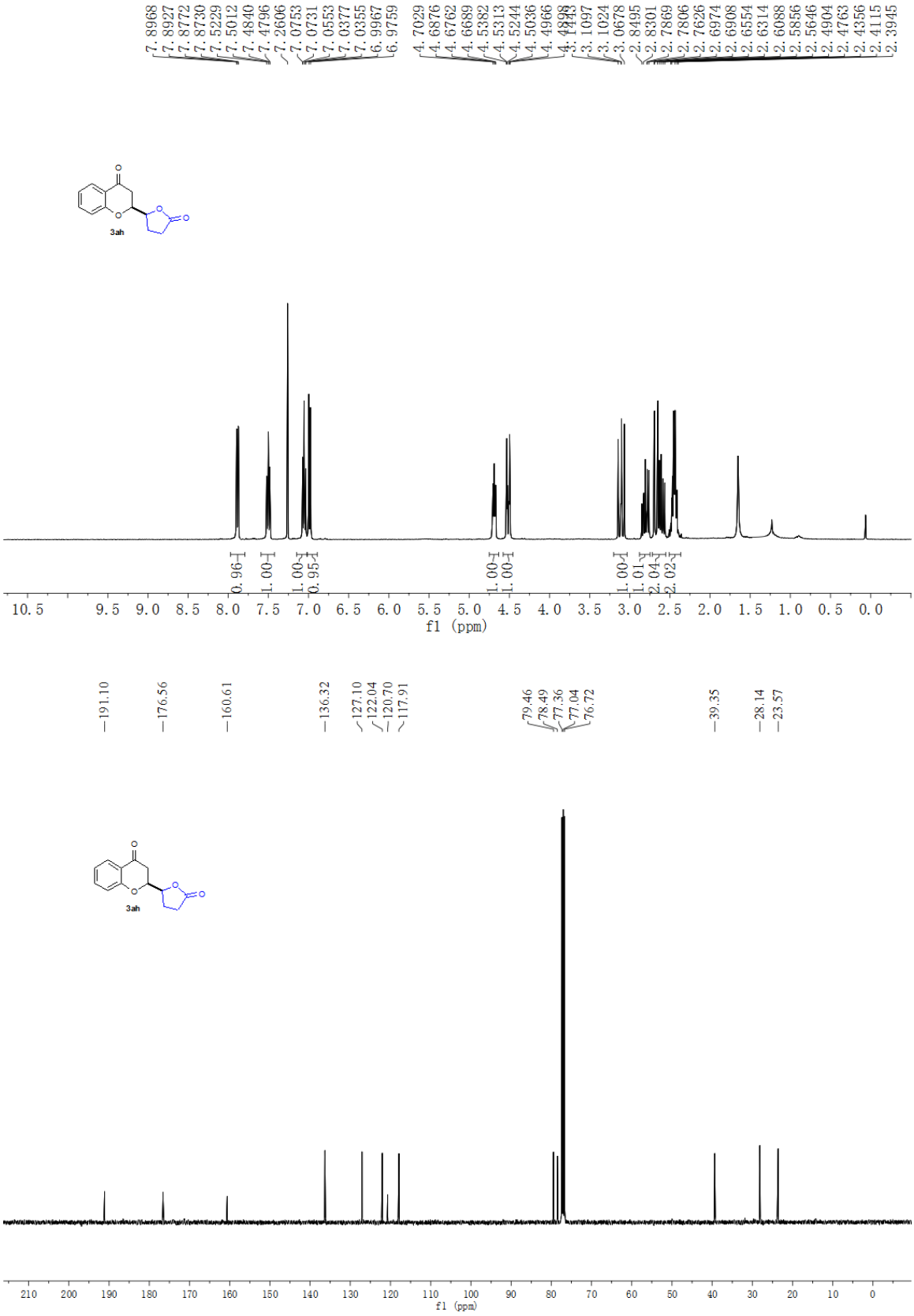


1-(6-Cyano-4-oxochroman-2-yl)ethyl pivalate (3rf)

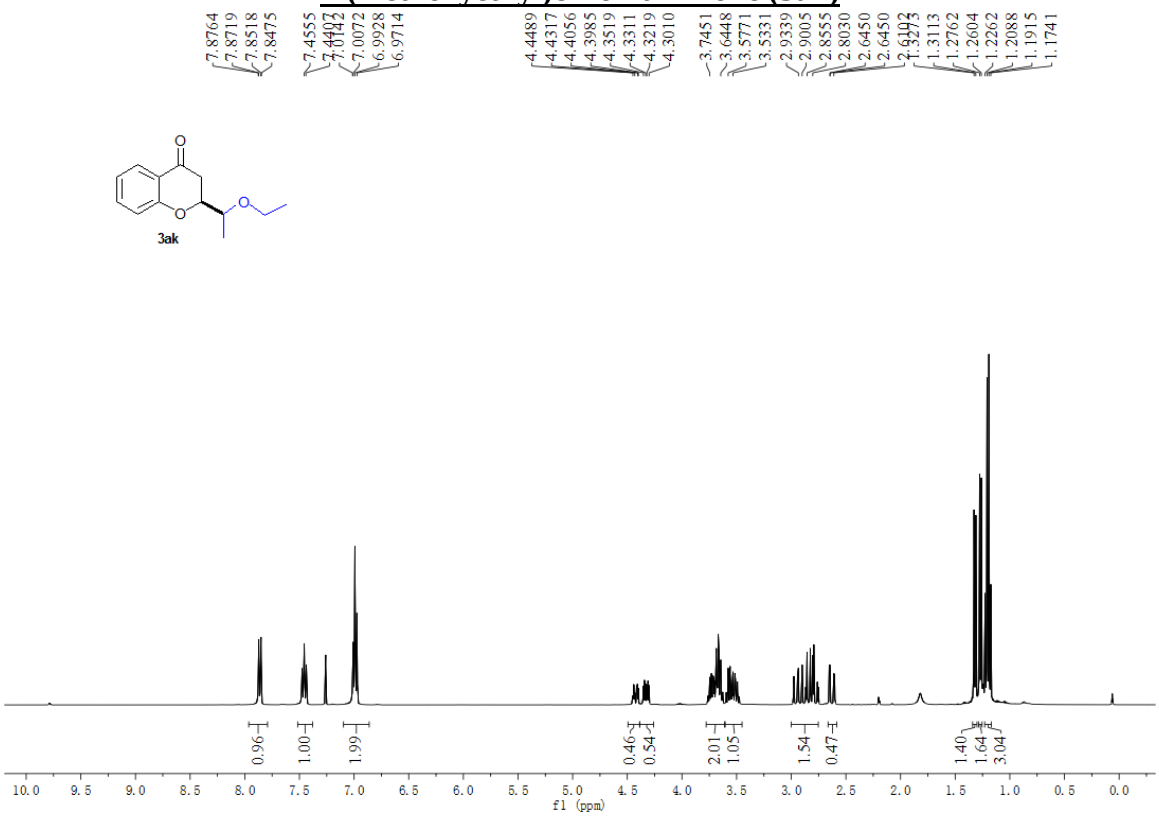


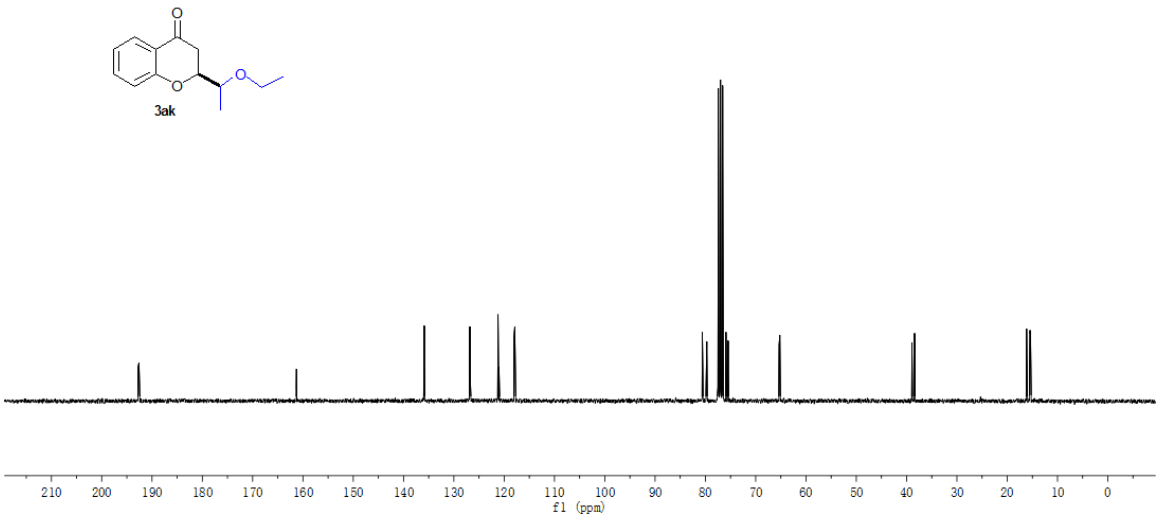


2-(5-oxotetrahydrofuran-2-yl)chroman-4-one (3ah)

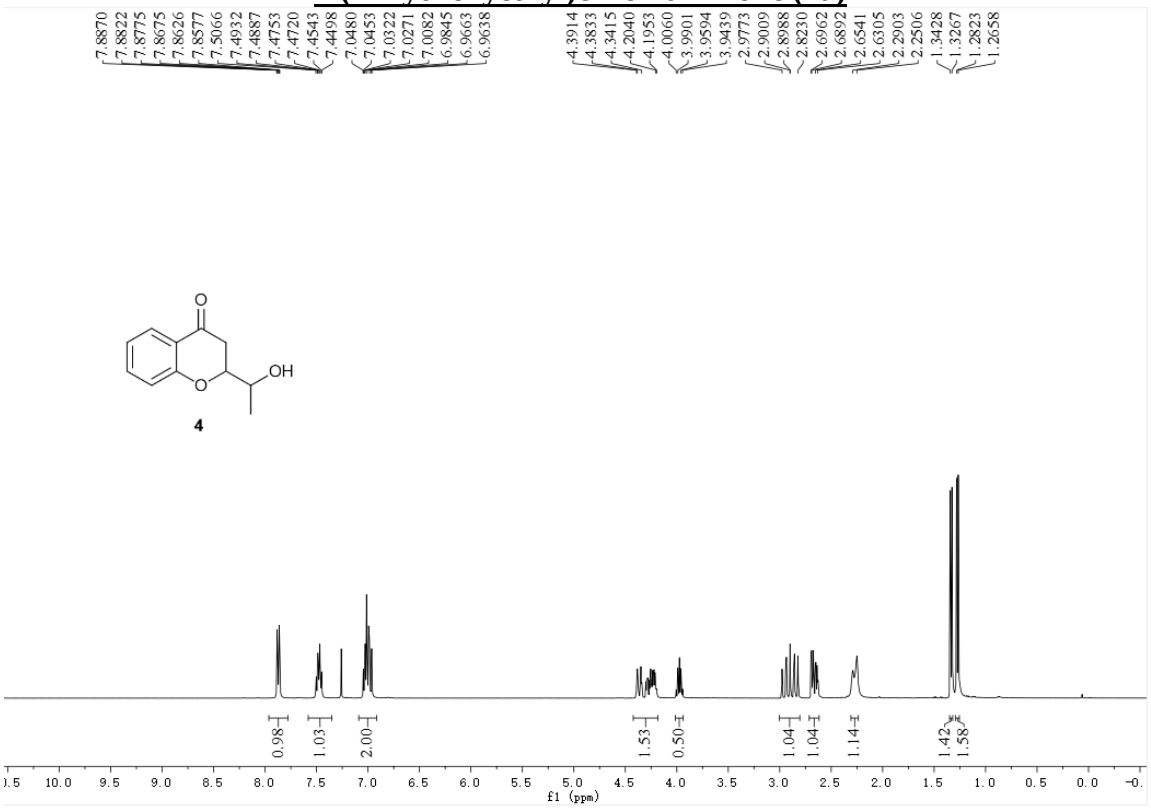


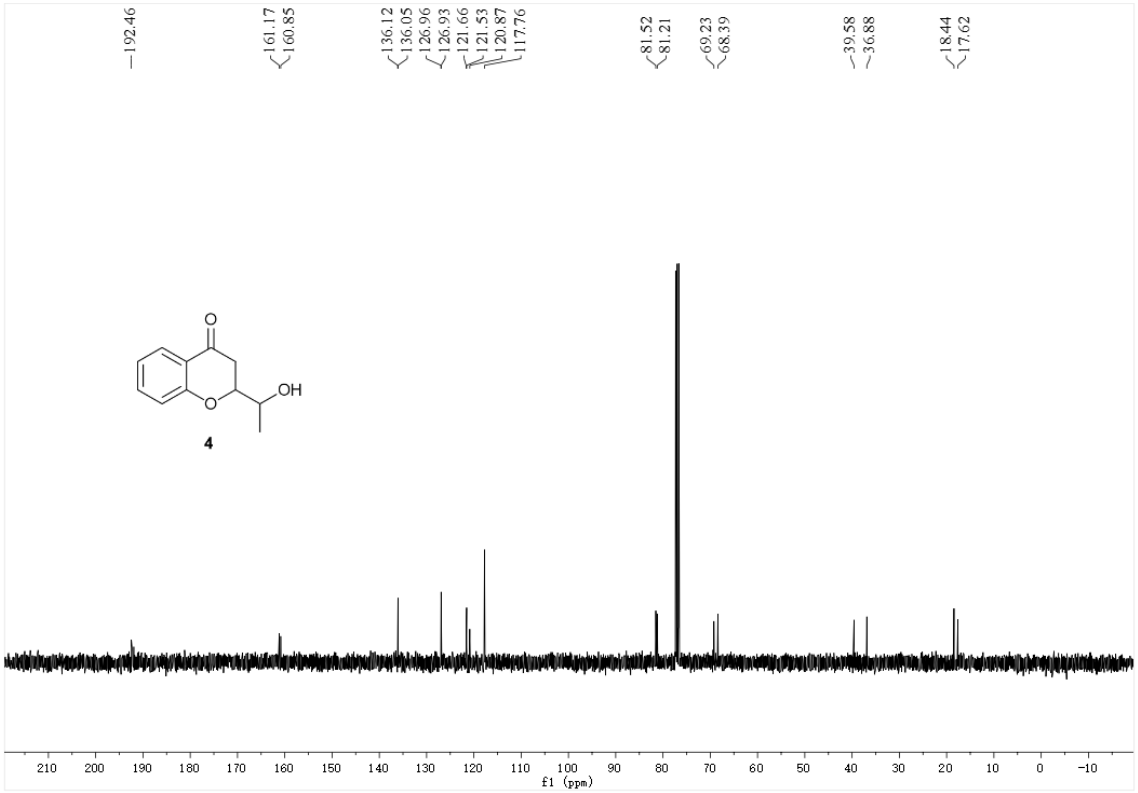
2-(1-ethoxyethyl)chroman-4-one (3ak)





2-(1-Hydroxyethyl)chroman-4-one (4a)





2-(Hydroxymethyl)chroman-4-one (4b)