Supporting Information

Metal-free oxidative decarbonylative alkylation of chromones with aliphatic aldehydes

Rongzhen Chen, Jin-Tao Yu* and Jiang Cheng

School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Jiangsu Province Key Laboratory of Fine Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China

E-mail: yujintao@cczu.edu.cn

1. 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 ppm relative to TMS, the coupling constants *J* are given in Hz. 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** (0.8 mmol), DTBP (0.6 mmol) and isopropanol (1 mL) were added into the sealed tubed. The reaction mixture was vigorously stirred at 120 ^{o}C for 15h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the products.

2. Mechanism Studies

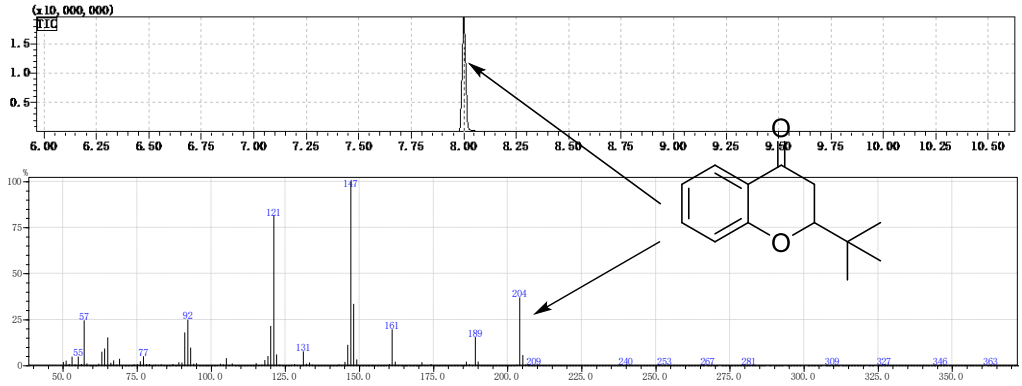
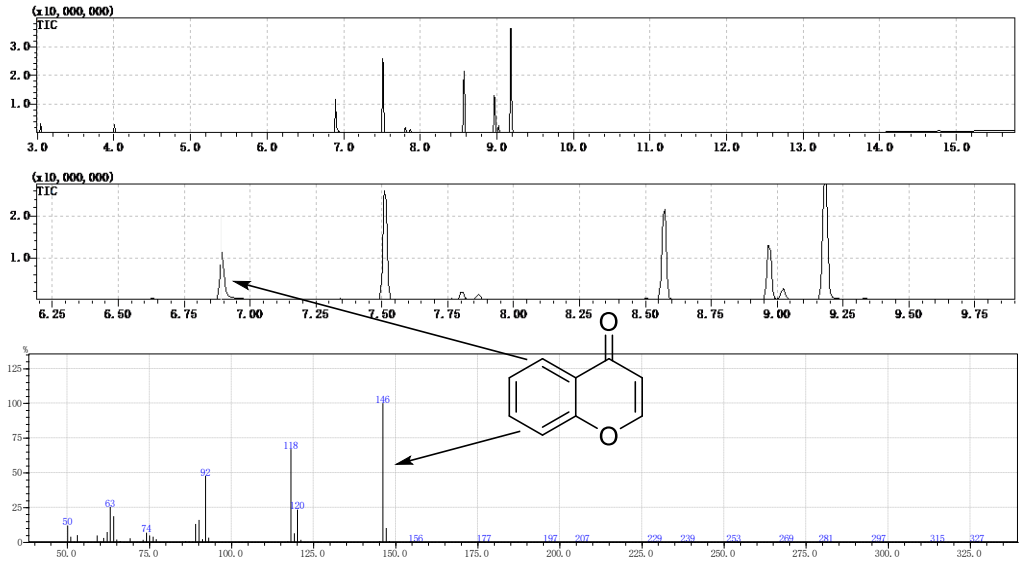


Figure S1 GC-MS spectra of the product **3aa**

Standard Procedure + BHT (3.0 equiv)



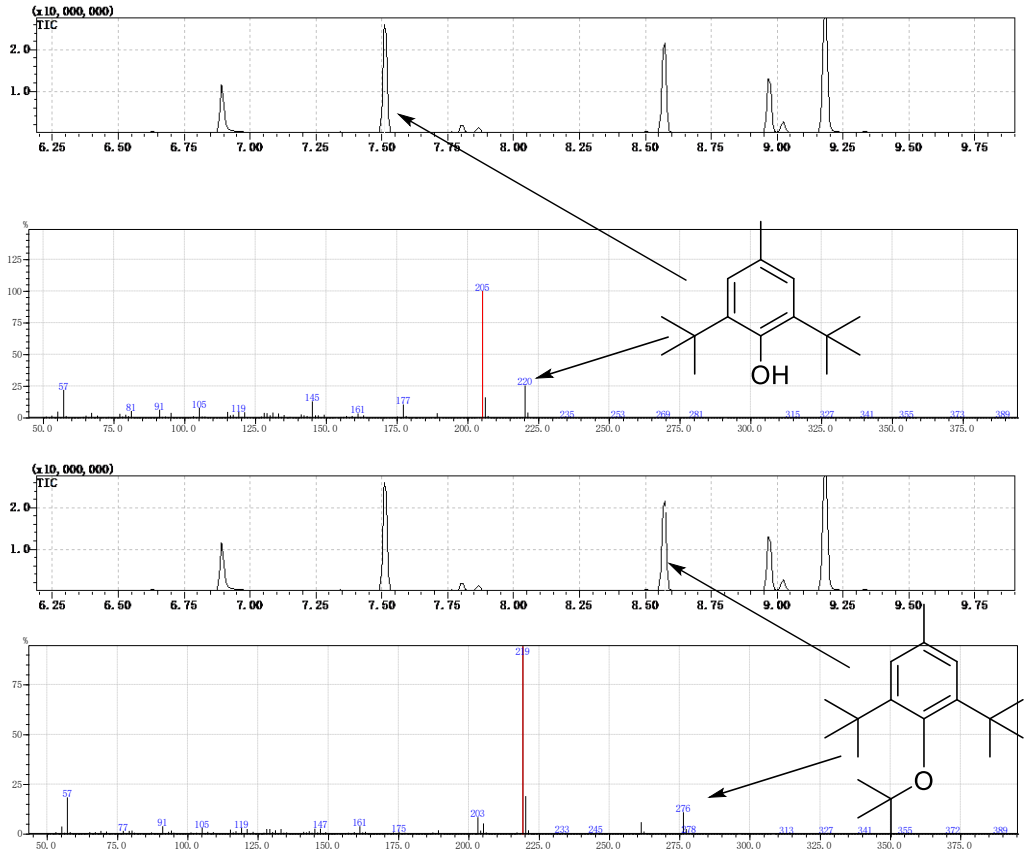


Figure S2 GC-MS spectra of the free radical capture results

Test for the evolution of CO gas

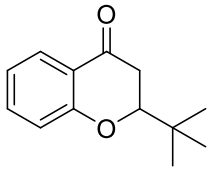
A piece of test strip prepared from PMA (phosphomolybdic acid)-$PdCl_2$ solution[1] was put into the reaction tube and sealed. After the completion of the reaction, the color of the test strip was changed from light yellow to dark blue (Figure S3).

Figure S3. The PMA-$PdCl_2$ test strip as prepared (left) and the PMA-$PdCl_2$ test strip in the reaction tube (right).

[1] A. Verma and S. kumar, *Org. Lett.*, 2016, **18**, 4388.

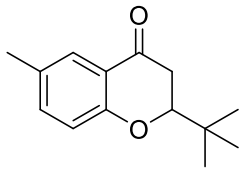
3. Characterization data of the products

2-(*tert*-butyl)chroman-4-one (3aa)[2]



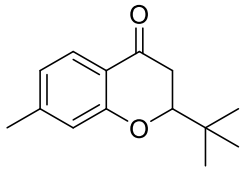
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.47-7.42 (m, 1H), 6.99-6.95 (m, 2H), 4.04 (dd, *J* = 12.6, 4.1 Hz, 1H), 2.72-2.61 (m, 2H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.5, 162.2, 135.9, 126.9, 121.0, 120.8, 117.9, 85.2, 38.4, 34.2, 25.5.

2-(tert-butyl)-6-methylchroman-4-one (3ba)



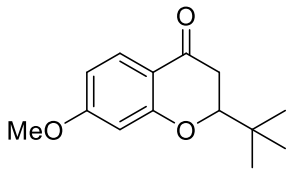
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (d, *J* = 1.6 Hz, 1H), 7.23 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 4.03-3.91 (m, 1H), 2.67-2.56 (m, 2H), 2.26 (s, 3H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.7, 160.3, 136.9, 130.3, 126.4, 120.3, 117.7, 85.2, 38.4, 34.1, 25.5, 21.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{19}O_2$ $(M+H)^+$ 219.1380, found 219.1381.

2-(tert-butyl)-7-methylchroman-4-one (3ca)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 8.4 Hz, 1H), 6.78-6.77 (m, 2H), 4.00 (dd, *J* = 12.8, 4.1 Hz, 1H), 2.68-2.55 (m, 2H), 2.32 (s, 3H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.2, 162.2, 147.3, 126.7, 122.4, 118.5, 117.9, 85.2, 38.4, 34.1, 25.5, 21.9. HRMS (ESI) *m/z* calcd for $C_{14}H_{19}O_2$ $(M+H)^+$ 219.1380, found 219.1381.

2-(tert-butyl)-7-methoxychroman-4-one (3da)

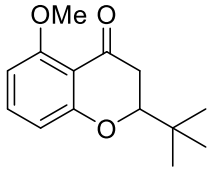


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 8.8 Hz, 1H), 6.49 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.36 (d, *J* = 2.3 Hz, 1H), 4.00-3.96 (m, 1H), 3.77 (s, 3H), 2.62-2.48 (m, 2H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$,

[2] D. Xiong, W. Zhou, Z. Lu, S. Zeng and J. Wang, *Chem. Commun.*, 2017, **53**, 6844.

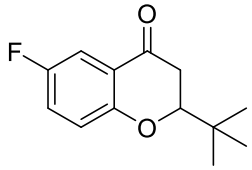
100 MHz): δ 191.9, 165.9, 164.1, 128.5, 114.6, 109.8, 100.5, 85.6, 55.6, 38.0, 34.1, 25.5. HRMS (ESI) *m/z* calcd for $C_{14}H_{19}O_3$ $(M+H)^+$ 235.1329, found 235.1328.

2-(tert-butyl)-5-methoxychroman-4-one (3ea)



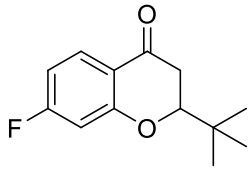
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72-7.27 (m, 1H), 6.55-6.51 (m, 1H), 6.44-6.41 (m, 1H), 3.96-3.91 (m, 1H), 3.85 (s, 3H), 2.67-2.49 (m, 2H), 0.98 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.1, 163.7, 160.5, 135.7, 111.1, 109.9, 103.4, 85.5, 56.1, 39.9, 33.9, 25.4. HRMS (ESI) *m/z* calcd for $C_{14}H_{19}O_3$ $(M+H)^+$ 235.1329, found 235.1328.

2-(tert-butyl)-6-fluorochroman-4-one (3fa)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.41 (m, 1H), 7.14-7.09 (m, 1H), 6.93-6.89 (m, 1H), 4.02-3.93 (m, 1H), 2.62-2.59 (m, 2H), 1.01 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.6, 158.3 (d, J_{C-F} =22.7 Hz), 155.7, 123.3 (d, J_{C-F} =24.3 Hz), 121.1 (d, J_{C-F} =6.4 Hz), 119.5 (d, J_{C-F} =7.3 Hz), 111.6 (d, J_{C-F} =23.0 Hz), 85.5, 38.1, 34.1, 25.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}FO_2$ $(M+H)^+$ 223.1129, found 223.1130.

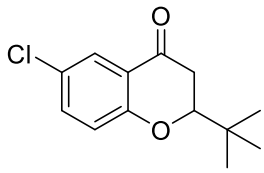
2-(tert-butyl)-7-fluorochroman-4-one (3ga)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.85 (m, 1H), 6.73-6.66 (m, 2H), 4.12-4.02 (m, 1H), 2.71-2.61 (m, 2H), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.0, 167.5 (d, J_{C-F} =254.3 Hz), 163.8 (d, J_{C-F} =13.6 Hz), 129.4 (d, J_{C-F} =11.4 Hz), 109.5 (d, J_{C-F} =22.6 Hz), 104.6 (d, J_{C-F} =24.1 Hz), 85.9, 38.1, 34.2, 25.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}FO_2$ $(M+H)^+$ 223.1129, found 223.1131.

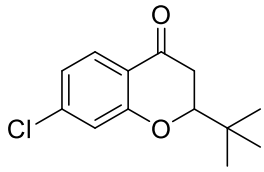
2-(tert-butyl)-6-chlorochroman-4-one (3ha)[3]

[3] E. R. Ashley, E. C. Sherer, B. Pio, R. K. Orr and R. T. Ruck, *ACS Catal.*, 2017, **7**, 1446.



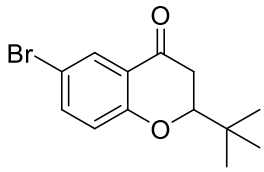
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.74 (m, 1H), 7.35-7.32 (m, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 4.05-3.95 (m, 1H), 2.63-2.58 (m, 2H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.2, 160.6, 135.6, 126.5, 126.1, 121.5, 119.6, 85.5, 38.1, 34.2, 25.5.

2-(tert-butyl)-7-chlorochroman-4-one (3ia)



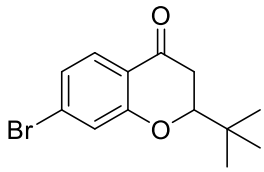
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75-7.72 (m, 1H), 6.98-6.89 (m, 2H), 4.08-3.98 (m, 1H), 2.64-2.58 (m, 2H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.2, 162.4, 141.6, 128.1, 121.8, 119.3, 118.0, 85.7, 38.2, 34.2, 25.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}ClO_2$ $(M+H)^+$ 239.0833, found 239.0836.

6-bromo-2-(tert-butyl)chroman-4-one (3ja)



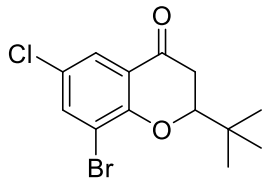
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.84 (m, 1H), 7.45-7.42 (m, 1H), 6.85-6.81 (m, 1H), 4.01-3.93 (m, 1H), 2.65-2.55 (m, 2H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.9, 160.9, 138.4, 129.2, 121.9, 120.0, 113.6, 85.5, 38.0, 34.2, 25.5. HRMS (ESI) *m/z* calcd for $C_{10}H_{11}O_3$ $(M+H)^+$ 179.0703, found 179.0704. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}BrO_2$ $(M+H)^+$ 283.0328, found 283.0332.

7-bromo-2-(tert-butyl)chroman-4-one (3ka)



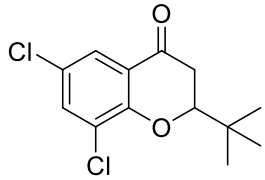
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 1.2 Hz, 1H), 7.06 (d, *J* = 8.4, 1.2 Hz, 1H), 4.06-3.96 (m, 1H), 2.67-2.57 (m, 2H), 1.01 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.4, 162.3, 130.2, 128.1, 124.6, 121.1, 119.6, 85.7, 38.2, 34.2, 25.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{16}BrO_2$ $(M+H)^+$ 283.0328, found 283.0332.

8-bromo-2-(tert-butyl)-6-chlorochroman-4-one (3la)



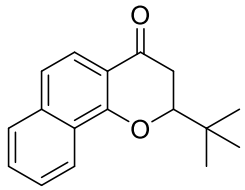
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.72 (d, *J* = 2.1 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 1H), 4.13-4.03 (m, 1H), 2.69-2.63 (m, 2H), 1.08 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.5, 157.1, 138.2, 126.6, 125.6, 121.9, 112.9, 86.3, 37.8, 34.5, 25.5. HRMS (ESI) *m/z* calcd for $C_{13}H_{15}BrClO_2$ $(M+H)^+$ 316.9938, found 316.9943.

2-(tert-butyl)-6,8-dichlorochroman-4-one (3ma)



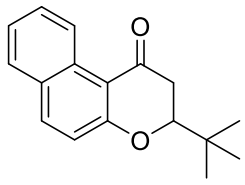
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (d, *J* = 2.5 Hz, 1H), 7.51 (d, *J* = 2.5 Hz, 1H), 4.14-4.05 (m, 1H), 2.75-2.66 (m, 2H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.5, 156.3, 135.3, 126.2, 124.9, 124.2, 122.2, 86.3, 37.9, 34.5, 25.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{15}Cl_2O_2$ $(M+H)^+$ 273.0444, found 273.0447.

2-(tert-butyl)-2,3-dihydro-4H-benzo[h]chromen-4-one (3na)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (dd, *J* = 8.3 Hz, 1H), 7.82 (dd, *J* = 8.7 Hz, 1H), 7.72 (dd, *J* = 8.0 Hz, 1H), 7.58-7.54 (m, 1H), 7.51-7.47 (m, 1H), 7.72 (dd, *J* = 8.7 Hz, 1H), 4.20-4.16 (m, 1H), 2.80-2.65 (m, 2H), 1.15 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.9, 160.2, 137.5, 129.5, 127.9, 126.2, 125.0, 123.5, 121.8, 120.7, 115.2, 86.1, 37.8, 34.4, 25.7. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}O_2$ $(M+H)^+$ 255.1380, found 255.1382.

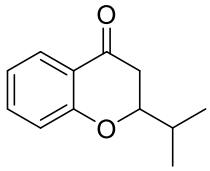
3-(tert-butyl)-2,3-dihydro-1H-benzo[f]chromen-1-one (3oa)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.46 (dd, *J* = 8.7 Hz, 1H), 7.86-7.81 (m, 1H), 7.71-7.60 (m, 1H), 7.42-7.38 (m, 1H), 7.09-7.04 (m, 1H), 4.16-4.13 (m, 1H), 2.86-2.77 (m, 1H), 2.71-2.65 (m, 1H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.5, 164.2, 137.2, 131.5, 129.5, 129.0, 128.3,

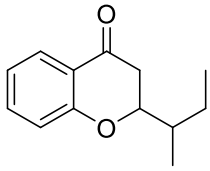
125.8, 124.7, 118.9, 112.2, 86.2, 39.6, 34.0, 25.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{19}O_2$ $(M+H)^+$ 255.1380, found 255.1381.

2-isopropylchroman-4-one (3ab)[2]



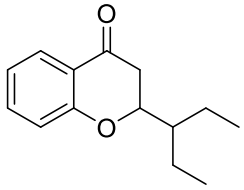
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.47-7.42 (m, 1H), 6.99-6.95 (m, 2H), 4.19-4.14 (m, 1H), 2.73-2.60 (m, 2H), 2.08-2.00 (m, 1H), 1.08-1.03 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.1, 161.9, 135.9, 126.9, 121.1, 120.9, 117.9, 82.5, 40.1, 32.2, 17.9.

2-(sec-butyl)chroman-4-one (3ac)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46-7.42 (m, 1H), 6.98-6.94 (m, 2H), 4.32-4.24 (m, 1H), 2.78-2.65 (m, 1H), 2.62-2.55 (m, 1H), 1.91-1.84 (m, 0.48H), 1.77-1.68 (m, 0.53H), 1.65-1.57 (m, 1H), 1.33-1.24 (m, 1H), 1.05-0.93 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.2, 193.1, 162.0, 161.9, 135.9, 135.8, 126.9, 121.1, 121.0, 120.9, 117.94, 117.91, 81.3, 81.1, 40.3, 39.5, 38.7, 38.5, 24.9, 24.8, 14.2, 14.1, 11.6, 11.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{17}O_2$ $(M+H)^+$ 205.1223, found 205.1224.

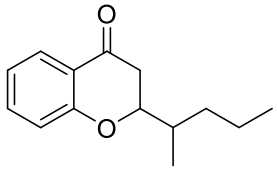
2-(pentan-3-yl)chroman-4-one (3ad)[4]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46-7.41 (m, 1H), 6.98-6.94 (m, 2H), 4.44-4.39 (m, 1H), 2.77-2.69 (m, 1H), 2.60-2.55 (m, 1H), 1.67-1.56 (m, 2H), 1.54-1.46 (m, 2H), 1.40-1.29 (m, 1H), 0.96-0.92 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.2, 162.1, 135.9, 126.9, 121.1, 121.0, 117.9, 79.5, 44.8, 39.9, 21.5, 21.3, 11.4.

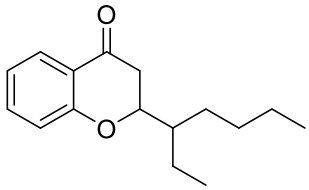
2-(pentan-2-yl)chroman-4-one (3ae)

[4] C. Vila, V. Hornillos, M. Fananas-Mastral and B. L. Feringa, *Chem. Commun.*, 2013, **49**, 5933.



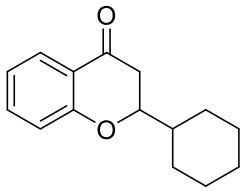
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.45-7.41 (m, 1H), 6.98-6.94 (m, 2H), 4.31-4.23 (m, 1H), 2.78-2.65 (m, 1H), 2.61-2.54 (m, 1H), 1.96-1.93 (m, 0.53H), 1.88-1.78 (m, 0.51H), 1.59-1.39 (m, 2H), 1.36-1.19 (m, 2H), 1.04-0.99 (m, 3H), 0.94-0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.2, 193.1, 162.0, 161.9, 135.9, 135.8, 126.9, 121.1, 121.0, 120.9, 117.94, 117.91, 81.6, 81.3, 40.3, 39.3, 36.8, 36.6, 34.4, 34.3, 20.2, 20.1, 14.6, 14.5, 14.3, 14.2. HRMS (ESI) *m/z* calcd for $C_{14}H_{19}O_2$ $(M+H)^+$ 219.1380, found 219.1382.

2-(heptan-3-yl)chroman-4-one (3af)



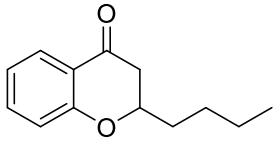
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.46-7.41 (m, 1H), 6.98-6.94 (m, 2H), 4.45-4.38 (m, 1H), 2.78-2.70 (m, 1H), 2.60-2.54 (m, 1H), 1.70-1.60 (m, 1.51H), 1.57-1.42 (m, 2.54H), 1.38-1.24 (m, 5H), 0.97-0.88 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3, 193.2, 162.12, 162.10, 135.9, 126.9, 121.03, 121.00, 117.9, 79.8, 79.7, 43.3, 43.2, 39.9, 39.8, 29.4, 29.3, 28.6, 28.5, 23.1, 23.0, 22.1, 21.9, 14.1, 14.0, 11.5, 11.4. HRMS (ESI) *m/z* calcd for $C_{16}H_{23}O_2$ $(M+H)^+$ 247.1693, found 247.1692.

2-cyclohexylchroman-4-one (3ag)[2]



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.84 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.45-7.41 (m, 1H), 6.98-6.93 (m, 2H), 4.19-4.14 (m, 1H), 2.74-2.59 (m, 2H), 1.98-1.95 (m, 1H), 1.81-1.68 (m, 5H), 1.34-1.07 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.1, 162.9, 135.9, 126.9, 121.0, 117.9, 81.9, 41.8, 40.2, 28.3, 28.2, 26.3, 26.0, 25.9.

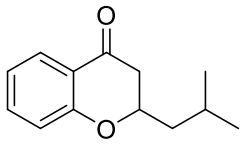
2-butylchroman-4-one (3ah)[5]



[5] D. Zhao, B. Beiring and F. Glorius, *Angew. Chem. Int. Ed.*, 2013, **52**, 8454.

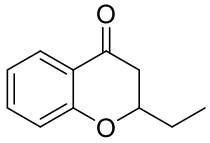
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48-7.44 (m, 1H), 7.01-6.95 (m, 2H), 4.46-4.39 (m, 1H), 2.67 (d, *J* = 7.9 Hz, 2H), 1.93-1.83 (m, 1H), 1.75-1.66 (m, 1H), 1.59-1.33 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.8, 162.7, 135.9, 126.9, 121.1, 121.0, 117.9, 77.9, 43.0, 34.7, 27.1, 22.5, 14.0.

2-isobutylchroman-4-one (3ai)[4]



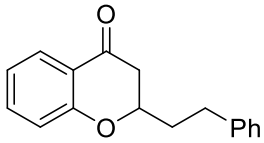
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.49-7.43 (m, 1H), 7.02-6.94 (m, 2H), 4.57-4.47 (m, 1H), 2.68-2.65 (m, 2H), 1.99-1.81 (m, 2H), 1.51-1.41 (m, 1H), 0.99-0.96 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.7, 162.7, 135.9, 126.9, 121.2, 121.1, 117.9, 76.3, 43.9, 43.4, 24.2, 23.0, 22.2.

2-ethylchroman-4-one (3aj)[2]



^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49-7.44 (m, 1H), 7.02-6.96 (m, 2H), 4.43-4.33 (m, 1H), 2.70-2.67 (m, 2H), 1.95-1.72 (m, 2H), 1.08 (t, *J* = 7.4, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.7, 162.7, 135.9, 126.9, 121.1, 121.0, 117.9, 79.1, 42.6, 27.9, 9.3.

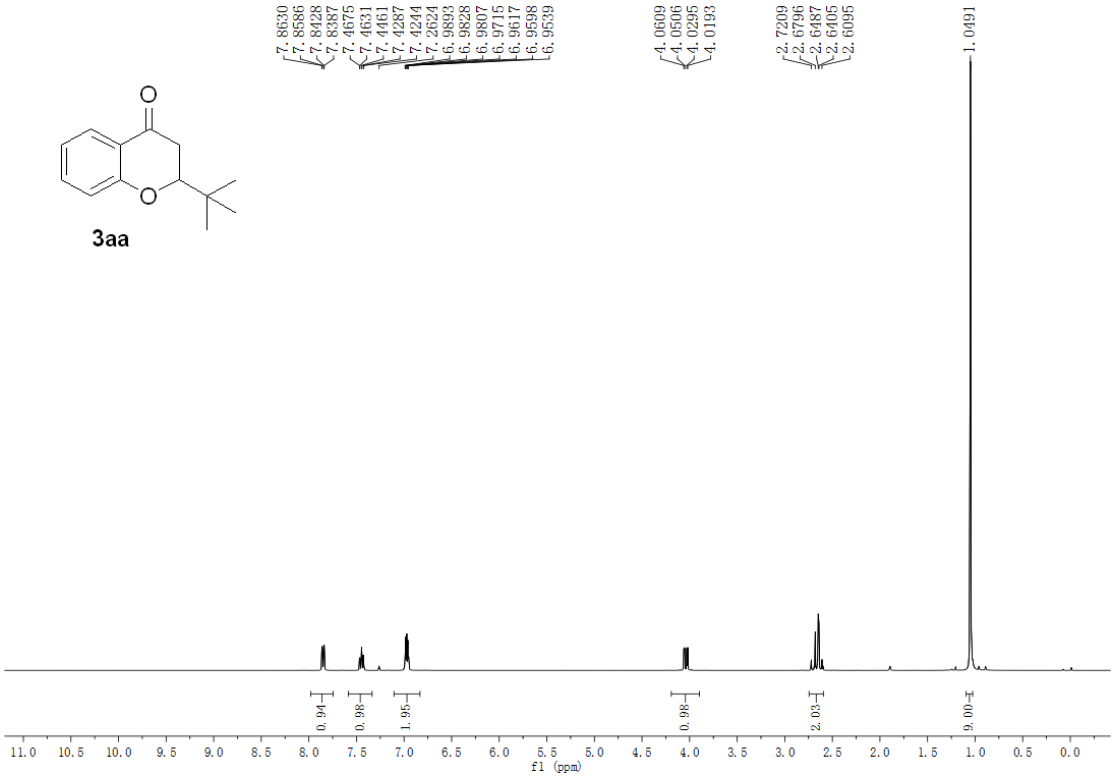
2-phenethylchroman-4-one (3ak)[6]



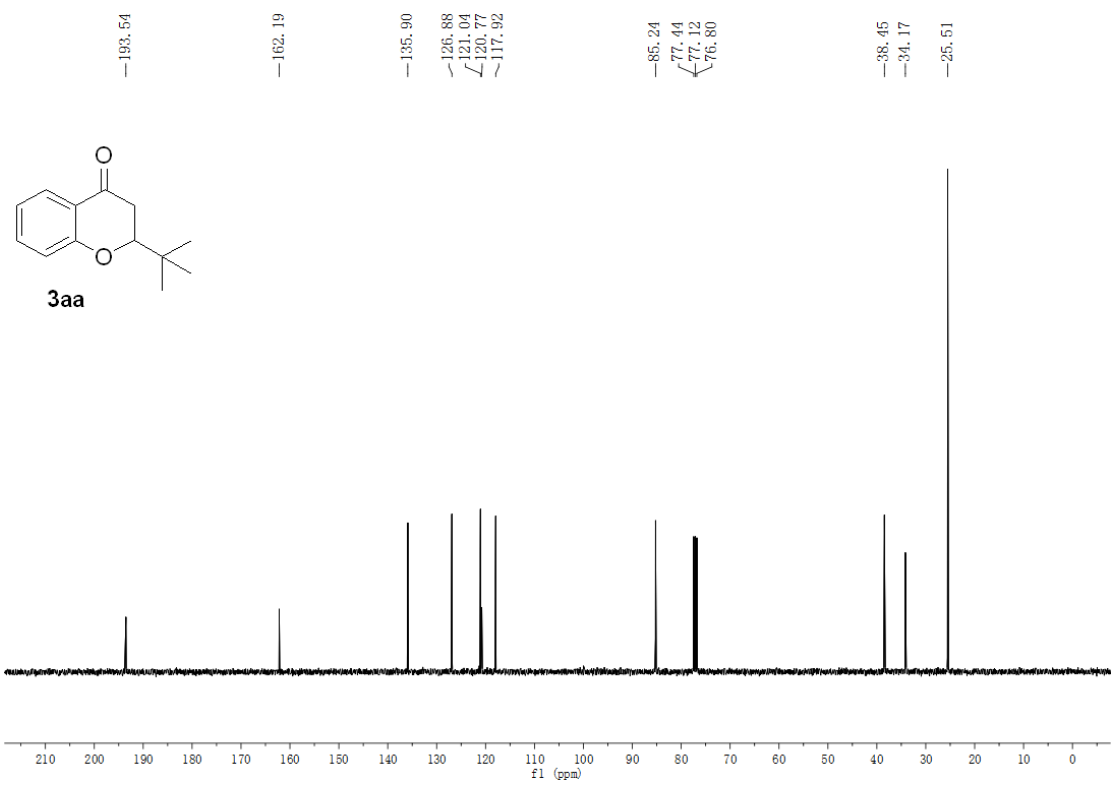
^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.88-7.85 (m, 1H), 7.49-7.44 (m, 1H), 7.31-7.26 (m, 2H), 7.23-7.16 (m, 3H), 7.02-6.97 (m, 2H), 4.46-4.36 (m, 1H), 2.97-2.77 (m, 2H), 2.70-2.63 (m, 2H), 2.27-2.15 (m, 1H), 2.03-1.91 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.3, 161.6, 140.9, 136.1, 128.6, 128.5, 127.0, 126.2, 121.3, 121.1, 117.9, 76.8, 43.0, 36.5, 31.2.

[6] M. Kawasaki, H. Yoshikai, H. Kakuda, N. Toyooka, A. Tanaka, M. Goto and T. Kometani, *Heterocycles*, 2006, **68**, 483.

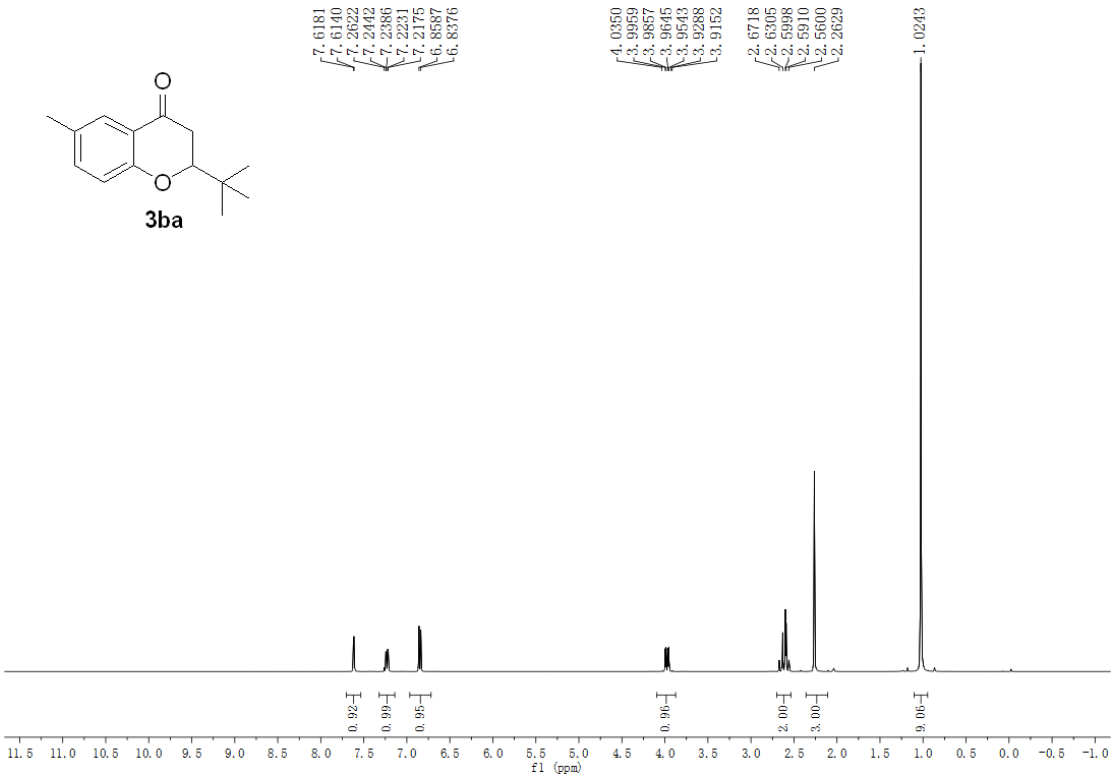
4. Copies of ^{1}H NMR and ^{13}C NMR spectra of the products

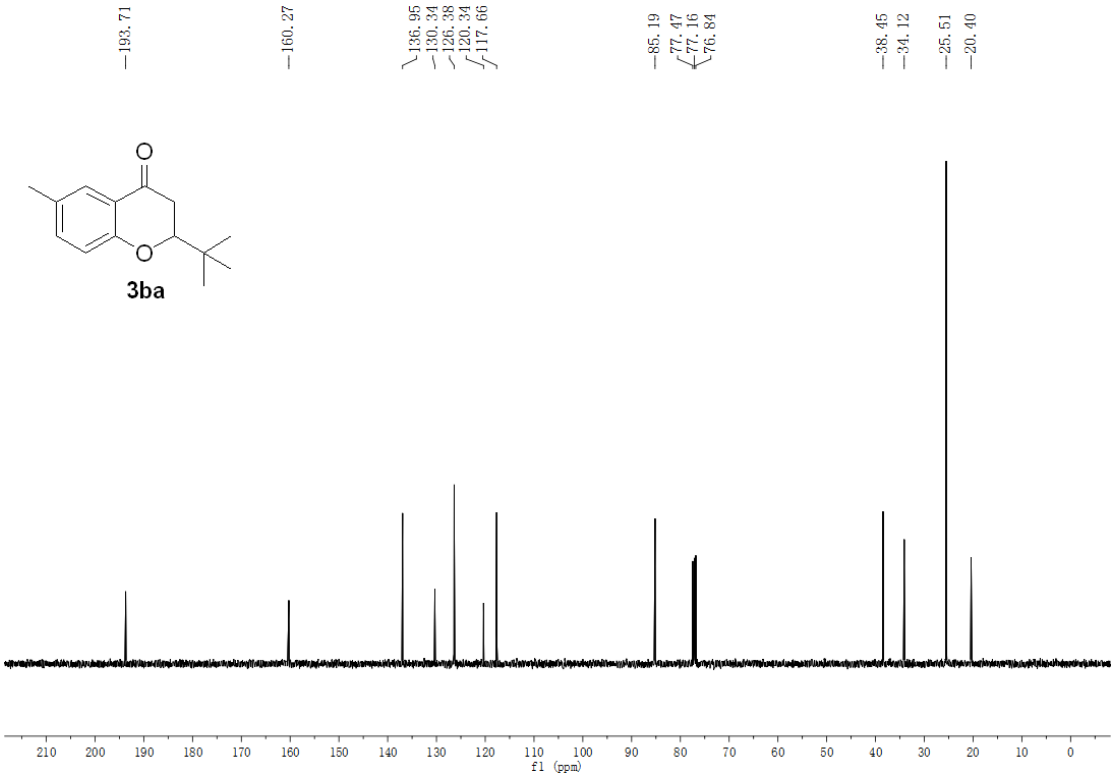


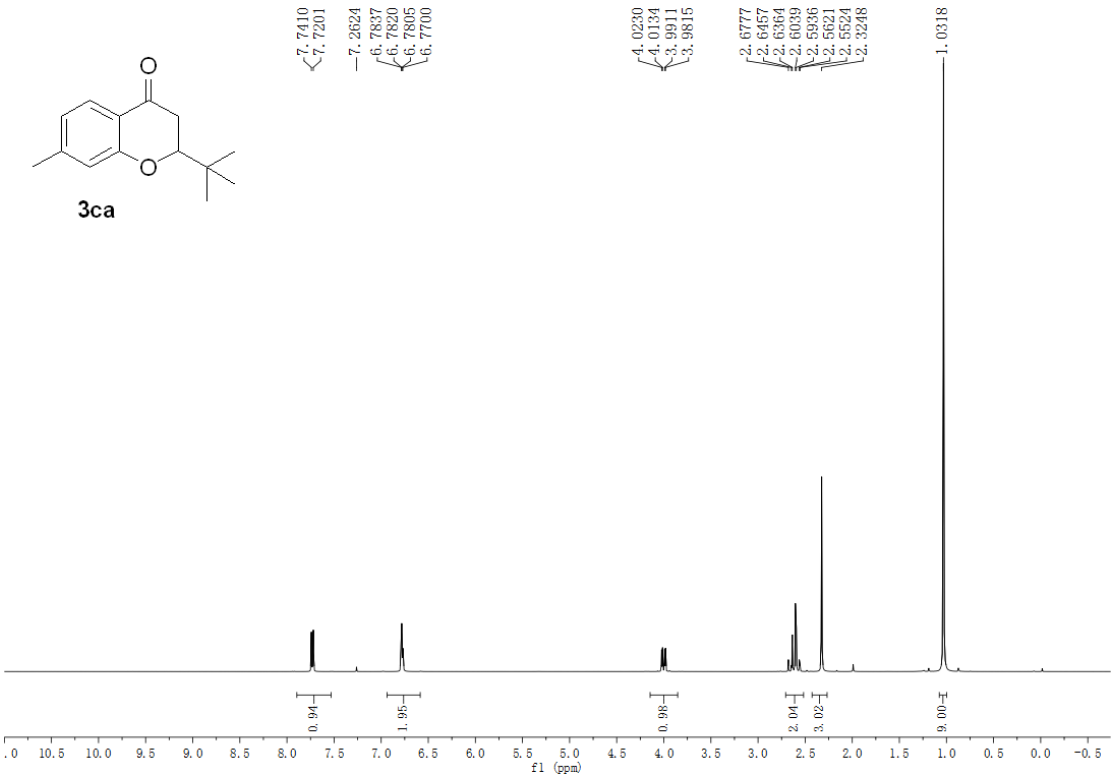
3aa

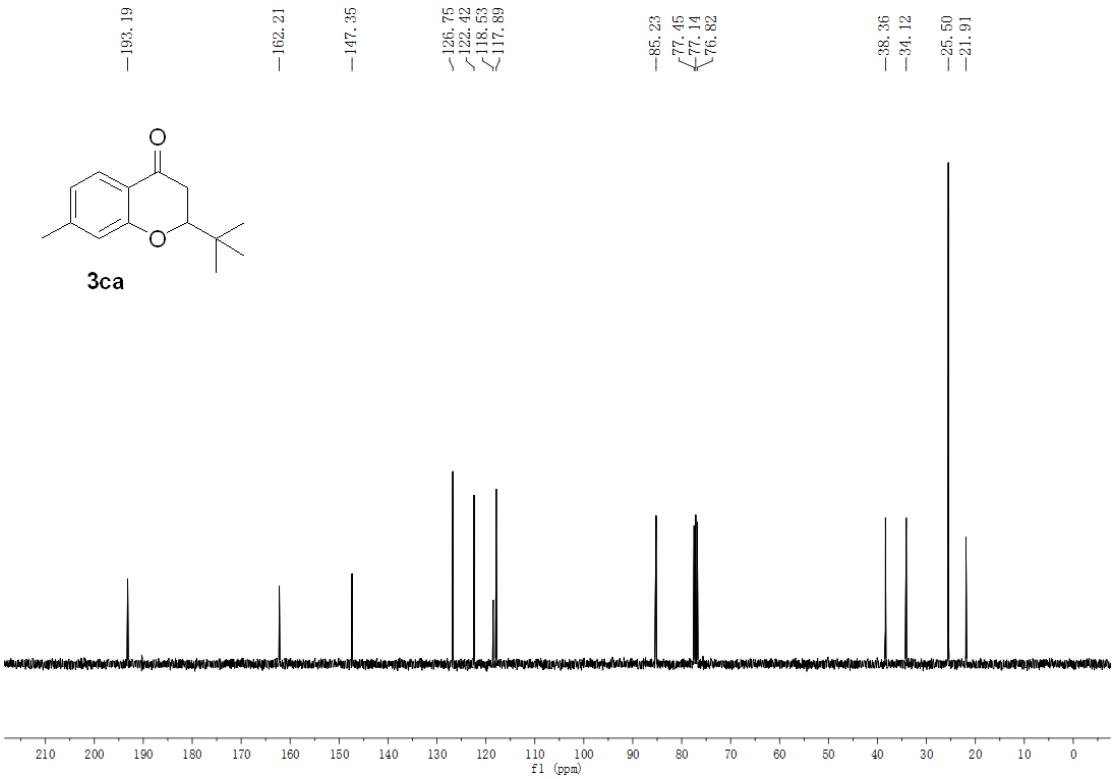


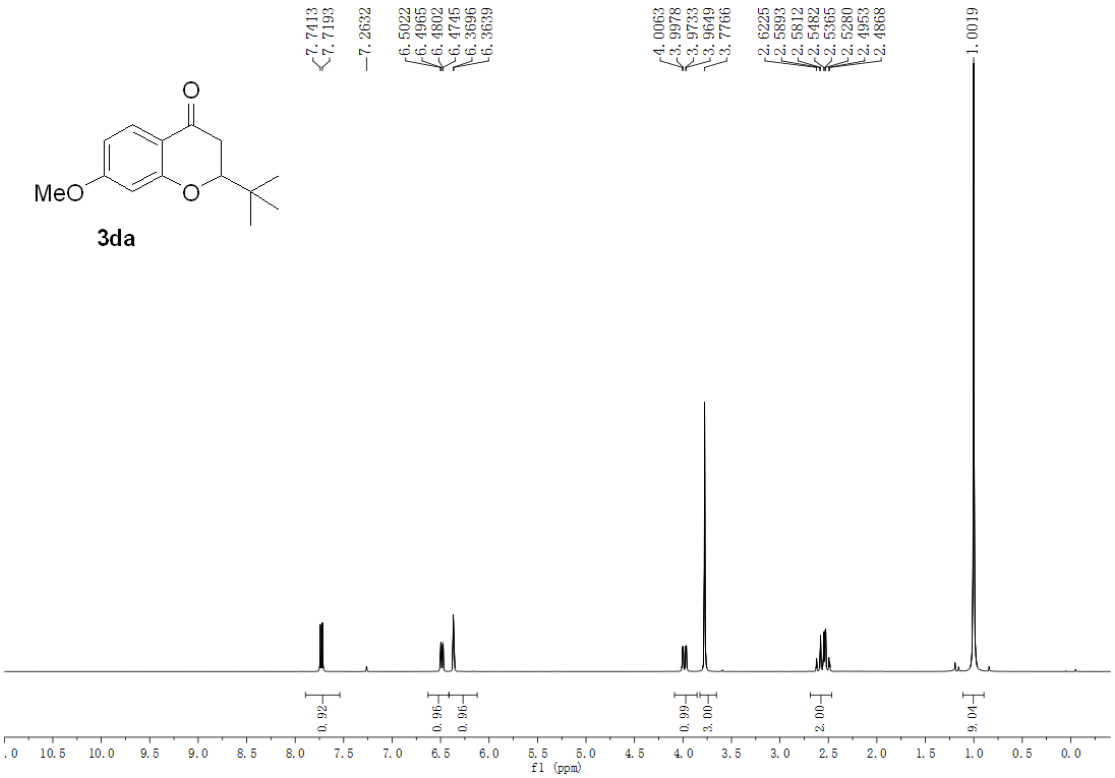
3aa


7.6181
7.6140
7.2622
7.2442
7.2386
7.2231
7.2175
6.8587
6.8376
4.0350
3.9959
3.9857
3.9645
3.9543
3.9288
3.9152
2.6718
2.6305
2.5998
2.5910
2.5600
2.2629
1.0243
3ba
0.92
0.99
0.95
0.96
2.00
3.00
9.06
f1 (ppm)


193.71
160.27
136.95
130.34
126.38
120.34
117.66
85.19
77.47
77.16
76.84
38.45
34.12
25.51
20.40
3ba
f1 (ppm)

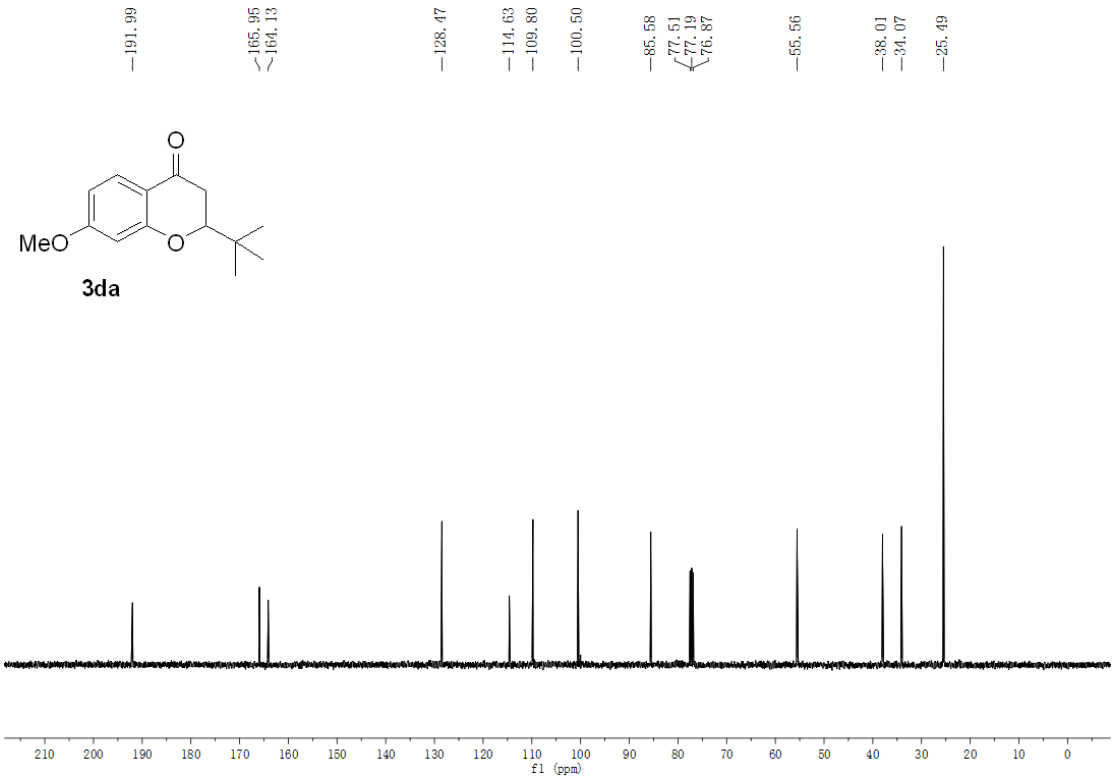

7.7410
7.7201
7.2624
6.7837
6.7820
6.7805
6.7700
4.0230
4.0134
3.9911
3.9815
2.6777
2.6457
2.6364
2.6039
2.5936
2.5621
2.5524
2.3248
1.0318
3ca
0.94
1.95
0.98
2.04
3.02
9.00
f1 (ppm)


193.19
162.21
147.35
126.75
122.42
118.53
117.89
85.23
77.45
77.14
76.82
38.36
34.12
25.50
21.91
3ca
f1 (ppm)


7.7413
7.7193
7.2632
6.5022
6.4965
6.4802
6.4745
6.3696
6.3639
4.0063
3.9978
3.9733
3.9649
3.7766
2.6225
2.5893
2.5812
2.5482
2.5365
2.5280
2.4953
2.4868
1.0019
0.92
0.96
0.96
0.99
3.00
2.00
9.04
f1 (ppm)

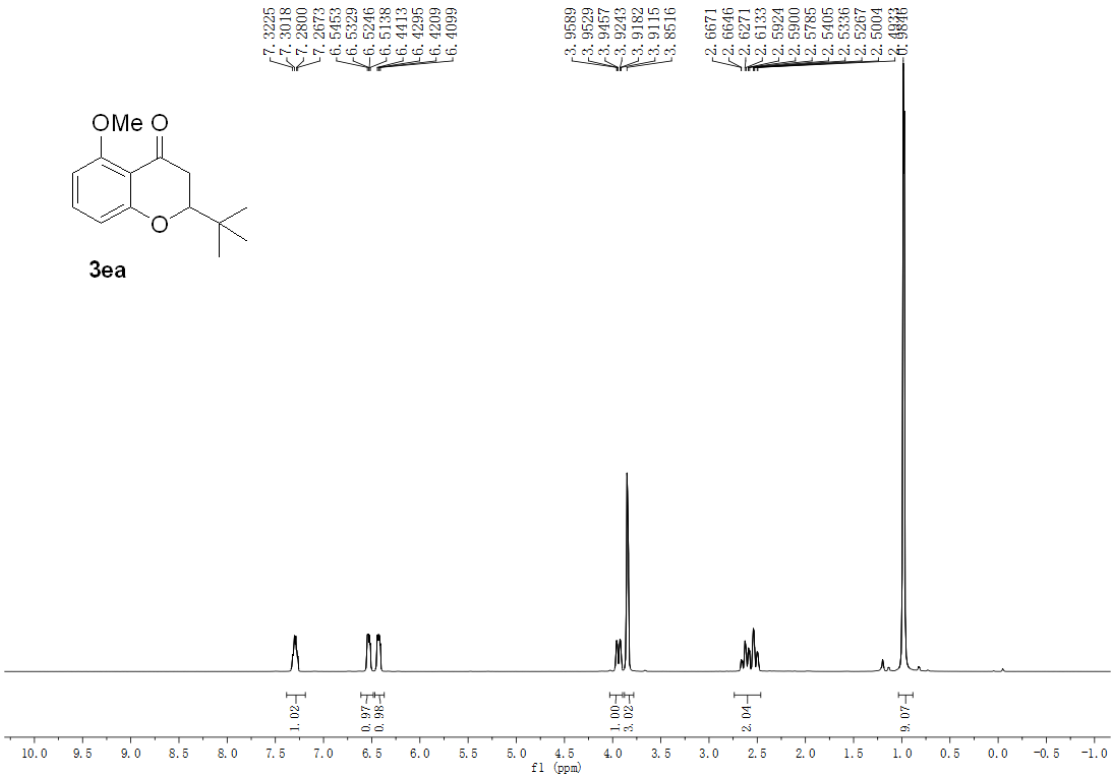
O
MeO
O

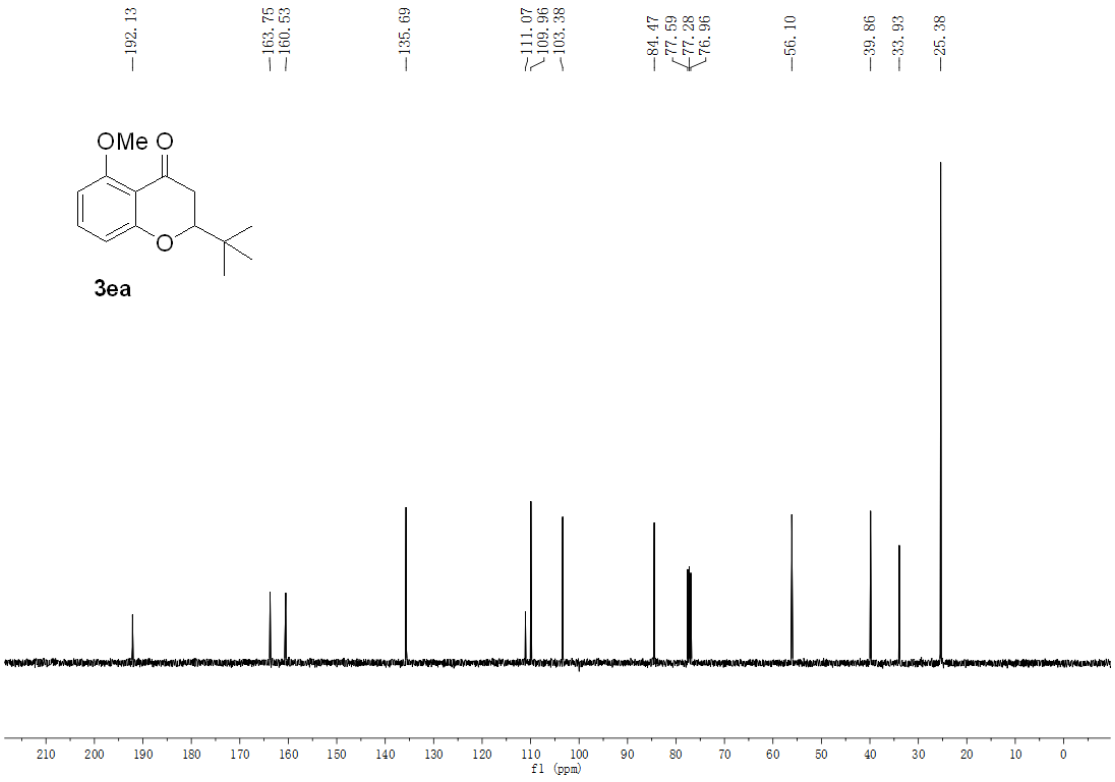
3da

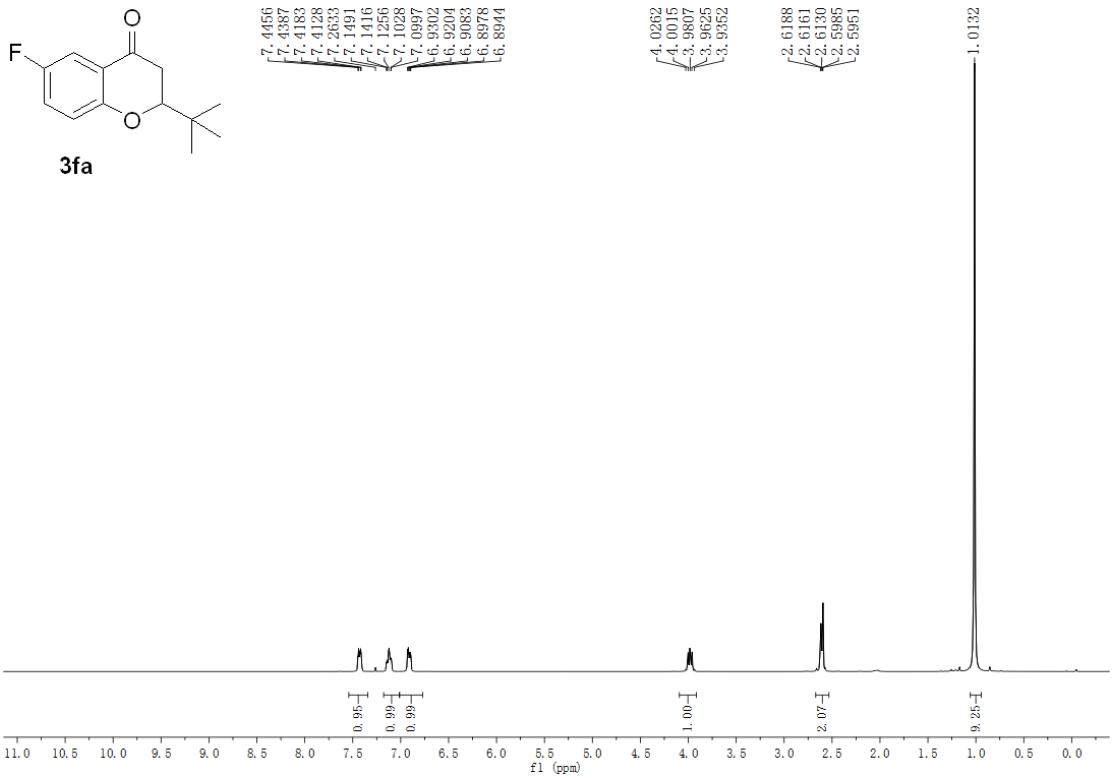

191.99
165.95
164.13
128.47
114.63
109.80
100.50
85.58
77.51
77.19
76.87
55.56
38.01
34.07
25.49
f1 (ppm)

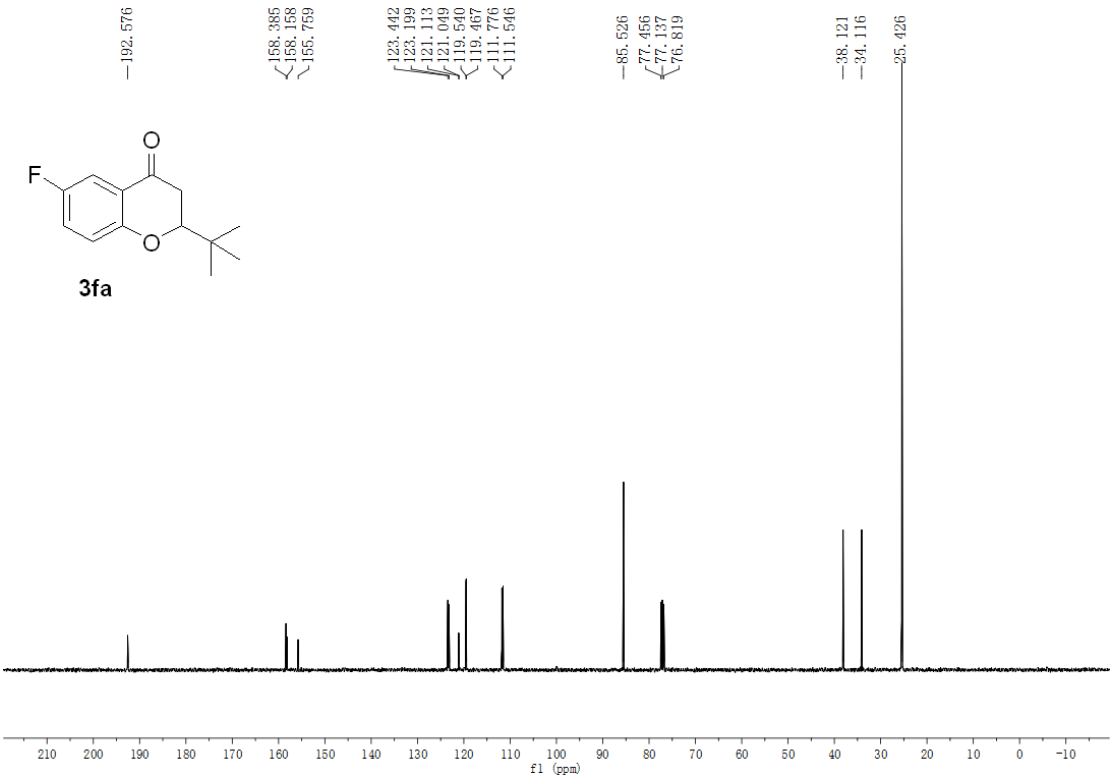
O
MeO
O

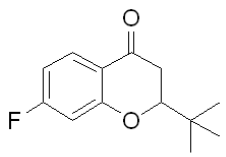
3da


7.3225
7.3018
7.2800
7.2673
6.5453
6.5329
6.5246
6.5138
6.4413
6.4295
6.4209
6.4099
3.9589
3.9529
3.9457
3.9243
3.9182
3.9115
3.8516
2.6671
2.6646
2.6271
2.6133
2.5924
2.5900
2.5785
2.5405
2.5336
2.5267
2.5004
2.4933
2.4846
OMe O
3ea
1.02
0.97
0.98
1.00
3.02
2.04
9.07
f1 (ppm)


192.13
163.75
160.53
135.69
111.07
109.96
103.38
84.47
77.59
77.28
76.96
56.10
39.86
33.93
25.38
OMe O
3ea
f1 (ppm)

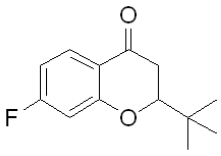

3fa
7.4456
7.4387
7.4183
7.4128
7.2633
7.1491
7.1416
7.1256
7.1028
7.0997
6.9302
6.9204
6.9083
6.8978
6.8944
4.0262
4.0015
3.9807
3.9625
3.9352
2.6188
2.6161
2.6130
2.5985
2.5951
1.0132
0.95
0.99
0.99
1.00
2.07
9.25
f1 (ppm)


3fa
192.576
158.385
158.158
155.759
123.442
123.199
121.113
121.049
119.540
119.467
111.776
111.546
85.526
77.456
77.137
76.819
38.121
34.116
25.426
f1 (ppm)


O
F
O

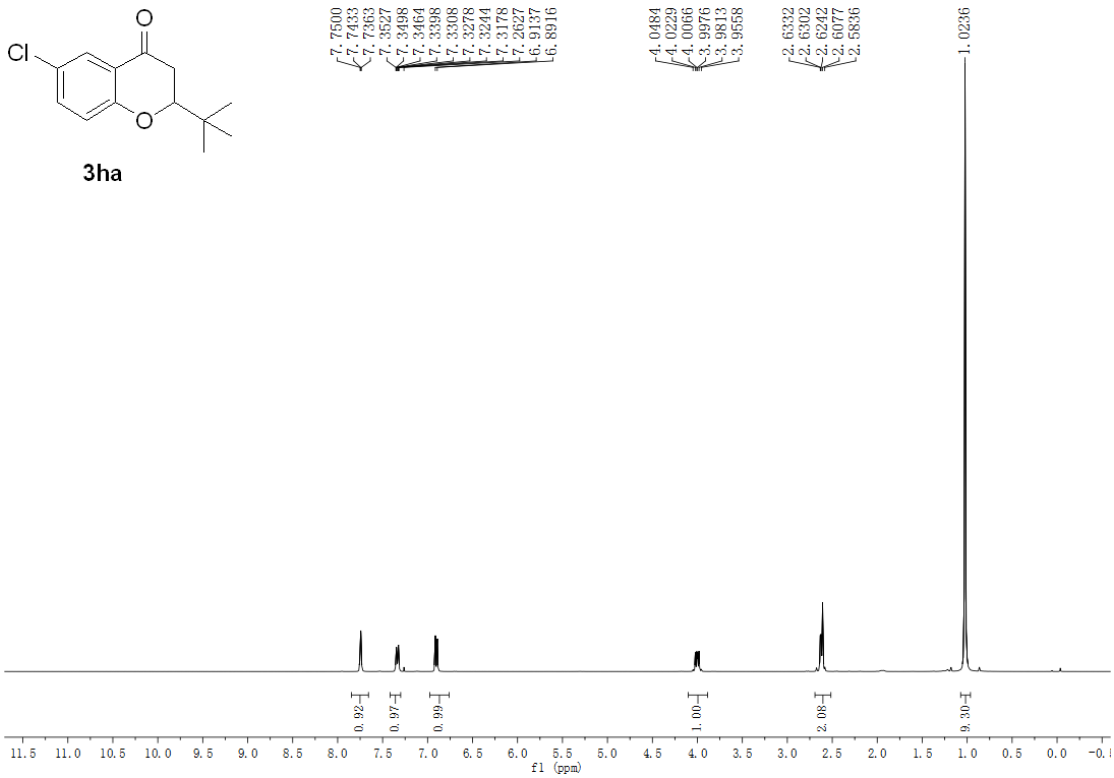
3ga

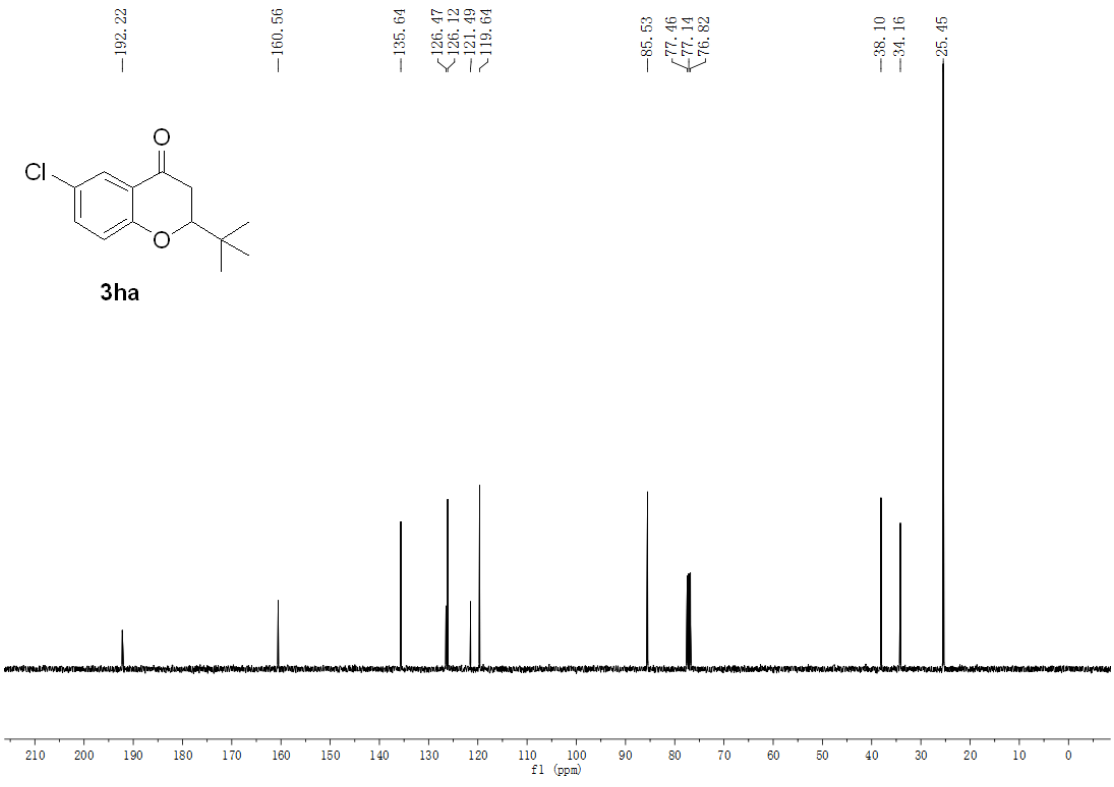
7.8956
7.8788
7.8740
7.8571
7.2630
6.7296
6.7236
6.7087
6.7028
6.6876
6.6817
6.6628
6.6571
4.1279
4.1224
4.0942
4.0826
4.0643
4.0527
4.0190
2.7157
2.6742
2.6519
2.6441
2.6405
2.6105
1.0496
0.94
1.95
1.00
2.05
9.12
f1 (ppm)

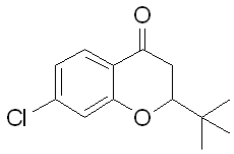

O
F
O

3ga

192.059
168.759
166.216
163.900
163.764
129.448
129.334
117.741
117.720
109.637
109.411
104.739
104.498
85.945
77.377
77.059
76.741
38.126
34.178
25.452
f1 (ppm)

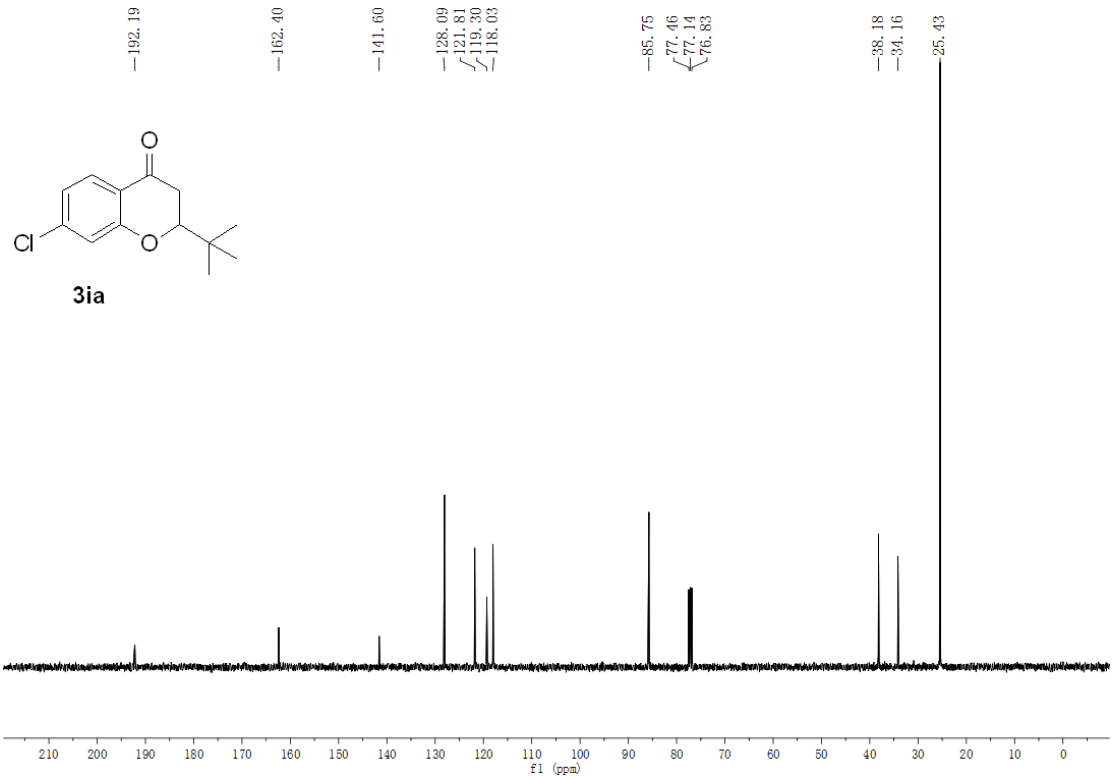

Cl
O
O
3ha
7.7500
7.7433
7.7363
7.3527
7.3498
7.3464
7.3398
7.3308
7.3278
7.3244
7.3178
7.2627
6.9137
6.8916
4.0484
4.0229
4.0066
3.9976
3.9813
3.9558
2.6332
2.6302
2.6242
2.6077
2.5836
1.0236
0.92
0.97
0.99
1.00
2.08
9.30
f1 (ppm)


192.22
160.56
135.64
126.47
126.12
121.49
119.64
85.53
77.46
77.14
76.82
38.10
34.16
25.45
Cl
O
O
3ha
f1 (ppm)


O
Cl
O

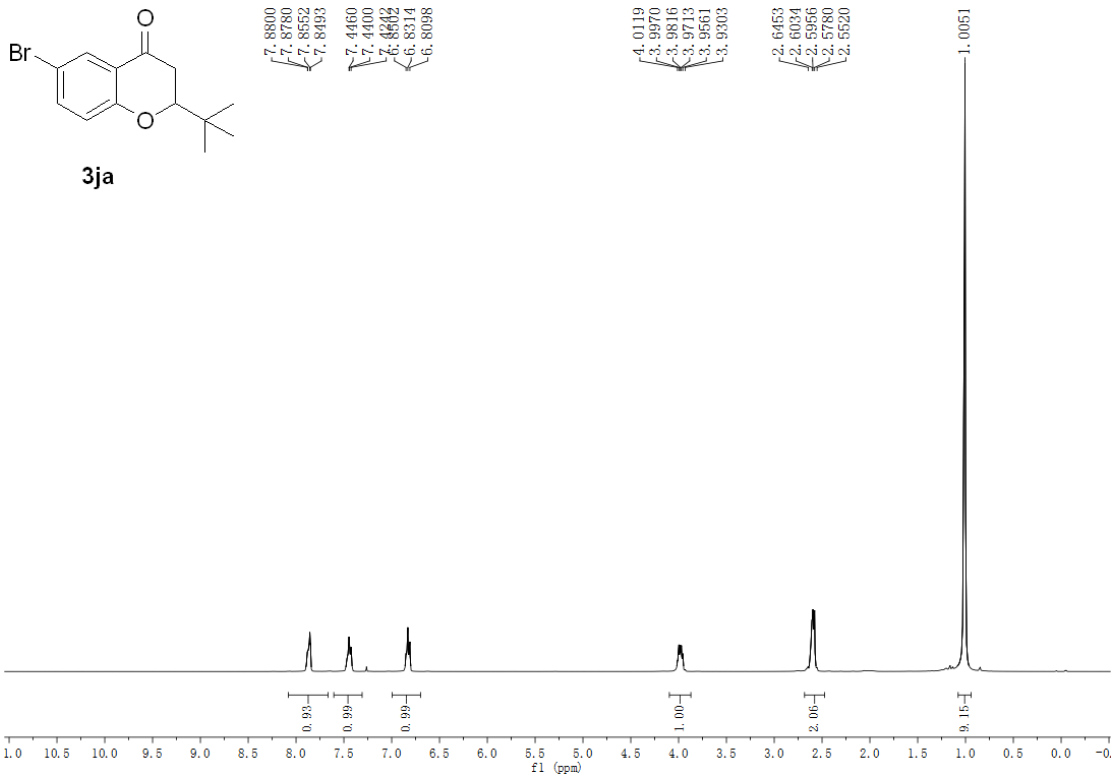
3ia

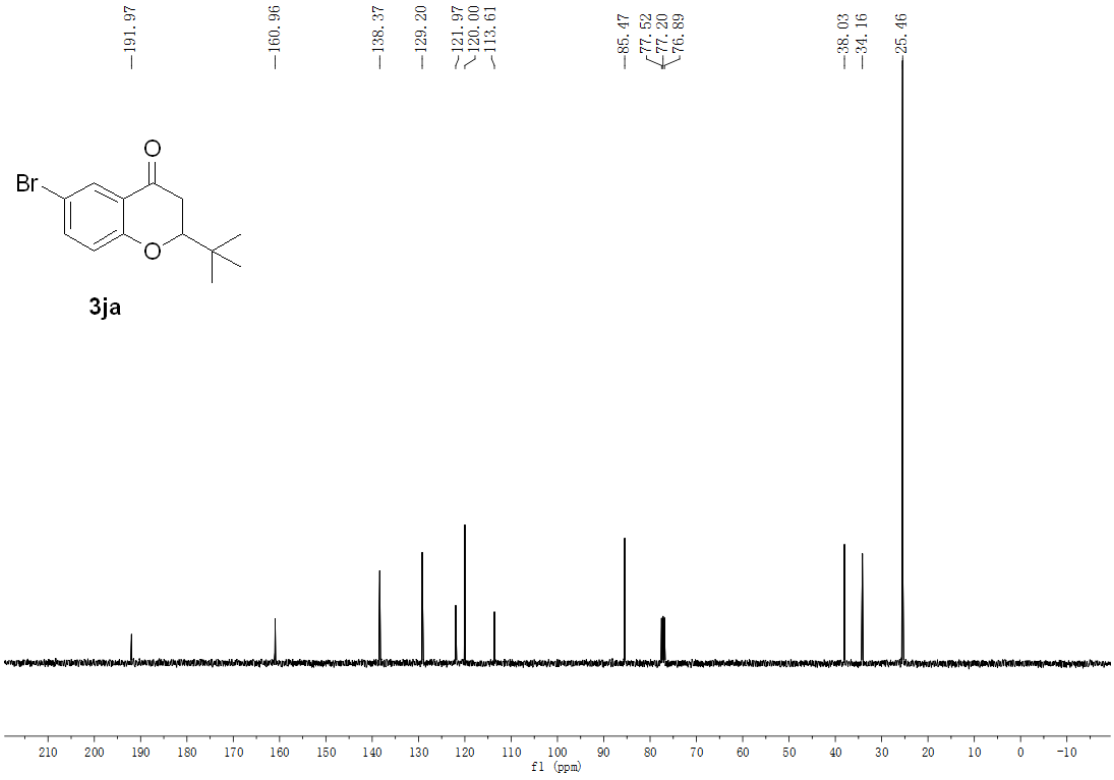
7.7554
7.7497
7.7349
7.7196
7.7161
7.2637
6.9839
6.9794
6.9657
6.9313
6.9265
6.9106
6.9060
6.8925
4.0801
4.0508
4.0375
4.0231
4.0094
3.9962
3.9802
2.6418
2.6261
2.6128
2.5987
2.5847
1.0244
0.96
1.93
1.00
2.03
9.37
f1 (ppm)


192.19
162.40
141.60
128.09
121.81
119.30
118.03
85.75
77.46
77.14
76.83
38.18
34.16
25.43
f1 (ppm)

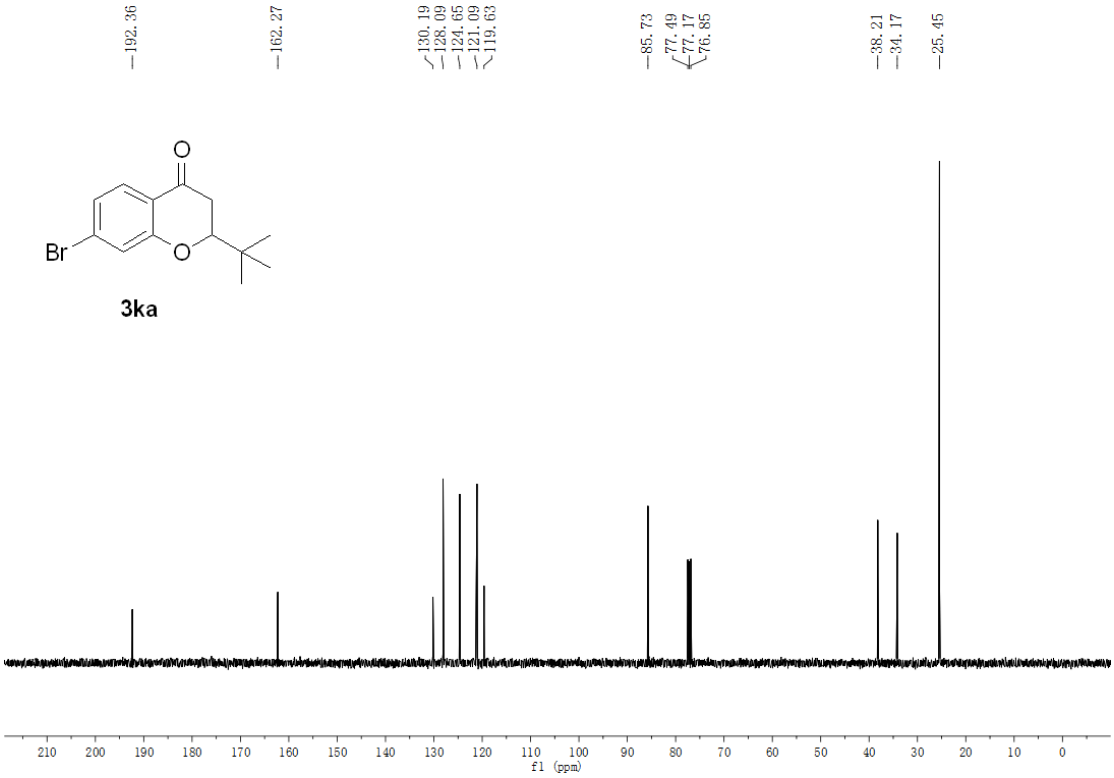
O
Cl
O

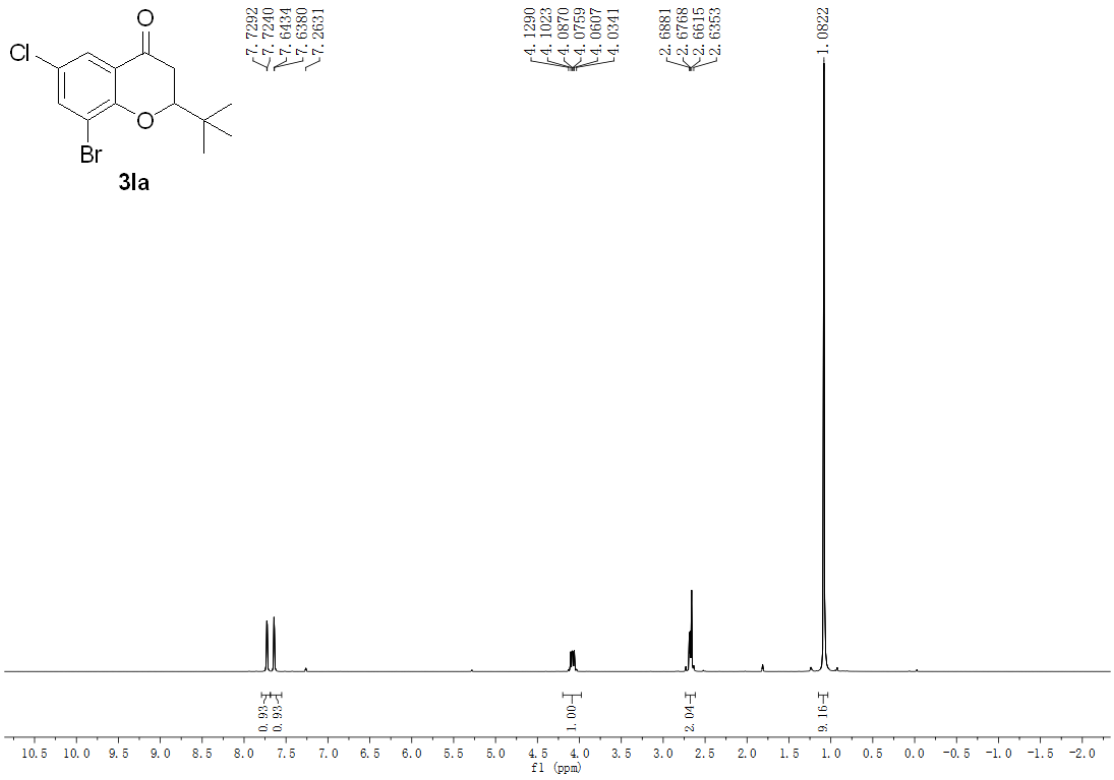
3ia

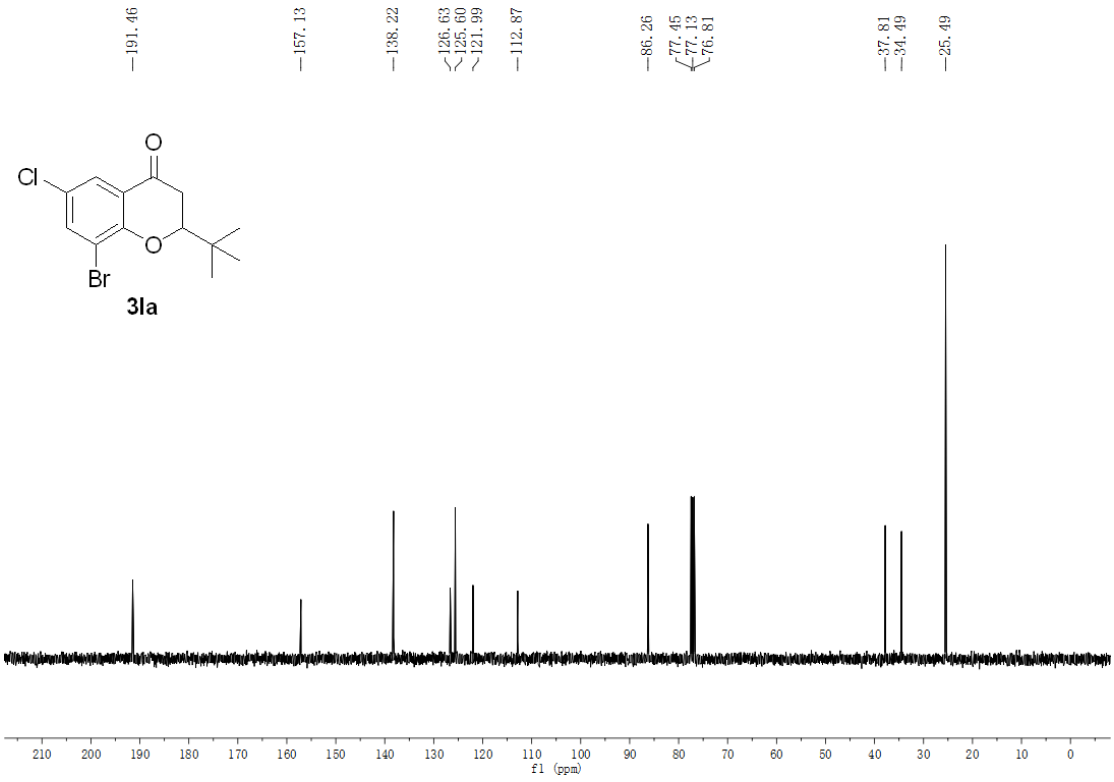

Br
O
O
3ja
7.8800
7.8780
7.8552
7.8493
7.4460
7.4400
6.8342
6.8314
6.8098
4.0119
3.9970
3.9816
3.9713
3.9561
3.9303
2.6453
2.6034
2.5956
2.5780
2.5520
1.0051
0.93
0.99
0.99
1.00
2.06
9.15
f1 (ppm)

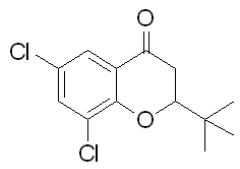

191.97
160.96
138.37
129.20
121.97
120.00
113.61
85.47
77.52
77.20
76.89
38.03
34.16
25.46
Br
O
O
3ja
f1 (ppm)


O
Br
O
3ka
7.6586
7.6376
7.2633
7.1533
7.1502
7.0744
7.0715
7.0534
7.0505
4.0629
4.0349
4.0208
4.0076
3.9934
3.9654
2.6691
2.6276
2.6137
2.5999
2.5723
1.0142
0.95
0.93
0.96
0.98
2.03
9.00
f1 (ppm)


192.36
162.27
130.19
128.09
124.65
121.09
119.63
85.73
77.49
77.17
76.85
38.21
34.17
25.45
O
Br
O
3ka
f1 (ppm)

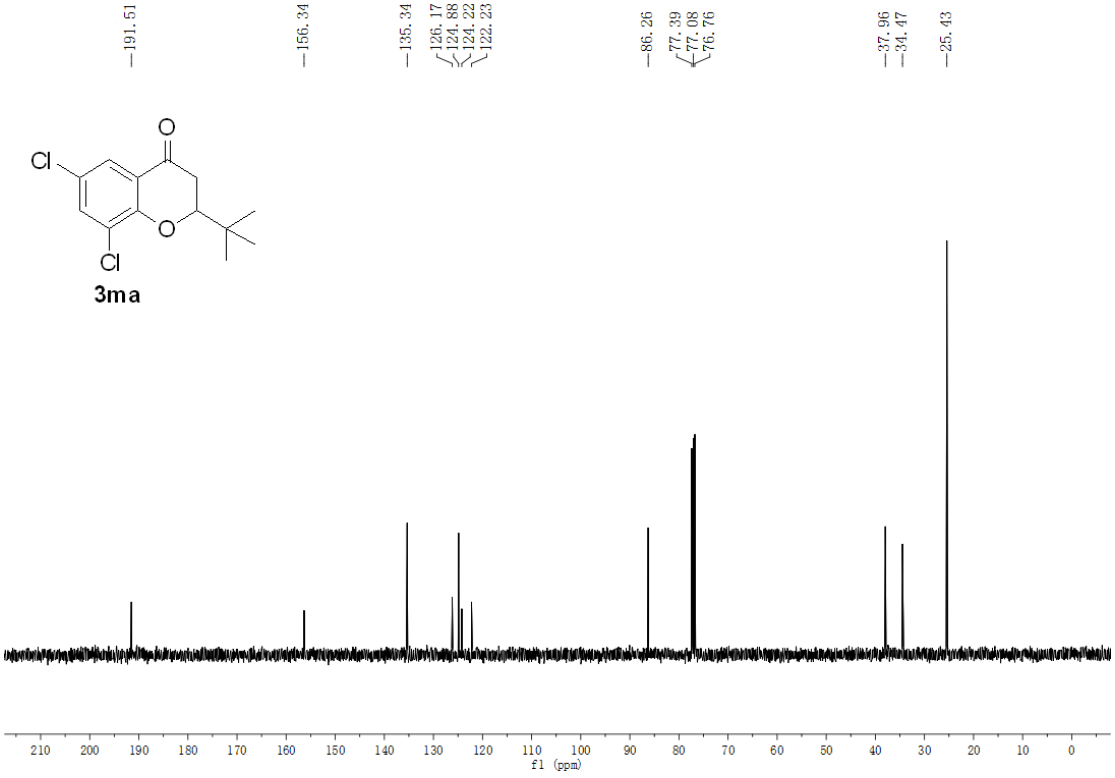

Cl
O
O
Br
3la
7.7292
7.7240
7.6434
7.6380
7.2631
4.1290
4.1023
4.0870
4.0759
4.0607
4.0341
2.6881
2.6768
2.6615
2.6353
1.0822
0.93
0.93
1.00
2.04
9.16
f1 (ppm)


191.46
157.13
138.22
126.63
125.60
121.99
112.87
86.26
77.45
77.13
76.81
37.81
34.49
25.49
Cl
O
O
Br
3la
f1 (ppm)


O
Cl
O
Cl

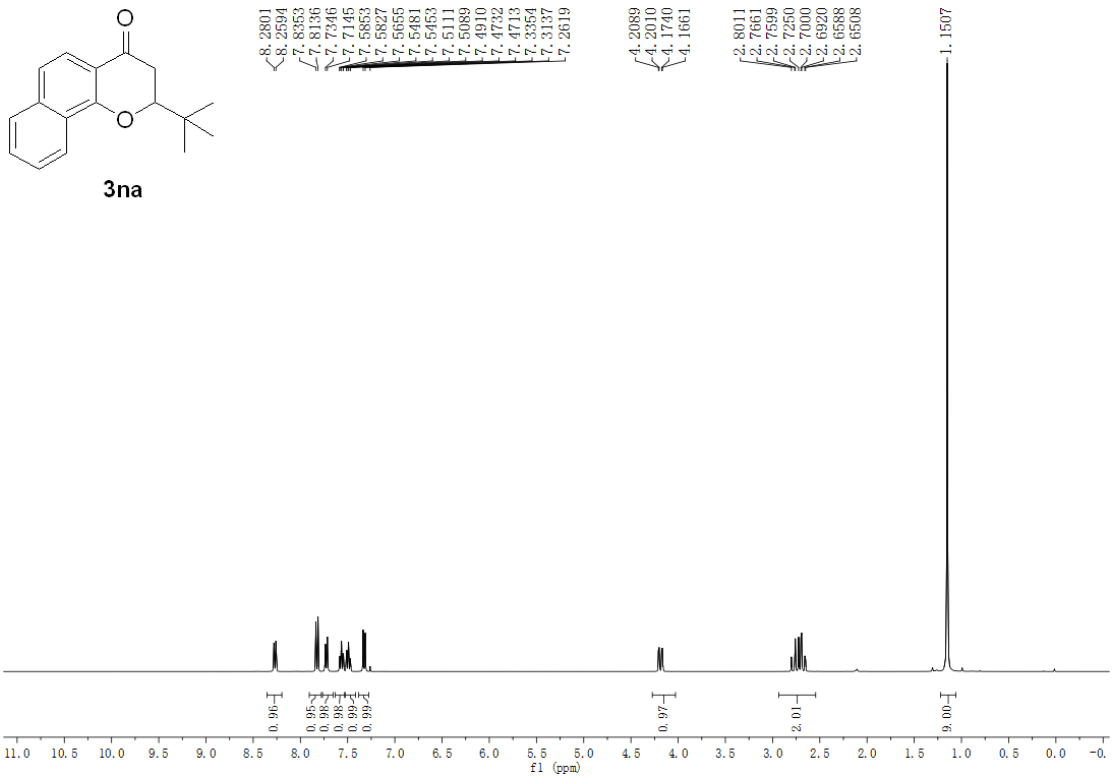
3ma

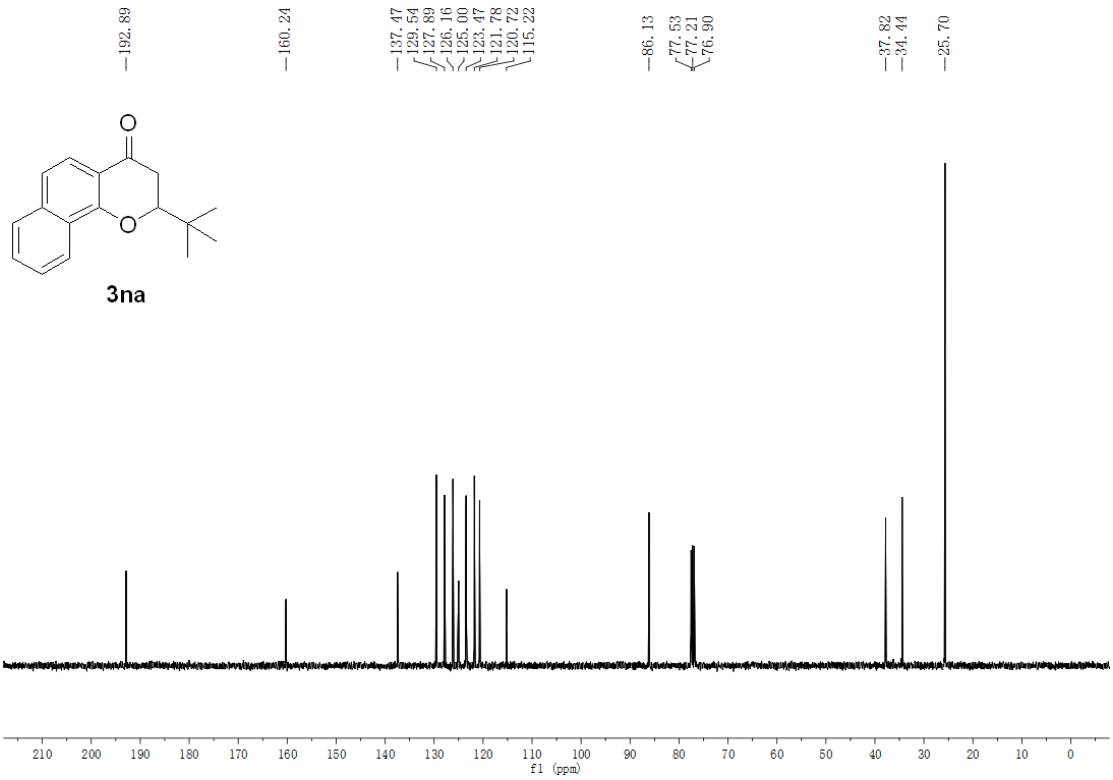
7.7196
7.7133
7.5112
7.5049
7.2630
4.1416
4.1163
4.0996
4.0913
4.0746
4.0494
2.7522
2.7104
2.7019
2.6853
2.6603
1.0896
0.93
0.95
1.00
2.05
9.26
f1 (ppm)

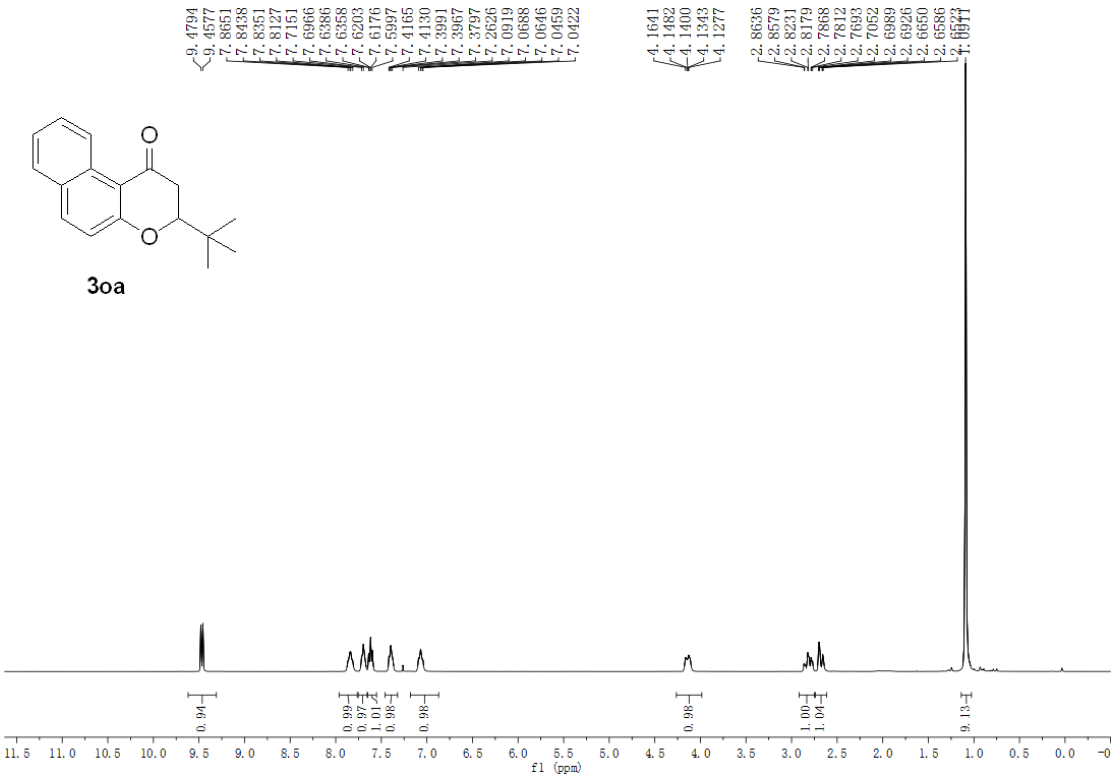

191.51
156.34
135.34
126.17
124.88
124.22
122.23
86.26
77.39
77.08
76.76
37.96
34.47
25.43
f1 (ppm)

O
Cl
O
Cl

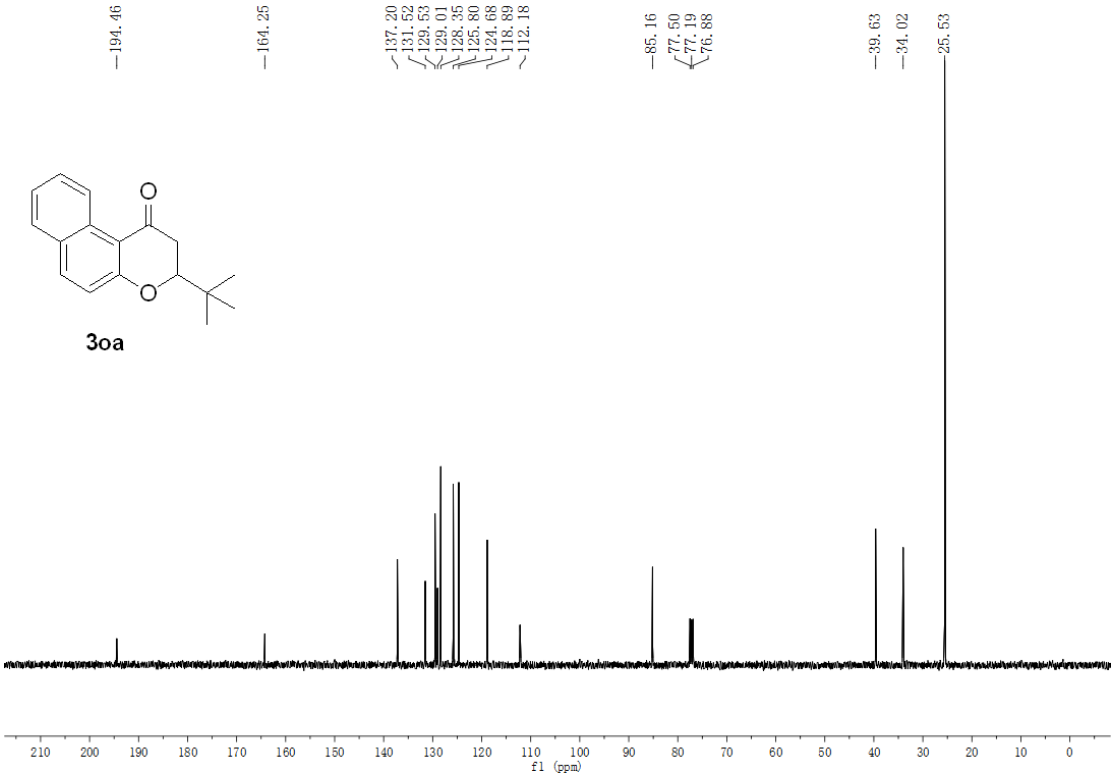
3ma


3na
8.2801
8.2594
7.8353
7.8136
7.7346
7.7145
7.5853
7.5827
7.5655
7.5481
7.5453
7.5111
7.5089
7.4910
7.4732
7.4713
7.3354
7.3137
7.2619
4.2089
4.2010
4.1740
4.1661
2.8011
2.7661
2.7599
2.7250
2.7000
2.6920
2.6588
2.6508
1.1507
0.96
0.95
0.98
0.98
0.99
0.99
0.97
2.01
9.00
f1 (ppm)

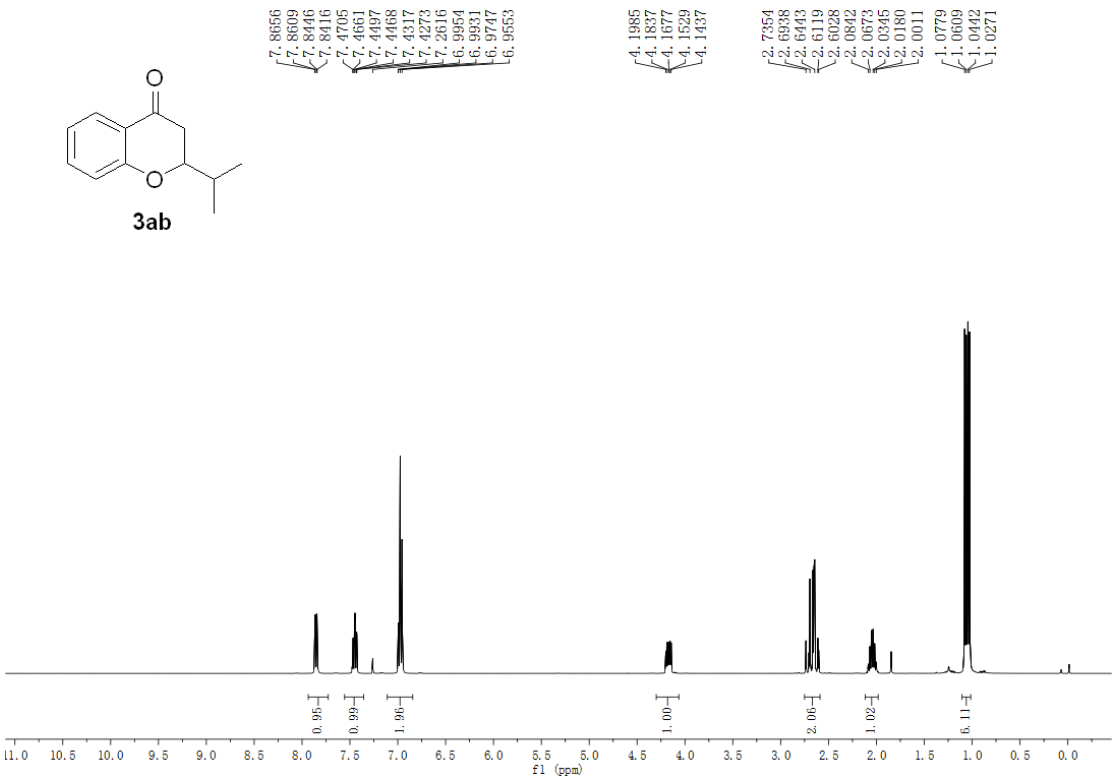

3na
192.89
160.24
137.47
129.54
127.89
126.16
125.00
123.47
121.78
120.72
115.22
86.13
77.53
77.21
76.90
37.82
34.44
25.70
f1 (ppm)

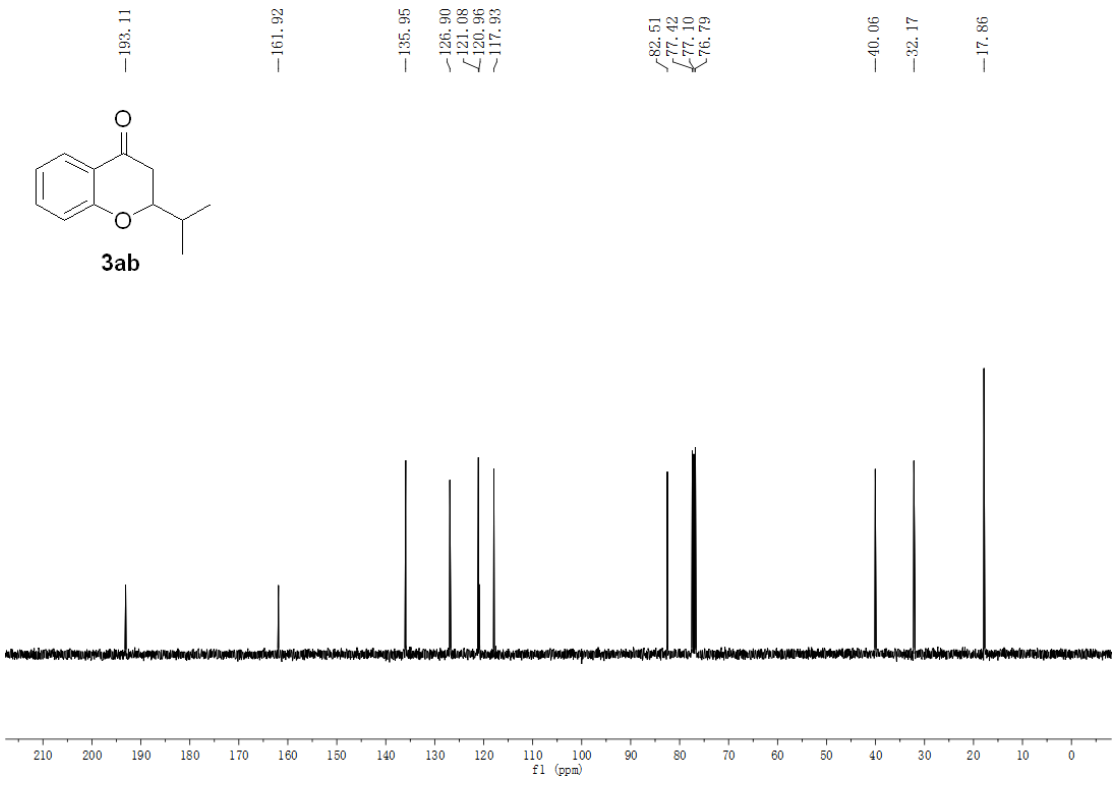

9.4794
9.4577
7.8651
7.8438
7.8351
7.8127
7.7151
7.6966
7.6386
7.6358
7.6203
7.6176
7.5997
7.4165
7.4130
7.3991
7.3967
7.3797
7.2626
7.0919
7.0688
7.0646
7.0459
7.0422
4.1641
4.1482
4.1400
4.1343
4.1277
2.8636
2.8579
2.8231
2.8179
2.7868
2.7812
2.7693
2.7052
2.6989
2.6926
2.6650
2.6586
1.0941
0.94
0.99
0.97
1.01
0.98
0.98
0.98
1.00
1.04
9.13
f1 (ppm)

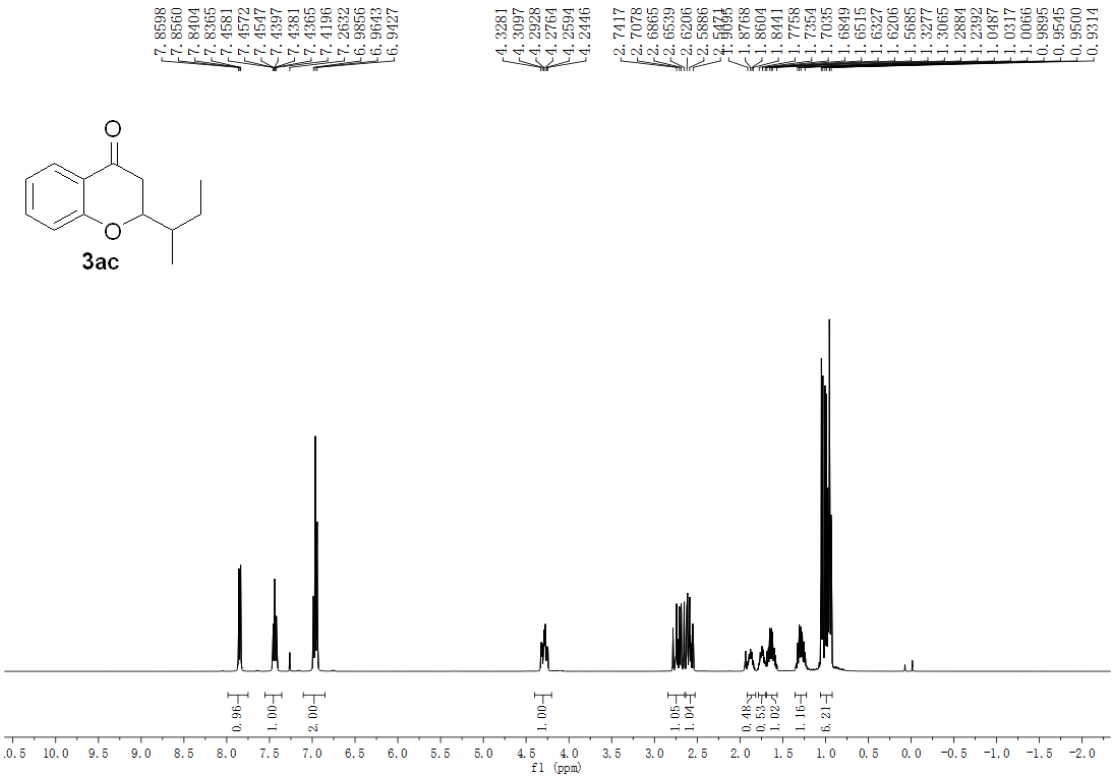
3oa

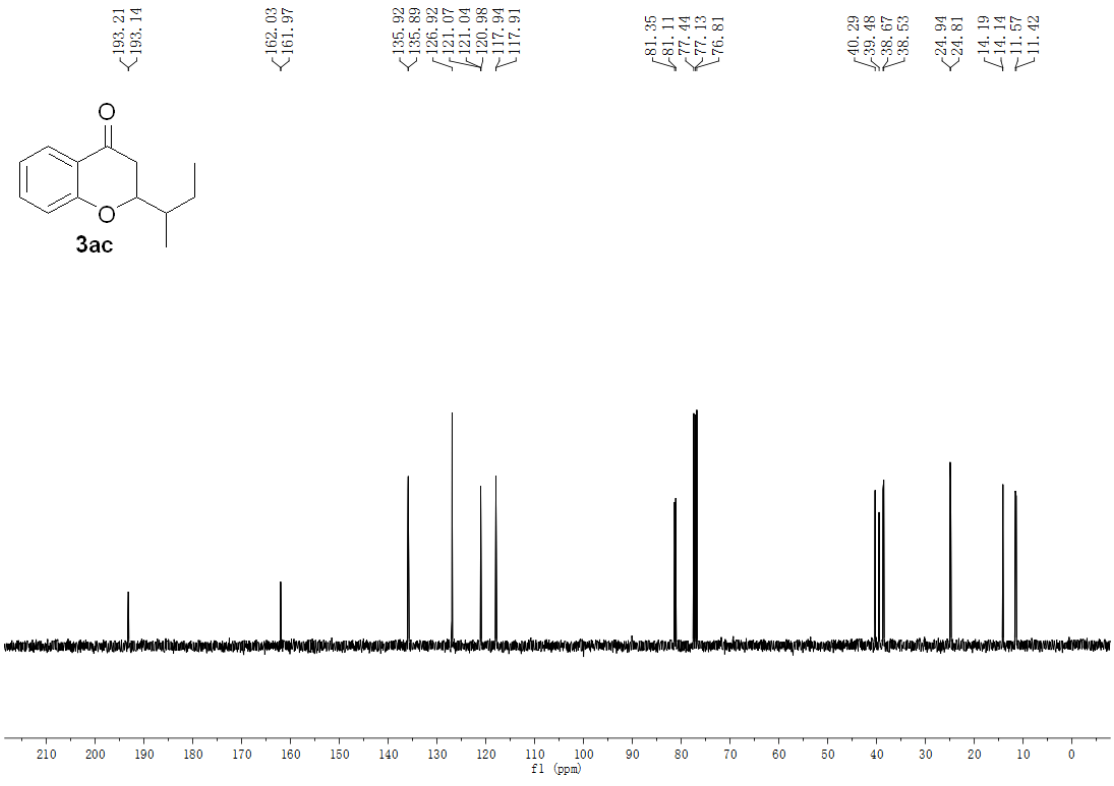

194.46
164.25
137.20
131.52
129.53
129.01
128.35
125.80
124.68
118.89
112.18
85.16
77.50
77.19
76.88
39.63
34.02
25.53
f1 (ppm)

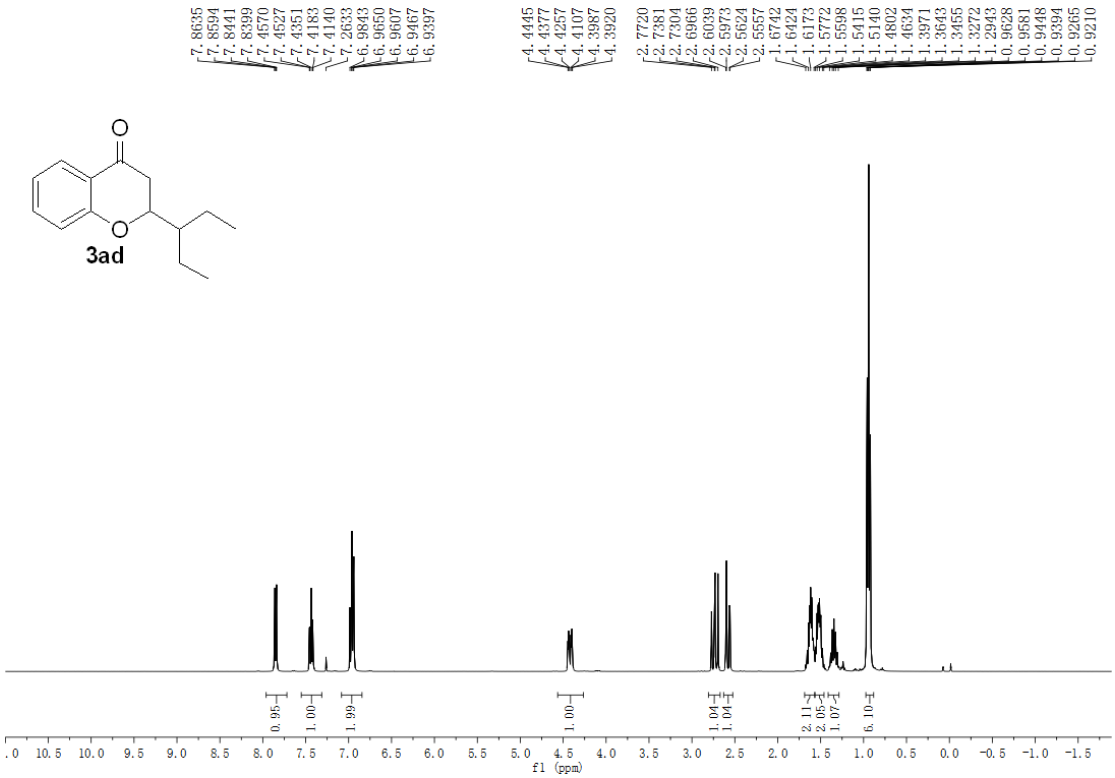
3oa

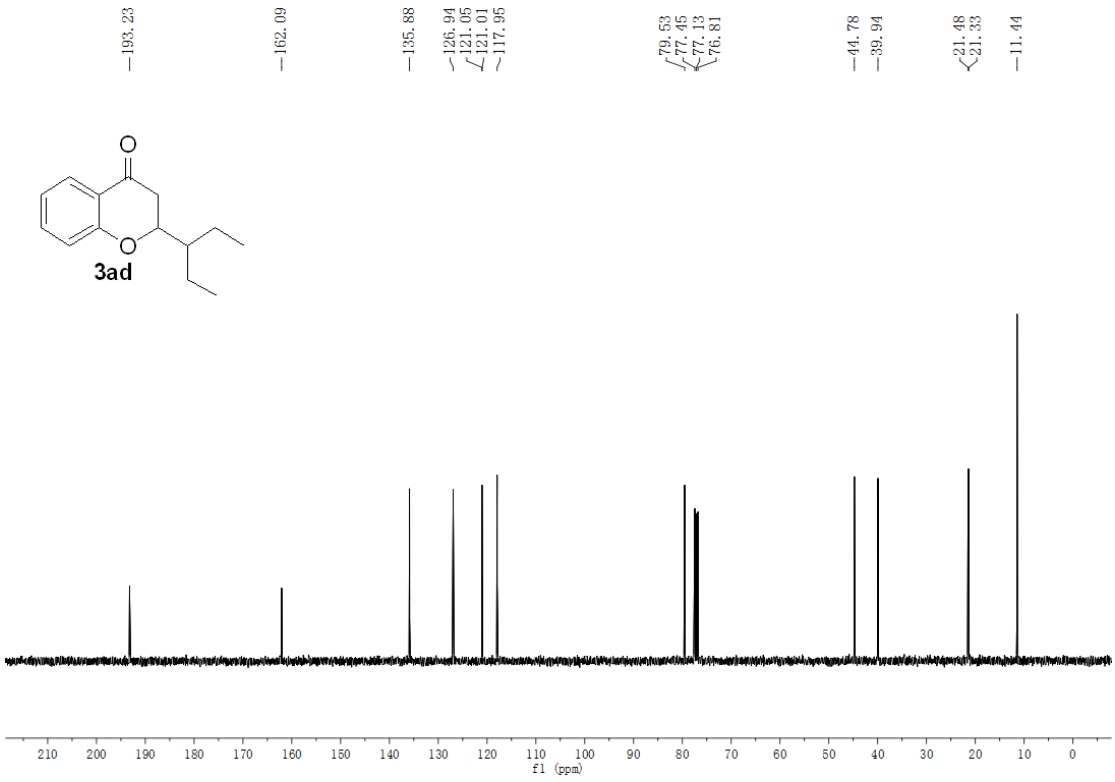

7.8656
7.8609
7.8446
7.8416
7.4705
7.4661
7.4497
7.4468
7.4317
7.4273
7.2616
6.9954
6.9931
6.9747
6.9553
4.1985
4.1837
4.1677
4.1529
4.1437
2.7354
2.6938
2.6443
2.6119
2.6028
2.0842
2.0673
2.0345
2.0180
2.0011
1.0779
1.0609
1.0442
1.0271
3ab
0.95
0.99
1.96
1.00
2.06
1.02
6.11
f1 (ppm)

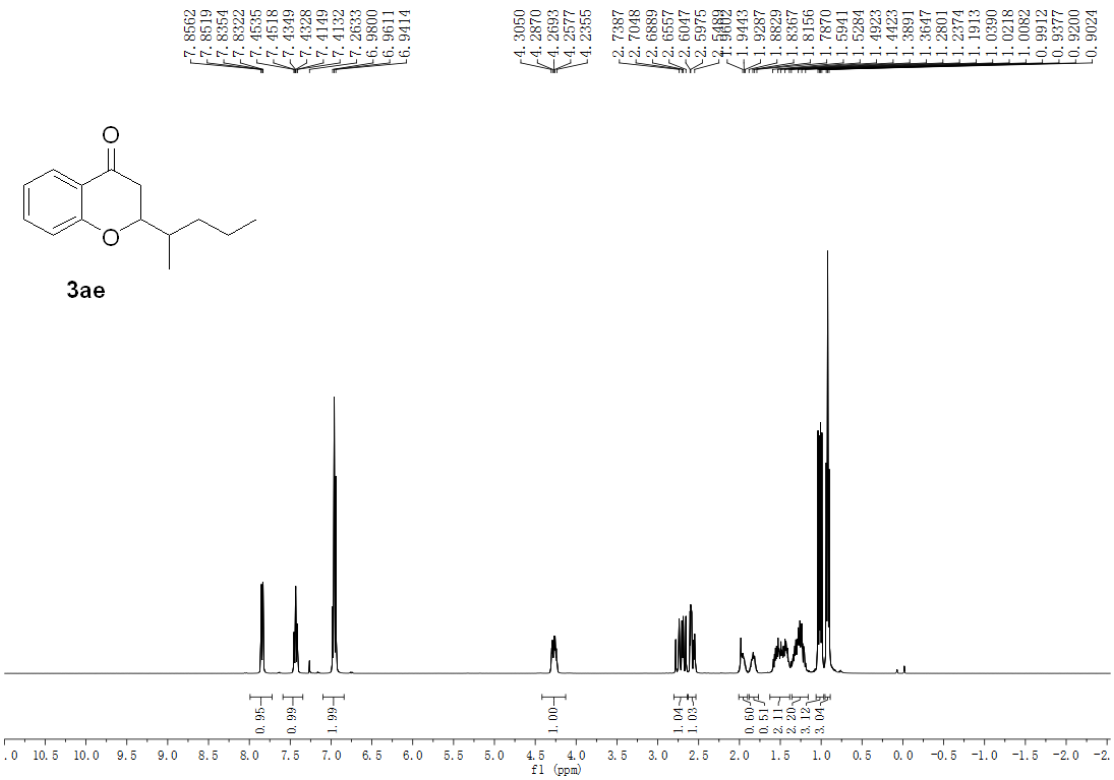

193.11
161.92
135.95
126.90
121.08
120.96
117.93
82.51
77.42
77.10
76.79
40.06
32.17
17.86
3ab
f1 (ppm)

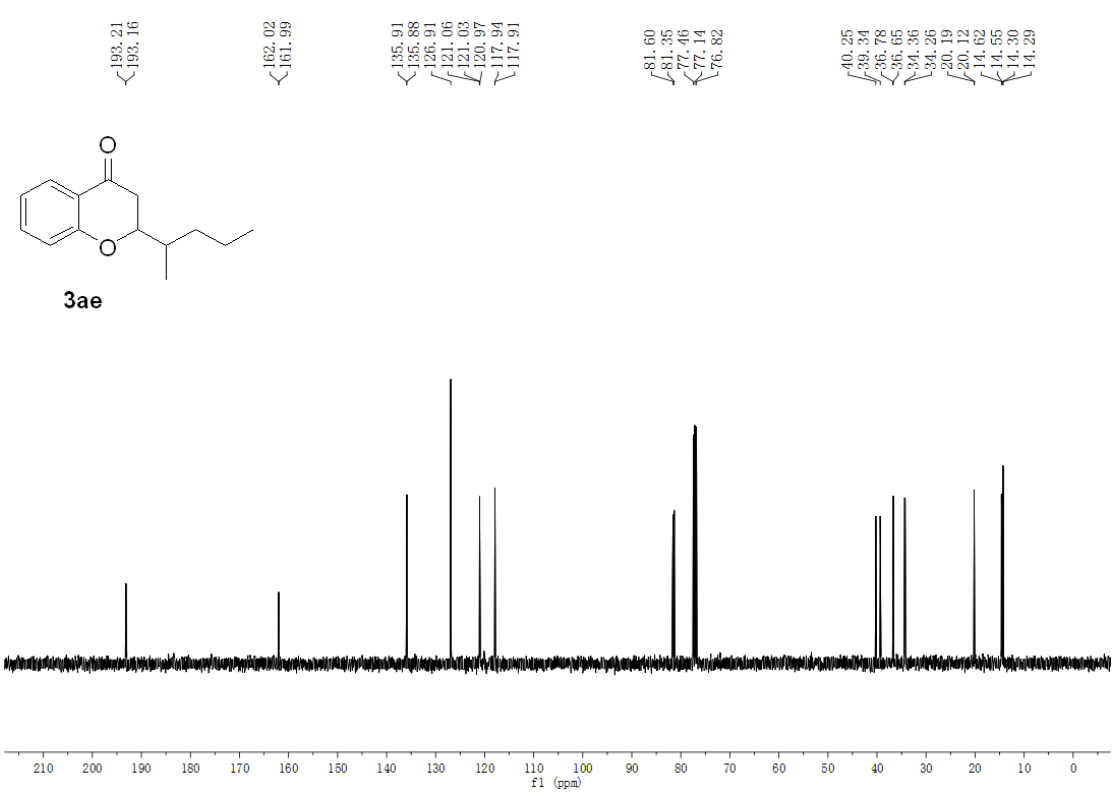

7.8598
7.8560
7.8404
7.8365
7.4581
7.4572
7.4547
7.4397
7.4381
7.4365
7.4196
7.2632
6.9856
6.9643
6.9427
4.3281
4.3097
4.2928
4.2764
4.2594
4.2446
2.7417
2.7078
2.6865
2.6539
2.6206
2.5886
1.8768
1.8604
1.8441
1.7758
1.7354
1.7035
1.6849
1.6515
1.6327
1.6206
1.5685
1.3277
1.3065
1.2884
1.2392
1.0487
1.0317
1.0066
0.9895
0.9545
0.9500
0.9314
O
O
3ac
0.96
1.00
2.00
1.00
1.05
1.04
0.48
0.53
1.02
1.16
6.21
f1 (ppm)

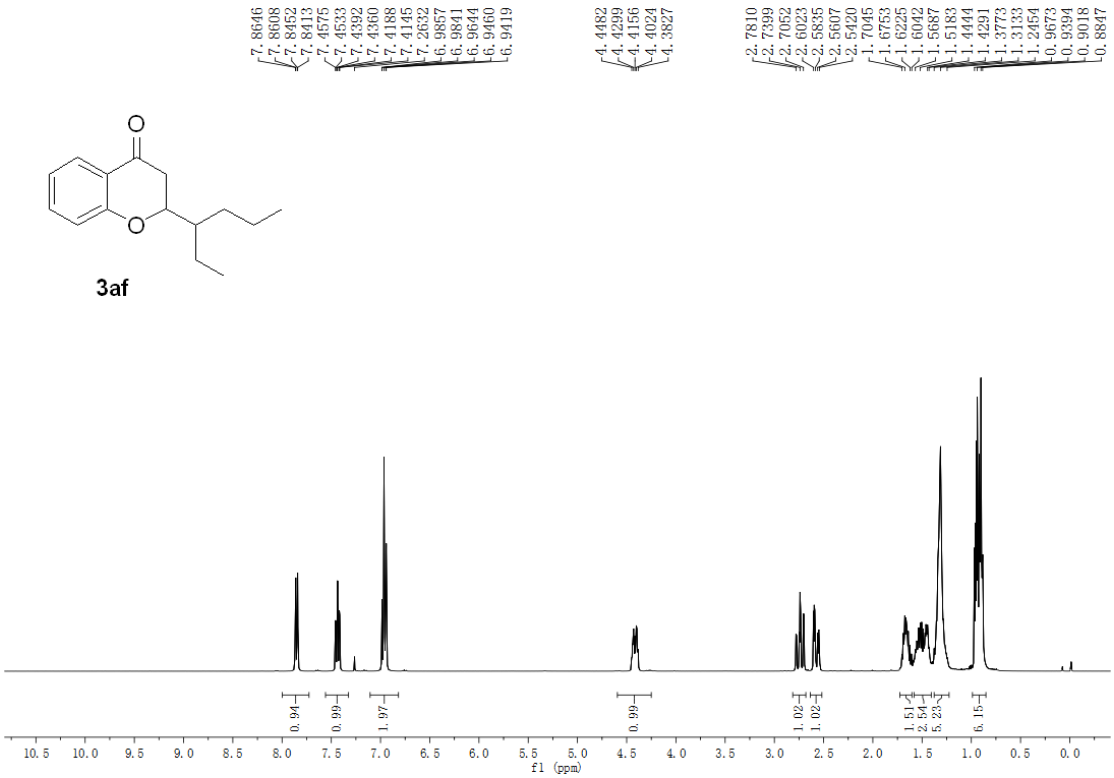

193.21
193.14
162.03
161.97
135.92
135.89
126.92
121.07
121.04
120.98
117.94
117.91
81.35
81.11
77.44
77.13
76.81
40.29
39.48
38.67
38.53
24.94
24.81
14.19
14.14
11.57
11.42
O
O
3ac
f1 (ppm)

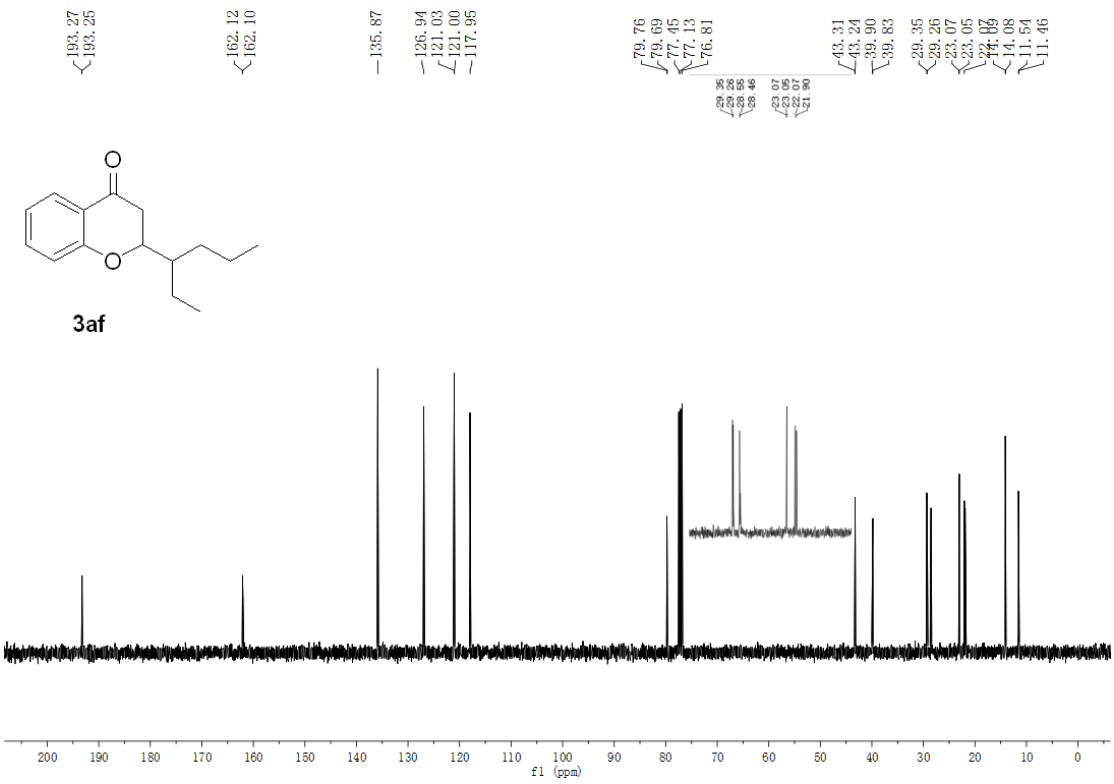

7.8635
7.8594
7.8441
7.8399
7.4570
7.4527
7.4351
7.4183
7.4140
7.2633
6.9843
6.9650
6.9607
6.9467
6.9397
4.4445
4.4377
4.4257
4.4107
4.3987
4.3920
2.7720
2.7381
2.7304
2.6966
2.6039
2.5973
2.5624
2.5557
1.6742
1.6424
1.6173
1.5772
1.5598
1.5415
1.5140
1.4802
1.4634
1.3971
1.3643
1.3455
1.3272
1.2943
1.0628
0.9581
0.9448
0.9394
0.9265
0.9210
O
O
3ad
0.95
1.00
1.99
1.00
1.04
1.04
2.11
2.05
1.07
6.10
f1 (ppm)

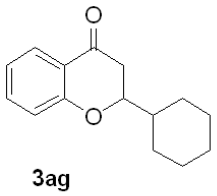

193.23
162.09
135.88
126.94
121.05
121.01
117.95
79.53
77.45
77.13
76.81
44.78
39.94
21.48
21.33
11.44
O
O
3ad
f1 (ppm)


7.8562
7.8519
7.8354
7.8322
7.4535
7.4518
7.4349
7.4328
7.4149
7.4132
7.2633
6.9800
6.9611
6.9414
4.3050
4.2870
4.2693
4.2577
4.2355
2.7387
2.7048
2.6889
2.6557
2.6047
2.5975
1.9443
1.9287
1.8829
1.8367
1.8156
1.7870
1.5941
1.5284
1.4923
1.4423
1.3891
1.3647
1.2801
1.2374
1.1913
1.0390
1.0218
1.0082
0.9912
0.9377
0.9200
0.9024
3ae
0.95
0.99
1.99
1.00
1.04
1.03
0.60
0.51
2.11
2.20
3.12
3.04
f1 (ppm)

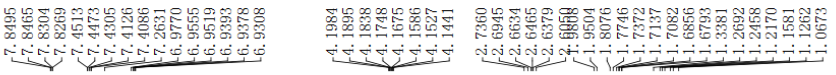

193.21
193.16
162.02
161.99
135.91
135.88
126.91
121.06
121.03
120.97
117.94
117.91
81.60
81.35
77.46
77.14
76.82
40.25
39.34
36.78
36.65
34.36
34.26
20.19
20.12
14.62
14.55
14.30
14.29
3ae
f1 (ppm)

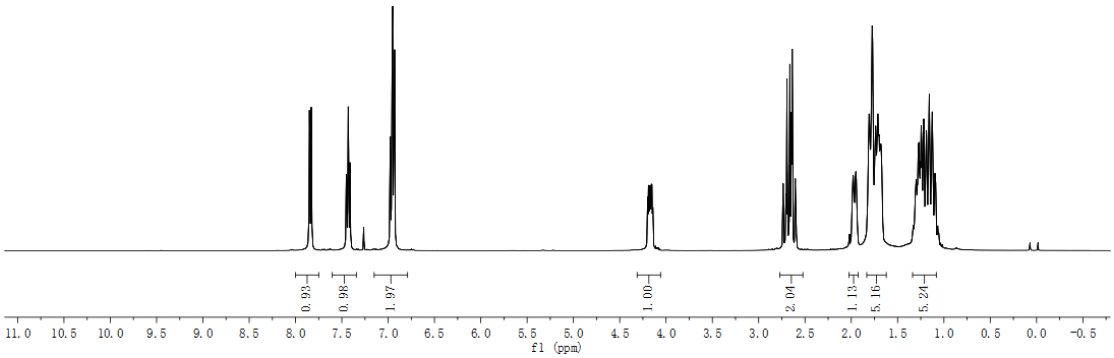

7.8646
7.8608
7.8452
7.8413
7.4575
7.4533
7.4392
7.4360
7.4188
7.4145
7.2632
6.9857
6.9841
6.9644
6.9460
6.9419
4.4482
4.4299
4.4156
4.4024
4.3827
2.7810
2.7399
2.7052
2.6023
2.5835
2.5607
2.5420
1.7045
1.6753
1.6225
1.6042
1.5687
1.5183
1.4444
1.4291
1.3773
1.3133
1.2454
0.9673
0.9394
0.9018
0.8847
3af
0.94
0.99
1.97
0.99
1.02
1.02
1.51
2.54
5.23
6.15
f1 (ppm)

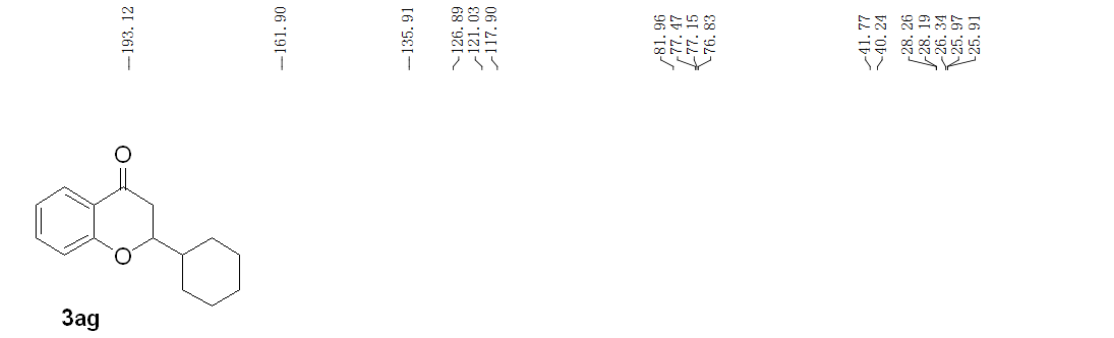

193.27
193.25
162.12
162.10
135.87
126.94
121.03
121.00
117.95
79.76
79.69
77.45
77.13
76.81
43.31
43.24
39.90
39.83
29.35
29.26
23.07
23.05
14.08
11.54
11.46
3af
f1 (ppm)



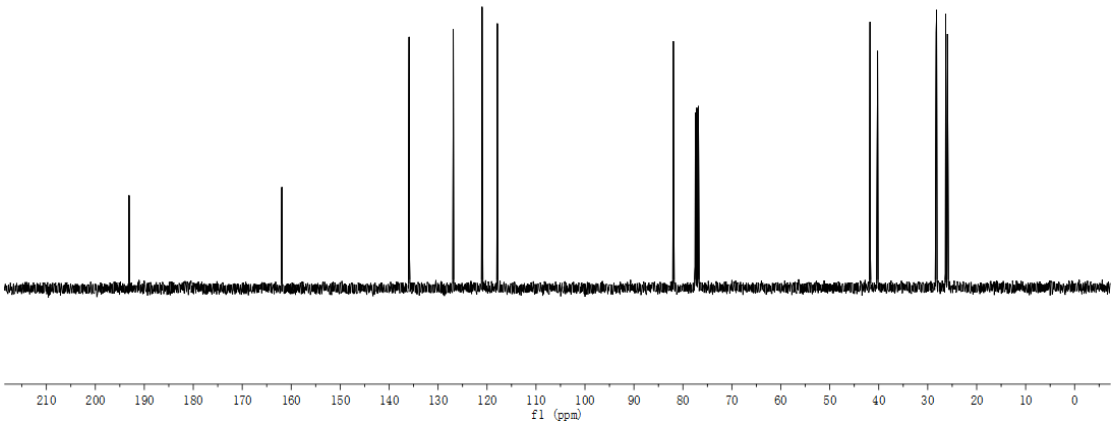
3ag

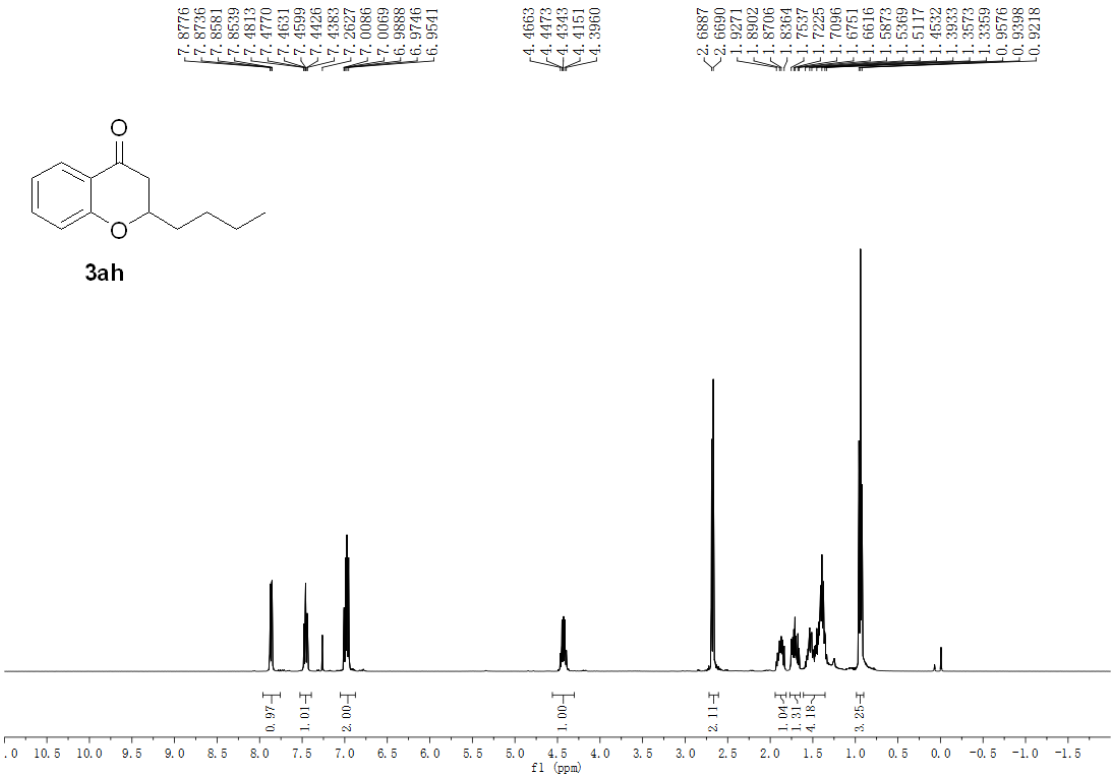

7.8495
7.8465
7.8304
7.8269
7.4513
7.4473
7.4305
7.4126
7.4086
7.2631
6.9770
6.9555
6.9519
6.9393
6.9378
6.9308
4.1984
4.1895
4.1838
4.1748
4.1675
4.1586
4.1527
4.1441
2.7360
2.6945
2.6634
2.6465
2.6379
1.9504
1.8076
1.7746
1.7372
1.7137
1.7082
1.6856
1.6793
1.3381
1.2692
1.2458
1.2170
1.1581
1.1262
1.0673

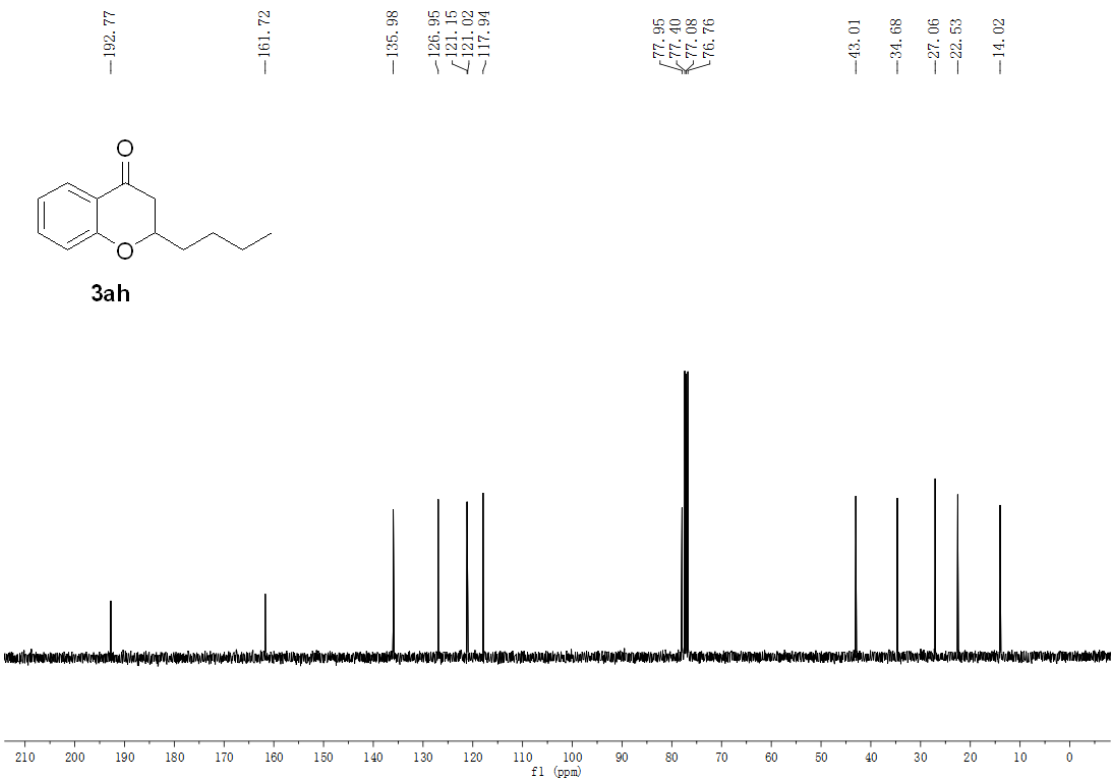

0.93
0.98
1.97
1.00
2.04
1.13
5.16
5.24
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

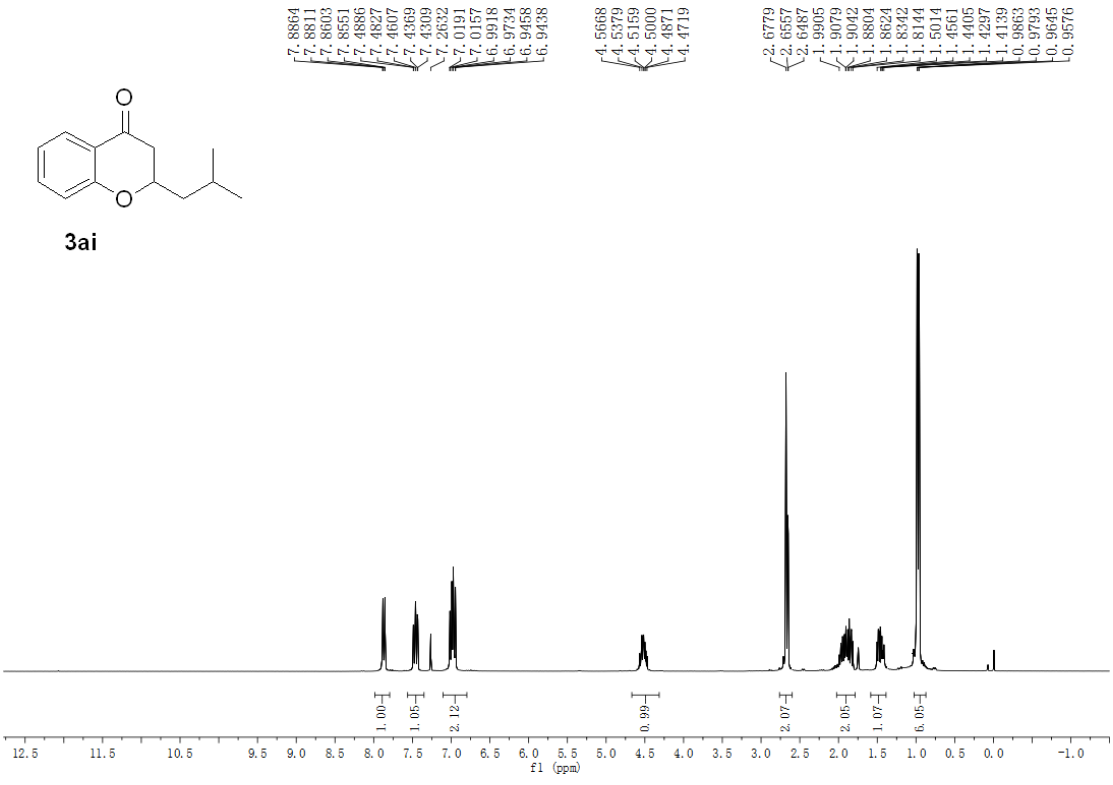

193.12
161.90
135.91
126.89
121.03
117.90
81.96
77.47
77.15
76.83
41.77
40.24
28.26
28.19
26.34
25.97
25.91

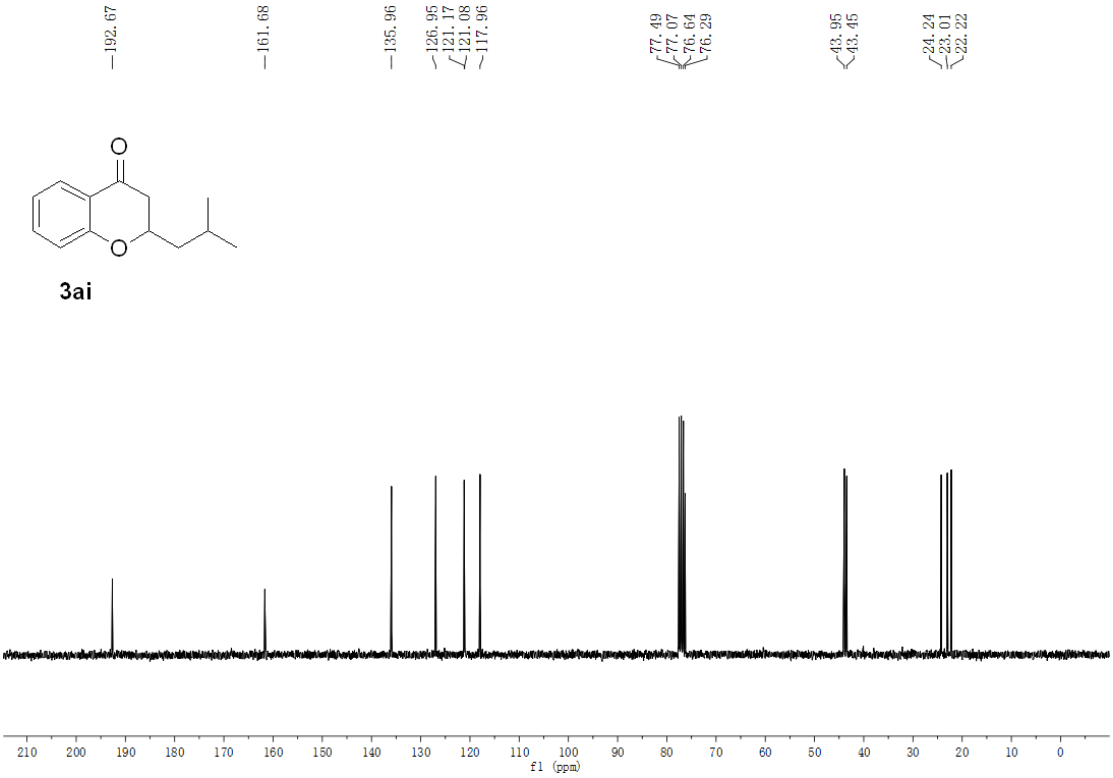
3ag

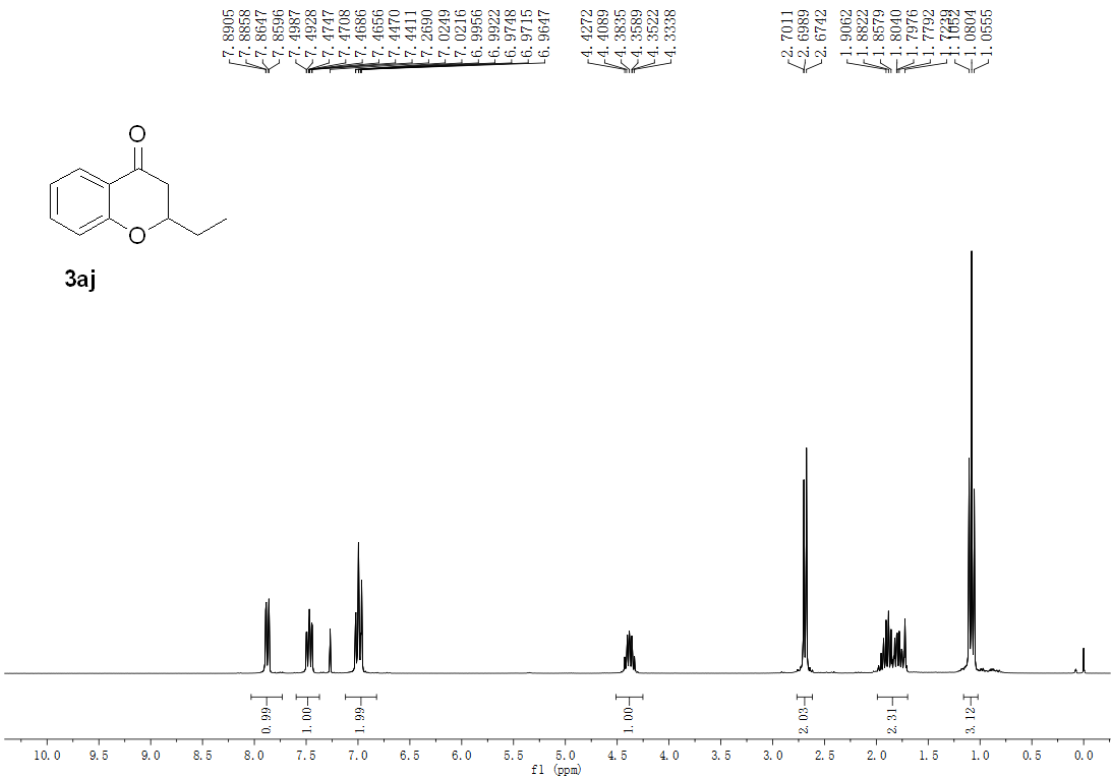

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

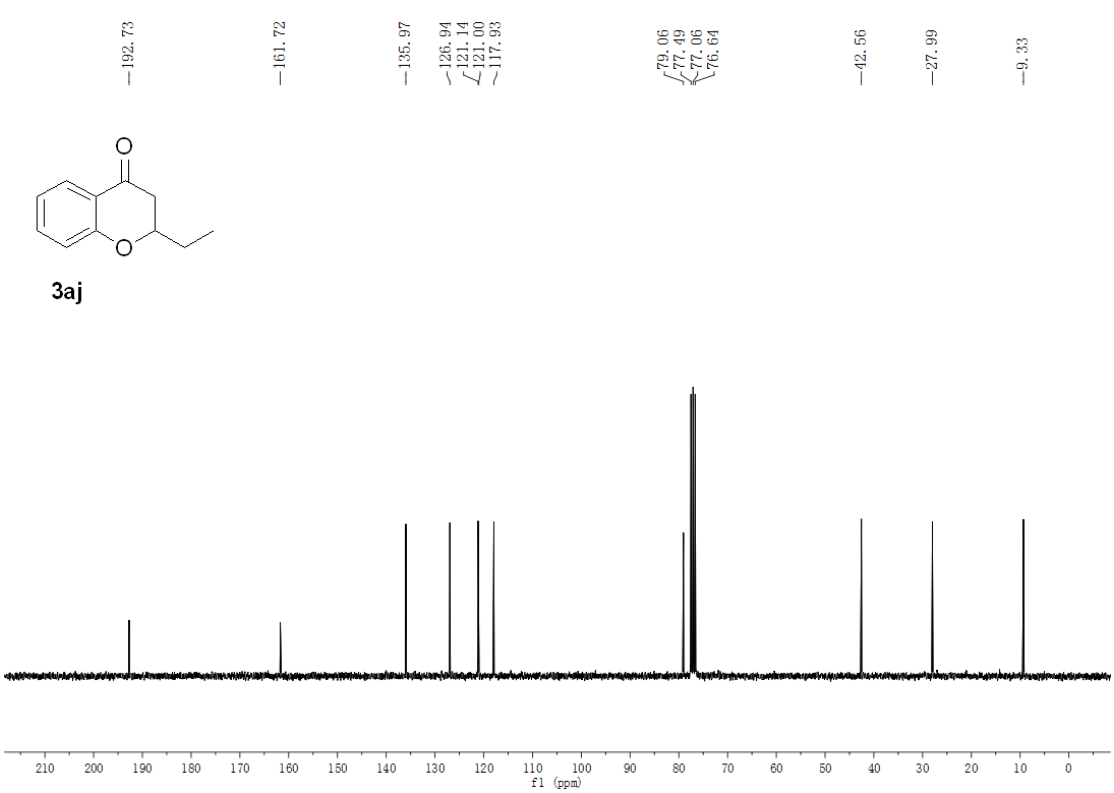

7.8776
7.8736
7.8581
7.8539
7.4813
7.4770
7.4631
7.4599
7.4426
7.4383
7.2627
7.0086
7.0069
6.9888
6.9746
6.9541
4.4663
4.4473
4.4343
4.4151
4.3960
2.6887
2.6690
1.9271
1.8902
1.8706
1.8364
1.7537
1.7225
1.7096
1.6751
1.6616
1.5873
1.5369
1.5117
1.4532
1.3933
1.3573
1.3359
0.9576
0.9398
0.9218
3ah
0.97
1.01
2.00
1.00
2.11
1.04
1.31
4.18
3.25
f1 (ppm)

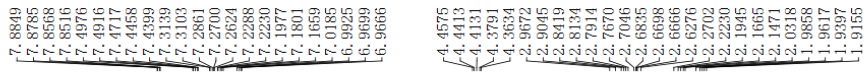

192.77
161.72
135.98
126.95
121.15
121.02
117.94
77.95
77.40
77.08
76.76
43.01
34.68
27.06
22.53
14.02
3ah
f1 (ppm)

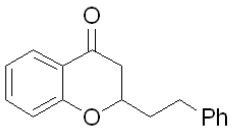

7.8864
7.8811
7.8603
7.8551
7.4886
7.4827
7.4607
7.4369
7.4309
7.2632
7.0191
7.0157
6.9918
6.9734
6.9458
6.9438
4.5668
4.5379
4.5159
4.5000
4.4871
4.4719
2.6779
2.6557
2.6487
1.9905
1.9079
1.9042
1.8804
1.8624
1.8342
1.8144
1.5014
1.4561
1.4405
1.4297
1.4139
0.9863
0.9793
0.9645
0.9576
O
O
3ai
1.00
1.05
2.12
0.99
2.07
2.05
1.07
6.05
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


192.67
161.68
135.96
126.95
121.17
121.08
117.96
77.49
77.07
76.64
76.29
43.95
43.45
24.24
23.01
22.22
O
O
3ai
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

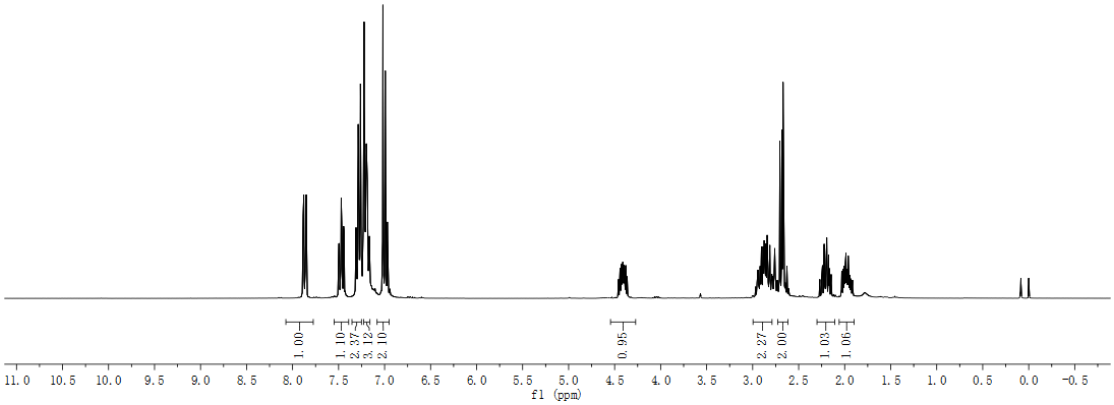

7.8905
7.8858
7.8647
7.8596
7.4987
7.4928
7.4747
7.4708
7.4686
7.4656
7.4470
7.4411
7.2690
7.0249
7.0216
6.9956
6.9922
6.9748
6.9715
6.9647
4.4272
4.4089
4.3835
4.3589
4.3522
4.3338
2.7011
2.6989
2.6742
1.9062
1.8822
1.8579
1.8040
1.7976
1.7792
1.1652
1.0804
1.0555
3aj
0.99
1.00
1.99
1.00
2.03
2.31
3.12
f1 (ppm)


192.73
161.72
135.97
126.94
121.14
121.00
117.93
79.06
77.49
77.06
76.64
42.56
27.99
9.33
3aj
f1 (ppm)

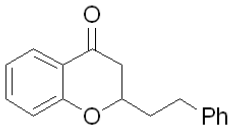

7.8849
7.8785
7.8568
7.8516
7.4976
7.4916
7.4717
7.4458
7.4399
7.3139
7.3103
7.2861
7.2700
7.2624
7.2288
7.2230
7.1977
7.1801
7.1659
7.0185
6.9925
6.9699
6.9666
4.4575
4.4413
4.4131
4.3791
4.3634
2.9672
2.9045
2.8419
2.8134
2.7914
2.7670
2.7046
2.6835
2.6698
2.6666
2.6276
2.2702
2.2230
2.1945
2.1665
2.1471
2.0318
1.9858
1.9617
1.9397
1.9155


O
O
Ph

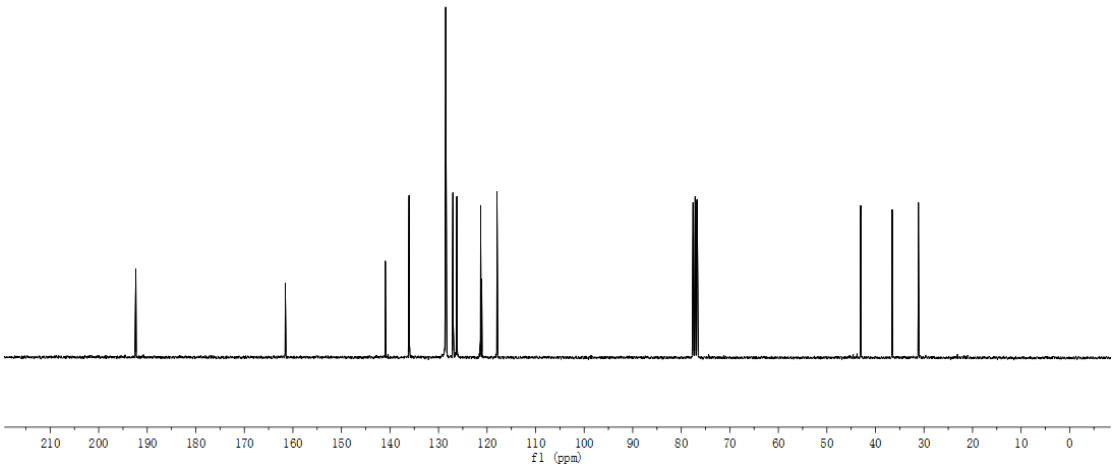
3ak


1.00
1.10
2.37
3.12
2.10
0.95
2.27
2.00
1.03
1.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


192.35
161.57
140.96
136.06
128.60
128.52
127.03
126.21
121.33
121.10
117.96
77.56
77.14
76.83
76.71
43.03
36.56
31.16


O
O
Ph

3ak


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)