Supporting Information

Metal-free radical addition/cyclization of alkynoates with xanthates towards 3-(β-carbonyl)coumarins

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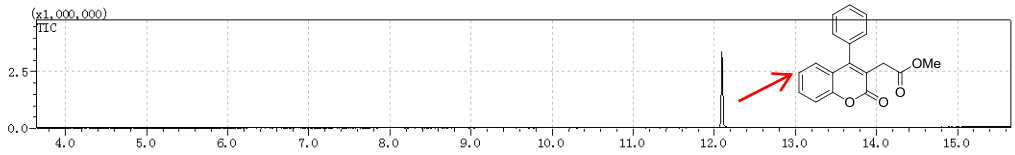
1. General experimental details

General Information: All chemicals were used as received without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature on a 300, 400 or 500 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 for the oxidative annulation of alkynoates with xanthates towards coumarins: Under N_2, the mixture of alkynoate **1** (0.2 mmol), xanthate **2** (0.6 mmol), DLP (0.6 mmol, 240 mg) and DCE (2 mL) were added into the tube and sealed. The reaction mixture was vigorously stirred at 85 ^{o}C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the products.

Mechanism Studies



GC (Residual time of **3aa**: 12.09 min)

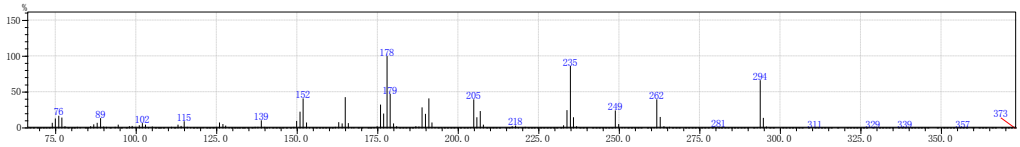
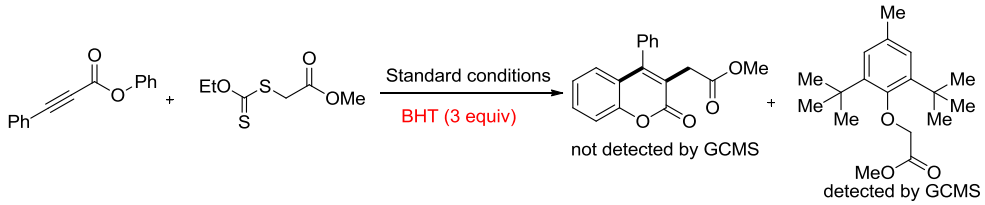
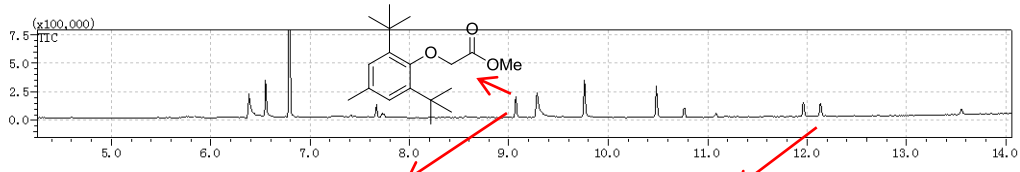


Figure S1 GC-MS spectra of the **3aa**

Standard Procedure + BHT (3.0 equiv)





MS (Residual time of adduct: 9.05 min); Residual time: 12.13 min, not not consistent with **3aa**

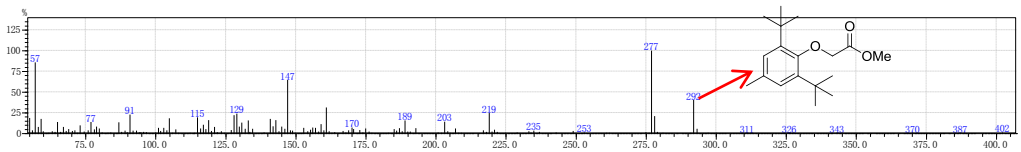
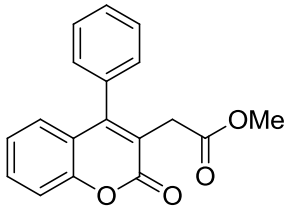


Figure S2 GC-MS spectra of the free radical capture results

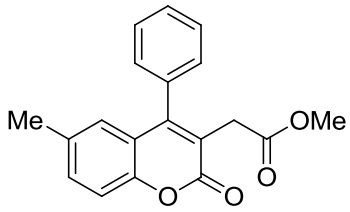
2. Experimental characterization data for compounds

Methyl 2-(2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3aa)



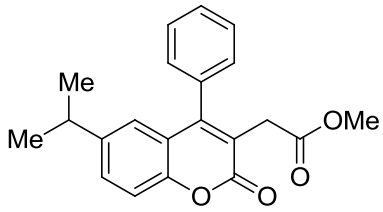
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (43.5 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.51 (m, 4H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.31-7.28 (m, 2H), 7.20-7.16 (m, 1H), 7.07-7.04 (m, 1H), 3.69 (m, 3H), 3.42 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.8, 161.6, 153.0, 152.9, 133.9, 131.4, 129.1, 129.0, 128.2, 127.6, 124.2, 120.4, 120.2, 116.8, 35.9, 31.1, 26.5, 25.7. HRMS (ESI) *m/z* calcd for $C_{18}H_{15}O_4$ $(M+H)^+$ 295.0965, found 295.0966.

Methyl 2-(7-methyl-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ba)



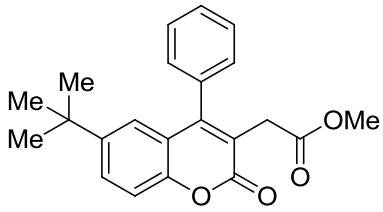
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (48.6 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.48 (m, 3H), 7.29-7.27 (m, 2H), 7.21 (s, 1H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 3.68 (s, 3H), 3.40 (s, 3H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 161.8, 153.1, 153.0, 142.6, 134.2, 129.0, 128.9, 128.2, 127.2, 125.4, 118.9, 118.0, 116.9, 52.2, 34.1, 22.6. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}O_4$ $(M+H)^+$ 309.1121, found 309.1119.

Methyl 2-(7-isopropyl-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ca)



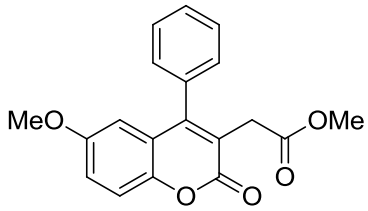
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (51.7 mg, 77%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48-7.39 (m, 3H), 7.21-7.17 (m, 3H), 6.98-6.94 (m, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 3.59 (s, 3H), 3.31 (s, 2H), 2.95-2.86 (m, 1H), 1.21 (s, 3H), 1.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.9, 161.8, 153.6, 153.1, 153.0, 134.2, 129.0, 128.9, 128.2, 127.4, 122.9, 119.0, 118.3, 114.3, 52.2, 34.14, 34.10, 22.6. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_4$ $(M+H)^+$ 337.1434, found 337.1436.

Methyl 2-(7-(*tert*-butyl)-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3da)



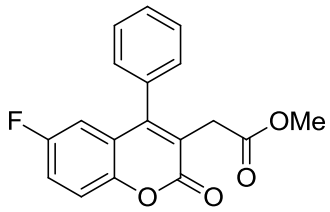
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (52.5 mg, 74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.54-7.48 (m, 3H), 7.41-7.40 (m, 1H), 7.29-7.25 (m, 2H), 7.22-7.18 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 3.67 (s, 3H), 3.39 (s, 2H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.9, 161.9, 155.9, 152.9, 152.8, 134.2, 129.0, 128.9, 128.2, 127.1, 121.7, 119.2, 117.9, 113.6, 52.2, 34.15, 34.10, 31.0. HRMS (ESI) *m/z* calcd for $C_{22}H_{23}O_4$ $(M+H)^+$ 351.1591, found 351.1594.

Methyl 2-(7-methoxy-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ea)



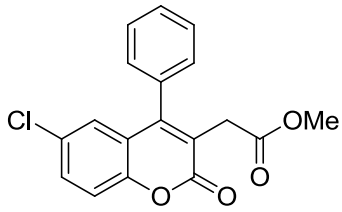
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 5:1) gives a yellow oil (48.6 mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.48 (m, 3H), 7.28-7.26 (m, 2H), 6.95-6.89 (m, 2H), 6.75-6.72 (m, 1H), 3.88 (s, 3H), 3.68 (s, 3H), 3.38 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.1, 162.4, 161.9, 154.6, 153.2, 134.3, 129.0, 128.9, 128.5, 128.1, 116.8, 114.0, 112.3, 110.6, 55.8, 52.1, 33.9. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}O_5$ $(M+H)^+$ 325.1071, found 325.1070.

Methyl 2-(7-fluoro-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3fa)



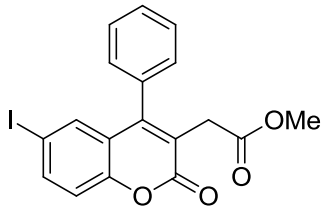
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (46.2 mg, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.77 (m, 1H), 7.56-7.48 (m, 4H), 7.28-7.25 (m, 2H), 6.74-6.88 (d, *J* = 8.3 Hz, 1H), 3.69 (s, 3H), 3.39 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.7, 164.1 (d, $J_{C\text{-}F}$ = 252.1 Hz), 161.2, 154.0 (d, *J* = 12.6 Hz), 152.6, 133.8, 129.33, 129.30, 129.2, 129.1, 128.1, 118.2 (d, $J_{C\text{-}F}$ = 235.3 Hz), 112.2 (d, $J_{C\text{-}F}$ = 22.4 Hz), 104.2 (d, $J_{C\text{-}F}$ = 25.4 Hz), 52.2, 34.0. HRMS (ESI) *m/z* calcd for $C_{18}H_{14}FO_4$ $(M+H)^+$ 313.0871, found 313.0872.

Methyl 2-(7-chloro-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ga)



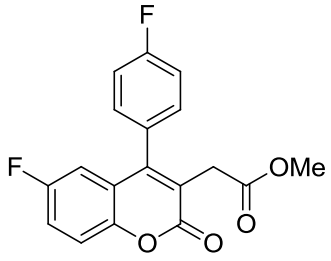
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (47.2 mg, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56-7.50 (m, 3H), 7.41-7.40 (m, 1H), 7.28-7.24 (m, 3H), 7.15-7.12 (m, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 3.68 (s, 3H), 3.39 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 160.9, 153.1, 152.4, 137.3, 133.6, 129.3, 129.1, 128.5, 128.1, 124.8, 120.2, 119.1, 117.0, 52.3, 34.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{14}ClO_4$ $(M+H)^+$ 329.0575, found 329.0577.

Methyl 2-(7-iodo-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ha)



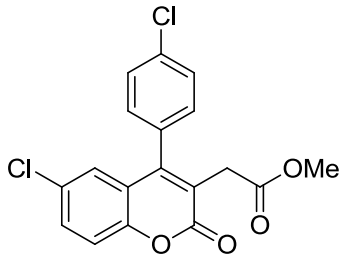
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (56.9 mg, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.50 (m, 3H), 7.41-7.40 (m, 1H), 7.28-7.24 (m, 3H), 7.15-7.12 (m, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 3.68 (s, 3H), 3.39 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5, 160.7, 152.7, 152.5, 133.5, 133.4, 129.3, 129.1, 128.6, 128.1, 125.8, 120.8, 120.0, 96.8, 52.3, 34.2. HRMS (ESI) *m/z* calcd for $C_{18}H_{14}IO_4$ $(M+H)^+$ 420.9931, found 420.9937.

Methyl 2-(6-fluoro-4-(4-fluorophenyl)-2-oxo-2*H*-chromen-3-yl)acetate (3ia)



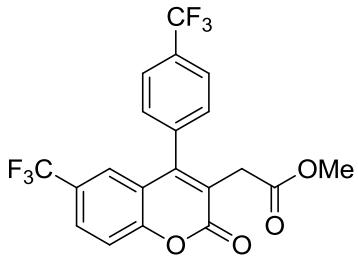
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (48.2 mg, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.22 (m, 3H), 7.14-7.11 (m, 1H), 7.04-7.00 (m, 1H), 6.95-6.90 (m, 1H), 3.69 (s, 3H), 3.39 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.6, 164.6 (d, $J_{C\text{-}F}$= 141.2 Hz), 162.6 (d, $J_{C\text{-}F}$= 136.2 Hz), 161.0, 153.9 (d, $J_{C\text{-}F}$= 12.5 Hz), 151.7, 130.1 (d, $J_{C\text{-}F}$= 8.7 Hz), 129.6 (d, $J_{C\text{-}F}$= 2.5 Hz), 129.0 (d, $J_{C\text{-}F}$= 10.0 Hz), 119.1, 117.1, 116.4 (d, $J_{C\text{-}F}$= 22.5 Hz), 112.4 (d, $J_{C\text{-}F}$= 22.5 Hz), 104.4 (d, $J_{C\text{-}F}$= 26.2 Hz), 52.3, 34.0. HRMS (ESI) *m/z* calcd for $C_{18}H_{13}F_2O_4$ $(M+H)^+$ 331.0776, found 331.0777.

Methyl 2-(6-chloro-4-(4-chlorophenyl)-2-oxo-2*H*-chromen-3-yl)acetate (3ja)



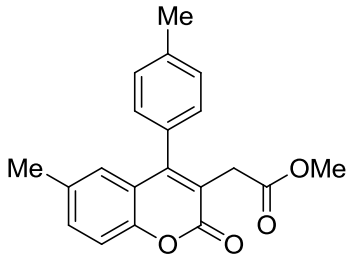
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (50.7 mg, 70%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55-7.52 (m, 2H), 7.42-7.41 (m, 1H), 7.25-7.21 (m, 2H), 7.18-7.14 (m, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 3.69 (s, 3H), 3.39 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.4, 160.6, 153.1, 151.2, 137.6, 135.7, 131.9, 129.6, 129.5, 128.2, 124.9, 120.5, 118.8, 117.1, 52.3, 34.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{13}Cl_2O_4$ $(M+H)^+$ 363.0185, found 363.0188.

Methyl 2-(2-oxo-6-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-2*H*-chromen-3-yl)acetate (3ka):



Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (53.3 mg, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.69 (s, 2H), 7.48-7.42 (m, 3H), 7.10 (d, *J* = 8.3 Hz, 1H), 3.71 (s, 3H), 3.42 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.0, 160.2, 152.5, 150.4, 136.9, 133.6, 132.0, 131.8, 128.8, 127.9, 126.3 (q, $J_{C\text{-}F}$ = 7.5 Hz), 123.3 (q, $J_{C\text{-}F}$ = 271.2 Hz), 123.0, 122.5, 120.9 (q, $J_{C\text{-}F}$ = 7.5 Hz), 114.4 (q, $J_{C\text{-}F}$ = 7.5 Hz), 52.5, 34.2. HRMS (ESI) *m/z* calcd for $C_{20}H_{13}F_6O_4$ $(M+H)^+$ 431.0713, found 431.0708.

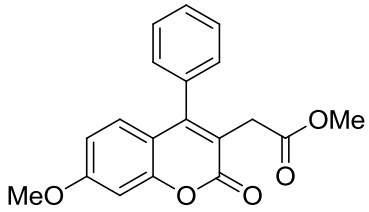
Methyl 2-(6-methyl-2-oxo-4-(*p*-tolyl)-2*H*-chromen-3-yl)acetate (3la)

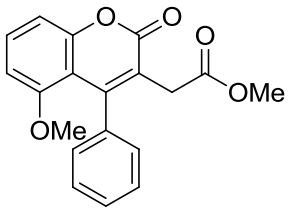


Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (49.6 mg, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, *J* = 7.8 Hz, 2H), 7.20-7.15 (m, 3H), 6.99-6.94 (m, 2H), 3.68 (s, 3H), 3.41 (s, 2H), 2.45 (s, 3H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 171.0, 161.8, 153.3, 152.9, 142.5, 138.9, 131.2,

129.6, 128.1, 127.3, 125.3, 118.9, 118.2, 116.9, 52.1, 34.1, 21.5, 21.3. HRMS (ESI) *m/z* calcd for $C_{20}H_{18}O_4$ $(M+H)^+$ 322.1205, found 322.1206.

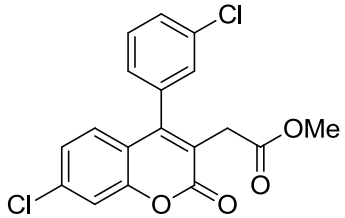
Methyl 2-(7-methoxy-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ma) and methyl 2-(5-methoxy-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ma')

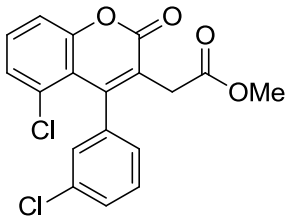




Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 5:1) gives a yellow oil (46.0 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.49 (m, 1H), 7.35-7.33 (m, 0.69H), 7.30-7.26 (m, 2.22H), 7.11-7.10 (m, 0.69H), 7.09-7.08 (m, 0.7H), 3.99 (s, 0.98H), 3.68-3.67 (t, 5.3H), 3.42-4.41 (d, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.8, 170.7, 161.8, 160.9, 155.8, 153.1, 152.7, 147.35, 147.30, 134.3, 134.0, 129.2, 129.0, 128.9, 128.2, 128.1, 123.8, 121.1, 120.9, 120.6, 120.4, 119.0, 118.3, 117.7, 113.3, 110.7, 56.4, 55.7, 52.2, 34.3. MS (EI): 324 (M^+).

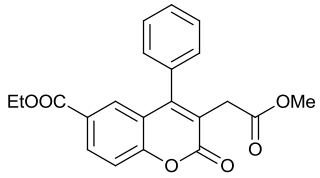
Methyl 2-(7-chloro-4-(3-chlorophenyl)-2-oxo-2*H*-chromen-3-yl)acetate (3na) and methyl 2-(5-methoxy-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3na')





Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (48.5 mg, 67%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.59 (m, 0.27H), 7.55-7.48 (m, 2.65H), 7.37-7.35 (m, 0.67H), 7.29 (s, 1H), 7.20-7.18 (m, 1H), 7.16-7.11 (m, 0.37H), 6.97-6.96 (m, 0.65H), 6.93-6.91 (m, 0.27H), 3.70 (s, 3H), 3.42 (s, 0.58H), 3.40 (s, 1.4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.3, 160.6, 151.3, 150.4, 135.4, 134.9, 132.0, 131.7, 130.7, 130.6, 129.9, 129.8, 129.6, 128.2, 128.1, 126.5, 126.4, 126.3, 124.4, 121.8, 121.1, 118.4, 52.4, 34.2. MS (EI): 362 (M^+).

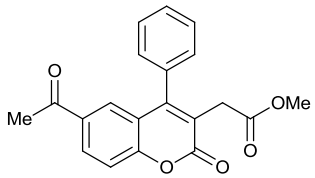
Ethyl 3-(2-methoxy-2-oxoethyl)-2-oxo-4-phenyl-2*H*-chromene-6-carboxylate (3oa)



Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1) gives a yellow oil (38.8 mg, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, J = 1.48 Hz, 1H), 7.80 (dd, J_1 = 8.3 Hz, J_2 = 1.60 Hz, 1H), 7.58-7.52 (m, 3H), 7.29-7.26 (m, 2H), 7.10 (d, J = 8.3 Hz, 1H), 4.44-4.38

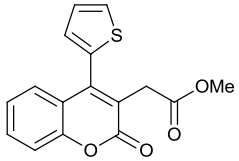
(q, 2H), 3.69 (s, 3H), 3.43 (s, 2H), 1.43-1.39 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.5, 165.2, 161.1, 152.5, 152.2, 133.5, 133.0, 129.4, 129.2, 128.2, 127.6, 124.8, 123.7, 122.3, 117.9, 61.7, 52.3, 34.3, 14.2. MS (EI): 366 (M^+).

Methyl 2-(6-acetyl-2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3pa)



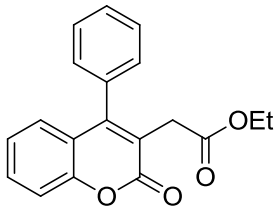
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 3:1) gives a yellow oil (32.9 mg, 49%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, J = 1.56 Hz, 1H), 7.72 (dd, J_1 = 8.3 Hz, J_2 = 1.68 Hz, 1H), 7.58-7.52 (m, 3H), 7.29-7.26 (m, 2H), 7.14 (d, J = 8.3 Hz, 1H), 3.69 (s, 3H), 3.44 (s, 2H), 2.64 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.6, 170.5, 161.0, 152.7, 152.1, 138.9, 133.4, 129.5, 129.2, 128.1, 127.9, 123.9, 123.4, 122.5, 116.8, 52.4, 34.3, 26.8. MS (EI): 336 (M^+).

Methyl 2-(2-oxo-4-(thiophen-2-yl)-2H-chromen-3-yl)acetate (3qa)



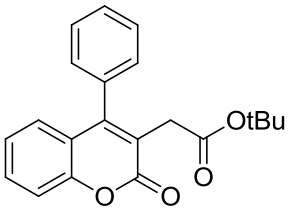
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 5:1) gives a yellow oil (25.2 mg, 42%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58-7.56 (m, 1H), 7.55-7.50 (m, 1H), 7.40-7.37 (m, 1H), 7.31-7.28 (m, 1H), 7.24-7.19 (m, 2H), 7.13-7.11 (m, 1H), 3.70 (s, 3H), 3.55 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 170.6, 161.1, 152.6, 146.6, 133.2, 131.7, 129.0, 128.0, 127.7, 127.4, 124.4, 122.7, 120.7, 116.8, 52.3, 34.5. MS (EI): 300 (M^+).

Ethyl 2-(2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ab)



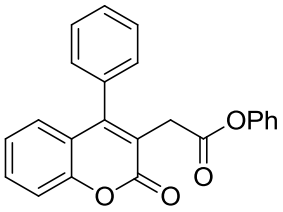
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (44.3 mg, 72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57-7.48 (m, 4H), 7.40-7.37 (m, 1H), 7.31-7.26 (m, 2H), 7.19-7.13 (m, 1H), 7.06-7.02 (m, 1H), 4.17-4.10 (q, 2H) 3.39 (s, 2H), 1.25-1.20 (t, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.3, 161.5, 152.94, 152.91, 134.0, 131.3, 129.1, 128.9, 128.2, 127.5, 124.2, 120.4, 120.3, 116.8, 61.1, 34.4, 14.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}O_4$ $(M+H)^+$ 309.1121, found 309.1120.

***tert*-Butyl 2-(2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ac)**



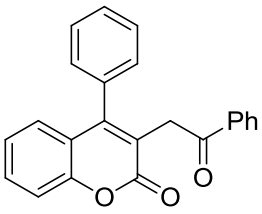
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (50.4 mg, 75%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56-7.46 (m, 4H), 7.40-7.37 (m, 1H), 7.30-7.26 (m, 2H), 7.18-7.12 (m, 1H), 7.04-7.01 (m, 1H), 3.32 (s, 2H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.5, 161.6, 152.9, 152.5, 134.2, 131.2, 128.9, 128.8, 128.2, 127.4, 124.1, 120.8, 120.5, 116.7, 81.2, 35.5, 27.9. HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_4$ $(M+H)^+$ 337.1434, found 337.1436.

Phenyl 2-(2-oxo-4-phenyl-2*H*-chromen-3-yl)acetate (3ad)



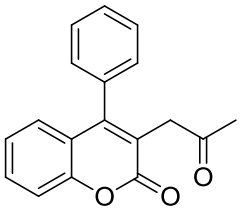
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (48.4 mg, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.52 (m, 4H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.39-7.35 (m, 4H), 7.24-7.19 (m, 2H), 7.08 (d, *J* = 7.7 Hz, 3H), 3.67 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.0, 161.5, 153.3, 152.9, 150.7, 133.9, 129.3, 129.2, 129.1, 128.2, 127.6, 125.9, 124.3, 121.5, 119.9, 116.8, 34.5. HRMS (ESI) *m/z* calcd for $C_{23}H_{17}O_4$ $(M+H)^+$ 357.1121, found 357.1124.

3-(2-Oxo-2-phenylethyl)-4-phenyl-2*H*-chromen-2-one (3ae)



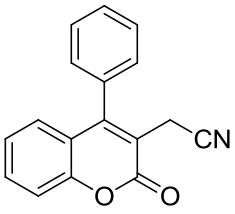
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (47.6 mg, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.92 (d, *J* = 7.0 Hz, 2H), 7.58-7.41 (m, 8H), 7.32-7.30 (m, 2H), 7.19-7.16 (m, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 196.3, 161.7, 153.2, 153.0, 136.6, 134.3, 133.2, 131.2, 129.0, 128.9, 128.5, 128.2, 128.1, 127.4, 124.1, 121.3, 120.6, 116.8, 38.8. HRMS (ESI) *m/z* calcd for $C_{23}H_{17}O_3$ $(M+H)^+$ 341.1172, found 341.1173.

3-(2-Oxopropyl)-4-phenyl-2*H*-chromen-2-one (3af)



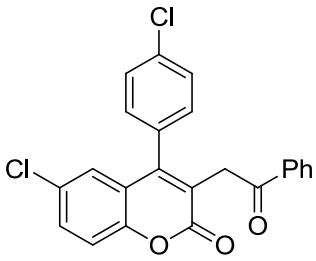
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (39.5 mg, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54-7.48 (m, 4H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.28-7.24 (m, 2H), 7.18-7.14 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 3.50 (s, 2H), 2.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.7, 161.6, 153.0, 152.9, 134.2, 131.2, 129.0, 128.9, 128.1, 127.4, 124.2, 121.0, 120.4, 116.7, 43.1, 30.2. HRMS (ESI) *m/z* calcd for $C_{18}H_{15}O_3$ $(M+H)^+$ 279.1016, found 279.1017.

2-(2-Oxo-4-phenyl-2*H*-chromen-3-yl)acetonitrile (3ag)



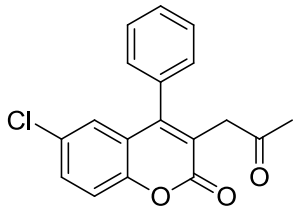
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (34.9 mg, 67%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.65-7.55 (m, 4H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.35-7.32 (m, 2H), 7.25-7.19 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 3.44 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.3, 154.6, 153.0, 132.9, 132.5, 129.8, 129.4, 127.9, 124.7, 119.8, 117.0, 116.4, 116.2, 17.5. HRMS (ESI) *m/z* calcd for $C_{17}H_{12}NO_2$ $(M+H)^+$ 262.0863, found 262.0862.

6-chloro-4-(4-chlorophenyl)-3-(2-oxo-2-phenylethyl)-2H-chromen-2-one (3je)



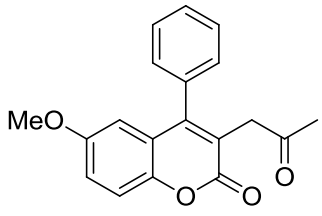
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (51.4 mg, 63%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.93-7.89 (m, 2H), 7.59-7.53 (m, 1H), 7.48-7.41 (m, 5H), 7.26-7.21(m, 2H), 7.15 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 4.04 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 195.9, 160.8, 153.1, 151.4, 137.3, 136.3, 135.5, 133.5, 132.2, 129.6, 129.4, 128.6, 128.2, 127.9, 124.8, 121.7, 118.9, 117.1, 38.7. HRMS (ESI) *m/z* calcd for $C_{23}H_{15}Cl_2O_3$ $(M+H)^+$ 409.0393, found 409.0398.

6-Chloro-3-(2-oxopropyl)-4-phenyl-2*H*-chromen-2-one (3gf)



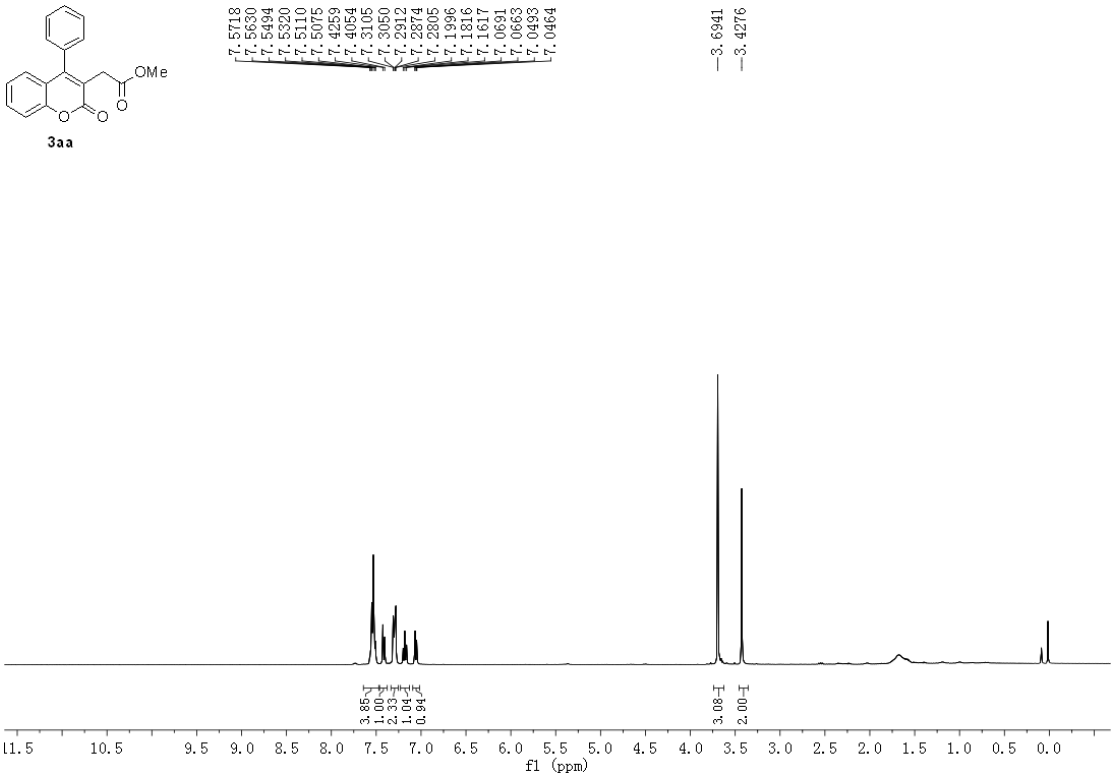
Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 8:1) gives a yellow oil (41.2 mg, 66%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53-7.48 (m, 3H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.26-7.20 (m, 2H), 7.12 (dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 3.48 (s, 2H), 2.18 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 204.5, 161.0, 153.0, 152.4, 137.1, 133.8, 129.2, 129.0, 128.3, 128.0, 124.7, 121.1, 119.1, 116.9, 43.0, 30.2. HRMS (ESI) *m/z* calcd for $C_{18}H_{14}ClO_3$ $(M+H)^+$ 313.0626, found 313.0628.

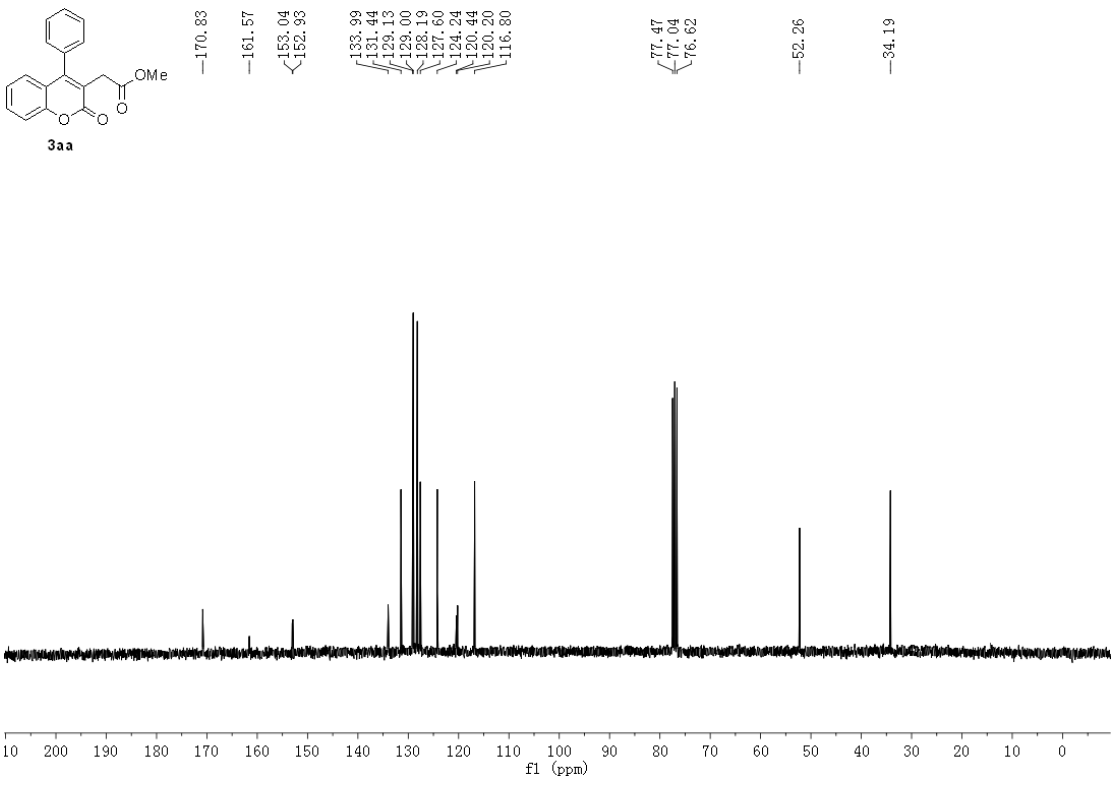
6-Methoxy-3-(2-oxopropyl)-4-phenyl-2*H*-chromen-2-one (3ef)

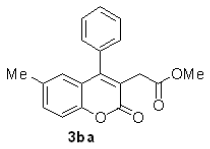


Flash column chromatography on a silica gel (petroleum ether/ethyl acetate = 5:1) gives a yellow oil (47.8 mg, 73%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51-7.46 (m, 3H), 7.25-7.20 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 6.72 (dd, J_1 = 8.8 Hz, J_2 = 2.5 Hz, 1H), 3.86 (s, 3H), 3.45 (s, 2H), 2.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 205.1, 162.3, 162.0, 154.5, 152.2, 134.5, 128.9, 128.8, 128.4, 128.0, 117.6, 114.0, 112.3, 100.6, 55.8, 42.9, 30.1. HRMS (ESI) *m/z* calcd for $C_{19}H_{17}O_4$ $(M+H)^+$ 309.1121, found 309.1122.

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



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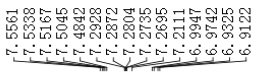
O
O
O

3ba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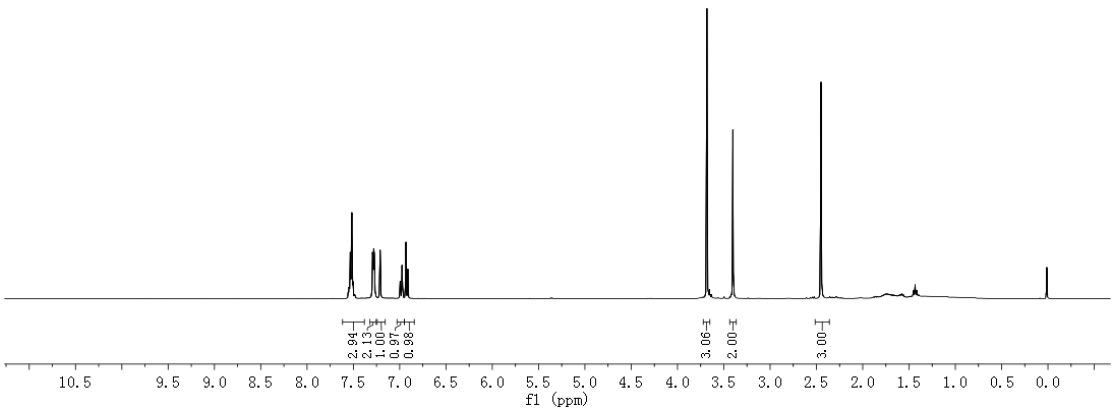
7.4842
7.2928
7.2872
7.2804
7.2735
7.2695
7.2111
6.9947
6.9742
6.9325
6.9122


3.6830
3.4021
2.4506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2.15
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3.00
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8.0
7.5
7.0
6.5
6.0
5.5
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3.5
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2.5
2.0
1.5
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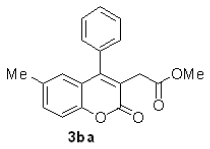
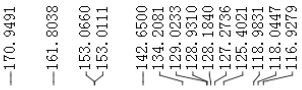
0.5
0.0
f1 (ppm)


Me
OMe
O
O
O

3ba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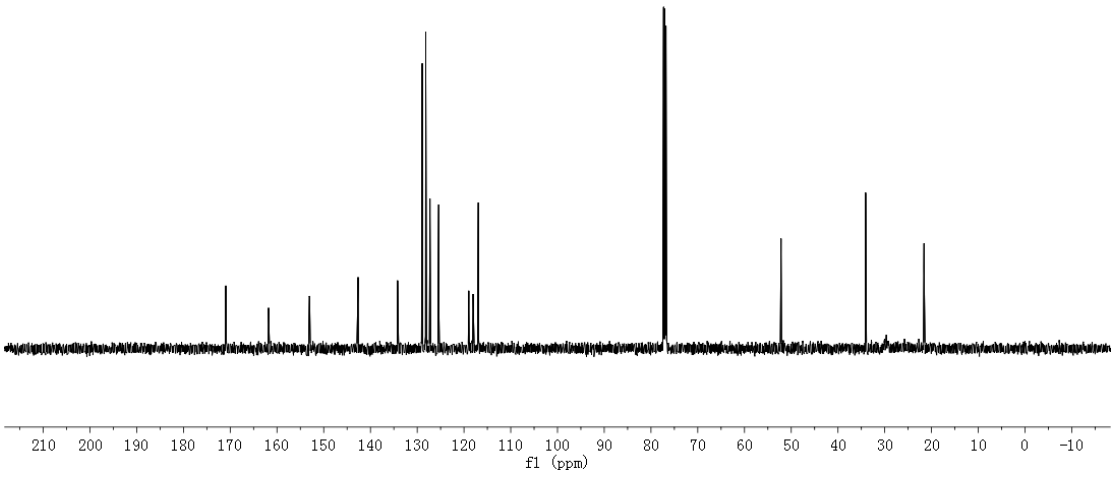
118.0447
116.9279


77.2960
77.0419
76.7877


52.1828


34.0943


21.5823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120
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100
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60
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40
30
20
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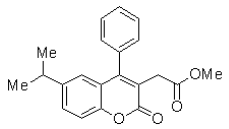
-10
f1 (ppm)


Me
Me
OMe
O
O

3ca


7.4791
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7.4455
7.4304
7.4247
7.4086
7.3937
7.2111
7.1953
7.1920
7.1789
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6.9742
6.9521
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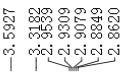
6.8913
6.8639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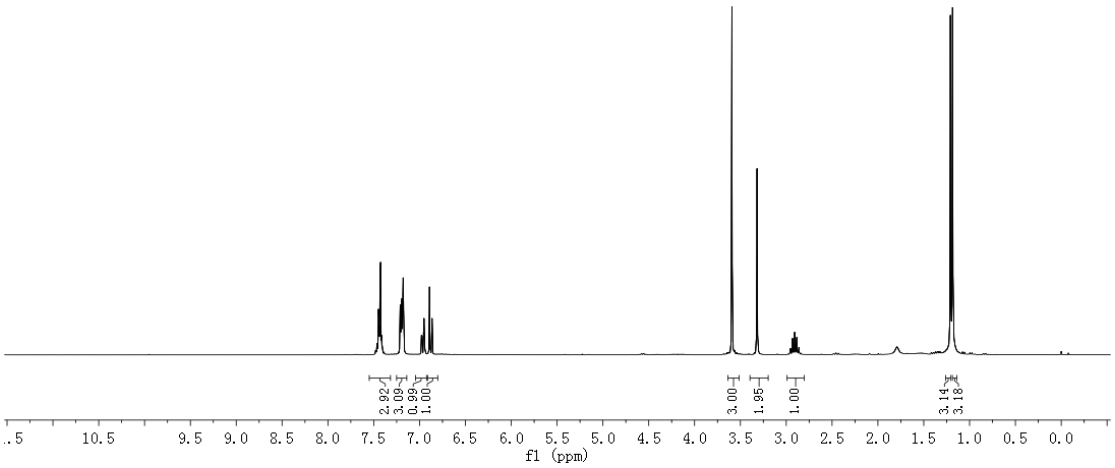
1.1856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3.00
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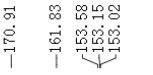
f1 (ppm)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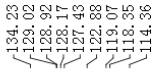
153.15
153.02


134.23
129.02
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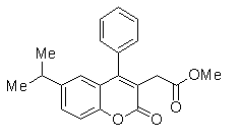
128.17
127.43
122.88
119.07
118.35
114.36

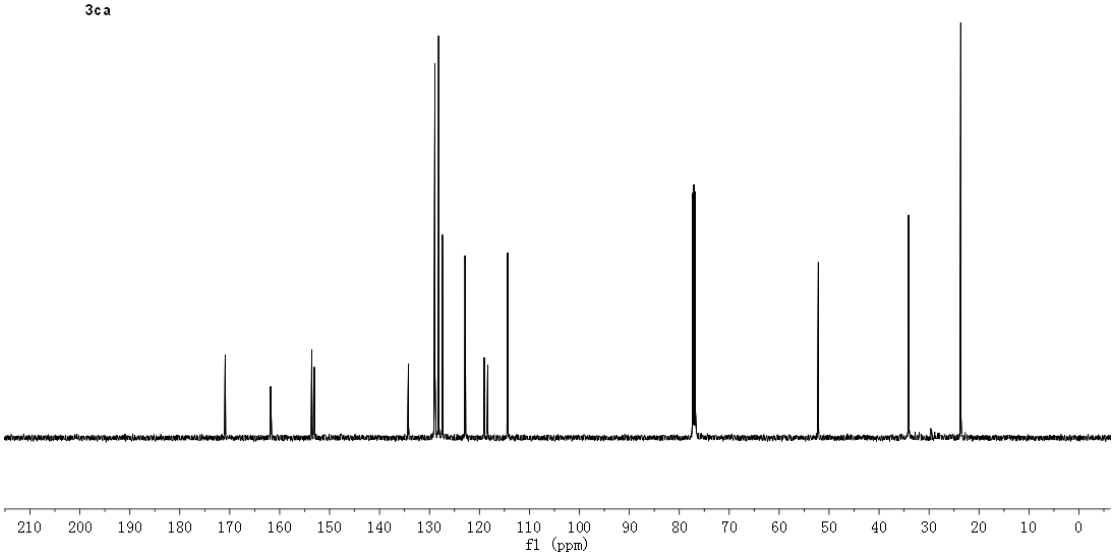

77.32
77.07
76.81


52.16


34.14
34.10
23.65


Me
Me
OMe
O
O

3ca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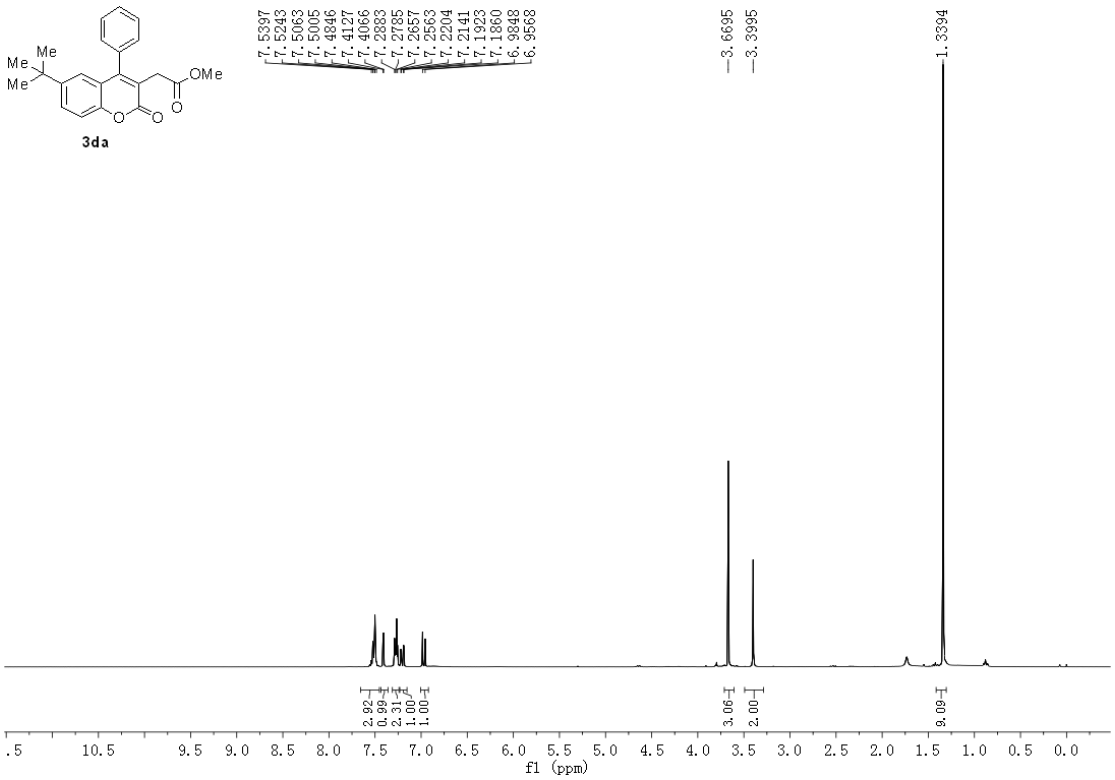
Me
Me
Me
OMe
O
O
3da
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7.2204
7.2141
7.1923
7.1860
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6.9568
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1.00
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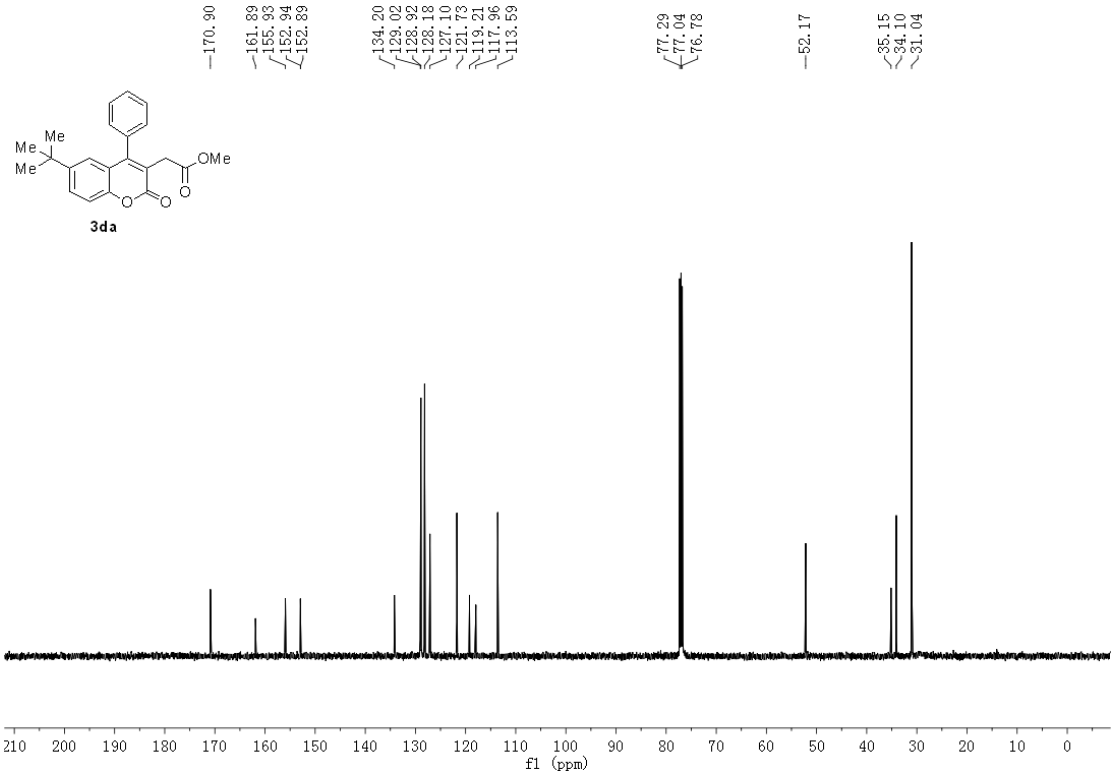
2.00
9.09
f1 (ppm)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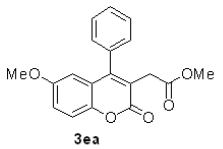
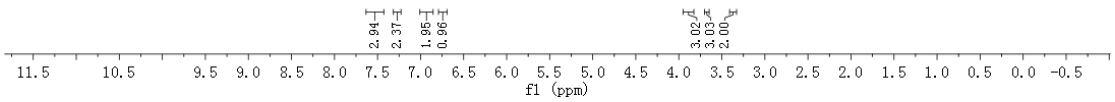
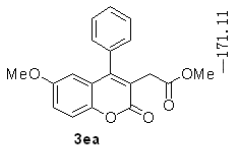
161.89
155.93
152.94
152.89
134.20
129.02
128.92
128.18
127.10
121.73
119.21
117.96
113.59
77.29
77.04
76.78
52.17
35.15
34.10
31.04
Me
Me
Me
OMe
O
O
3da
f1 (ppm)


MeO
OMe
O
O
3ea


7.5516
7.5430
7.5294
7.5121
7.4992
7.4830
7.2886
7.2808
7.2692
7.2654
6.9568
6.9346
6.9047
6.8986
6.7552
6.7490
6.7330
6.7268
3.8821
3.6836
3.3826


2.94
2.37
1.96
0.96
3.02
3.03
2.00
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
-0.5
f1 (ppm)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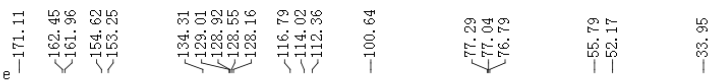
OMe
O
O
3ea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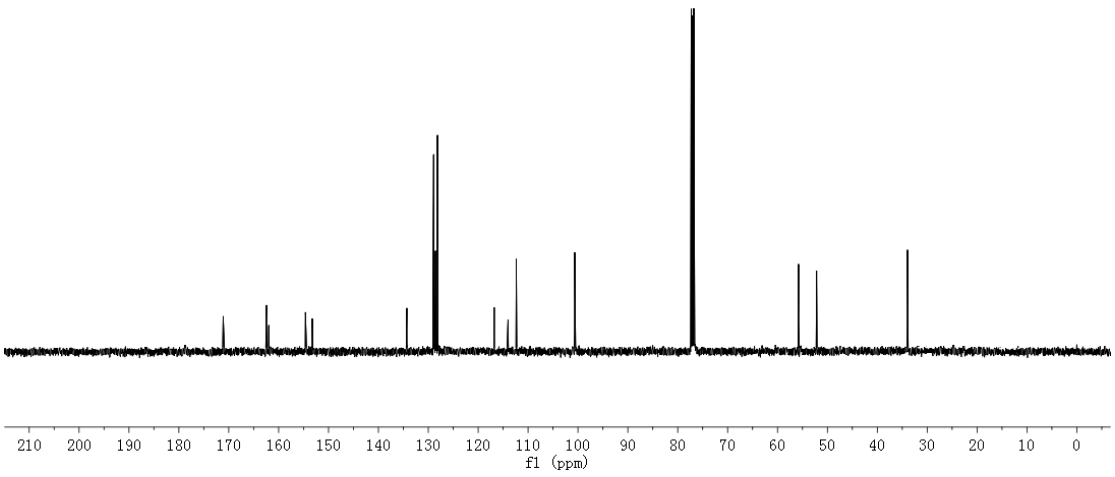
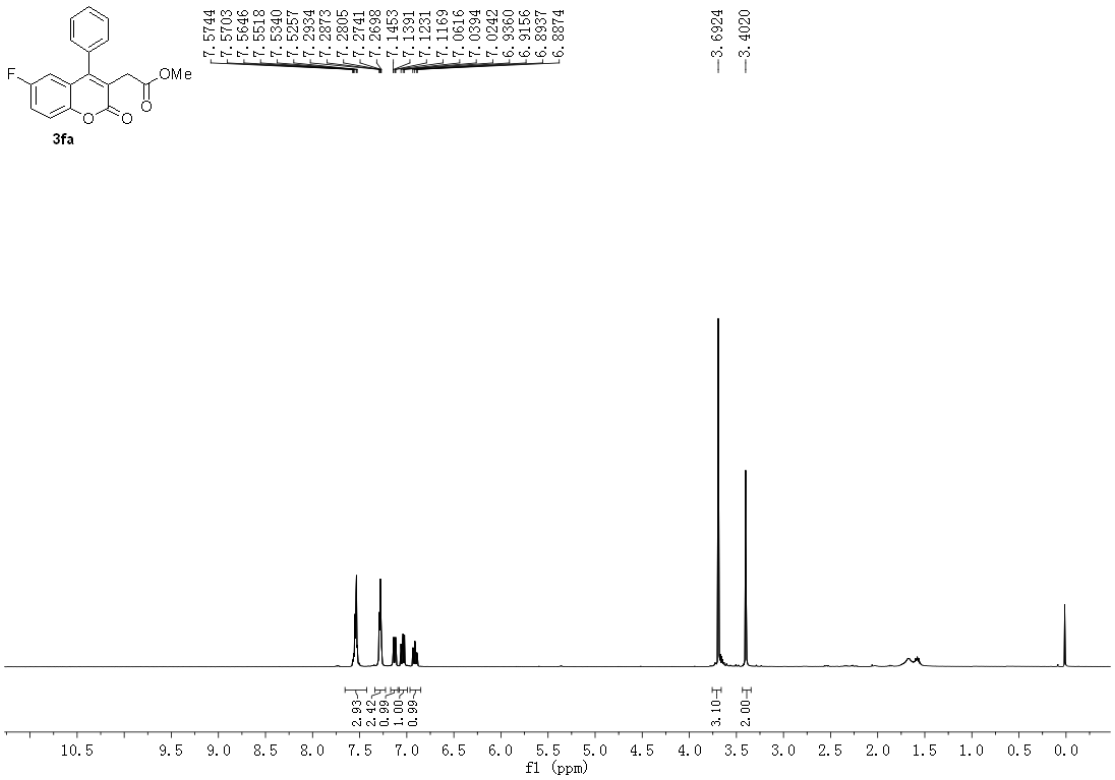
162.45
161.96
154.62
153.25
134.31
129.01
128.92
128.55
128.16
116.79
114.02
112.36
100.64
77.29
77.04
76.79
55.79
52.17
33.95


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


F
OMe
O
O
3fa
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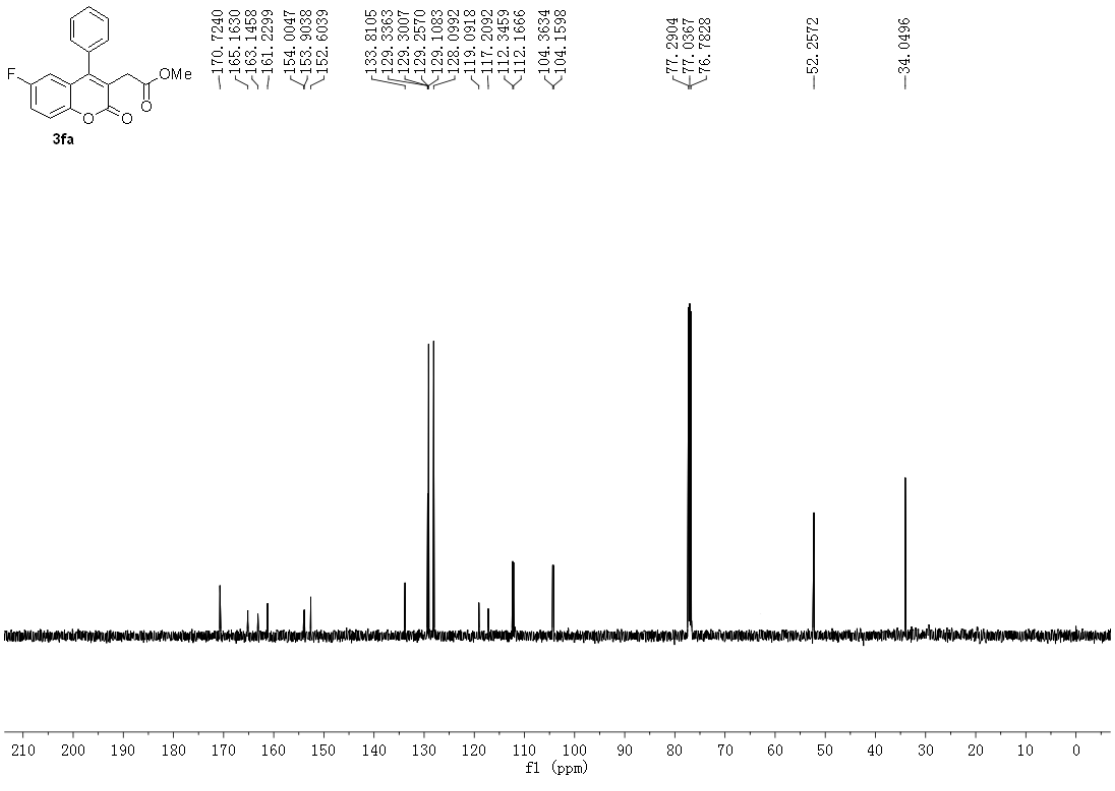
7.5703
7.5646
7.5518
7.5340
7.5257
7.2934
7.2873
7.2805
7.2741
7.2698
7.1453
7.1391
7.1231
7.1169
7.0616
7.0394
7.0242
6.9360
6.9156
6.8937
6.8874
3.6924
3.4020
2.93
2.42
0.99
1.00
0.99
3.10
2.00
f1 (ppm)


F
OMe
O
O
3fa
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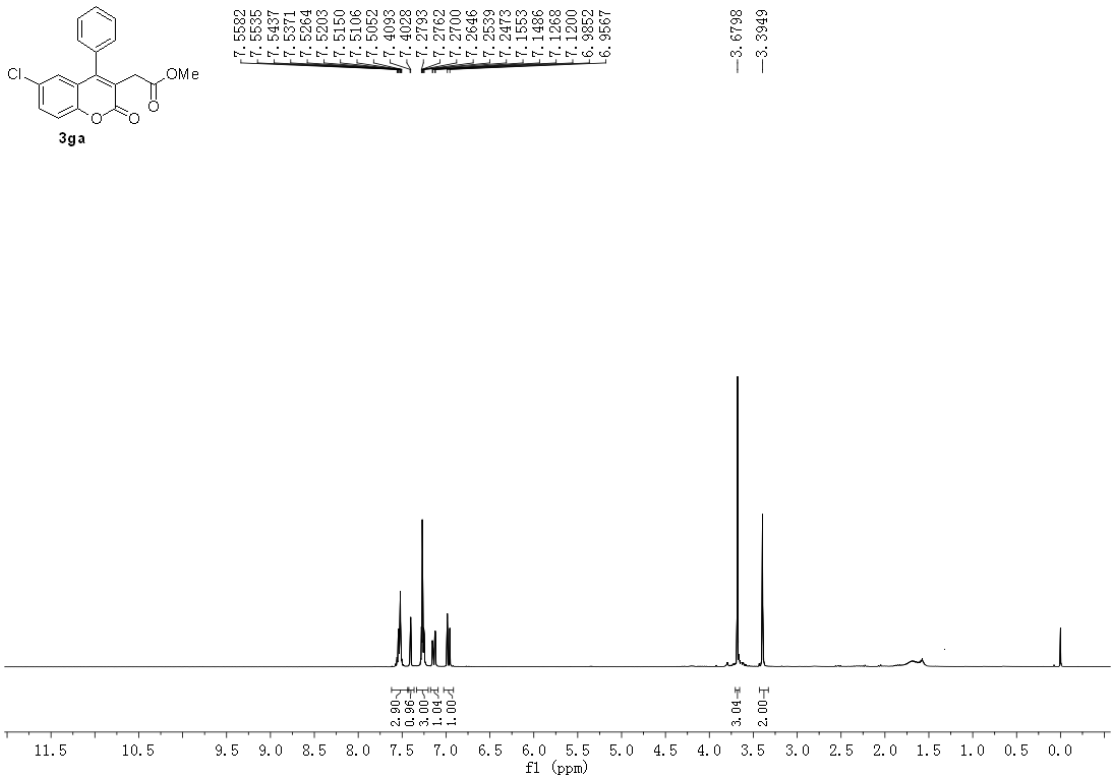
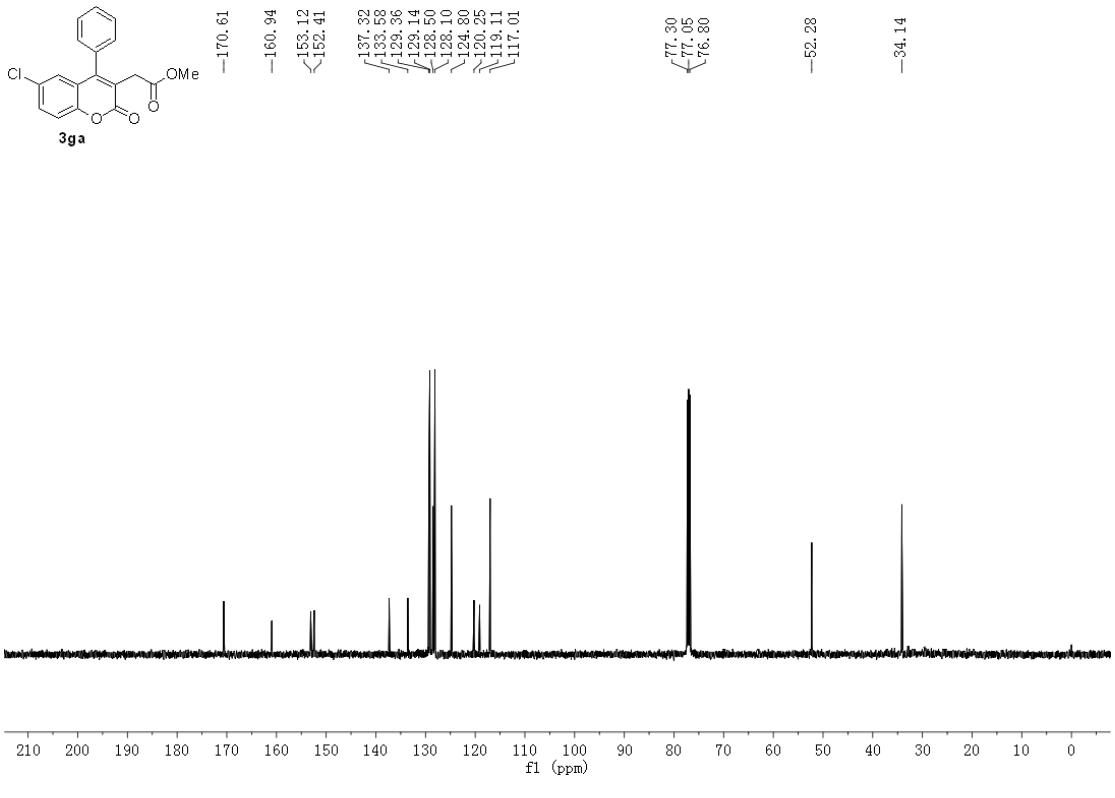
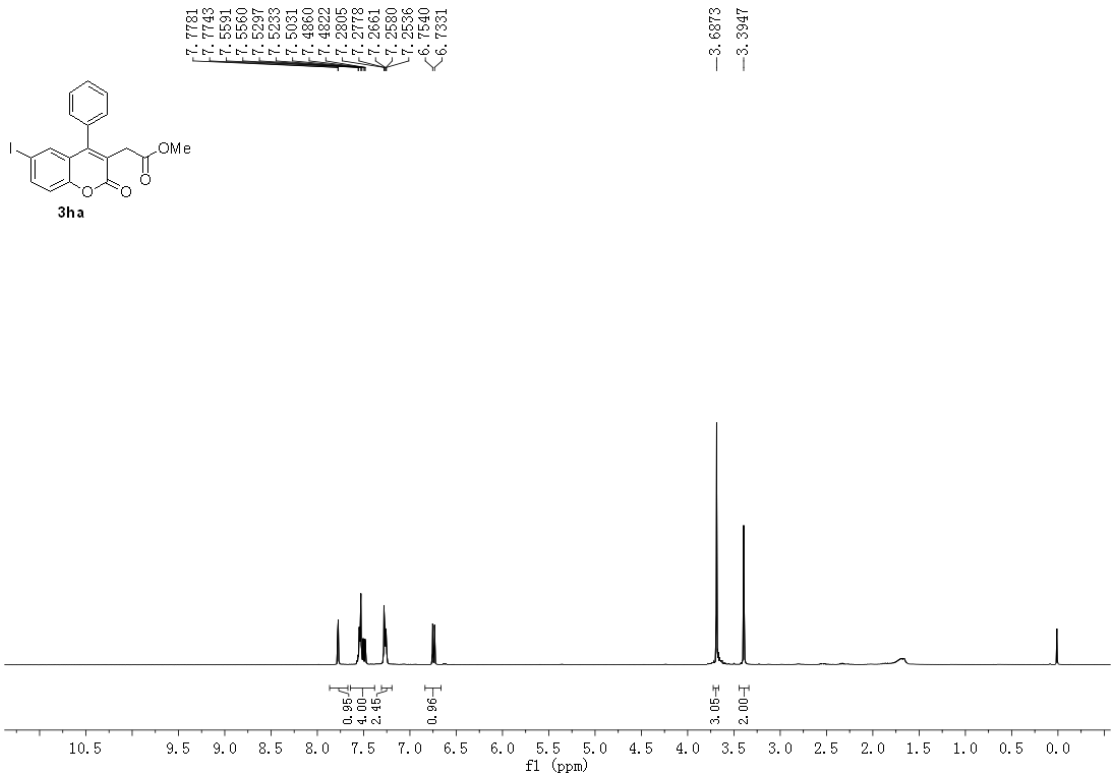
165.1630
163.1458
161.2299
154.0047
153.9038
152.6039
133.8105
129.3363
129.3007
129.2570
129.1083
128.0992
119.0918
117.2092
112.3459
112.1666
104.3634
104.1598
77.2904
77.0367
76.7828
52.2572
34.0496
f1 (ppm)


Cl
OMe
O
O
3ga
7.5582
7.5535
7.5437
7.5371
7.5264
7.5203
7.5150
7.5106
7.5052
7.4093
7.4028
7.2793
7.2762
7.2700
7.2646
7.2539
7.2473
7.1553
7.1486
7.1268
7.1200
6.9852
6.9567
3.6798
3.3949
2.90
0.96
3.00
1.04
1.00
3.04
2.00
f1 (ppm)


Cl
OMe
O
O
3ga
170.61
160.94
153.12
152.41
137.32
133.58
129.36
129.14
128.50
128.10
124.80
120.25
119.11
117.01
77.30
77.05
76.80
52.28
34.14
f1 (ppm)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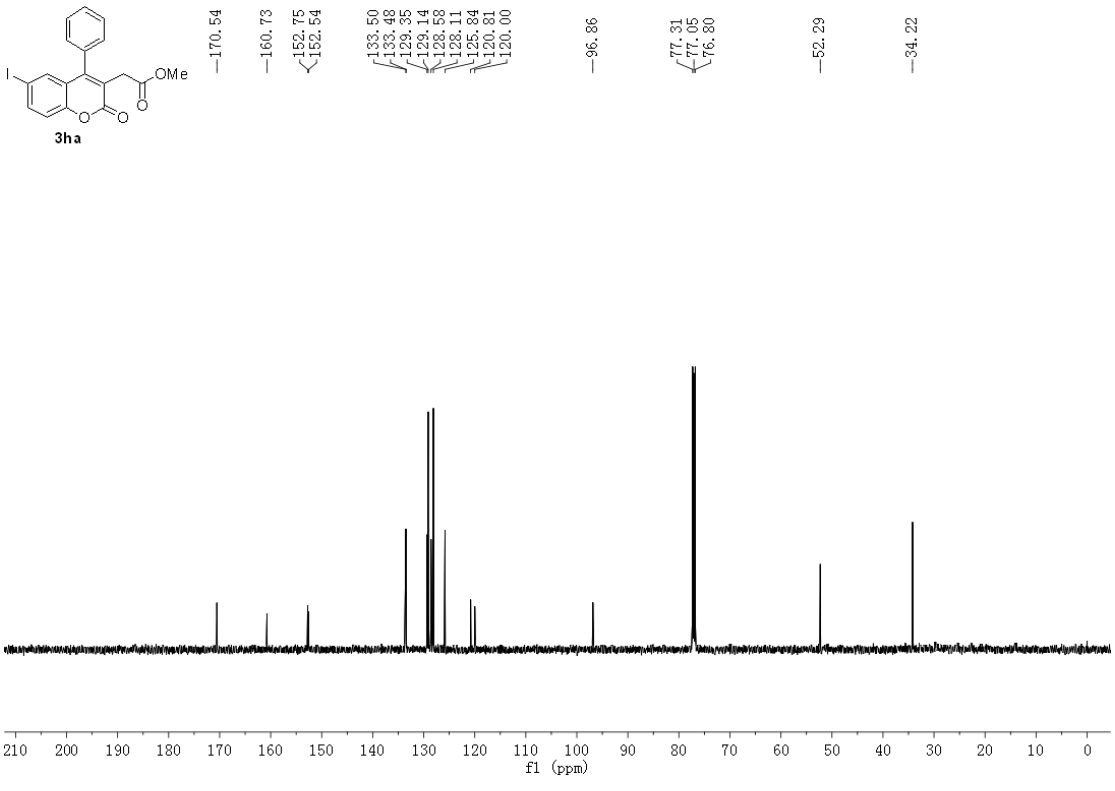
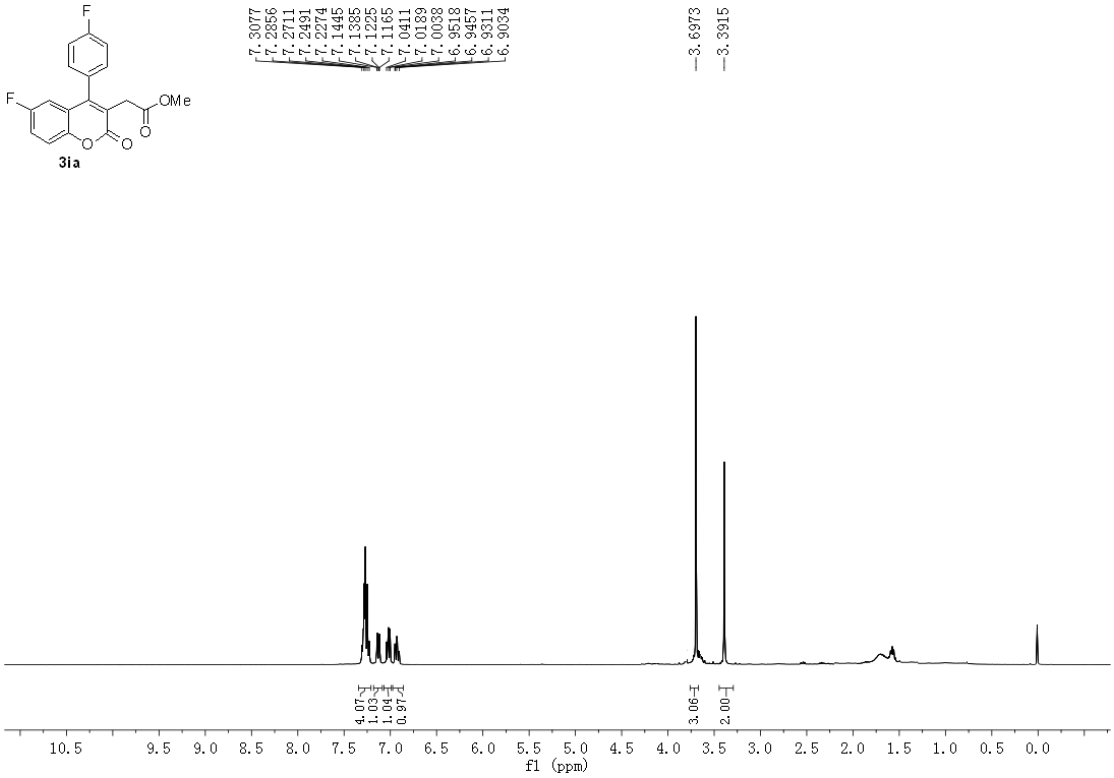
7.7743
7.5591
7.5560
7.5297
7.5233
7.5031
7.4860
7.4822
7.2805
7.2778
7.2661
7.2580
7.2536
6.7540
6.7331
3.6873
3.3947
I
OMe
O
O
3ha
0.95
4.00
2.45
0.96
3.05
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.54
160.73
152.75
152.54
133.50
133.48
129.35
129.14
128.58
128.11
125.84
120.81
120.00
96.86
77.31
77.05
76.80
52.29
34.22
I
OMe
O
O
3ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
OMe
O
O
3ia
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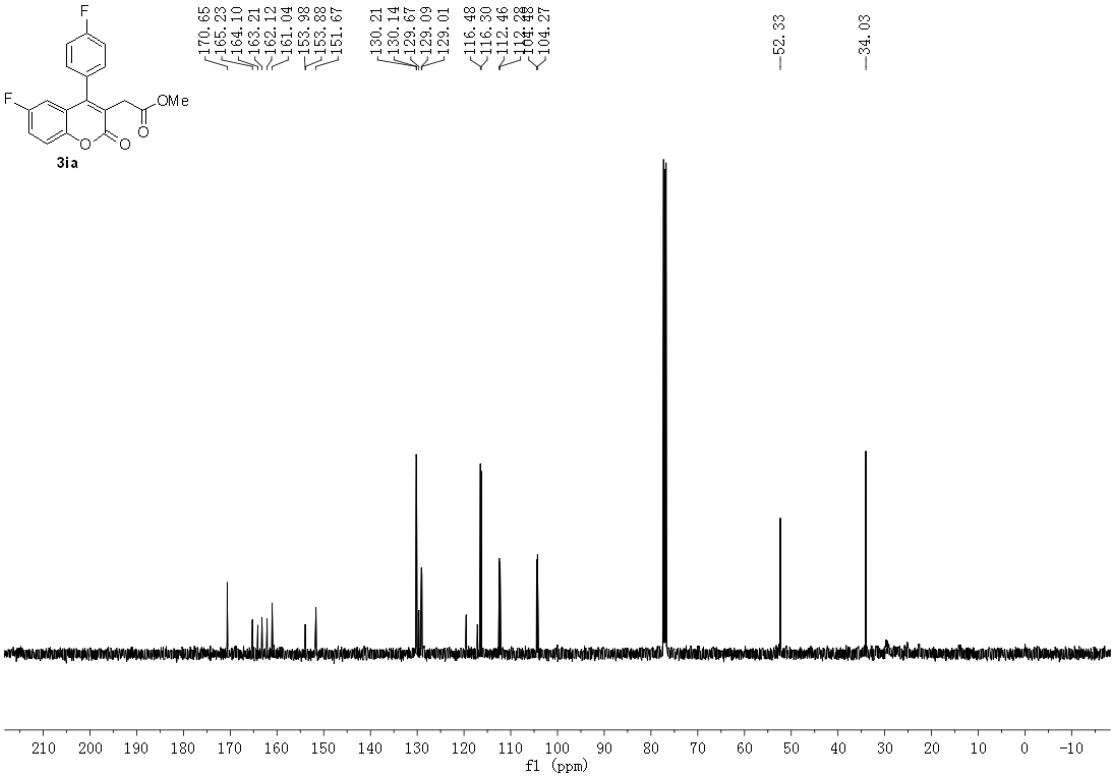
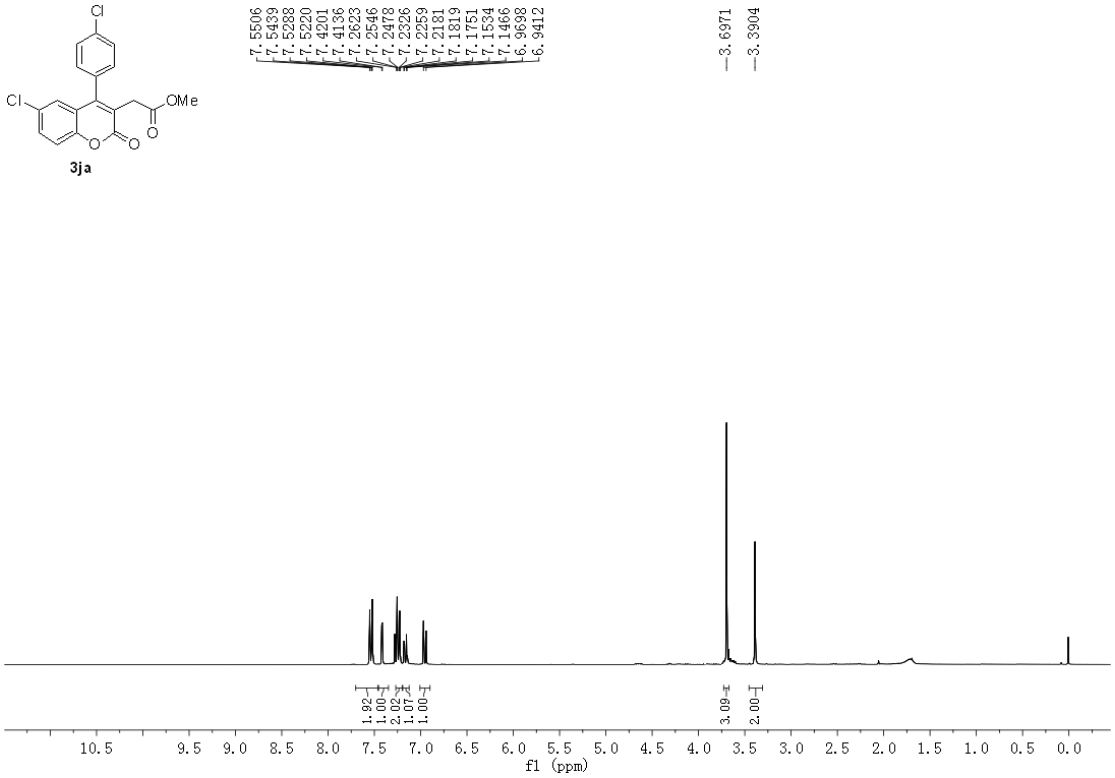
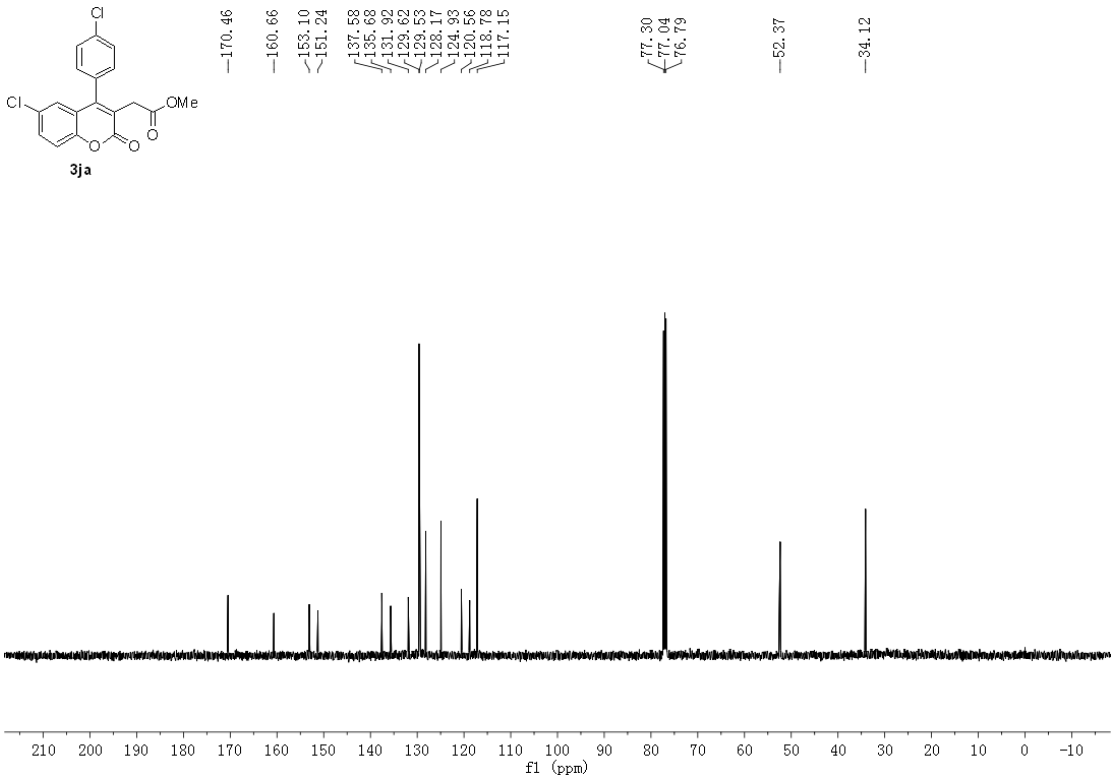
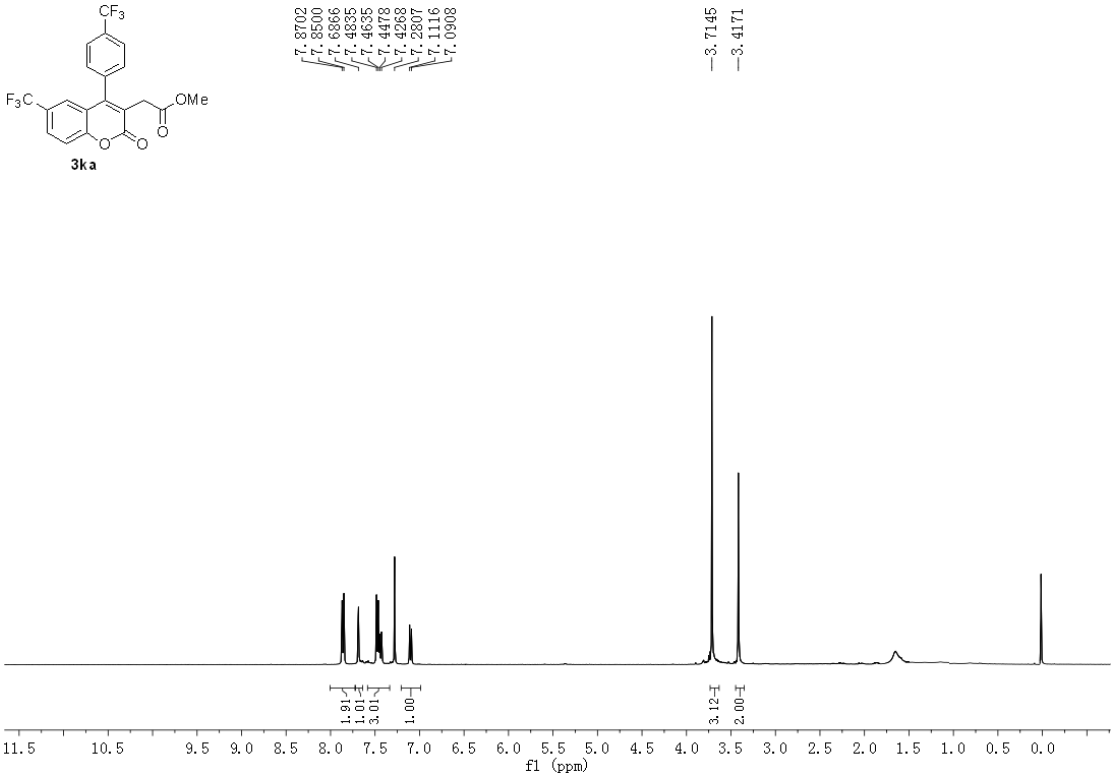
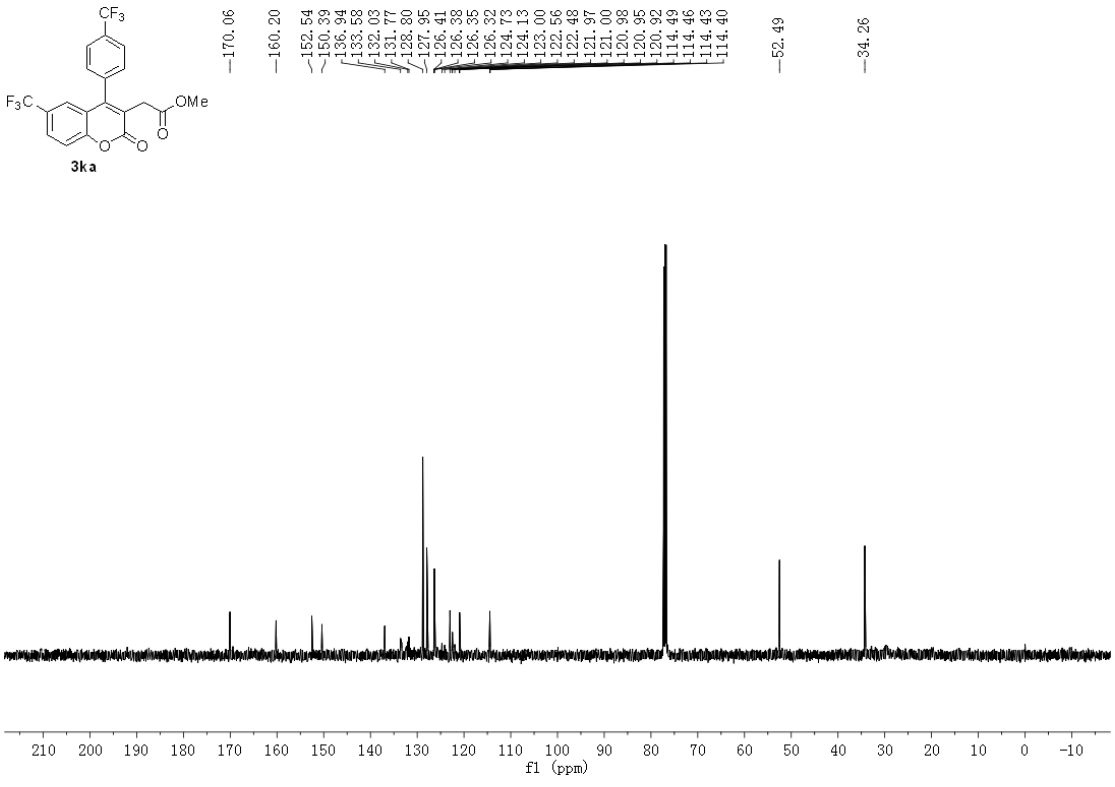
7.2856
7.2711
7.2491
7.2274
7.1445
7.1385
7.1225
7.1165
7.0411
7.0189
7.0038
6.9618
6.9457
6.9311
6.9034
3.6973
3.3915
4.07
1.03
1.04
0.97
3.06
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


F
F
OMe
O
O
3ia
170.65
165.23
164.10
163.21
162.12
161.04
153.98
153.88
151.67
130.21
130.14
129.67
129.09
129.01
116.48
116.30
112.46
104.27
52.33
34.03
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
Cl
OMe
O
O
O
3ja
7.5506
7.5439
7.5288
7.5220
7.4201
7.4136
7.2623
7.2546
7.2478
7.2326
7.2259
7.2181
7.1819
7.1751
7.1534
7.1466
6.9698
6.9412
3.6971
3.3904
1.92
1.00
2.02
1.07
1.00
3.09
2.00
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
f1 (ppm)


Cl
Cl
OMe
O
O
O
3ja
170.46
160.66
153.10
151.24
137.58
135.68
131.92
129.62
129.53
128.17
124.93
120.56
118.78
117.15
77.30
77.04
76.79
52.37
34.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3ka
7.8702
7.8500
7.6866
7.4835
7.4635
7.4478
7.4268
7.2807
7.1116
7.0908
3.7145
3.4171
1.91
1.01
3.01
1.00
3.12
2.00
f1 (ppm)


3ka
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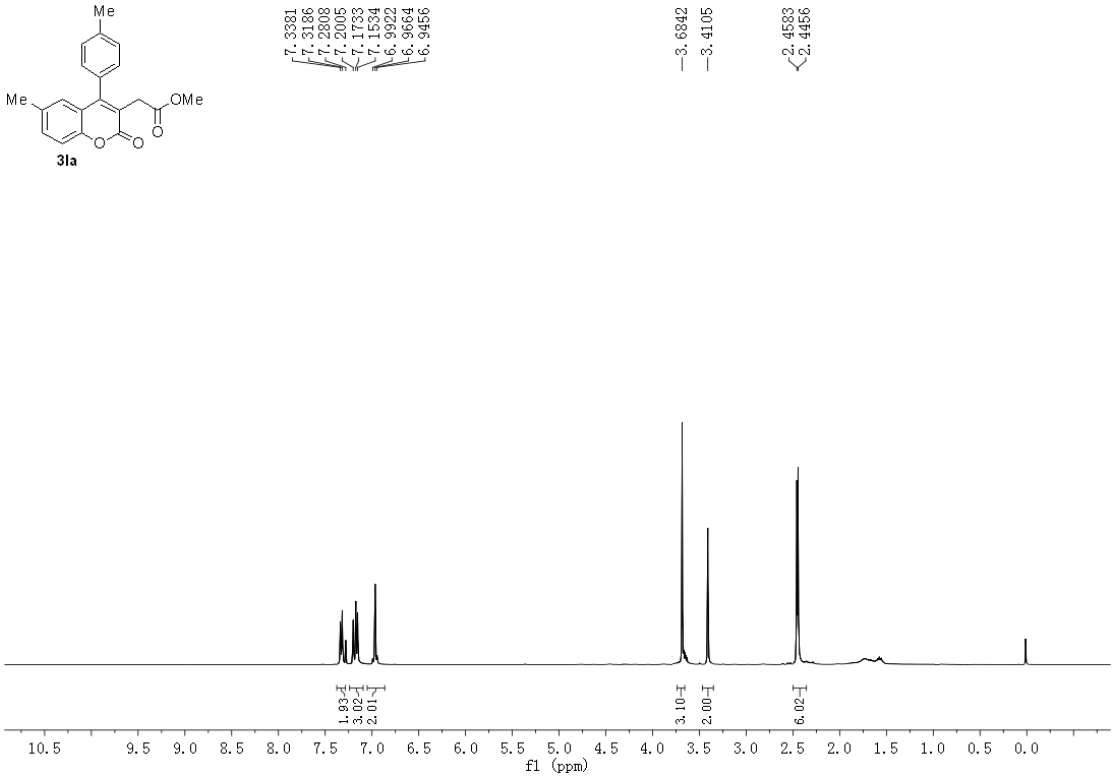
152.54
150.39
136.94
133.58
132.03
131.77
128.80
127.95
126.41
126.38
126.35
126.32
124.73
124.13
123.00
122.56
122.48
121.97
121.00
120.98
120.95
120.92
114.49
114.46
114.43
114.40
52.49
34.26
f1 (ppm)


Me
Me
OMe
O
O
3la
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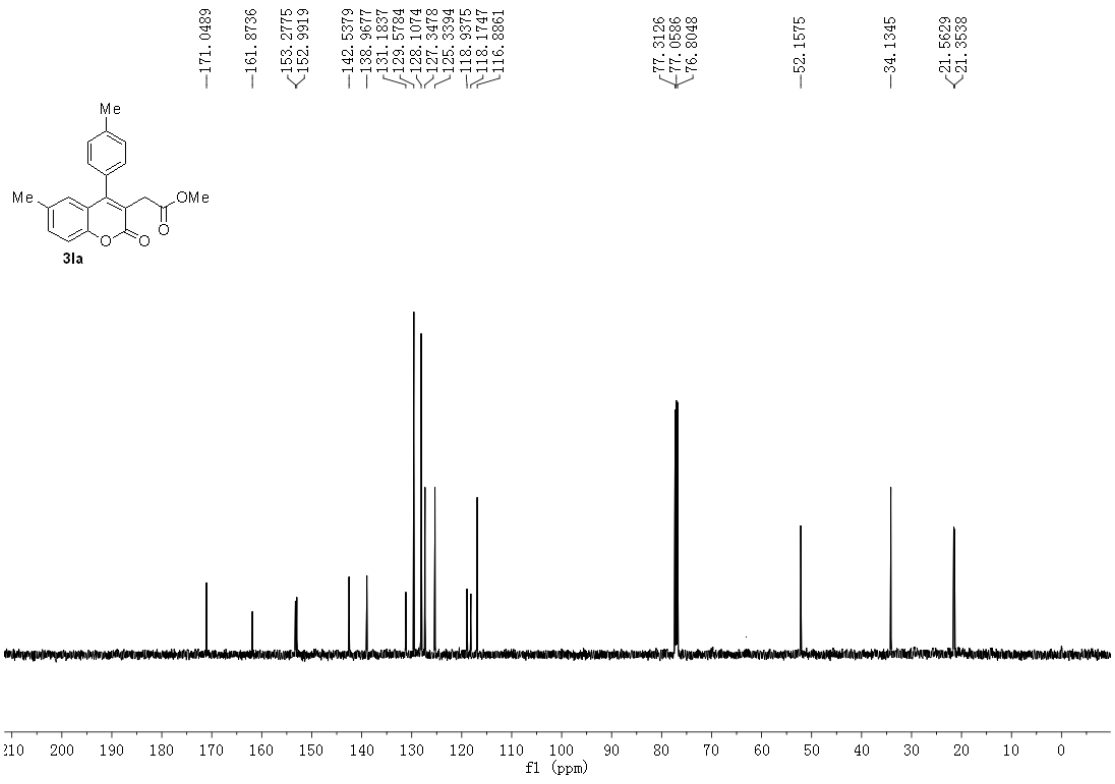
7.3186
7.2808
7.2005
7.1733
7.1534
6.9922
6.9664
6.9456
3.6842
3.4105
2.4583
2.4456
1.93
3.02
2.01
3.10
2.00
6.02
10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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142.5379
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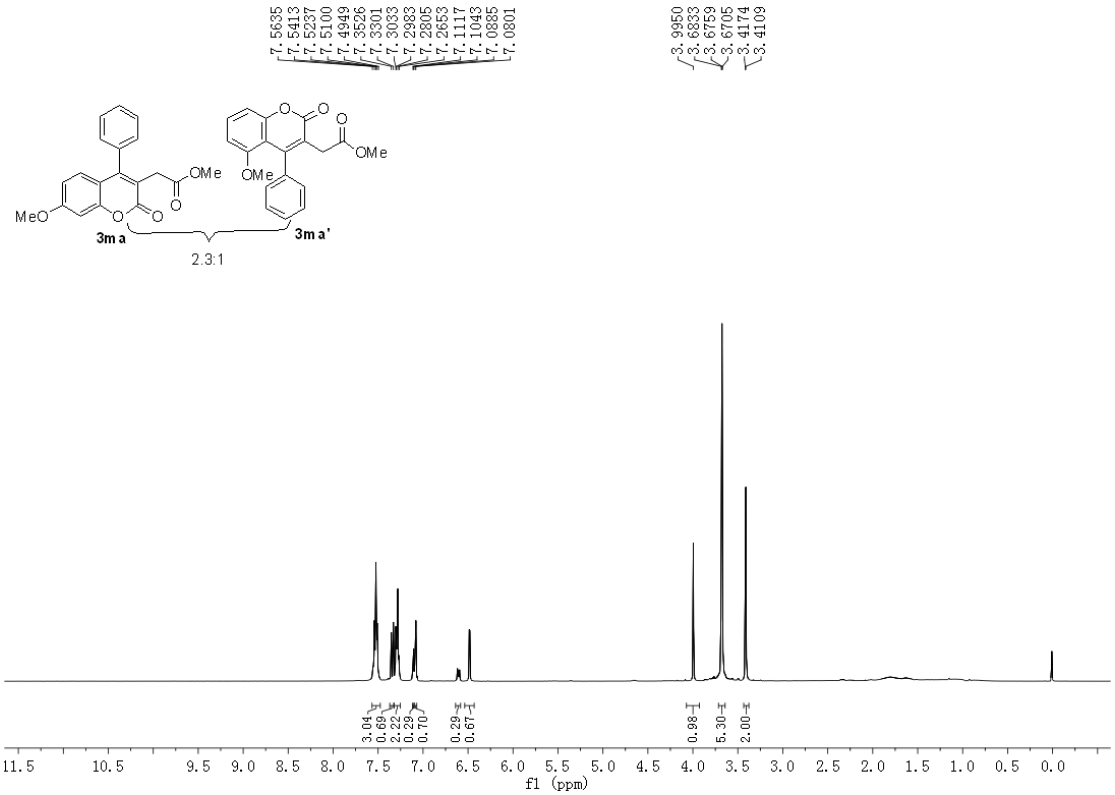
131.1837
129.5784
128.1074
127.3478
125.3394
118.9375
118.1747
116.8861
77.3126
77.0586
76.8048
52.1575
34.1345
21.5629
21.3538
Me
Me
OMe
O
O
3la
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.5237
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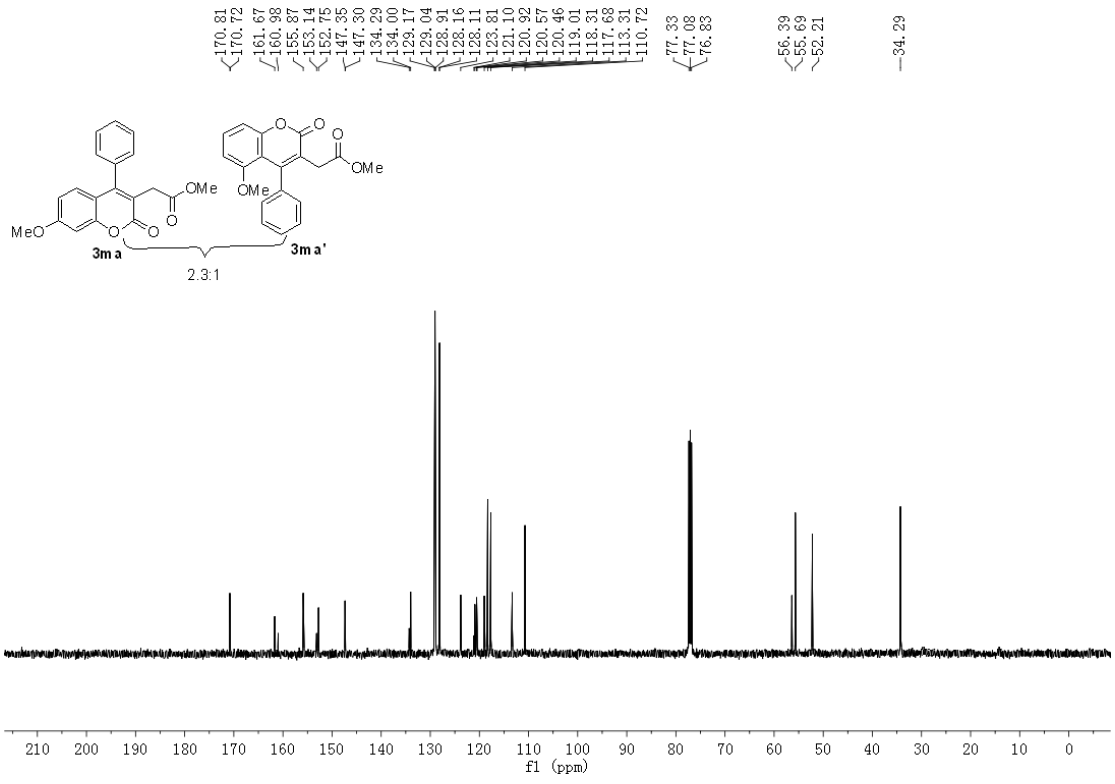
7.4949
7.3526
7.3301
7.3033
7.2983
7.2805
7.2653
7.1117
7.1043
7.0885
7.0801
3.9950
3.6833
3.6759
3.6705
3.4174
3.4109
OMe
OMe
OMe
MeO
3m a
3m a'
2.3:1
3.04
0.69
2.22
0.29
0.70
0.29
0.67
0.98
5.30
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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170.72
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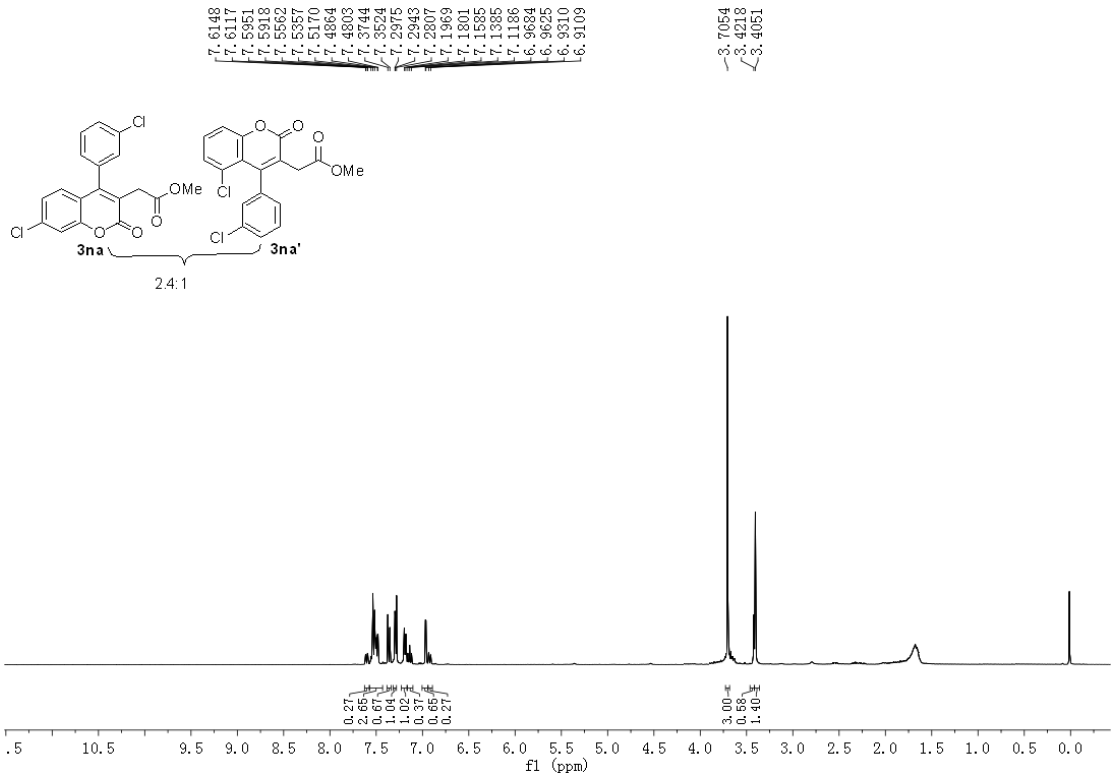
155.87
153.14
152.75
147.35
147.30
134.29
134.00
129.17
129.04
128.91
128.16
128.11
123.81
121.10
120.92
120.57
120.46
119.01
118.31
117.68
113.31
110.72
77.33
77.08
76.83
56.39
55.69
52.21
34.29
OMe
OMe
OMe
MeO
3m a
3m a'
2.3:1
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.5562
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7.5170
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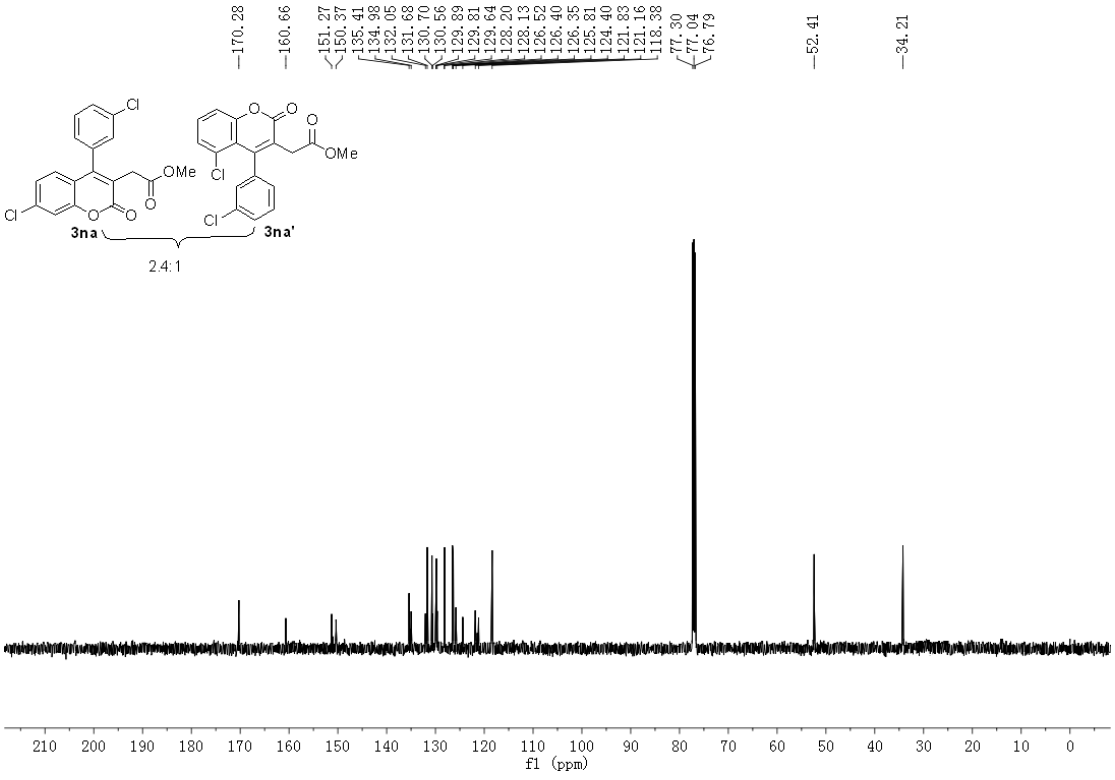
7.4803
7.3744
7.3524
7.2975
7.2943
7.2807
7.1969
7.1801
7.1585
7.1385
7.1186
6.9684
6.9625
6.9310
6.9109
3.7054
3.4218
3.4051
OMe
OMe
3na
3na'
2.4:1
0.27
2.65
0.67
1.04
1.02
0.37
0.65
0.27
3.00
0.58
1.40
f1 (ppm)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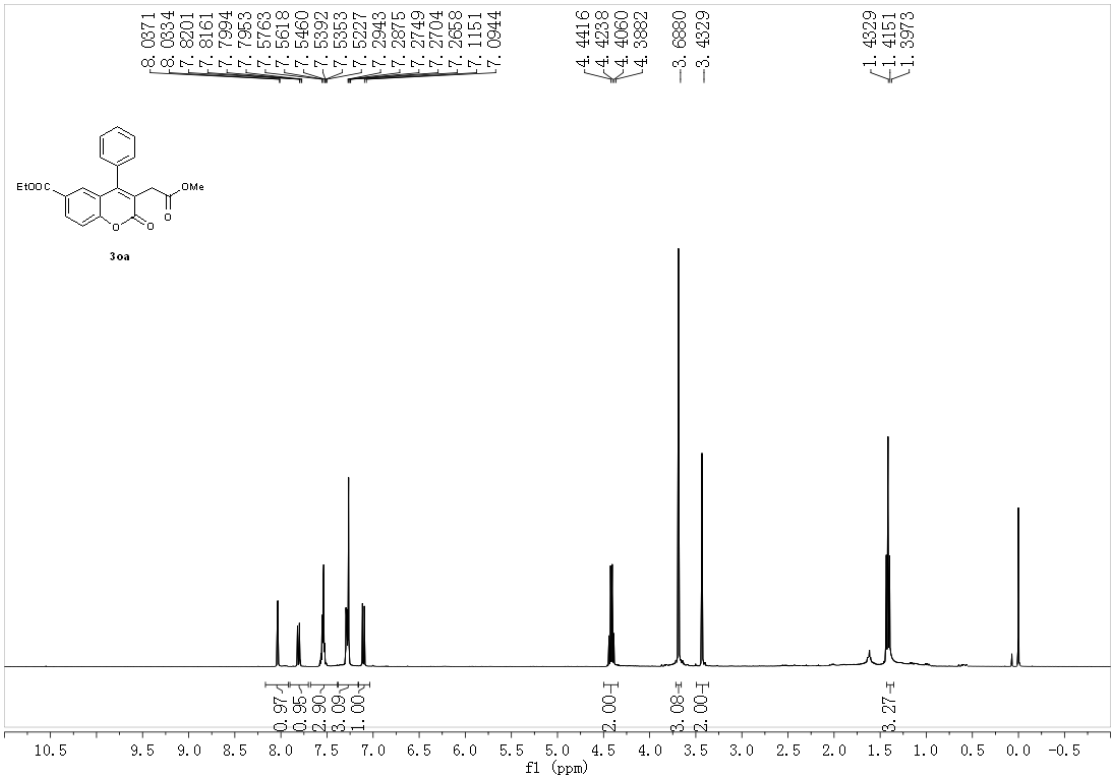
160.66
151.27
150.37
135.41
134.98
132.05
131.68
130.70
130.56
129.89
129.81
129.64
128.20
128.13
126.52
126.40
126.35
125.81
124.40
121.83
121.16
118.38
77.30
77.04
76.79
52.41
34.21
OMe
OMe
3na
3na'
2.4:1
f1 (ppm)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8.8201
7.8161
7.7994
7.7963
7.5763
7.5618
7.5460
7.5392
7.5353
7.5227
7.2943
7.2875
7.2749
7.2704
7.2658
7.1151
7.0944
4.4416
4.4238
4.4060
4.3882
3.6880
3.4329
1.4329
1.4151
1.3973
EtOOC
OMe
3oa
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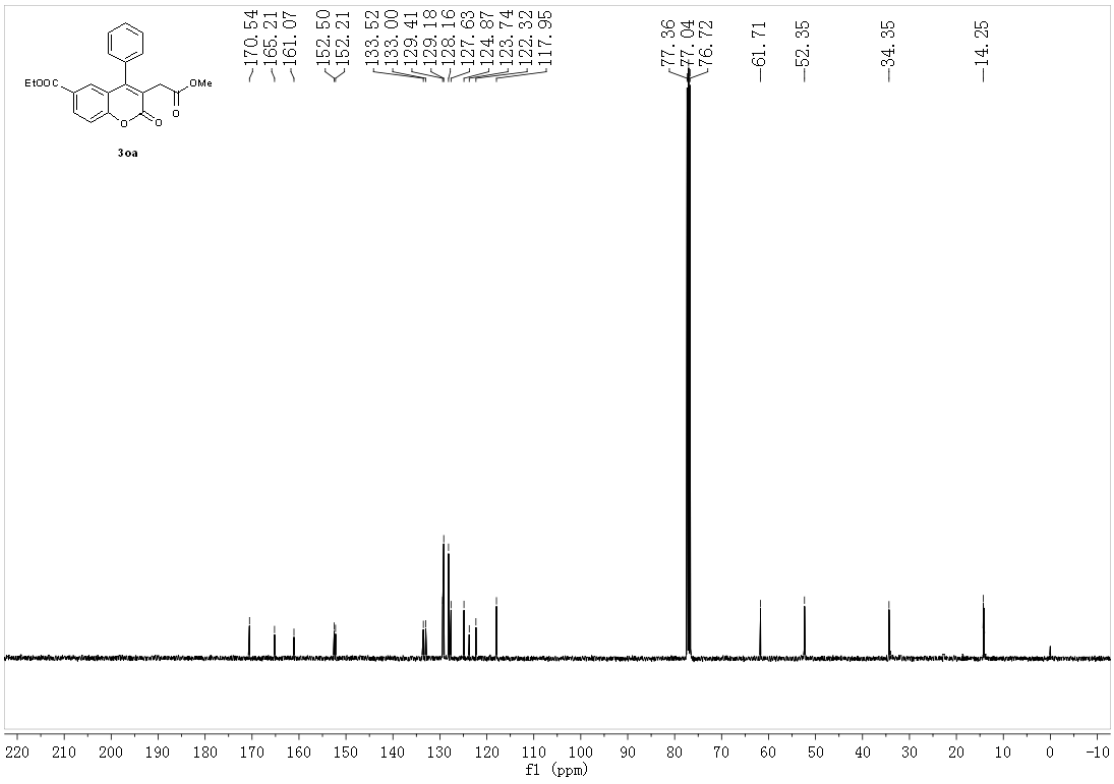
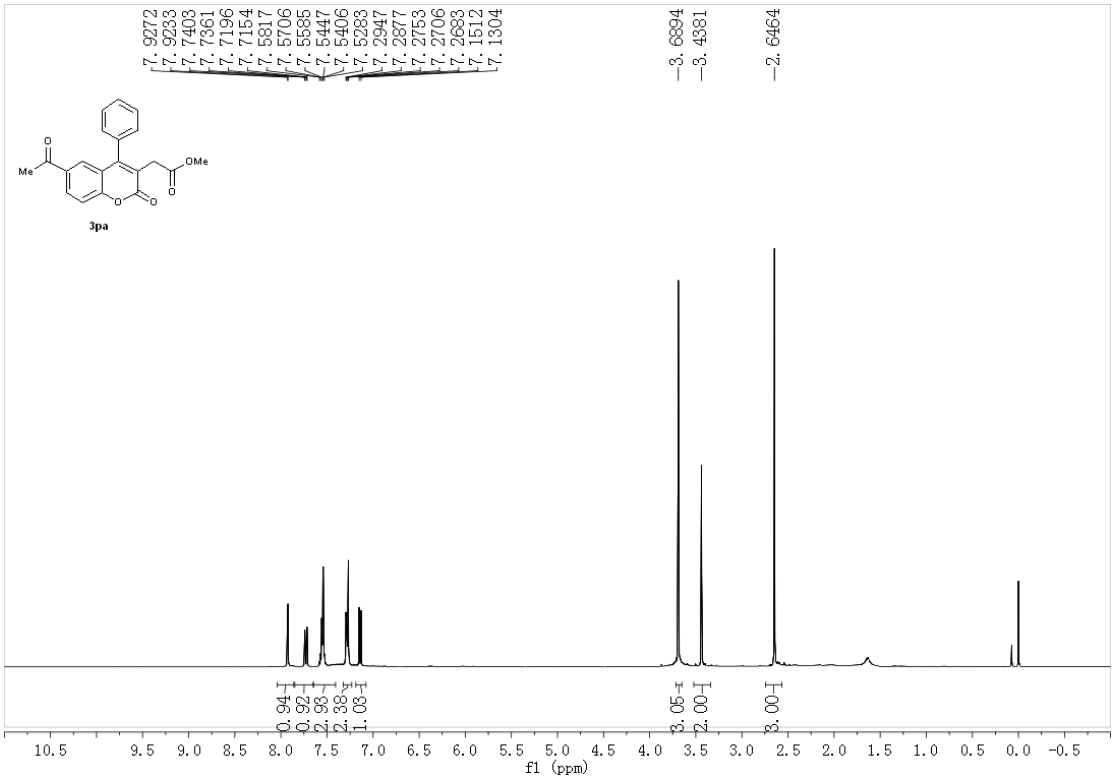
0.96
2.90
3.09
1.00
2.00
3.08
2.00
3.27
f1 (ppm)


170.54
165.21
161.07
152.50
152.21
133.52
133.00
129.41
129.18
128.16
127.63
124.87
123.74
122.32
117.95
77.36
77.04
76.72
61.71
52.35
34.35
14.25
EtOOC
OMe
3oa
f1 (ppm)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7.9233
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7.7196
7.7154
7.5817
7.5706
7.5585
7.5447
7.5406
7.5283
7.2947
7.2877
7.2753
7.2706
7.2683
7.1512
7.1304
3.6894
3.4381
2.6464
Me
OMe
3pa
0.94
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3.05
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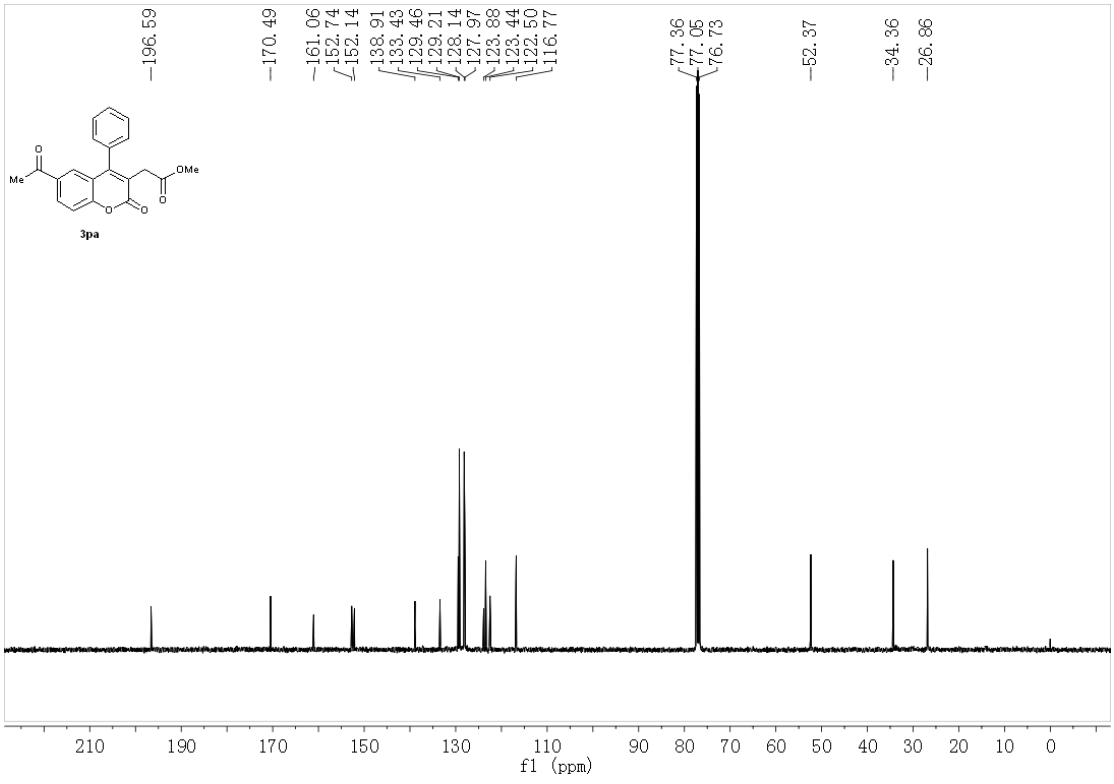
3.00
f1 (ppm)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77.05
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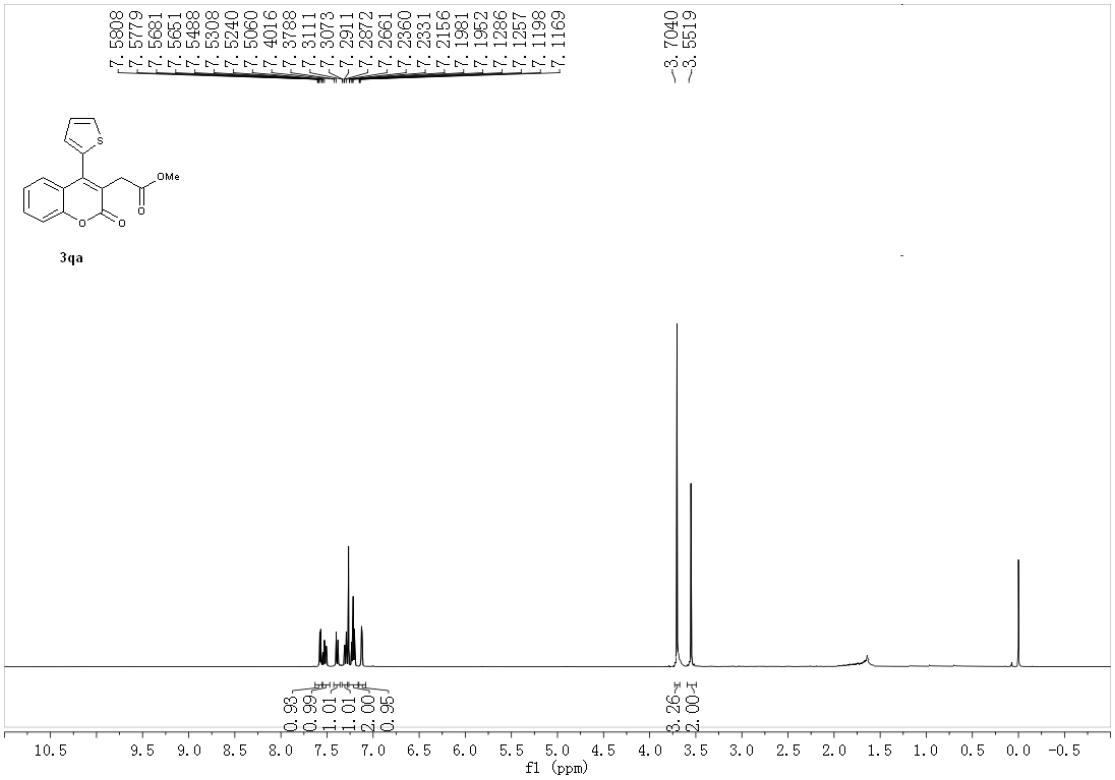
26.86
Me
OMe
3pa
f1 (ppm)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7.3111
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7.2911
7.2872
7.2661
7.2360
7.2331
7.2156
7.1981
7.1962
7.1286
7.1257
7.1198
7.1169
3.7040
3.5519
OMe
O
O
O
S
3qa
0.93
0.99
1.01
1.01
2.00
0.95
3.26
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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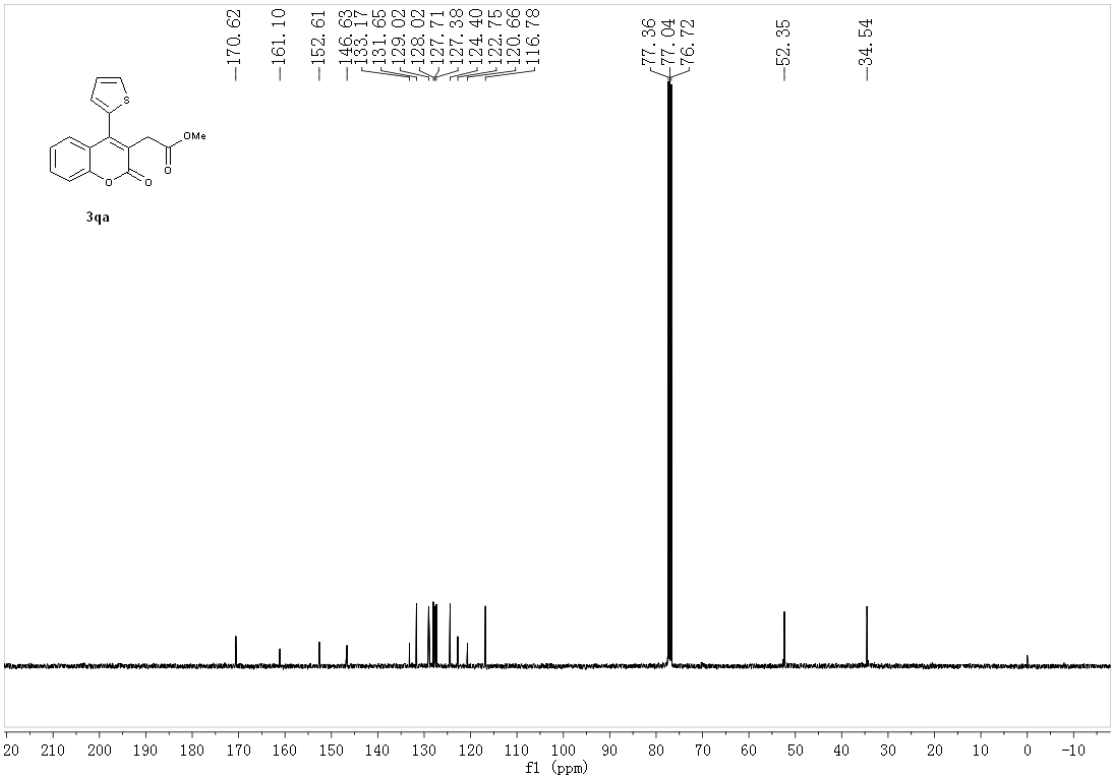
f1 (ppm)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77.36
77.04
76.72
52.35
34.54
OMe
O
O
O
S
3qa
20
210
200
190
180
170
160
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140
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120
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100
90
80
70
60
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40
30
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0
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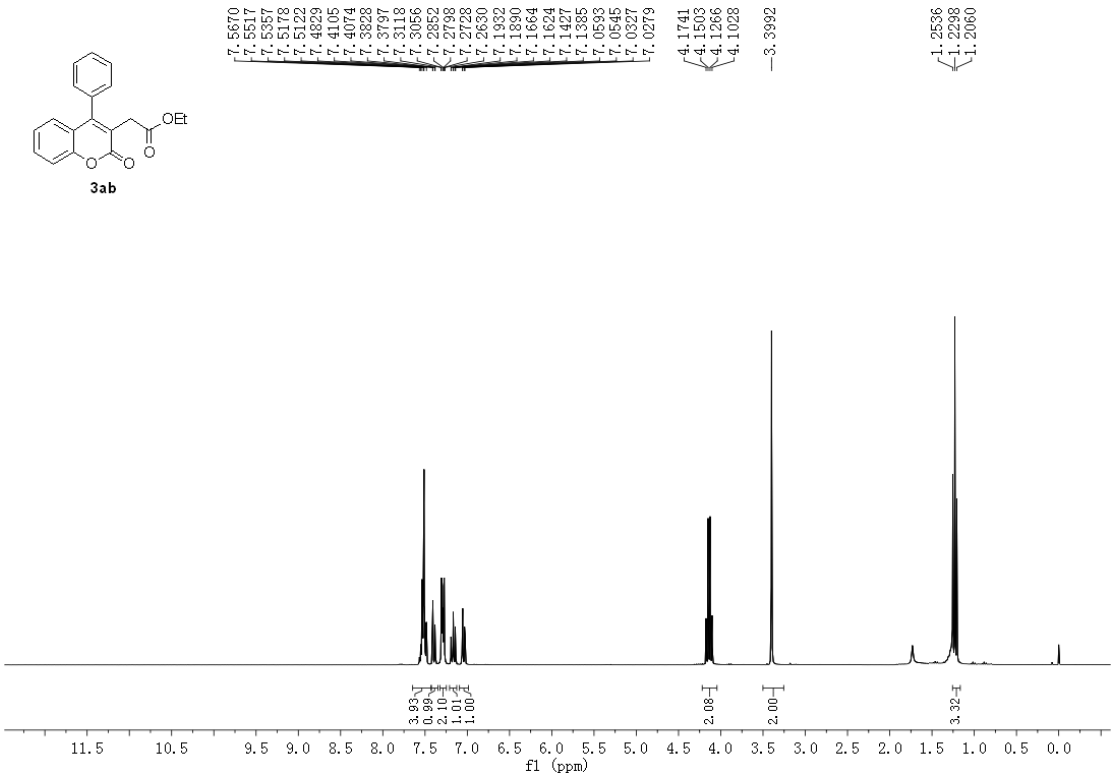
f1 (ppm)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7.2798
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7.1932
7.1890
7.1664
7.1624
7.1427
7.1385
7.0593
7.0545
7.0327
7.0279
4.1741
4.1503
4.1266
4.1028
3.3992
1.2536
1.2298
1.2060
OEt
O
O
3ab
3.93
0.99
2.10
1.01
1.00
2.08
2.00
3.32
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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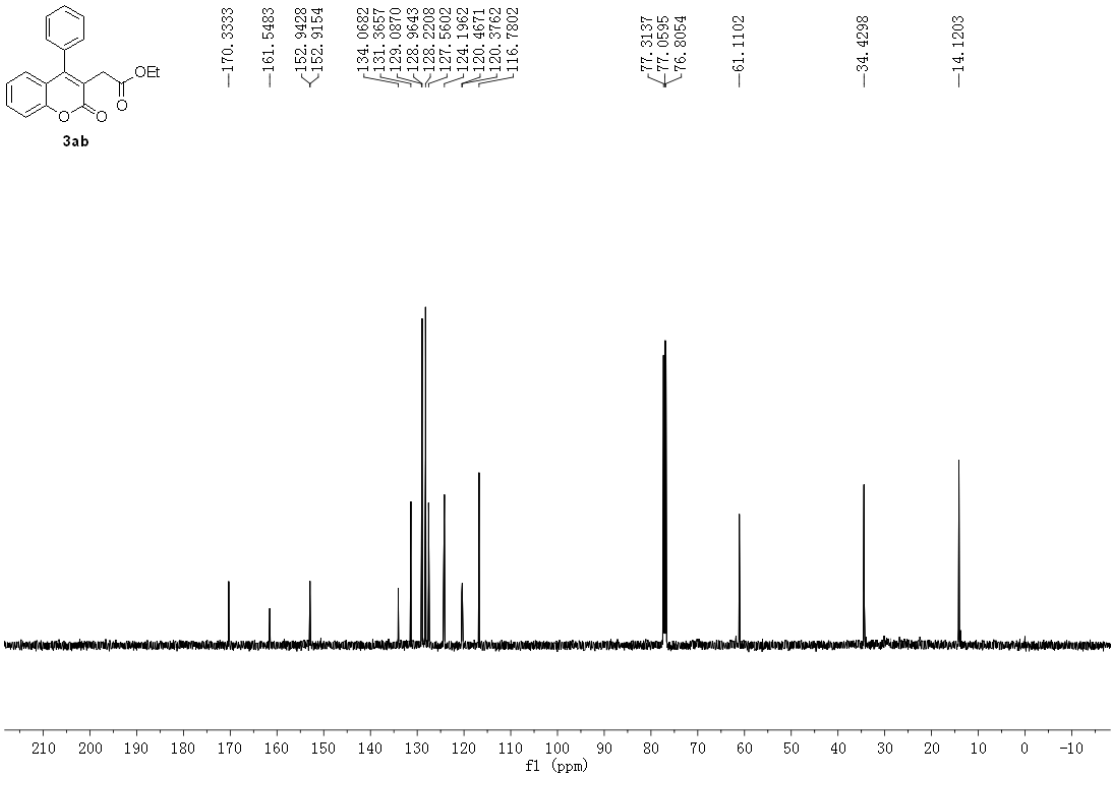
0.0
f1 (ppm)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77.0595
76.8054
61.1102
34.4298
14.1203
OEt
O
O
3ab
210
200
190
180
170
160
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140
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120
110
100
90
80
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0
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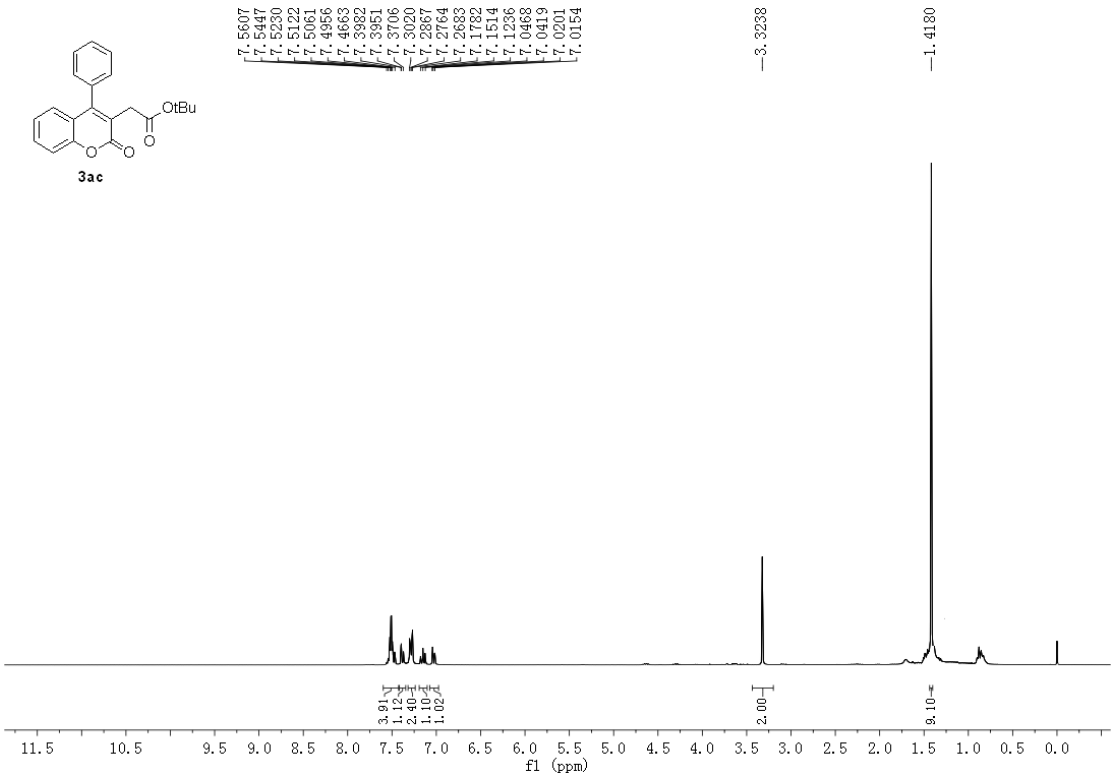
f1 (ppm)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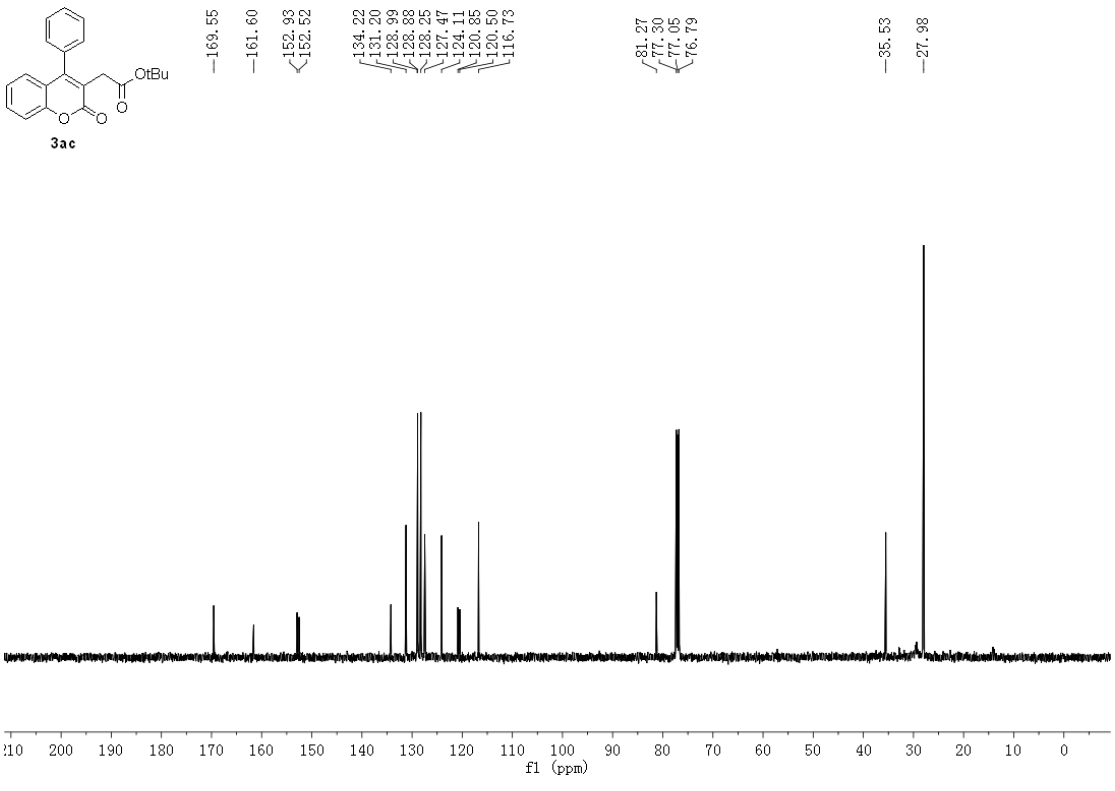
7.2764
7.2683
7.1782
7.1514
7.1236
7.0468
7.0419
7.0201
7.0154
3.3238
1.4180
OtBu
O
O
3ac
3.91
1.12
2.40
1.10
1.02
2.00
9.10
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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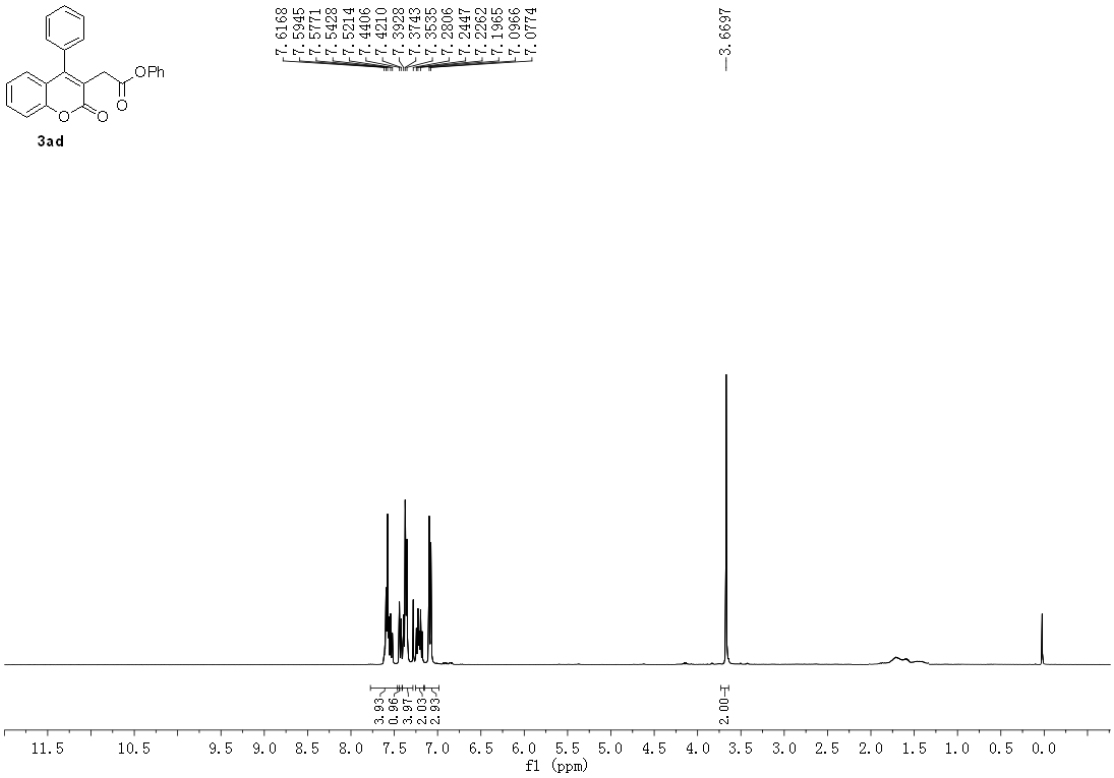
128.88
128.25
127.47
124.11
120.85
120.50
116.73
81.27
77.30
77.05
76.79
35.53
27.98
OtBu
O
O
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

OPh
O
O

3ad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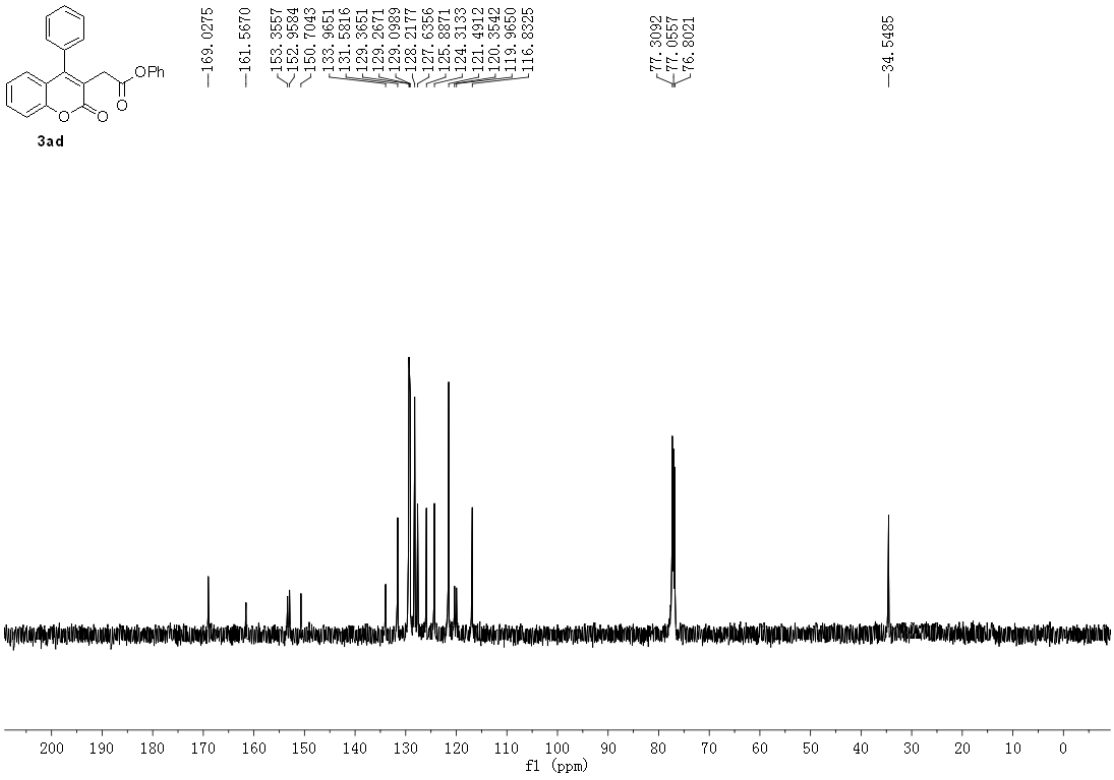
7.2447
7.2262
7.1965
7.0966
7.0774
3.6697
3.93
0.96
3.87
2.93
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

OPh
O
O

3ad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131.5816
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124.3133
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120.3542
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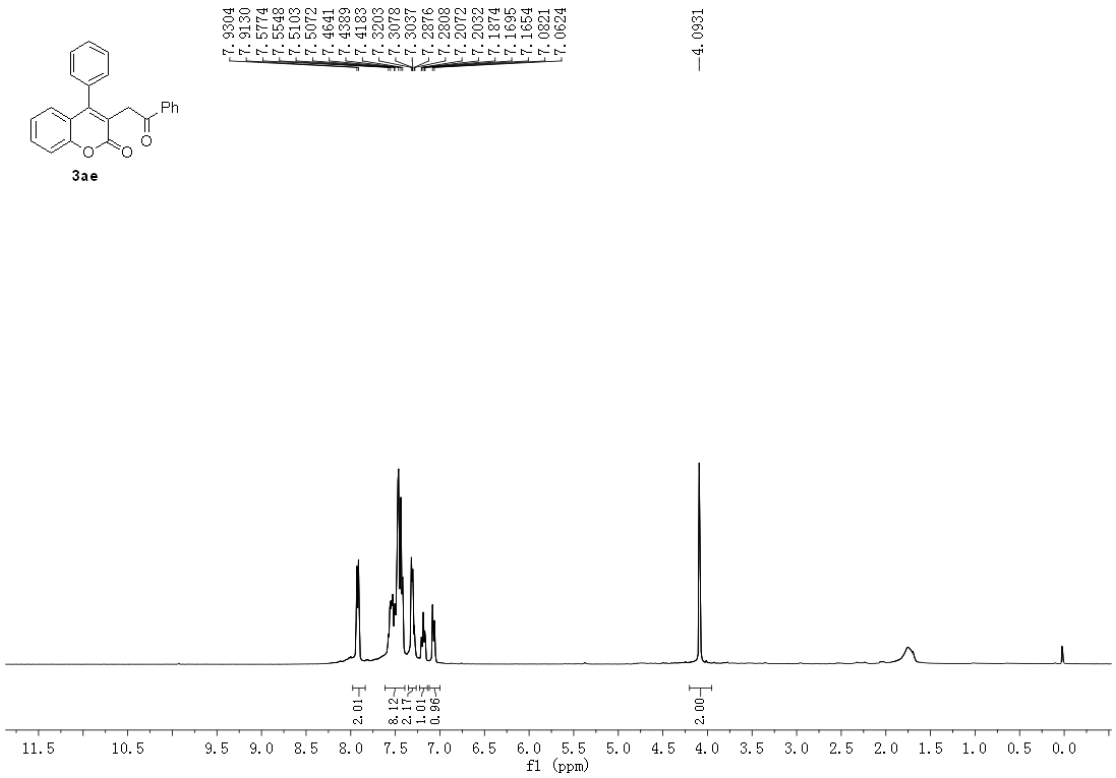
77.3092
77.0557
76.8021
34.5485
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.3037
7.2876
7.2808
7.2072
7.2032
7.1874
7.1695
7.1654
7.0821
7.0624
4.0931
Ph
O
O
3ae
2.01
8.12
2.17
1.01
0.96
2.00
11.5 10.5 9.5 9.0 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
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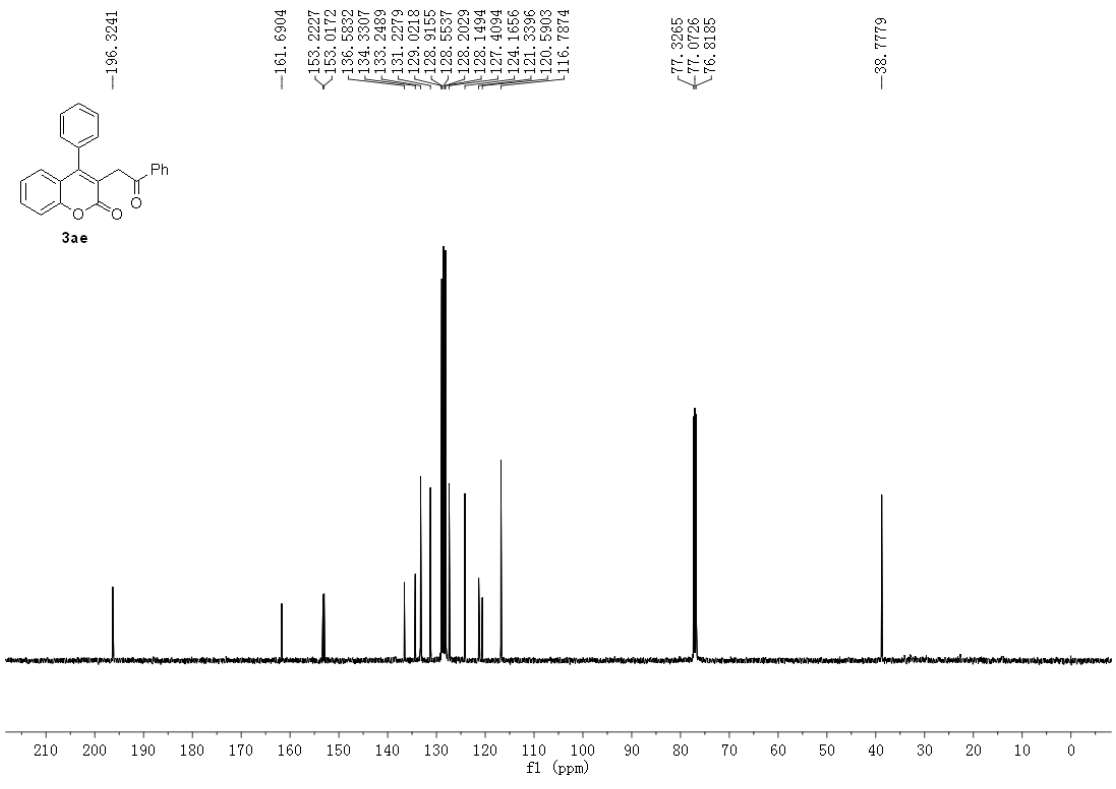
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128.9155
128.5537
128.2029
128.1494
127.4094
124.1656
121.3396
120.5903
116.7874
77.3265
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76.8185
38.7779
Ph
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O
3ae
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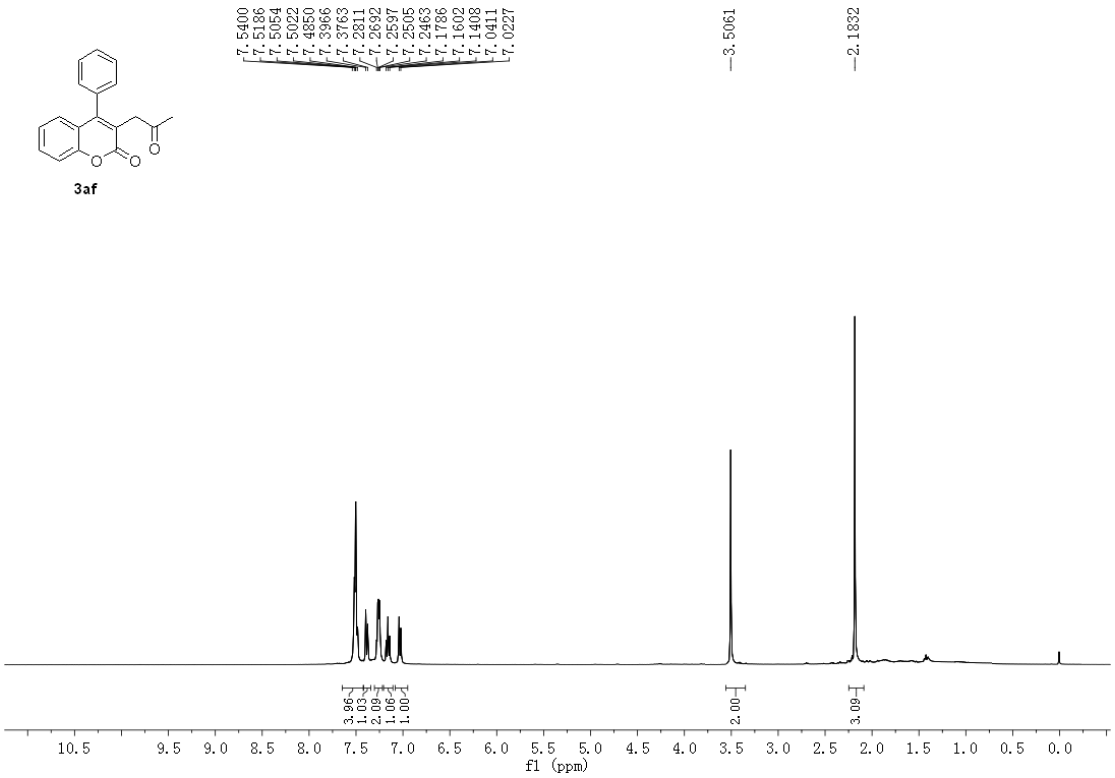
f1 (ppm)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7.2463
7.1786
7.1602
7.1408
7.0411
7.0227
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1.03
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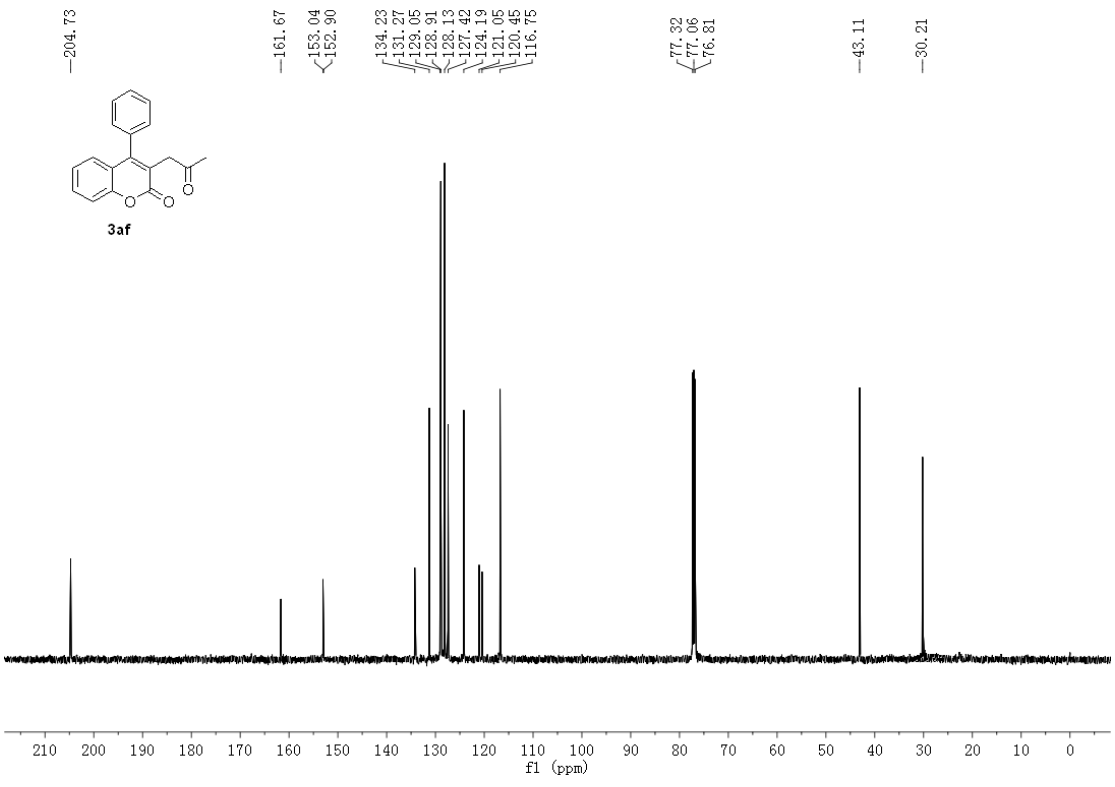
1.06
1.00
2.00
3.09
f1 (ppm)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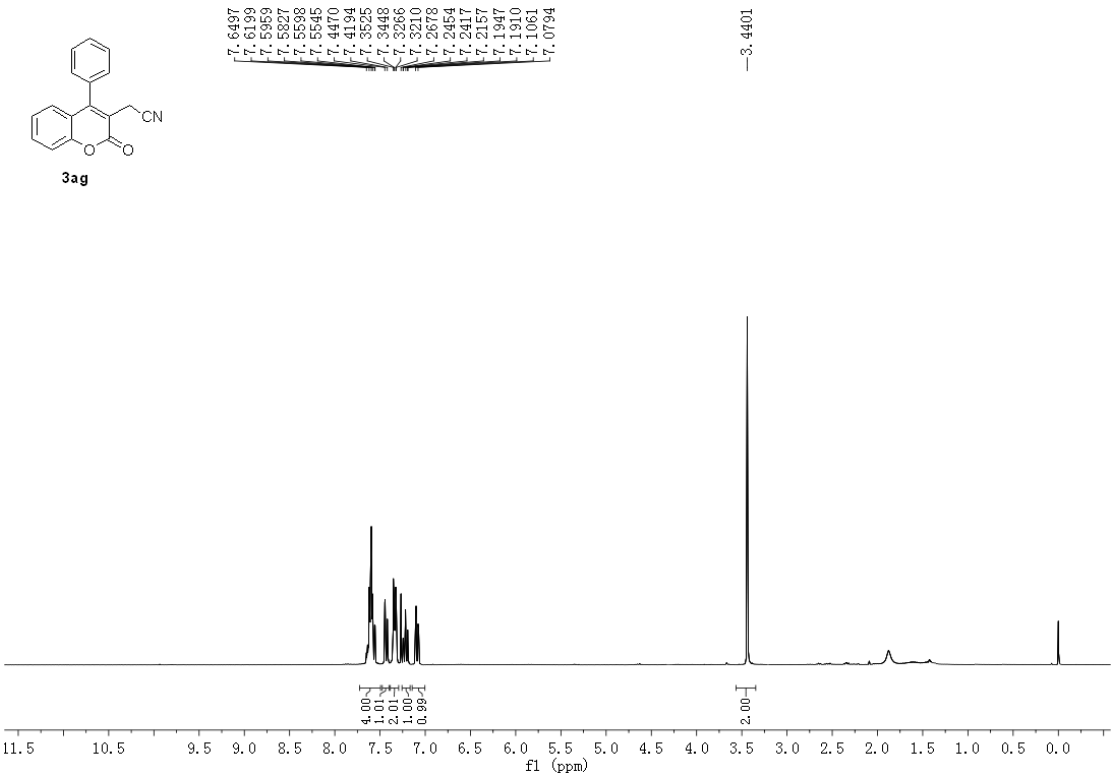
3af
f1 (ppm)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7.3266
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7.2417
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7.1910
7.1061
7.0794
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CN
O
O
3ag
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1.01
2.01
1.00
0.99
2.00
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10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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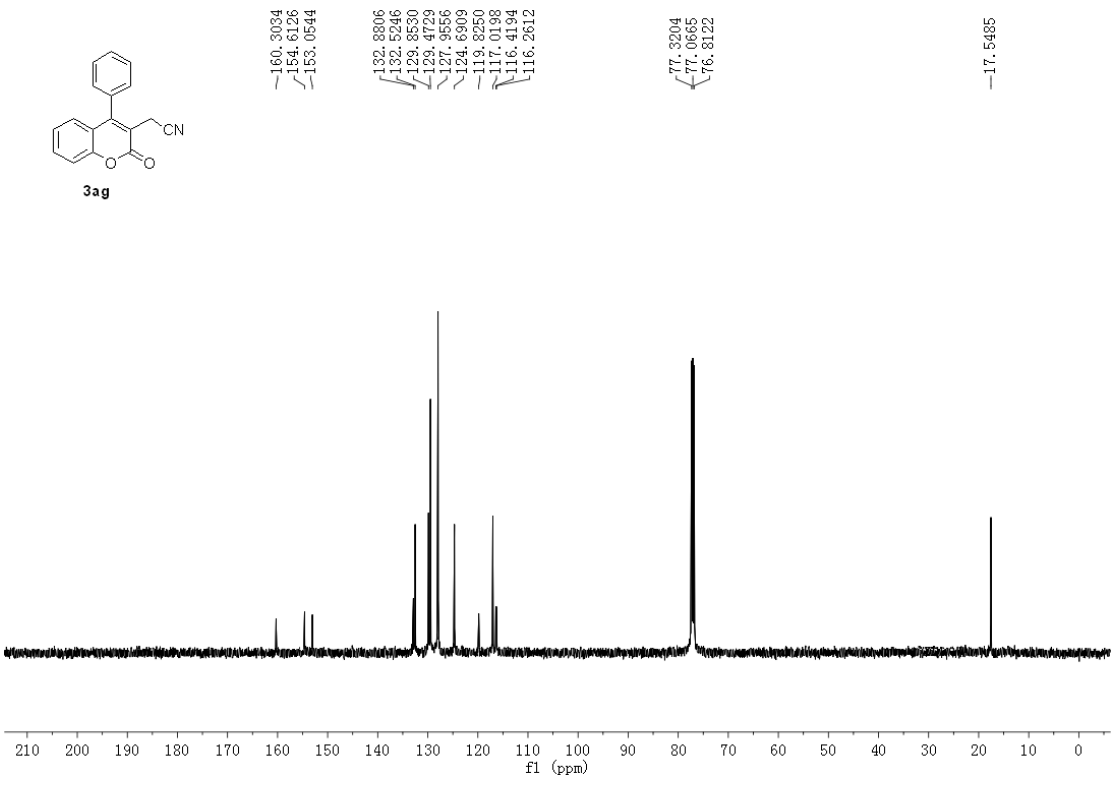
f1 (ppm)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117.0198
116.4194
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77.3204
77.0665
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CN
O
O
3ag
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200
190
180
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130
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10
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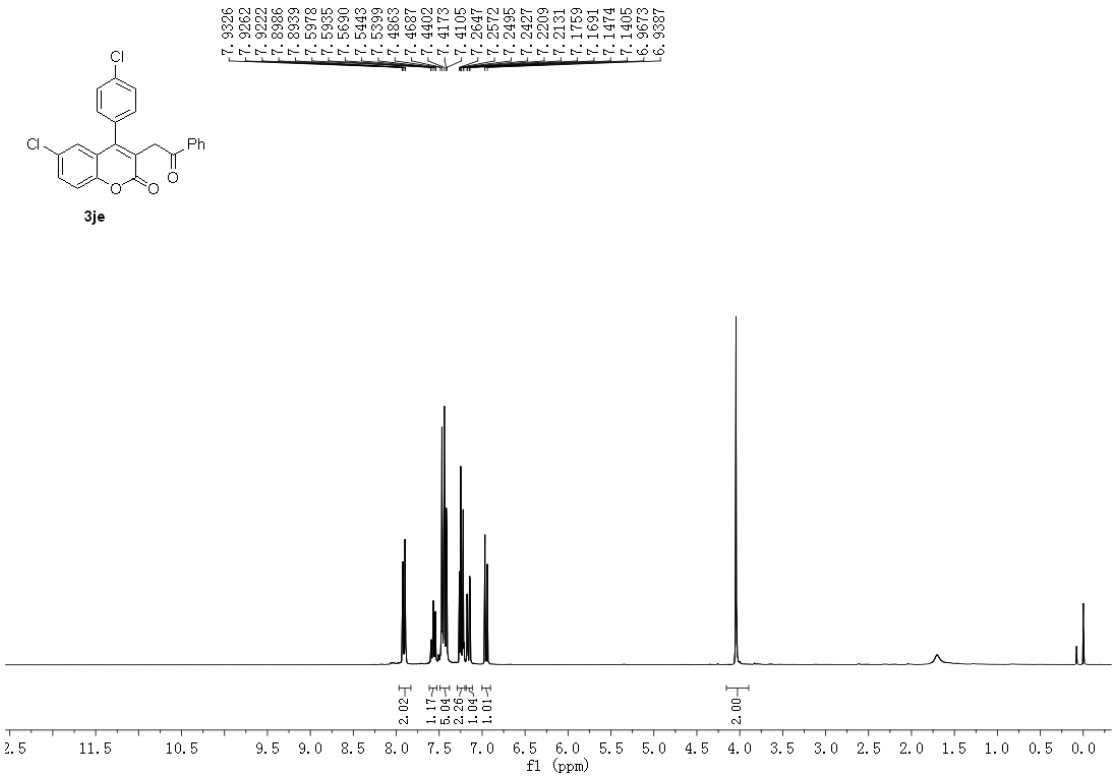
f1 (ppm)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7.4687
7.4402
7.4173
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7.2647
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7.2495
7.2427
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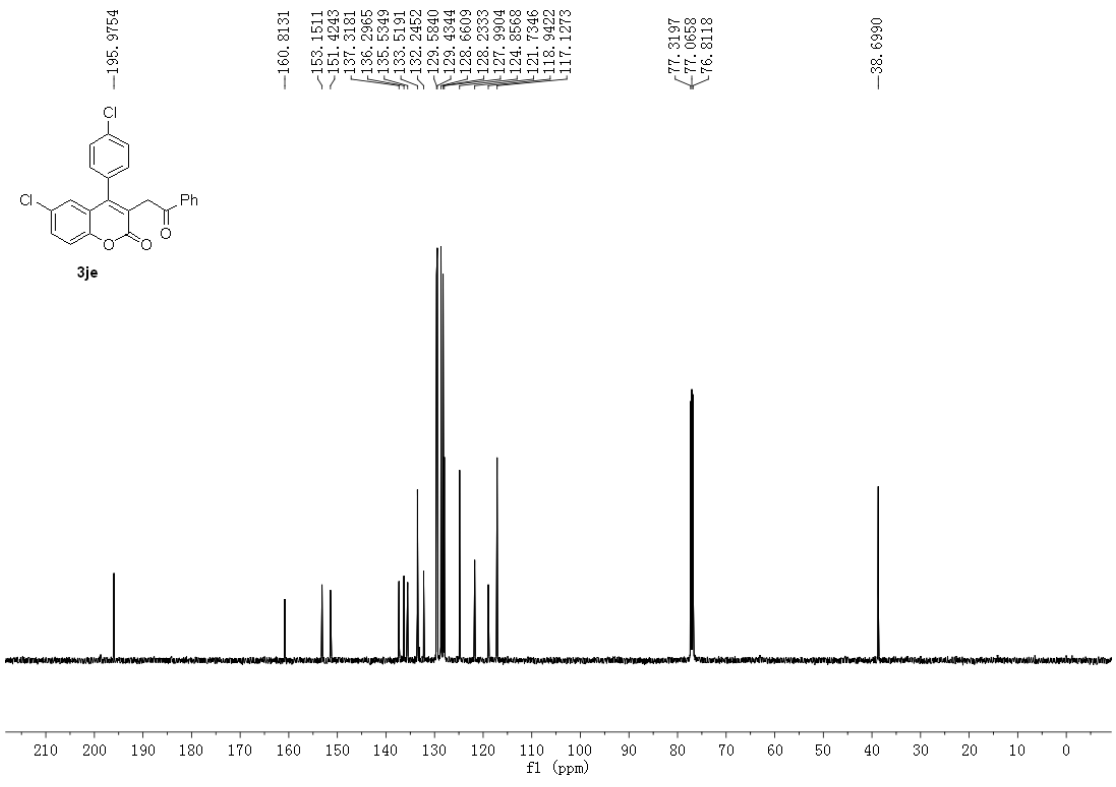
7.2131
7.1759
7.1691
7.1474
7.1405
6.9673
6.9387
Cl
Cl
Ph
O
O
3je
2.02
1.17
5.04
2.26
1.04
1.01
2.00
f1 (ppm)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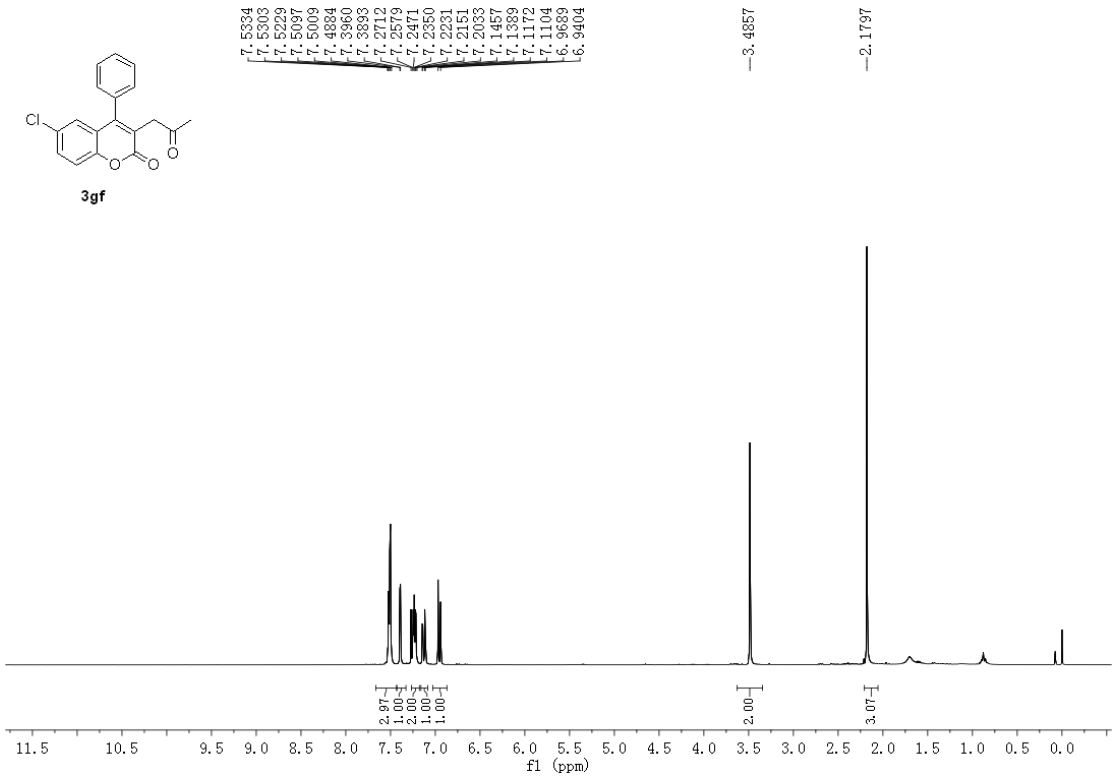
38.6990
Cl
Cl
Ph
O
O
3je
f1 (ppm)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6.9404
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2.00
1.00
1.00
2.00
3.07
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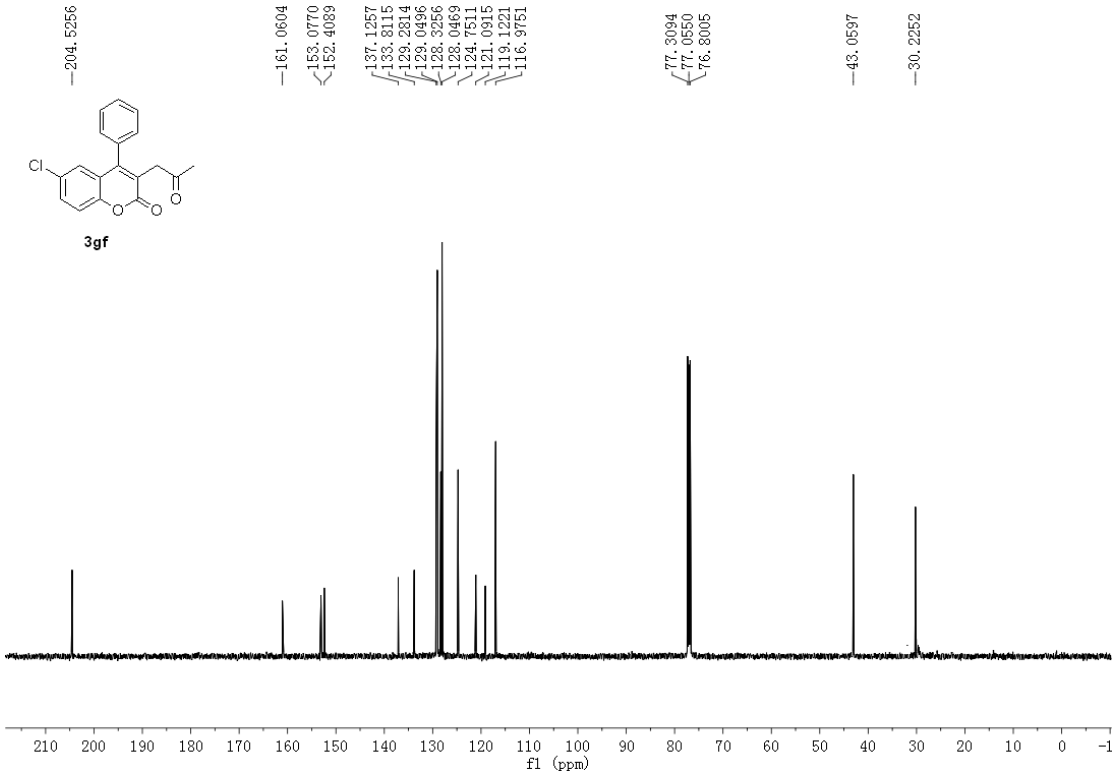
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77.0550
76.8005
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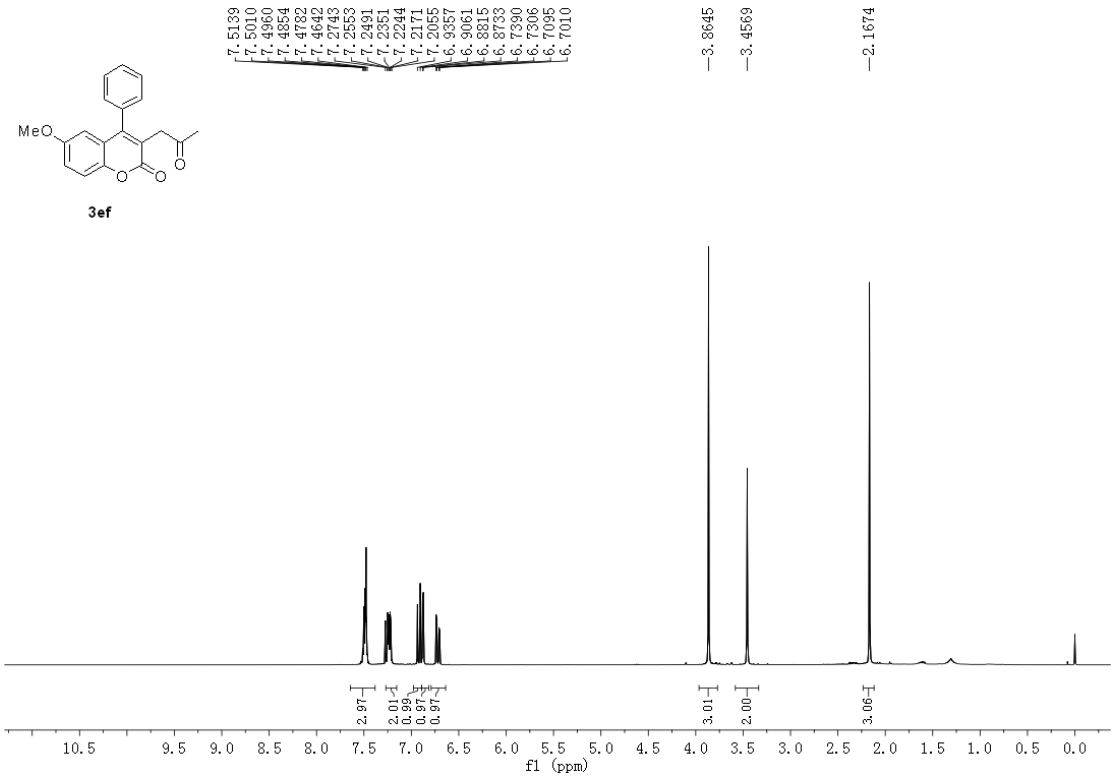
f1 (ppm)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6.8815
6.8733
6.7390
6.7306
6.7095
6.7010
3.8645
3.4569
2.1674
MeO
O
O
3ef
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2.00
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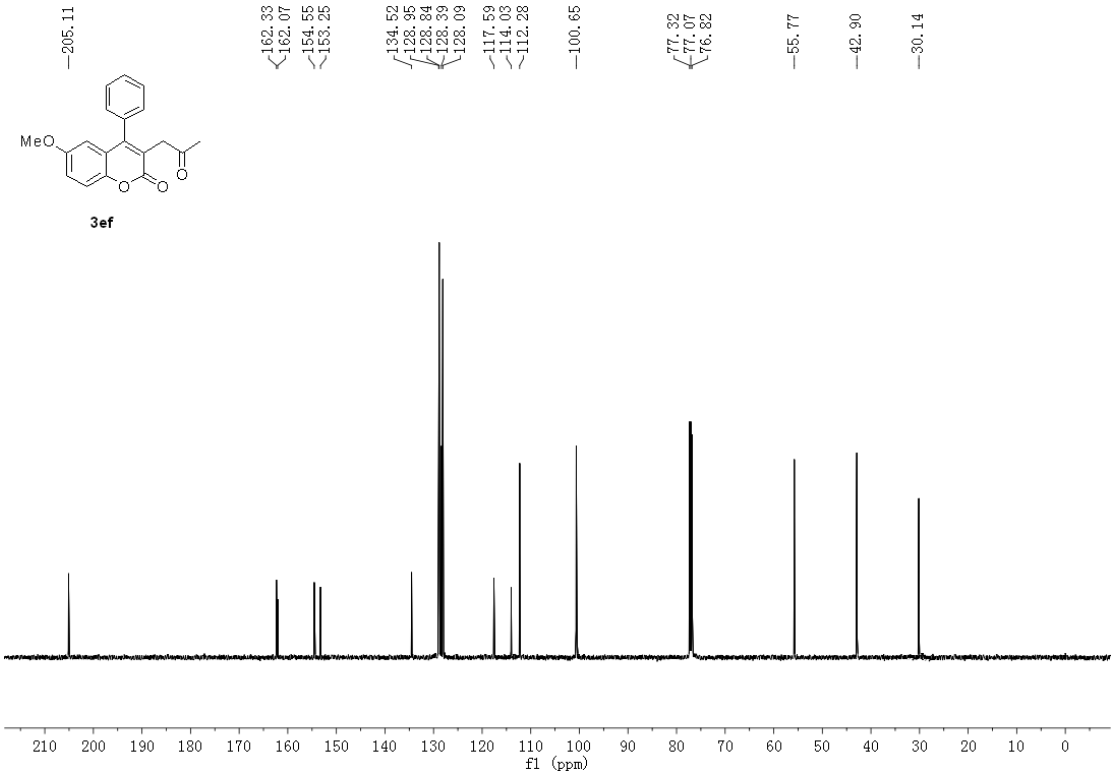
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100.65
77.32
77.07
76.82
55.77
42.90
30.14
MeO
O
O
3ef
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200
190
180
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150
140
130
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100
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70
60
50
40
30
20
10
0
f1 (ppm)