

**Metal-free Catalytic Cascade to Chromones: Direct
Coupling of Salicylaldehydes and Activated Alkynes
Triggered by Aryloxy Radical**

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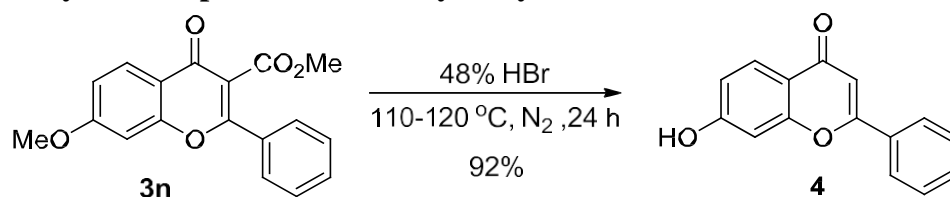
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General experimental procedure

^1H - and ^{13}C -NMR spectra were recorded on Varian 600 MHz spectrometers in CDCl_3 (with tetramethylsilane) solutions and chemical shifts (δ , ppm) were determined with internal solvent signal as reference (7.26 for ^1H NMR and 77.0 for ^{13}C NMR). Flash column chromatography was performed on Silica Gel (300-400 mesh) with an appropriate solvent system (see details below).

Decarboxylation of product **3n** to 7-hydroxyflavone **4**¹



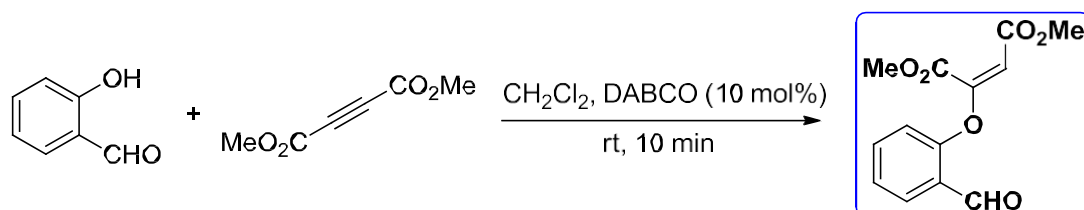
A mixture of methyl 7-methoxyflavone-3-carboxylate (**3n**, 0.20 mmol) and 48% aqueous hydrobromic acid (3.0 mL) was heated at 110-120 °C under nitrogen atmosphere for 24 h. After completion of the reaction, the excess hydrobromic acid was distilled off under reduced pressure, and the residue was purified by silica gel column with petroleum ether/ethyl acetate (10:1) as the eluent to give the analytically pure 7-hydroxyflavone (**4**)² as a white solid in 92% yield. ^1H NMR ($\text{DMSO}-d_6$, 600 MHz, ppm) δ 10.82 (s, br, 1 H), 8.04 (dd, $J = 8.22, 1.38$ Hz, 2 H), 7.89 (d, $J = 8.64$ Hz, 1 H), 7.59-7.53 (m, 3 H), 7.00 (d, $J = 2.22$ Hz, 1 H), 6.93 (dd, $J = 8.67, 2.28$ Hz, 1 H), 6.88 (s, 1 H). ^{13}C NMR ($\text{DMSO}-d_6$, 150 MHz, ppm) δ 176.8, 163.2, 162.4, 157.9, 131.9, 131.7, 129.5, 127.0, 126.6, 116.6, 115.5, 107.1, 103.0. And the spectra data are in accordance with literature.¹

General procedure for the syntheses of methyl arylpropiolates³

To a solution of aryl iodide (2.0 mmol) and methyl propiolate (672.6 mg, 8.0 mmol) in anhydrous THF (6.0 mL) were added $\text{PdCl}_2(\text{PPh}_3)_2$ (28.1 mg, 2 mol%), CuI (15.3 mg, 4 mol%), and anhydrous K_2CO_3 (1.104 g, 8.0 mmol) under N_2 atmosphere. The obtained mixture was stirred at 65 °C for 10 h. Then THF was evaporated under vacuum and the residue was extracted with EtOAc. After concentration, the crude product was purified by silica gel column chromatography with petroleum

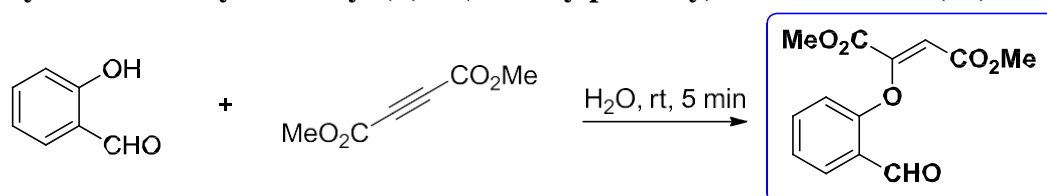
ether/EtOAc (15:1 to 12:1) as the eluent to give the analytically pure methyl arylpropiolate. Methyl arylpropiolates **2p-r** were obtained according to the above procedures in 70-85% isolated yields.

Synthesis of ethyl dimethyl (*E*)-2-(2-formylphenoxy)-2-butenedioate (**5a**)⁴



Dimethyl 2-butynedioate (284.2 mg, 2.0 mmol), DABCO (22.4 mg, 0.2 mmol), and salicylaldehyde (244.3 mg, 2.0 mmol) were stirred in CH₂Cl₂ (16 mL) at room temperature for 10 min. The solvent was evaporated under vacuum and the residue was purified by silica gel column chromatography with petroleum ether/EtOAc (5:1) as the eluent to give 81% total yield (428.1 mg) of the vinyl ethers, with *E*-isomer **5a** as the major product, and *Z*-isomer **5b** as the minor product (*E/Z* 91:9). ¹H NMR (CDCl₃, 600 MHz, ppm) δ 10.53 (s, 0.08 H; *Z*-isomer) 10.27 (s, 1 H; *E*-isomer), 7.96 (dd, *J* = 7.80, 1.62 Hz, 1 H; *E*-isomer), 7.91 (dd, *J* = 7.74, 1.62 Hz, 0.09 H; *Z*-isomer), 7.66 (td, *J* = 7.80, 1.74 Hz, 1 H; *E*-isomer), 7.48 (td, *J* = 7.80, 1.74 Hz, 0.11 H; *Z*-isomer), 7.39 (t, *J* = 7.59 Hz, 1 H; *E*-isomer), 7.19 (d, *J* = 8.22 Hz, 1 H; *E*-isomer), 7.17 (d, *J* = 7.38 Hz, 0.09 H; *Z*-isomer), 6.82 (d, *J* = 8.28 Hz, 0.10 H; *Z*-isomer), 6.74 (s, 0.08 H; *Z*-isomer), 5.23 (s, 1 H; *E*-isomer), 3.91 (s, 3 H; *E*-isomer), 3.76 (s, 0.26 H; *Z*-isomer), 3.70 (s, 0.27 H; *Z*-isomer), 3.68 (s, 3 H; *E*-isomer).

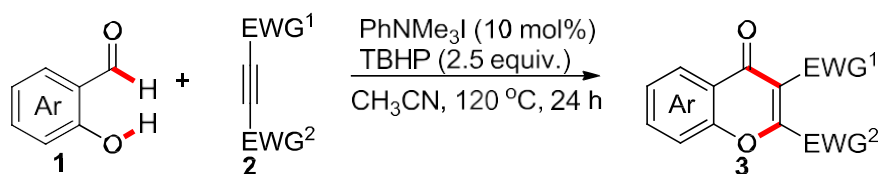
Synthesis of ethyl dimethyl (*Z*)-2-(2-formylphenoxy)-2-butenedioate (**5b**)⁵



Salicylaldehyde (244.3 mg, 2.0 mmol) was dissolved in aqueous solution of K₂CO₃ (0.276 g, 2.0 mmol), and then dimethyl 2-butynedioate (284.2 mg, 2.0 mmol) was added to the resulting solution. The reaction mixture was stirred vigorously at room

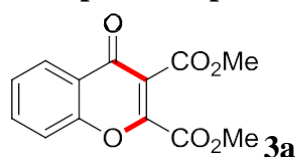
temperature for 5 min., and was extracted with EtOAc (20 mL × 3). After concentration, the crude product was purified by silica gel column chromatography with petroleum ether/EtOAc (5:1) as the eluent to give 67% total yield (354.1 mg) of vinyl ethers, with *Z*-isomer **5b** as the major product, and *E*-isomer **5a** as the minor product (*E/Z* 4:96). ¹H NMR (CDCl₃, 600 MHz, ppm) δ 10.54 (s, 1 H; *Z*-isomer), 10.28 (s, 0.03 H; *E*-isomer), 7.96 (dd, *J* = 7.74, 1.68 Hz, 0.04 H; *E*-isomer), 7.91 (dd, *J* = 7.74, 1.74 Hz, 1 H; *Z*-isomer), 7.66 (td, *J* = 7.80, 1.74 Hz, 0.05 H; *E*-isomer), 7.49 (td, *J* = 7.82, 1.80 Hz, 1 H; *Z*-isomer), 7.40 (t, *J* = 7.56 Hz, 0.05 H; *E*-isomer), 7.18 (t, *J* = 7.53 Hz, 1 H; *Z*-isomer), 6.83 (dd, *J* = 8.22, 0.36 Hz, 1 H; *Z*-isomer), 6.74 (s, 1 H; *Z*-isomer), 5.23 (s, 0.04 H), 3.92 (s, 0.09 H; *E*-isomer), 3.76 (s, 3 H; *Z*-isomer), 3.71 (s, 3 H; *Z*-isomer), 3.69 (s, 0.13 H; *E*-isomer).

General procedure for the synthesis of chromones

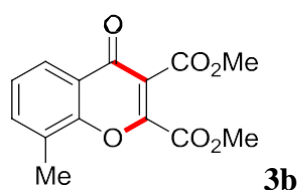


To an oven-dried reaction vessel was charged with trimethylphenylammonium iodide (5.3 mg, 0.02 mmol, 10 mol%), salicylaldehydes (0.20 mmol, 1.0 equiv.), anhydrous acetonitrile (2.0 mL), alkynes (0.30 mmol, 1.5 equiv.), and *tert*-butyl hydroperoxide (90 μ L, 5.0-6.0 M in decane, 2.5 equiv.) sequentially. Then the flask was sealed directly, placed into an oil bath, and stirred at 120 °C. After 24 h, the resulting mixture was cooled to room temperature, filtered through a short silica gel pad, and washed with ethyl acetate. After concentrated under vacuum, the residue was purified by silica gel column with petroleum ether/ethyl acetate as the eluent to give the analytically pure chromones.

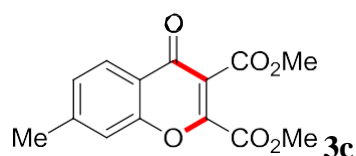
The spectroscopic data of chromones



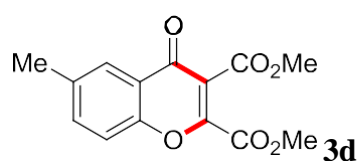
Dimethyl chromone-2,3-dicarboxylate (3a).⁶ Pale yellow solid. Isolated yield 71% (37.6 mg, from 24.5 mg of **1a**), eluent: petroleum ether/EtOAc 6:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 8.21 (d, *J* = 7.98 Hz, 1 H), 7.77 (t, *J* = 7.83 Hz, 1 H), 7.58 (d, *J* = 8.52 Hz, 1 H), 7.47 (t, *J* = 7.53 Hz, 1 H), 4.00 (s, 3 H), 3.96 (s, 3 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 174.9, 163.7, 160.2, 155.1, 149.5, 135.3, 126.4, 126.1, 123.6, 122.4, 118.6, 53.9, 53.2. HR-ESI-MS: [M+Na]⁺ *m/z* calcd. for C₁₃H₁₀O₆Na: 285.0375; found 285.0374.



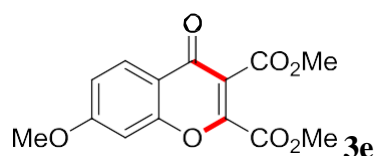
Dimethyl 8-methylchromone-2,3-dicarboxylate (3b). Pale yellow solid. Isolated yield 63% (35.5 mg, from 27.8 mg of **1b**), eluent: petroleum ether/EtOAc 6:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 8.01 (d, *J* = 7.92 Hz, 1 H), 7.57 (d, *J* = 7.26 Hz, 1 H), 7.33 (t, *J* = 7.65 Hz, 1 H), 4.00 (s, 3 H), 3.95 (s, 3 H), 2.51 (s, 3 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 175.2, 163.7, 160.3, 153.6, 149.2, 136.1, 128.2, 125.9, 123.53, 123.47, 122.0, 53.8, 53.1, 15.3. HR-ESI-MS: [M+H]⁺ *m/z* calcd. for C₁₄H₁₃O₆: 277.0712; found 277.0710.



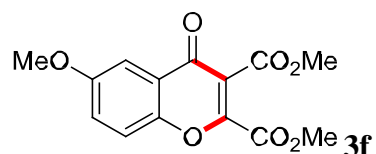
Dimethyl 7-methylchromone-2,3-dicarboxylate (3c). Pale yellow solid. Isolated yield 73% (40.9 mg, from 27.6 mg of **1c**), eluent: petroleum ether/EtOAc 6:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 8.09 (d, *J* = 8.16 Hz, 1 H), 7.38 (s, 1 H), 7.28 (dd, *J* = 8.16, 0.84 Hz, 1 H), 4.00 (s, 3 H), 3.96 (s, 3 H), 2.51 (s, 3 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 174.7, 163.8, 160.3, 155.3, 149.1, 147.0, 128.0, 125.8, 122.4, 121.4, 118.2, 53.8, 53.1, 21.9. HR-ESI-MS: [M+Na]⁺ *m/z* calcd. for C₁₄H₁₂O₆Na: 299.0532; found 299.0527.



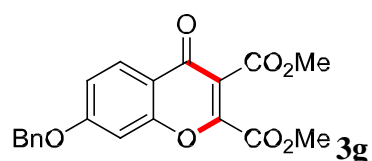
Dimethyl 6-methylchromone-2,3-dicarboxylate (3d). Pale yellow solid. Isolated yield 75% (41.9 mg, from 27.5 mg of **1d**), eluent: petroleum ether/EtOAc 6:1. ^1H NMR (CDCl_3 , 600 MHz, ppm) δ 7.96 (s, 1 H), 7.56 (dd, $J = 8.61, 2.04$ Hz, 1 H), 7.46 (d, $J = 8.64$ Hz, 1 H), 3.99 (s, 3 H), 3.95 (s, 3 H), 2.45 (s, 3 H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm) δ 174.9, 163.8, 160.3, 153.4, 149.2, 136.7, 136.5, 125.2, 123.3, 122.2, 118.3, 53.8, 53.1, 20.9. HR-ESI-MS: $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{14}\text{H}_{13}\text{O}_6$: 277.0712; found 277.0709.



Dimethyl 7-methoxychromone-2,3-dicarboxylate (3e). Pale yellow solid. Isolated yield 80% (47.1 mg, from 30.7 mg of **1e**), eluent: petroleum ether/EtOAc 40:1. ^1H NMR (CDCl_3 , 400 MHz, ppm) δ 8.08 (d, $J = 8.94$ Hz, 1 H), 7.00 (dd, $J = 8.91, 2.40$ Hz, 1 H), 6.93 (d, $J = 2.34$ Hz, 1 H), 3.98 (s, 3 H), 3.94 (s, 3 H), 3.90 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm) δ 173.9, 165.3, 163.8, 160.2, 157.0, 148.8, 127.3, 122.7, 117.4, 116.1, 100.4, 56.0, 53.8, 53.1. HR-ESI-MS: $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{14}\text{H}_{13}\text{O}_7$: 293.0661; found 293.0658.

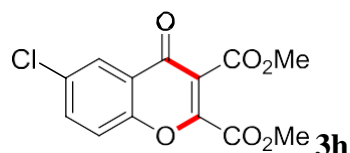


Dimethyl-6-methoxychromone-2,3-dicarboxylate (3f). Pale yellow solid. Isolated yield 78% (45.4 mg, from 30.2 mg of **1f**), eluent: petroleum ether/EtOAc 5:1. ^1H NMR (CDCl_3 , 600 MHz, ppm) δ 7.51-7.49 (m, 2 H), 7.33 (dt, $J = 9.24, 2.61$ Hz, 1 H), 3.98 (s, 3 H), 3.95 (s, 3 H), 3.88 (s, 3 H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm) δ 174.7, 163.9, 160.3, 157.8, 149.9, 149.0, 125.4, 124.4, 121.5, 120.0, 104.9, 56.0, 53.8, 53.1. HR-ESI-MS: $[\text{M}+\text{Na}]^+$ m/z calcd. for $\text{C}_{14}\text{H}_{12}\text{O}_7\text{Na}$: 315.0481; found 315.0478.

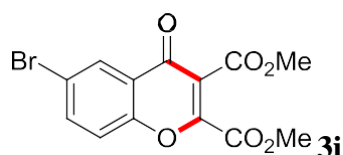


Dimethyl 7-benzyloxychromone-2,3-dicarboxylate (3g).⁷ White solid. Isolated yield 63% (46.4 mg, from 45.5 mg of **1g**), eluent: petroleum ether/EtOAc 8:1. ^1H NMR

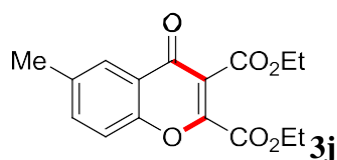
(CDCl₃, 600 MHz, ppm) δ 8.12 (dd, $J = 8.94, 1.92$ Hz, 1 H), 7.44-7.40 (m, 4 H), 7.39-7.36 (m, 1 H), 7.11-7.09 (m, 1 H), 7.03 (d, $J = 2.22$ Hz, 1 H), 5.17 (s, 2 H), 3.99 (s, 3 H), 3.96 (s, 3 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 174.0, 164.3, 163.8, 160.2, 157.0, 148.9, 135.2, 128.8, 128.5, 127.51, 127.49, 122.7, 117.7, 116.6, 101.5, 70.8, 53.8, 53.1. HR-ESI-MS: [M+H]⁺ m/z calcd. for C₂₀H₁₇O₇: 369.0974; found 369.0974.



Dimethyl 6-chlorochromone-2,3-dicarboxylate (3h). White solid. Isolated yield 52% (30.8 mg, from 31.2 mg of **1h**), eluent: petroleum ether/EtOAc 6:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 8.17 (d, $J = 2.58$ Hz, 1 H), 7.71 (dd, $J = 8.97, 2.64$ Hz, 1 H), 7.55 (d, $J = 8.94$ Hz, 1 H), 4.01 (s, 3 H), 3.97 (s, 3 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 173.8, 163.3, 159.9, 153.4, 149.6, 135.5, 132.6, 125.4, 124.5, 122.3, 120.3, 54.0, 53.3. HR-ESI-MS: [M+Na]⁺ m/z calcd. for C₁₃H₉ClO₆Na: 318.9985; found 318.9984.

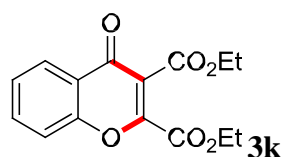


Dimethyl 6-bromochromone-2,3-dicarboxylate (3i). White solid. Isolated yield 57% (38.9 mg, from 40.2 mg of **1i**), eluent: petroleum ether/EtOAc 5:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 8.33 (d, $J = 2.40$ Hz, 1 H), 7.85 (dd, $J = 8.91, 2.46$ Hz, 1 H), 7.49 (d, $J = 8.94$ Hz, 1 H), 4.00 (s, 3 H), 3.97 (s, 3 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 173.6, 163.3, 159.9, 153.9, 149.6, 138.3, 128.6, 124.8, 122.4, 120.5, 120.1, 54.0, 53.3. HR-ESI-MS: [M+Na]⁺ m/z calcd. for C₁₃H₉BrO₆Na: 362.9480, 364.9460; found 362.9476, 364.9459.

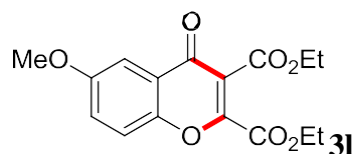


Diethyl 6-methylchromone-2,3-dicarboxylate (3j). Pale yellow solid. Isolated yield 69% (42.4 mg, from 27.4 mg of **1d**), eluent: petroleum ether/EtOAc 6:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 7.92 (s, 1 H), 7.52 (dd, $J = 8.49, 2.16$ Hz, 1 H), 7.44 (td, $J = 8.64, 2.76$ Hz, 1 H), 4.43-4.39 (m, 4 H), 2.42 (s, 3 H), 1.40-1.35 (m, 6 H). ¹³C NMR

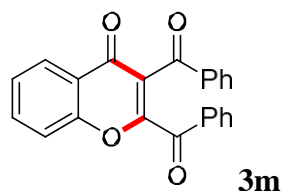
(CDCl₃, 150 MHz, ppm) δ 175.1, 163.4, 159.8, 153.4, 149.3, 136.5, 136.4, 125.1, 123.3, 122.3, 118.3, 63.3, 62.2, 20.9, 14.0, 13.9. HR-ESI-MS: [M+H]⁺ m/z calcd. for C₁₆H₁₇O₆: 305.1025; found 305.1023.



Diethyl chromone-2,3-dicarboxylate (3k). White solid. Isolated yield 65% (38.2 mg, from 24.6 mg of **1a**), eluent: petroleum ether/EtOAc 6:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 8.19-8.18 (m, 1 H), 7.76-7.73 (m, 1 H), 7.57 (d, J = 8.04 Hz, 1 H), 7.45 (td, J = 7.56, 0.96 Hz, 1 H), 4.45-4.41 (m, 4 H), 1.40-1.38 (m, 6 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 175.1, 163.2, 159.7, 155.2, 149.5, 135.2, 126.3, 126.0, 123.6, 122.5, 118.6, 63.4, 62.3, 14.0, 13.9. HR-ESI-MS: [M+Na]⁺ m/z calcd. for C₁₅H₁₄O₆Na: 313.0688; found 313.0688.

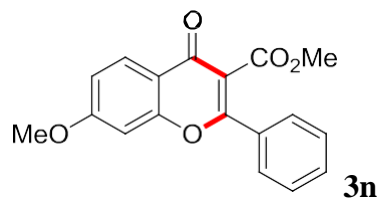


Diethyl 6-methoxychromone-2,3-dicarboxylate (3l). Very viscous yellow oil. Isolated yield 69% (44.3 mg, from 30.5 mg of **1f**), eluent: petroleum ether/EtOAc 6:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 7.50-7.48 (m, 2 H), 7.32-7.29 (m, 1 H), 4.43-4.00 (m, 4 H), 1.40-1.35 (m, 6 H). ¹³C NMR (CDCl₃, 150 MHz, ppm) δ 174.9, 163.4, 159.7, 157.7, 150.0, 149.1, 125.3, 124.4, 121.6, 120.1, 104.8, 63.3, 62.2, 55.9, 14.0, 13.9. HR-ESI-MS: [M+H]⁺ m/z calcd. for C₁₆H₁₇O₇: 321.0974; found 321.0971.

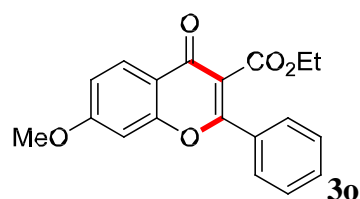


(4-Oxo-4H-chromene-2,3-diyl)bis(phenylmethanone) (3m).⁸ White solid. Isolated yield 70% (52.0 mg, from 25.6 mg of **1a**), eluent: petroleum ether/EtOAc 5:1. ¹H NMR (CDCl₃, 600 MHz, ppm) δ 8.27 (d, J = 7.92 Hz, 1 H), 7.95 (d, J = 7.44 Hz, 2 H), 7.89 (dd, J = 8.22, 1.02 Hz, 2 H), 7.79 (td, J = 7.82, 1.32 Hz, 1 H), 7.65 (t, J = 7.44 Hz, 1 H), 7.58-7.49 (m, 5 H), 7.44 (t, J = 7.77 Hz, 2 H). ¹³C NMR (CDCl₃, 150 MHz,

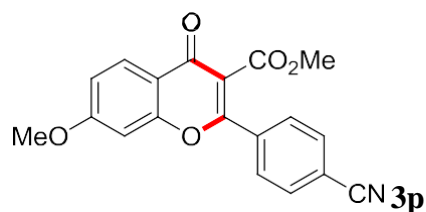
ppm) δ 191.6, 187.3, 175.9, 158.5, 155.1, 136.8, 135.1, 134.7, 134.2, 133.7, 130.1, 129.2, 128.8, 128.6, 126.5, 126.3, 126.0, 124.2, 118.5. HR-ESI-MS: $[M+H]^+$ m/z calcd. for $C_{23}H_{15}O_4$: 355.0970; found 355.0967.



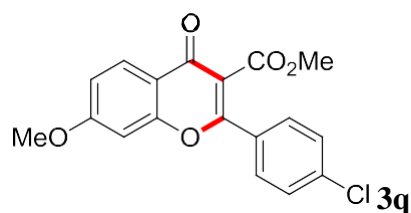
Methyl 7-methoxy-flavone-3-carboxylate (3n). Pale yellow solid. Isolated yield 47% (29.4 mg, from 30.5 mg of **1e**), eluent: petroleum ether/EtOAc 8:1. 1H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.16 (d, $J = 8.94$ Hz, 1 H), 7.72 (dd, $J = 7.92, 1.44$ Hz, 2 H), 7.55 (td, $J = 7.38, 2.28$ Hz, 1 H), 7.50 (td, $J = 7.41, 1.44$ Hz, 2 H), 7.01 (dd, $J = 8.91, 2.40$ Hz, 1 H), 6.91 (d, $J = 2.34$ Hz, 1 H), 3.92 (s, 3 H), 3.79 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 174.3, 165.7, 164.6, 162.6, 157.6, 132.0, 131.5, 128.8, 127.9, 127.5, 118.0, 116.9, 115.0, 100.3, 55.9, 52.7. HR-ESI-MS: $[M+H]^+$ m/z calcd. for $C_{18}H_{15}O_5$: 311.0919; found 311.0917.



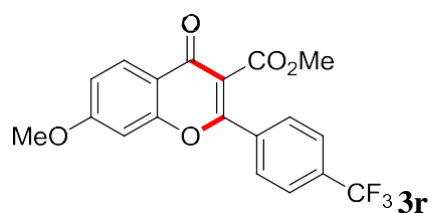
Ethyl 7-methoxy-flavone-3-carboxylate (3o). Very viscous yellow oil. Isolated yield 49% (32.4 mg, from 30.9 mg of **1e**), eluent: petroleum ether/EtOAc 8:1. 1H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.16 (d, $J = 8.88$ Hz, 1 H), 7.74 (d, $J = 7.32$ Hz, 2 H), 7.54 (t, $J = 7.38$ Hz, 1 H), 7.49 (t, $J = 7.50$ Hz, 2 H), 7.00 (dd, $J = 8.88, 2.28$ Hz, 1 H), 6.91 (d, $J = 2.28$ Hz, 1 H), 4.26 (q, $J = 7.14$ Hz, 2 H), 3.92 (s, 3 H), 1.16 (t, $J = 7.14$ Hz, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 174.3, 165.1, 164.5, 162.6, 157.6, 132.0, 131.4, 128.7, 128.0, 127.5, 118.3, 117.0, 114.9, 100.3, 61.8, 55.9, 13.8. HR-ESI-MS: $[M+Na]^+$ m/z calcd. for $C_{19}H_{16}O_5Na$: 347.0895; found 347.0890.



Methyl 4'-cyano-7-methoxy-flavone-3-carboxylate (3p). White solid. Isolated yield 55% (36.7 mg, from 30.3 mg of **1e**), eluent: petroleum ether/EtOAc 3:1. ^1H NMR (CDCl_3 , 600 MHz, ppm) δ 8.15 (d, $J = 8.94$ Hz, 1 H), 7.84 (d, $J = 8.46$ Hz, 2 H), 7.79 (d, $J = 8.46$ Hz, 2 H), 7.03 (dd, $J = 8.94, 2.34$ Hz, 1 H), 6.91 (d, $J = 2.28$ Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm) δ 173.8, 165.1, 164.9, 160.2, 157.5, 136.1, 132.5, 128.7, 127.6, 119.0, 117.7, 116.8, 115.4, 115.1, 100.3, 56.0, 53.0. HR-ESI-MS: $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{19}\text{H}_{14}\text{NO}_5$: 336.0872; found 336.0869.



Methyl 4'-chloro-7-methoxy-flavone-3-carboxylate (3q). Pale yellow solid. Isolated yield 47% (32.8 mg, from 30.7 mg of **1e**), eluent: petroleum ether/EtOAc 7:1. ^1H NMR (CDCl_3 , 600 MHz, ppm) δ 8.14 (d, $J = 8.88$ Hz, 1 H), 7.67 (d, $J = 8.58$ Hz, 2 H), 7.48 (d, $J = 8.52$ Hz, 2 H), 7.01 (dd, $J = 8.91, 2.34$ Hz, 1 H), 6.90 (d, $J = 2.28$ Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm) δ 174.1, 165.5, 164.7, 161.3, 157.5, 137.9, 130.3, 129.3, 129.1, 127.5, 118.1, 116.8, 115.1, 100.3, 55.9, 52.9. HR-ESI-MS: $[\text{M}+\text{H}]^+$ m/z calcd. for $\text{C}_{18}\text{H}_{14}\text{ClO}_5$: 345.0530; found 345.0528.



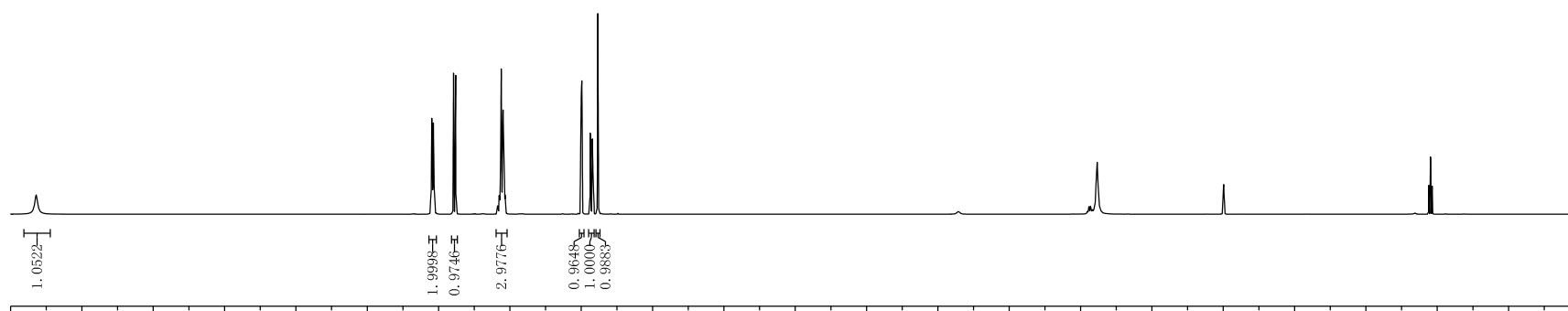
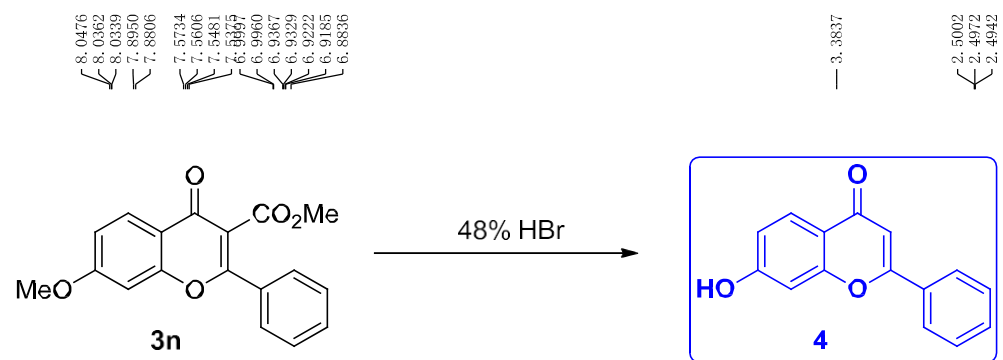
Methyl 4'-trifluoromethyl-7-methoxy-flavone-3-carboxylate (3r). Yellow solid. Isolated yield 51% (38.9 mg, from 30.6 mg of **1e**), eluent: petroleum ether/EtOAc 7:1. ^1H NMR (CDCl_3 , 600 MHz, ppm) δ 8.15 (d, $J = 8.94$ Hz, 1 H), 7.85 (d, $J = 8.22$ Hz, 2 H), 7.76 (d, $J = 8.28$ Hz, 2 H), 7.02 (dd, $J = 8.91, 2.28$ Hz, 1 H), 6.91 (d, $J = 2.28$ Hz, 1 H), 3.92 (s, 3 H), 3.80 (s, 3 H). ^{13}C NMR (CDCl_3 , 150 MHz, ppm) δ 174.0, 165.3, 164.8, 160.8, 157.5, 135.3, 133.1 (q, $J_{\text{C-F}} = 32.8$ Hz), 128.4, 127.6, 125.8 (q, $J_{\text{C-F}} = 3.7$ Hz), 123.5 (q, $J_{\text{C-F}} = 301.6$ Hz), 118.7, 116.8, 115.3, 100.3, 55.9, 52.9. ^{19}F NMR

(CDCl₃, 564.6 MHz, ppm) δ -63.1. HR-ESI-MS: [M+Na]⁺ *m/z* calcd. for C₁₉H₁₃F₃O₅Na: 401.0613; found 401.0607.

Reference

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Copy of the ^1H and ^{13}C NMR spectra of 7-hydroxyflavone (4) (via decarboxylation and demethylation of compound 3n)



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
f1 (ppm)

— 176.8117

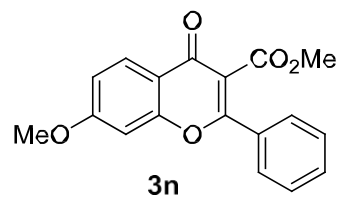
163.2045
162.3508
— 157.9285

131.9336
131.7371
129.4823
126.9660
126.5832

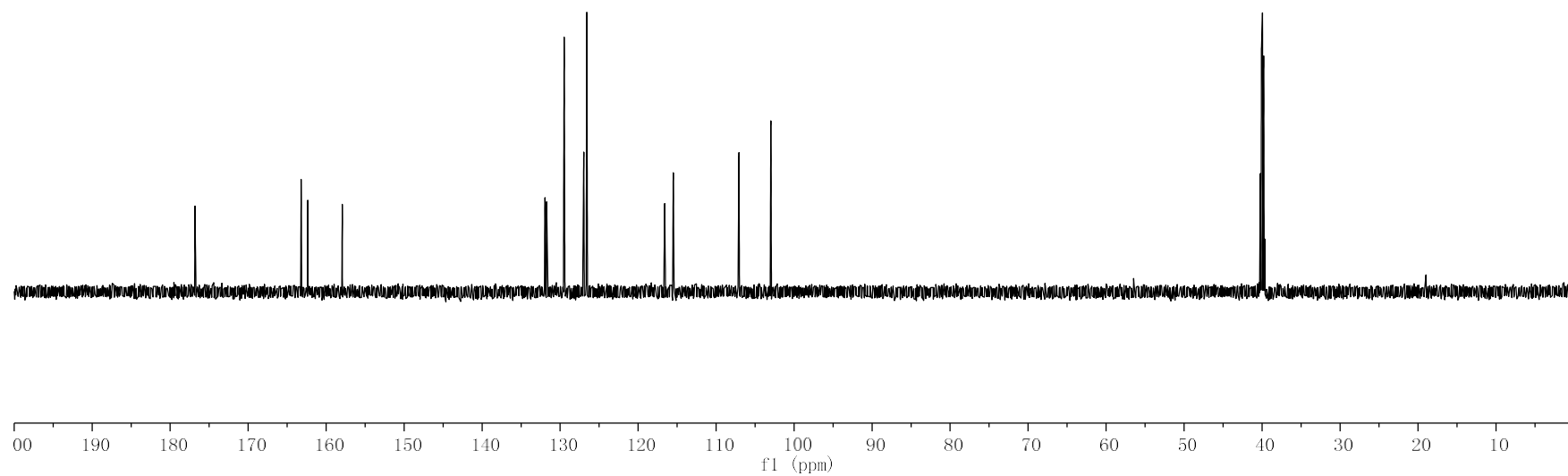
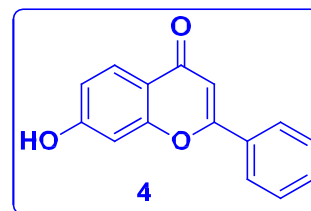
116.6020
115.4938

107.0687
— 102.9881

40.3591
40.2202
40.0806
39.9416
39.8018
39.6629
39.5216



48% HBr



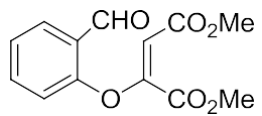
Copy of the ^1H NMR spectra of (*E*)-2-(2-formylphenoxy)-2-butenedioate (5a)

10.5330
10.2745

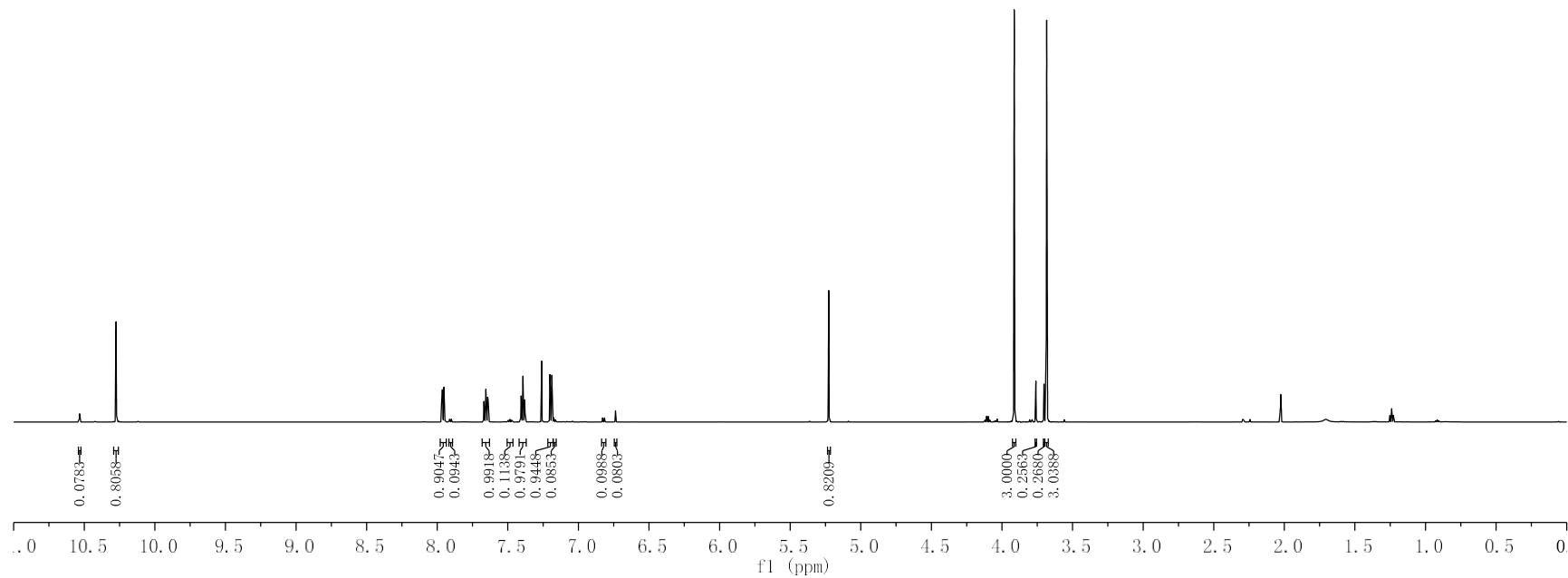
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7.9523
7.9496
7.9128
7.9101
7.8999
7.8972
7.6567
7.6556
7.6540
7.4055
7.3929
7.2014
6.8866
6.8148
6.7372

5.2266

3.9130
3.7593
3.7021
3.6835



5a, with trace amount of 5b
5a/5b 91:9



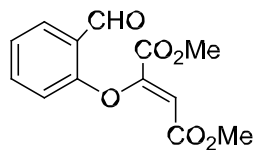
Copy of the ¹H NMR spectra of (Z)-2-(2-formylphenoxy)-2-butenedioate (5b)

10.5410
10.2822

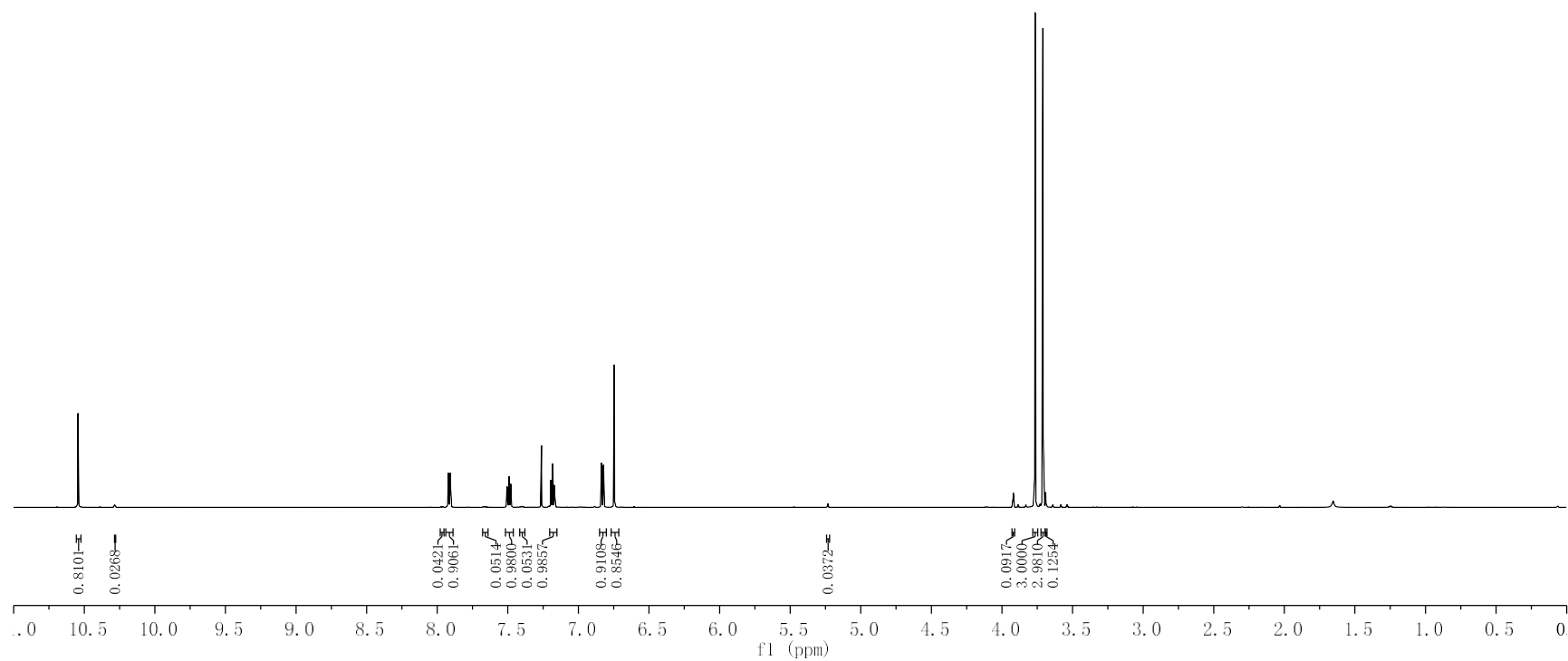
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7.9590
7.9562
7.9205
7.9176
7.9076
7.9047
7.4913
7.4896
7.4885
7.4869
7.2598
7.1926
7.1860
6.8335
6.8329
6.8198
6.7443

5.2324

3.9181
3.7635
3.7077
3.6891



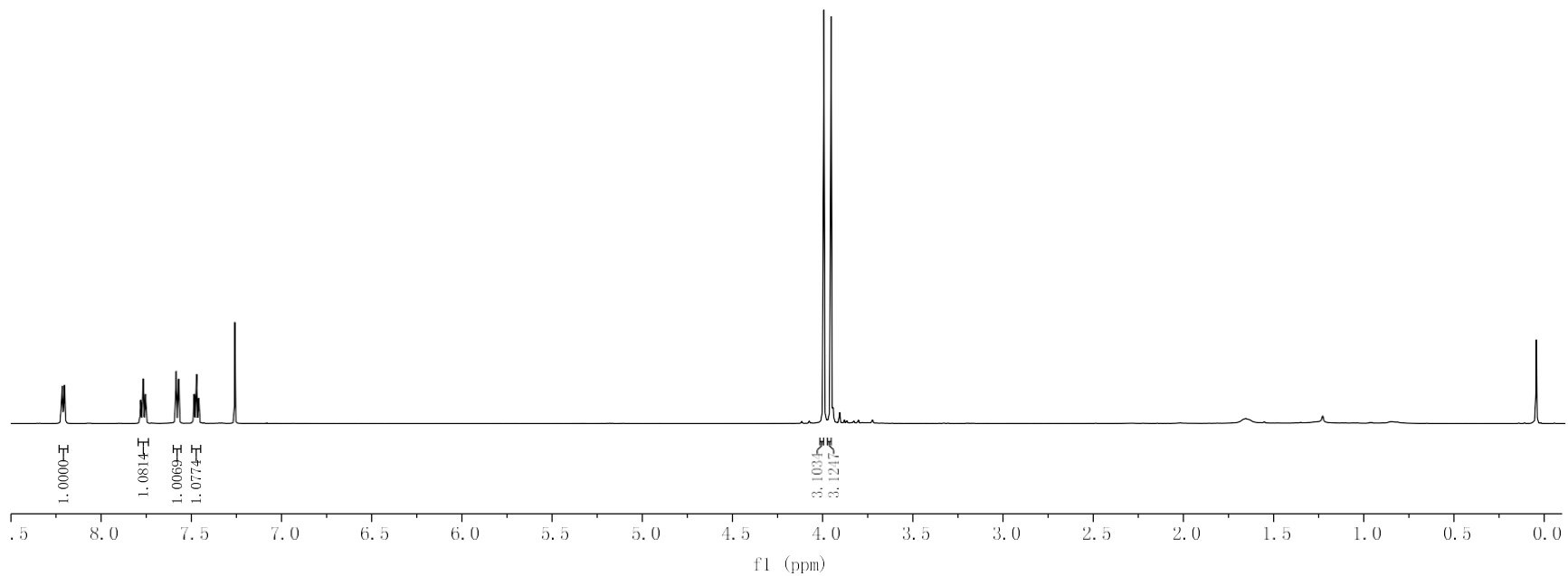
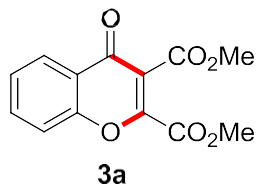
5b, with trace amount of 5a
5a/5b 4:96

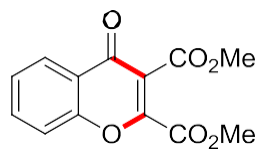


Copies of the ^1H , ^{13}C and ^{19}F NMR spectra of chromones 3a-r

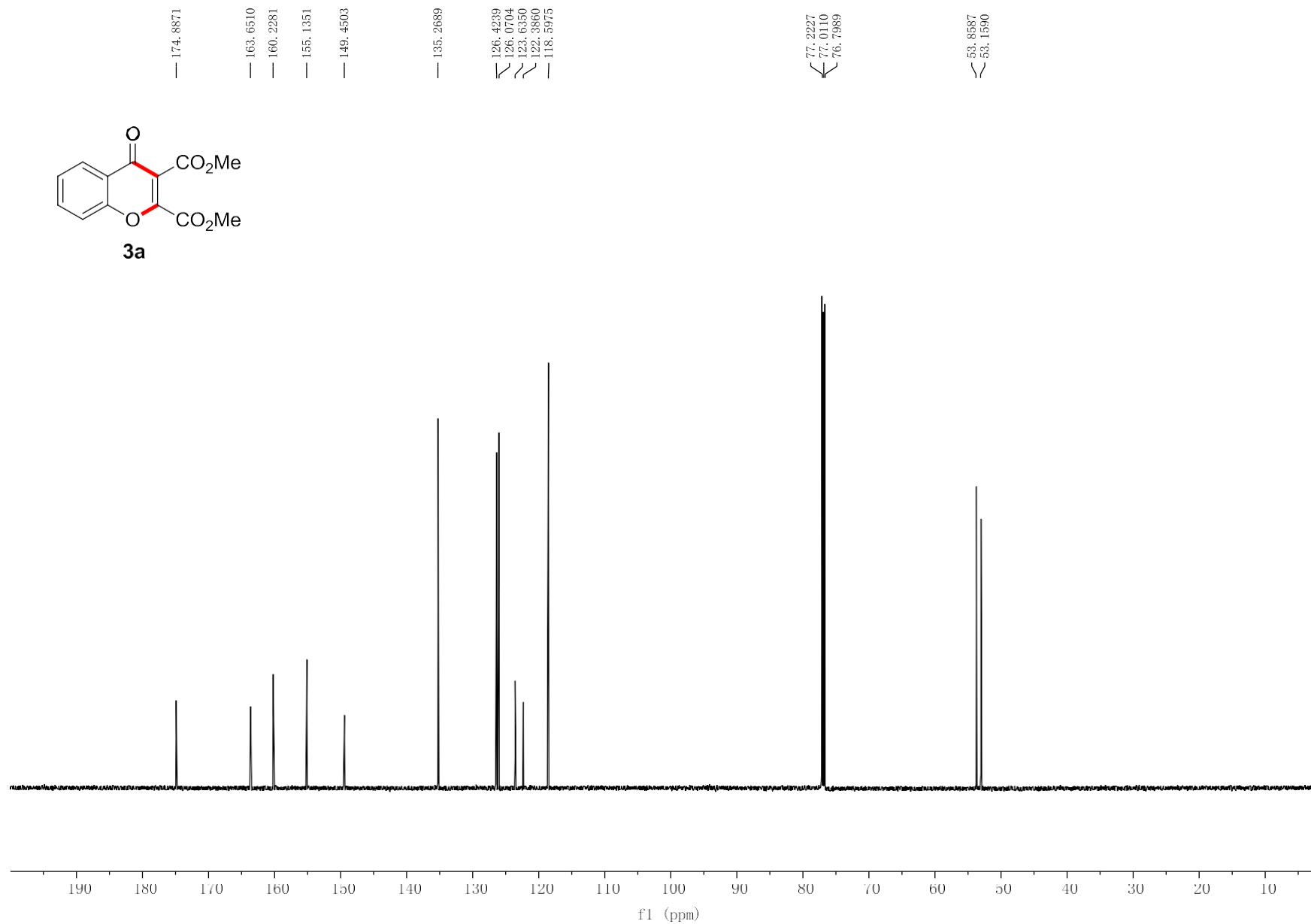
8.2143
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7.5835
7.5693
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7.4709
7.4586
7.2597

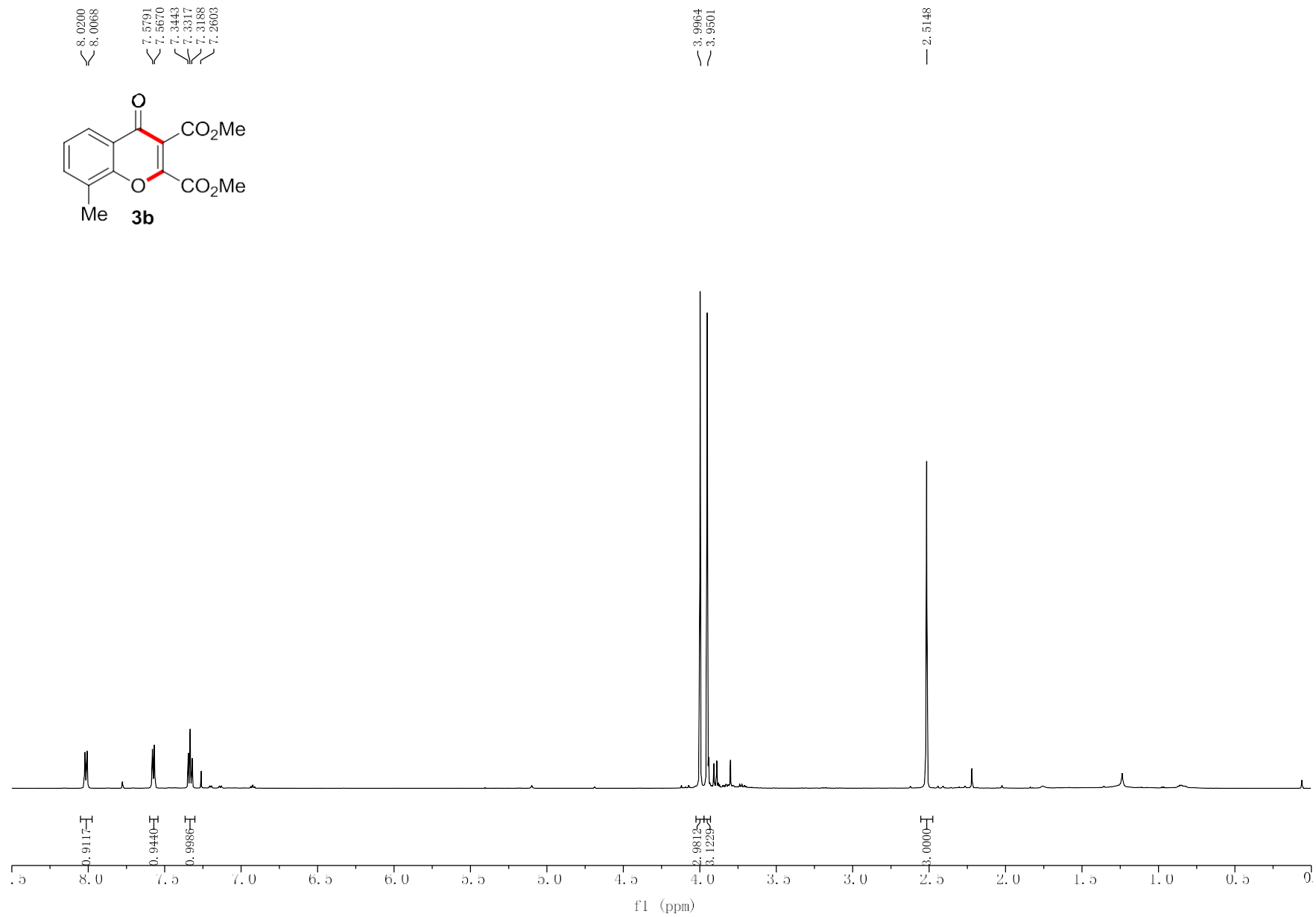
4.0019
3.9617

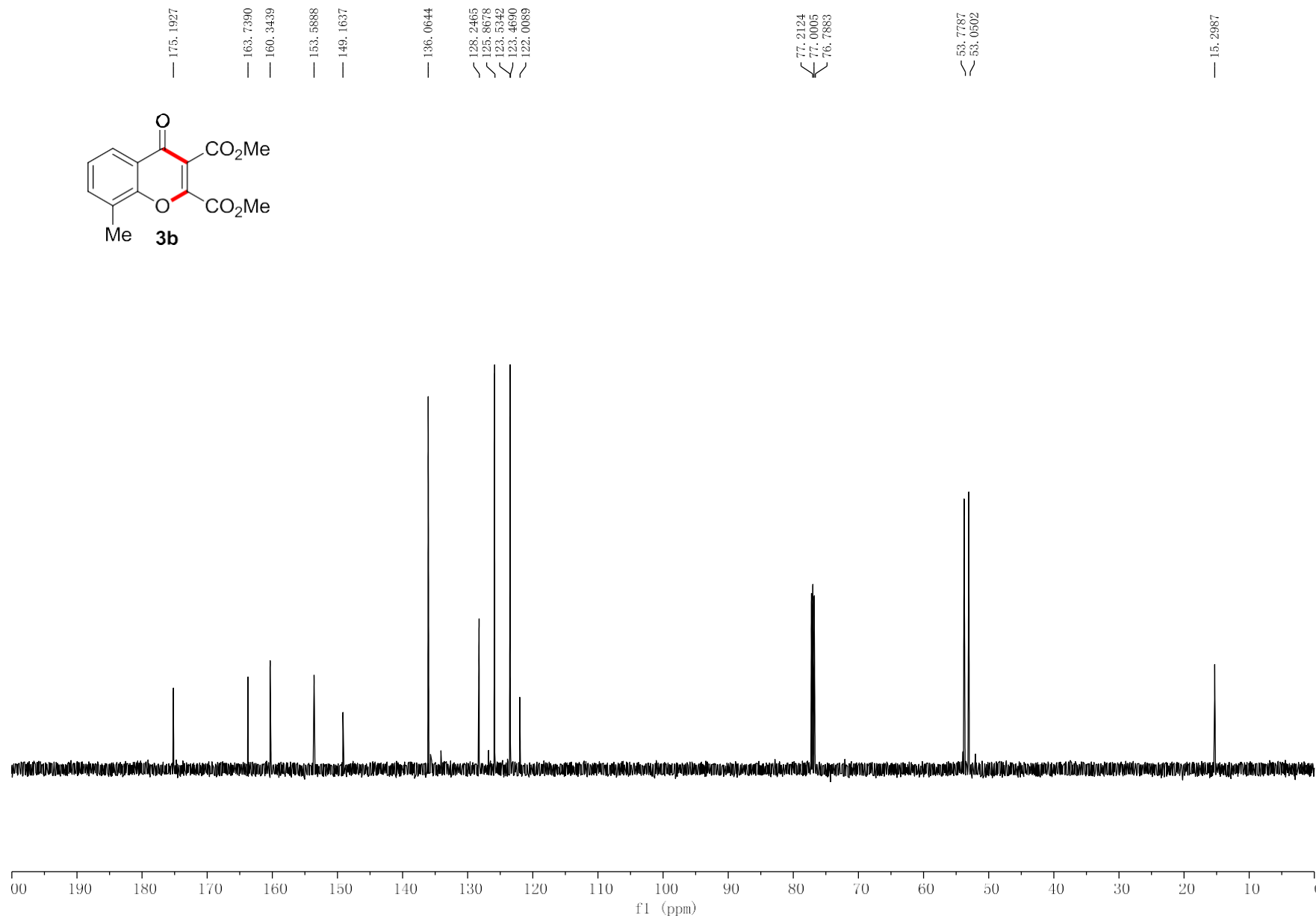
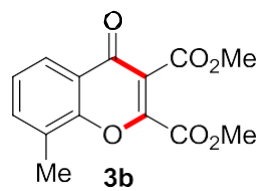


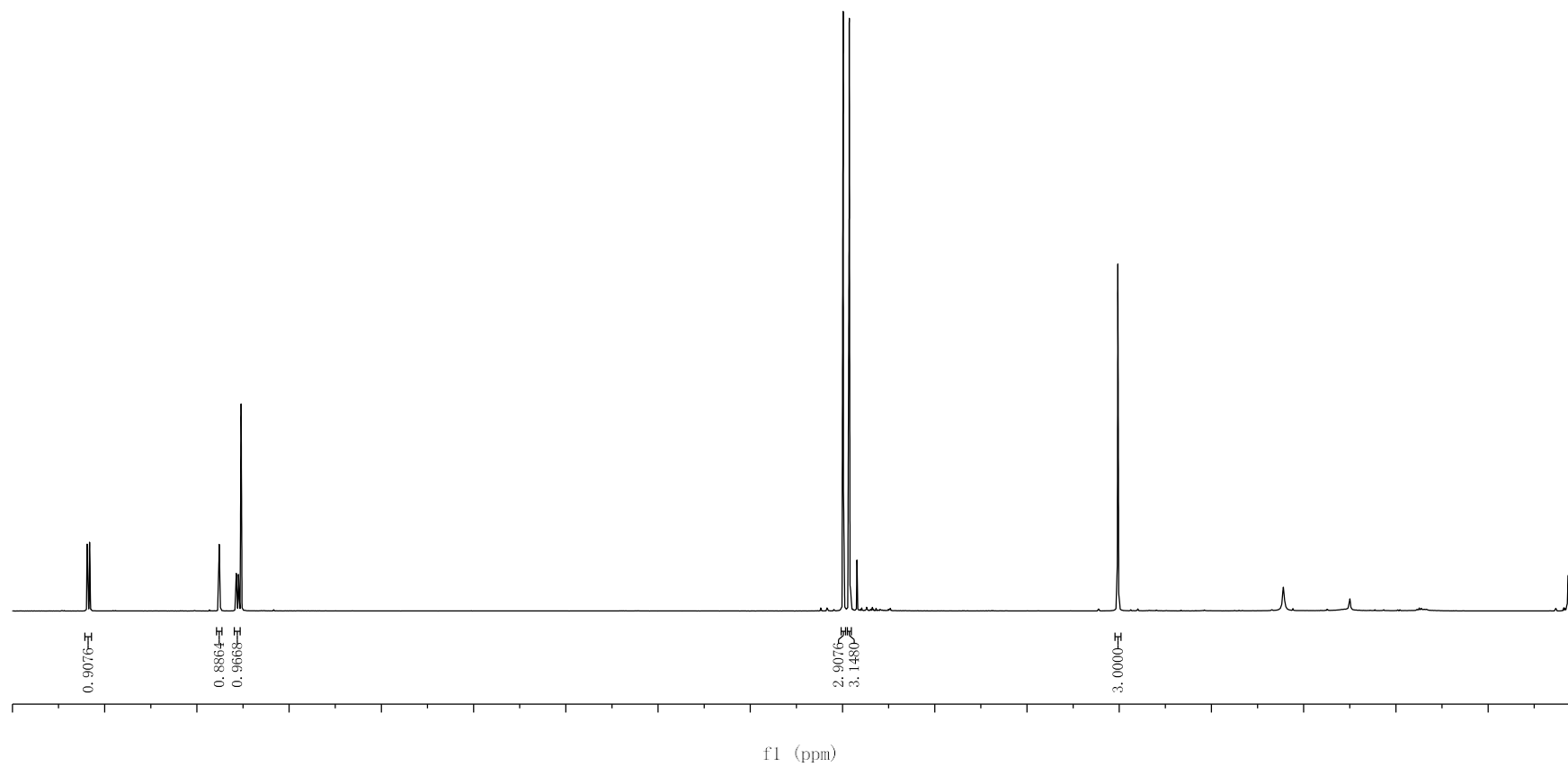
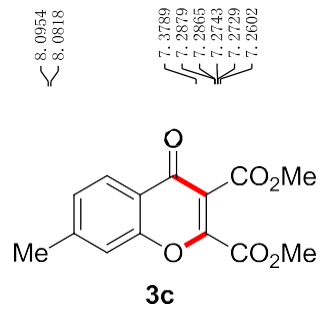


3a





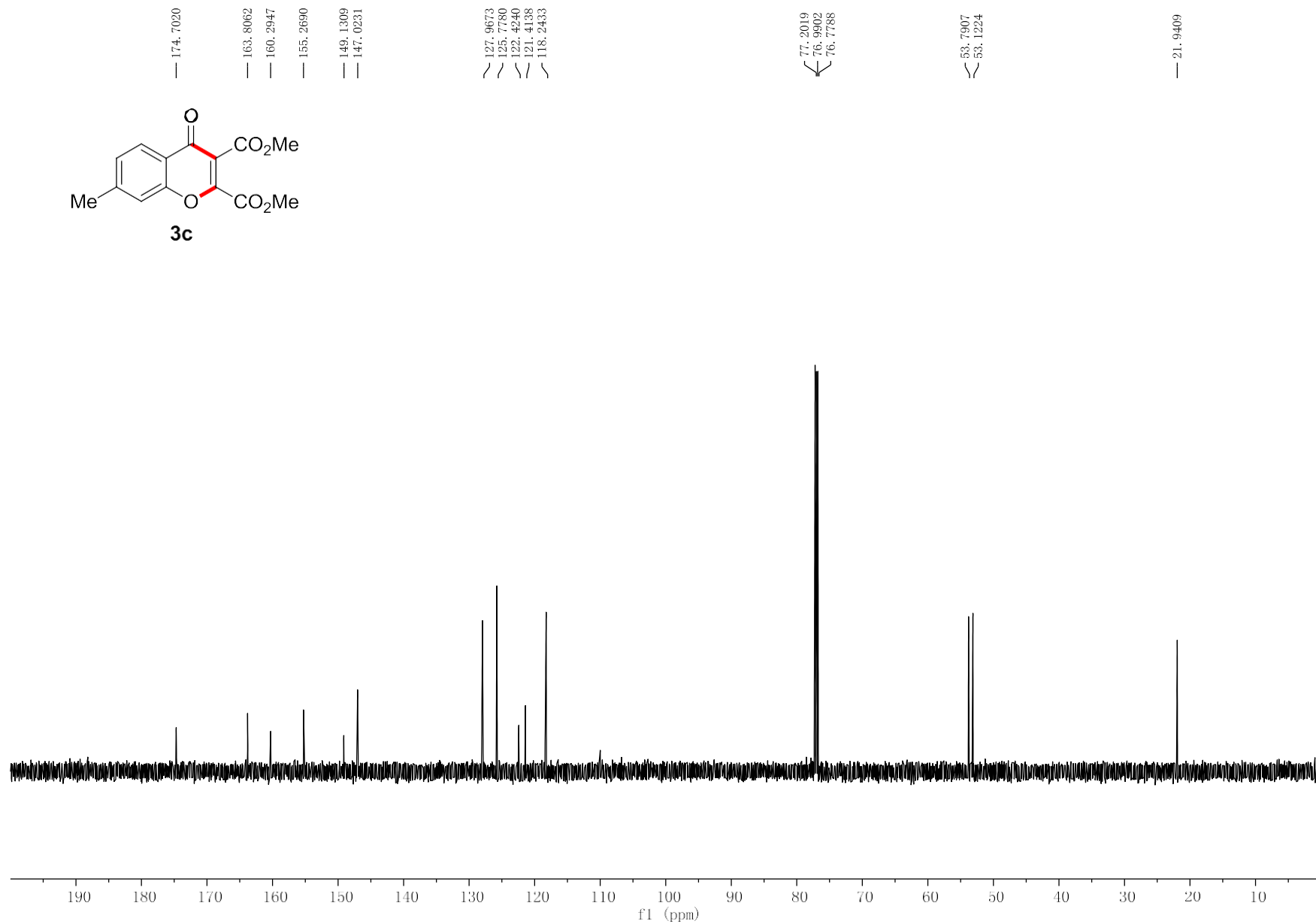
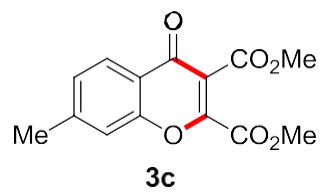


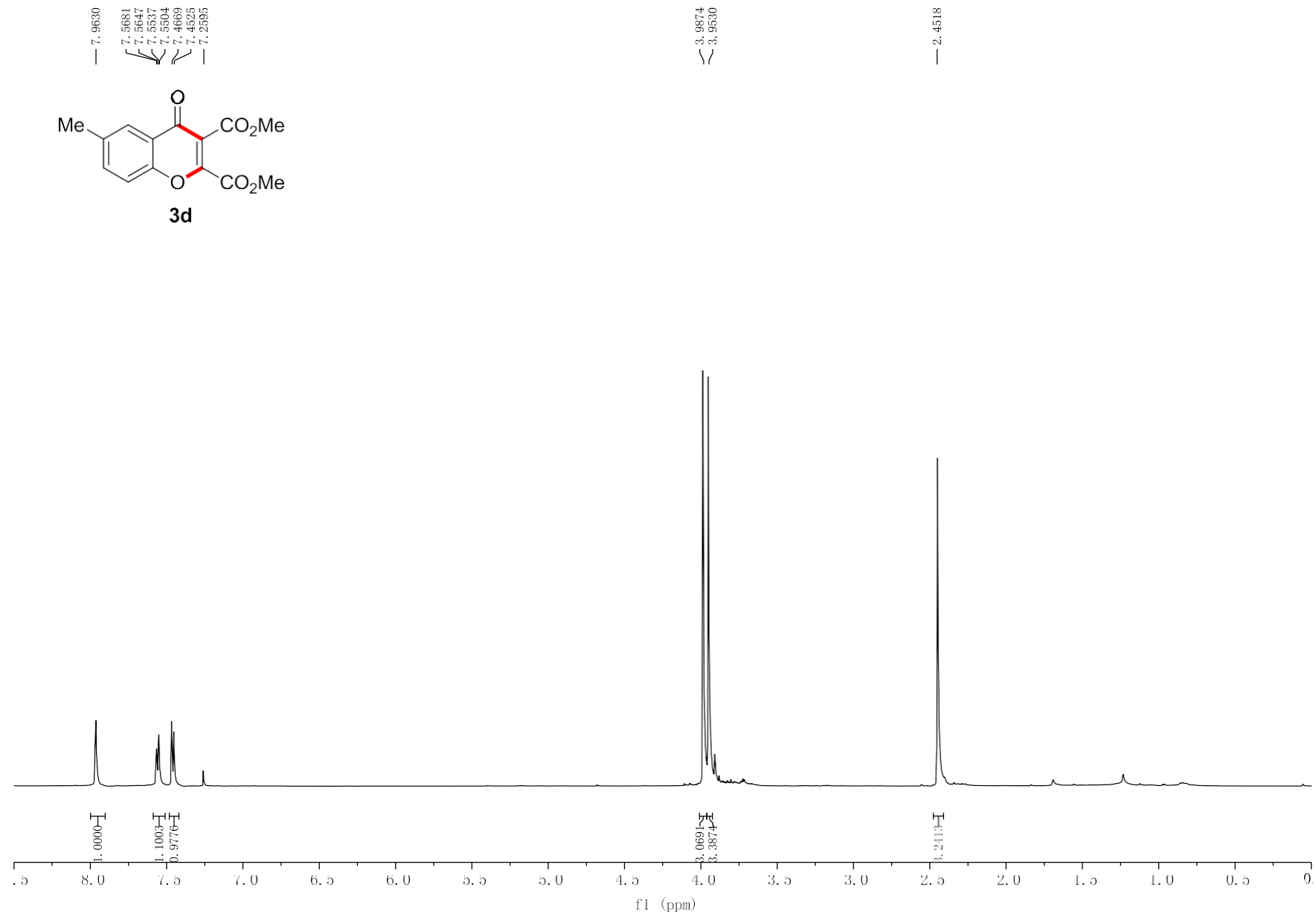
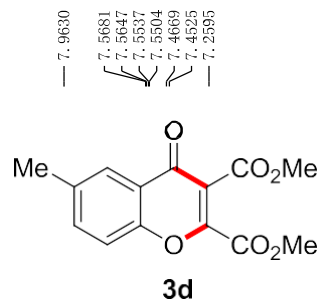


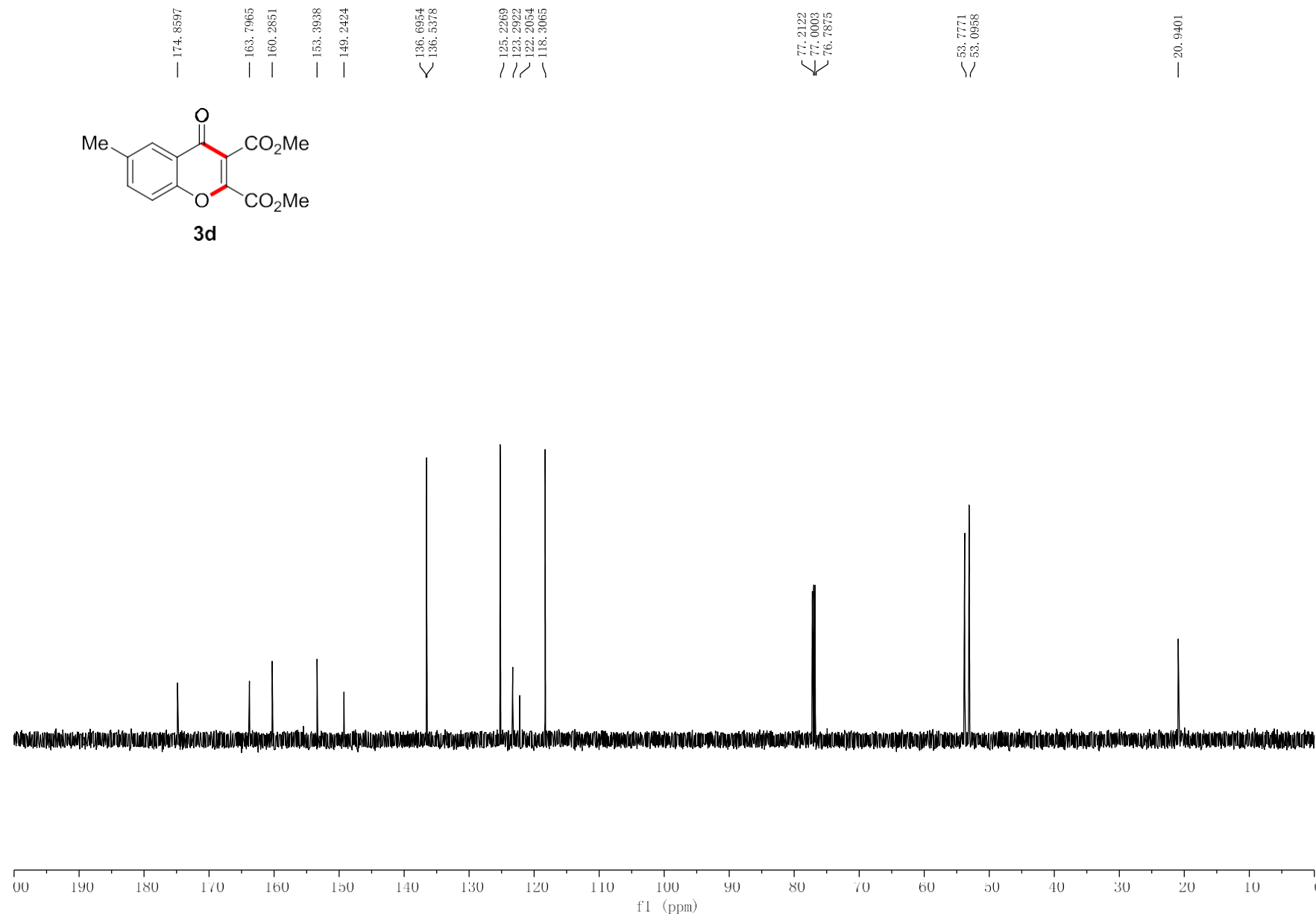
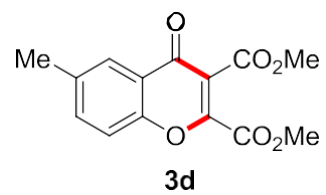
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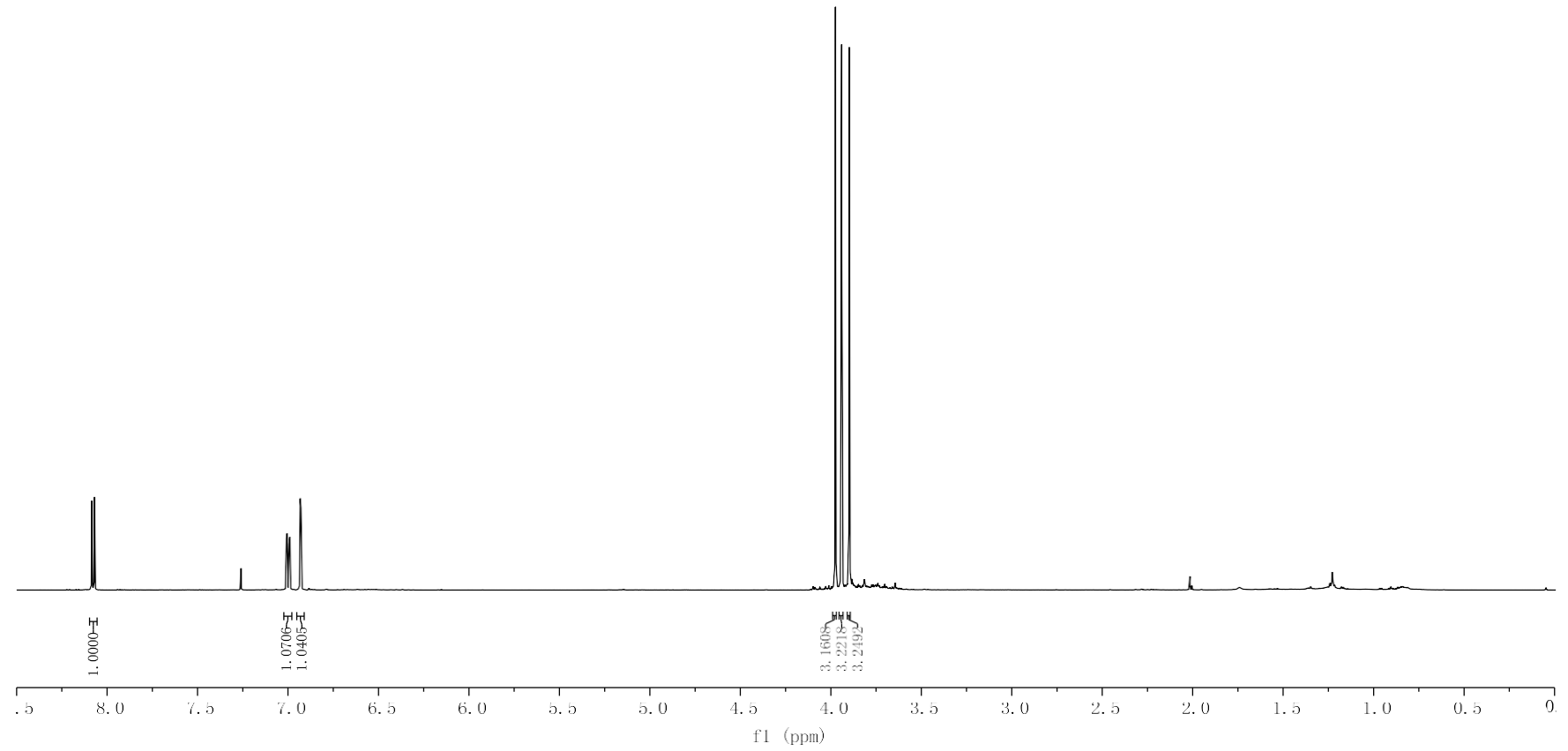
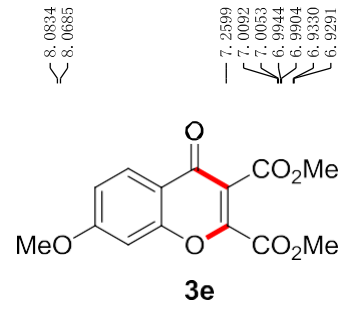
f1 (ppm)

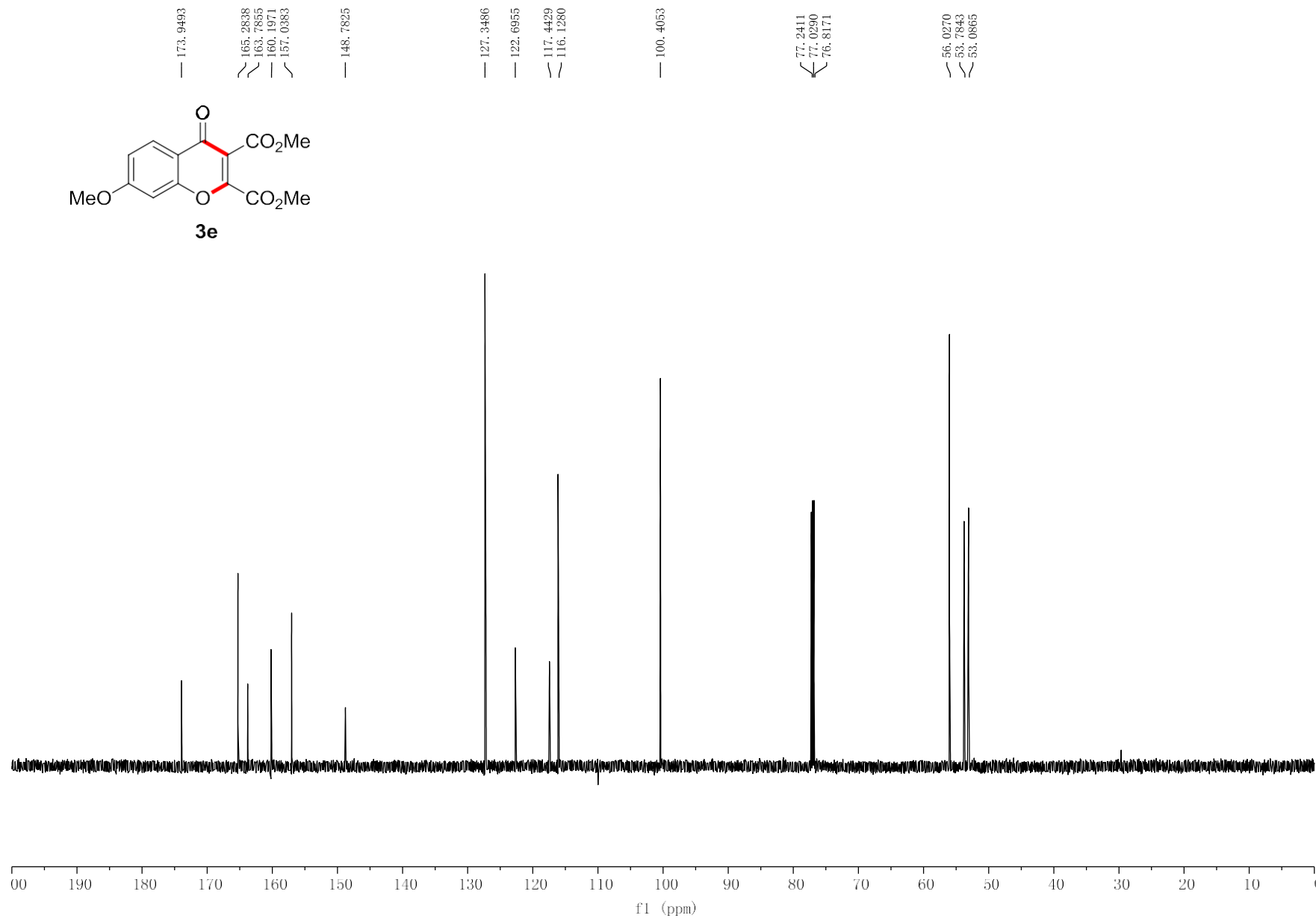
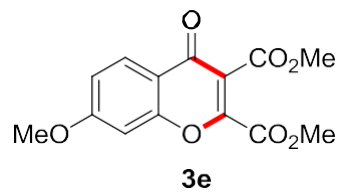
S21

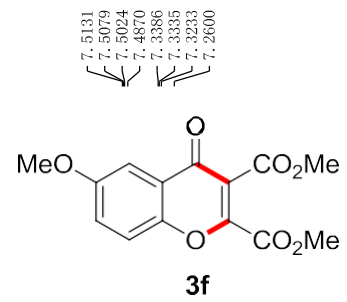




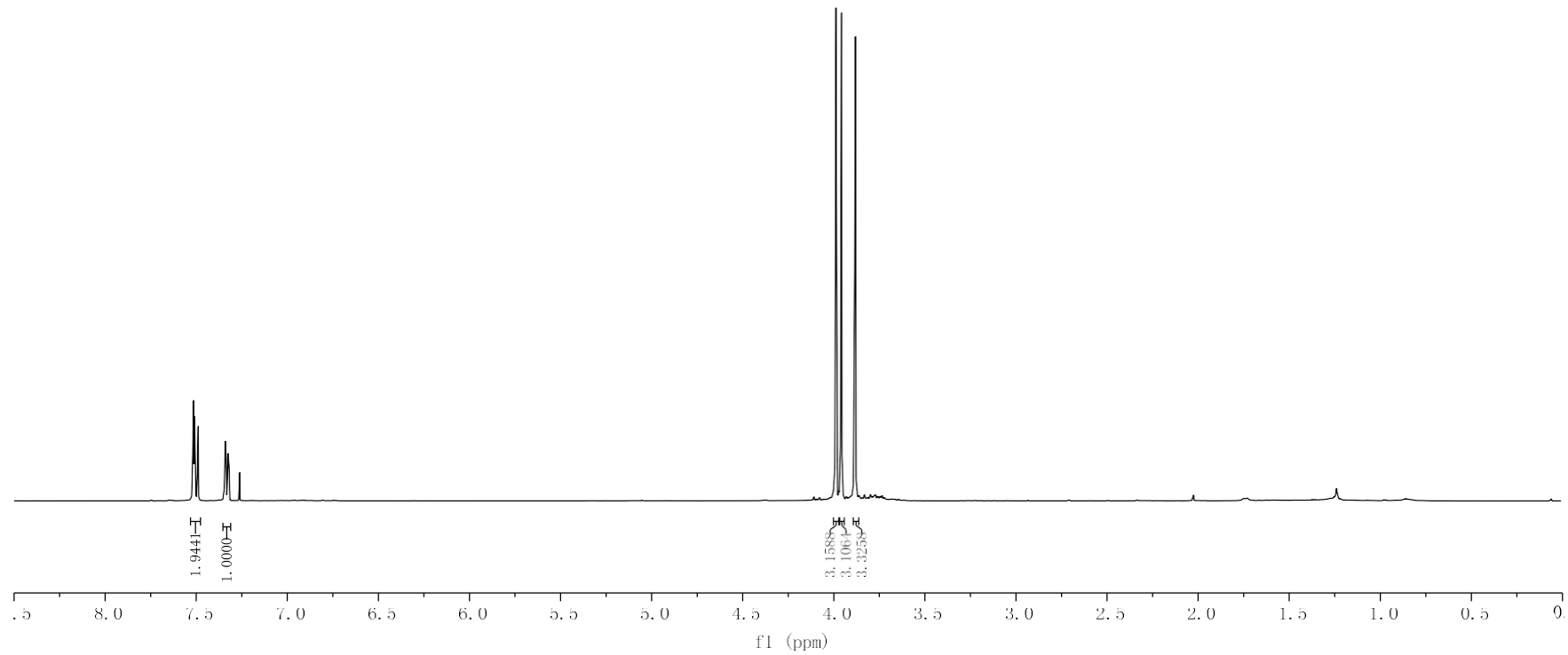


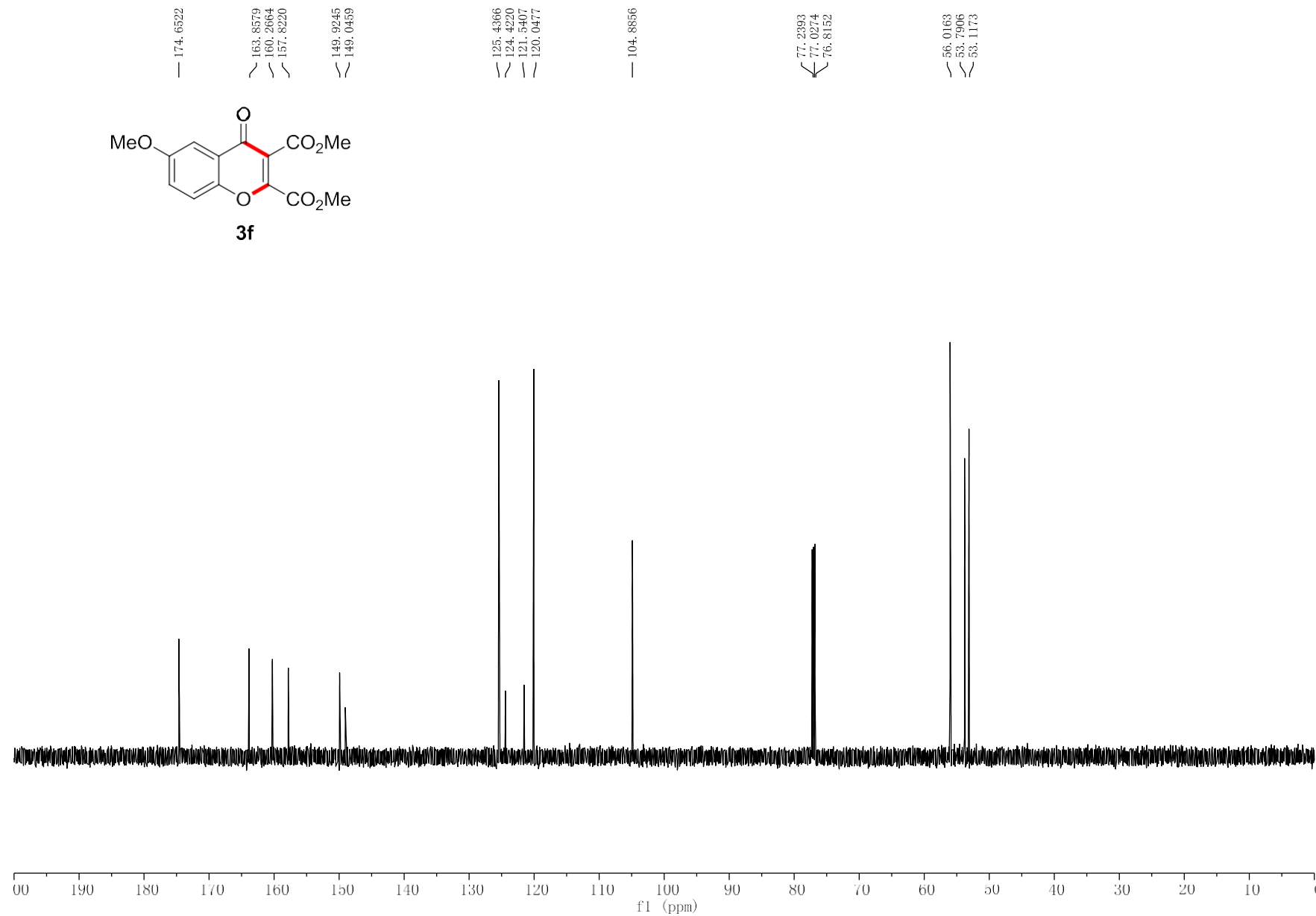
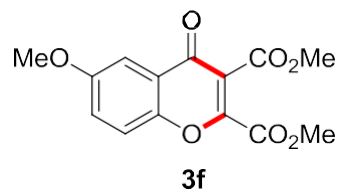




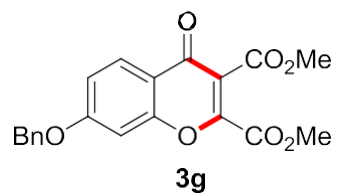


3.9829
3.9530
3.8766



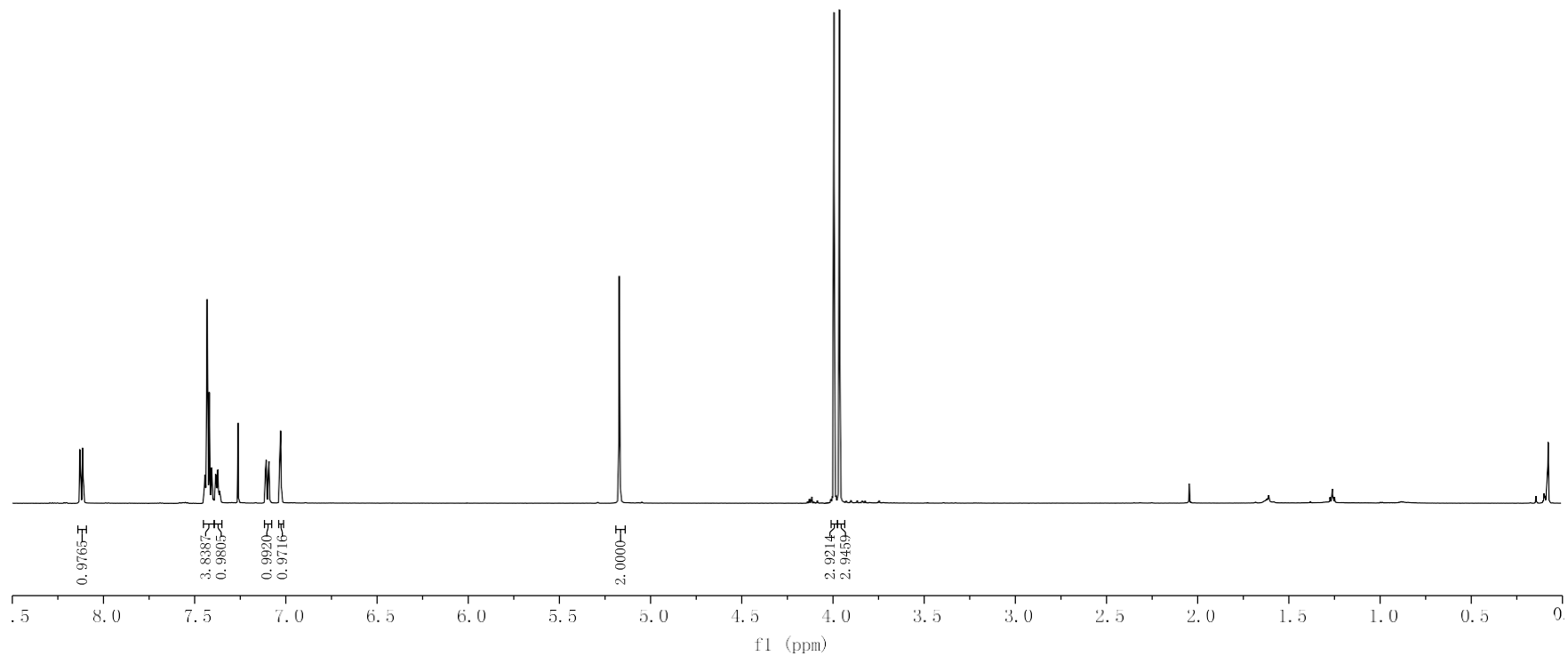


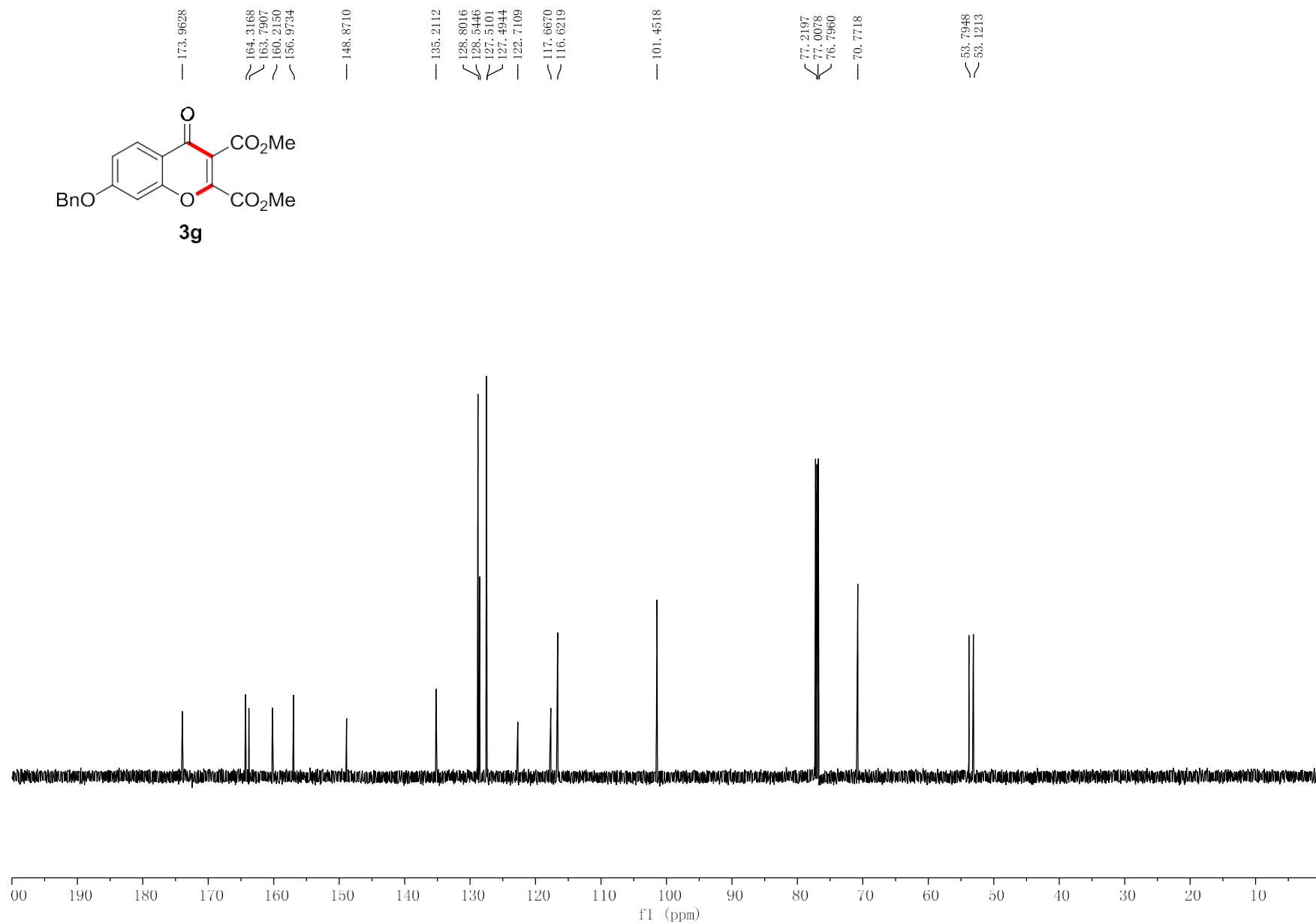
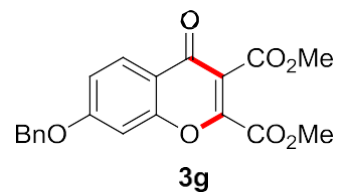
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7.3795
7.3770
7.3718
7.3642
7.3610
7.2597
7.1098
7.1060
7.1036
7.0949
7.0911
7.0887
7.0302
7.0265

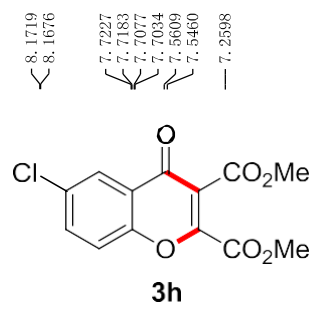


5.1681

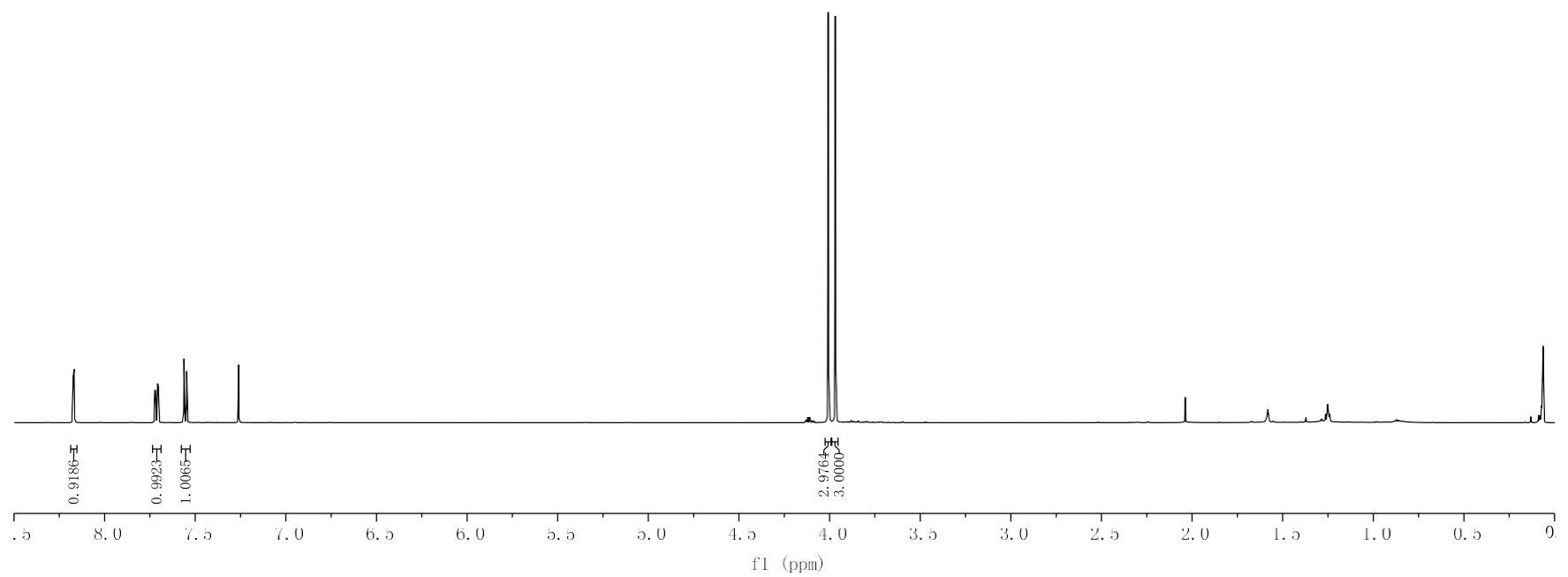
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3.9609

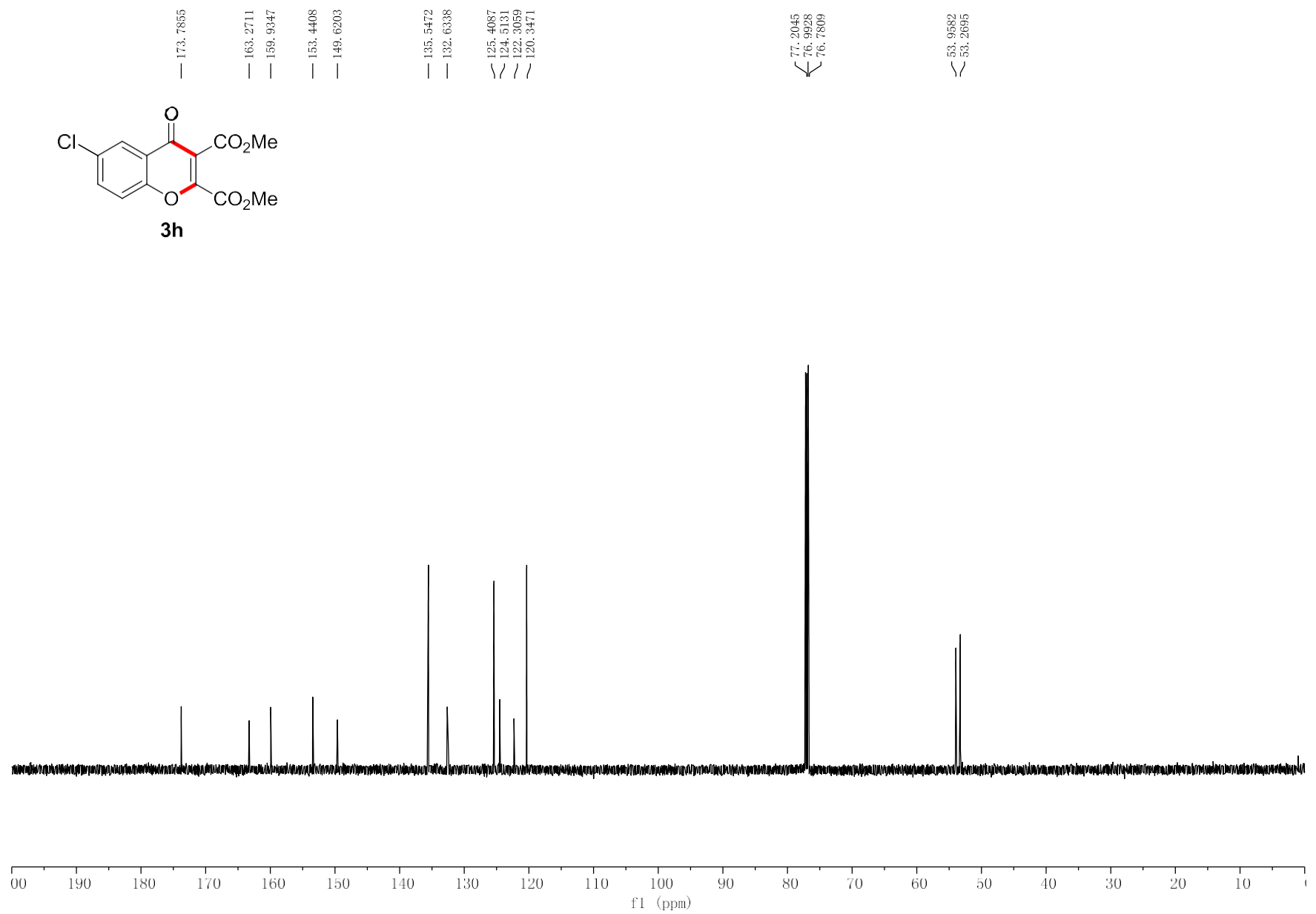
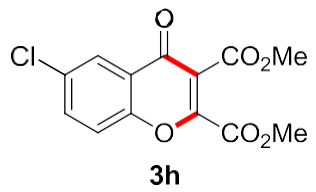






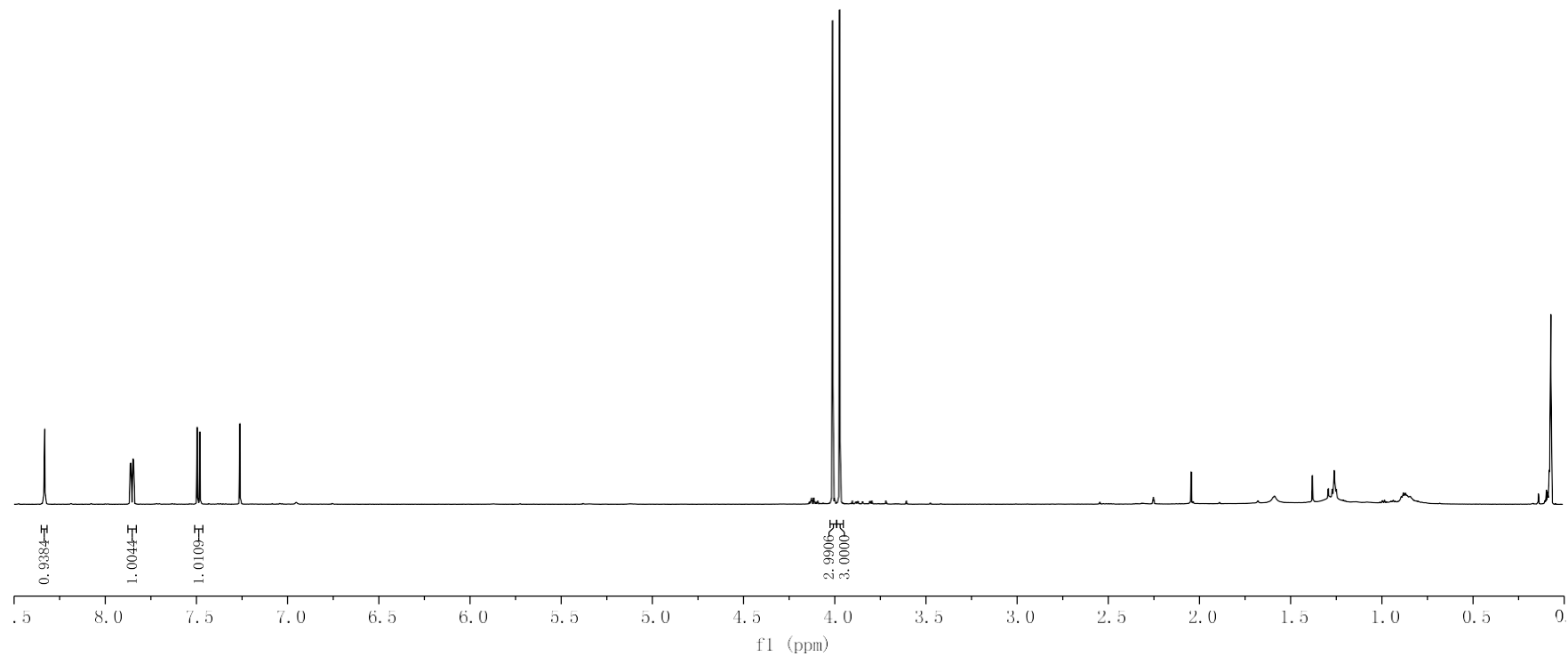
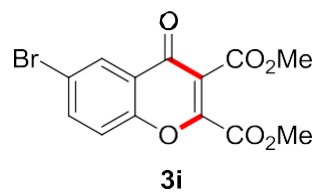
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3.9684

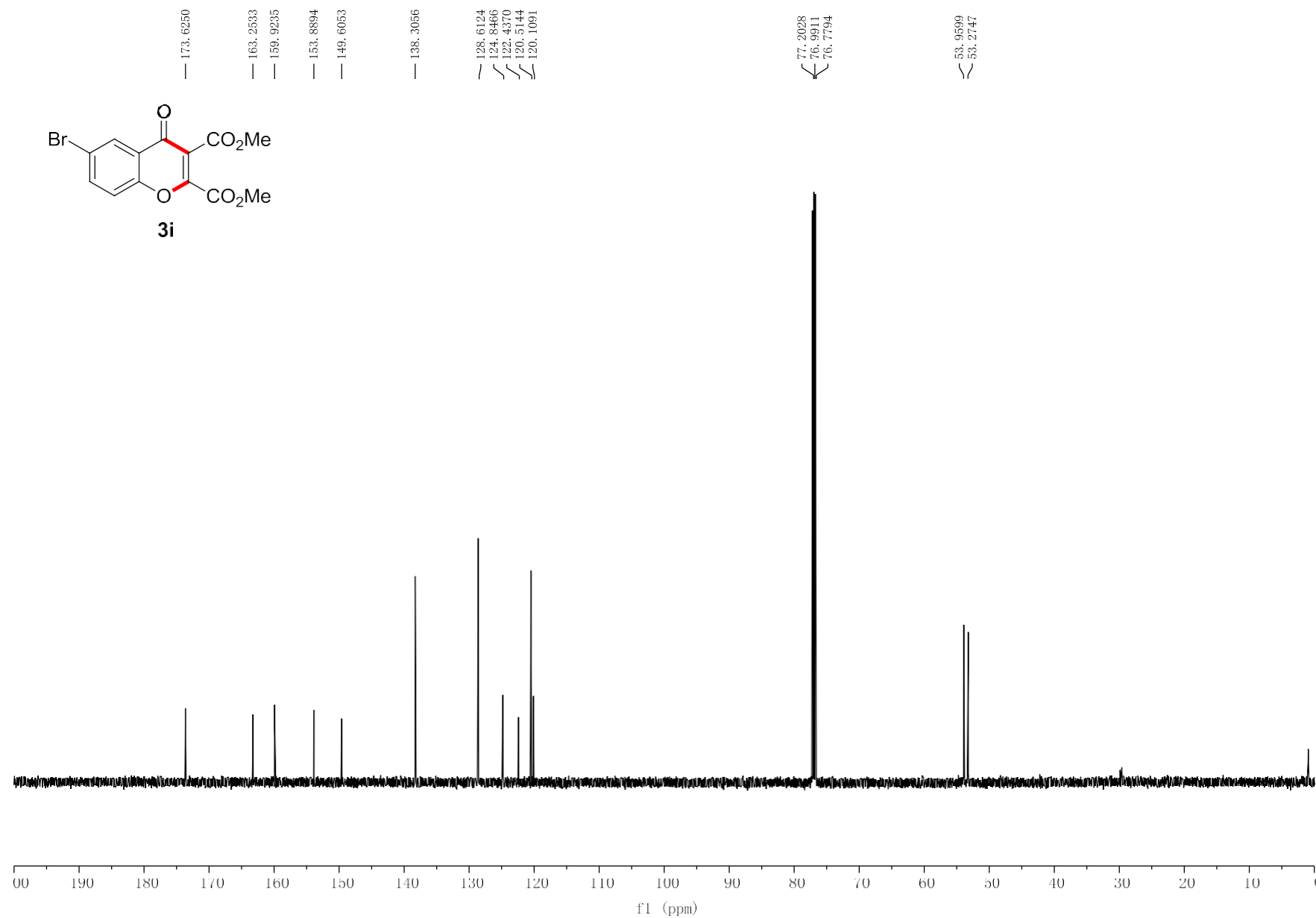


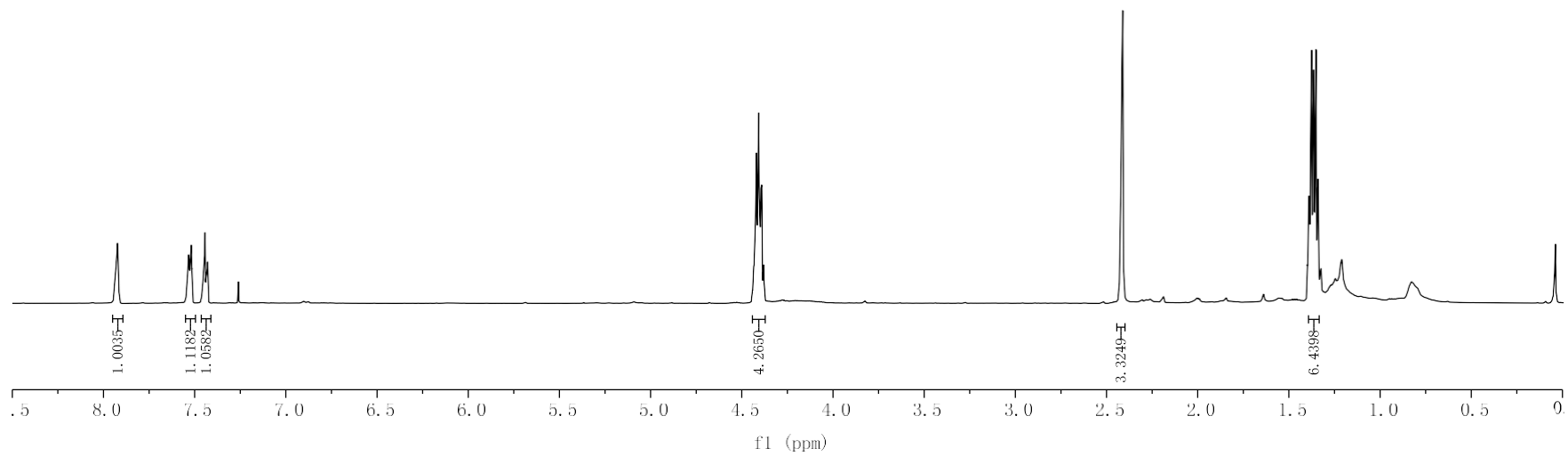
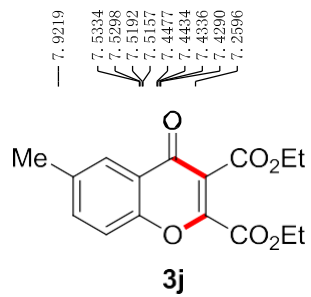


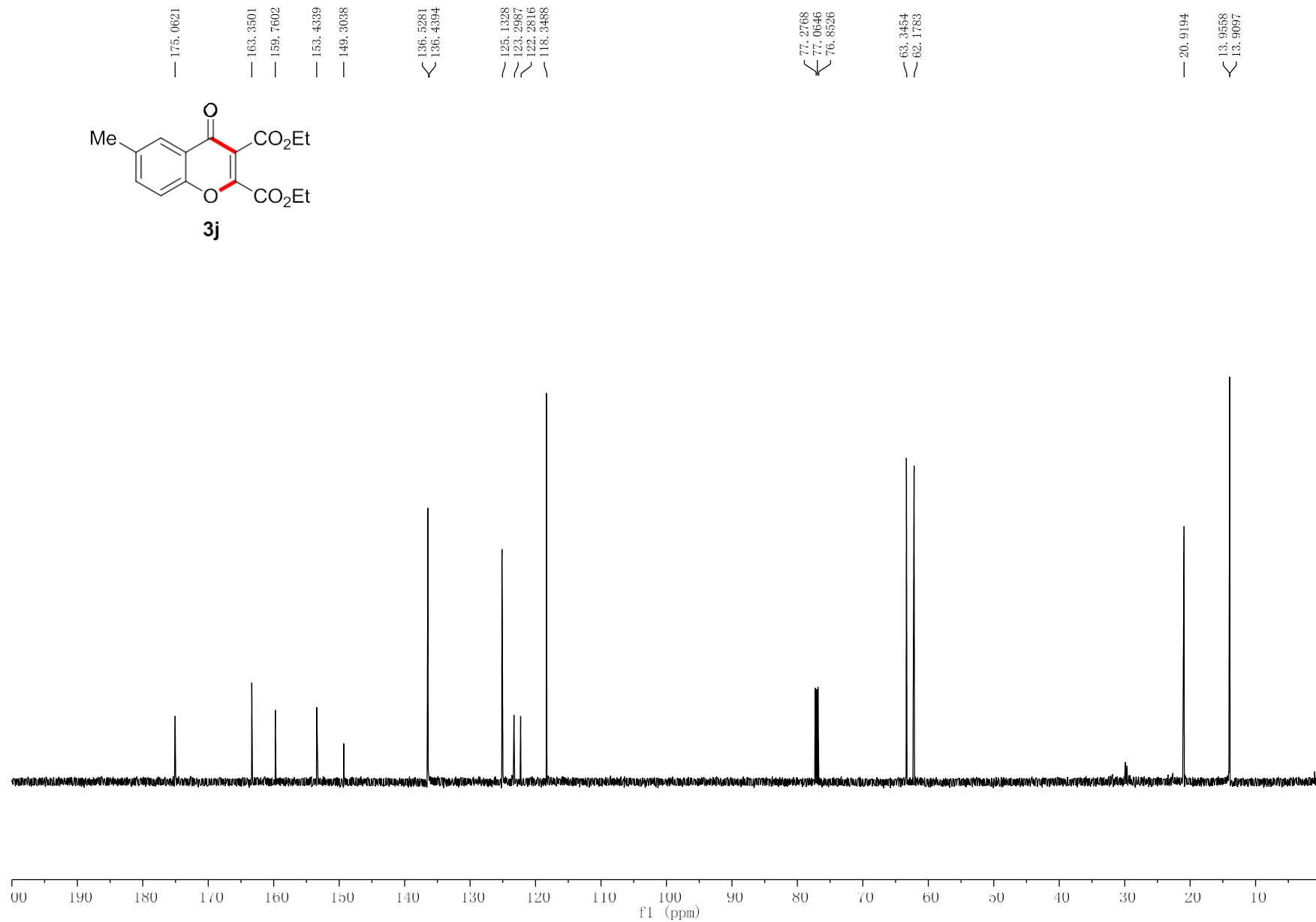
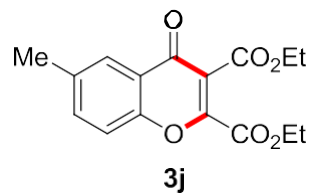
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7.4796
7.2597

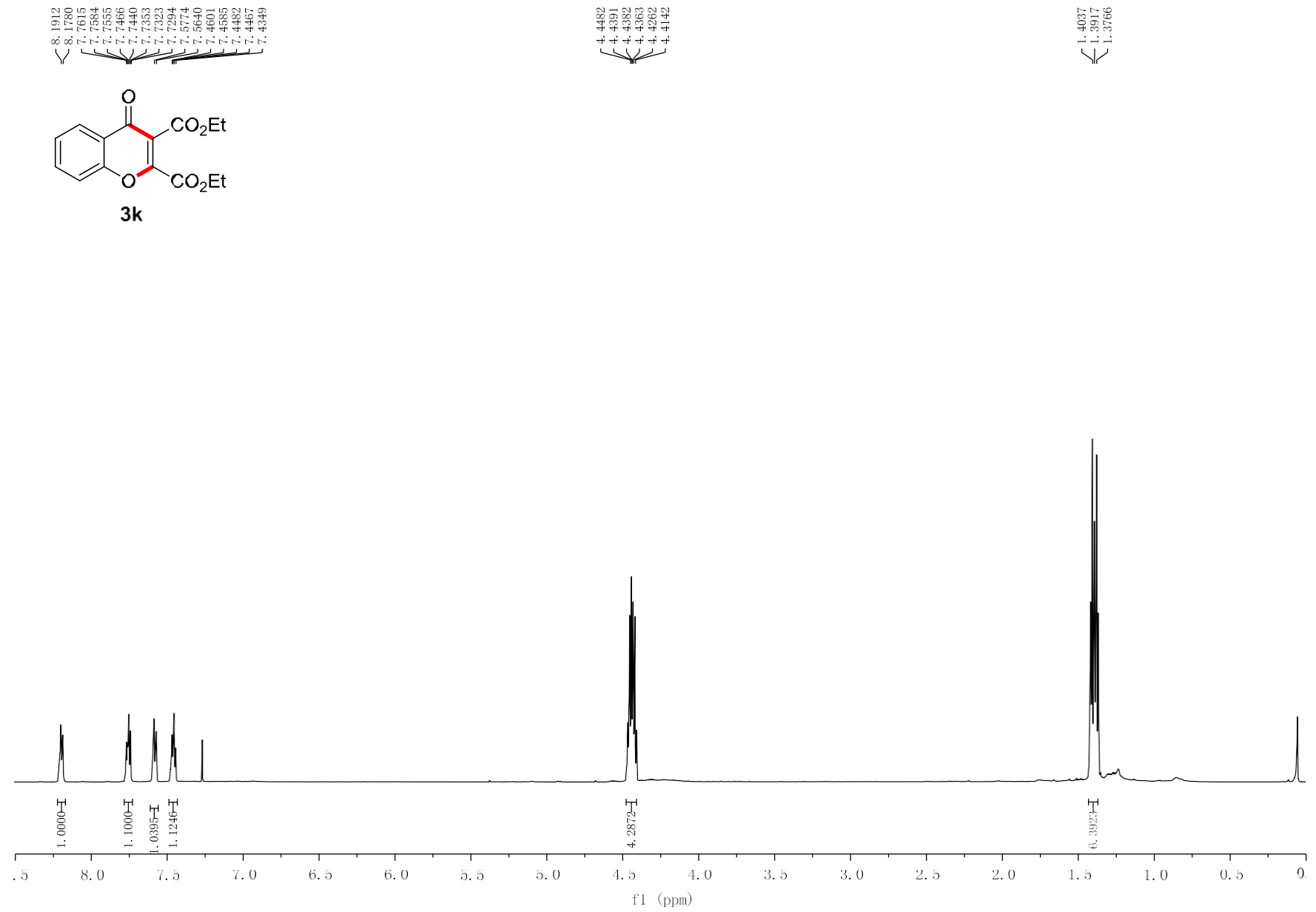
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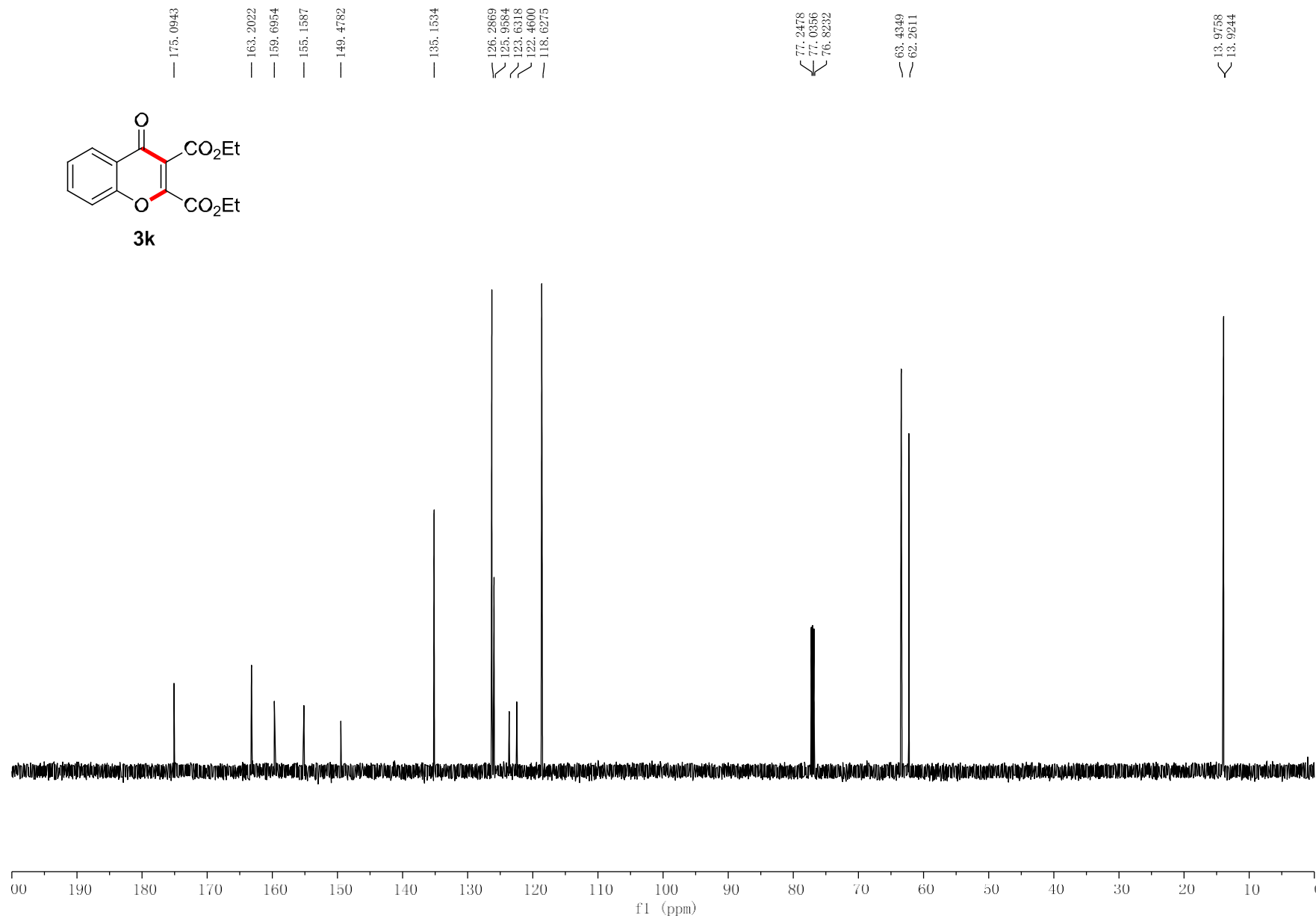
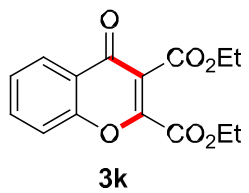


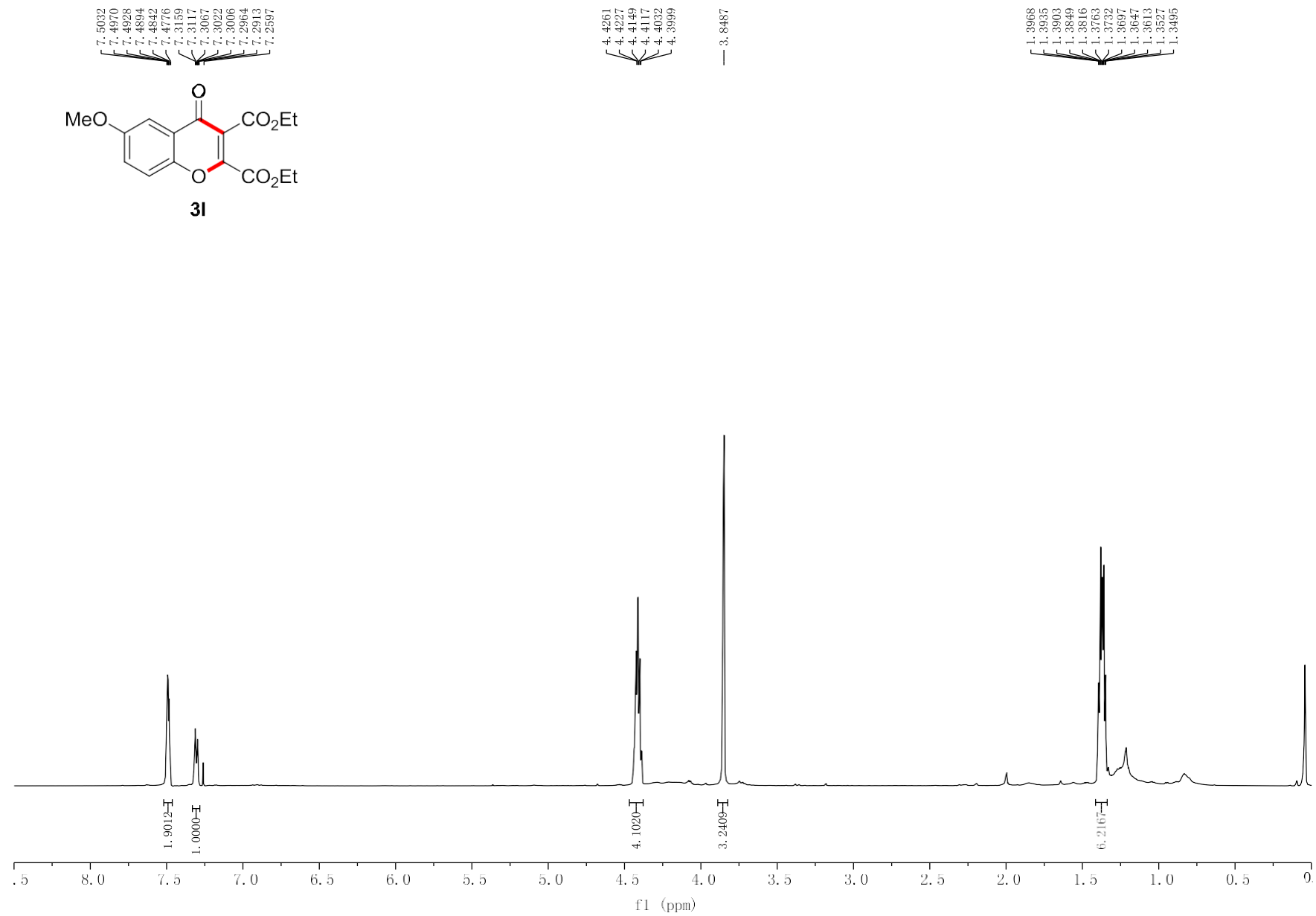


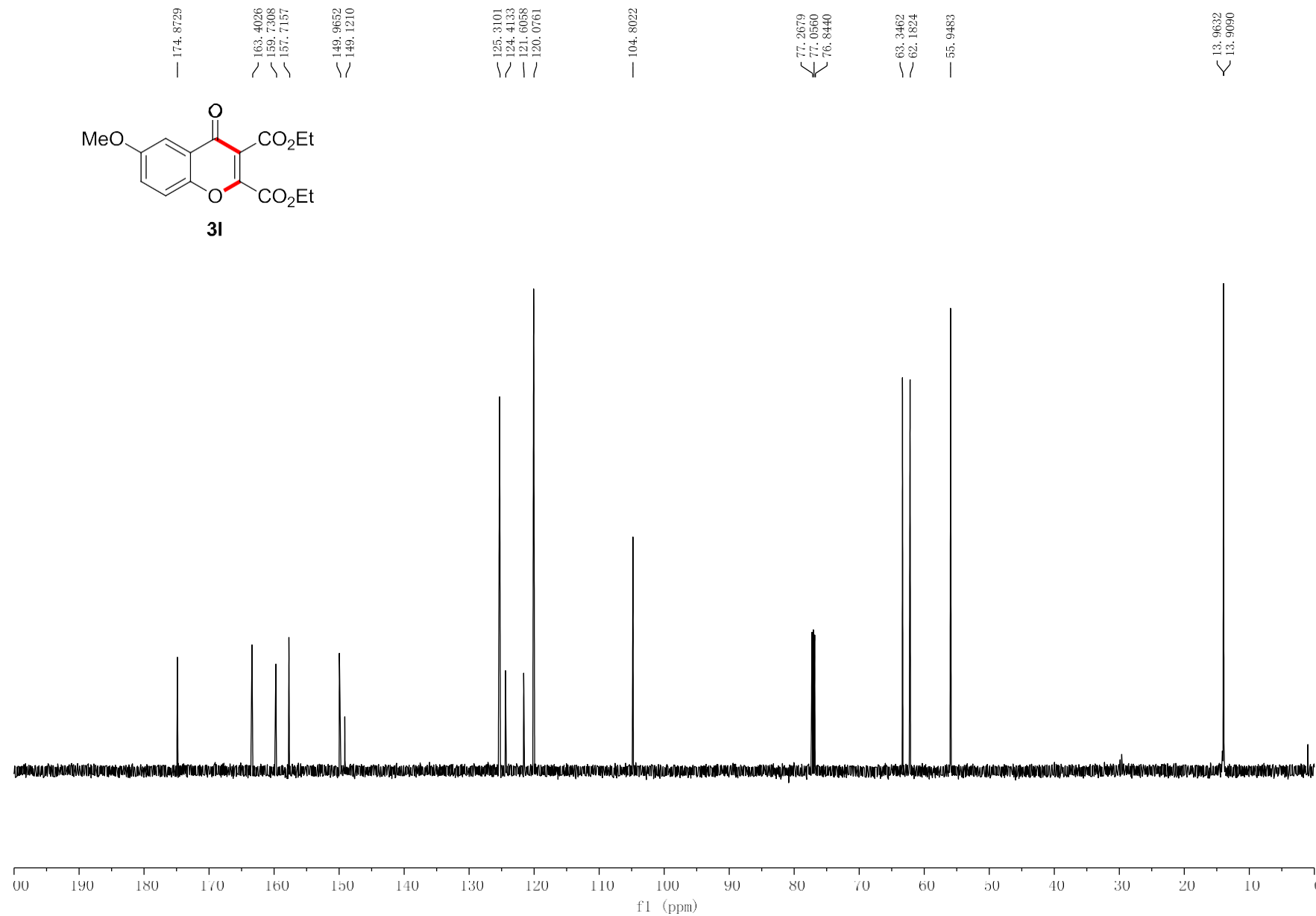
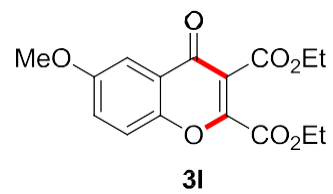


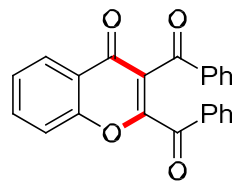






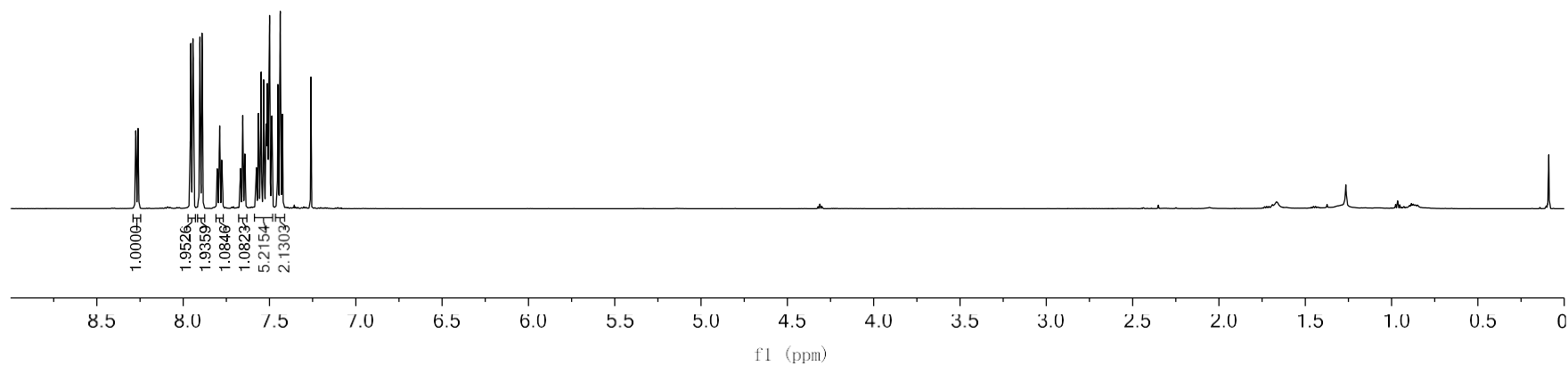




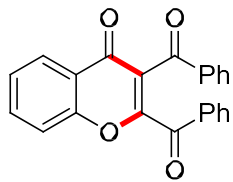


3m

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7.7765
7.7742
7.6673
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7.6425
7.5761
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7.5483
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7.4249
7.2602



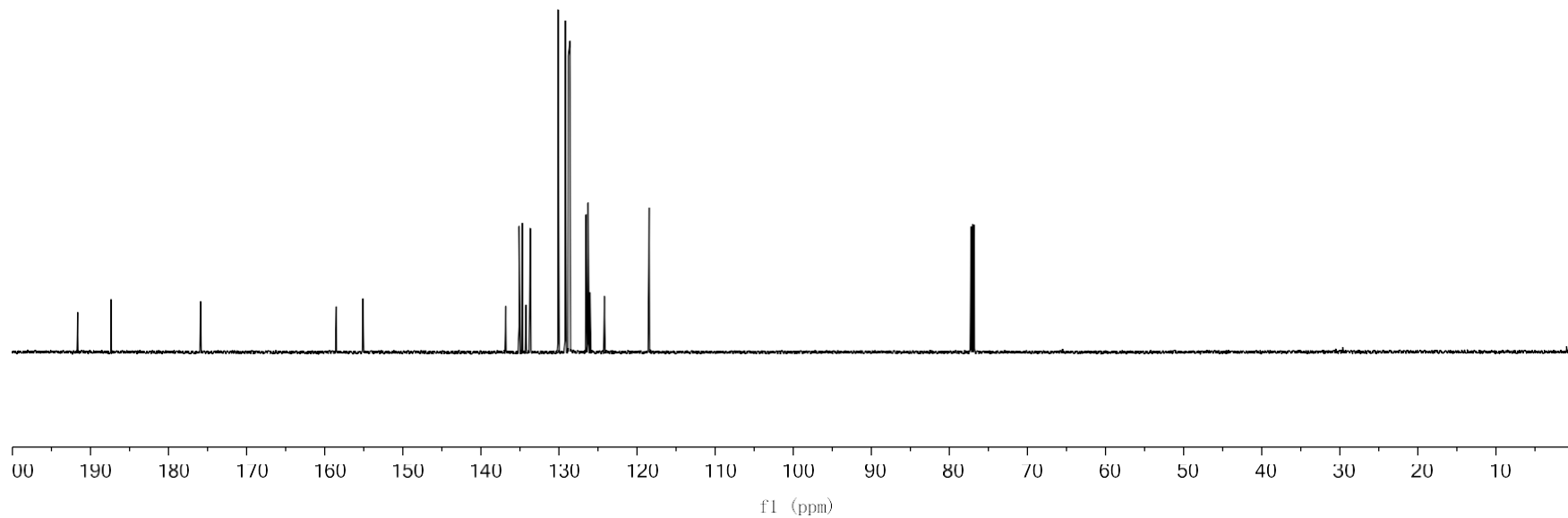
— 191.6204
— 187.3425
— 175.8932



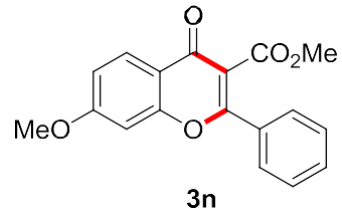
3m

— 158.5036
— 155.0969
— 136.8185
— 135.1104
— 134.6925
— 134.2035
— 133.6890
— 130.1306
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— 126.5317
— 126.2790
— 126.0425
— 124.1918
— 118.4615

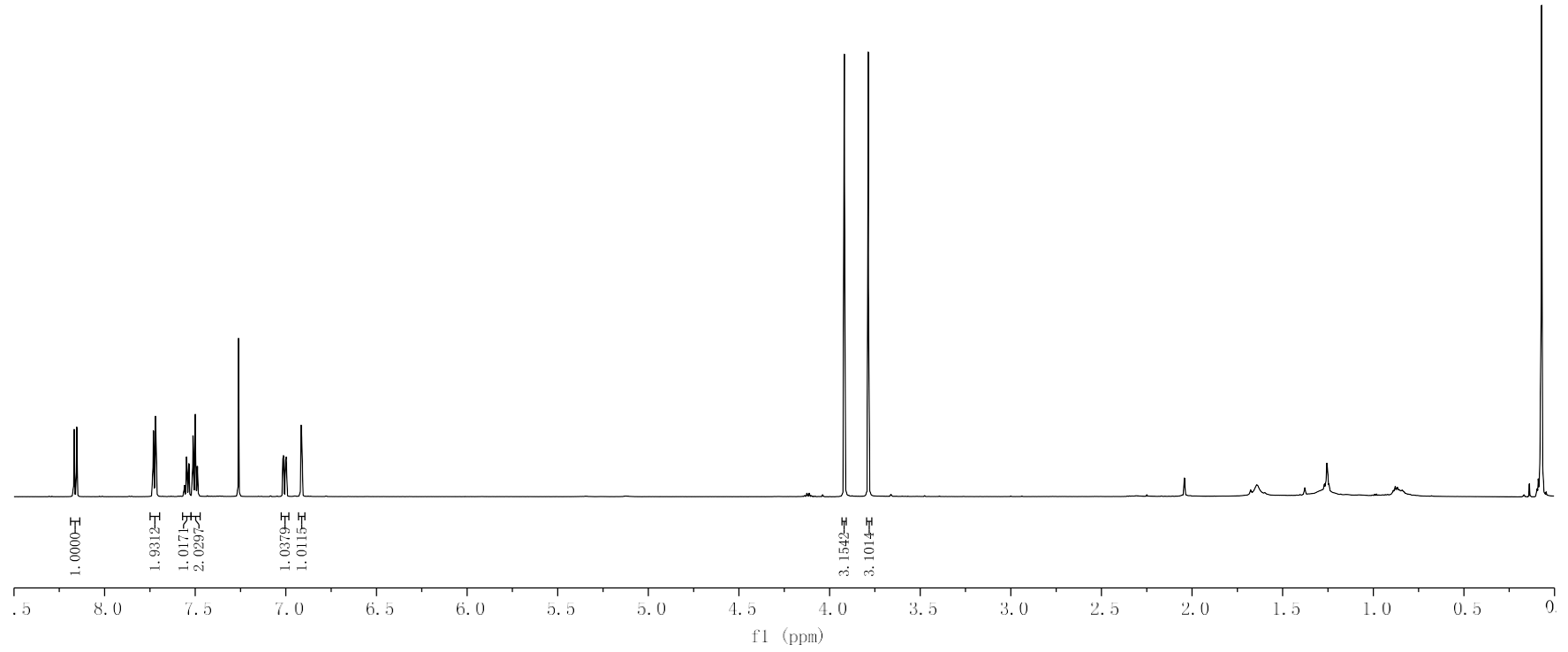
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— 77.0554
— 76.8435

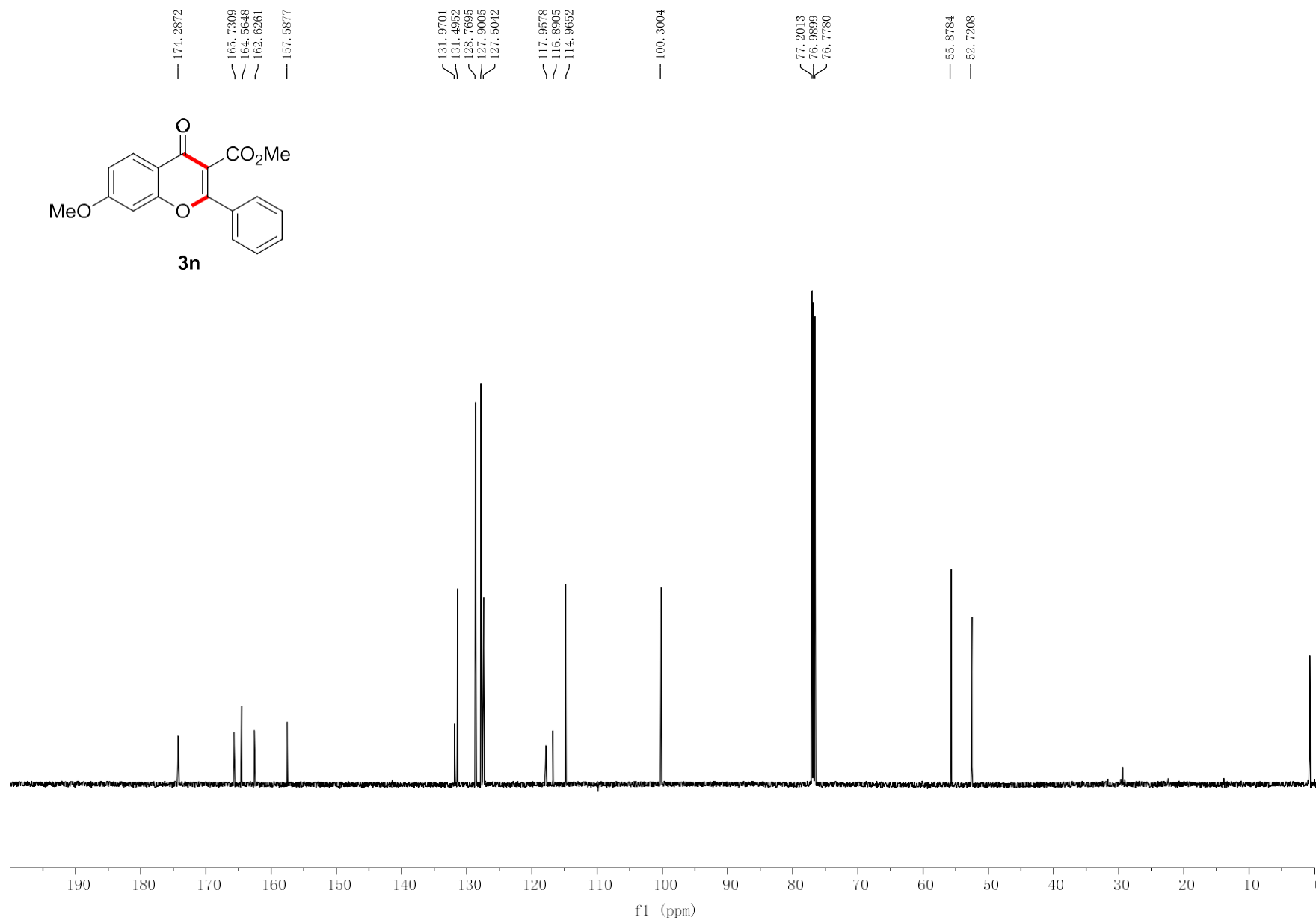
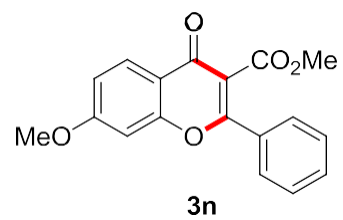


8.1678
8.1529
7.7296
7.7176
7.7152
7.6466
7.5343
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7.4983
7.4866
7.0157
7.0117
7.0008
6.9969
6.9153
6.9114

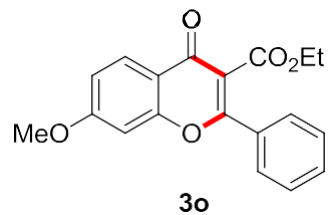


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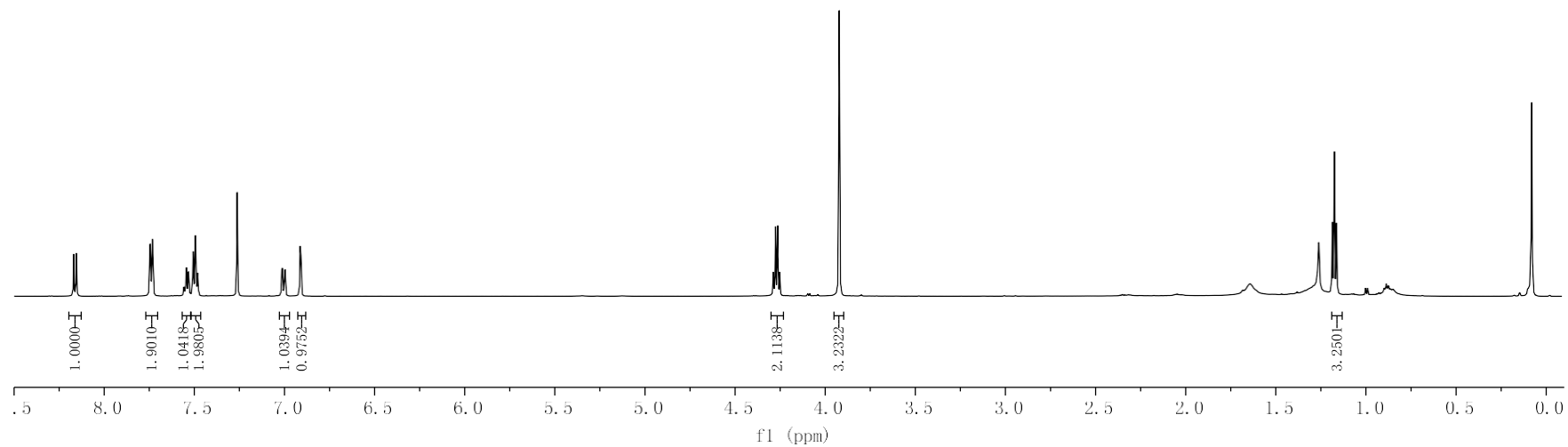


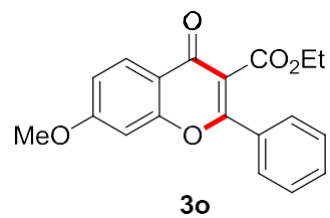
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7.5044
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7.0120
7.0082
6.9972
6.9934
6.9100
6.9062



4.2813
4.2694
4.2575
4.2456
3.9155

1.1763
1.1644
1.1525





— 174.3212
 (165.1386
 (164.5243
 — 162.5741
 — 157.6061

(132.0467
 (131.4071
 (128.6832
 (128.0122
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(118.2711
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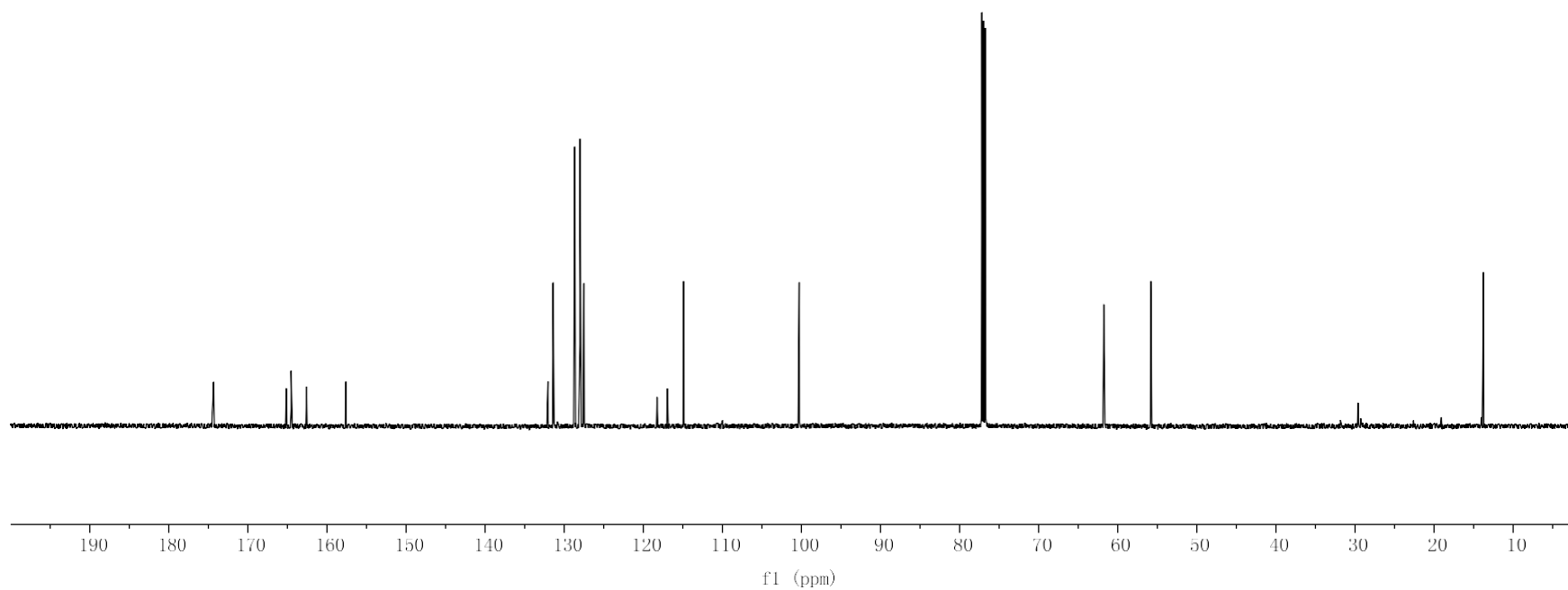
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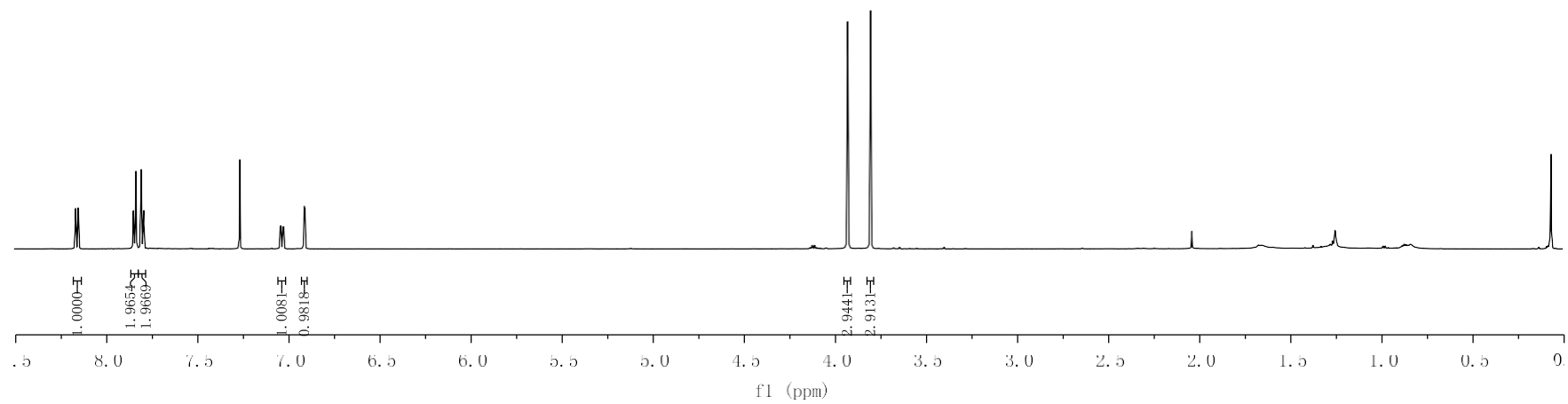
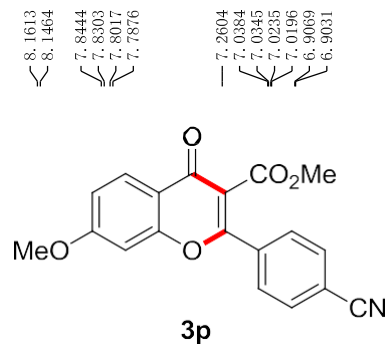
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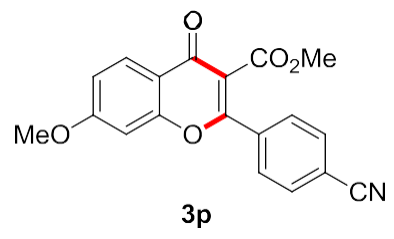
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— 55.8726

— 13.8141







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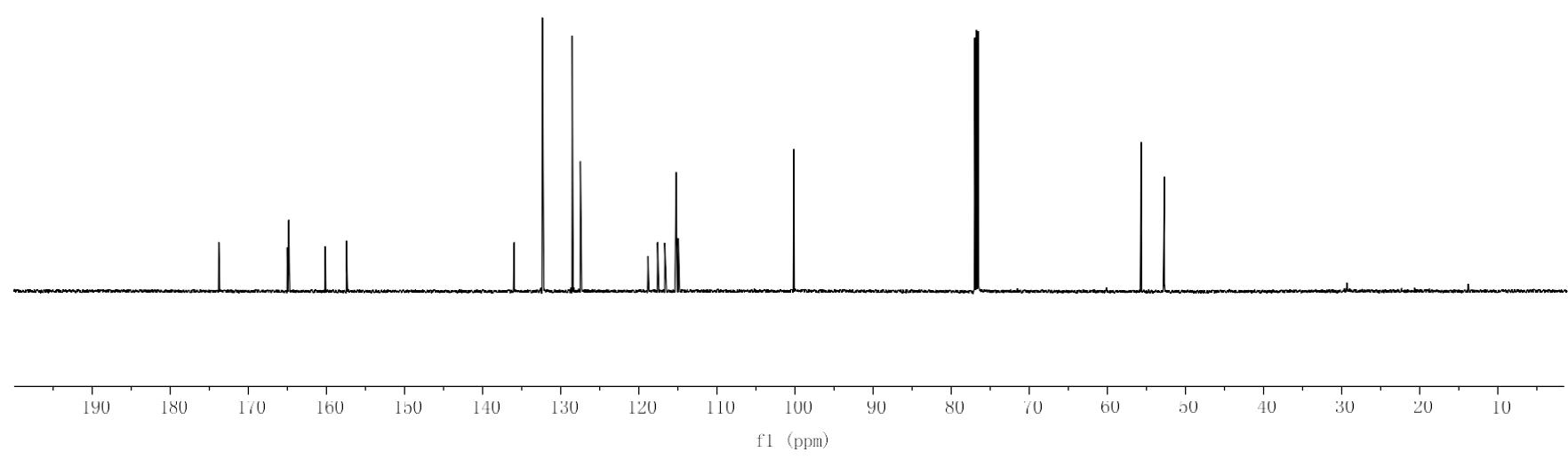
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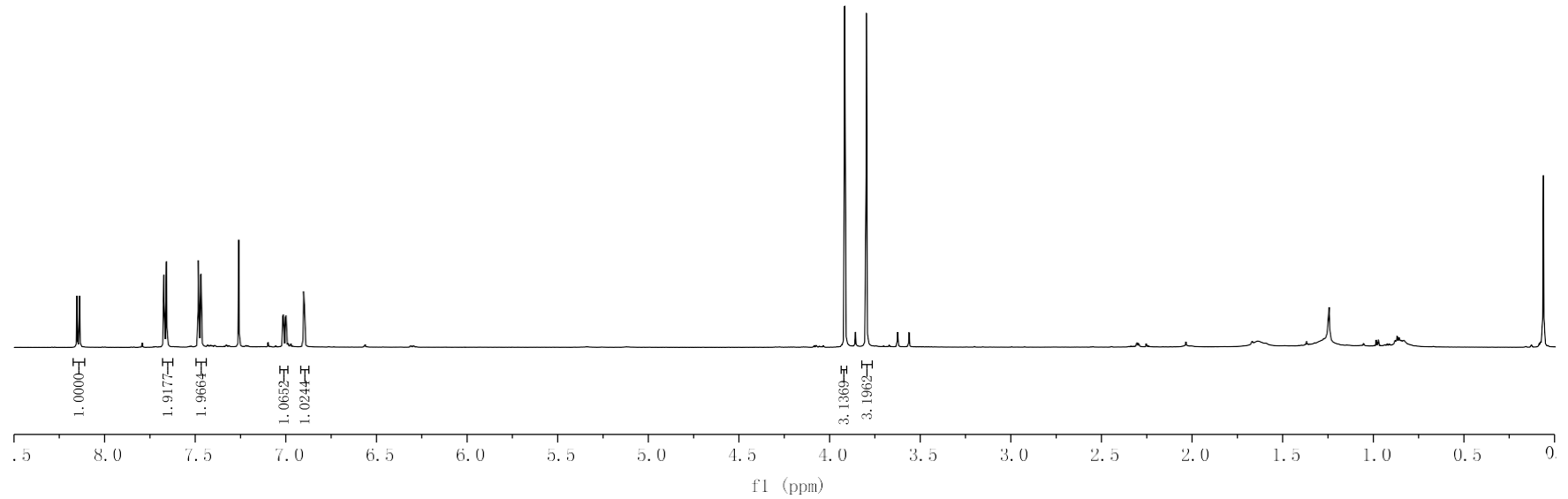
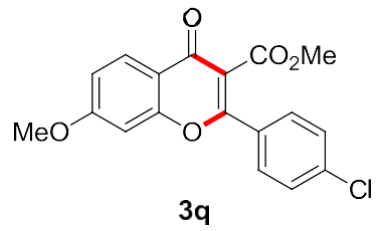
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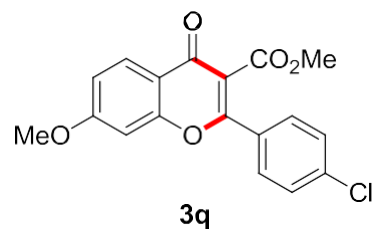
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7.0139
7.0029
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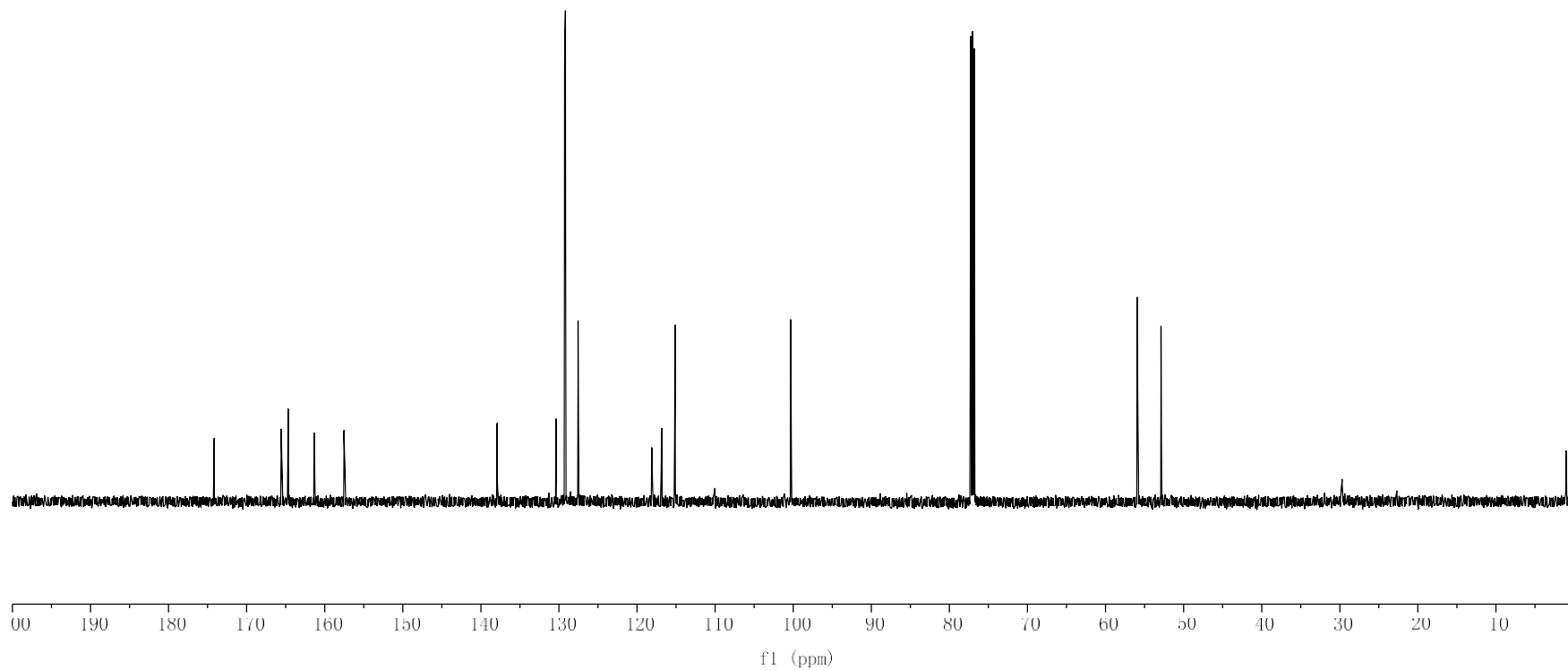
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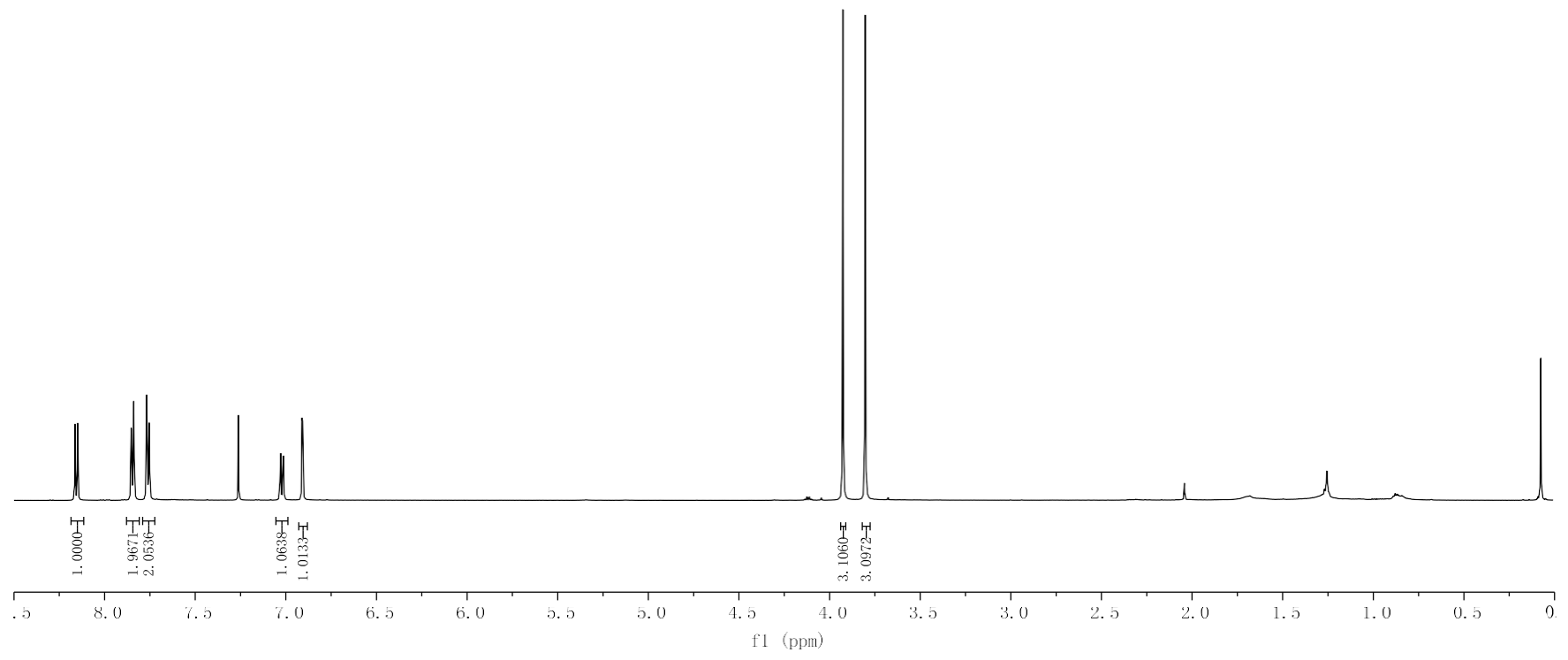
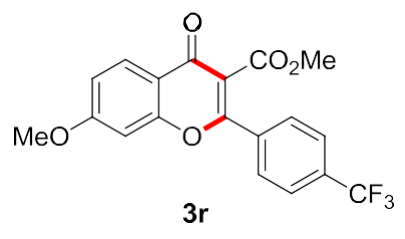
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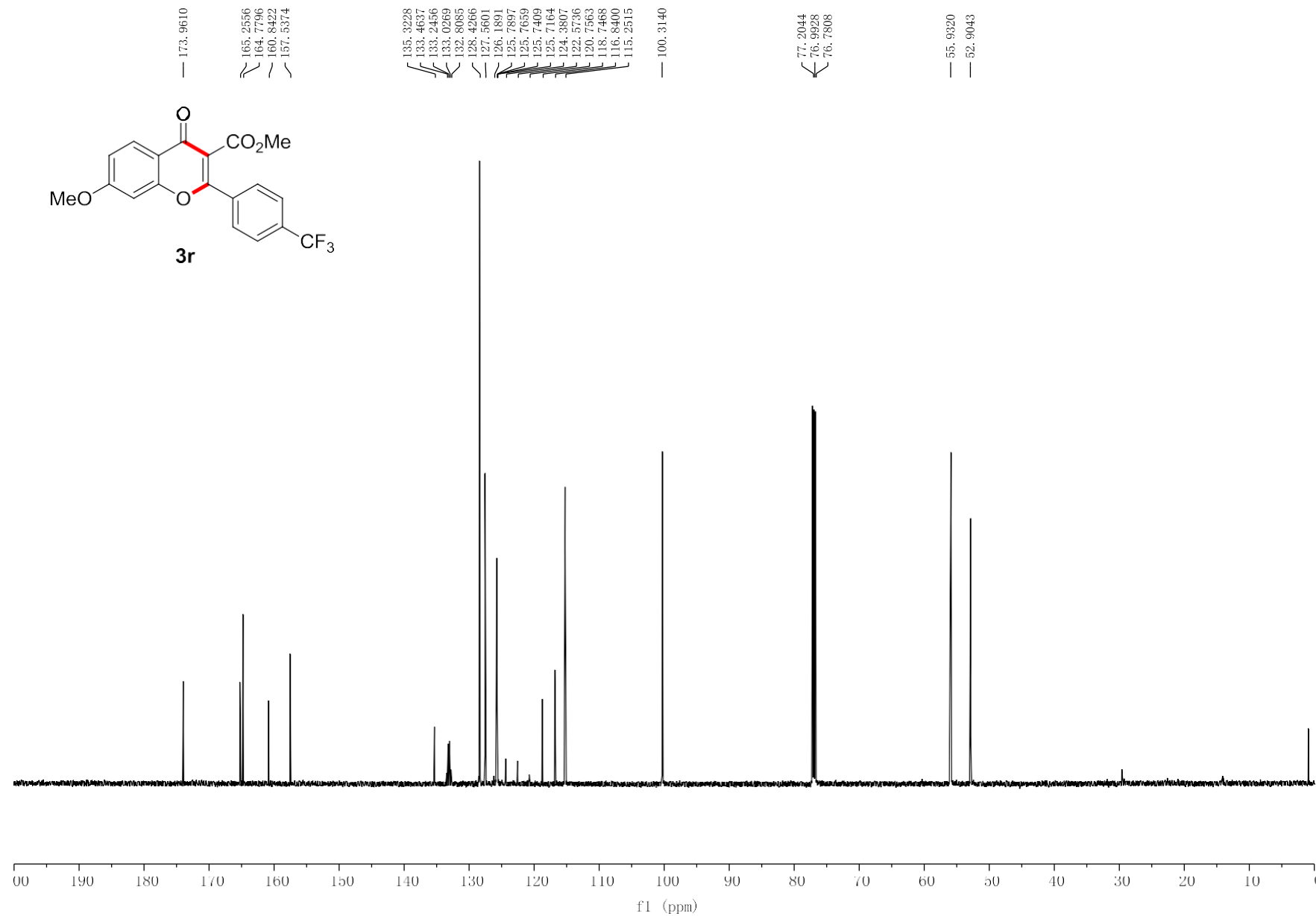
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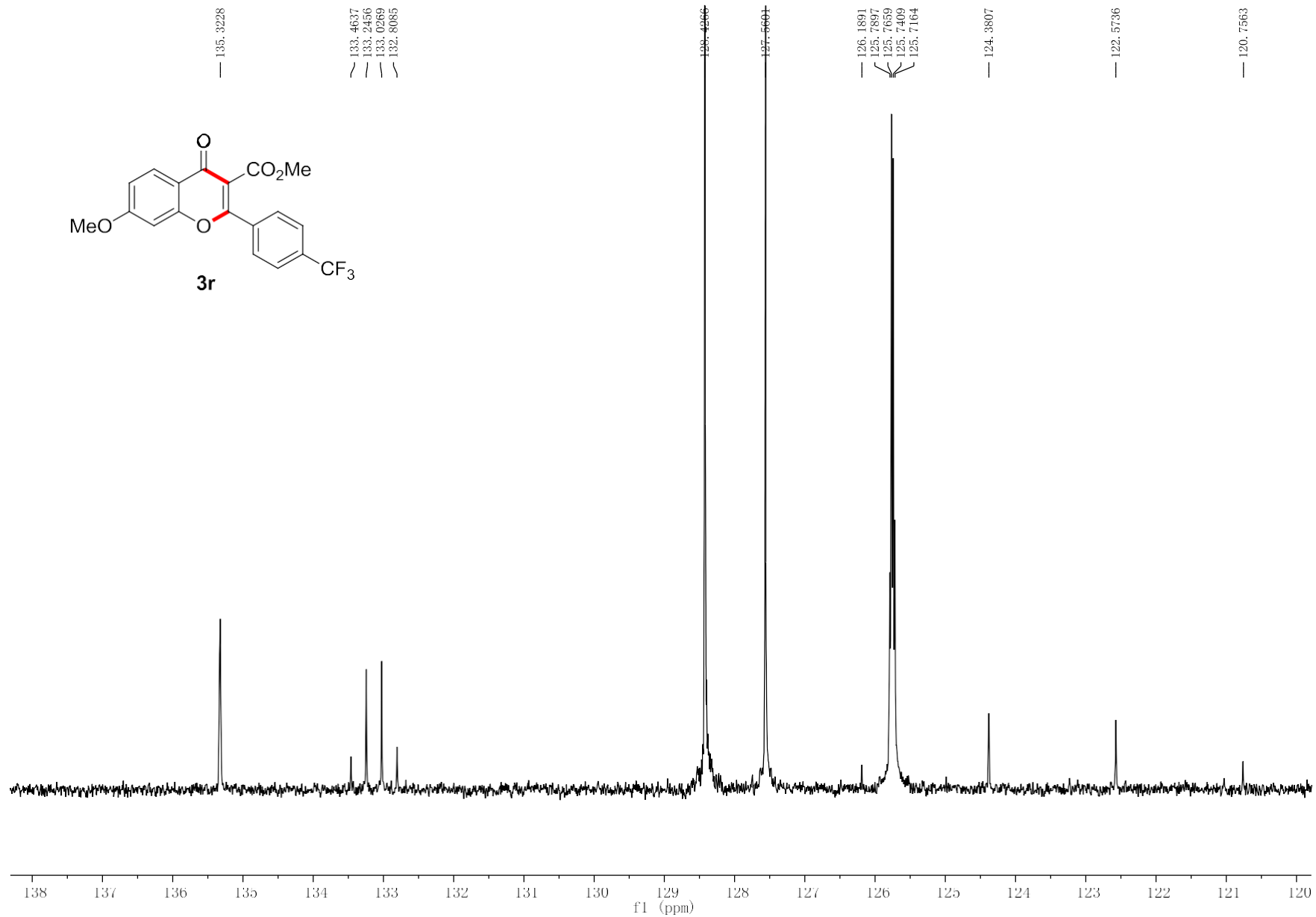
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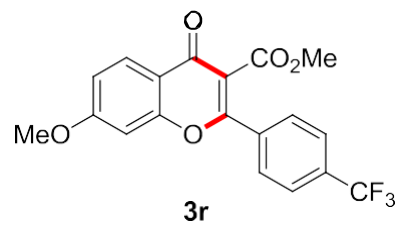


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7.0107
6.9091
6.9053
3.9228
3.7992









— 63.0530

