Supporting Information

Rh(III)-catalyzed C-H annulation of sulfoxonium ylides with iodonium ylides towards isocoumarins

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Table of Contents

1. General information

Unless otherwise noted, all reactions were carried out without exclusion of air or moisture. Commercial solvents and reagents were used without further purification. Analytical thin layer chromatography (TLC) was performed using silica gel GF254 plates. Column chromatography was performed using silica gel (200-300 mesh) eluting with petroleum ether and ethyl acetate. NMR spectra were recorded on 400 MHz or 600 MHz spectrometers in the solvent indicated. Chemical shifts are reported downfield from TMS (= 0.00) for ^{1}H NMR. For ^{13}C NMR, chemical shifts are reported in the scale relative to $CDCl_3$ (= 77.00). HR-MS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer. Melting points were determined using a Büchi B-540 capillary melting point apparatus.**1a-1s**[1], **2a-2h**[2], **2i**[3], **2j**[4], **2K-2m**[2] and **2n**[5] are known compounds and prepared according to the corresponding literature.

2. Reaction Procedure

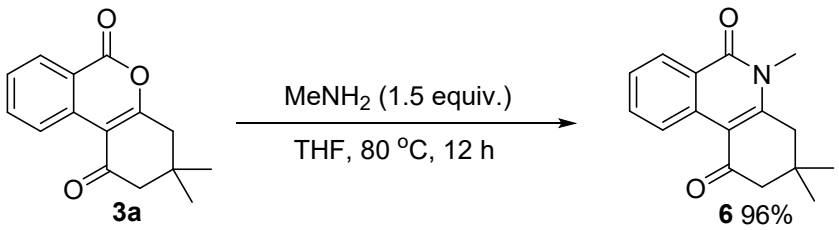
2.1 General procedure for the synthesis of products 3

A mixture of 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **1a** (39.2 mg, 0.20 mmol), 5,5-dimethyl-2-(phenyl-λ^3-iodanylidene)cyclohexane-1,3-dione **2a** (102.6mg, 0.30 mmol), $[Rh^*CpCl_2]_2$ (3.1mg, 2.5 mol %) and NaOPiv (24.8 mg, 0.20 mmol) in HFIP (1.0 mL) was stirred at 40 ^{o}C for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel (200-300 mesh) column chromatography using hexane/ethyl acetate (6:1) as the eluant to afford **3a** as a white solid.

2.2 General Procedure for the gram scale reaction

A mixture of 2-(dimethyl(oxo)-λ^6-sulfanylidene)-1-phenylethan-1-one **1a** (0.98 g, 5.0 mmol), 2-(phenyl-λ^3-iodanylidene)cyclohexane-1,3-dione **2b** (2.56 g, 7.5 mmol), $[Rh^*CpCl_2]_2$ (40.3 mg, 1.3 mol %) and NaOPiv (0.62 g, 5.0 mmol) in HFIP (15.0 mL) was stirred at 40 ^{o}C for 12 hours. The resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel (200-300 mesh) column chromatography using hexane/ethyl acetate (5:1) as the eluant to afford **4a** as a white solid.

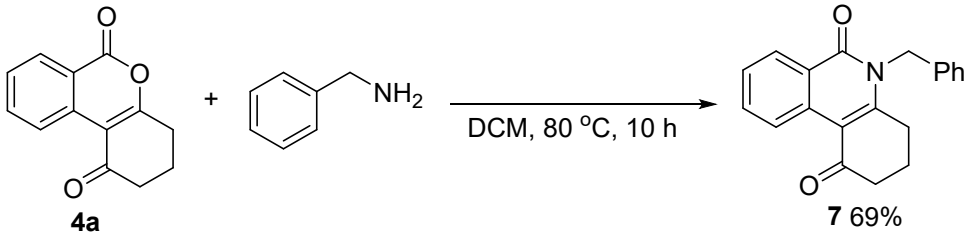
2.3 Further transformation of compound 3a



3a **6** 96%

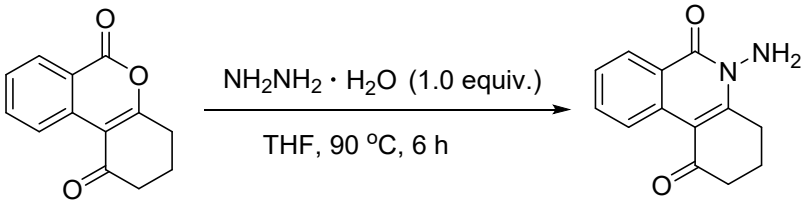
A mixture of **3a** (48.4 mg, 0.2 mmol), methylamine (27.9 mg, 0.3 mmol, 30 wt. % solution in methanol) in THF (2.0 mL) was stirred at 80 °C for 12 hours. Then the resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude product was purified by silica gel chromatography using PE/EA (3:1) to afford the product **6** in 96% yield.

2.4 Further transformation of compound 4a



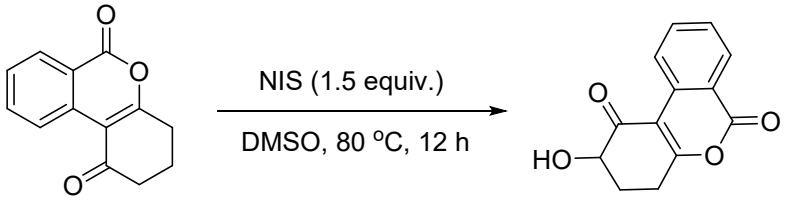
4a **7** 69%

A mixture of **4a** (42.8 mg, 0.2 mmol), phenylmethanamine (30.2 mg, 0.3 mmol) in DCM (2.0 mL) was stirred at 80 °C for 10 hours. Then the resulting mixture was cooled to room temperature, solvent was removed under vacuo and the crude product was purified by silica gel chromatography using PE/EA (3:1) to afford the product **7** in 69% yield.



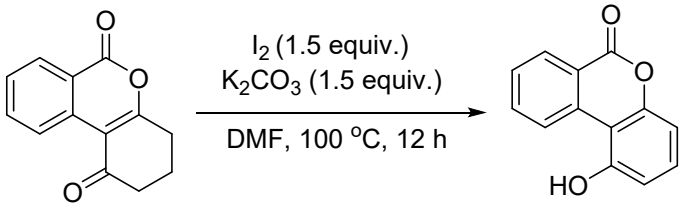
4a **8** 84%

A mixture of **4a** (42.8 mg, 0.2 mmol) and $NH_2NH_2{\cdot}H_2O$ (10.1 mg, 0.2 mmol) in THF (2.0 mL) was stirred at 90 °C for 6 hours. After completion of the reaction as indicated by thin-layer chromatography (TLC), solvent was removed under vacuo. The crude reaction mixtur were washed with H_2O, extracted with ethyl acetate and purified by silica gel column chromatography using PE/EA (3:1) to afford **8** in 84% yield.



4a **9** 75%

A mixture of **4a** (42.8 mg, 0.2 mmol), *N*-Iodosuccinamide (67.2 mg, 0.3 mmol) in DMSO (2.0 mL) was stirred at 80 °C for 12 hours. After completion of the reaction as indicated by thin-layer chromatography (TLC), the reaction mixture was washed with NH_4Cl solution. The product was extracted with ethyl acetate, dried over sodium sulphate, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel column chromatography using PE/EA (2:1) to afford **9** in 75% yield.

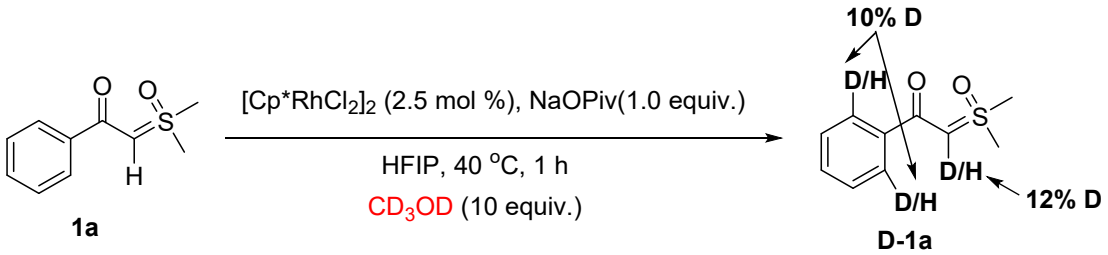


4a **10** 62%

A mixture of **4a** (42.8 mg, 0.2 mmol), K_2CO_3 (41.4 mg, 0.3 mmol) and iodine (76.2 mg, 0.3 mmol) in DMF (2.0 mL) was stirred at 100 °C for 12 hours. After completion of the reaction as indicated by thin-layer chromatography (TLC), the reaction mixture was washed with $Na_2S_2O_3$ solution. The product was extracted with ethyl acetate, solvent was removed under vacuo and the crude reaction mixture was purified by silica gel column chromatography using PE/EA (2:1) to afford **10** in 62% yield.

3. Isotope labeling experiments

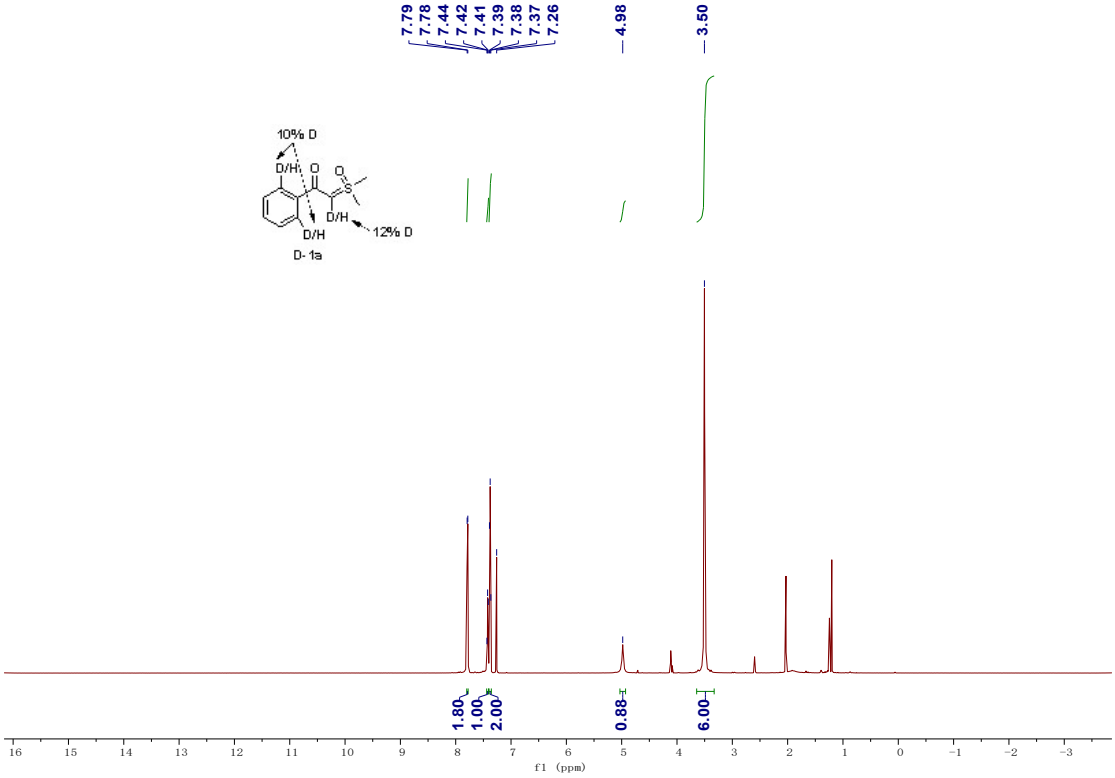
3.1 H/D exchange experiment



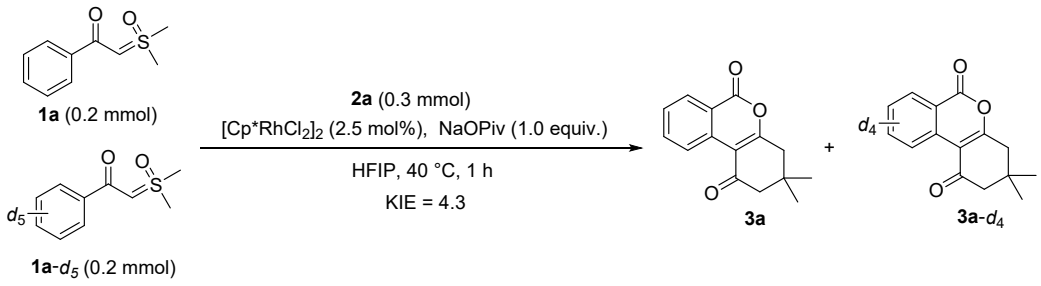
1a **D-1a**

Ylide **1a** (0.20 mmol, 39.2 mg), $[Cp^*RhCl_2]_2$ (2.5 mol %, 3.1 mg), NaOPiv (0.20 mmol, 24.8 mg) and CD_3OD (2.0 mmol, 72.0 mg) were dissolved in HFIP (1.0 mL). The mixture was stirred at 40 °C under air for 1 h. The resulting mixture was cooled

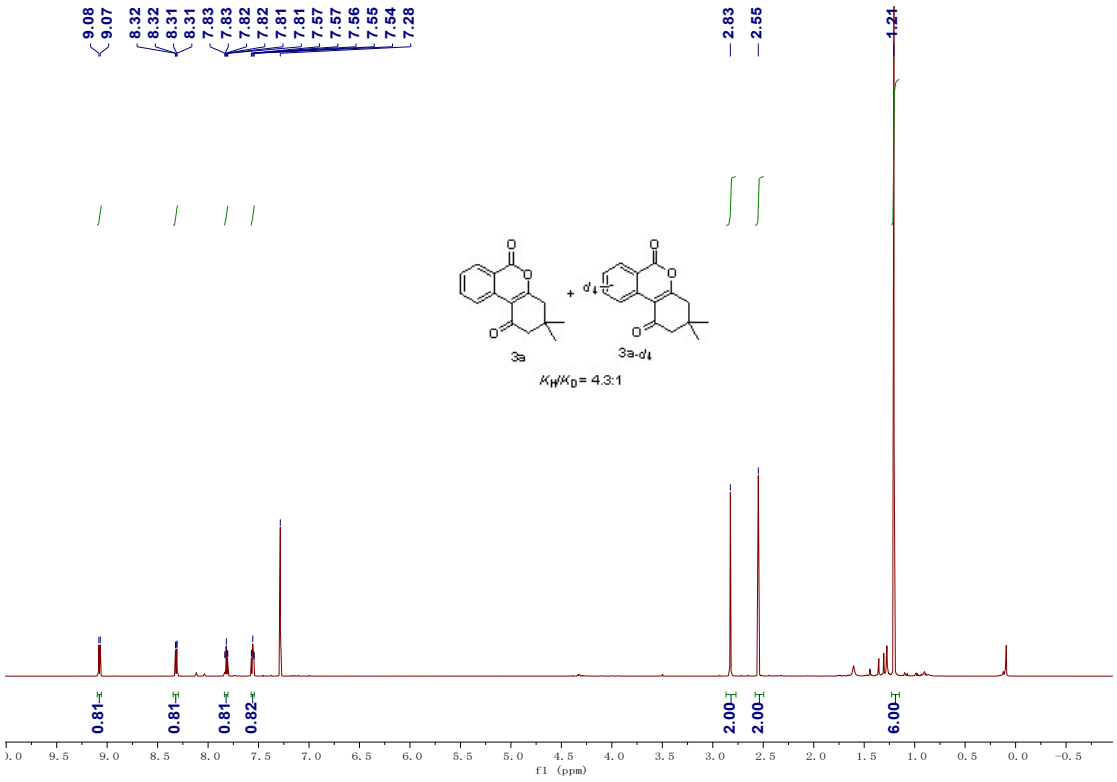
to room temperature and solvent was removed under vacuo. Purification was performed by flash column chromatography on silica gel (5% MeOH in EtOAc) to give the D-**1a**.

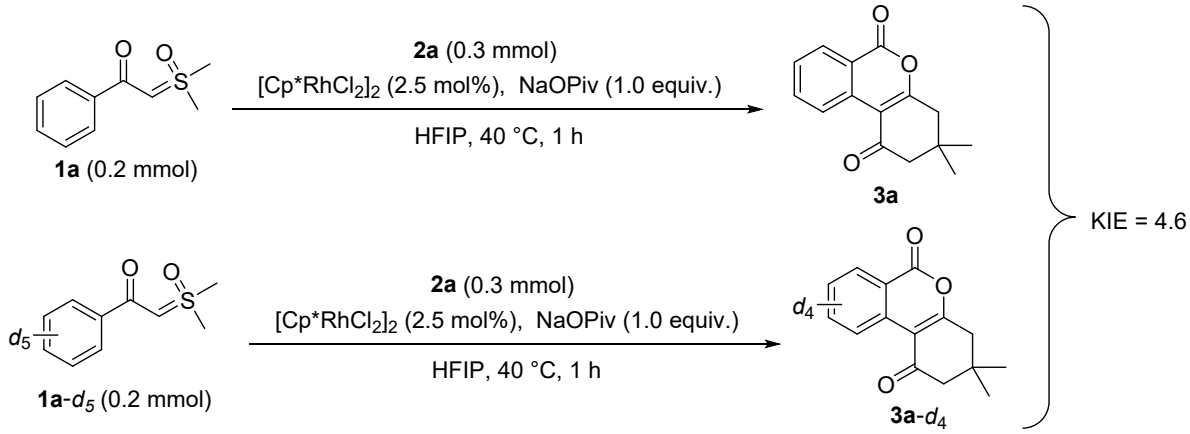


3.2 Kinetic isotope effect

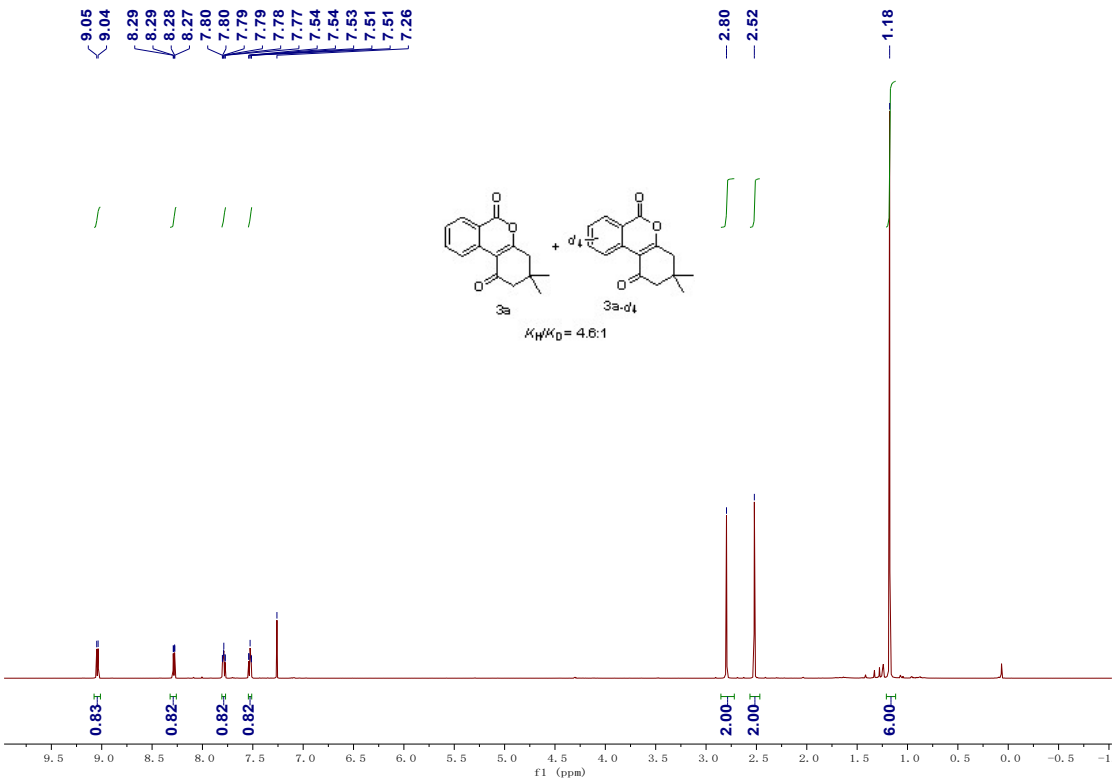


Ylide **1a** (0.20 mmol, 39.2 mg), **1a**-d_5 (0.20 mmol, 40.2 mg), **2a** (0.3 mmol, 102.6 mg), $[Cp^*RhCl_2]_2$ (2.5 mol %, 3.1 mg) and NaOPiv (0.20 mmol, 24.8 mg) were dissolved in HFIP (1.0 mL). The mixture was stirred at 40 ℃ for 1 h. The resulting mixture was cooled to room temperature and solvent was removed under vacuo. Purification was performed by flash column chromatography on silica gel using EtOAc/Hexane (1:6) as the eluant to provide a mixture of **3a** and **3a**-d_4. The ratio of **3a** and **3a**-d_4 was determined to be 4.3:1 by ^{1}H NMR integration method.

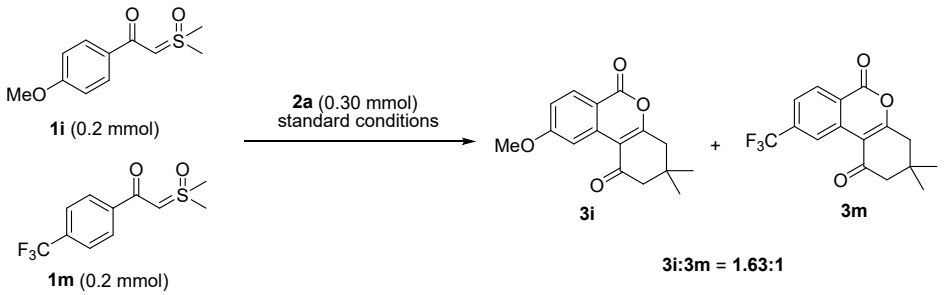




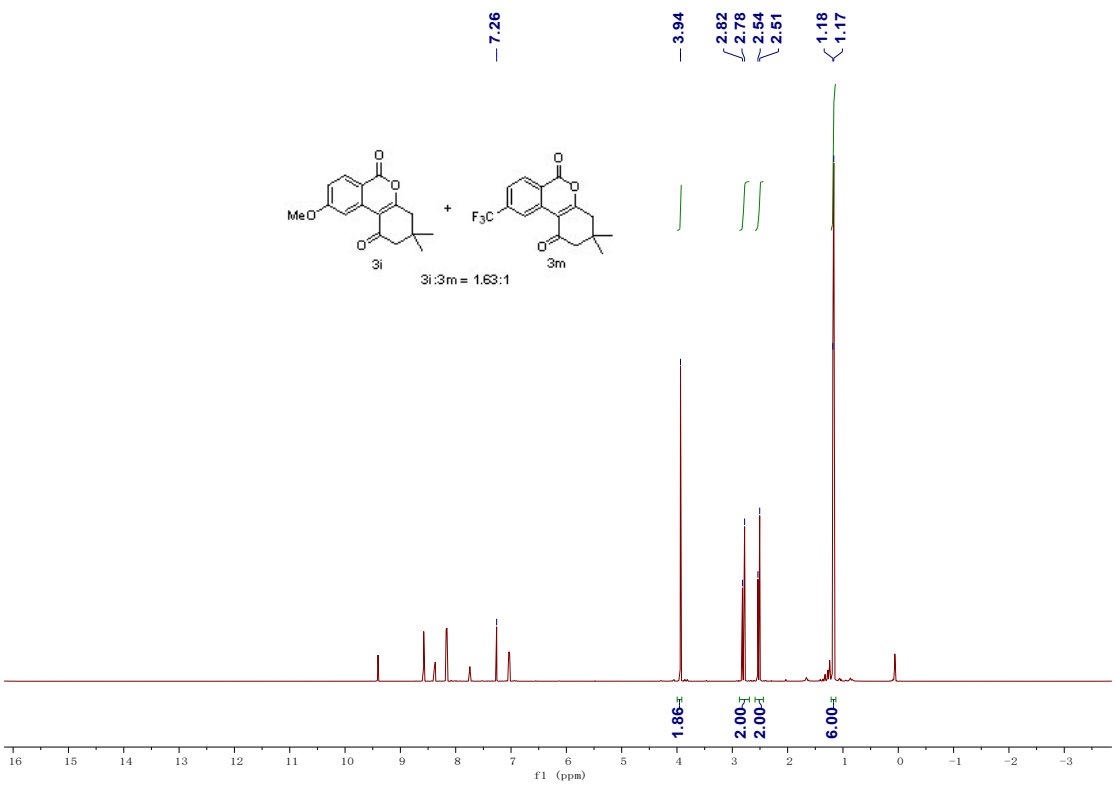
In a round bottom flask, a mixture of ylide **1a** (0.20 mmol, 39.2 mg), **2a** (0.3 mmol, 102.6 mg), $[Cp^*RhCl_2]_2$ (2.5 mol %, 3.1 mg) and NaOPiv (0.20 mmol, 24.8 mg) were dissolved in HFIP (1.0 mL). The mixture was stirred at 40 ℃ for 1 h. At the same time, in another round bottom flask, a solution of **1a**-d_5 (40.2mg, 0.20 mmol), **2a** (102.6 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (3.1mg, 2.5 mol %) and NaOPiv (0.20 mmol, 24.8mg) in HFIP (1.0 mL) was stirred at 40 °C for 1 h. These two mixtures were rapidly combined, and all the volatiles were rapidly removed under a reduced pressure. The residue was purified by silica gel chromatography using EtOAc/Hexane (1:6) as the eluant to provide a mixture of **3a** and **3a**-d_4. Upon analyzing the corresponding ^1H NMR spectrum, the KIE (K_H/K_D) was about 4.6.



4. Competition experiments

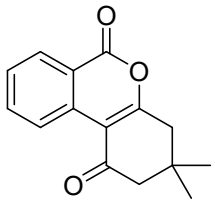


A solution of ylide **1i** (45.2 mg, 0.20 mmol) and **1m** (52.8 mg, 0.20 mmol), 5,5-dimethyl-2-(phenyl-λ^3-iodanylidene)cyclohexane-1,3-dione **2a** (102.6 mg, 0.30 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 2.5 mol %) and NaOPiv (24.8 mg, 0.20 mmol) in HFIP (1.0 mL) was stirred at 40 ^oC under open air for 12 hours. The solvent was removed under vacuo and the crude reaction mixture was directly loaded on silica gel column chromatography and purified using EtOAc/Hexane (1:4) as the eluant to afford a mixture of compounds **3i** and **3m**. The ratio of **3i** and **3m** was determined to be 1.63:1 by ^1H NMR.



5. Analytical data and copies of NMR spectra

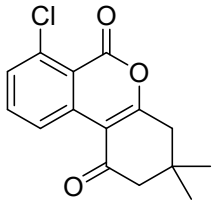
5.1 Analytical data for products



3a

3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

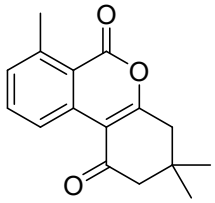
Compound **3a** was isolated as a white solid (44.1 mg, 91% yield). M.P.: 140-141 °C . ^{1}H NMR (**400 MHz, $CDCl_3$**) δ 9.03 (d, *J* = 8.3 Hz, 1H), 8.35 - 8.23 (m, 1H), 7.83 - 7.73 (m, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 2.79 (s, 2H), 2.51 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (**100 MHz, $CDCl_3$**) *δ* 196.9, 167.9, 160.7, 135.6, 133.8, 129.5, 128.3, 125.8, 119.7, 110.5, 52.8, 42.5, 31.9, 28.1. **HRMS (ESI)** m/z calcd for $C_{15}H_{15}O_3^+$ [M + H^+]: 243.1016; found: 243.1015.



3b

7-chloro-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

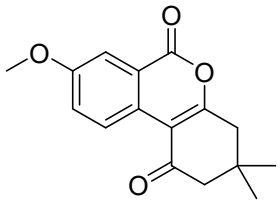
Compound **3b** was isolated as a white solid (18.3 mg, 33% yield). M.P.: 145-146 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.05 (d, J = 7.9 Hz, 1H), 7.64 (t, J = 8.1 Hz, 1H), 7.54 (d, J = 7.4 Hz, 1H), 2.78 (s, 2H), 2.52 (s, 2H), 1.16 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.4, 168.7, 156.9, 136.8, 136.8, 135.3, 131.4, 124.4, 116.9, 110.0, 53.0, 42.4, 31.8, 28.1. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}ClO_3^+$ [M + H^+]: 277.0626; found: 277.0630.



3c

3,3,7-trimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

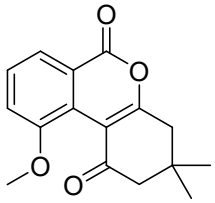
Compound **3c** was isolated as a white solid (10.3 mg, 20% yield). M.P.: 121-123 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 8.94 (d, J = 8.3 Hz, 1H), 7.66 - 7.58 (m, 1H), 7.32 (d, J = 7.5 Hz, 1H), 2.79 (s, 3H), 2.76 (s, 2H), 2.50 (s, 2H), 1.16 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.8, 167.9, 159.7, 143.4, 135.3, 134.8, 131.4, 123.6, 118.1, 110.5, 53.1, 42.5, 31.8, 28.1, 23.8. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}O_3^+$ [M + H^+]: 257.1172; found: 257.1169.



3d

8-methoxy-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

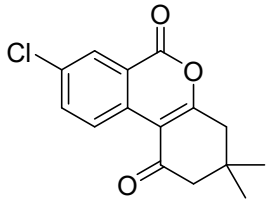
Compound **3d** was isolated as a white solid (22.3 mg, 41% yield). M.P.: 144-145 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 8.97 (d, J = 9.1 Hz, 1H), 7.68 (d, J = 2.9 Hz, 1H), 7.36 (dd, J = 9.1, 2.9 Hz, 1H), 3.90 (s, 3H), 2.78 (s, 2H), 2.50 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 197.1, 165.8, 160.9, 159.3, 127.6, 127.4, 124.6, 121.1, 110.6, 110.3, 55.6, 52.8, 42.3, 32.0, 28.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}O_4^+$ [M + H^+]: 273.1121; found: 273.1118.



3d'

10-methoxy-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

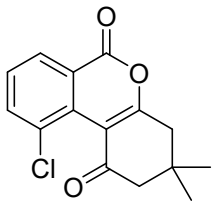
Compound **3d'** was isolated as a white solid (6.5 mg, 12% yield). M.P.: 152-153 °C . ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 7.86 (d, J = 7.8 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 3.90 (s, 3H), 2.73 (s, 2H), 2.57 (s, 2H), 1.18 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 193.8, 163.3, 160.8, 155.3, 129.4, 123.0, 122.3, 121.5, 118.0, 113.4, 56.3, 52.6, 42.0, 33.1, 28.7. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}O_4^+$ [M + H^+]: 273.1121; found: 273.1119.



3e

8-chloro-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

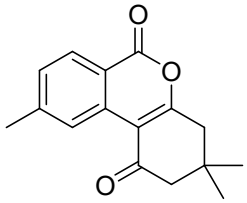
Compound **3e** was isolated as a white solid (20.5 mg, 37% yield). M.P.: 153-154 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.03 (d, J = 8.9 Hz, 1H), 8.24 (d, J = 2.3 Hz, 1H), 7.72 (dd, J = 8.9, 2.4 Hz, 1H), 2.79 (s, 2H), 2.52 (s, 2H), 1.18 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.7, 168.1, 159.6, 135.8, 134.4, 132.2, 128.9, 127.6, 121.2, 110.1, 52.7, 42.4, 32.0, 28.1. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}ClO_3^+$ [M + H^+]: 277.0626; found: 277.0621.



3e'

10-chloro-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

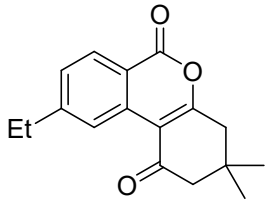
Compound **3e** was isolated as a white solid (6.6 mg, 12% yield). M.P.: 120-121 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 8.23 - 8.17 (m, 1H), 7.83 - 7.79 (m, 1H), 7.48 (t, J = 7.9 Hz, 1H), 2.78 (s, 2H), 2.61 (s, 2H), 1.22 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 193.4, 165.6, 159.8, 137.5, 131.6, 131.2, 129.0, 128.4, 123.4, 113.7, 52.1, 42.1, 32.8, 28.6. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}ClO_3^+$ [M + H^+]: 277.0626; found: 277.0620.



3f

3,3,9-trimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

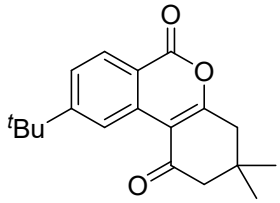
Compound **3f** was isolated as a white solid (47.6 mg, 93% yield). M.P.: 131-132 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 8.85 (s, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 2.78 (s, 2H), 2.53 - 2.47 (m, 5H), 1.17 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 197.1, 168.1, 160.8, 147.0, 133.8, 129.6, 129.6, 125.8, 117.2, 110.5, 52.9, 42.6, 31.9, 28.1, 22.5. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}O_3^+$ [M + H^+]: 257.1172; found: 257.1175.



3g

9-ethyl-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

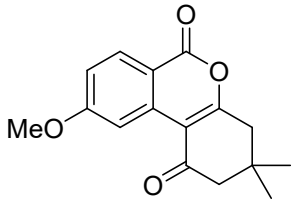
Compound **3g** was isolated as a white solid (49.1 mg, 91% yield). M.P.: 123-124 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 8.90 - 8.85 (m, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.35 (dd, J = 8.4, 1.8 Hz, 1H), 2.81-2.75 (m, 4H), 2.50 (s, 2H), 1.28 (t, J = 7.8 Hz, 3H), 1.16 (s, 6H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 197.0, 168.0, 160.7, 153.0, 133.9, 129.7, 128.4, 124.8, 117.4, 110.5, 52.9, 42.5, 31.9, 29.6, 28.1, 15.1. **HRMS (ESI)** m/z calcd for $C_{17}H_{19}O_3^+$ [M + H^+]: 271.1329; found: 271.1326.



3h

9-(*tert*-butyl)-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

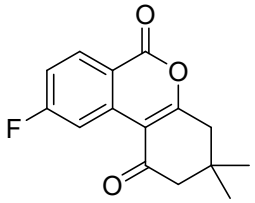
Compound **3h** was isolated as a white solid (55.8 mg, 94% yield). M.P.: 147-149 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9.13 (d, J = 1.8 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 8.4, 1.8 Hz, 1H), 2.79 (s, 2H), 2.51 (s, 2H), 1.39 (s, 9H), 1.17 (s, 6H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 197.2, 168.0, 160.7, 159.8, 133.8, 129.4, 126.1, 122.4, 117.2, 110.7, 53.0, 42.6, 35.8, 31.9, 31.0, 28.1. **HRMS (ESI)** m/z calcd for $C_{19}H_{23}O_3^+$ [M + H^+]: 299.1642; found: 299.1641.



3i

9-methoxy-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

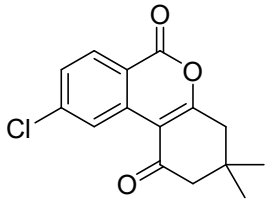
Compound **3i** was isolated as a white solid (50.7 mg, 94% yield). M.P.: 143-144 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 8.64 - 8.56 (m, 1H), 8.18 (dd, J = 8.9, 1.6 Hz, 1H), 7.08 - 7.01 (m, 1H), 3.95 (s, 3H), 2.78 (s, 2H), 2.51 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 197.2, 168.9, 165.4, 160.4, 136.3, 131.6, 117.1, 112.6, 110.3, 107.9, 55.7, 52.9, 42.6, 31.9, 28.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}O_4^+$ [M + H^+]: 273.1121; found: 273.1134.



3j

9-fluoro-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

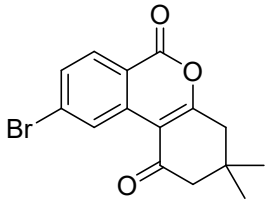
Compound **3j** was isolated as a white solid (45.0 mg, 87% yield). M.P.: 117-118 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 8.76 (dd, J = 11.3, 2.5 Hz, 1H), 8.27 (dd, J = 8.8, 5.9 Hz, 1H), 7.20 (td, J = 8.7, 2.5 Hz, 1H), 2.79 (s, 2H), 2.51 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.5, 169.1, 167.2 (d, J = 256.1 Hz), 159.7, 136.5 (d, J = 12.3 Hz), 132.7 (d, J = 10.6 Hz), 116.6 (d, J = 23.5 Hz), 116.1 (d, J = 2.2 Hz), 112.4 (d, J = 26.2 Hz), 109.9 (d, J = 3.1 Hz), 52.5, 42.5, 31.9, 28.1. ^{19}F NMR (**396 MHz**, **$CDCl_3$**) δ -98.84. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}FO_3^+$ [M + H^+]: 261.0921; found: 261.0924.



3k

9-chloro-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

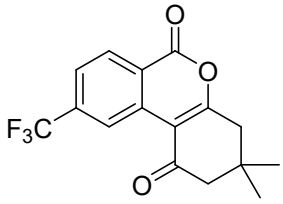
Compound **3k** was isolated as a white solid (49.6 mg, 89% yield). M.P.: 155-156 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.12 - 9.05 (m, 1H), 8.21 - 8.15 (m, 1H), 7.51 - 7.44 (m, 1H), 2.79 (s, 2H), 2.52 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.5, 169.1, 159.9, 142.7, 135.0, 131.0, 128.9, 125.7, 118.0, 109.7, 52.6, 42.5, 31.9, 28.1. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}ClO_3^+$ [M + H^+]: 277.0626; found: 277.0638.



3l

9-bromo-3,3-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

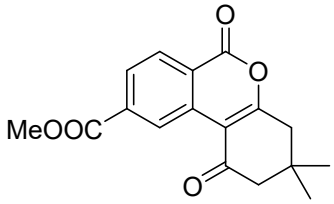
Compound **3l** was isolated as a white solid (55.2 mg, 86% yield). M.P.: 159-160 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.35 - 9.23 (m, 1H), 8.15 - 8.06 (m, 1H), 7.69 - 7.59 (m, 1H), 2.80 (s, 2H), 2.52 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.5, 169.0, 160.1, 135.0, 131.9, 131.7, 131.0, 128.8, 118.4, 109.6, 52.6, 42.6, 31.9, 28.1. **HRMS (ESI)** m/z calcd for $C_{15}H_{14}BrO_3^+$ [M + H^+]: 321.0121; found: 321.0136.



3m

3,3-dimethyl-9-(trifluoromethyl)-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

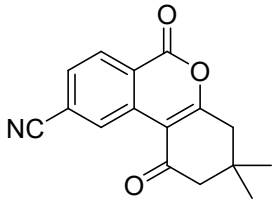
Compound **3m** was isolated as a white solid (35.4 mg, 57% yield). M.P.: 169-170 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.42 (s, 1H), 8.45 - 8.34 (m, 1H), 7.75 (d, J = 8.3 Hz, 1H), 2.83 (s, 2H), 2.55 (s, 2H), 1.19 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.5, 169.1, 159.6, 136.8 (d, J = 32.8 Hz), 134.3, 130.3, 124.7 (q, J = 3.5 Hz), 123.3 (q, J = 3.9 Hz), 122.2, 121.9, 109.9, 52.6, 42.5, 32.0, 28.1. ^{19}F NMR (**396 MHz**, **$CDCl_3$**) δ -63.38. **HRMS (ESI)** m/z calcd for $C_{16}H_{14}F_3O_3^+$ [M + H^+]: 311.0890; found: 311.0904.



3n

3,3-dimethyl-1,6-dioxo-2,3,4,6-tetrahydro-1H-benzo[c]chromene-9-carboxylate

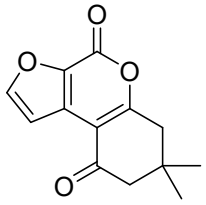
Compound **3n** was isolated as a white solid (33.0 mg, 55% yield). M.P.: 156-157 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.71 - 9.63 (m, 1H), 8.38 - 8.28 (m, 1H), 8.20 - 8.11 (m, 1H), 3.99 (s, 3H), 2.82 (s, 2H), 2.55 (s, 2H), 1.20 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.5, 168.4, 166.0, 160.0, 136.2, 133.9, 129.7, 128.8, 127.2, 122.6, 110.2, 52.7, 52.7, 42.4, 31.9, 28.1. **HRMS (ESI)** m/z calcd for $C_{17}H_{17}O_5^+$ [M + H^+]: 301.1071; found: 301.1083.



3o

3,3-dimethyl-1,6-dioxo-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromene-9-carbonitrile

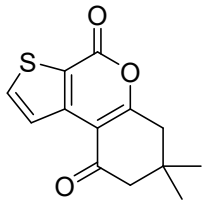
Compound **3o** was isolated as a white solid (16.1 mg, 30% yield). M.P.: 142-143°C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.46 (dd, J = 0.8 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.75 (dd, J = 8.0, 1.2 Hz, 1H), 2.84 (s, 2H), 2.56 (s, 2H), 1.20 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.3, 169.5, 159.2, 134.3, 130.7, 130.3, 130.3, 122.5, 119.0, 117.6, 109.3, 52.5, 42.5, 32.0, 28.1. **HRMS (ESI)** m/z calcd for $C_{16}H_{14}NO_3^+$ [M +H^+]: 268.0968; found: 268.0963.



3p

7,7-dimethyl-7,8-dihydro-4*H*-furo[2,3-*c*]chromene-4,9(6*H*)-dione

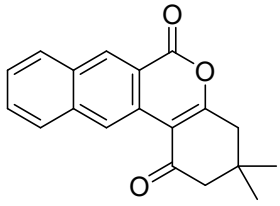
Compound **3p** was isolated as a white solid (16.3 mg, 35% yield). M.P.: 143-144 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 7.85 (d, J = 1.8 Hz, 1H), 7.36 (d, J = 1.8 Hz, 1H), 2.78 (s, 2H), 2.47 (s, 2H), 1.17 (s, 6H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 195.0, 169.0, 152.0, 151.3, 136.8, 132.5, 110.1, 109.1, 51.0, 41.6, 32.8, 28.2. **HRMS (ESI)** m/z calcd for $C_{13}H_{13}O_4^+$ [M +H^+]: 233.0808; found: 233.0802.



3q

7,7-dimethyl-7,8-dihydro-4*H*-thieno[2,3-*c*]chromene-4,9(6*H*)-dione

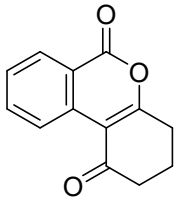
Compound **3q** was isolated as a white solid (44.0 mg, 89% yield). M.P.: 128-129 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 8.27 - 8.18 (m, 1H), 7.94 - 7.87 (m, 1H), 2.82 (s, 2H), 2.50 (s, 2H), 1.18 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 195.1, 169.3, 156.8, 143.5, 137.7, 126.0, 122.8, 111.4, 51.5, 41.8, 32.4, 28.2. **HRMS (ESI)** m/z calcd for $C_{13}H_{12}NaO_3S^+$ [M + Na^+]: 271.0399; found: 271.0413.



3r

3,3-dimethyl-3,4-dihydro-1*H*-naphtho[2,3-*c*]chromene-1,6(2*H*)-dione

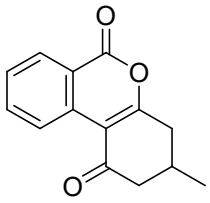
Compound **3r** was isolated as a white solid (45.6 mg, 78% yield). M.P.: 184-185 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.51 (s, 1H), 8.89 (s, 1H), 8.04 - 7.95 (m, 2H), 7.69 - 7.62 (m, 1H), 7.60 - 7.53 (m, 1H), 2.81 (s, 2H), 2.56 (s, 2H), 1.20 (s, 6H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 197.3, 166.8, 161.0, 136.8, 132.0, 131.7, 129.5, 129.2, 129.0, 127.7, 127.2, 125.4, 118.0, 110.6, 52.9, 42.5, 31.9, 28.2. **HRMS (ESI)** m/z calcd for $C_{19}H_{17}O_3^+$ [M +H^+]: 293.1172; found: 293.1181.



4a

3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

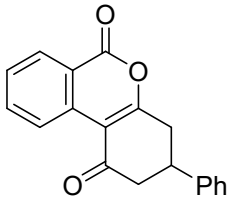
Compound **4a** was isolated as a white solid (36.8 mg, 86% yield). M.P.: 128-129 °C. ^{1}H NMR (**400 MHz**, **$CDCl_3$**) δ 9.03 (d, J = 8.3 Hz, 1H), 8.30 - 8.22 (m, 1H), 7.81 - 7.75 (m, 1H), 7.56 - 7.49 (m, 1H), 2.93 (t, J = 6.0 Hz, 2H), 2.65 (t, J = 6.8 Hz, 2H), 2.17 (p, J = 6.4 Hz, 2H). ^{13}C NMR (**100 MHz**, **$CDCl_3$**) δ 196.9, 169.4, 160.4, 135.6, 134.0, 129.5, 128.4, 126.0, 119.8, 111.5, 38.9, 28.9, 19.9.



4b

3-methyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

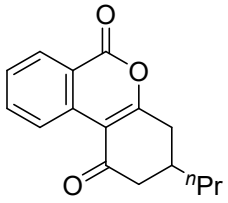
Compound **4b** was isolated as a white solid (36.9 mg, 81% yield). M.P.: 123-124 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9.02 (d, J = 8.4 Hz, 1H), 8.25 (dd, J = 8.4, 1.2 Hz, 1H), 7.80 - 7.73 (m, 1H), 7.54 - 7.47 (m, 1H), 2.96 - 2.89 (m, 1H), 2.72 - 2.61 (m, 2H), 2.47 - 2.32 (m, 2H), 1.18 (d, J = 6.6 Hz, 3H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 196.8, 168.8, 160.5, 135.5, 133.9, 129.5, 128.3, 125.8, 119.7, 111.1, 47.1, 36.8, 27.6, 20.7.



4c

3-phenyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

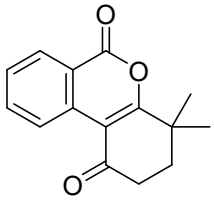
Compound **4c** was isolated as a white solid (51.2 mg, 88% yield). M.P.: 168-169 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9.06 (d, J = 8.4 Hz, 1H), 8.27 (dd, J = 7.8, 1.2 Hz, 1H), 7.82 - 7.76 (m, 1H), 7.57 - 7.50 (m, 1H), 7.42 - 7.36 (m, 2H), 7.34 - 7.28 (m, 3H), 3.60 - 3.52 (m, 1H), 3.21 - 3.09 (m, 2H), 2.98 - 2.85 (m, 2H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 195.9, 168.5, 160.3, 141.4, 135.6, 133.7, 129.5, 129.0, 128.5, 127.4, 126.5, 125.9, 119.7, 111.2, 45.8, 37.9, 36.3.



4d

3-propyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

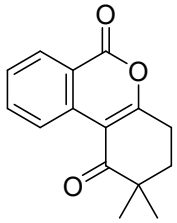
Compound **4d** was isolated as a white solid (48.6 mg, 95% yield). M.P.: 113-114 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9 .02 (d, J = 8.4 Hz, 1H), 8.25 (dd, J = 7.8, 1.2 Hz, 1H), 7.79 - 7.74 (m, 1H), 7.53 - 7.48 (m, 1H), 2.98 - 2.90 (m, 1H), 2.76 - 2.69 (m, 1H), 2.68 - 2.60 (m, 1H), 2.40 - 2.23 (m, 2H), 1.50 - 1.36 (m, 4H), 0.94 (t, J = 7.8 Hz, 3H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 196.9, 169.0, 160.5, 135.5, 133.9, 129.5, 128.3, 125.8, 119.7, 111.2, 45.4, 37.4, 35.1, 32.2, 19.5, 13.9. **HRMS (ESI)** m/z calcd for $C_{16}H_{17}O_3^+$ [M +H^+]: 257.1172; found: 257.1164.



4e

4,4-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

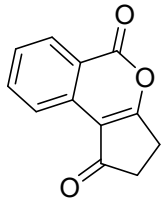
Compound **4e** was isolated as a white solid (22.8 mg, 47% yield). M.P.: 119-120 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9.05 (d, J = 8.4 Hz, 1H), 8.28 (dd, J = 7.8, 1.2 Hz, 1H), 7.80 - 7.75 (m, 1H), 7.56 - 7.48 (m, 1H), 2.70 (t, J = 7.2 Hz, 2H), 2.03 (t, J = 7.2 Hz, 2H), 1.46 (s, 6H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 197.0, 174.3, 160.6, 135.5, 134.1, 129.4, 128.4, 126. 3, 119.8, 110.0, 36.1, 35.8, 34.8, 26.2.



4e'

2,2-dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

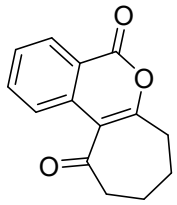
Compound **4e'** was isolated as a white solid (22.8 mg, 47% yield). M.P.: 136-137 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9.02 (d, J = 8.4 Hz, 1H), 8.27 (dd, J = 8.4, 1.2 Hz, 1H), 7.79 - 7.74 (m, 1H), 7.54 - 7.47 (m, 1H), 2.93 (t, J = 6.6 Hz, 2H), 2.00 (t, J = 6.6 Hz, 2H), 1.23 (s, 6H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 201.7, 167.4, 160.6, 135.5, 134.4, 129.5, 128.3, 126.1, 120.0, 109.7, 42.0, 33.1, 25.6, 24.5.



4f

2,3-dihydrocyclopenta[*c*]isochromene-1,5-dione

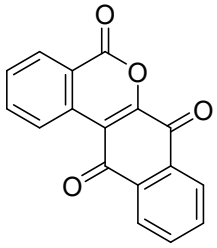
Compound **4f** was isolated as a white solid (37.2 mg, 93% yield). M.P.: 123-124 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 8.48 (d, *J* = 7.8 Hz, 1H), 8.30 - 8.23 (m, 1H), 7.83 - 7.78 (m, 1H), 7.59 - 7.54 (m, 1H), 3.06 - 2.98 (m, 2H), 2.77 - 2.71 (m, 2H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) *δ* 200.3, 180.4, 161.0, 135.8, 131.8, 130.4, 129.0, 123.2, 118.6, 114.5, 34.6, 25.8.



4g

7,8,9,10-tetrahydrocyclohepta[*c*]isochromene-5,11-dione

Compound **4g** was isolated as a white solid (11.1 mg, 24% yield). M.P.: 145-146 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) *δ* 8.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.76 - 7.69 (m, 1H), 7.53 - 7.47 (m, 1H), 2.97 - 2.92 (m, 2H), 2.83 - 2.78 (m, 2H), 1.99 - 1.92 (m, 4H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) *δ* 202.6, 163.5, 161.1, 135.2, 134.5, 129.6, 128.2, 124.6, 119.6, 116.3, 43.0, 32.3, 23.1, 22.4.

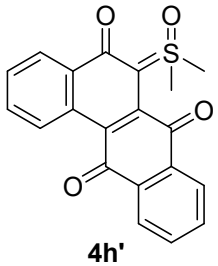


4h

5*H*-dibenzo[*c*,*g*]chromene-5,7,12-trione

Compound **4h** was isolated as a yellow solid (47.7 mg, 86% yield). M.P.: 251-252 °C.

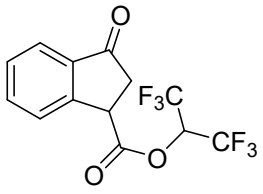
^{1}H NMR (**600 MHz**, **$CDCl_3$**) *δ* 9.32 (d, *J* = 7.8 Hz, 1H), 8.44 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.25 - 8.20 (m, 2H), 7.97 - 7.92 (m, 1H), 7.87 - 7.78 (m, 2H), 7.77 - 7.72 (m, 1H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) *δ* 183.5, 176.6, 158.7, 150.9, 135.9, 134.9, 134.2, 132.4, 132.1, 131.3, 130.4, 130.3, 128.7, 127.1, 126.7, 122.9, 116.7. **HRMS (ESI)** m/z calcd for $C_{17}H_9O_4^+$ [M +H^+]: 277.0495; found: 277.0487.



4h'

6-(dimethyl(oxo)-λ^6-sulfanylidene)tetraphene-5,7,12(6*H*)-trione

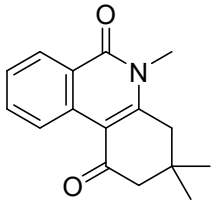
Compound **4h'** was isolated as a maroon solid (7.1 mg, 10% yield). M.P.: 263-264 °C. ^{1}H NMR (**600 MHz**, **CDCl$_3$**) δ 9.56 (d, *J* = 8.4 Hz, 1H), 8.41 - 8.36 (m, 1H), 8.20 - 8.16 (m, 1H), 7.97 - 7.93 (m, 1H), 7.77 - 7.70 (m, 2H), 7.68 - 7.62 (m, 1H), 7.59 - 7.51 (m, 1H), 4.01 (s, 6H). ^{13}C NMR (**150 MHz**, **CDCl$_3$**) *δ* 185.9, 182.6, 174.1, 142.2, 134.3, 134.0, 133.8, 133.6, 132.6, 132.5, 132.1, 129.1, 127.9, 126.7, 125.4, 124.9, 119.0, 97.7, 43.8. **HRMS (ESI)** m/z calcd for $C_{20}H_{15}O_4S^+$ [M +H$^+$]: 351.0686; found: 351.0680.



4i

1,1,1,3,3,3-hexafluoropropan-2-yl-3-oxo-2,3-dihydro-1*H*-indene-1-carboxylate

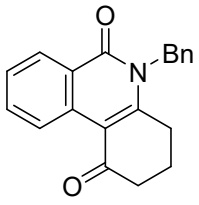
Compound **4i** was isolated as a white solid (41.3 mg, 63% yield). M.P.: 102-103 °C. ^{1}H NMR (**600 MHz**, **CDCl$_3$**) *δ* 7.82 (d, *J* = 7.8 Hz, 1H), 7.72 - 7.64 (m, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 5.86 - 5.76 (m, 1H), 4.50 (dd, *J* = 8.4, 3.6 Hz, 1H), 3.16 (dd, *J* = 19.2, 3.6 Hz, 1H), 2.99 (dd, *J* = 19.2, 8.4 Hz, 1H). ^{13}C NMR (**150 MHz**, **CDCl$_3$**) *δ* 202.4, 169.0, 148.7, 136.3, 135.4, 129.5, 126.3, 124.4, 121.2 - 121.1 (m), 119.4 - 119.2 (m), 67.2 (p, *J* = 35.0 Hz), 42.8, 39.0. ^{19}F NMR (**565 MHz, CDCl$_3$**) δ -72.99 (q, *J* = 8.5 Hz, 3F), -73.17 (q, *J* = 8.5 Hz, 3F). **HRMS (ESI)** m/z calcd for $C_{13}H_9F_6O_3^+$ [M +H$^+$]: 327.0450; found: 327.0453.



6

3,3,5-trimethyl-3,4-dihydrophenanthridine-1,6(2*H*,5*H*)-dione

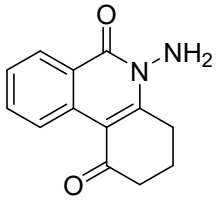
Compound **6** was isolated as a white solid (49.1 mg, 96% yield). M.P.: 150-151 °C. ^{1}H NMR (**600 MHz**, **CDCl$_3$**) *δ* 9.23 (d, *J* = 8.4 Hz, 1H), 8.39 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.72 - 7.66 (m, 1H), 7.48 - 7.43 (m, 1H), 3.63 (s, 3H), 2.81 (s, 2H), 2.47 (s, 2H), 1.15 (s, 6H). ^{13}C NMR (**150 MHz**, **CDCl$_3$**) *δ* 196.8, 162.9, 152.2, 133.5, 133.3, 127.6, 126.8, 125.8, 123.7, 110.4, 52.1, 42.6, 31.8, 31.2, 28.3. **HRMS (ESI)** m/z calcd for $C_{16}H_{18}NO_2^+$ [M +H$^+$]: 256.1332; found: 256.1324.



7

5-benzyl-3,4-dihydrophenanthridine-1,6(2*H*,5*H*)-dione

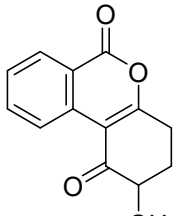
Compound **7** was isolated as a white solid (41.8 mg, 69% yield). M.P.: 173-174 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9.23 (d, J = 7.8 Hz, 1H), 8.47 (dd, J = 8.4, 1.2 Hz, 1H), 7.79 - 7.73 (m, 1H), 7.56 - 7.49 (m, 1H), 7.33 (t, J = 6.6 Hz, 2H), 7.29 - 7.25 (m, 1H), 7.14 (d, J = 7.2 Hz, 2H), 5.51 (s, 2H), 2.93 (t, J = 6.6 Hz, 2H), 2.59 (t, J = 6.0 Hz, 2H), 2.04 (p, J = 6.0 Hz, 2H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 196.7, 162.8, 154.2, 136.0, 134.0, 133.6, 129.0, 128.0, 127.6, 127.1, 126.3, 126.0, 124.1, 111.9, 47.3, 38.6, 28.4, 20.9.



8

5-amino-3,4-dihydrophenanthridine-1,6(2*H*,5*H*)-dione

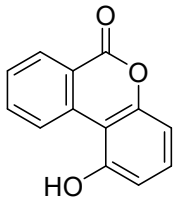
Compound **8** was isolated as a white solid (38.3 mg, 84% yield). M.P.: 187-188 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 9.24 (d, J = 9.0 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.48 (t, J = 7.8 Hz, 1H), 5.03 (s, 2H), 3.24 (t, J = 6.6 Hz, 2H), 2.60 (t, J = 6.6 Hz, 2H), 2.14 (p, J = 6.6 Hz, 2H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 196.8, 161.9, 154.8, 133.7, 133.6, 127.3, 126.8, 126.2, 122.9, 110.4, 38.8, 27.3, 20.6. **HRMS (ESI)** m/z calcd for $C_{13}H_{13}N_2O_2^+$ [M +H^+]: 229.0972; found: 229.0965.



9

2-hydroxy-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione

Compound **9** was isolated as a white solid (34.5 mg, 75% yield). M.P.: 186-187 °C. ^{1}H NMR (**600 MHz**, **$CDCl_3$**) δ 8.95 (d, J = 8.4 Hz, 1H), 8.30 (dd, J = 8.4, 1.2 Hz, 1H), 7.84 - 7.79 (m, 1H), 7.59 - 7.54 (m, 1H), 4.31 (dd, J = 13.8, 5.4 Hz, 1H), 3.96 (s, 1H), 3.17 - 3.08 (m, 1H), 3.01 - 2.95 (m, 1H), 2.58 - 2.54 (m, 1H), 2.13 - 2.00 (m, 1H). ^{13}C NMR (**150 MHz**, **$CDCl_3$**) δ 197.7, 168.9, 160.0, 135.8, 133.3, 129.8, 128.9, 125.3, 119.5, 109.5, 72.0, 28.4, 27.2.

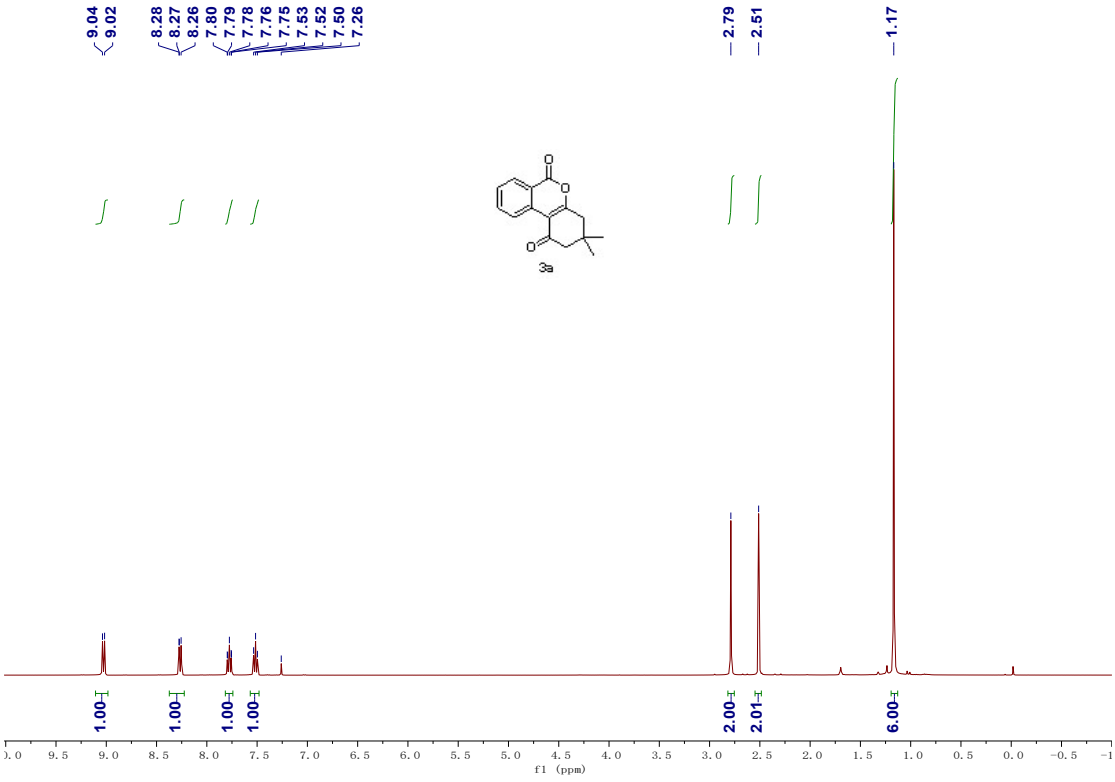


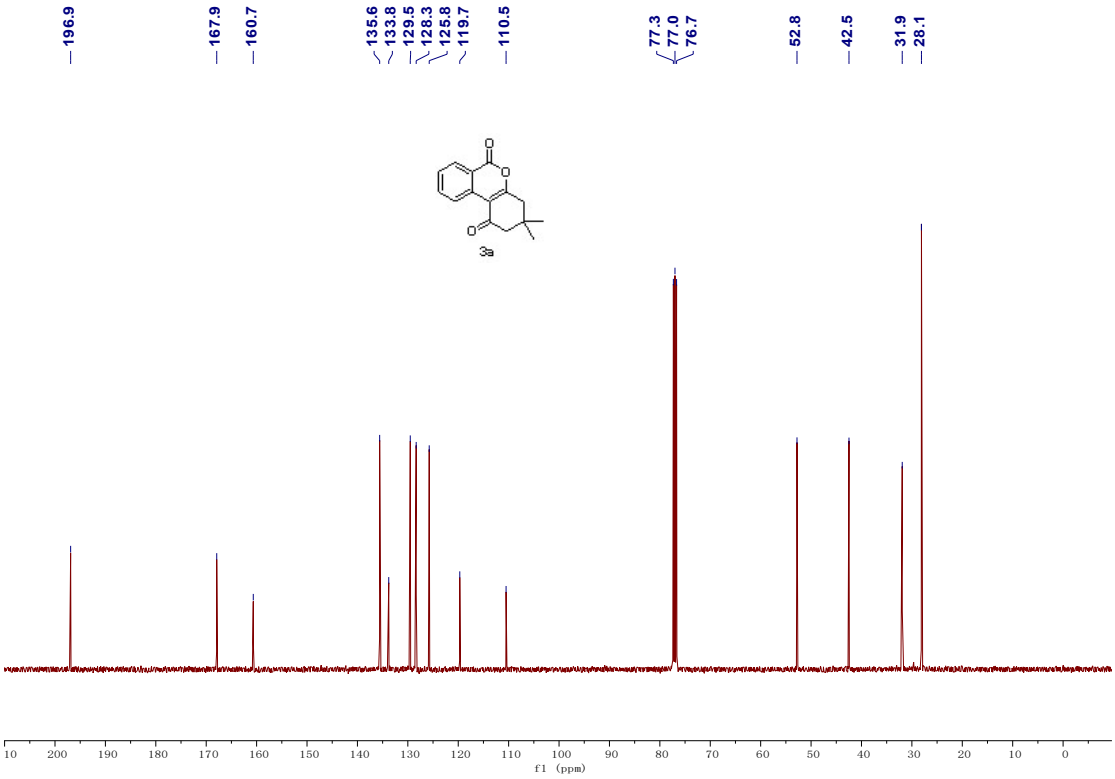
10

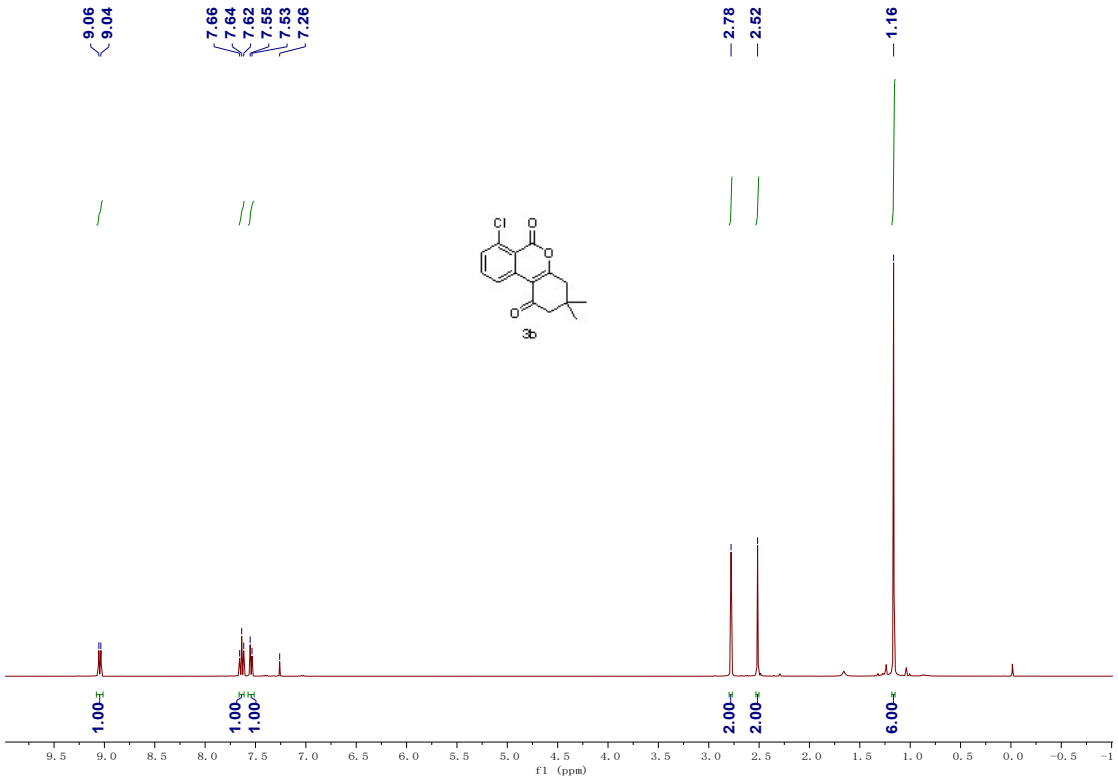
1-hydroxy-6*H*-benzo[*c*]chromen-6-one

Compound **10** was isolated as a yellow solid (26.3 mg, 62% yield). M.P.: 241-242 °C. ^{1}H NMR (**600 MHz**, **DMSO-d_6**) δ 11.05 (s, 1H), 9.14 (d, J = 8.4 Hz, 1H), 8.27 (dd, J = 7.8, 1.2 Hz, 1H), 7.93 - 7.89 (m, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 8.4 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H). ^{13}C NMR (**150 MHz**, **DMSO-d_6**) δ 160.4, 156.6, 152.1, 135.0, 134.5, 130.2, 129.4, 127.9, 127.1, 120.0, 112.0, 107.7, 106.0.

5.2 Copies of NMR spectra.



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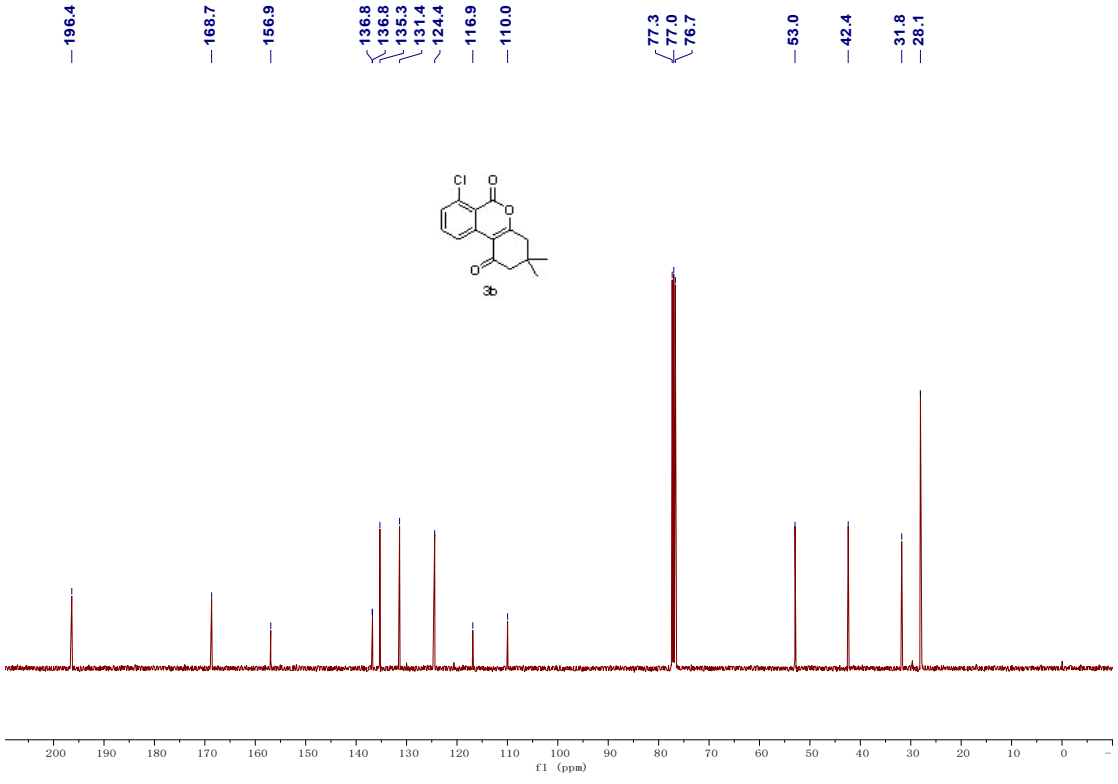
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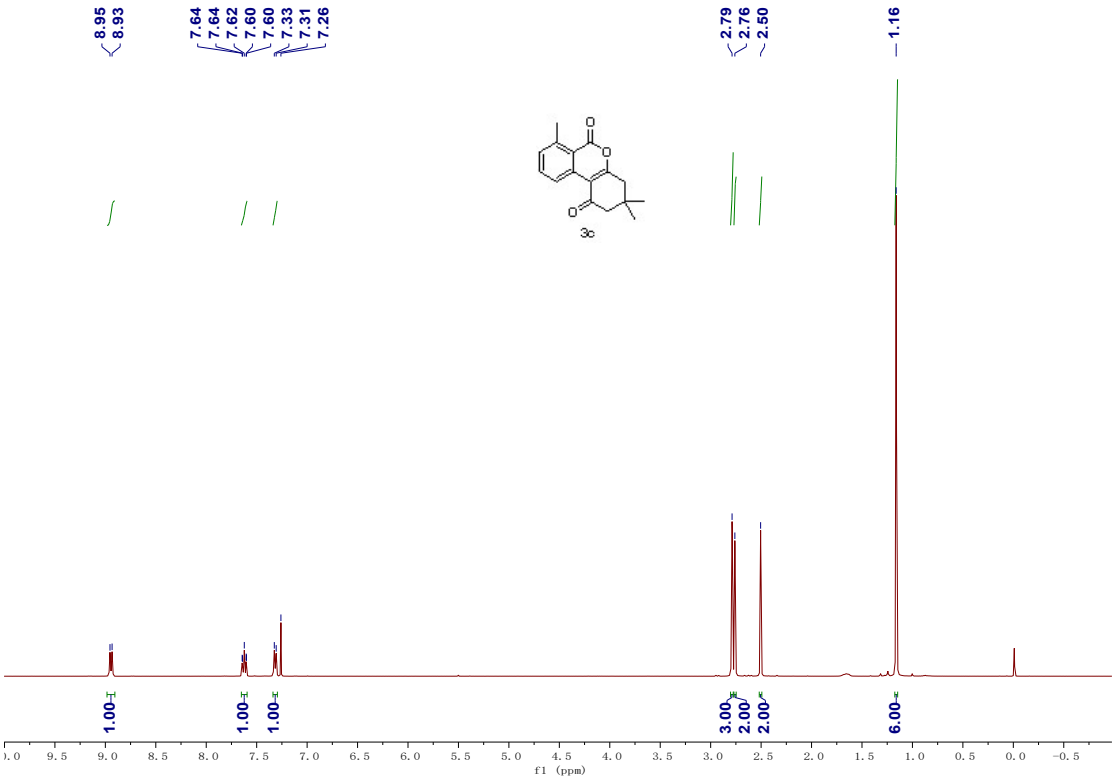
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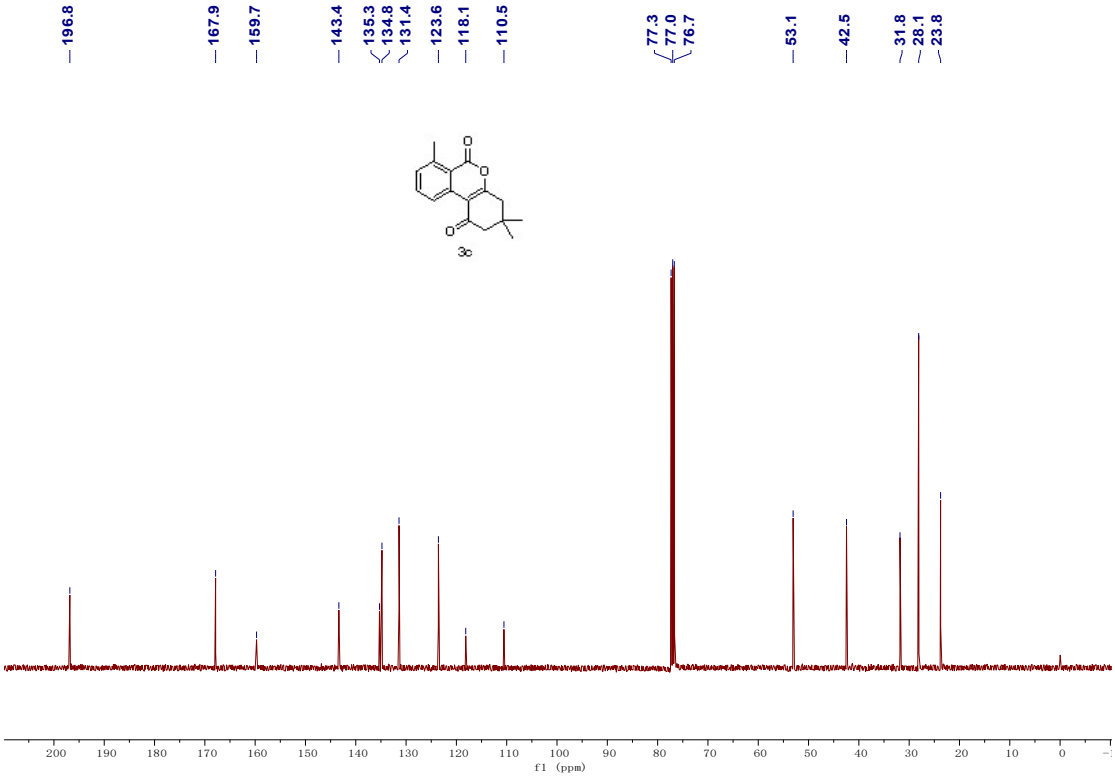
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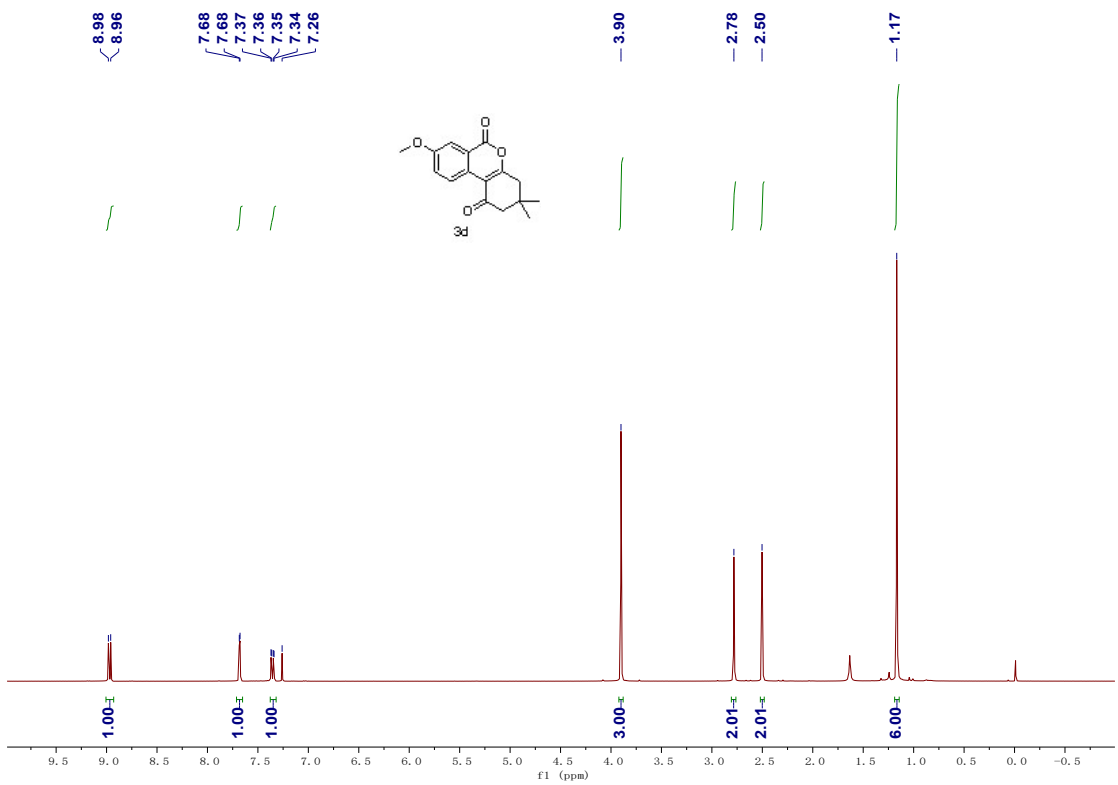
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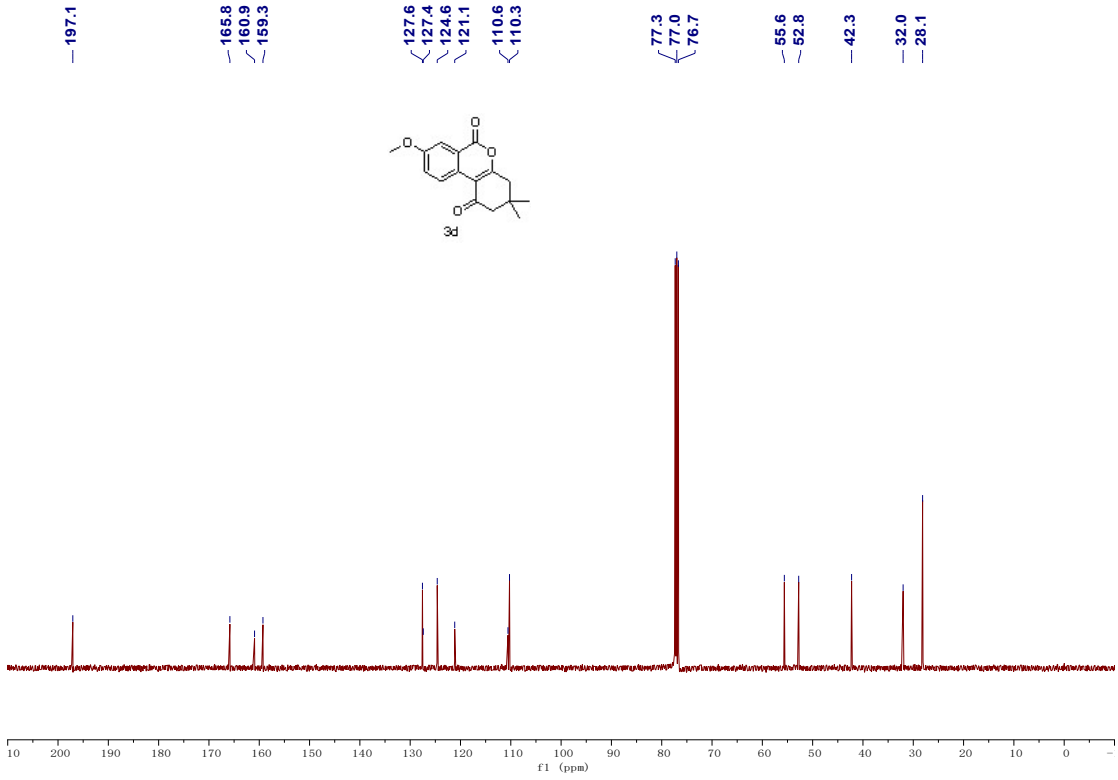
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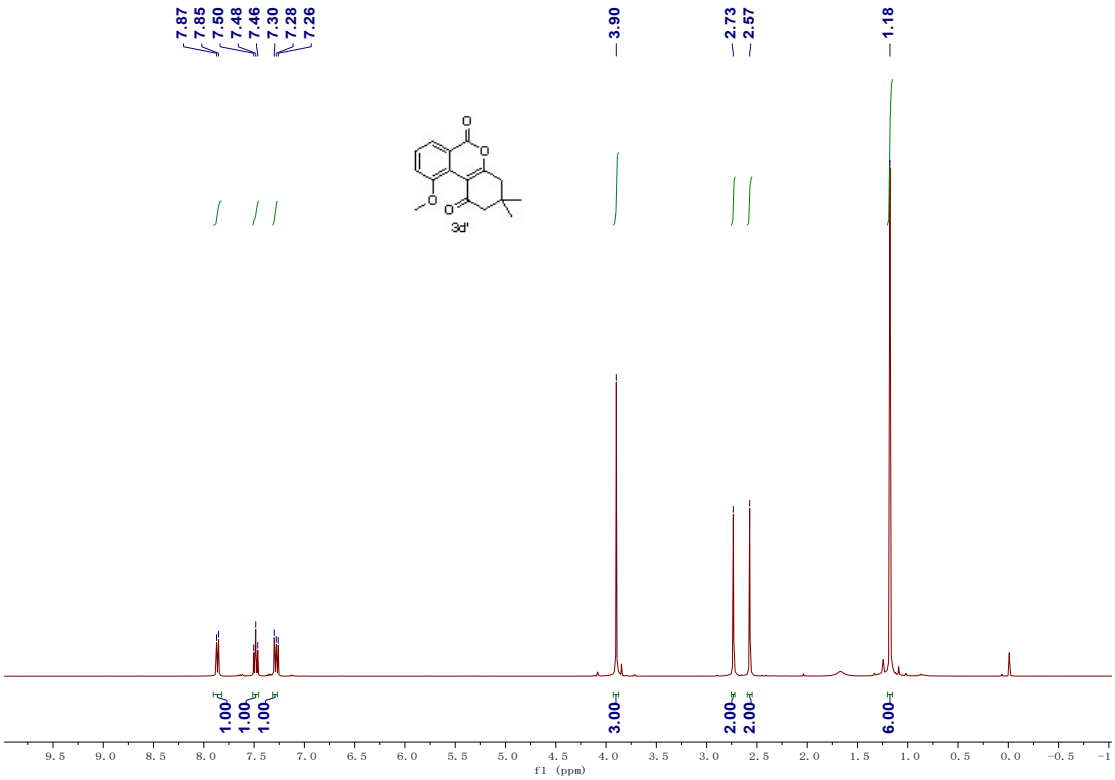
f1 (ppm)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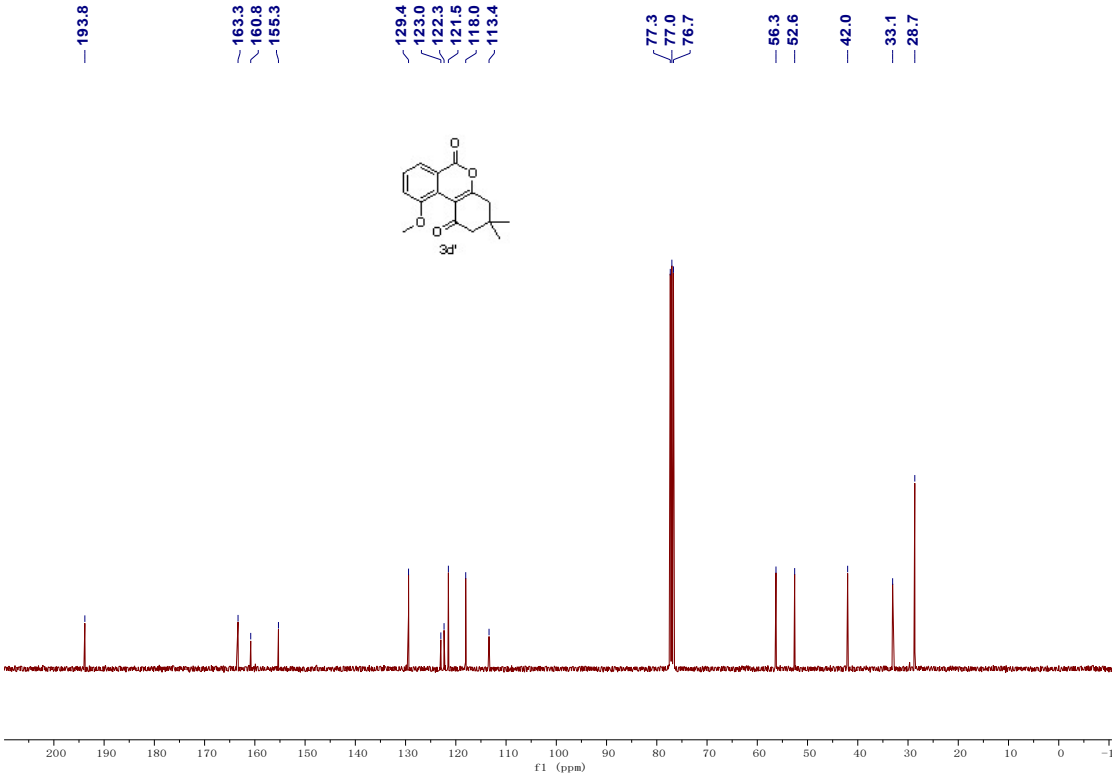
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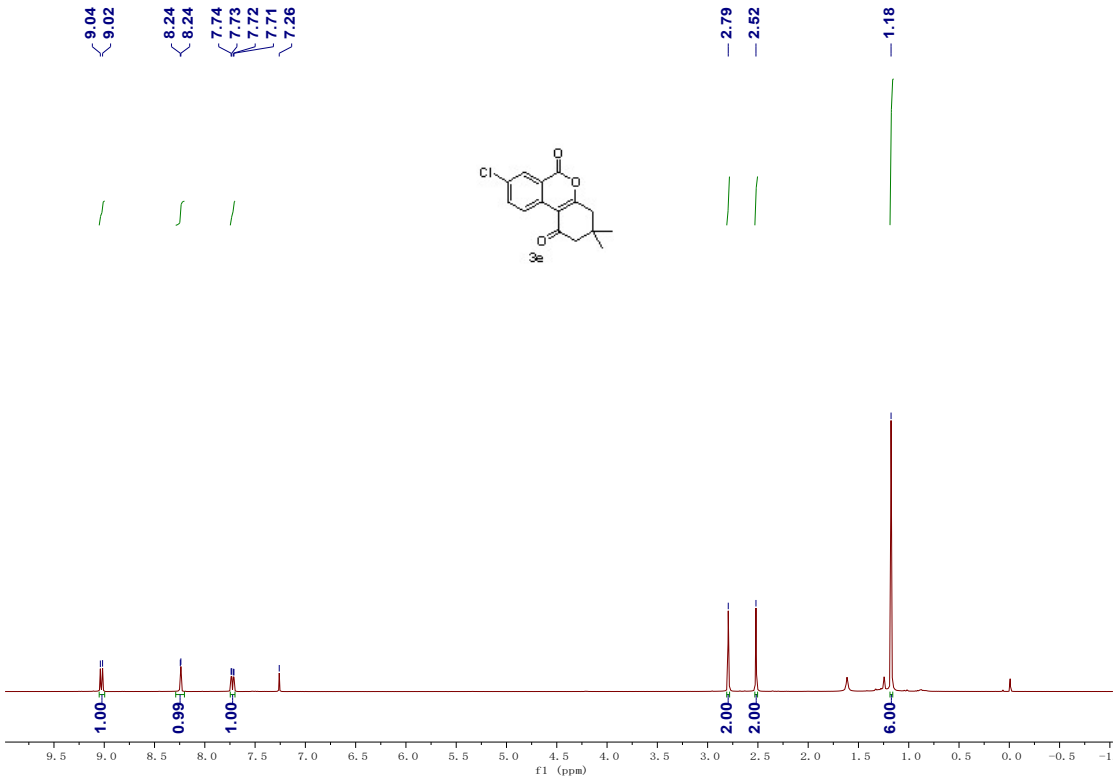
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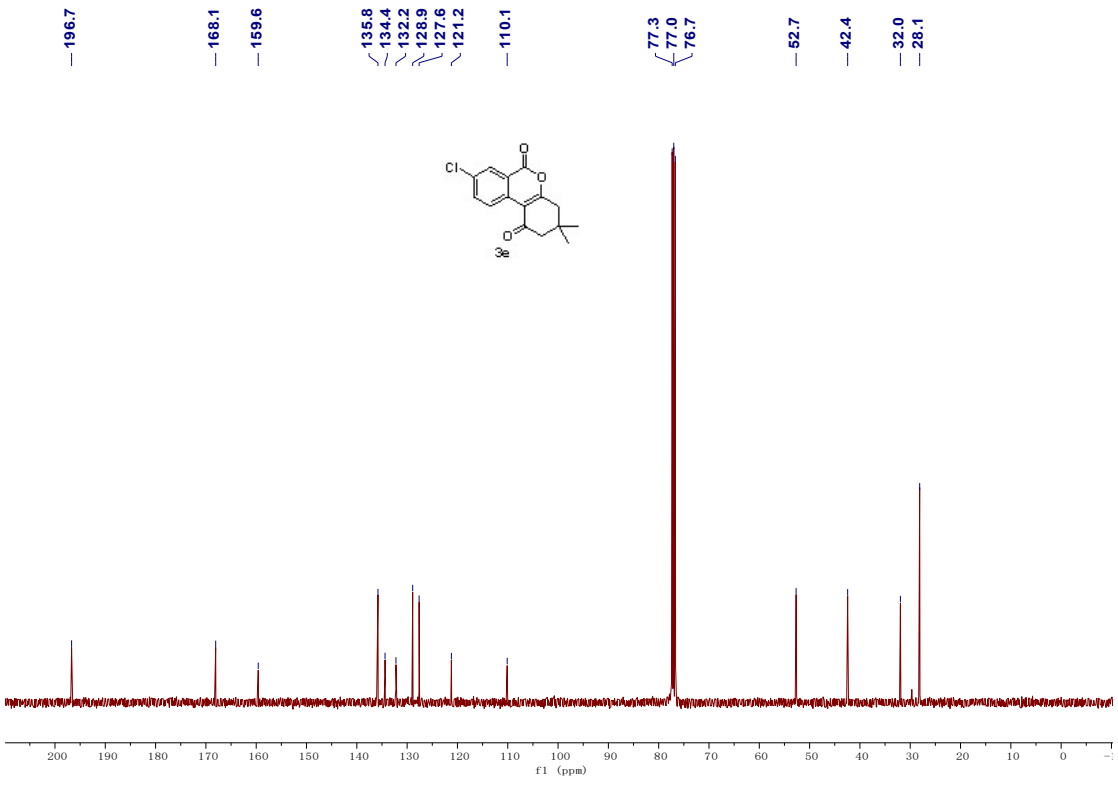
f1 (ppm)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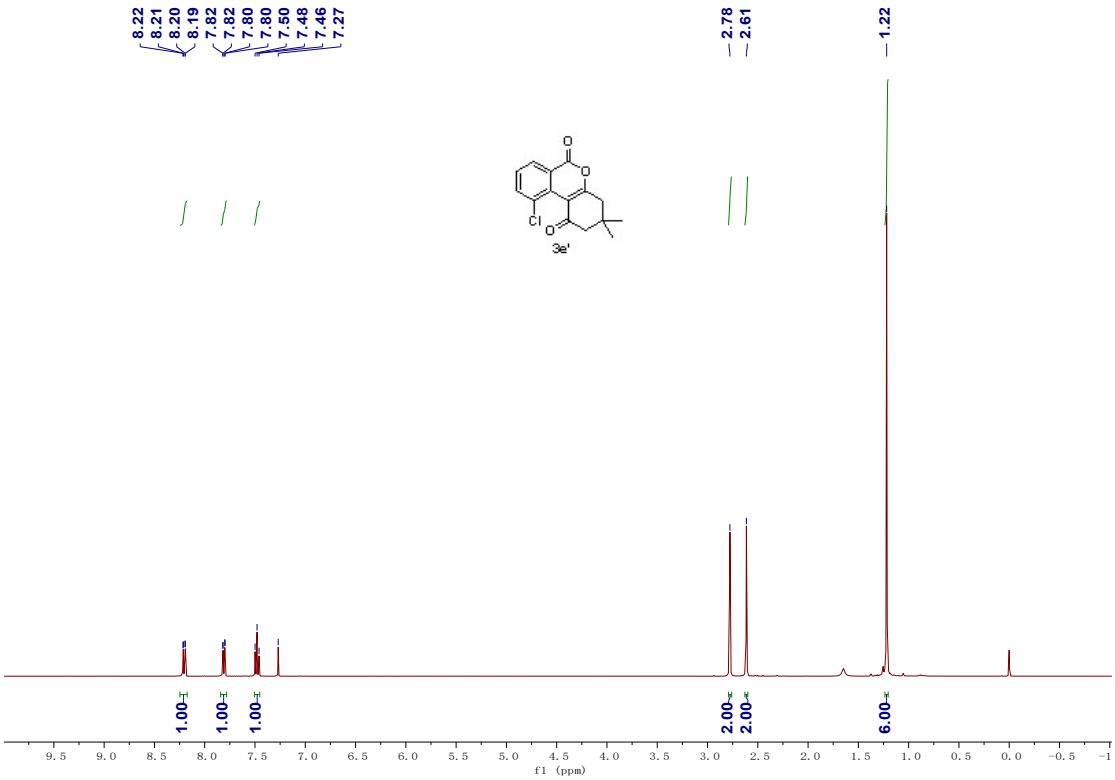
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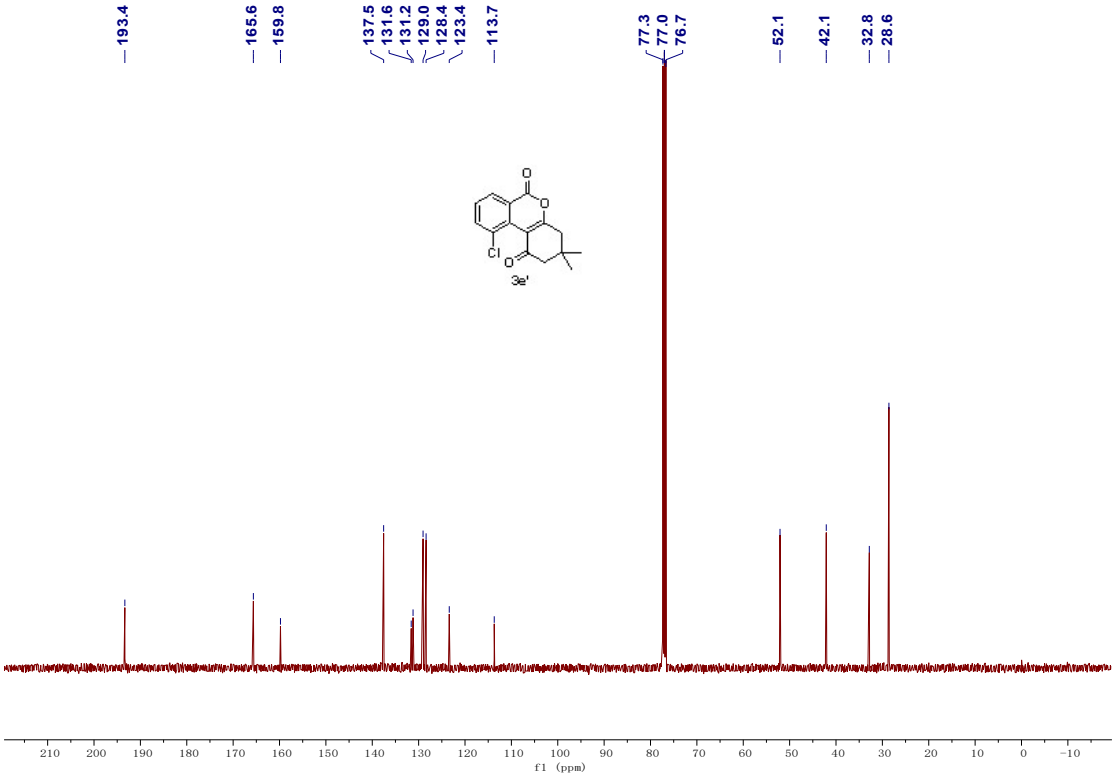
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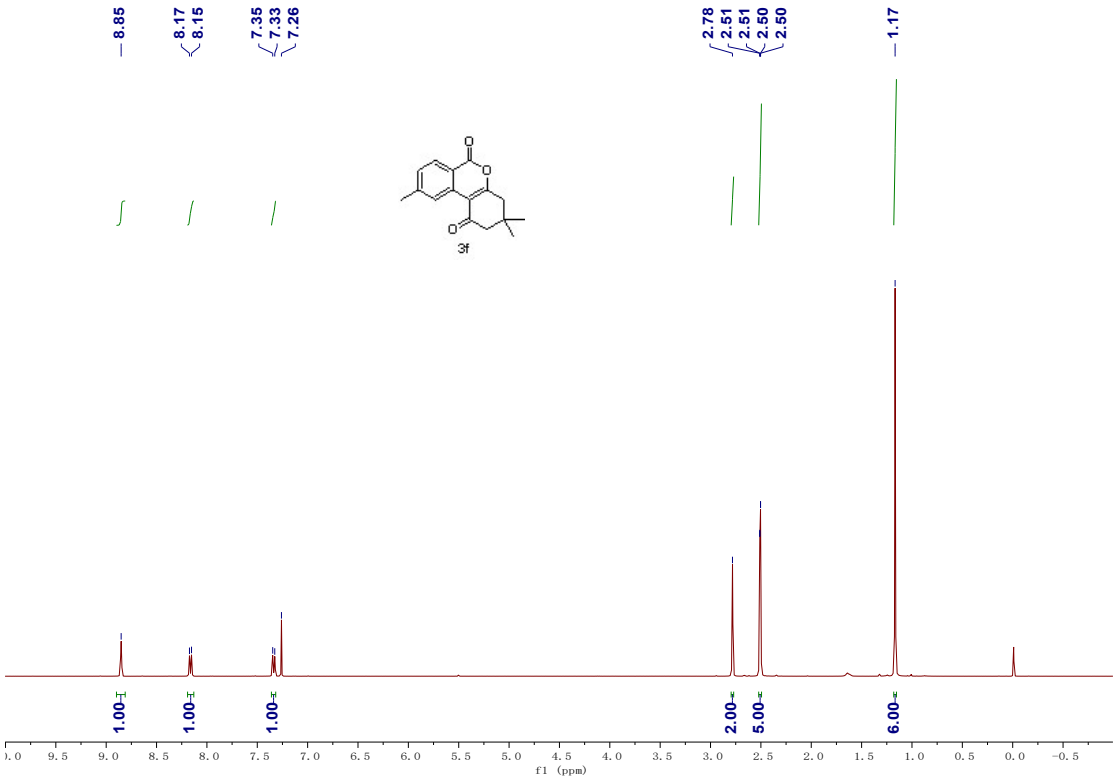
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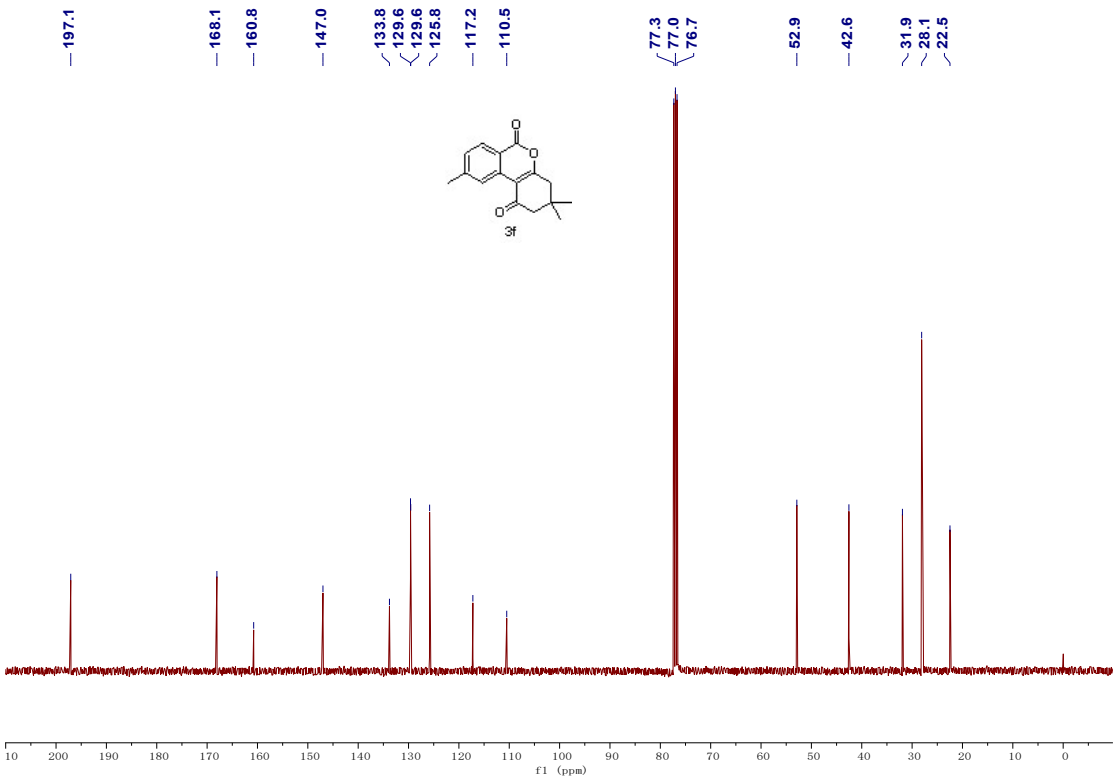
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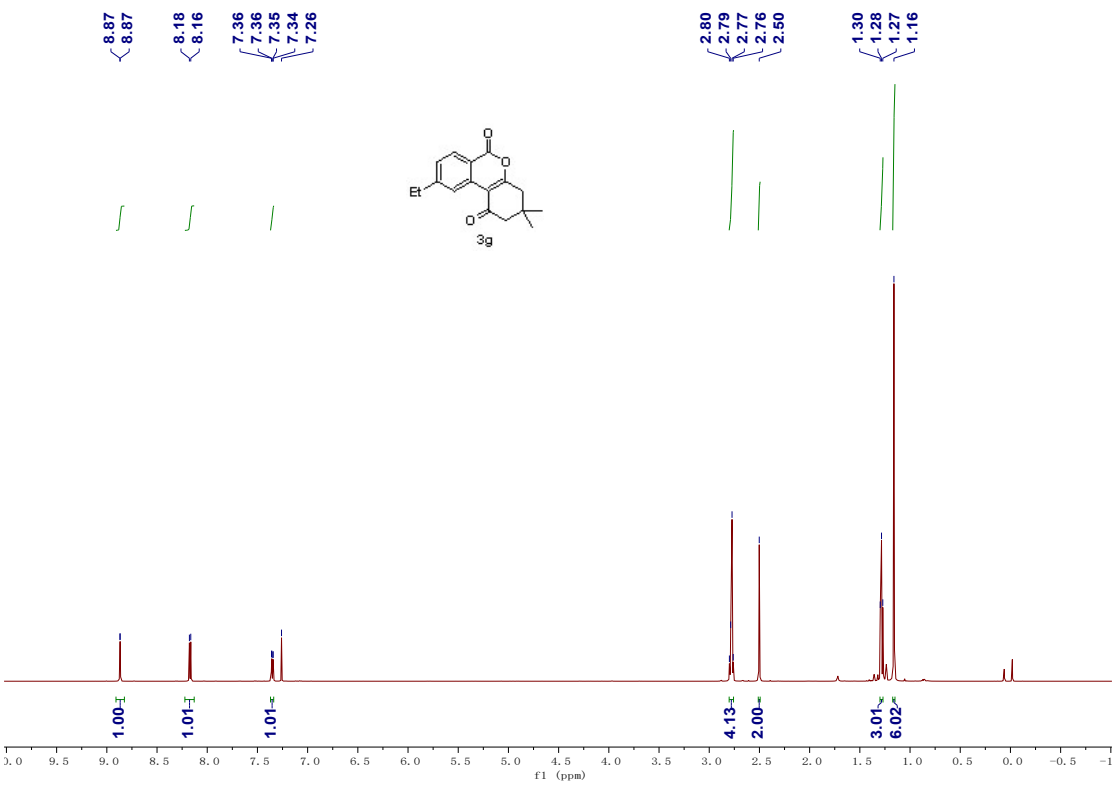
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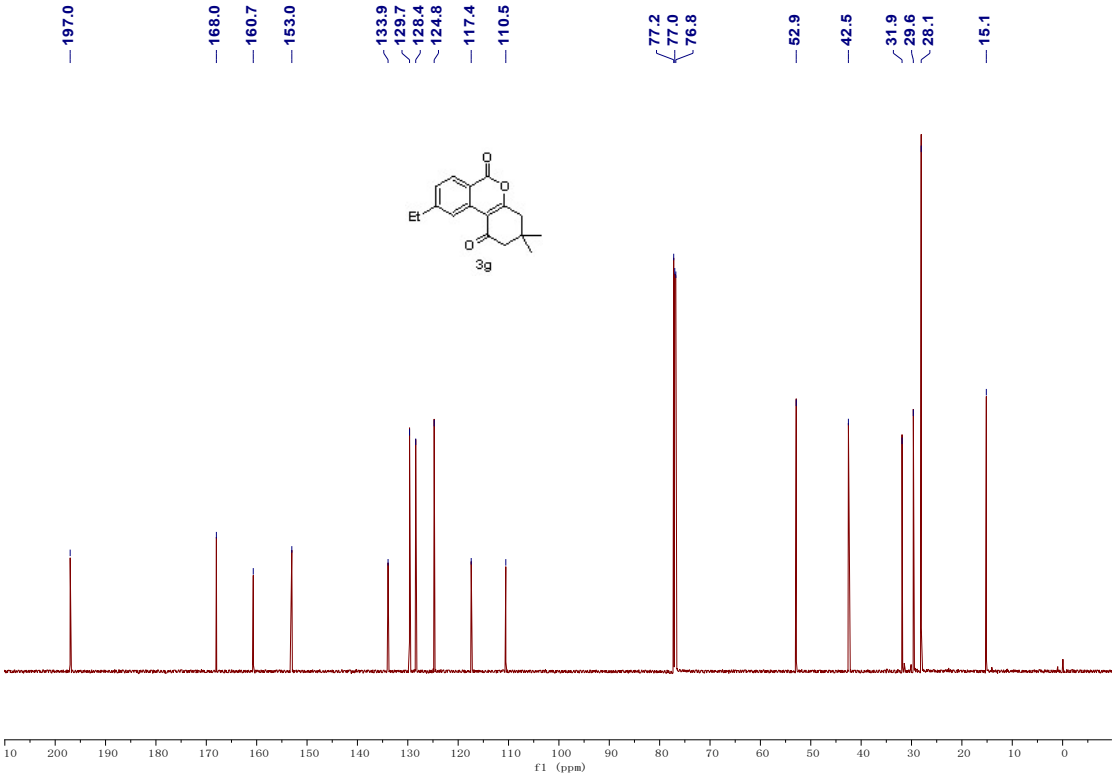
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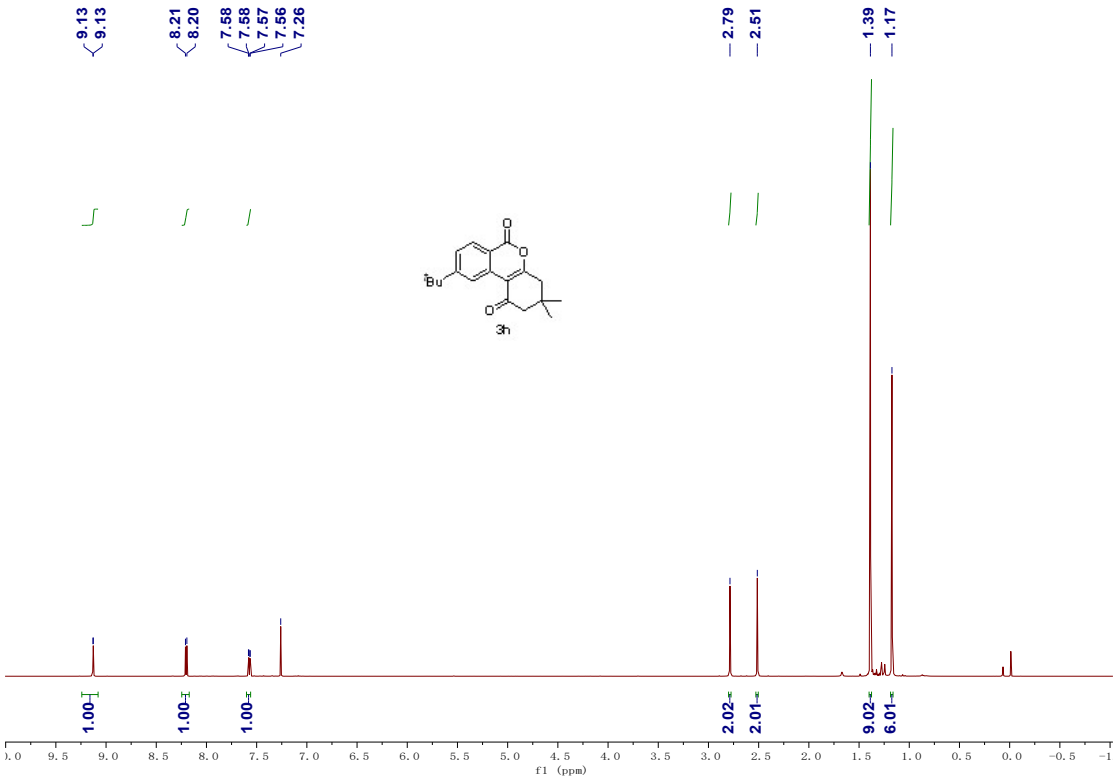
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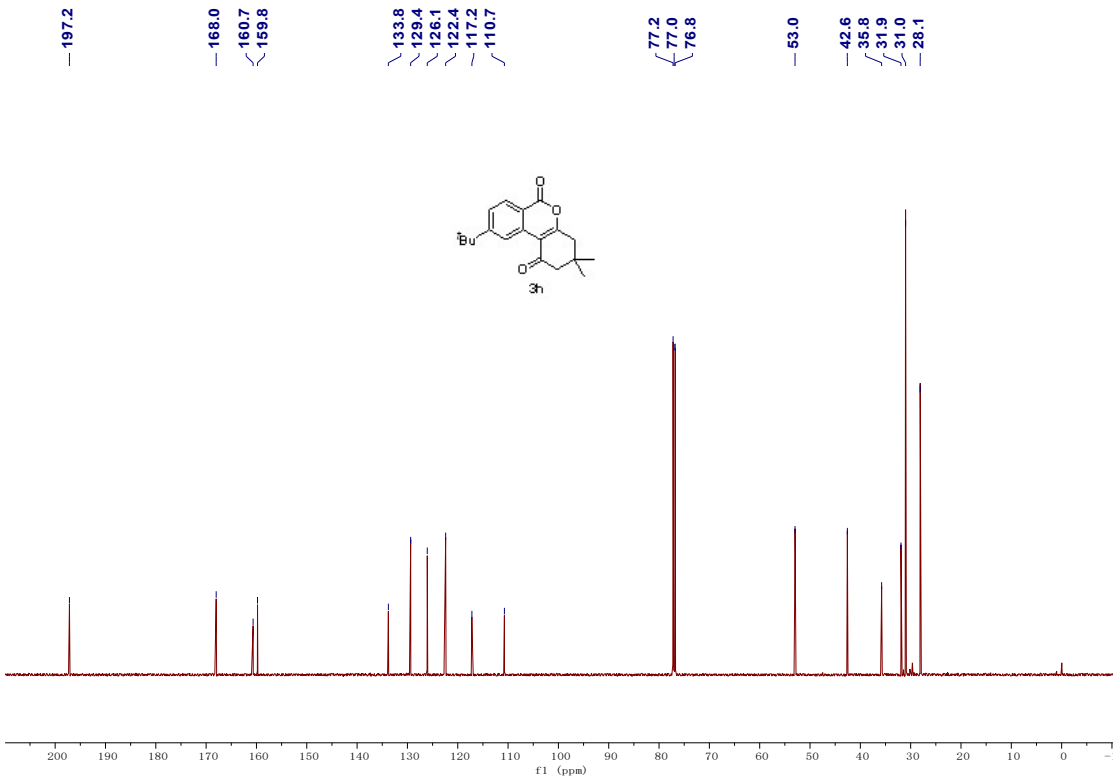
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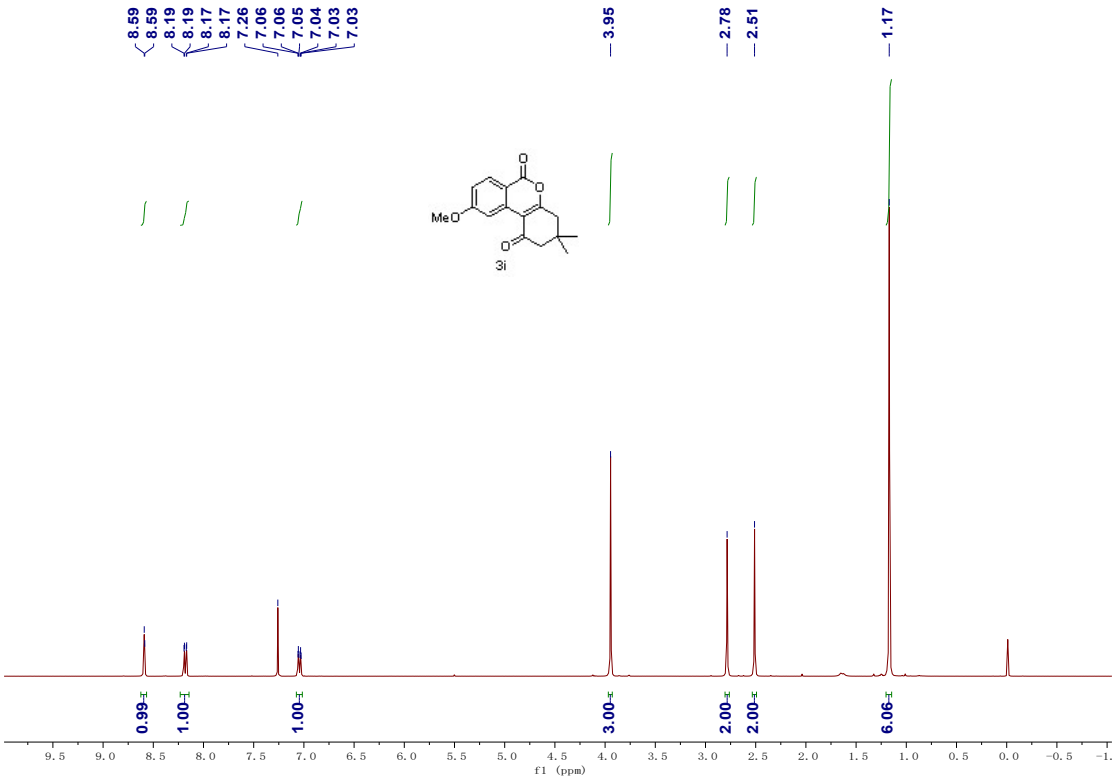
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3.95
2.78
2.51
1.17
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O
3i
0.99
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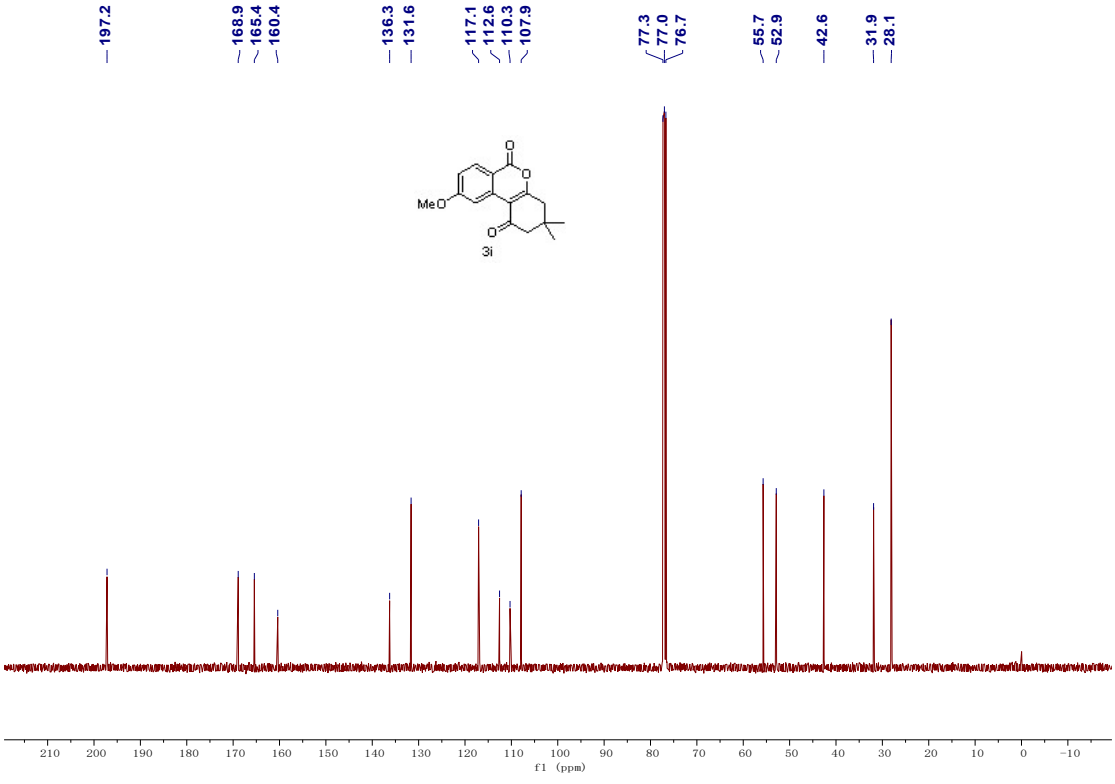
1.00
3.00
2.00
2.00
6.06
f1 (ppm)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160.4
136.3
131.6
117.1
112.6
110.3
107.9
77.3
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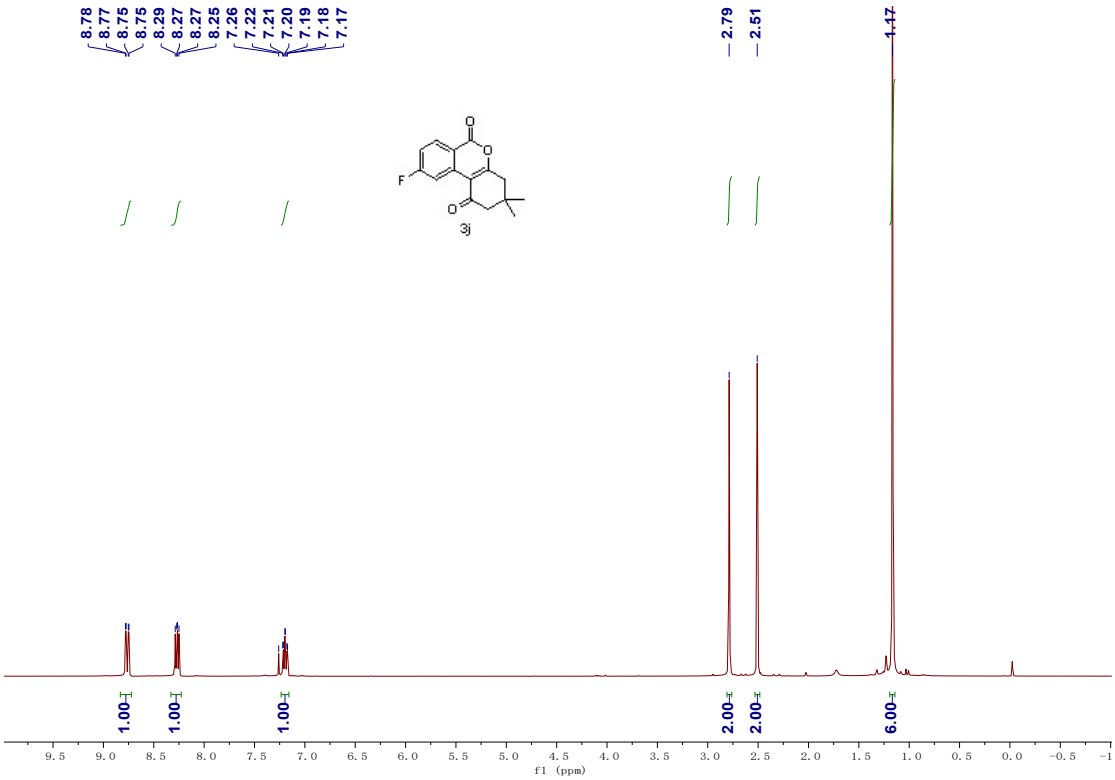
76.7
55.7
52.9
42.6
31.9
28.1
MeO
O
O
O
3i
f1 (ppm)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8.77
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8.25
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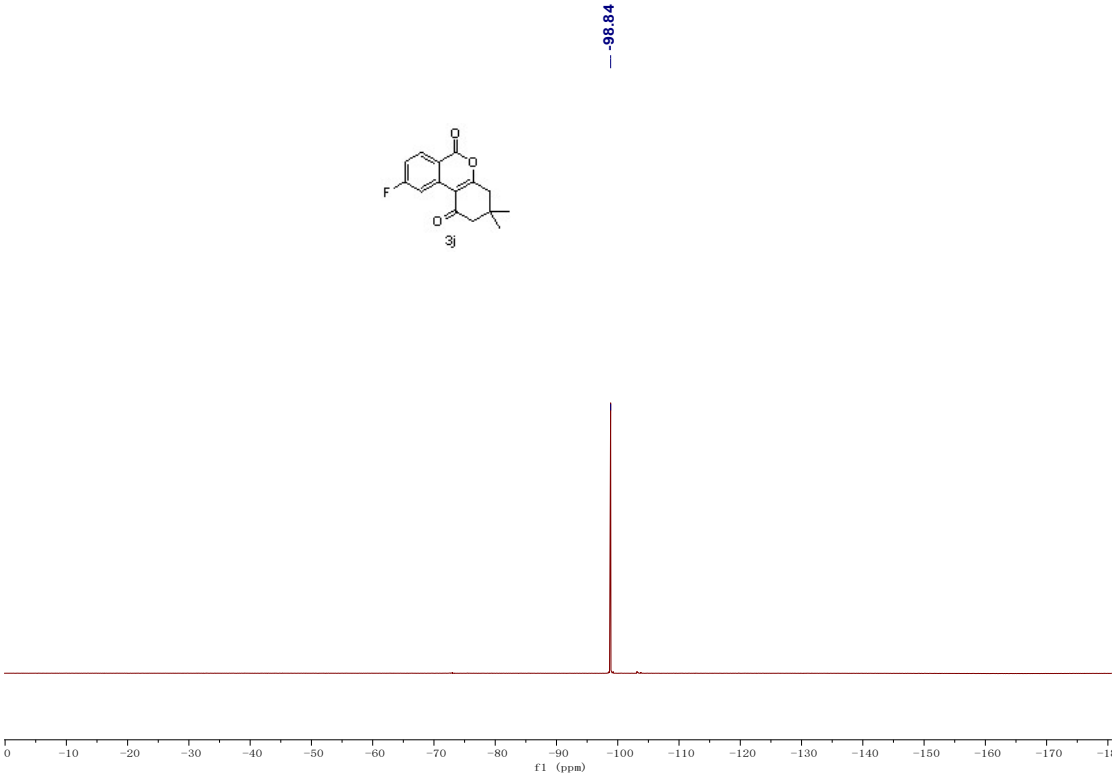
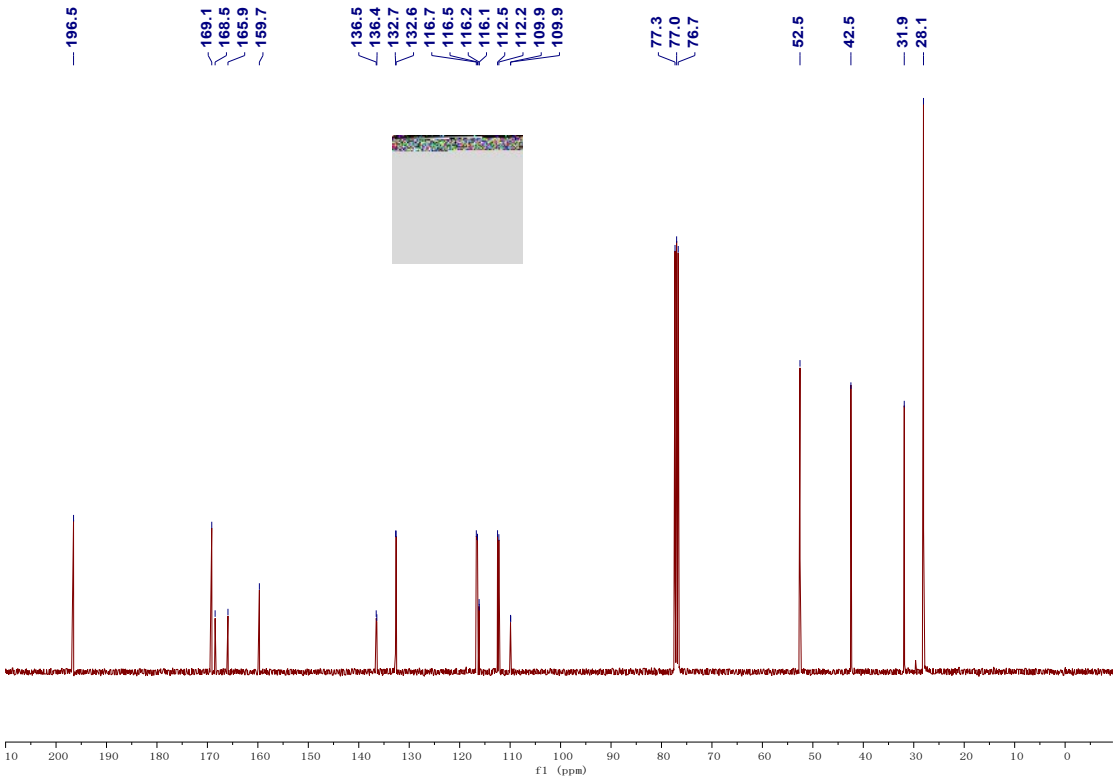
7.22
7.21
7.20
7.19
7.18
7.17
2.79
2.51
1.17
3j
1.00
1.00
1.00
2.00
2.00
6.00
f1 (ppm)


-98.84
3j
f1 (ppm)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136.4
132.7
132.6
116.7
116.5
116.2
116.1
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112.2
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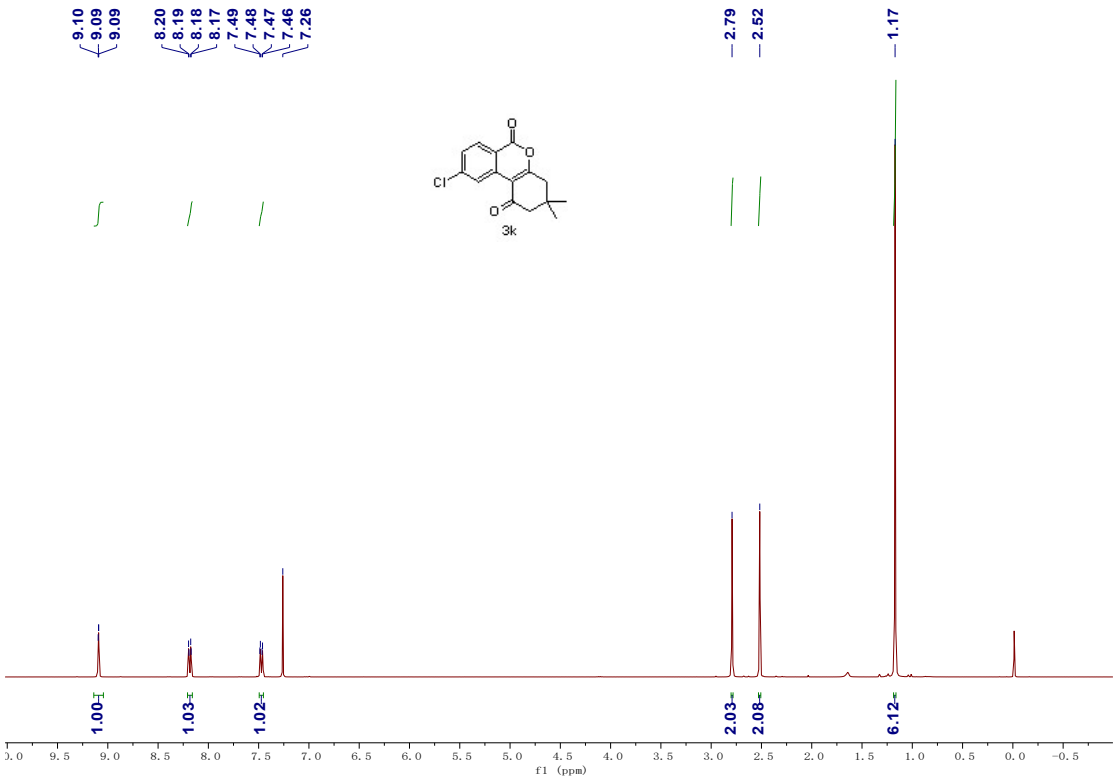
109.9
77.3
77.0
76.7
52.5
42.5
31.9
28.1
f1 (ppm)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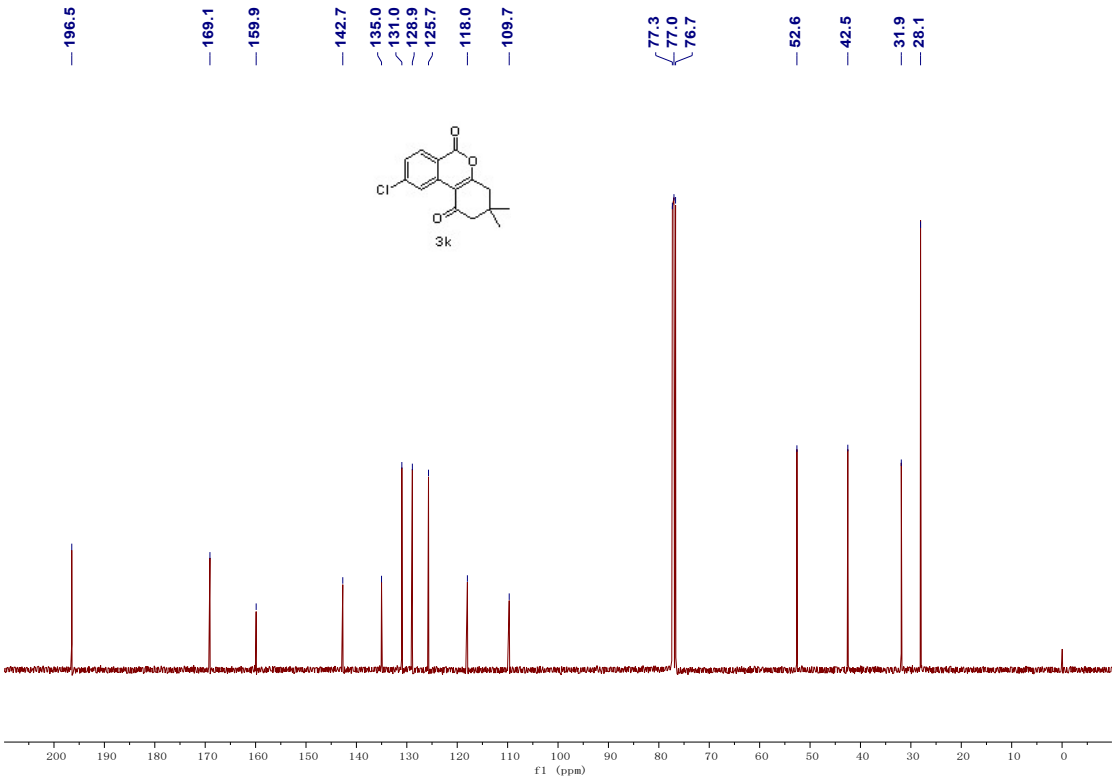
9.09
9.09
8.20
8.19
8.18
8.17
7.49
7.48
7.47
7.46
7.26
2.79
2.52
1.17
Cl
O
O
O
3k
1.00
1.03
1.02
2.03
2.08
6.12
f1 (ppm)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125.7
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76.7
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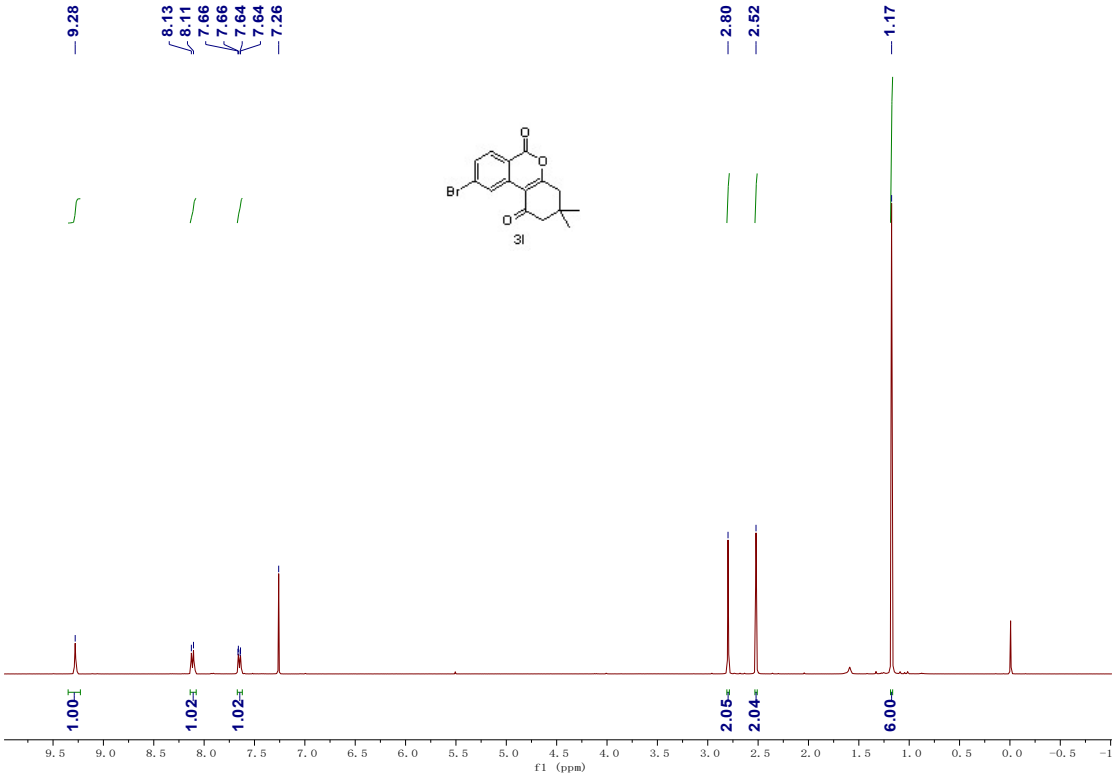
42.5
31.9
28.1
Cl
O
O
O
3k
f1 (ppm)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8.13
8.11
7.66
7.66
7.64
7.64
7.26
2.80
2.52
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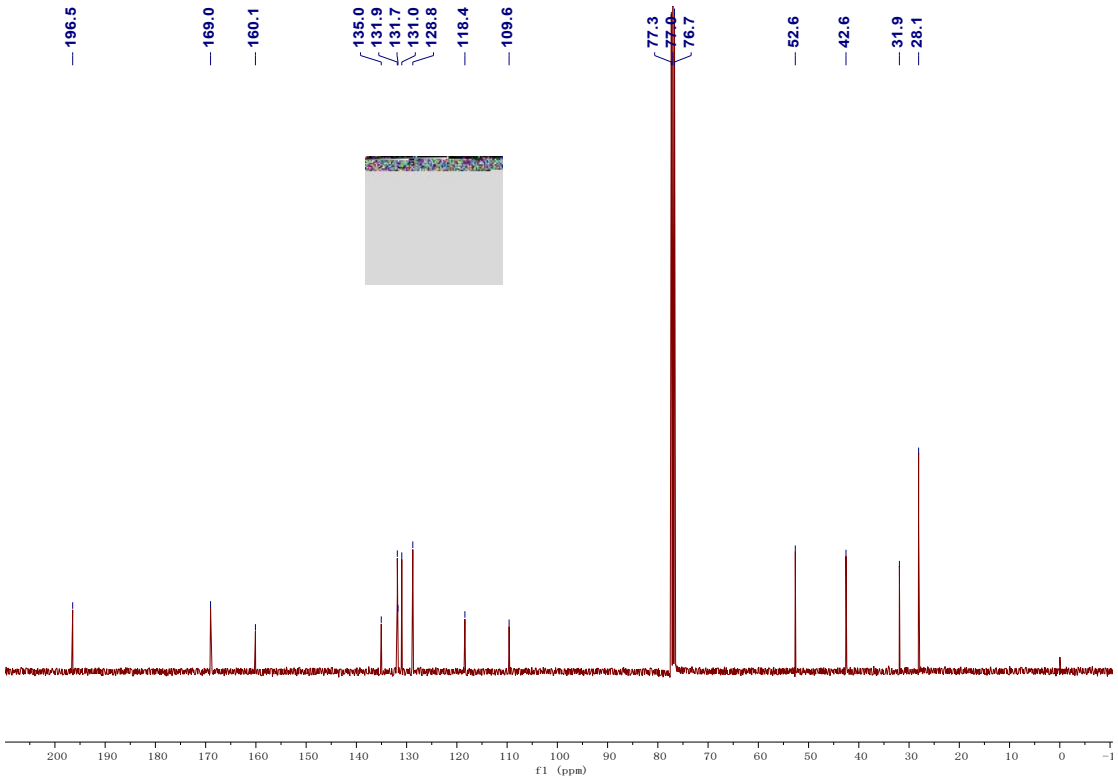
O
O
O
3l
1.00
1.02
1.02
2.05
2.04
6.00
f1 (ppm)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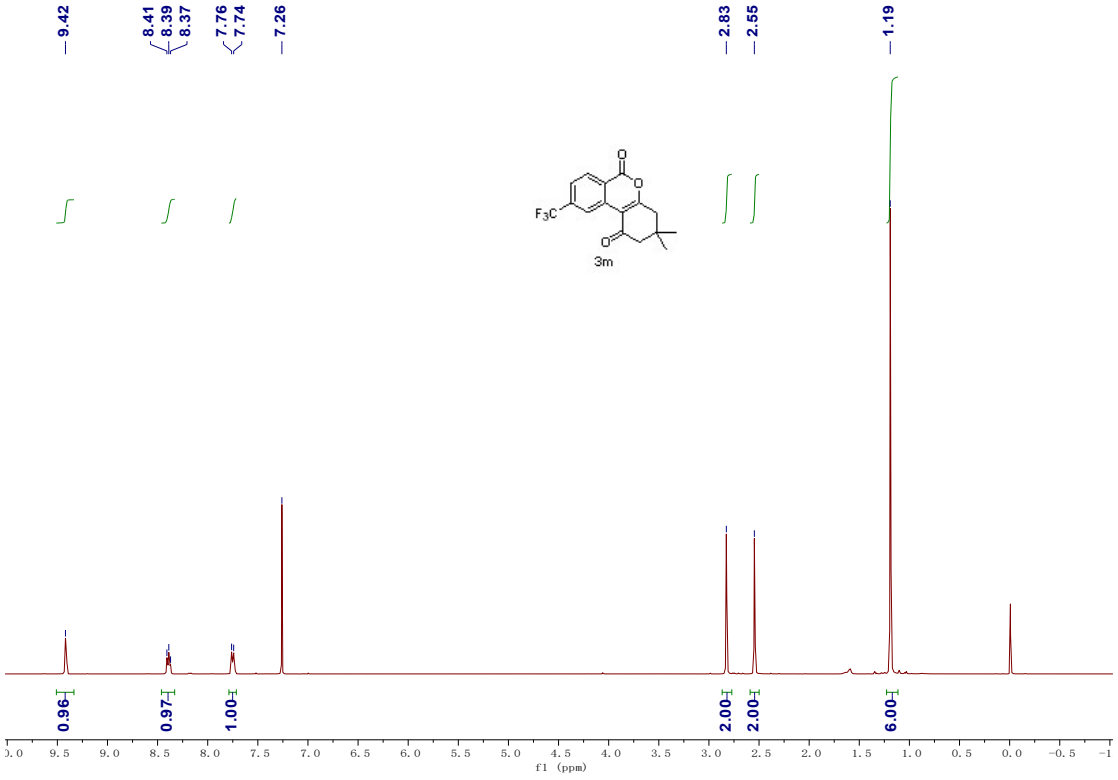
135.0
131.9
131.7
131.0
128.8
118.4
109.6
77.3
77.0
76.7
52.6
42.6
31.9
28.1
f1 (ppm)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8.41
8.39
8.37
7.76
7.74
7.26
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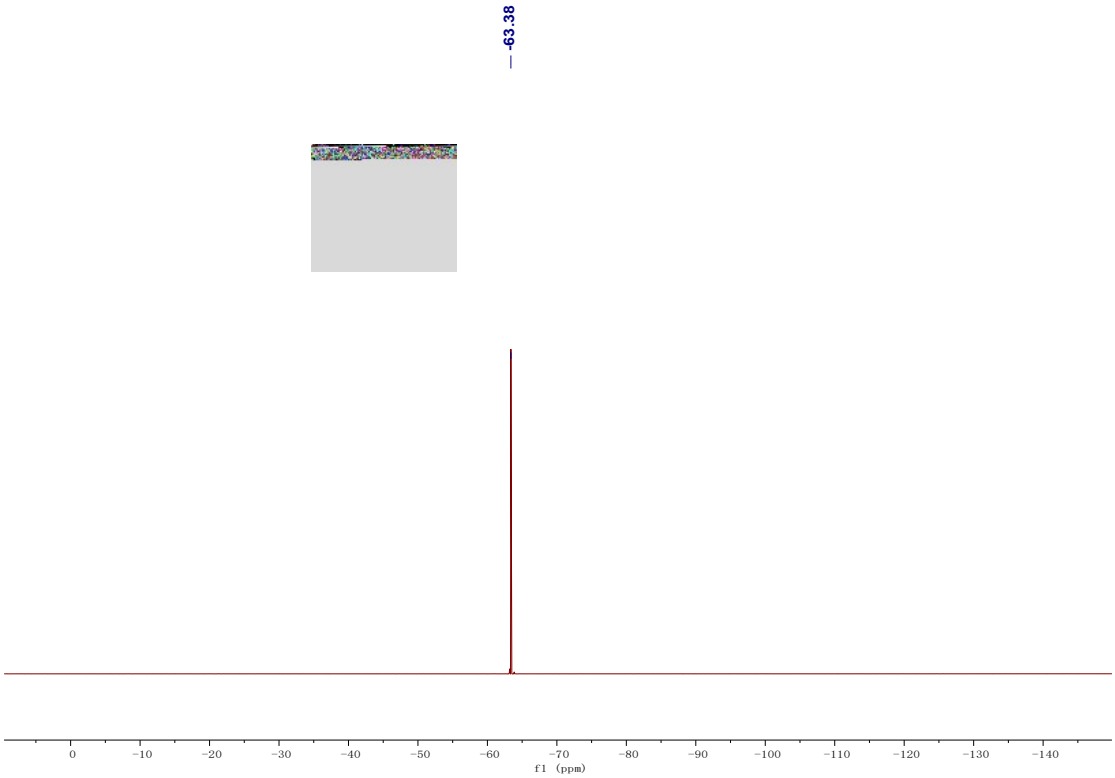
2.55
1.19
F3C
3m
0.96
0.97
1.00
2.00
2.00
6.00
f1 (ppm)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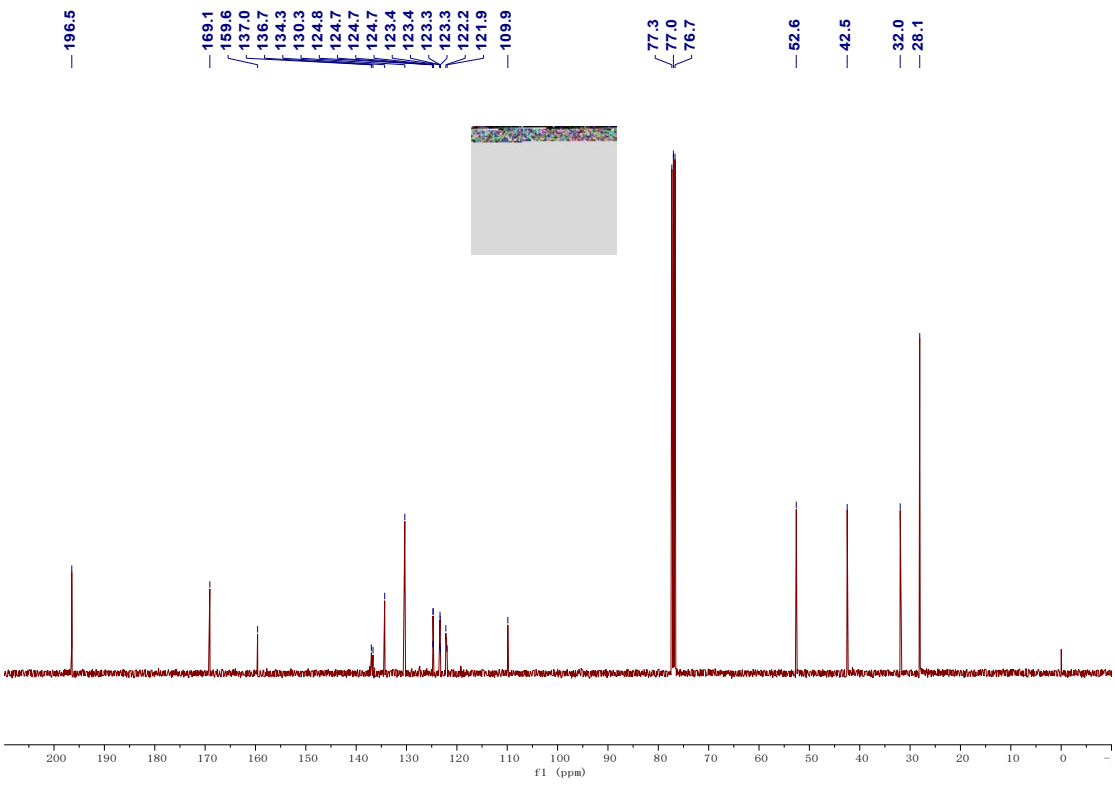
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)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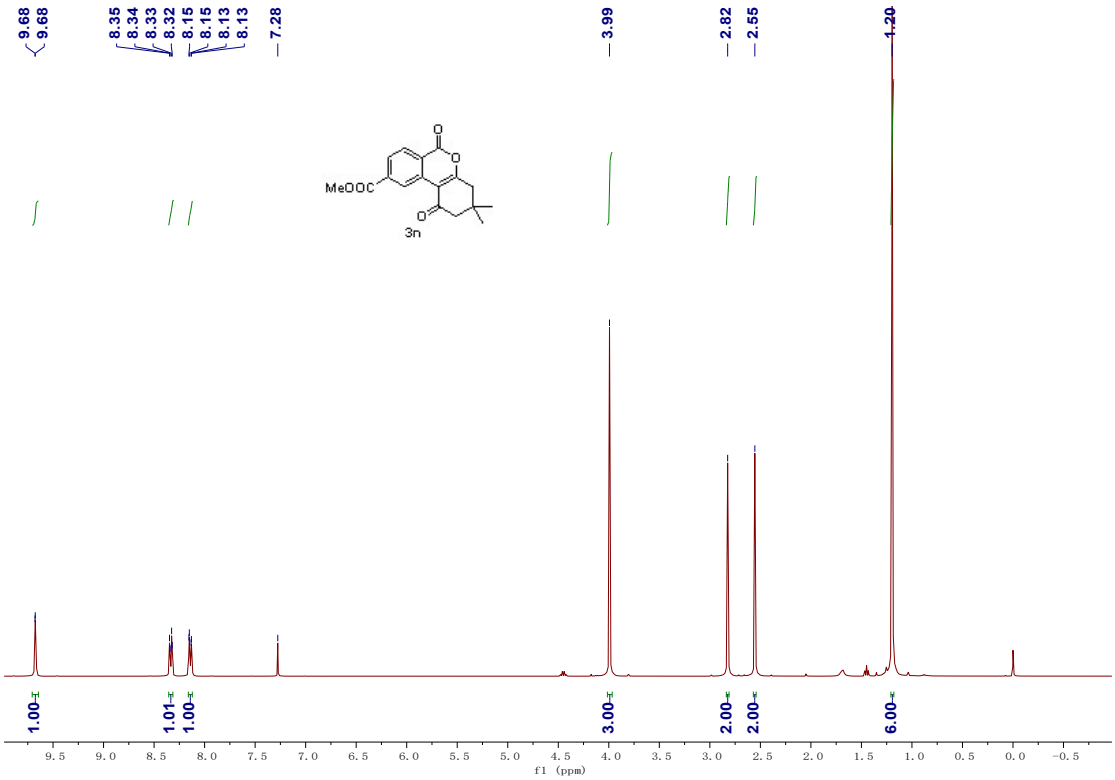
136.7
134.3
130.3
124.8
124.7
124.7
124.7
123.4
123.4
123.3
123.3
122.2
121.9
109.9
77.3
77.0
76.7
52.6
42.5
32.0
28.1
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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9.68
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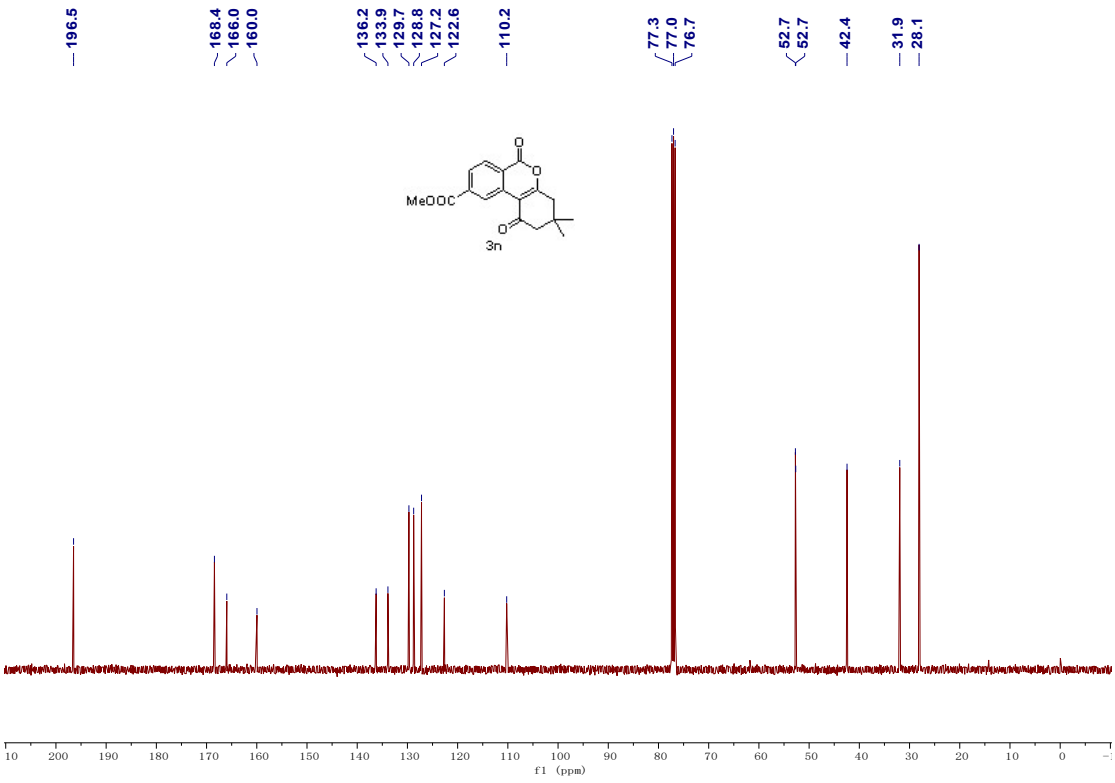
8.34
8.33
8.32
8.15
8.15
8.13
8.13
7.28
3.99
2.82
2.55
1.20
MeOOC
3n
1.00
1.01
1.00
3.00
2.00
2.00
6.00
f1 (ppm)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168.4
166.0
160.0
136.2
133.9
129.7
128.8
127.2
122.6
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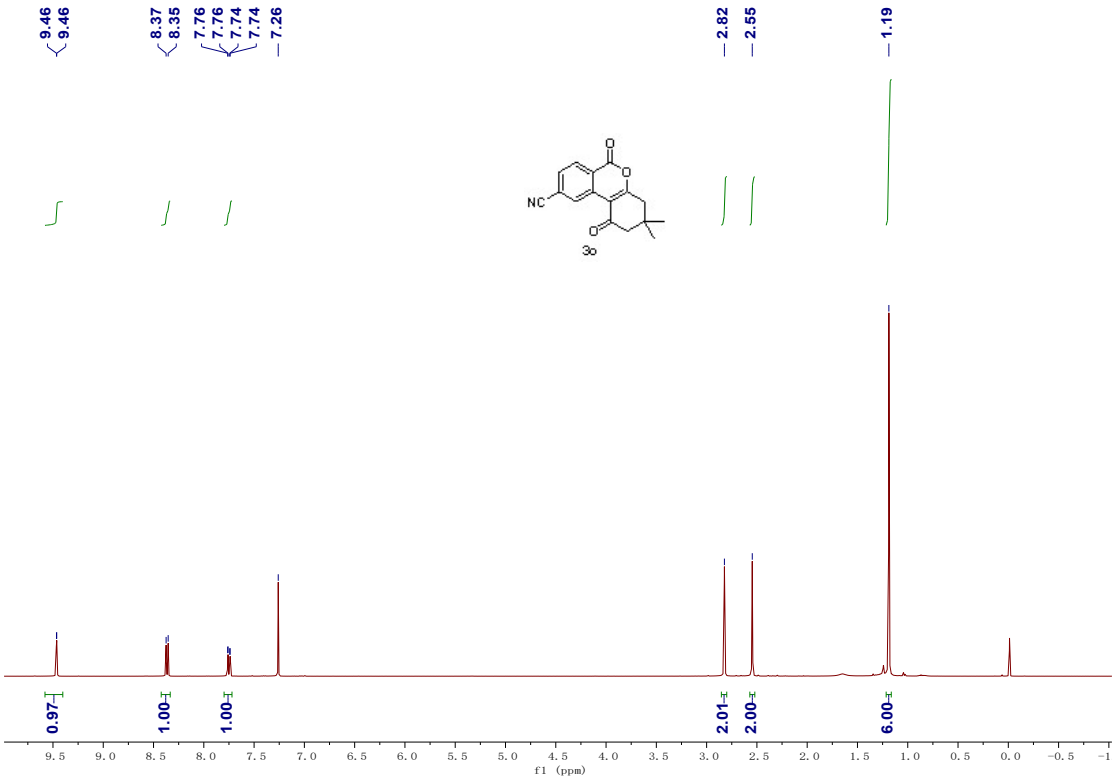
77.3
77.0
76.7
52.7
52.7
42.4
31.9
28.1
MeOOC
3n
f1 (ppm)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8.37
8.35
7.76
7.76
7.74
7.74
7.26
2.82
2.55
1.19
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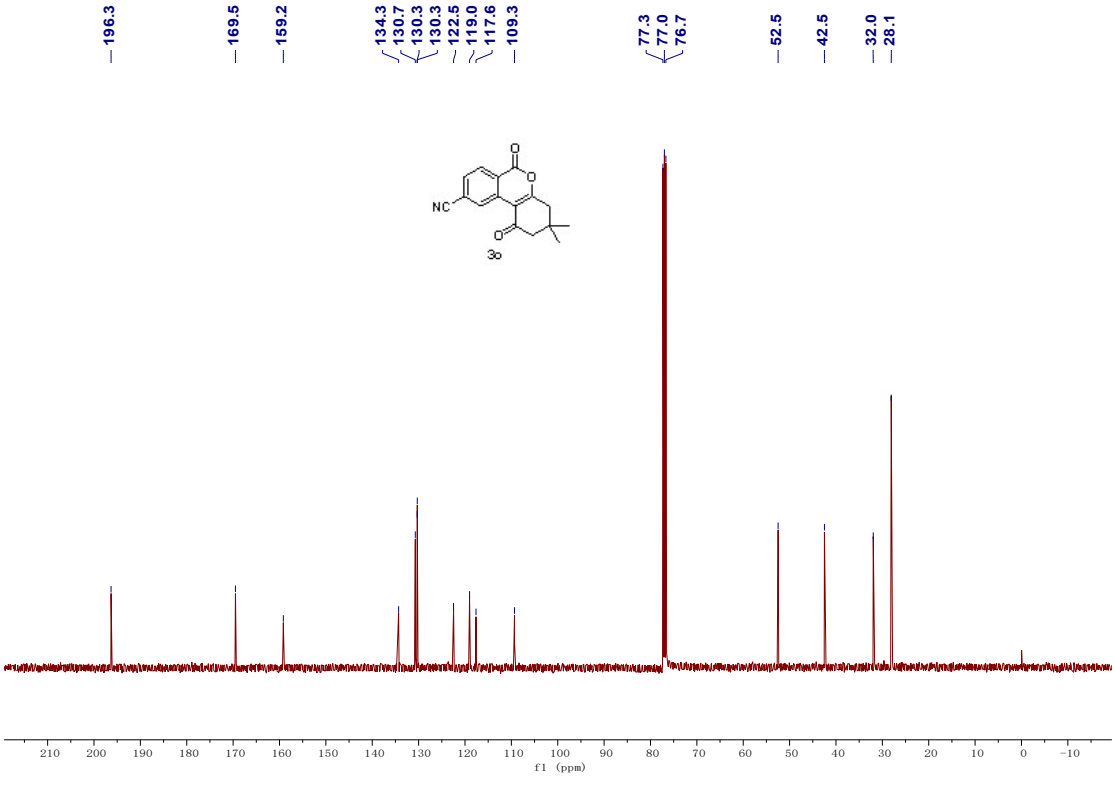
O
O
O
3o
0.97
1.00
1.00
2.01
2.00
6.00
f1 (ppm)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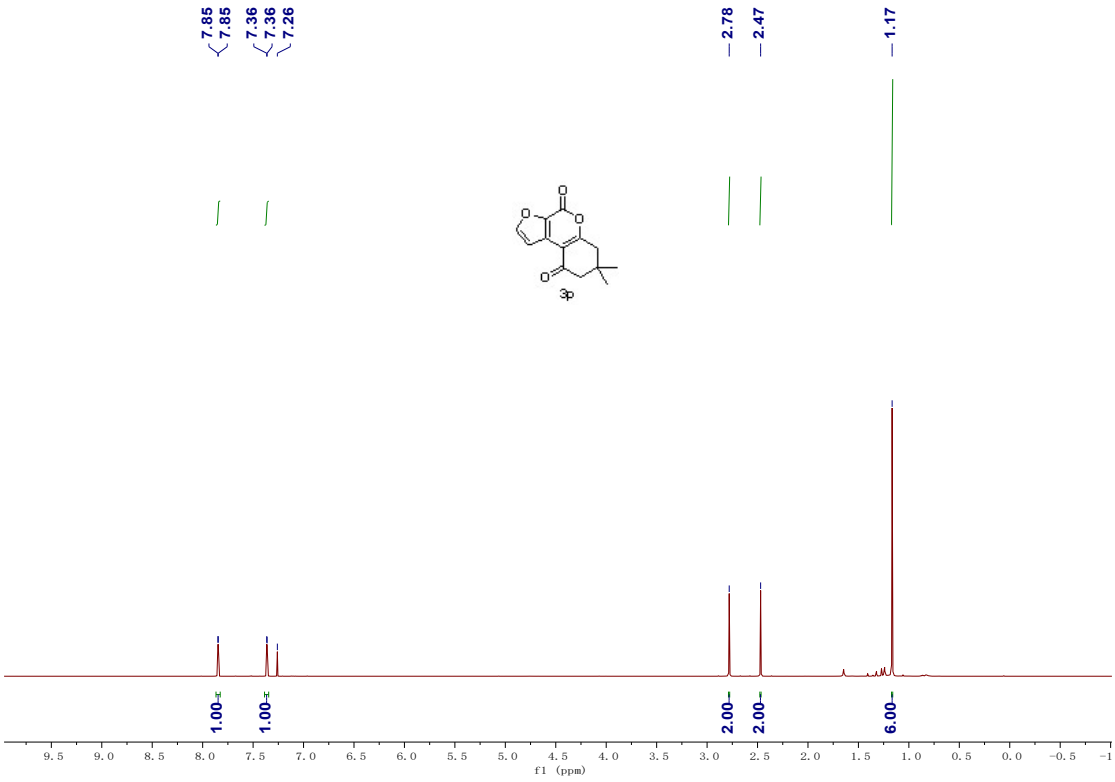
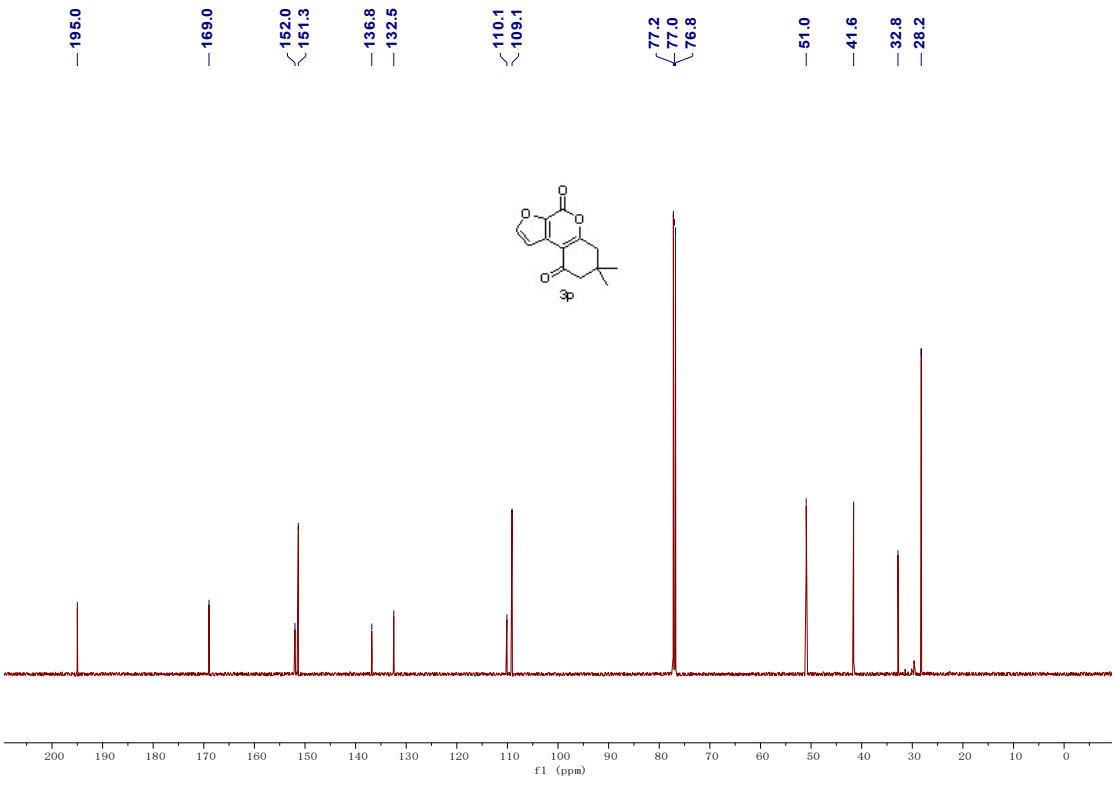
169.5
159.2
134.3
130.7
130.3
130.3
122.5
119.0
117.6
109.3
77.3
77.0
76.7
52.5
42.5
32.0
28.1
NC
O
O
O
3o
f1 (ppm)


7.85
7.85
7.36
7.36
7.26
2.78
2.47
1.17
3p
1.00
1.00
2.00
2.00
6.00
f1 (ppm)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151.3
136.8
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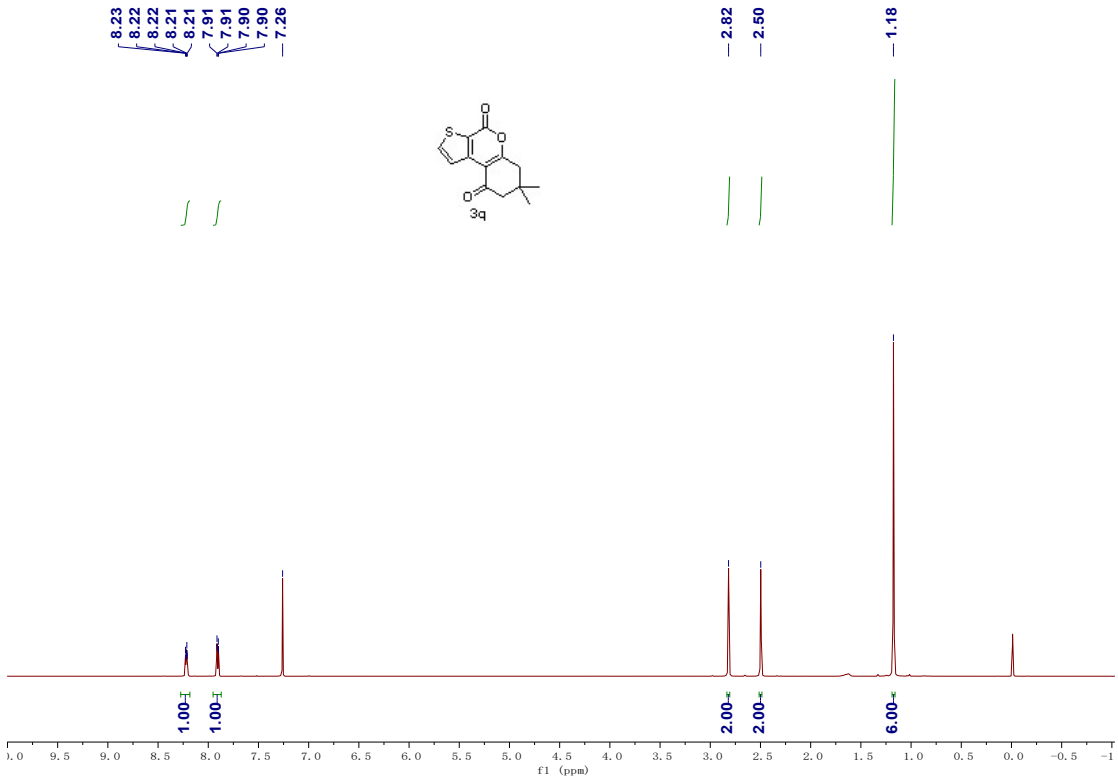
109.1
77.2
77.0
76.8
51.0
41.6
32.8
28.2
3p
f1 (ppm)


8.23
8.22
8.22
8.21
8.21
7.91
7.91
7.90
7.90
7.26
2.82
2.50
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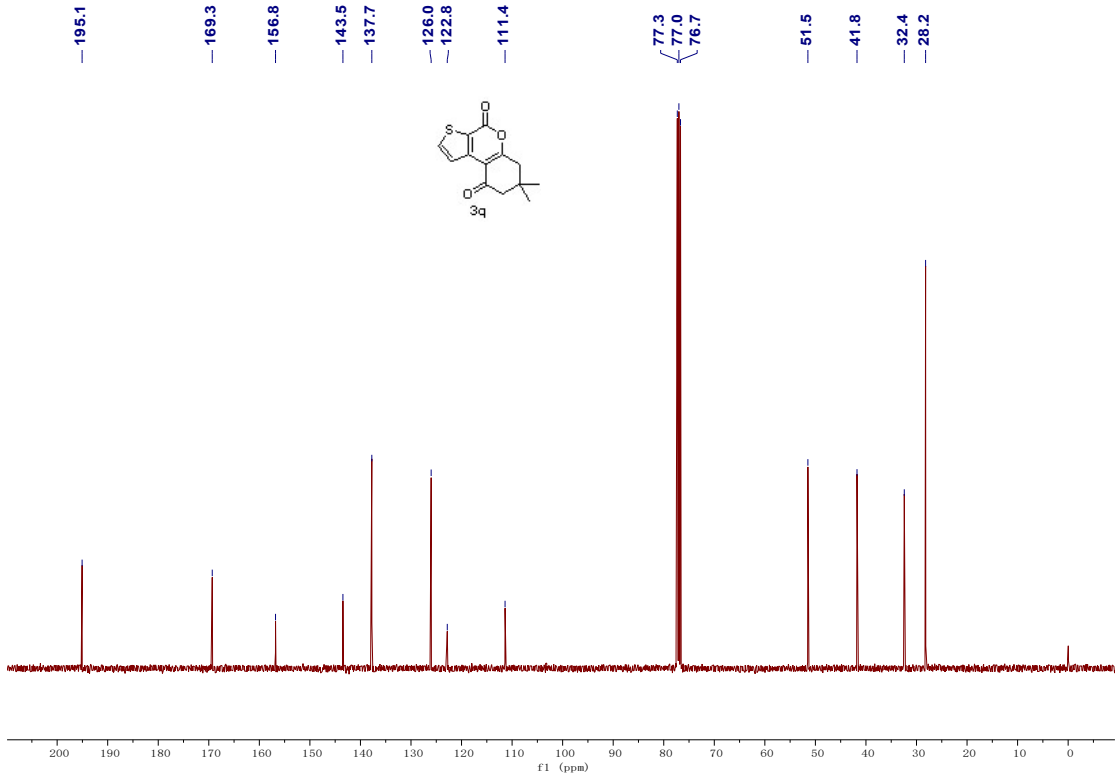
1.00
2.00
2.00
6.00
f1 (ppm)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169.3
156.8
143.5
137.7
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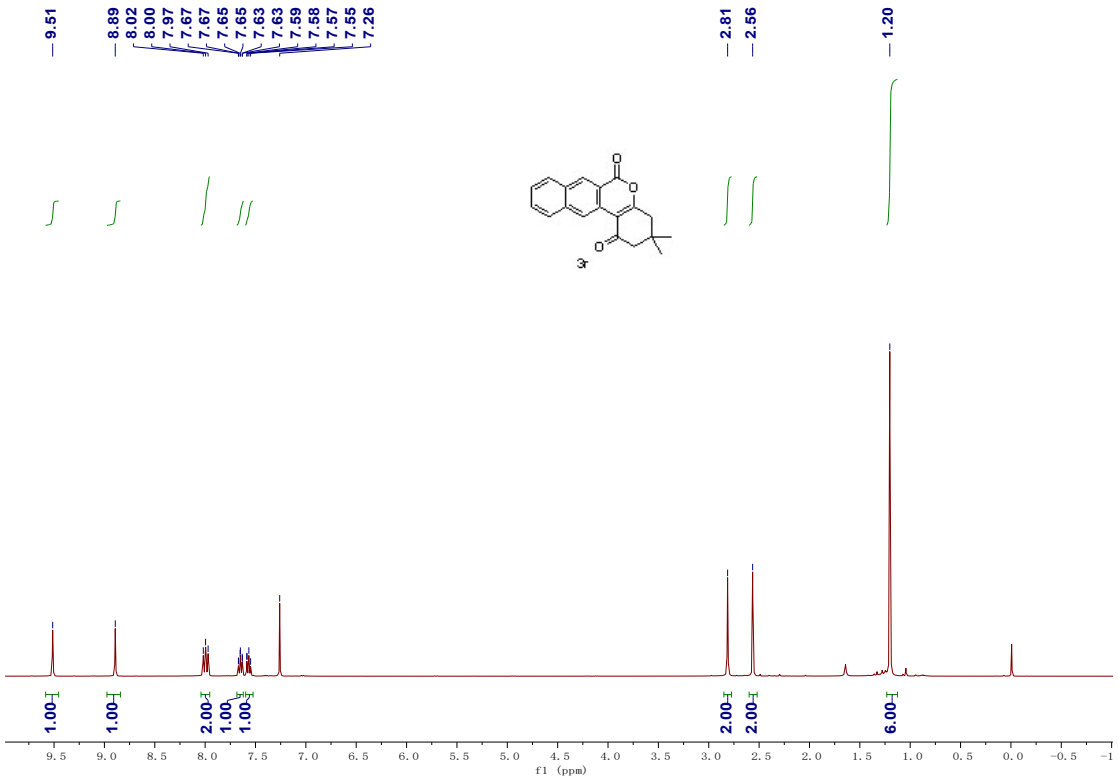
111.4
77.3
77.0
76.7
51.5
41.8
32.4
28.2
3q
f1 (ppm)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7.63
7.63
7.59
7.58
7.57
7.55
7.26
2.81
2.56
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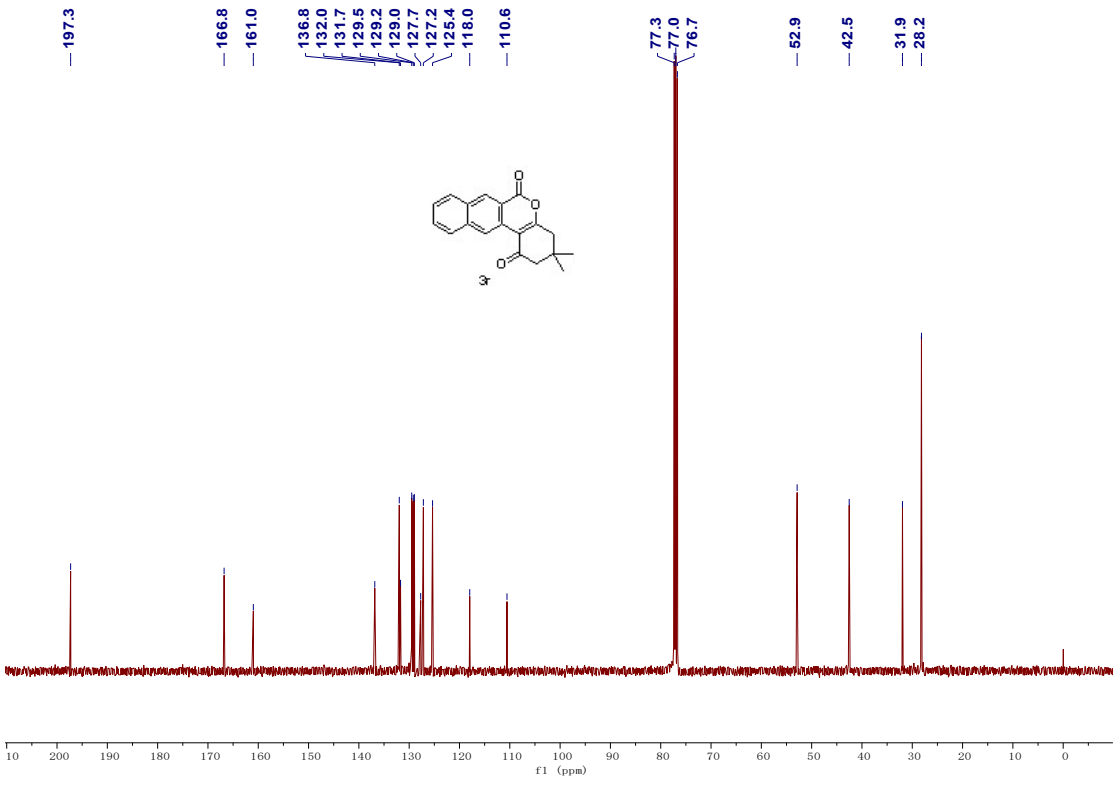
1.00
2.00
1.00
1.00
2.00
2.00
6.00
f1 (ppm)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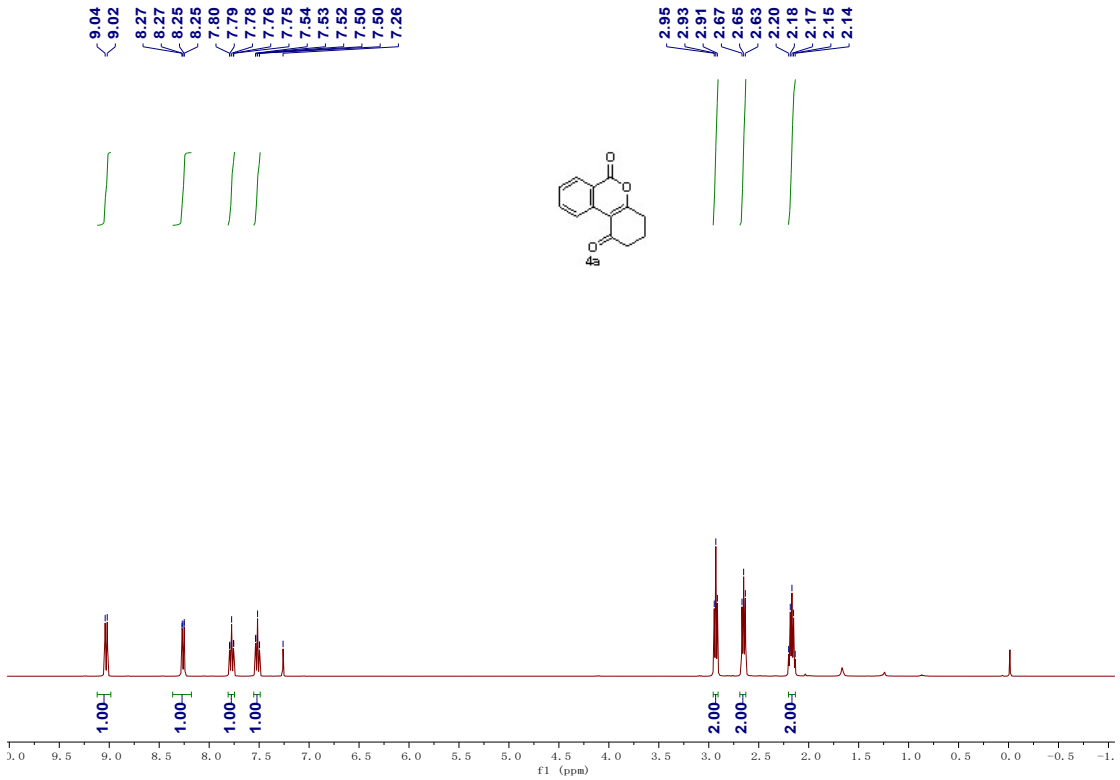
136.8
132.0
131.7
129.5
129.2
129.0
127.7
127.2
125.4
118.0
110.6
77.3
77.0
76.7
52.9
42.5
31.9
28.2
f1 (ppm)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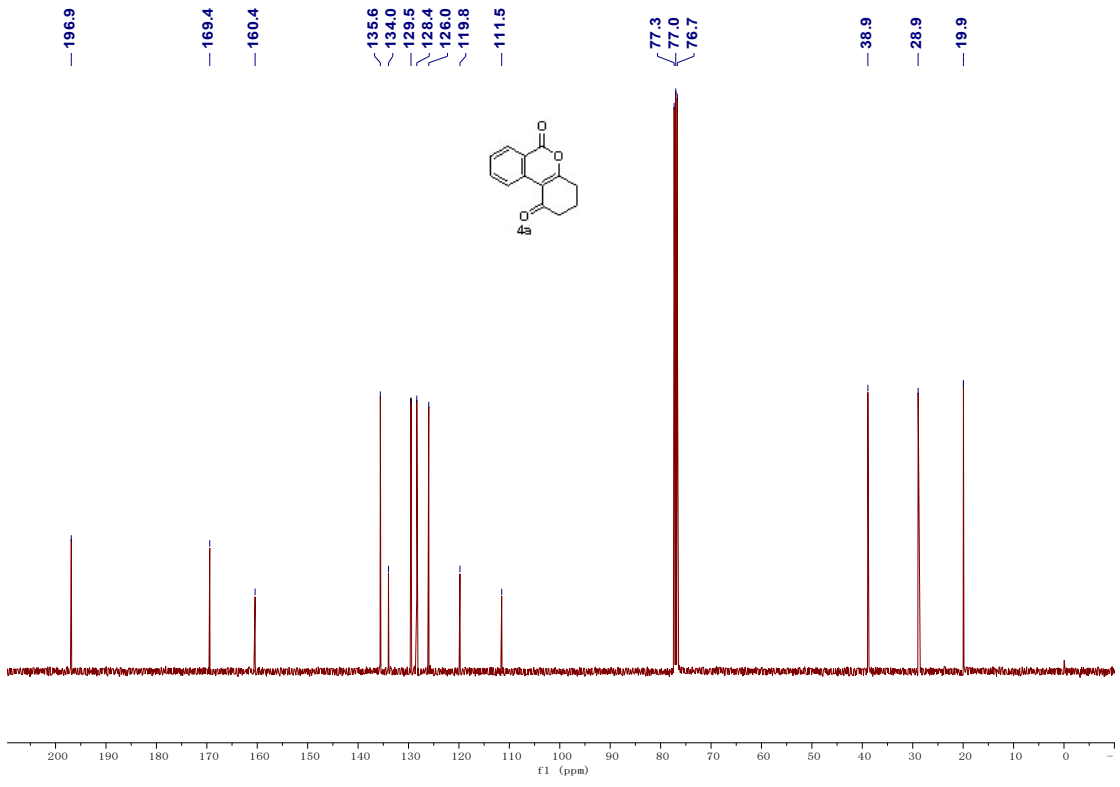
7.54
7.53
7.52
7.50
7.50
7.26
2.95
2.93
2.91
2.67
2.65
2.63
2.20
2.18
2.17
2.15
2.14
4a
1.00
1.00
1.00
1.00
2.00
2.00
2.00
f1 (ppm)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169.4
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129.5
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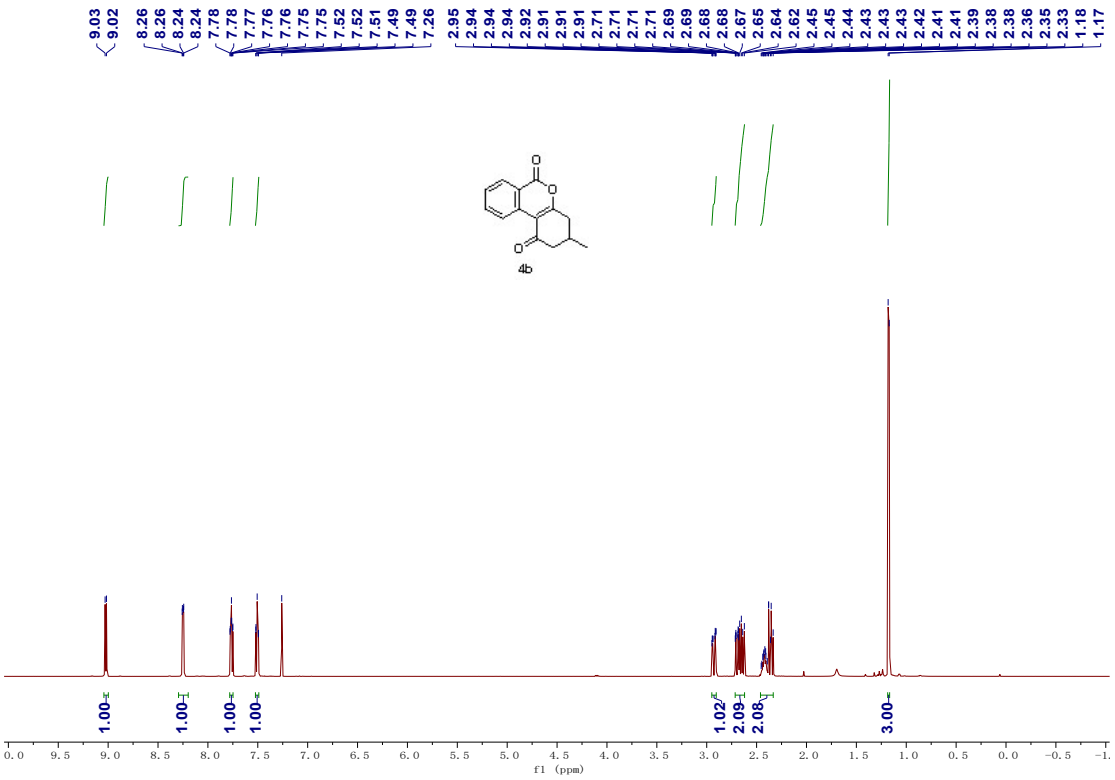
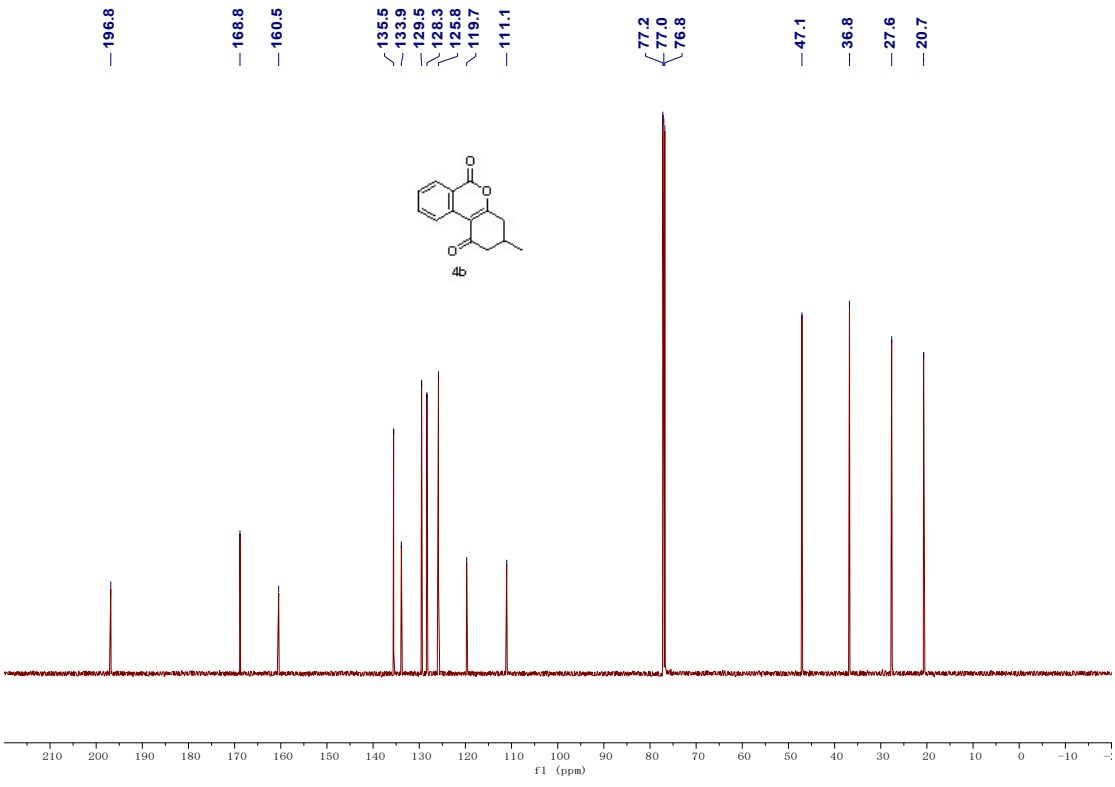
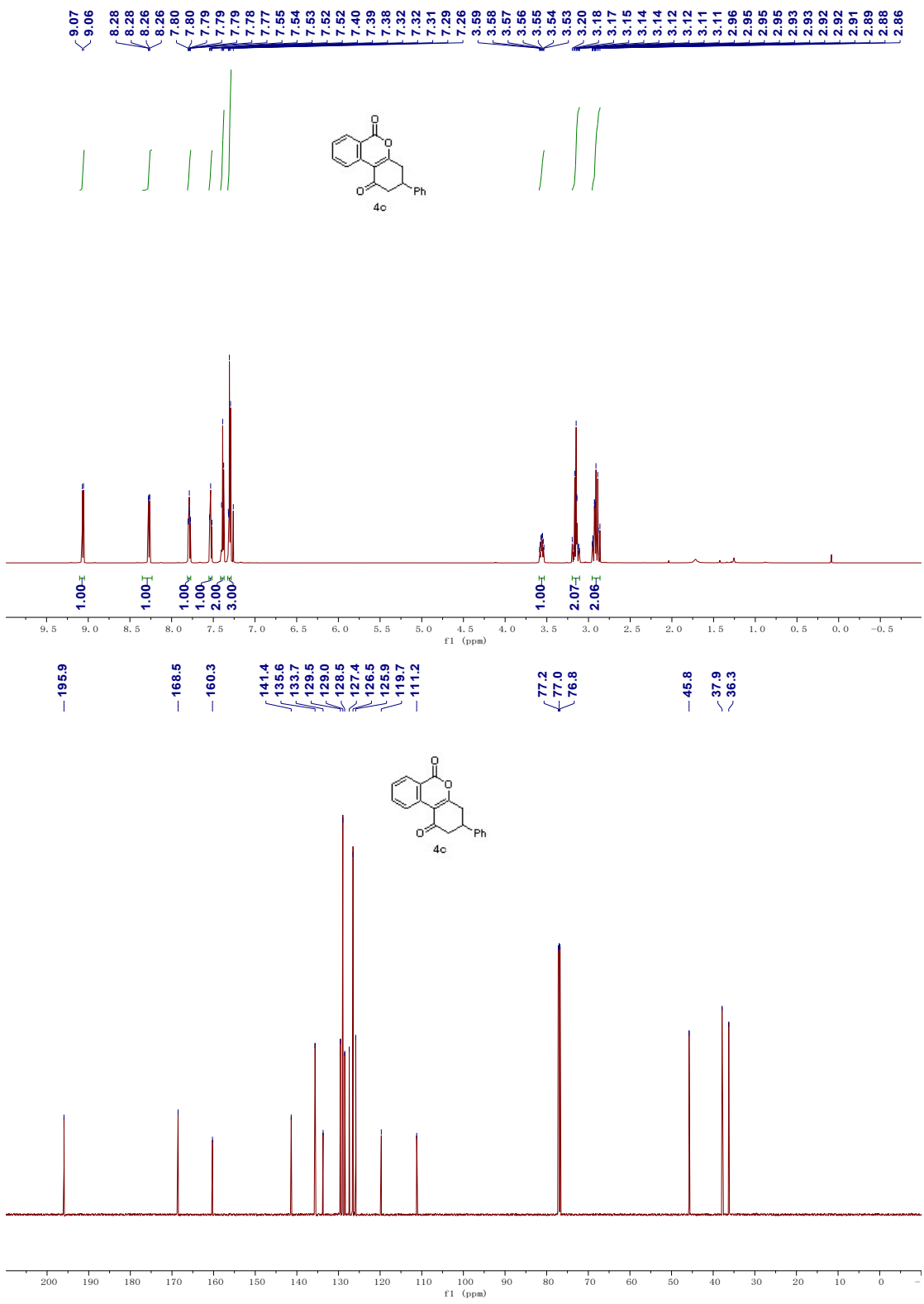
126.0
119.8
111.5
77.3
77.0
76.7
38.9
28.9
19.9
4a
f1 (ppm)


9.03 9.02 8.26 8.26 8.24 8.24 7.78 7.78 7.77 7.76 7.76 7.75 7.75 7.52 7.51 7.49 7.49 7.26
2.95 2.94 2.94 2.94 2.92 2.91 2.91 2.91 2.71 2.71 2.71 2.71 2.69 2.69 2.68 2.68 2.67 2.65 2.64 2.62 2.45 2.45 2.44 2.43 2.43 2.43 2.42 2.41 2.41 2.39 2.38 2.38 2.36 2.35 2.33 1.18 1.17
4b
1.00 1.00 1.00 1.00 1.02 2.09 2.08 3.00
f1 (ppm)


196.8 168.8 160.5 135.5 133.9 129.5 128.3 125.8 119.7 111.1 77.2 77.0 76.8 47.1 36.8 27.6 20.7
4b
f1 (ppm)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7.79
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7.77
7.55
7.54
7.53
7.52
7.52
7.40
7.39
7.38
7.32
7.32
7.31
7.29
7.26
3.59
3.58
3.57
3.56
3.55
3.54
3.53
3.20
3.18
3.17
3.15
3.14
3.14
3.12
3.12
3.11
3.11
2.96
2.95
2.95
2.93
2.93
2.92
2.92
2.91
2.89
2.88
2.86
O
O
O
Ph
4c
1.00
1.00
1.00
1.00
2.00
3.00
1.00
2.07
2.06
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)
195.9
168.5
160.3
141.4
135.6
133.7
129.5
129.0
128.5
127.4
126.5
125.9
119.7
111.2
77.2
77.0
76.8
45.8
37.9
36.3
O
O
O
Ph
4c
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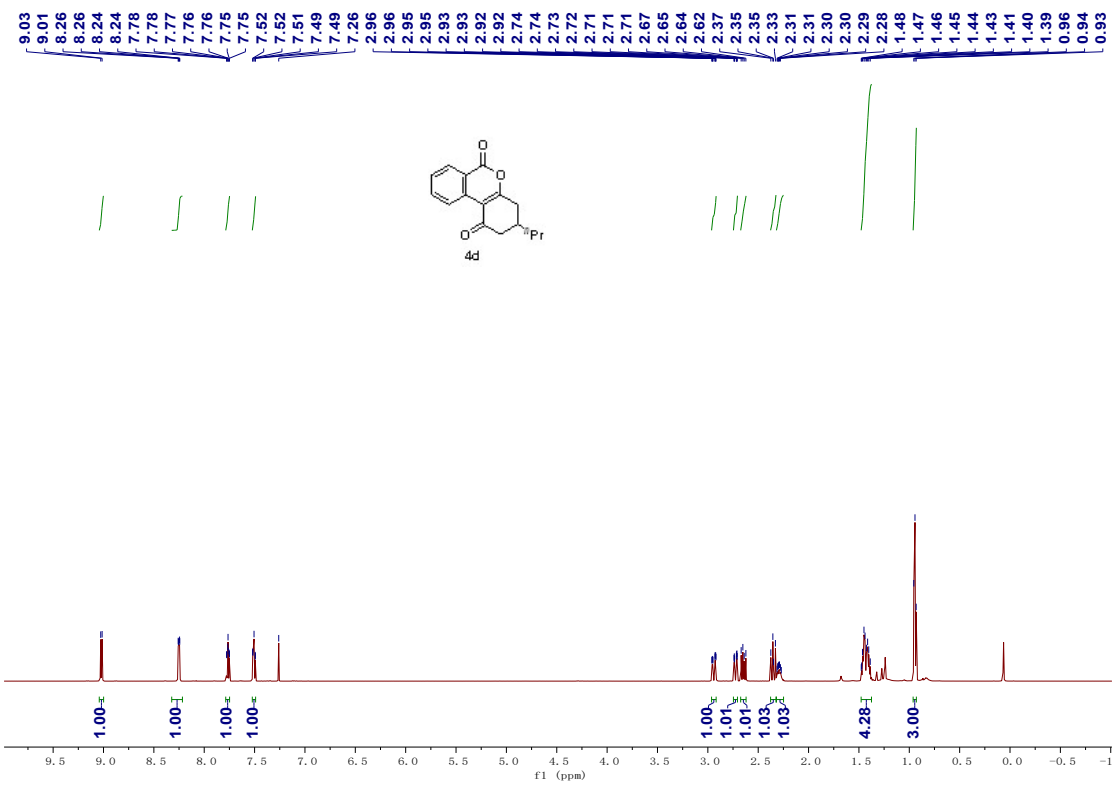
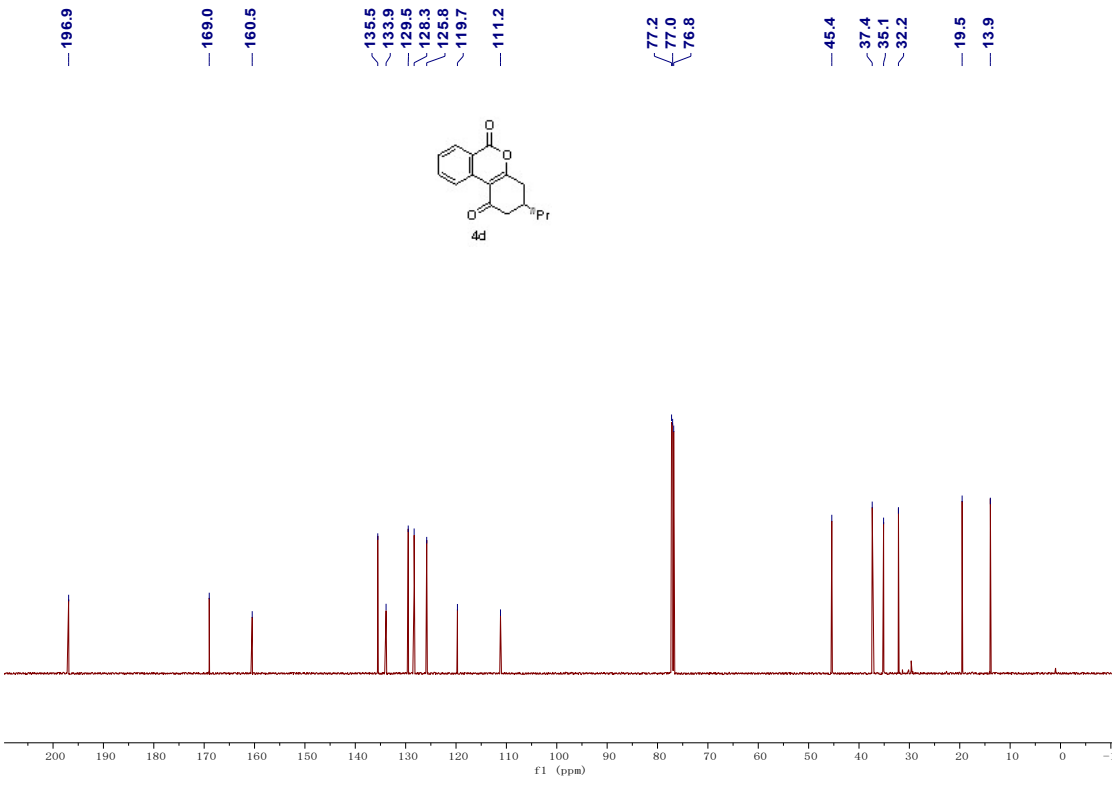
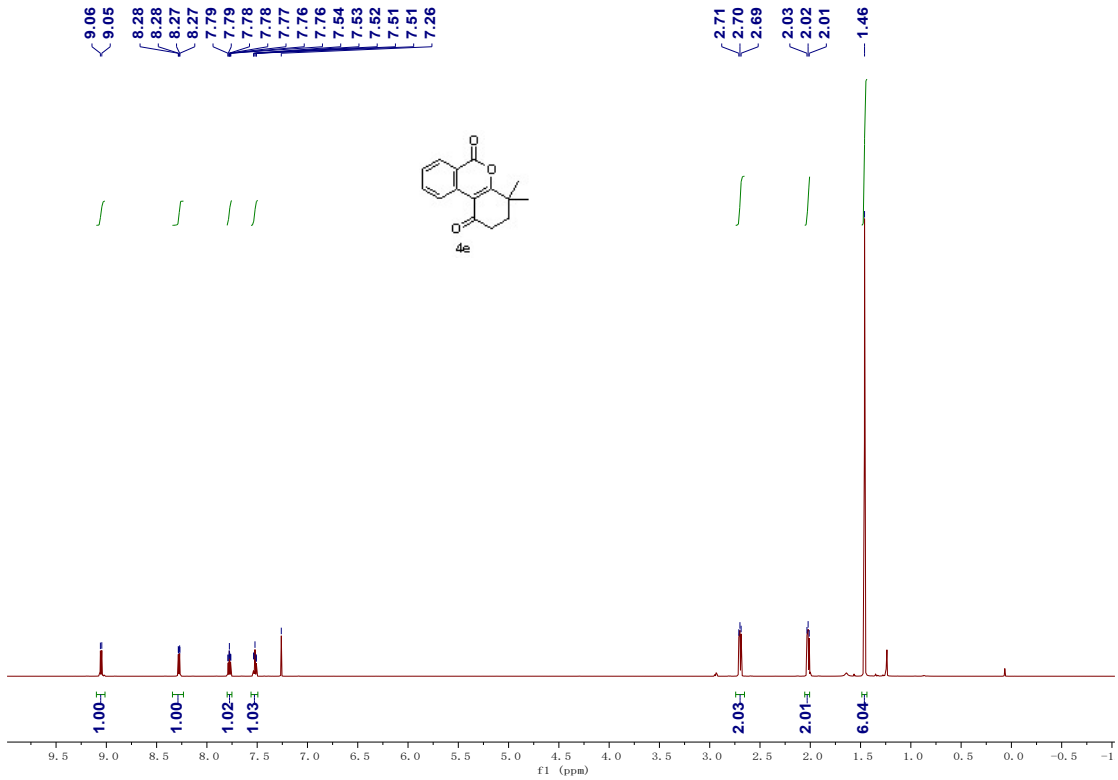
f1 (ppm)


9.03 9.01 8.26 8.26 8.24 8.24 7.78 7.78 7.77 7.76 7.76 7.75 7.75 7.52 7.52 7.51 7.49 7.49 7.26
2.96 2.96 2.95 2.95 2.93 2.92 2.92 2.74 2.74 2.73 2.72 2.71 2.71 2.71 2.67 2.65 2.64 2.62 2.37 2.35 2.35 2.33 2.31 2.31 2.30 2.30 2.29 2.28 1.48 1.47 1.46 1.45 1.44 1.43 1.41 1.40 1.39 0.96 0.94 0.93
O
O
O
nPr
4d
1.00 1.00 1.00 1.00 1.00 1.01 1.01 1.03 1.03 4.28 3.00
f1 (ppm)


196.9 169.0 160.5 135.5 133.9 129.5 128.3 125.8 119.7 111.2 77.2 77.0 76.8 45.4 37.4 35.1 32.2 19.5 13.9
O
O
O
nPr
4d
f1 (ppm)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7.79
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7.77
7.76
7.76
7.54
7.53
7.52
7.51
7.51
7.26
2.71
2.70
2.69
2.03
2.02
2.01
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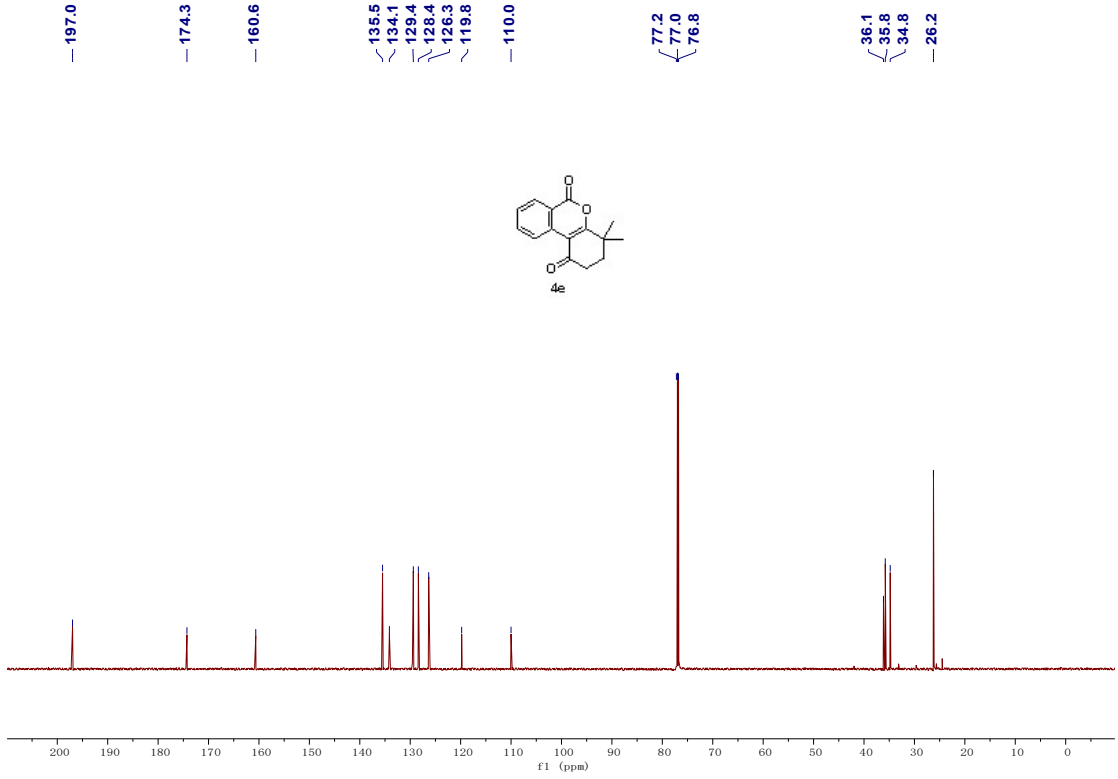
4e
1.00
1.00
1.02
1.03
2.03
2.01
6.04
f1 (ppm)


197.0
174.3
160.6
135.5
134.1
129.4
128.4
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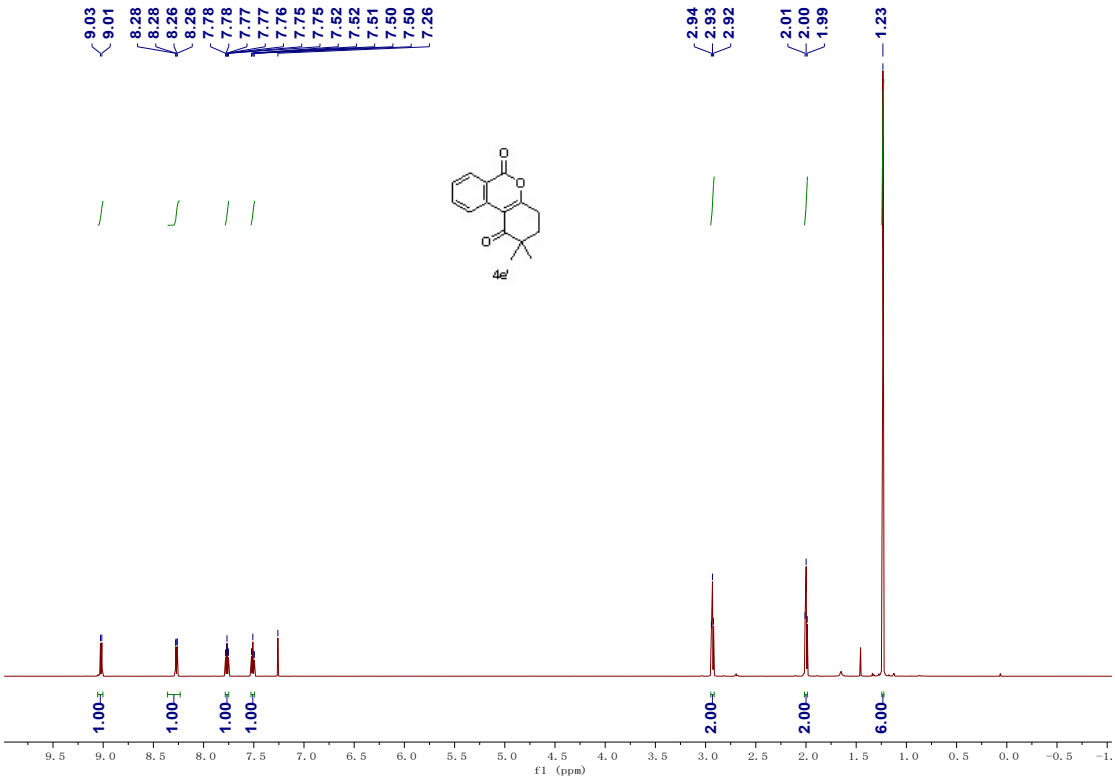
77.2
77.0
76.8
36.1
35.8
34.8
26.2
4e
f1 (ppm)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7.26
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2.92
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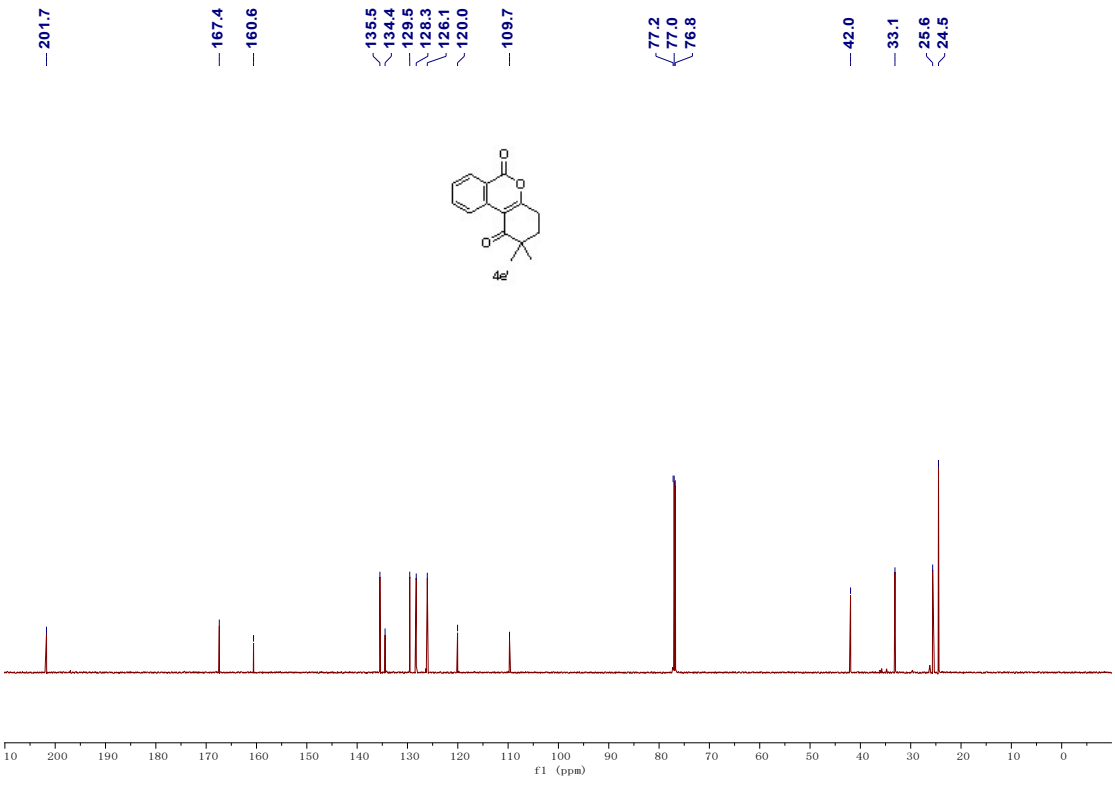
2.00
1.99
1.23
4e'
1.00
1.00
1.00
1.00
2.00
2.00
6.00
f1 (ppm)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76.8
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25.6
24.5
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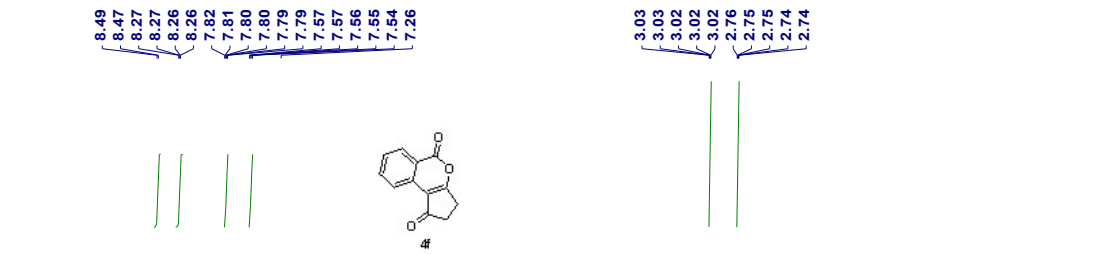
f1 (ppm)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7.57
7.56
7.55
7.54
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3.02
3.02
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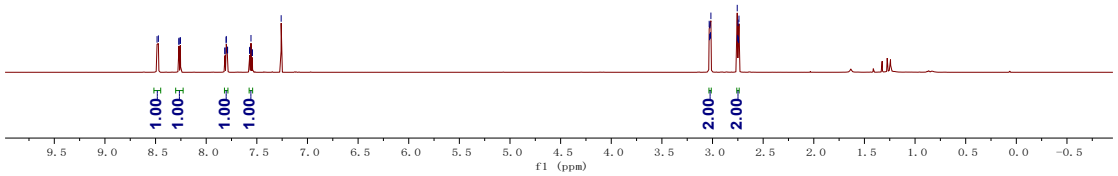
2.74
4f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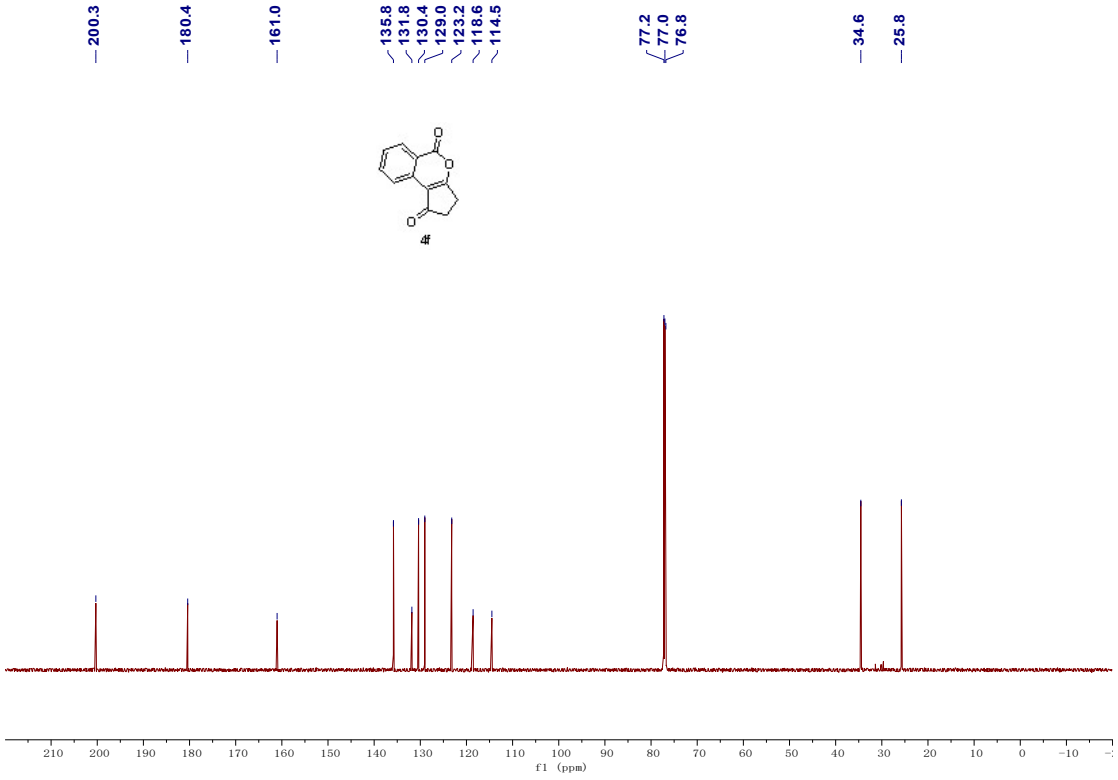
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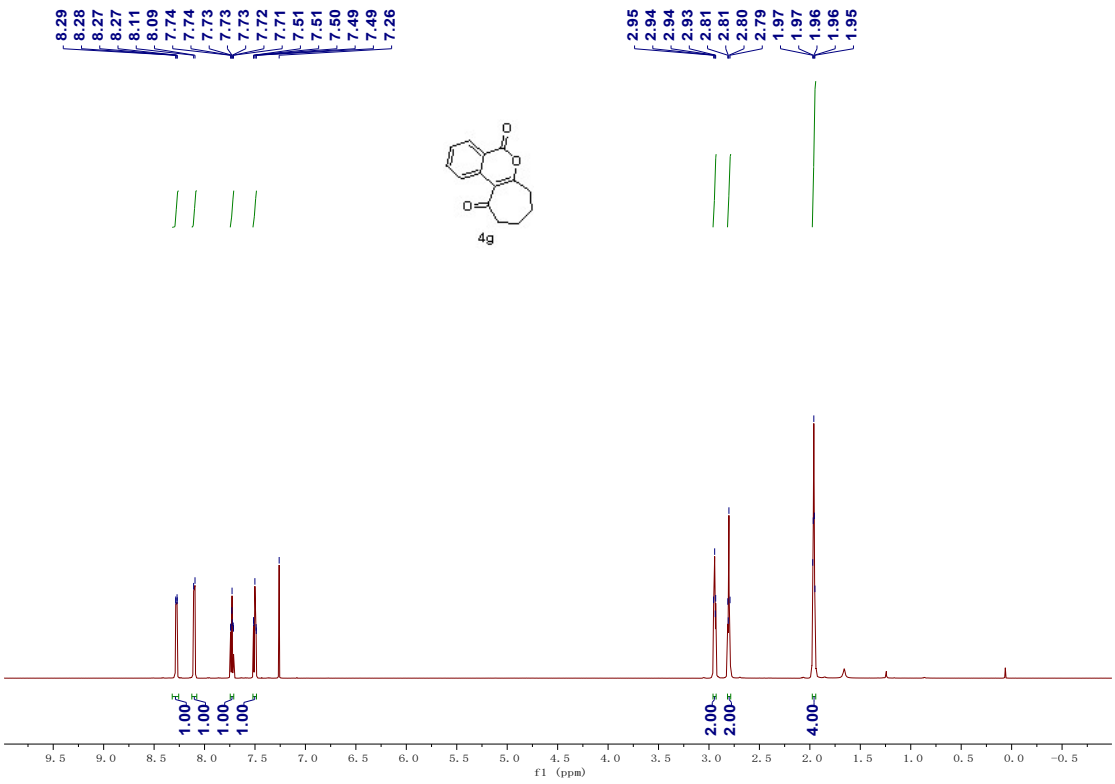
25.8
4f
f1 (ppm)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7.50
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7.26
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2.94
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2.79
1.97
1.97
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4g
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1.00
1.00
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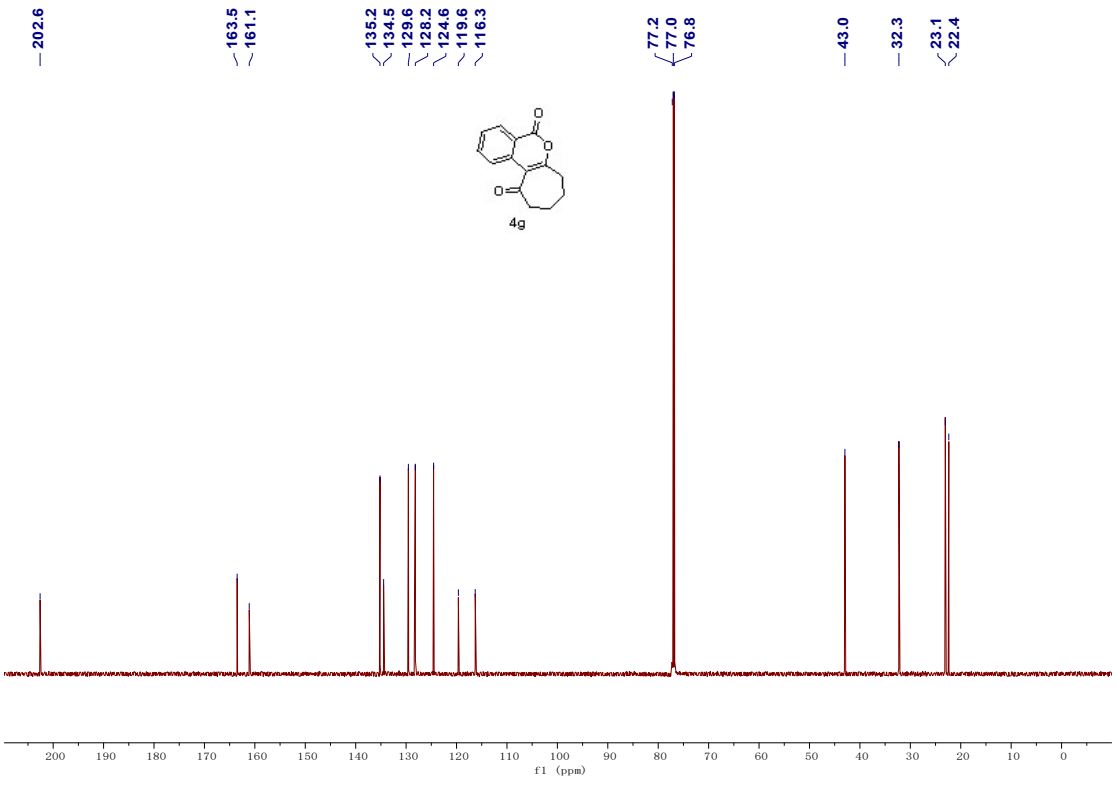
4.00
f1 (ppm)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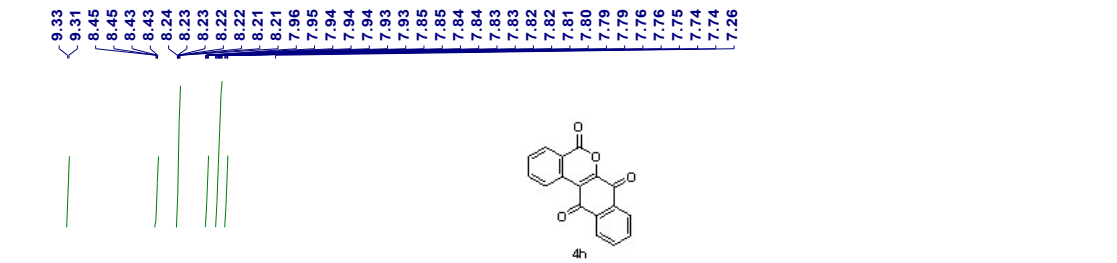
23.1
22.4
4g
f1 (ppm)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7.94
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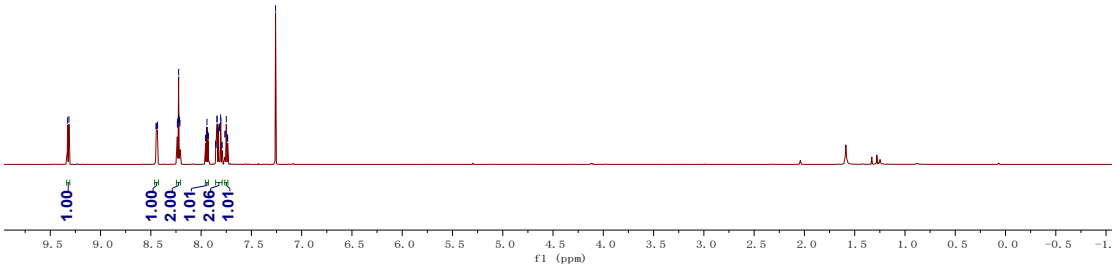
7.26
4h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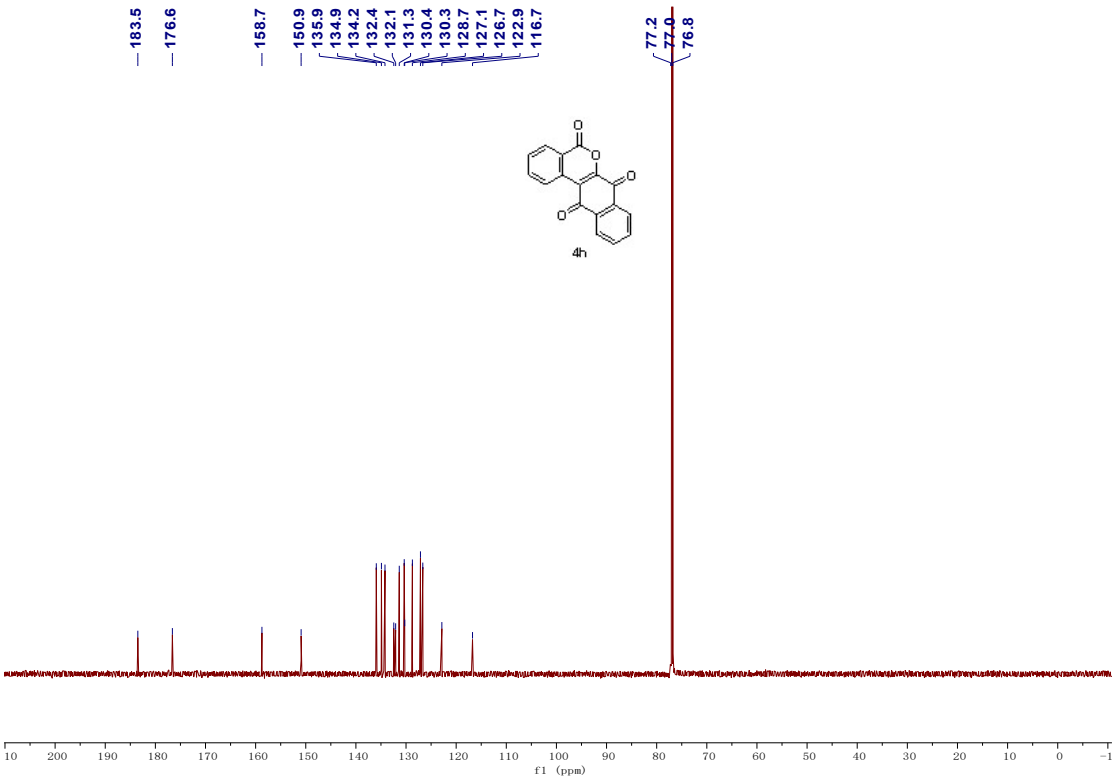
1.01
f1 (ppm)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134.9
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132.4
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131.3
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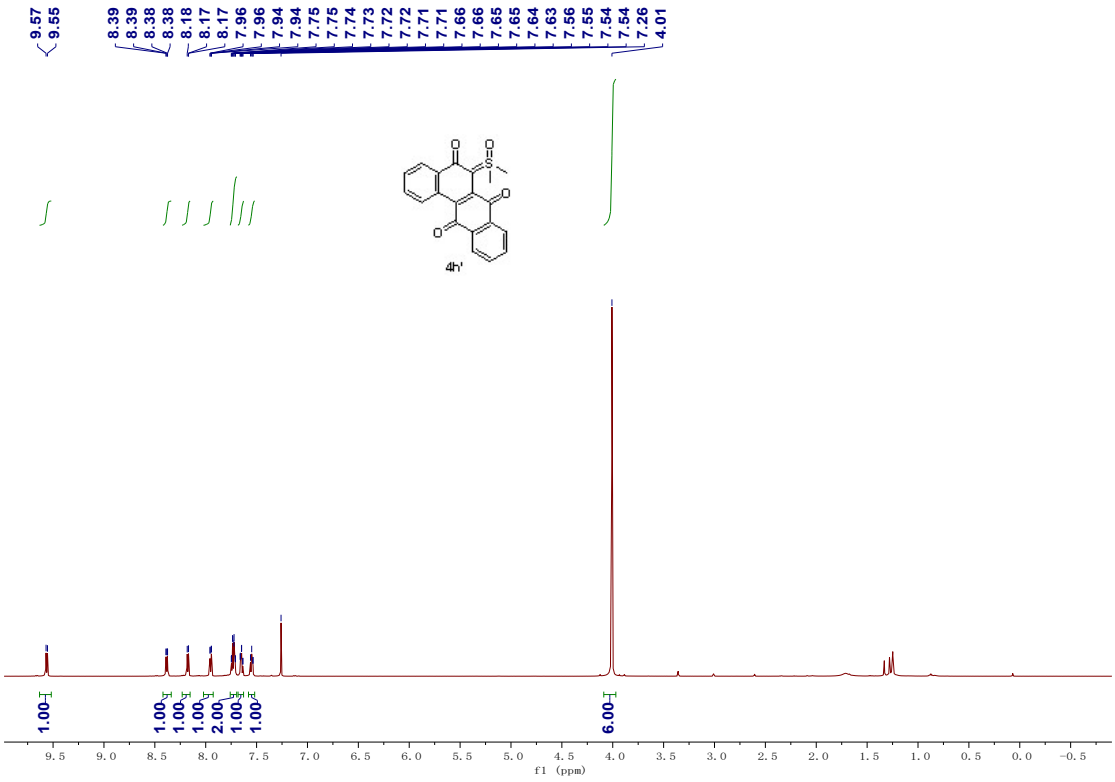
128.7
127.1
126.7
122.9
116.7
77.2
77.0
76.8
4h
f1 (ppm)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8.17
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7.96
7.94
7.94
7.75
7.75
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7.72
7.72
7.71
7.71
7.66
7.66
7.65
7.65
7.64
7.63
7.56
7.55
7.54
7.54
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4.01
4h'
1.00
1.00
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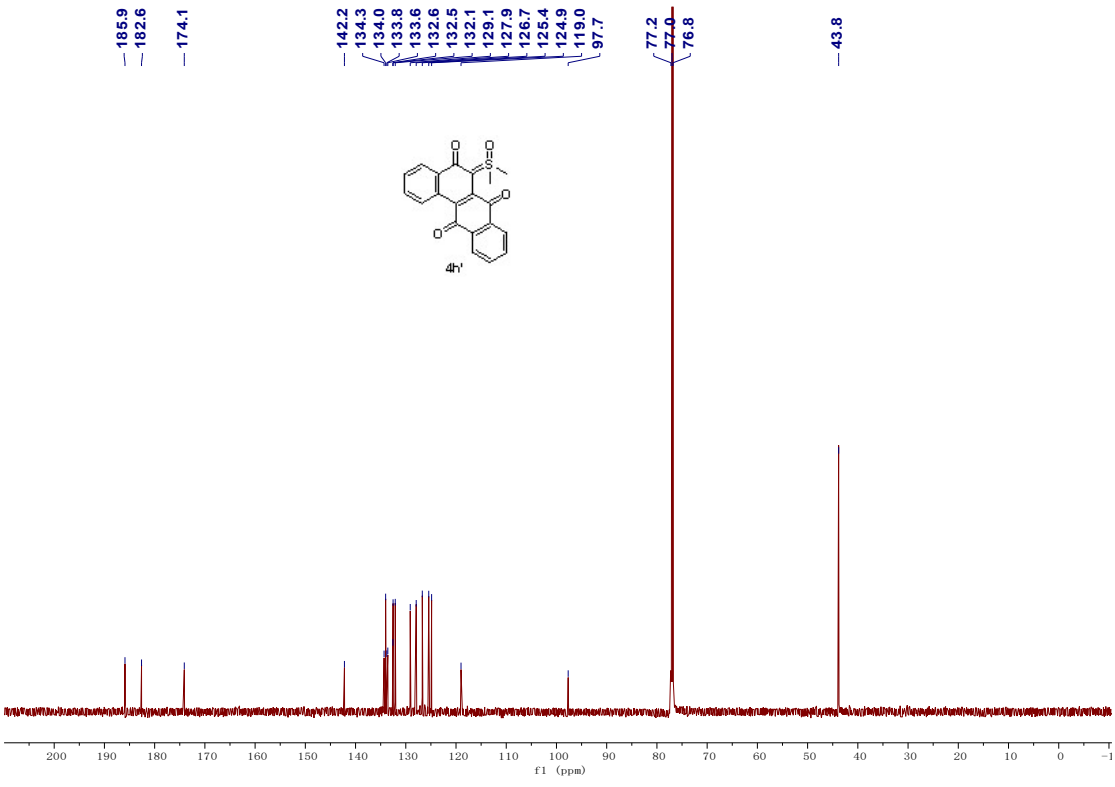
2.00
1.00
1.00
6.00
f1 (ppm)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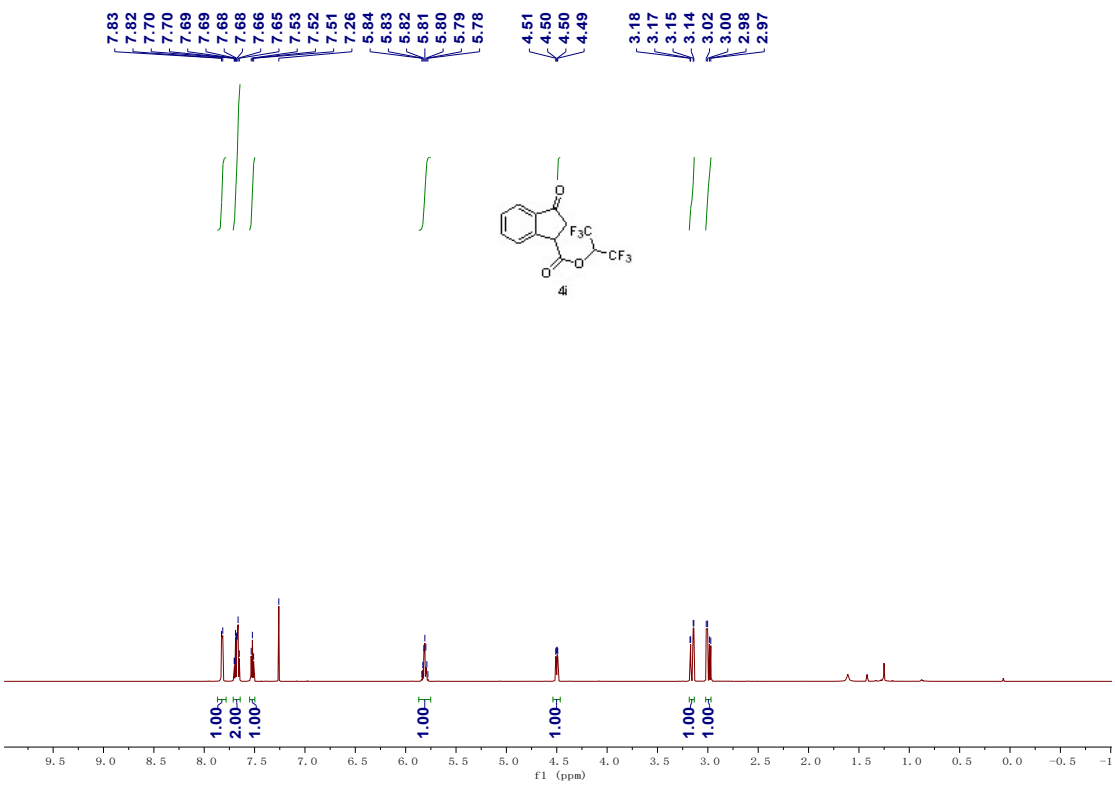
134.0
133.8
133.6
132.6
132.5
132.1
129.1
127.9
126.7
125.4
124.9
119.0
97.7
77.2
77.0
76.8
43.8
4h'
f1 (ppm)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5.83
5.82
5.81
5.80
5.79
5.78
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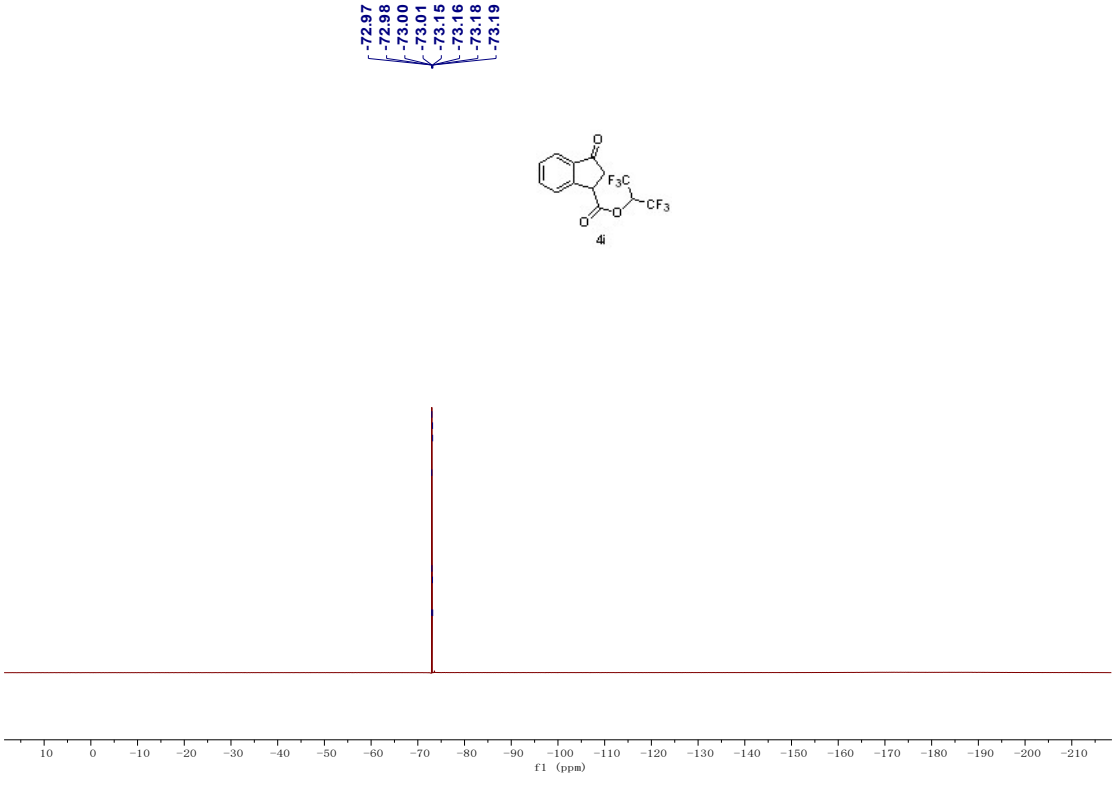
4.50
4.50
4.49
3.18
3.17
3.15
3.14
3.02
3.00
2.98
2.97
F3C
CF3
O
O
O
4i
1.00
2.00
1.00
1.00
1.00
1.00
1.00
f1 (ppm)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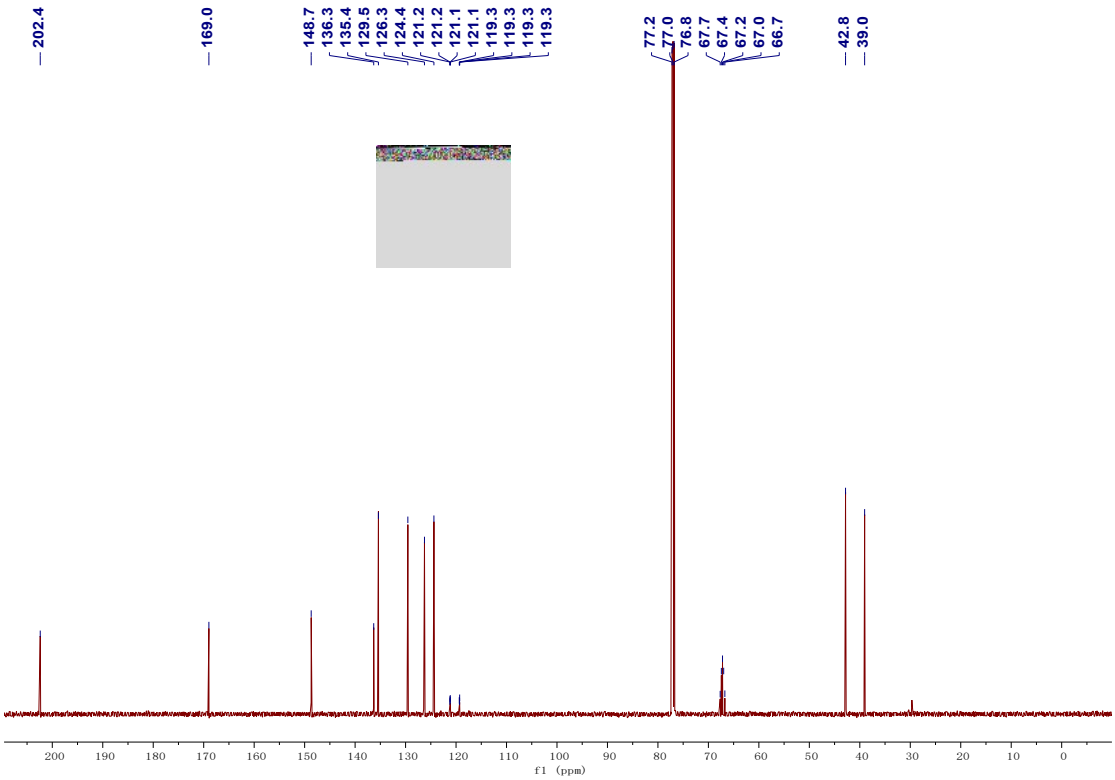
F3C
CF3
O
O
O
4i
f1 (ppm)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124.4
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121.2
121.1
121.1
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119.3
119.3
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76.8
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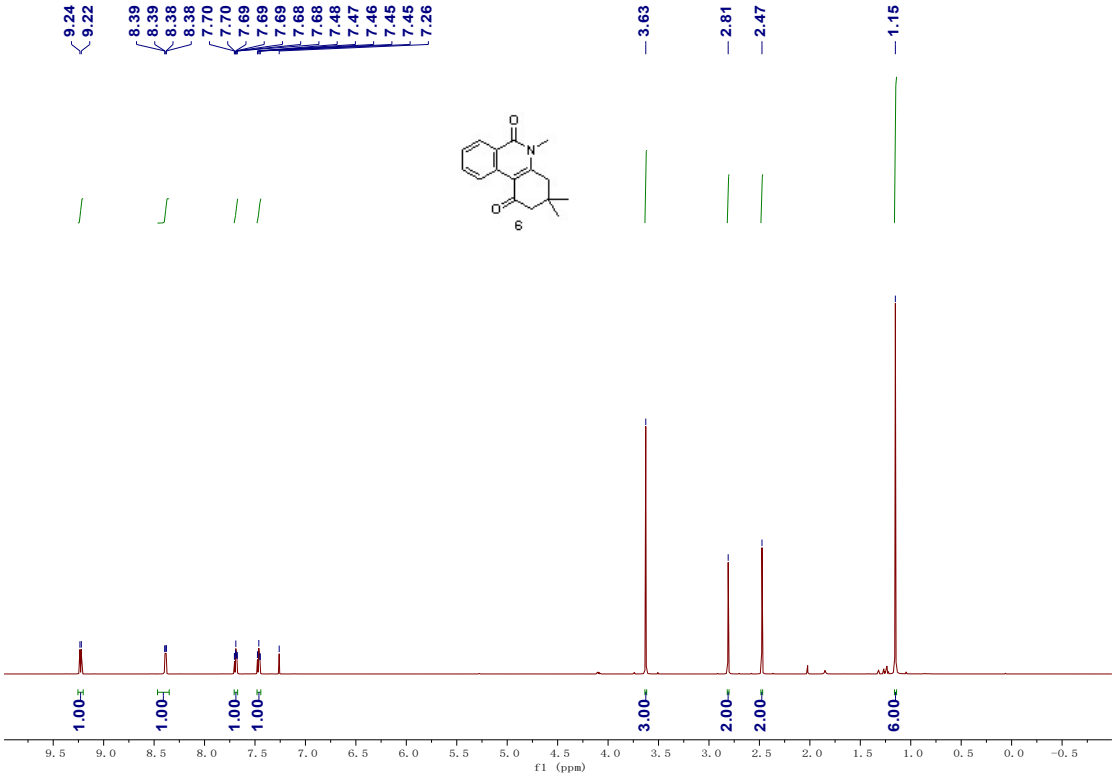
67.4
67.2
67.0
66.7
42.8
39.0
f1 (ppm)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7.45
7.26
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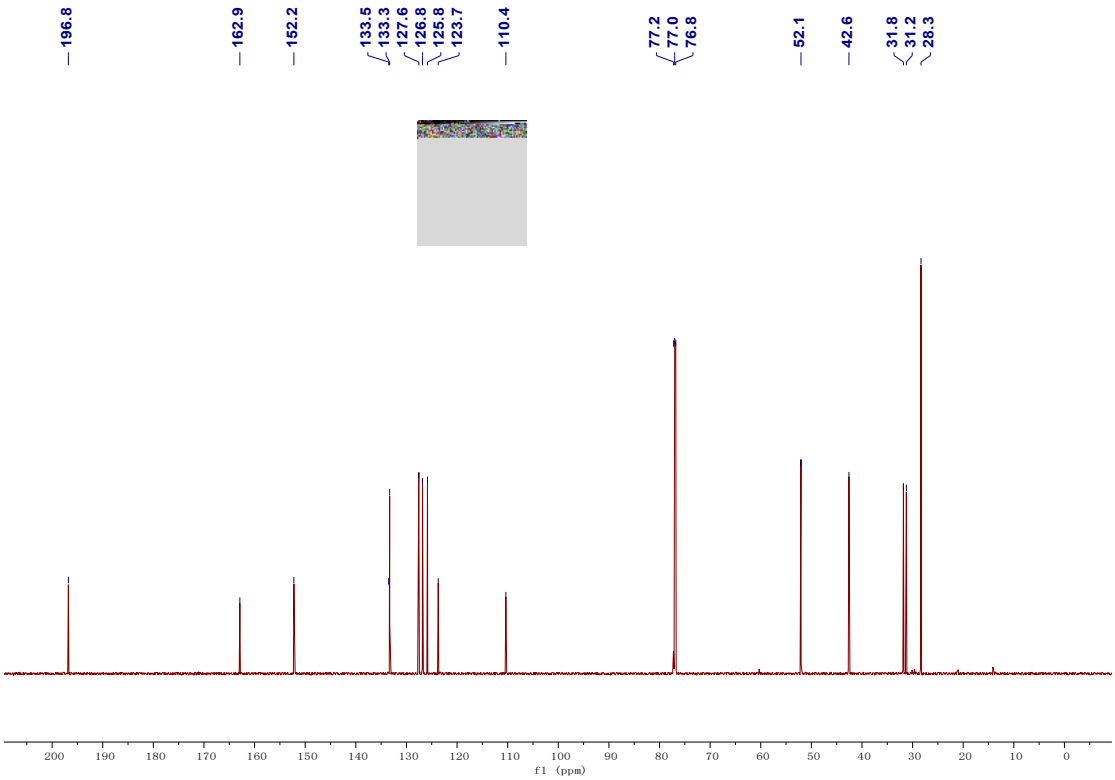
2.00
6.00
f1 (ppm)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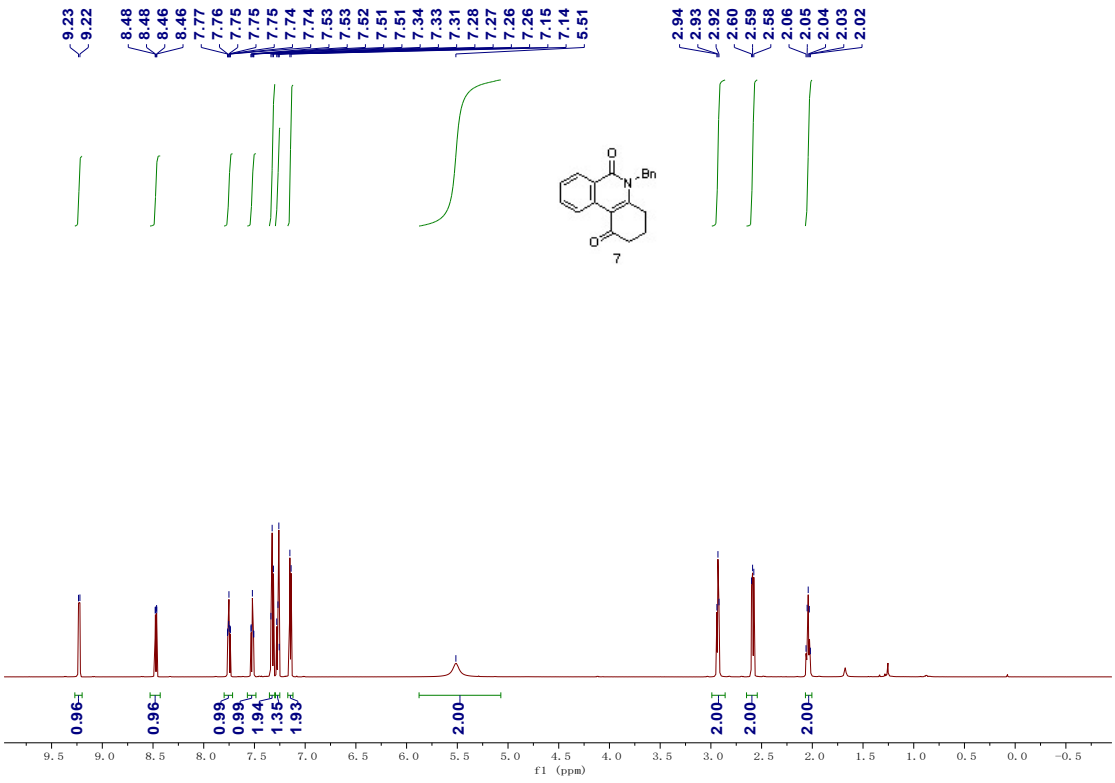
28.3
f1 (ppm)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2.58
2.06
2.05
2.04
2.03
2.02
Bn
7
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0.96
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0.99
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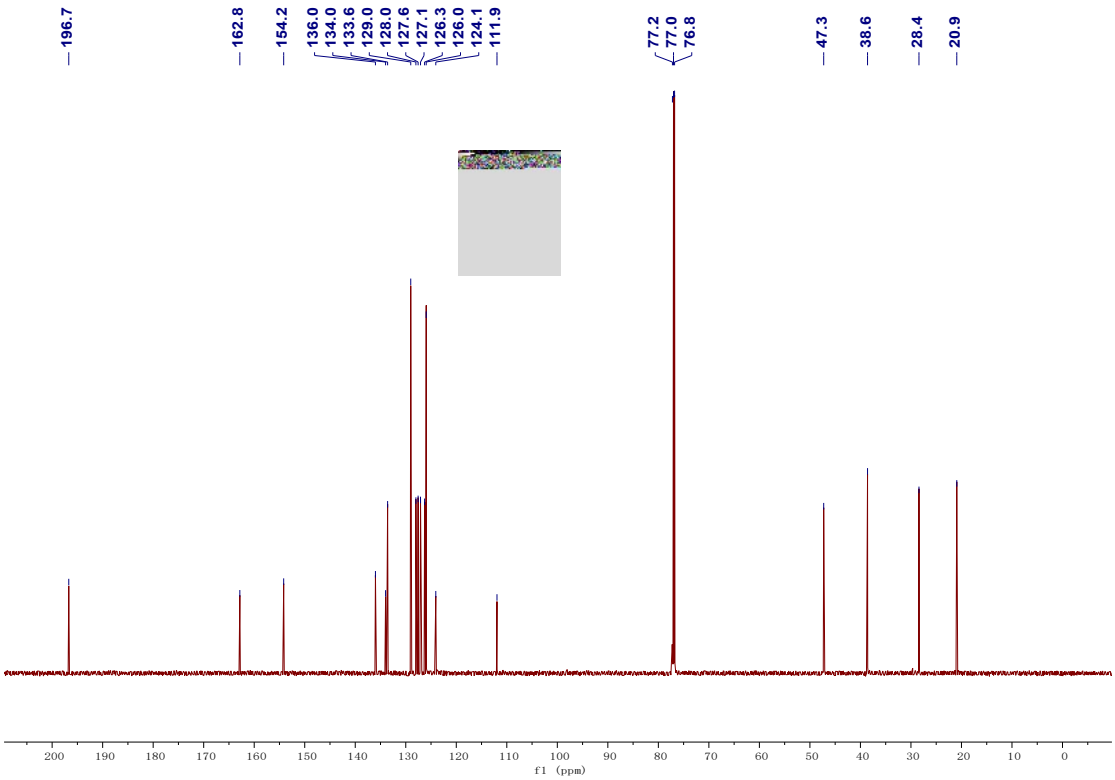
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111.9
77.2
77.0
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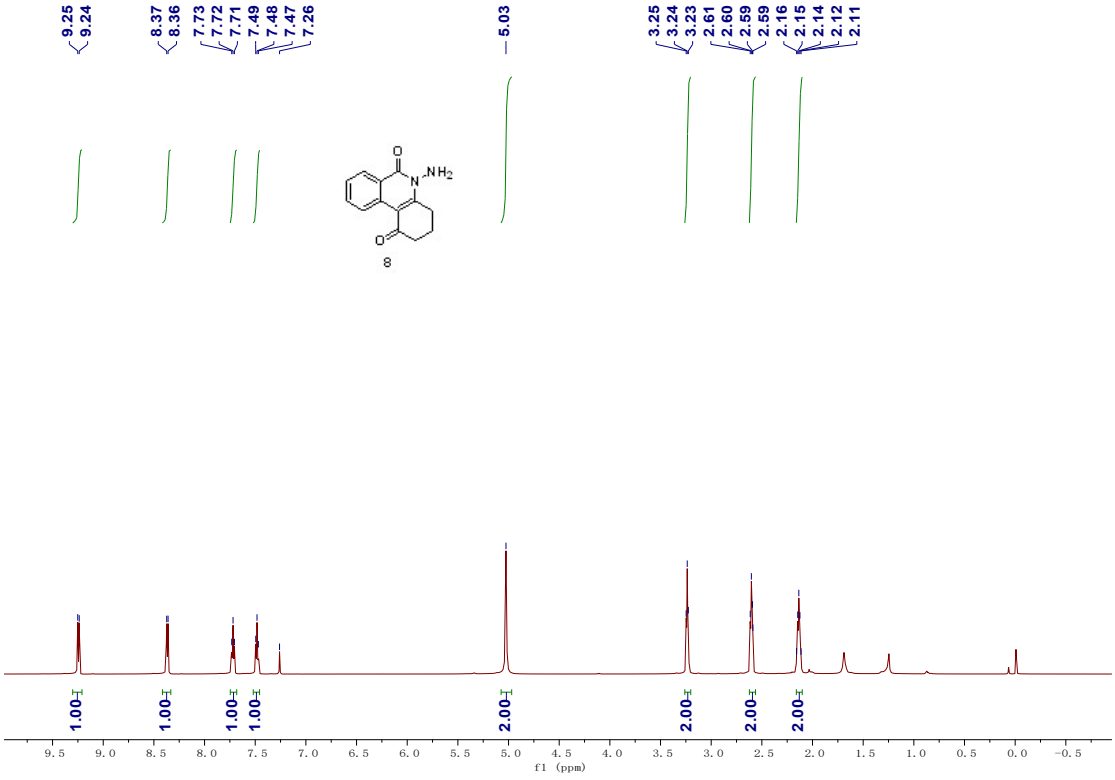
47.3
38.6
28.4
20.9
f1 (ppm)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3.24
3.23
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2.59
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2.15
2.14
2.12
2.11
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O
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1.00
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2.00
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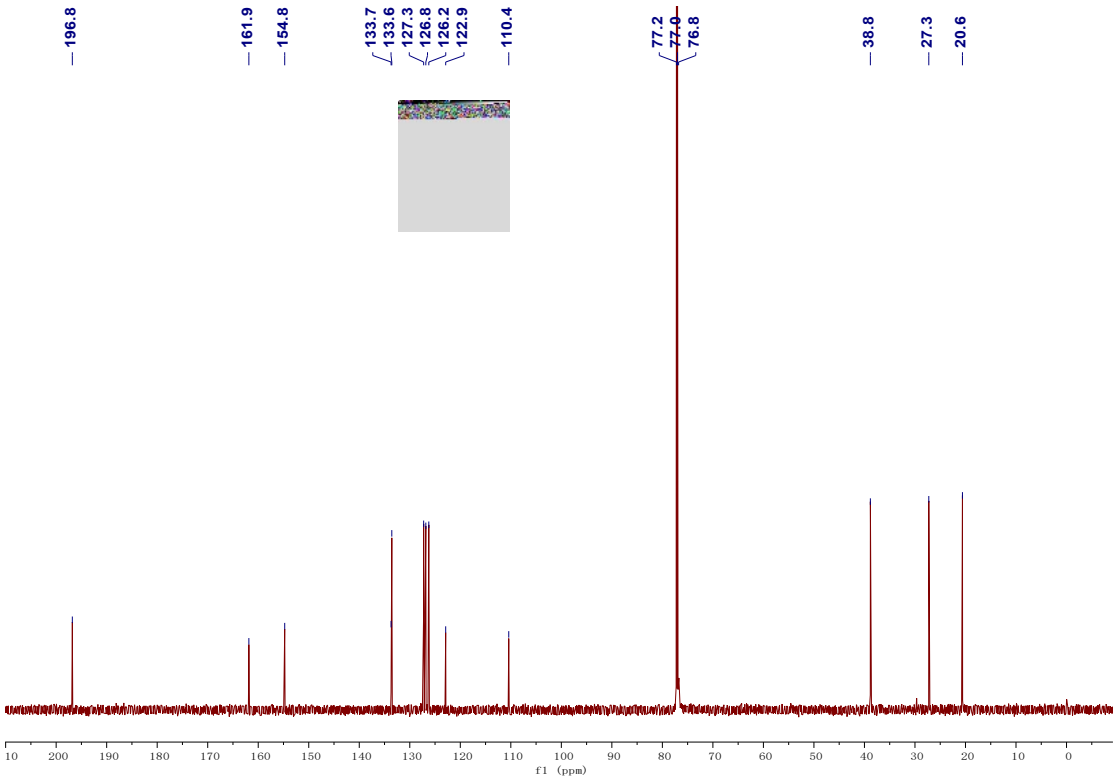
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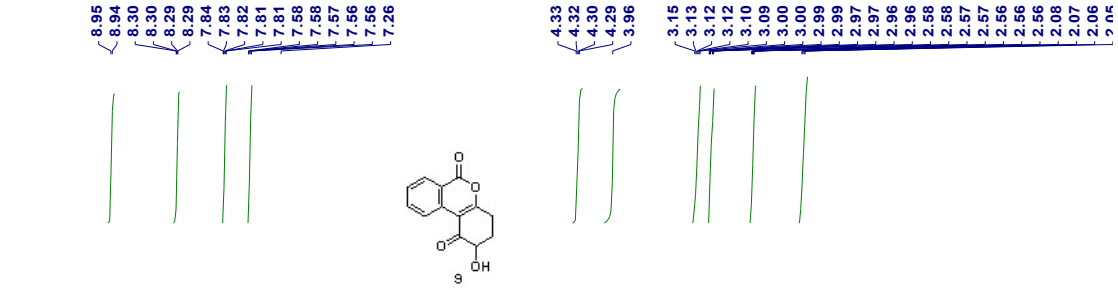
20.6
f1 (ppm)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7.26
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3.00
3.00
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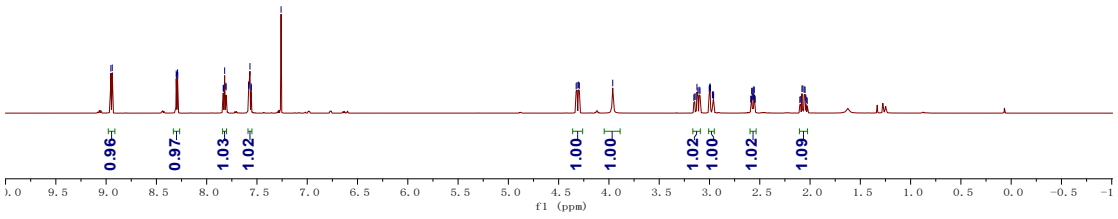
2.07
2.06
O
O
O
OH
9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1.02
1.00
1.02
1.09
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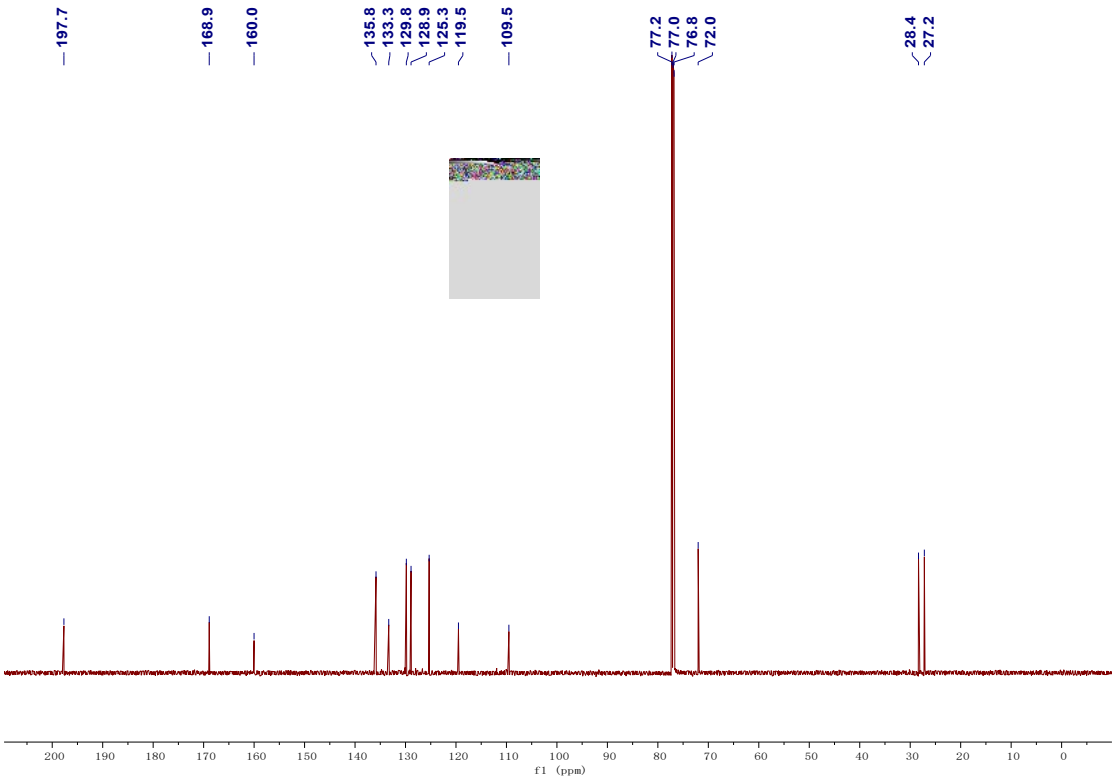
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76.8
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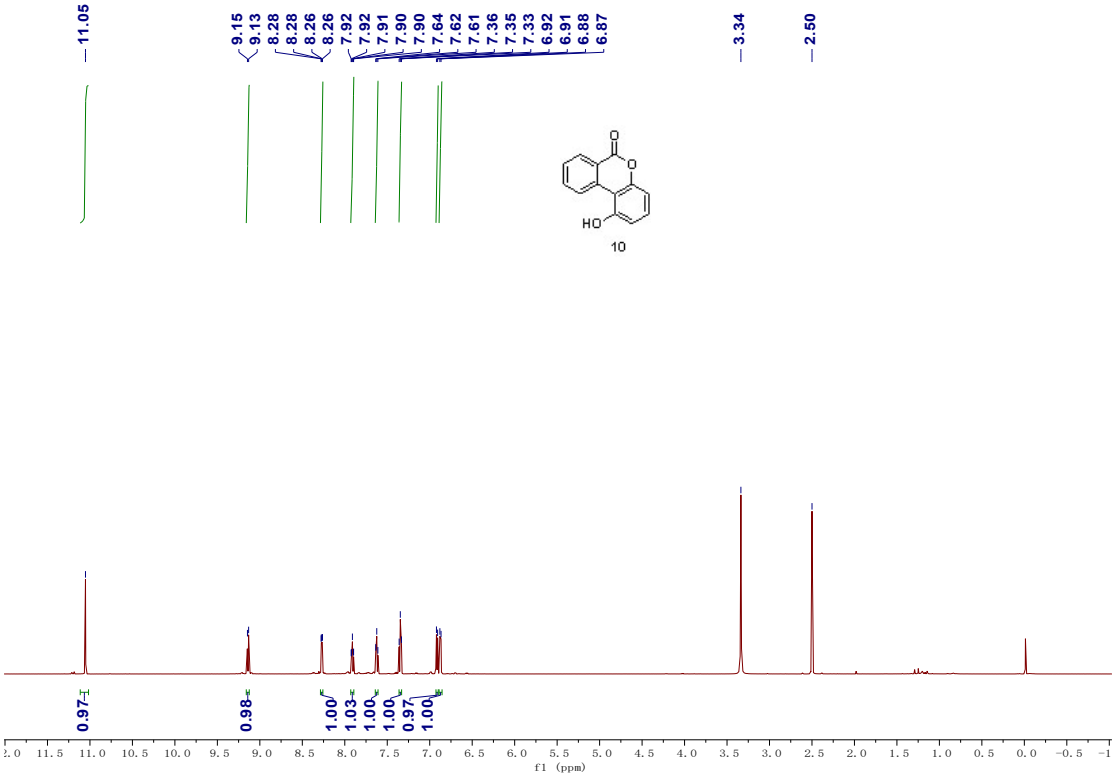
27.2
f1 (ppm)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7.62
7.61
7.36
7.35
7.33
6.92
6.91
6.88
6.87
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0.98
1.00
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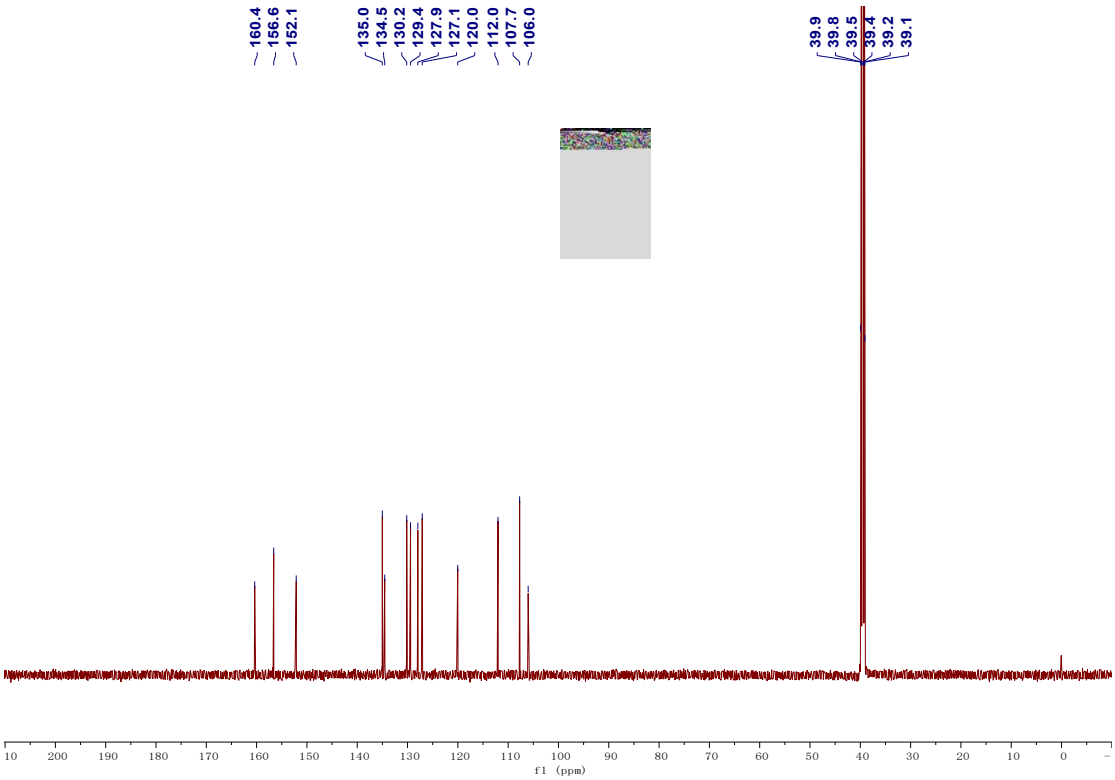
1.00
f1 (ppm)



6. References.

1. S. Mayakrishnan, M. Tamizmani and N. U. Maheswari, *Chem. Commun.*, 2020, **56**, 15462-15465.
2. S. Pradhan, K. Mishra and Y. R. Lee, *Chem. Eur. J.*, 2019, **25**, 10886-10894.
3. C. Li, C. Chen, Q. An, T. Yang, Z. Sang, Y. Yang, Y. Ju, A. Tong and Y. Luo, *Eur. J. Med. Chem.*, 2019, **162**, 543-554.
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