Supporting Information

Rh(III)-catalyzed oxidative C−H bond arylation with hydroquinones: sustainable synthesis of dibenzo[*b*,*d*]pyran-6-ones and benzo[*d*]naphtho[1,2-*b*]pyran-6-ones†

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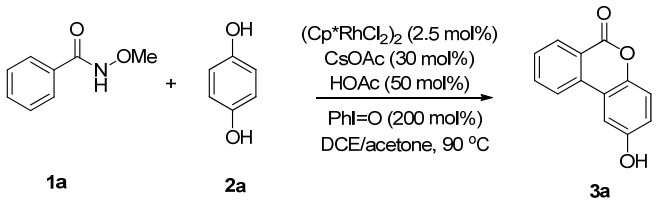
I. General Information

All Rhodium-catalyzed reactions were carried out without any particular precautions to extrude moisture or oxygen.

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300−400 mesh). Melting points were corrected. The ^{1}H NMR and ^{13}C NMR spectra were determined at 25 ºC on a 500 MHz and 125 MHz, respectively, and TMS as internal standard. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

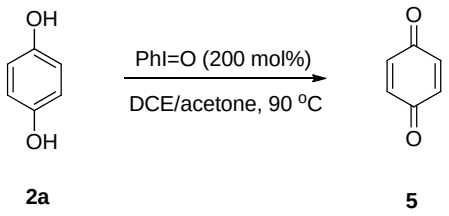
II. Typical Procedures of Compounds 3a-3q and 4a-4c



General procedure for the synthesis of 3a-3q and 4a-4c (**3a** as an example):

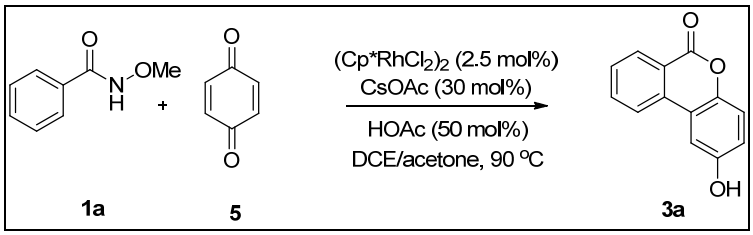
Without any particular precautions to extrude oxygen or moisture, to a stirred solution of **2a** (44.0 mg, 0.4 mmol) in DCE (1.0 mL)/acetone (1.0 mL) in a sealed tube, PhI=O (88.0 mg, 0.4 mmol), **1a** (30.2 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), CsOAc (11.5 mg, 0.06 mmol) and HOAc (6.0 uL, 0.1 mmol) were added successively. After heated at 90 °C for 5 h, the starting material **1a** was consumed as indicated by TLC. The reaction mixture was cooled to room temperature and diluted with water (15 mL), then extracted with EtOAc (10 mL×3), the organic phase was combined and washed with saturated Na_2CO_3 solution. After dried over Na_2SO_4, the organic phase was concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1, v/v) to afford the product **3a** (98% yield).

III. Mechanism experiments



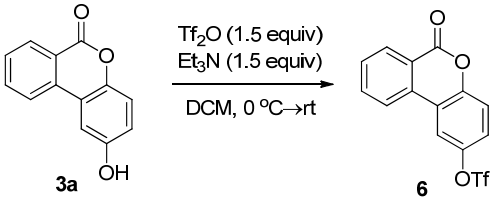
2a (44.0 mg, 0.4 mmol) was added into the mixture of DCE (1.0 mL)/acetone (1.0 mL) in a sealed tube, followed by PhI=O (88.0 mg, 0.4 mmol). After heated at 90 °C for 10 min, the reaction mixture was cooled to room temperature and was concentrated in vacuo. The ^{1}H NMR spectrum of the crude product shows that benzoquinone **5** was obtained in 61% yield (*p*-xylene as the

internal standard).

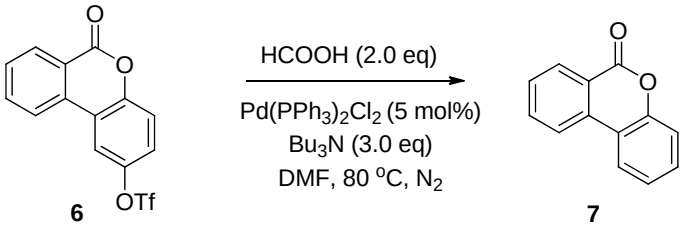


1a (30.2 mg, 0.2 mmol), **5** (43.2 mg, 0.4 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), CsOAc (11.5 mg, 0.06 mmol) and HOAc (6.0 uL, 0.1 mmol) were added into the mixture of DCE (1.0 mL)/acetone (1.0 mL) in a sealed tube. After heated at 90 °C for 3 h, the starting material **1a** was consumed as indicated by TLC. The reaction mixture was cooled to room temperature and diluted with water (15 mL), then extracted with EtOAc (10 mL×3), the organic phase was combined and washed with saturated Na_2CO_3 solution. After dried over Na_2SO_4, the organic phase was concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1, v/v) to afford the product **3a** (99% yield).

IV. Procedures for synthesis of 7 and 8

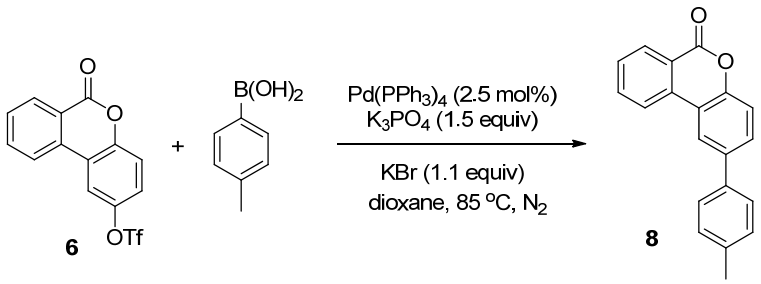


To an ice-bath cooled solution of **3a** (42.4 mg, 0.2 mmol) in DCM (1.0 mL) at, Et_3N (41.7 uL, 0.3 mmol) and $(CF_3SO_2)_2O$ (50.4 uL, 0.3 mmol) were added successively. The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was diluted with brine (10 mL) and extracted with DCM (2×10 mL). The combined organics were dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/ EtOAc = 10/1, v/v) to afford the product **6** in 85% yield.



An oven-dried 25 mL Schlenk tube was charged with $Pd(PPh_3)_2Cl_2$ (7.0 mg, 0.01 mmol), and was evacuated and refilled with N_2 three times. Then DMF (1.0 mL), Bu_3N (144 uL, 0.6 mmol) and HCOOH (15.2 uL, 0.4 mmol) were added successively. The reaction mixture was stirred at 80°C for 7 h. It was cooled to room temperature and diluted with brine (10 mL), then extracted with

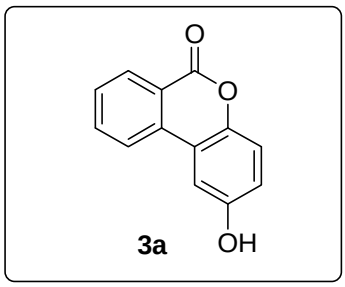
EtOAc (2 ×10 mL). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/Et_2O = 30/1, v/v) to afford the product **7** in 76% yield.



An oven-dried 25 mL Schlenk tube was charged with **6** (68.8 mg, 0.2 mmol), *p*-tolylboronic acid (29.9 mg, 0.22 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol), K_3PO_4 (63.6 mg, 0.3 mmol) and KBr (26.2 mg, 0.22 mmol) and was evacuated and refilled with N_2 three times, followed by adding dioxane (1.0 mL). The reaction mixture was stirred at 85°C for 5 h. The reaction mixture was cooled to room temperature and diluted with brine (10 mL), then extracted with EtOAc (2 ×10 mL). The combined organics were dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/Et_2O = 50/1, v/v) to afford the product **8** in 84% yield.

V. Analytical Data of Compounds 3a-3q and 4a-4c , 7 and 8

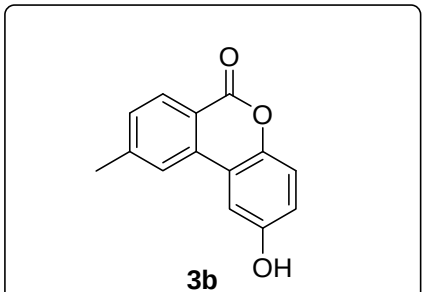
2-hydroxy-6H-benzo[c]chromen-6-one **(3a)**



3a

Yellowish solid, m.p. 161−162 ^{o}C. **^{1}H NMR** (500 MHz, DMSO): δ 6.99 (dd, *J* = 3.0, 8.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 3.0 Hz, 1H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.92 (t, *J* = 7.0 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 9.75 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 108.7, 118.6, 118.7, 118.9, 121.1, 123.0, 129.7, 130.3, 134.8, 135.7, 144.4, 154.7, 160.9. Calcd for ($C_{13}H_9O_3^+$ $[M+H]^+$) 213.0546. Found 213.0562.

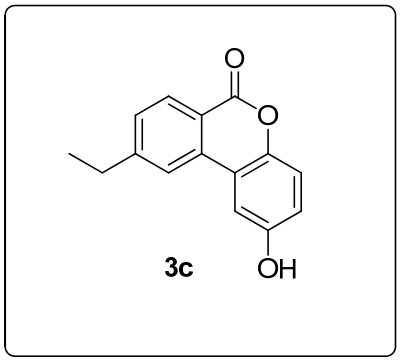
2-hydroxy-9-methyl-6H-benzo[c]chromen-6-one **(3b)**



3b

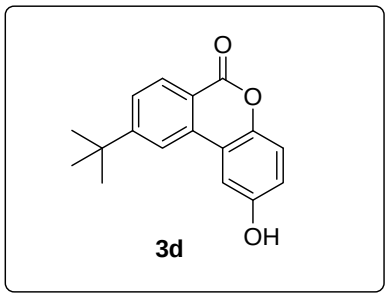
Yellowish solid, m.p. 224−225 ^{o}C. **^{1}H NMR** (500 MHz, DMSO): δ 2.48 (s, 3H), 6.97 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 2.5 Hz, 1H), 8.07 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 9.70 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 22.1, 108.7, 118.6, 118.7, 118.8, 123.0, 130.3, 130.8, 134.7, 144.6, 146.6, 154.7, 160.9. Calcd for ($C_{14}H_{11}O_3^+$ $[M+H]^+$) 227.0703. Found 227.0698.

9-ethyl-2-hydroxy-6H-benzo[c]chromen-6-one **(3c)**



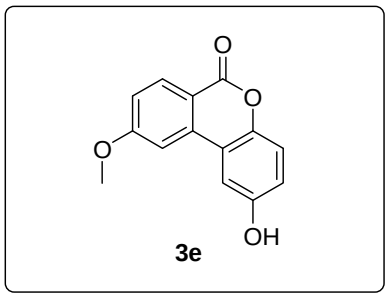
Yellowish solid, m.p. 135−136 °C. **^{1}H NMR** (500 MHz, DMSO): δ 1.28 (t, *J* = 7.5 Hz, 3H), 2.82 (q, *J* = 7.5 Hz, 2H), 6.99 (dd, *J* = 2.5, 8.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 2.5 Hz, 1H), 8.09 (s, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 9.67 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 15.5, 29.0, 108.7, 118.5, 118.7, 118.8, 121.8, 129.6, 130.4, 134.8, 144.5, 152.4, 154.6, 160.8. Calcd for ($C_{15}H_{13}O_3^+$ $[M+H]^+$) 241.0859. Found 241.0875.

9-tert-butyl-2-hydroxy-6H-benzo[c]chromen-6-one **(3d)**



Yellowish solid, m.p. 248−249 °C. **^{1}H NMR** (500 MHz, DMSO): δ 1.41 (s, 9H), 6.99 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.73 (s,1H), 7.74 (d, J = 9.5 Hz, 1H), 8.18 (d, J = 9.5 Hz, 1H), 8.19 (s, 1H), 9.67 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 31.2, 36.0, 108.8, 118.6, 118.7, 118.9, 119.1, 127.3, 130.2, 134.5, 144.6, 154.6, 159.0, 160.8. **HRMS** (ESI-TOF) Calcd for ($C_{17}H_{17}O_3^+$ $[M+H]^+$) 269.1172. Found 269.1177.

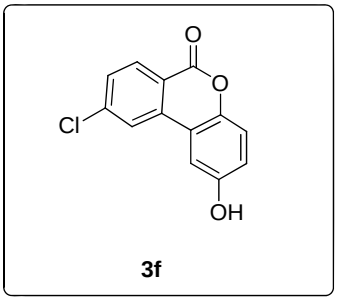
2-hydroxy-9-methoxy-6H-benzo[c]chromen-6-one **(3e)**



Brown solid, m.p. 187−188 °C. **^{1}H NMR** (500 MHz, DMSO): δ 4.00 (s, 3H), 7.01 (dd, *J* = 2.0, 7.0 Hz, 1H), 7.22−7.26 (m, 2H), 7.69 (d, *J* = 2.0 Hz, 2H), 8.17 (d, *J* = 8.5 Hz, 1H), 9.68 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 56.5, 105.9, 109.2, 114.0, 117.6, 118.5, 118.7, 119.1, 132.6, 137.2, 144.8, 154.6, 160.6, 165.1. **HRMS** (ESI-TOF) Calcd for ($C_{14}H_{11}O_4^+$ $[M+H]^+$) 243.0652.

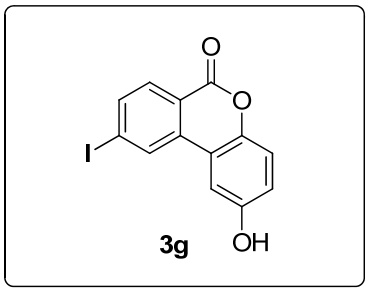
Found 243.0660.

9-chloro-2-hydroxy-6H-benzo[c]chromen-6-one **(3f)**



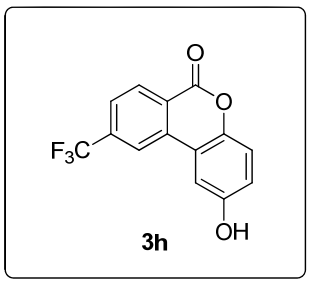
Yellowish solid, m.p. 192−193 °C. **^{1}H NMR** (500 MHz, DMSO): δ 7.01 (dd, *J* = 2.5, 8.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 2.5 Hz, 1H), 7.64 (dd, *J* = 2.0, 8.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.30 (d, *J* = 2.0 Hz, 1H), 9.76 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 109.2, 117.8, 118.6, 119.6, 119.8, 122.9, 129.7, 132.3, 136.6, 141.1, 144.7, 154.8, 160.2. Calcd for ($C_{13}H_8ClO_3^+$ $[M+H]^+$) 247.0156. Found 247.0147.

2-hydroxy-9-iodo-6H-benzo[c]chromen-6-one **(3g)**



Yellowish solid, m.p. 190−191 °C. **^{1}H NMR** (500 MHz, DMSO): δ 7.02 (dd, *J* = 2.5, 8.5 Hz, 1H), 7.26 (d, *J* = 8.5 Hz, 1H), 7.65 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 8.67 (s, 1H), 9.72 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 105.2, 109.1, 117.5, 118.6, 119.4, 120.4, 131.6, 131.7, 136.1, 138.5, 144.7, 154.8, 160.7. Calcd for ($C_{13}H_8IO_3^+$ $[M+H]^+$) 338.9513. Found 338.9520.

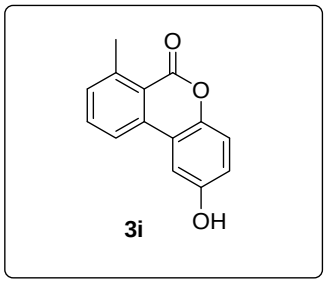
2-hydroxy-9-(trifluoromethyl)-6H-benzo[c]chromen-6-one **(3h)**



Yellowish solid, m.p. 138−139 °C. **^{1}H NMR** (500 MHz, DMSO): δ 7.04 (dd, *J* = 3.0, 9.0 Hz, 1H), 7.26 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 3.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.57 (s, 1H), 9.75 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 109.3, 117.9, 118.7, 119.8, 120.4

(d, *J* = 3.9 Hz), 124.0 (q, *J* = 271.9 Hz), 124.2, 125.6 (d, *J* = 3.4 Hz), 131.6, 135.0 (q, *J* = 32.1 Hz), 135.6, 144.6, 154.9, 160.0. **HRMS** (ESI-TOF) Calcd for ($C_{14}H_8FO_3^+$ $[M+H]^+$) 281.0420. Found 281.0419.

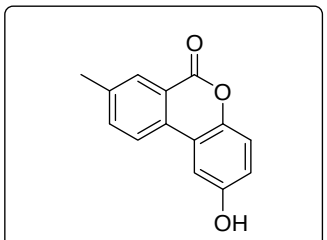
2-hydroxy-7-methyl-6H-benzo[c]chromen-6-one **(3i)**



3i

Yellowish solid, m.p. 159−160 °C. **^{1}H NMR** (500 MHz, DMSO): δ 2.76 (s, 3H), 6.97 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 9.67 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 23.8, 108.8, 118.1, 118.8, 118.9, 119.4, 121.0, 132.8, 134.9, 136.1, 143.6, 144.4, 154.5, 160.2. Calcd for ($C_{14}H_{11}O_3^+$ $[M+H]^+$) 227.0703. Found 227.0708.

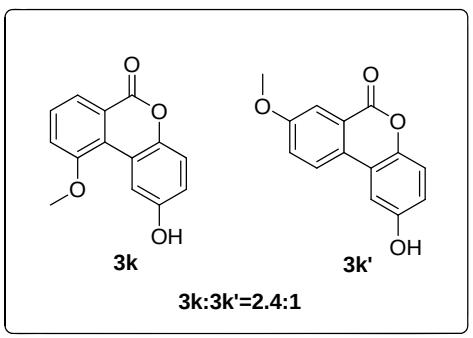
2-hydroxy-8-methyl-6H-benzo[c]chromen-6-one **(3j)**



3j

Yellow solid, m.p. 162−163 °C. **^{1}H NMR** (500 MHz, DMSO): δ 2.47 (s, 3H), 6.97 (d, *J* = 6.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.57 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 8.06 (s, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 9.69 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 21.2, 108.4, 118.4, 118.5, 118.8, 120.9, 123.0, 129.9, 132.3, 136.8, 139.6, 144.1, 154.7, 160.9. Calcd for ($C_{14}H_{11}O_3^+$ $[M+H]^+$) 227.0703. Found 227.0702.

2-hydroxy-10-methoxy-6H-benzo[c]chromen-6-one **(3k);**
2-hydroxy-8-methoxy-6H-benzo[c]chromen-6-one **(3k')**

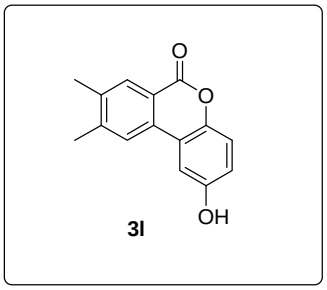


3k **3k'**

3k:3k'=2.4:1

Yellowish solid, **^{1}H NMR** (500 MHz, DMSO): δ 3.91 (s, 3H), 4.07 (s, 1.27H), 6.92-6.96 (m, 1.33H), 7.24 (d, *J* = 9.0 Hz, 1.27H), 7.51−7.53 (m, 1.9H), 7.63−7.66 (m, 1.80H), 7.92 (d, *J* = 7.5 Hz, 0.36H), 8.21 (dd, *J* = 2.5, 8.5 Hz, 0.96H), 8.40 (s, 0.38H), 9.67 (s, 0.92H). **^{13}C NMR** (125 MHz, DMSO): δ 56.1, 56.8, 108.1, 111.7, 114.1, 117.6, 117.7, 117.8, 118.0, 118.4, 118.8, 122.2, 122.3, 124.0, 124.9, 128.0, 130.2, 143.6, 154.1, 154.8, 160.1, 160.7. Calcd for ($C_{14}H_{11}O_4^+$ $[M+H]^+$) 243.0652. Found 243.0653.

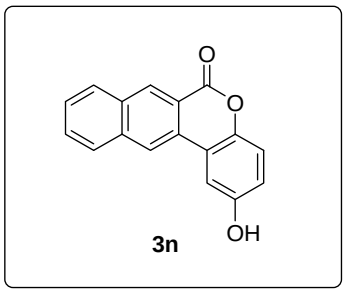
2-hydroxy-8,9-dimethyl-6H-benzo[c]chromen-6-one **(3l)**



3l

Yellowish solid, m.p. 177−178 ^{o}C. **^{1}H NMR** (500 MHz, DMSO): δ 2.36 (s, 3H), 2.43 (s, 3H), 6.95 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 2.5 Hz, 1H), 7.97 (s, 1H), 8.05 (s, 1H), 9.66 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 19.7, 20.5, 108.5, 118.3, 118.4, 118.7, 118.8, 123.5, 130.3, 132.6, 138.9, 144.3, 145.8, 154.6, 160.9. Calcd for ($C_{15}H_{13}O_3^+$ $[M+H]^+$) 241.0859. Found 241.0876.

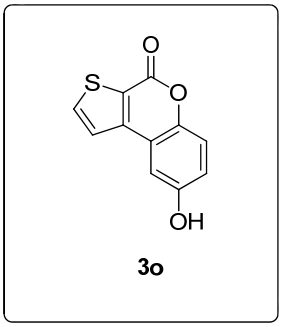
2-hydroxy-6H-naphtho[2,3-c]chromen-6-one **(3n)**



3n

Yellowish solid, m.p. 165−166 ^{o}C. **^{1}H NMR** (500 MHz, DMSO): δ 6.99 (dd, *J* = 2.5, 8.5Hz, 1H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.76−7.79 (m, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 8.86 (s, 1H), 8.99 (s, 1H), 9.74 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 108.9, 118.5, 118.8, 119.1, 119.4, 122.0, 127.8, 128.7, 129.8, 129.9, 130.1, 132.4, 132.5, 136.3, 144.0, 154.8, 161.1. Calcd for ($C_{17}H_{11}O_3^+$ $[M+H]^+$) 263.0703. Found 263.0712.

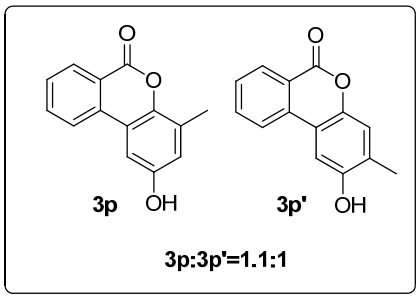
8-hydroxy-4H-thieno[2,3-c]chromen-4-one **(3o)**



3o

Light brown solid, m.p. 169−170 °C. **^{1}H NMR** (500 MHz, DMSO): δ 7.01 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.97 (d, *J* = 5.0 Hz, 1H), 8.37 (d, *J* = 5.0 Hz, 1H), 9.80 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 109.6, 118.1, 118.4, 118.7, 124.0, 124.1, 138.9, 145.4, 145.9, 154.7, 157.1. Calcd for ($C_{11}H_7O_3S^+$ $[M+H]^+$) 219.0110. Found 219.0115.

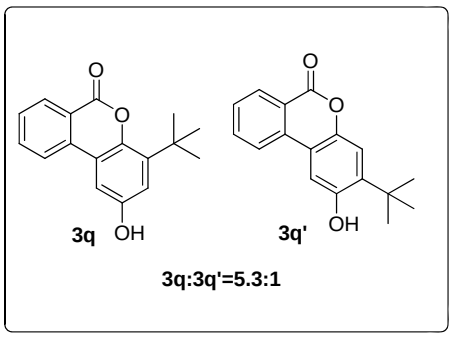
2-hydroxy-4-methyl-6H-benzo[c]chromen-6-one **(3p);**
2-hydroxy-3-methyl-6H-benzo[c]chromen-6-one **(3p')**



3p:3p'=1.1:1

Yellowish solid, **^{1}H NMR** (500 MHz, DMSO): δ 2.22 (s, 3H), 2.33 (s, 2.67H), 6.88 (d, *J* = 2.5 Hz, 0.83H), 7.17 (s, 0.88H), 7.43 (d, *J* = 2.5 Hz, 0.89H), 7.51 (s, 1.01H), 7.62−7.67 (m, 1.93H), 7.90-7.94 (m, 1.85H), 8.09 (d, *J* = 8.5 Hz, 1.01H), 8.23 (t, *J* = 7.5 Hz, 2.67H), 9.60 (s, 0.81H), 9.67 (s, 0.92H). **^{13}C NMR** (125 MHz, DMSO): δ 16.0, 16.6, 106.3, 107.4, 115.9, 118.4, 119.2, 120.1, 120.7, 120.9, 122.3, 123.1, 127.5, 129.1, 129.2, 129.5, 130.2, 130.3, 134.9, 135.0, 135.7, 135.8, 142.9, 144.3, 152.9, 154.1, 160.8, 161.0. Calcd for ($C_{14}H_{11}O_3^+$ $[M+H]^+$) 227.0703. Found 227.0712.

4-(tert-butyl)-2-hydroxy-6H-benzo[c]chromen-6-one **(3q);**
3-(tert-butyl)-2-hydroxy-6H-benzo[c]chromen-6-one **(3q')**

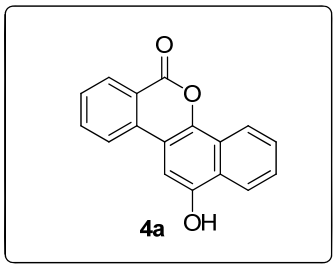


3q:3q'=5.3:1

Yellowish solid, m.p. 129−130 °C. **^{1}H NMR** (500 MHz, DMSO): δ 1.39 (s, 1.70H), 1.45 (s, 9H), 7.00 (d, *J* = 2.5 Hz, 0.98H), 7.15 (s, 0.17H), 7.50 (d, *J* = 2.5 Hz, 0.98H), 7.52 (s, 0.19) 7.66 (t, *J* =

8.0 Hz, 1.22H) 7.92 (t, *J* = 8.0 Hz, 1.13H), 8.04 (d, *J* = 8.0 Hz, 0.10H), 8.25 (dd, *J* = 8.0, 14.0 Hz, 2.09H), 9.63 (s, 0.86H). **^{13}C NMR** (125 MHz, DMSO): δ 30.1, 35.1, 106.5, 116.9, 119.0, 120.5, 123.2, 129.5, 129.9, 135.3, 135.7, 139.2, 143.2, 154.0, 160.3. Calcd for ($C_{17}H_{17}O_3^+$ $[M+H]^+$) 269.1172. Found 269.1170.

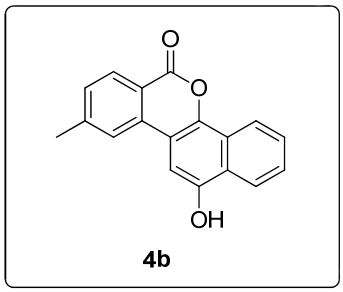
12-hydroxy-6H-dibenzo[c,h]chromen-6-one **(4a)**



4a

Brown solid, m.p. 193−194 °C. **^{1}H NMR** (500 MHz, DMSO): δ 7.51 (s, 1H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 2H), 8.00 (t, *J* = 7.5 Hz, 1H), 8.20 (t, *J* = 9.0 Hz, 2H), 8.32 (d, *J* = 8.0 Hz, 2H), 10.48 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 100.4, 113.5, 121.2, 121.7, 122.9, 124.5, 126.4, 127.4, 128.1, 129.5, 130.4, 135.2, 136.0, 140.3, 150.5, 160.8. **HRMS** (ESI-TOF) Calcd for ($C_{17}H_{11}O_3^+$ $[M+H]^+$) 263.0703. Found 263.0694.

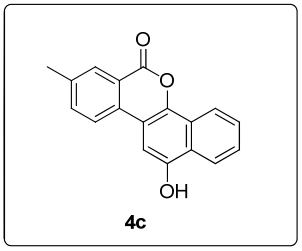
12-hydroxy-9-methyl-6H-dibenzo[c,h]chromen-6-one **(4b)**



4b

Brown solid, m.p. 248−249 °C. **^{1}H NMR** (500 MHz, DMSO): δ 2.54 (s, 3H), 7.48 (s, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.94 (s, 1H), 8.17-8.21 (m, 2H), 8.30 (d, *J* = 8.0 Hz, 1H), 10.41 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 22.2, 100.5, 113.5, 118.8, 121.6, 122.8, 122.9, 124.5, 126.4, 127.3, 128.0, 130.4, 130.6, 135.1, 140.4, 146.6, 150.5,160.7. Calcd for ($C_{18}H_{13}O_3^+$ $[M+H]^+$) 277.0859. Found 277.0853.

12-hydroxy-8-methyl-6H-dibenzo[c,h]chromen-6-one **(4c)**

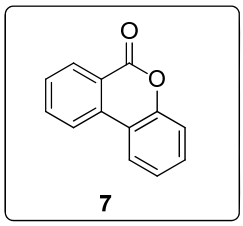


4c

Brown solid, m.p. 236−237 °C. **^{1}H NMR** (500 MHz, DMSO): δ 2.51 (s, 3H), 7.50 (s, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 1H), 8.14

(s, 1H)，8.22 (d, *J* = 8.5 Hz, 1H)，8.32 (d, *J* = 8.0 Hz, 1H)，10.47 (s, 1H). **^{13}C NMR** (125 MHz, DMSO): δ 21.3, 100.4, 113.7, 121.1, 121.6, 123.0, 124.5, 126.2, 127.2, 128.1, 130.1, 132.7, 137.1, 139.5, 139.9, 150.5, 160.9. Calcd for ($C_{18}H_{13}O_3^+$ $[M+H]^+$) 277.0859. Found 277.0868.

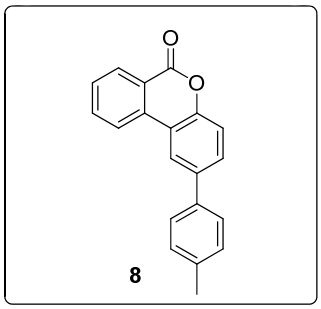
6H-benzo[c]chromen-6-one (7)



7

White solid, m.p. 91−92°C. **^{1}H NMR** (500 MHz, $CDCl_3$): **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.34−7.40 (m, 2H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.84 (t, *J* = 7.0 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 117.8, 118.0, 121.3, 121.7, 122.8, 124.5, 128.9, 130.4, 130.6, 134.7, 134.8, 151.3, 161.2. Calcd for ($C_{13}H_9O_2^+$ $[M+H]^+$) 197.0597. Found 197.0606.

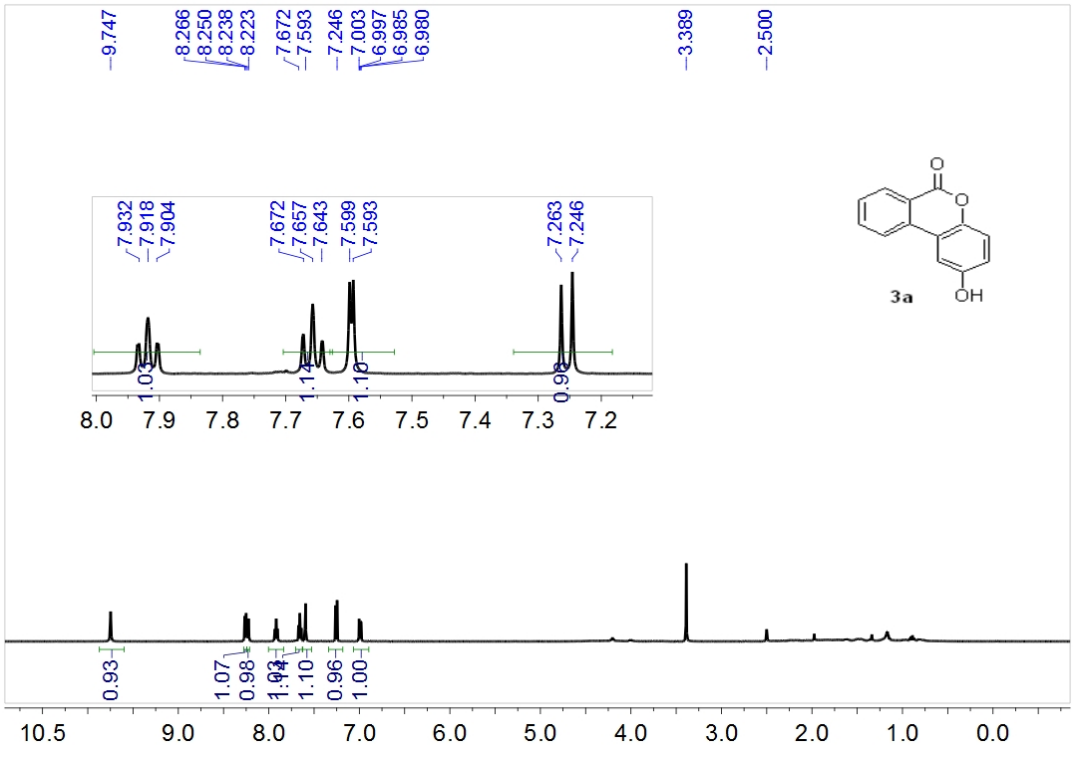
2-(p-tolyl)-6H-benzo[c]chromen-6-one (8)

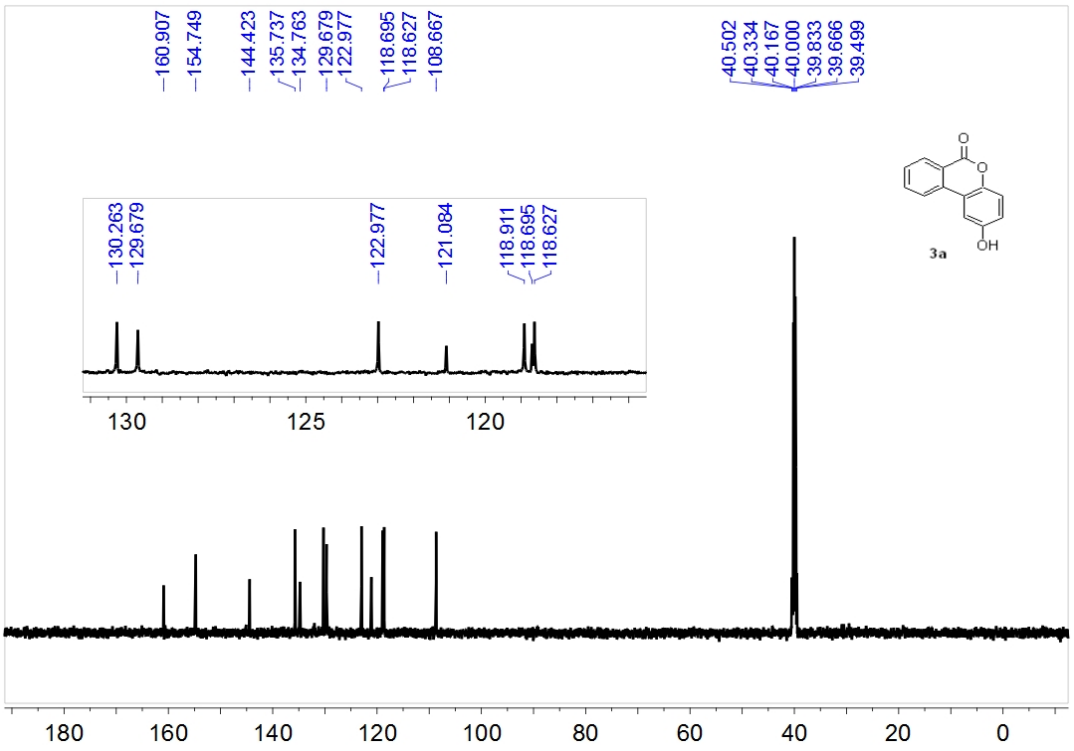


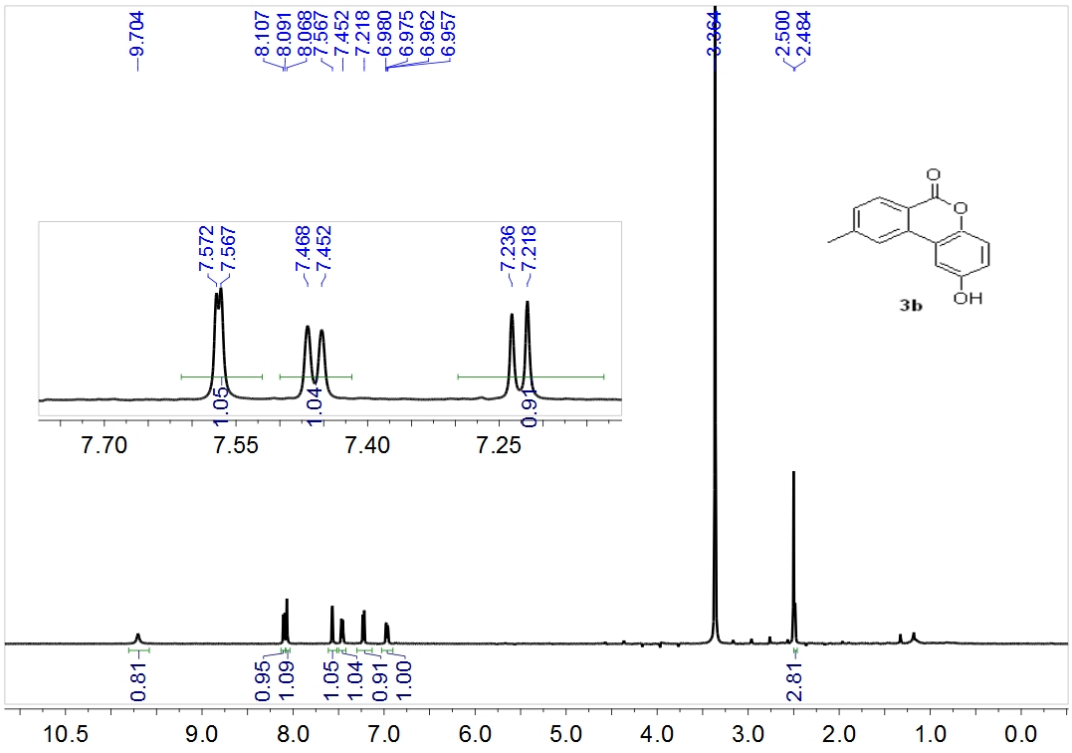
8

White solid, m.p. 137−138°C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.68 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.23 (s, 1H), 8.44 (d, *J* = 8.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.1, 118.0, 118.1, 121.0, 121.4, 121.7, 127.0, 129.0, 129.3, 129.7, 130.7, 134.8, 134.9, 137.2, 137.6, 137.9, 150.5, 161.2. Calcd for ($C_{20}H_{15}O_2^+$ $[M+H]^+$) 287.1067. Found 287.1070

VI. Copies of ^{1}H NMR and ^{13}C NMR spectra



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2.484
7.572
7.567
7.468
7.452
7.236
7.218
1.05
1.04
0.91
7.70
7.55
7.40
7.25
3b
OH
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0.95
1.09
1.05
1.04
0.91
1.00
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7.0
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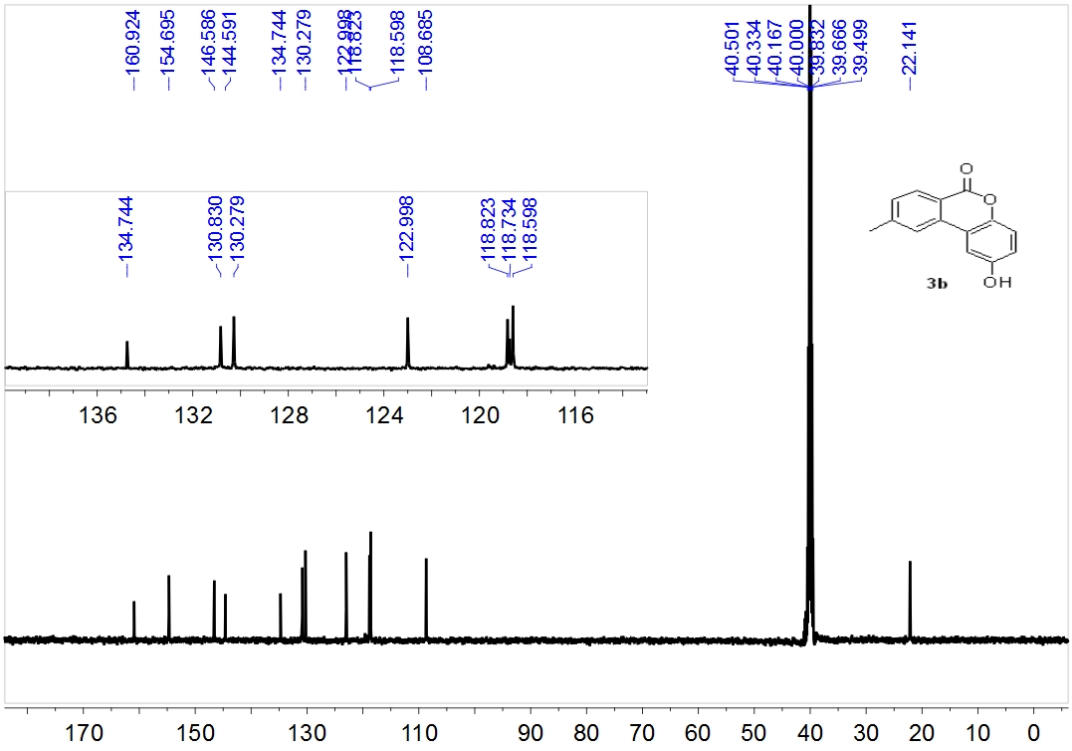
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130.830
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118.823
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118.598
136
132
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120
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3b
OH
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70
60
50
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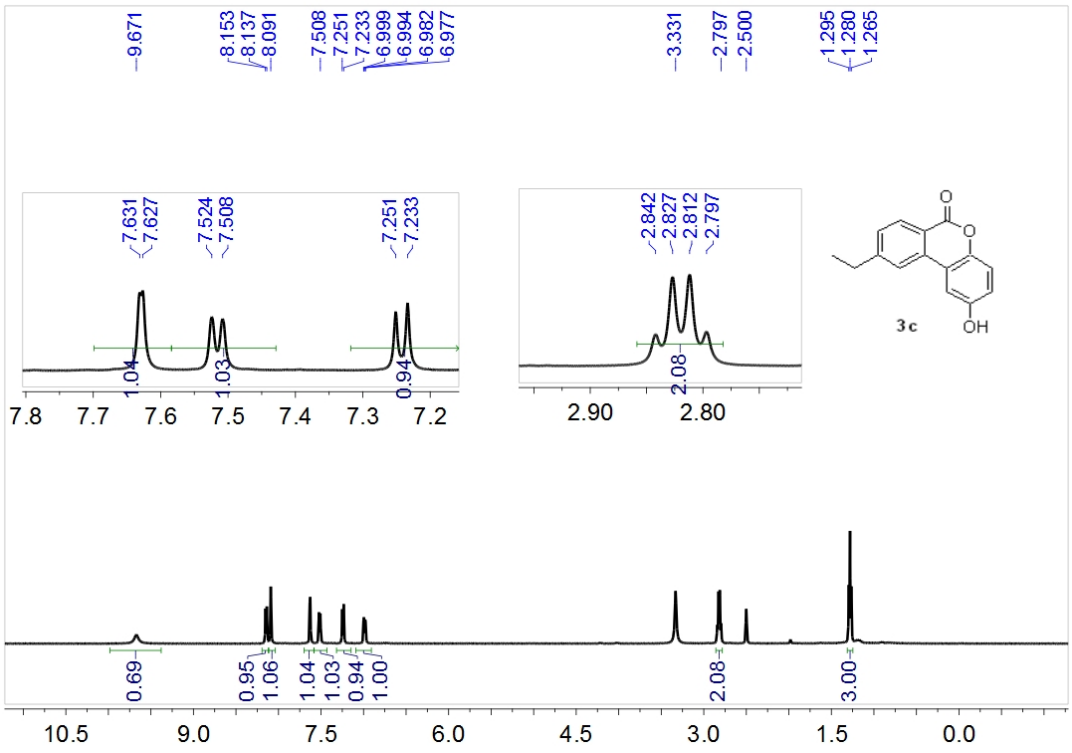
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2.500
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1.280
1.265
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7.627
7.524
7.508
7.251
7.233
1.04
1.03
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7.6
7.5
7.4
7.3
7.2
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6.0
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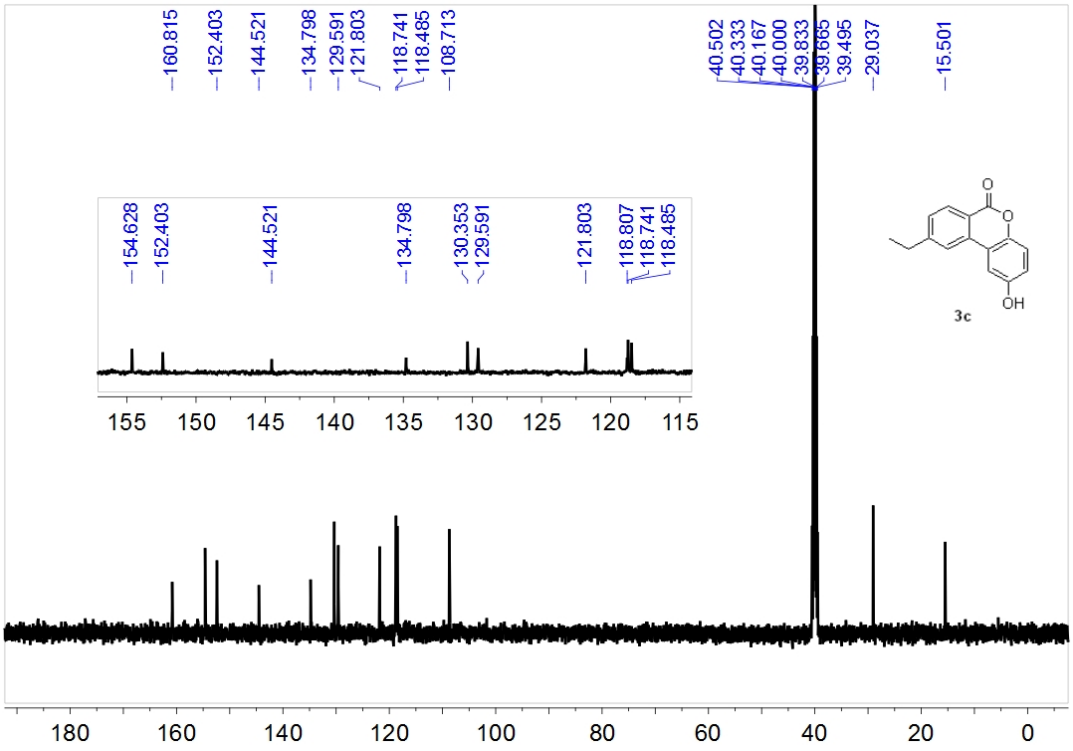
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40.000
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15.501
154.628
152.403
144.521
134.798
130.353
129.591
121.803
118.807
118.741
118.485
155
150
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140
135
130
125
120
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3c
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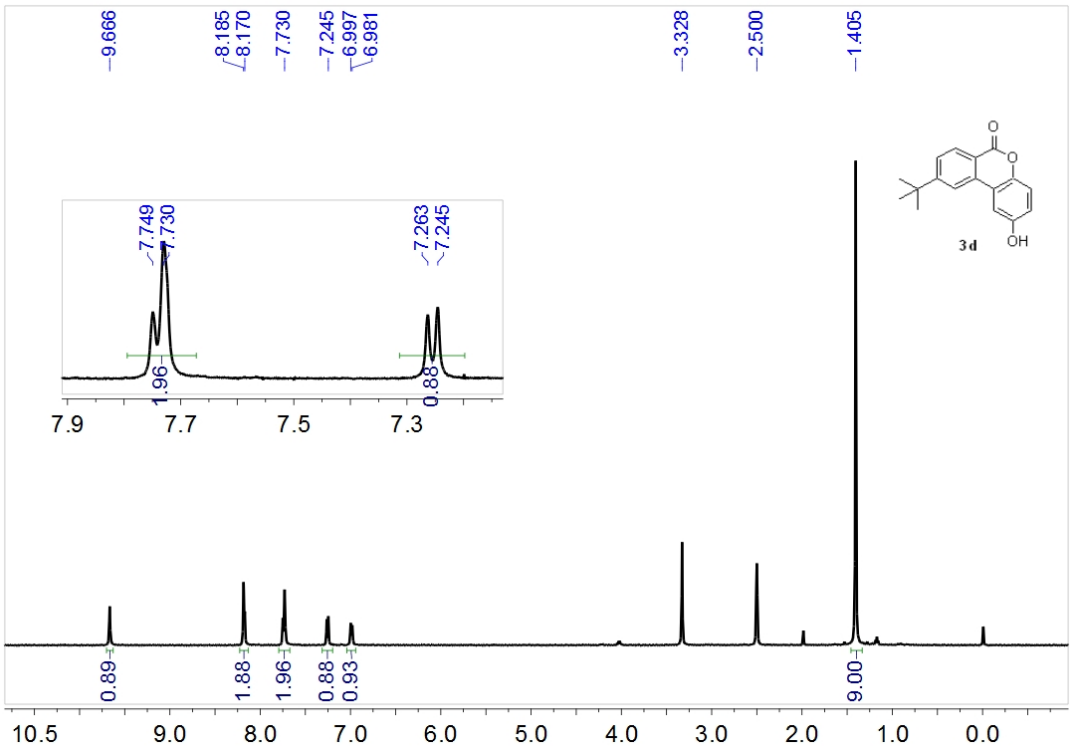
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7.5
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5.0
4.0
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1.0
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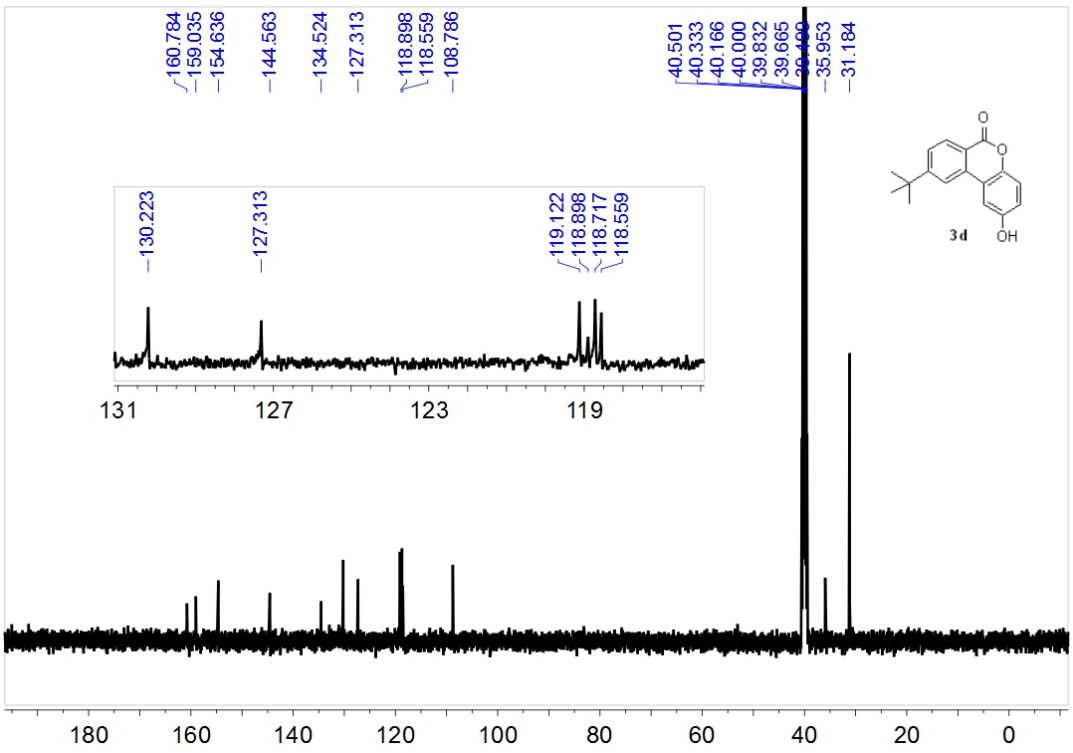
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130.223
127.313
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123
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3d
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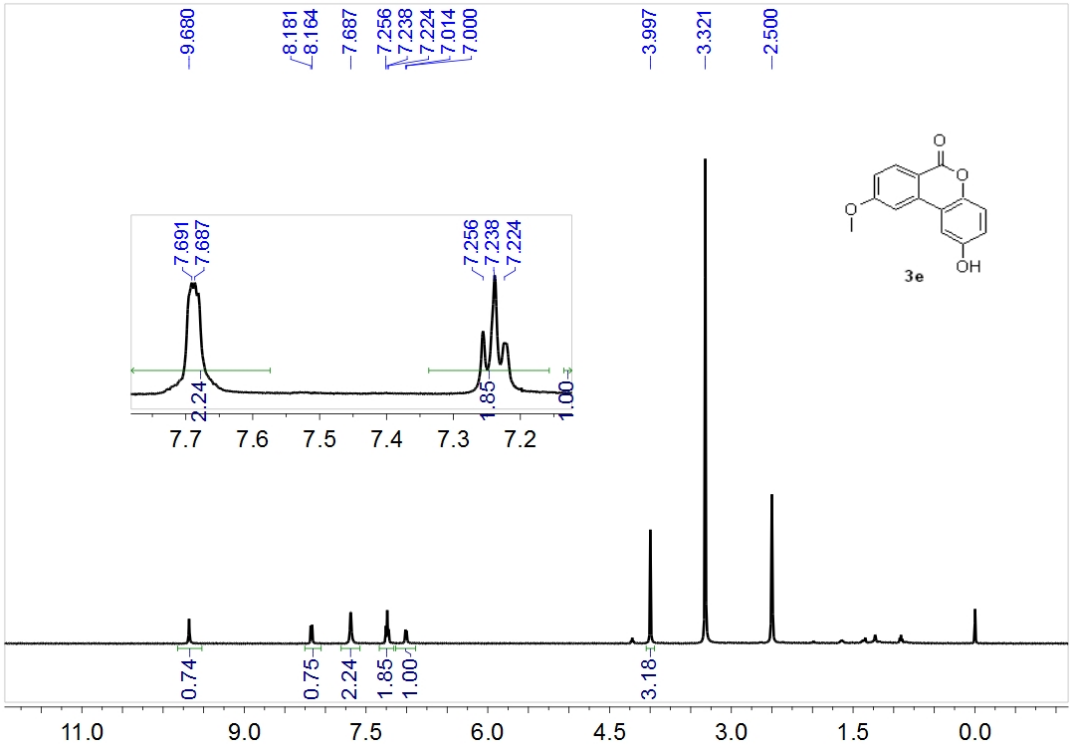
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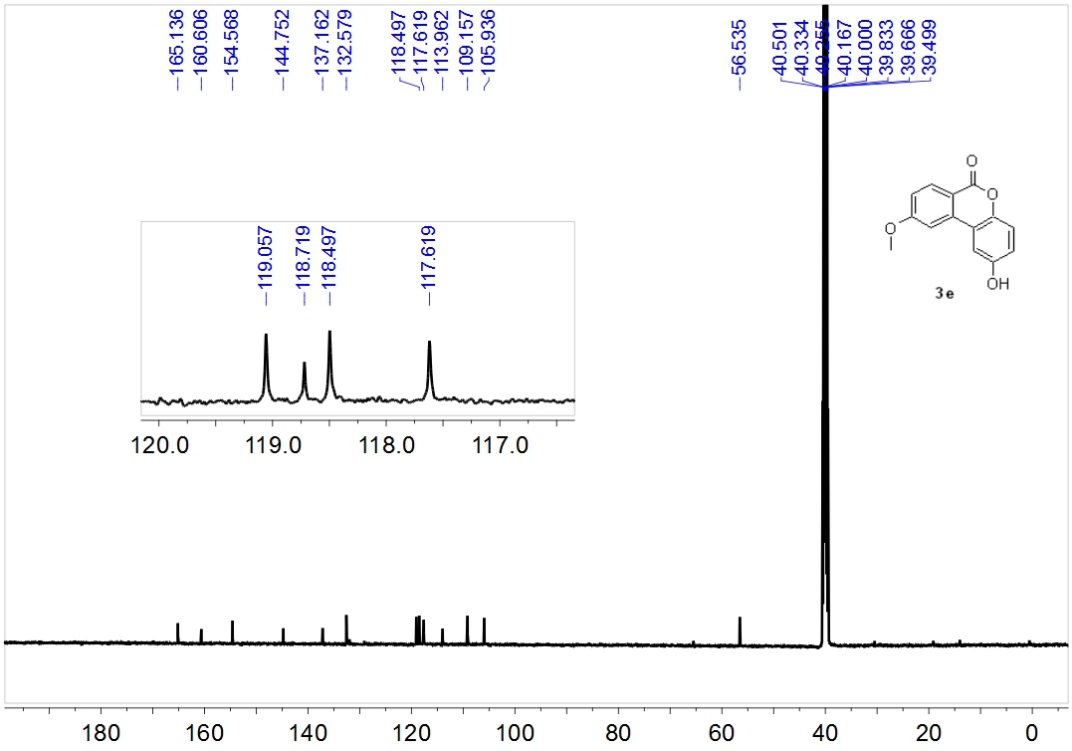
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40.167
40.000
39.833
39.666
39.499
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118.719
118.497
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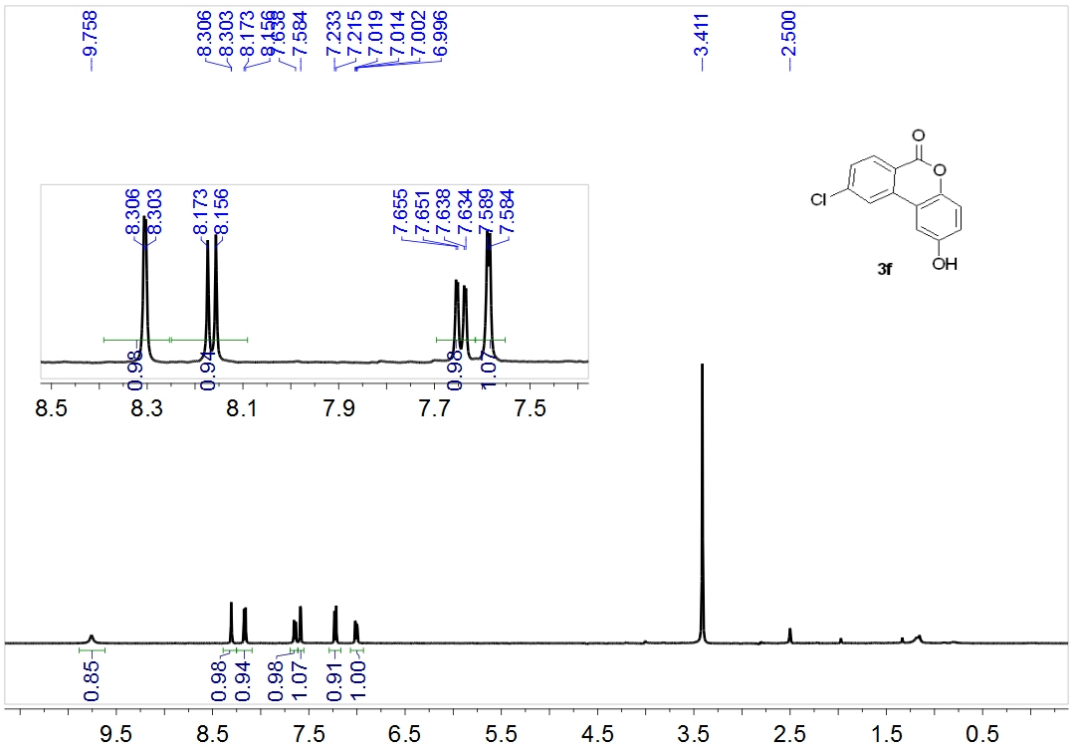
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7.655
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8.5
8.3
8.1
7.9
7.7
7.5
Cl
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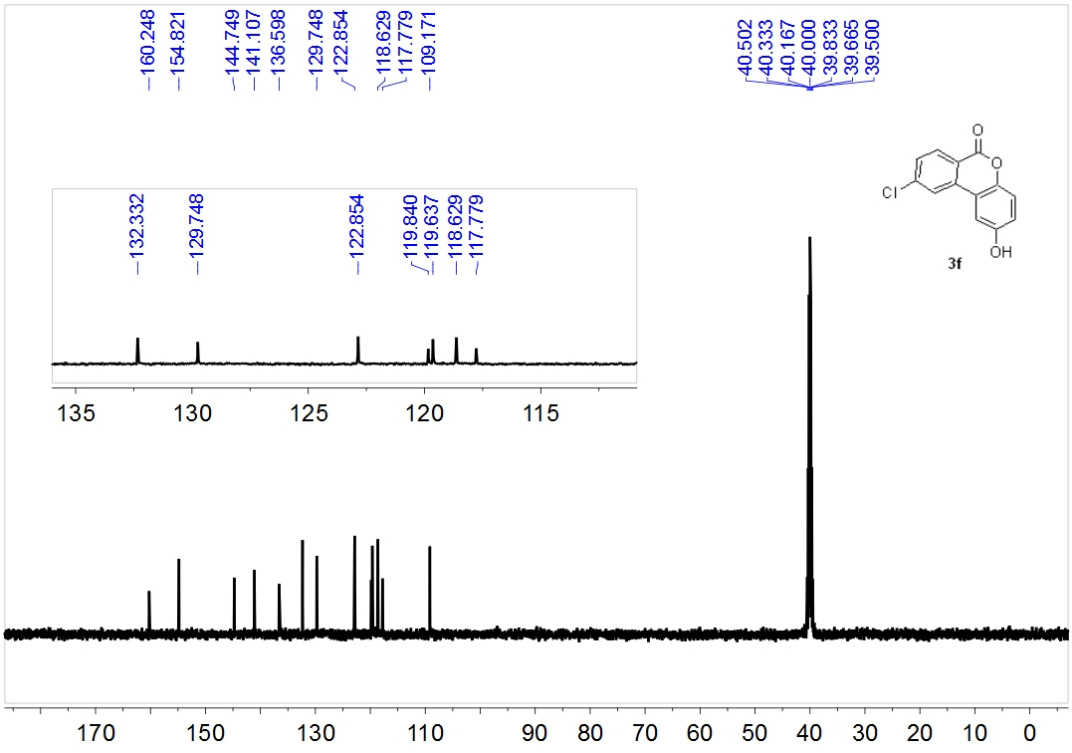
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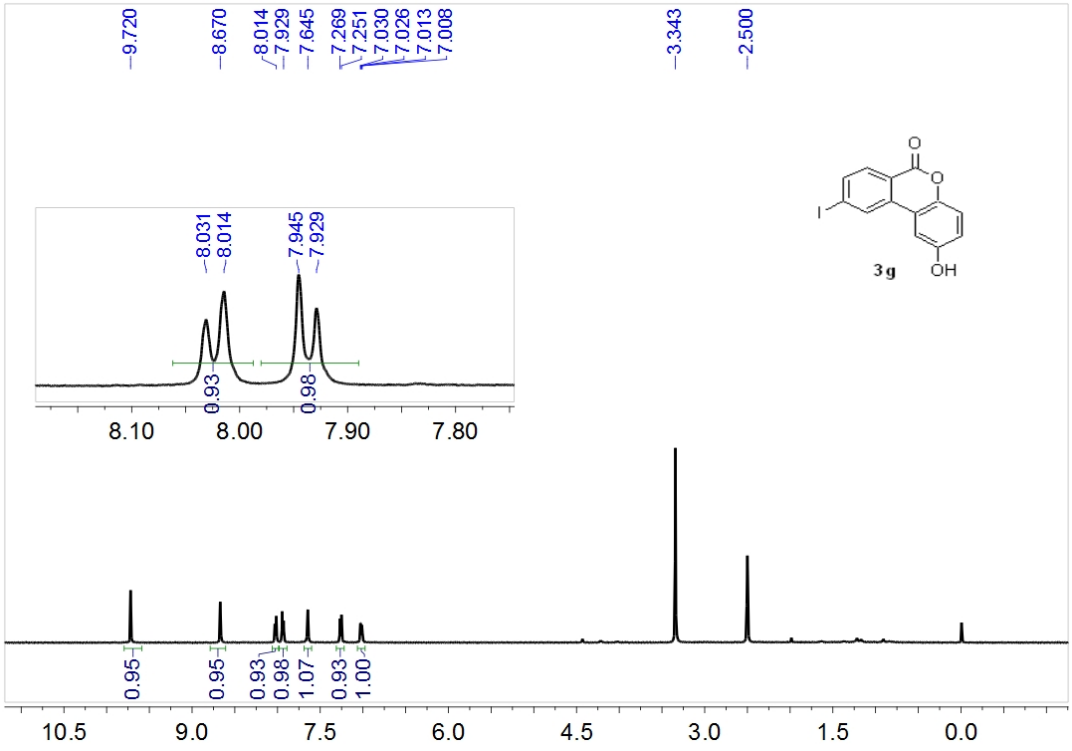
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6.0
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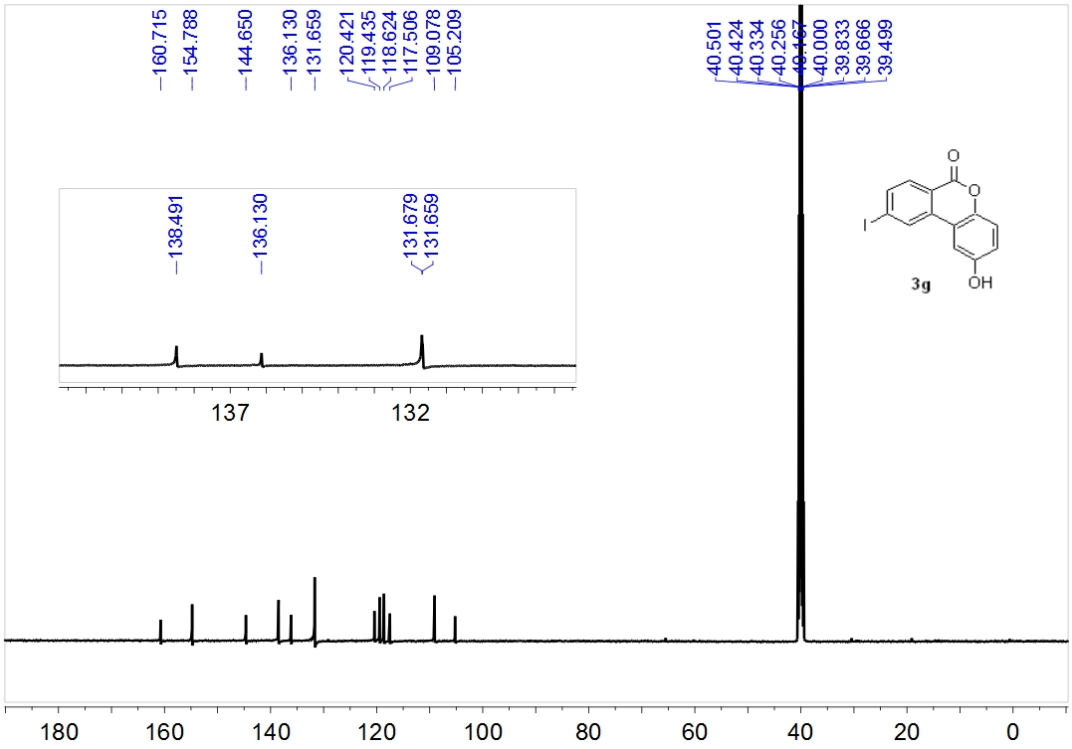
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140
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60
40
20
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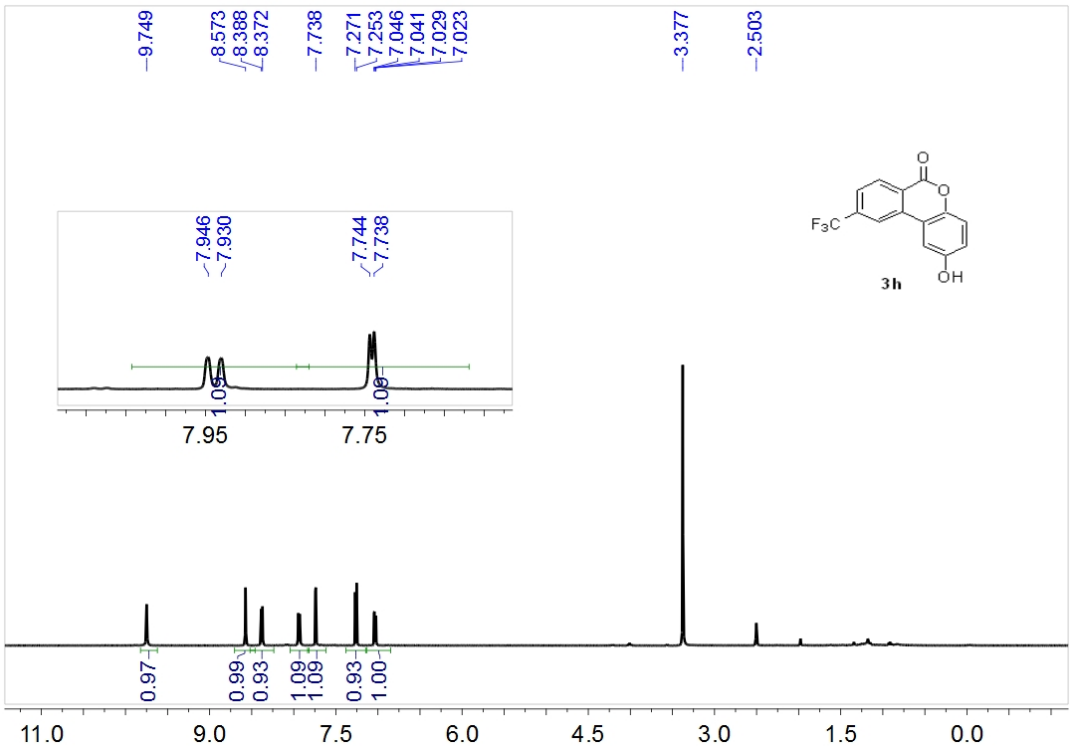
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7.253
7.046
7.041
7.029
7.023
3.377
2.503
7.946
7.930
7.744
7.738
1.09
1.09
7.95
7.75
F3C
O
O
OH
3h
0.97
0.99
0.93
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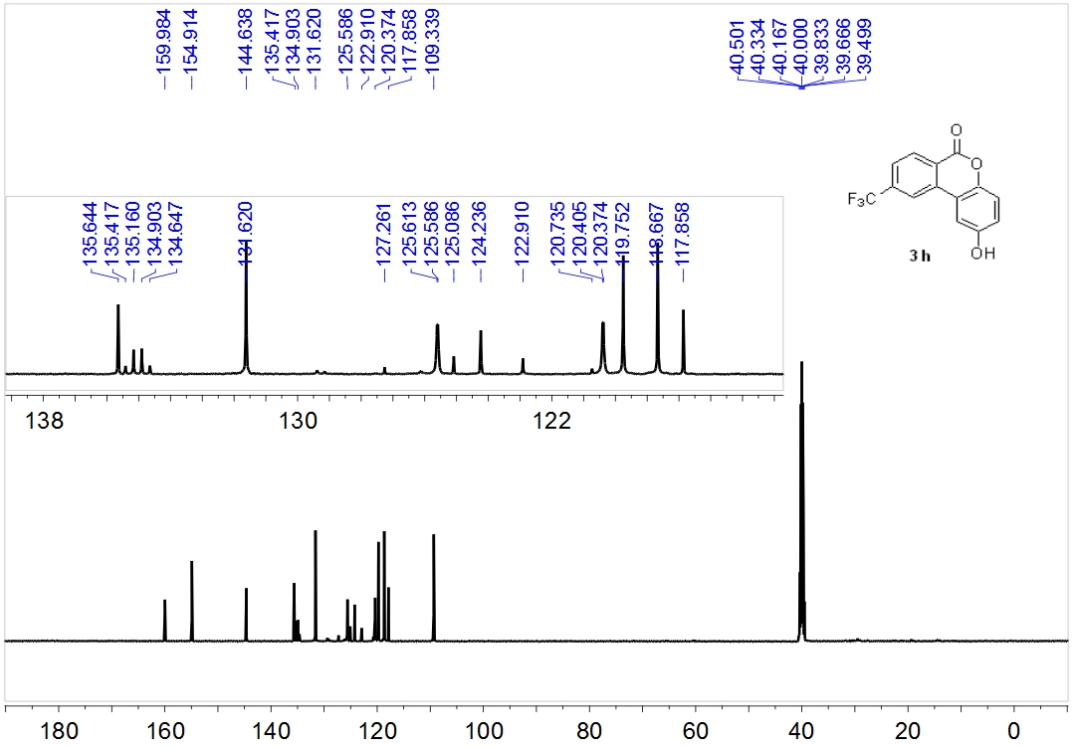
0.0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120.735
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120.374
119.752
118.667
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F3C
O
O
OH
3h
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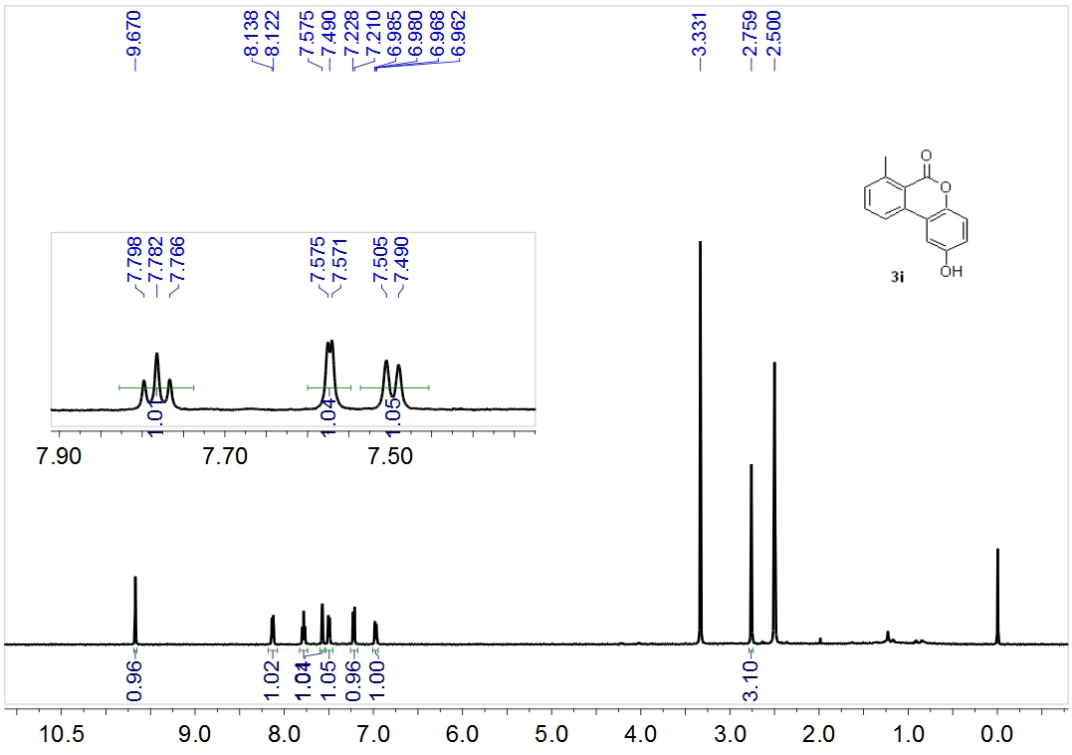
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7.798
7.782
7.766
7.575
7.571
7.505
7.490
1.01
1.04
1.05
7.90
7.70
7.50
3i
OH
0.96
1.02
1.04
1.05
0.96
1.00
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8.0
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6.0
5.0
4.0
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2.0
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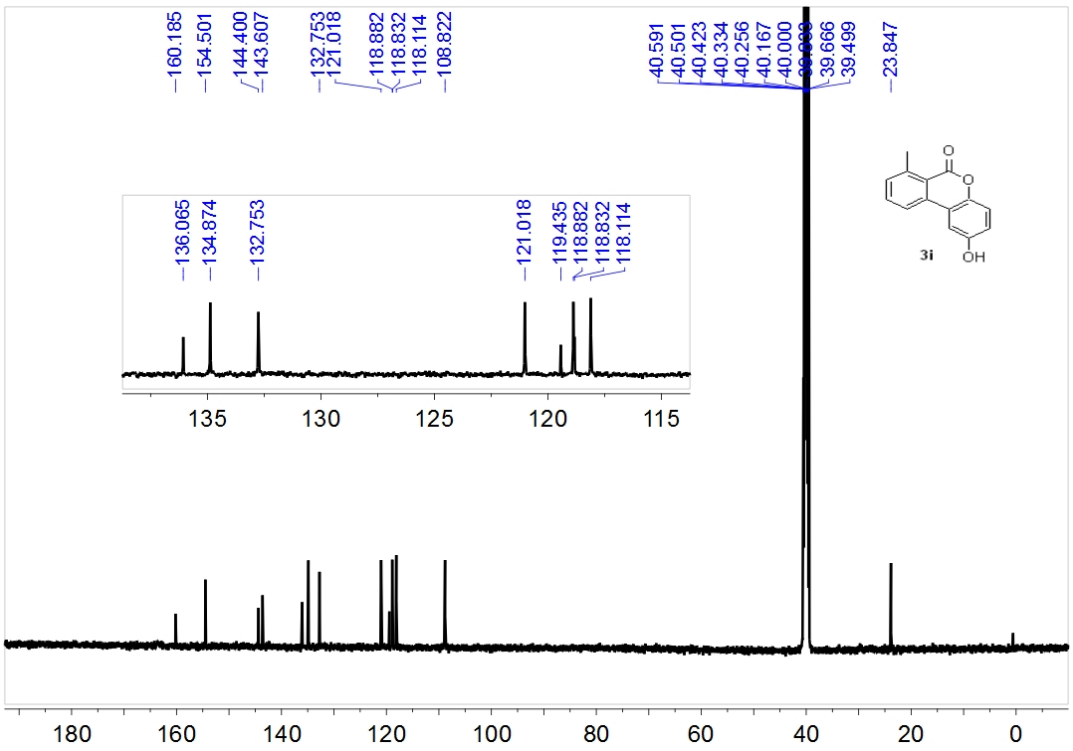
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118.832
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40.423
40.334
40.256
40.167
40.000
39.833
39.666
39.499
23.847
136.065
134.874
132.753
121.018
119.435
118.882
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130
125
120
115
3i
OH
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140
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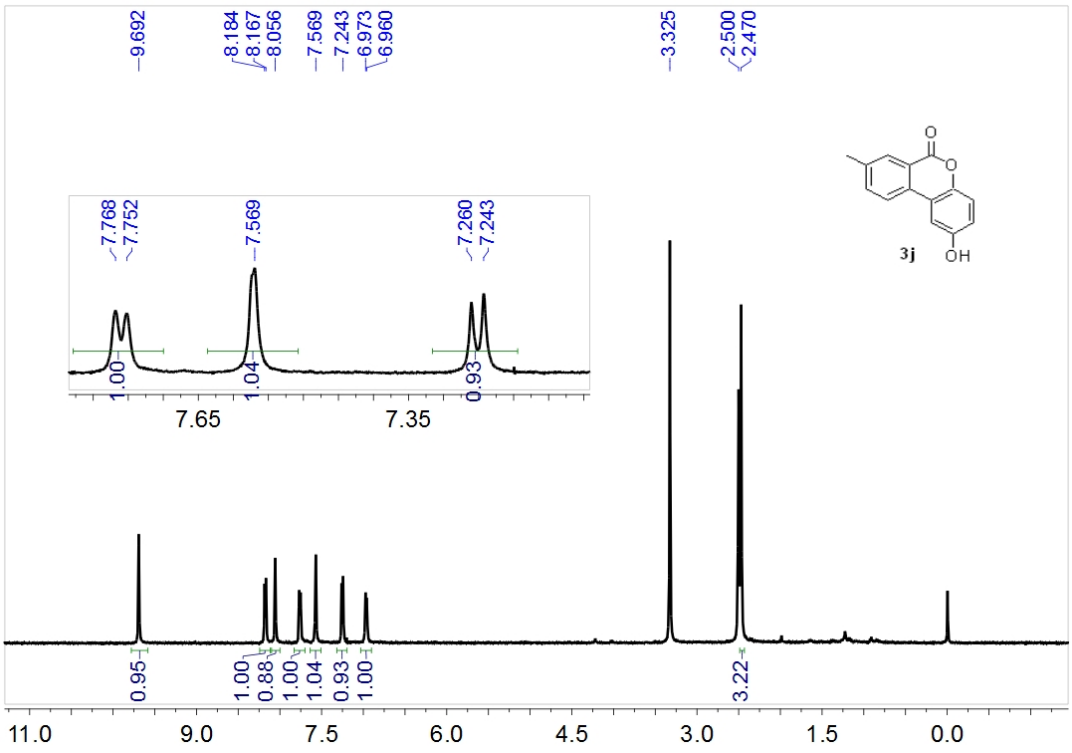
20
0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6.960
3.325
2.500
2.470
7.768
7.752
7.569
7.260
7.243
1.00
1.04
0.93
7.65
7.35
3j
OH
0.95
1.00
0.88
1.00
1.04
0.93
1.00
3.22
11.0
9.0
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6.0
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3.0
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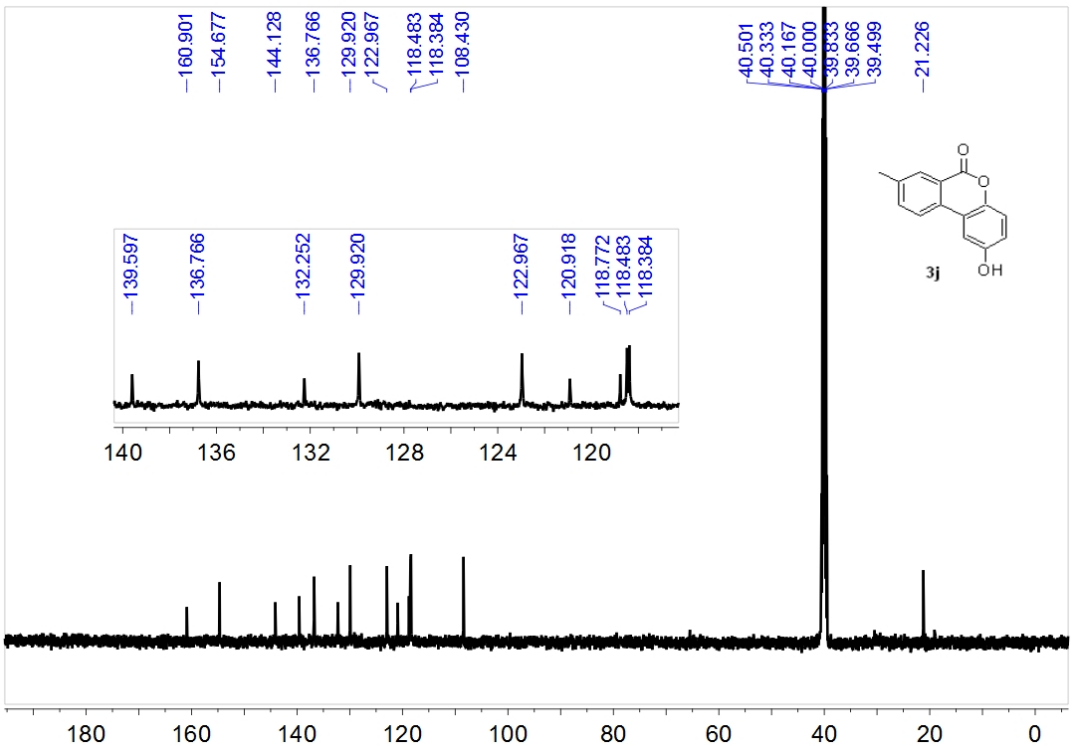
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118.384
108.430
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40.000
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39.666
39.499
21.226
139.597
136.766
132.252
129.920
122.967
120.918
118.772
118.483
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128
124
120
3j
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140
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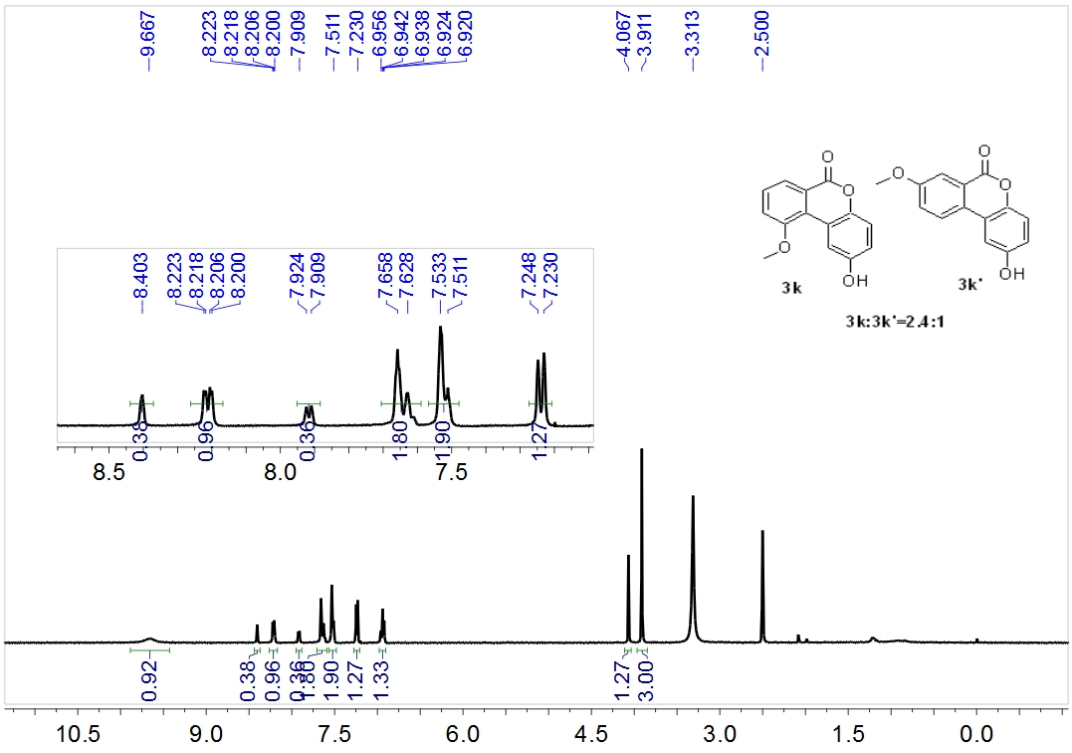
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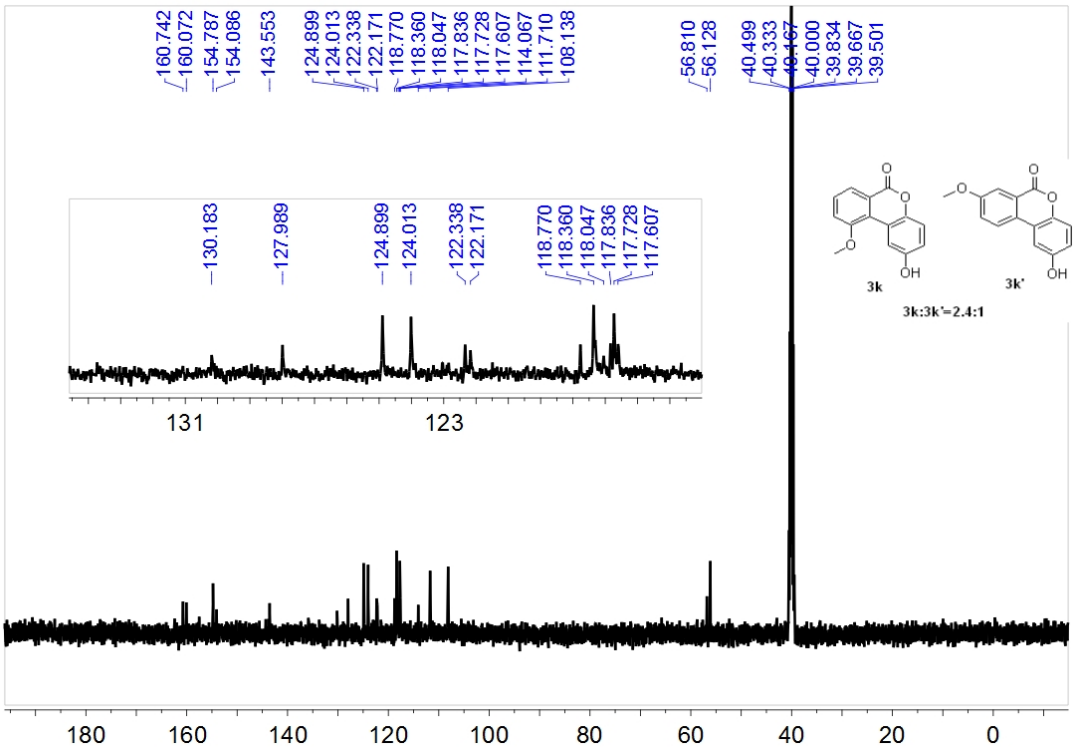
8.206
8.200
7.909
7.511
7.230
6.956
6.942
6.938
6.924
6.920
4.067
3.911
3.313
2.500
8.403
8.223
8.218
8.206
8.200
7.924
7.909
7.658
7.628
7.533
7.511
7.248
7.230
0.38
0.96
0.36
1.80
1.90
1.27
8.5
8.0
7.5
3k
3k'
3k:3k'=2.4:1
0.92
0.38
0.96
0.36
0.38
1.90
1.27
1.33
1.27
3.00
10.5
9.0
7.5
6.0
4.5
3.0
1.5
0.0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118.770
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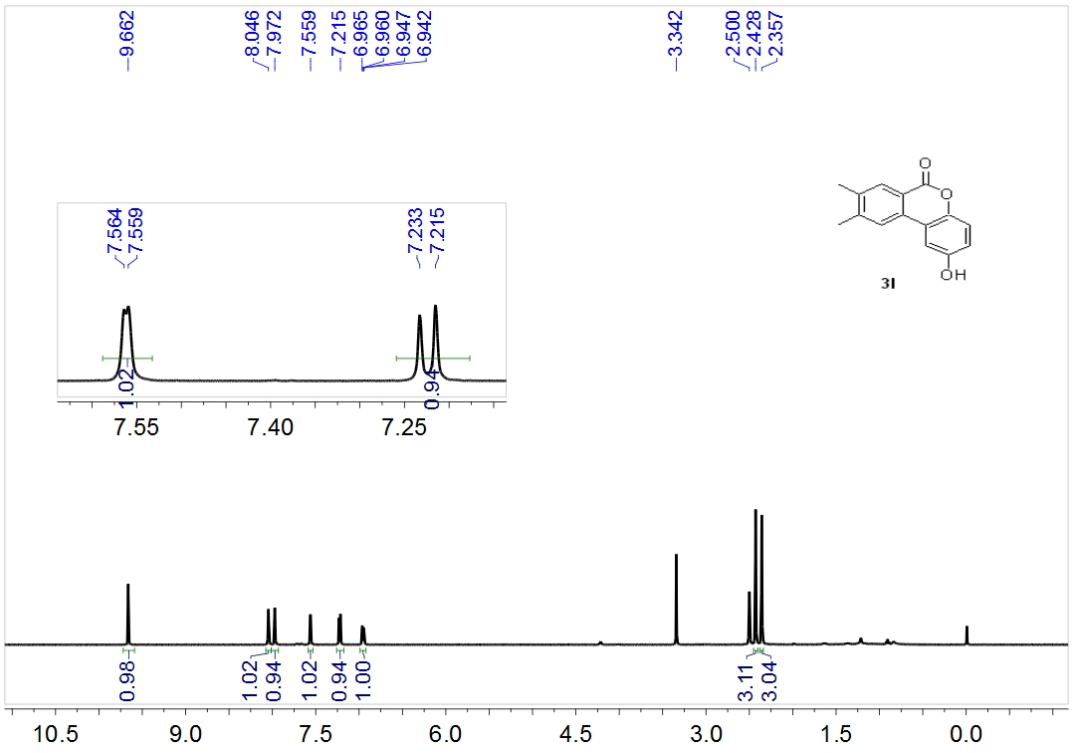
118.047
117.836
117.728
117.607
114.067
111.710
108.138
56.810
56.128
40.499
40.333
40.167
40.000
39.834
39.667
39.501
130.183
127.989
124.899
124.013
122.338
122.171
118.770
118.360
118.047
117.836
117.728
117.607
131
123
3k
3k'
3k:3k'=2.4:1
180
160
140
120
100
80
60
40
20
0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7.215
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6.960
6.947
6.942
3.342
2.500
2.428
2.357
7.564
7.559
7.233
7.215
1.02
0.94
7.55
7.40
7.25
3I
OH
0.98
1.02
0.94
1.02
0.94
1.00
3.11
3.04
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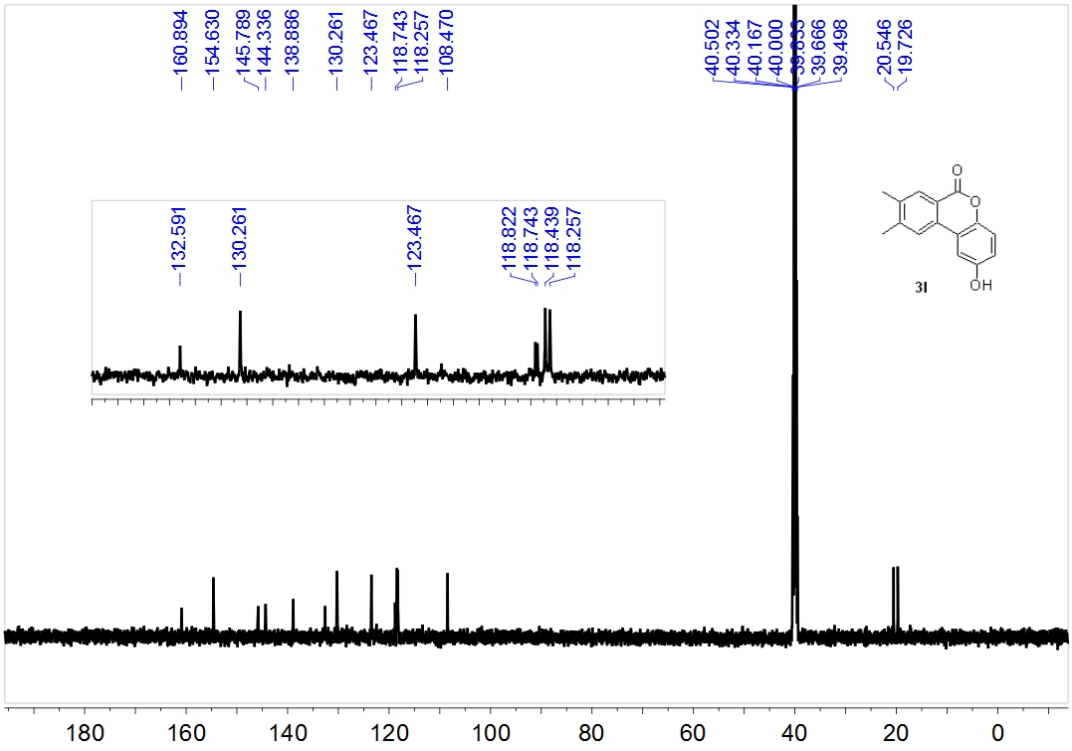
7.5
6.0
4.5
3.0
1.5
0.0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130.261
123.467
118.743
118.257
108.470
40.502
40.334
40.167
40.000
39.833
39.666
39.498
20.546
19.726
132.591
130.261
123.467
118.822
118.743
118.439
118.257
3I
OH
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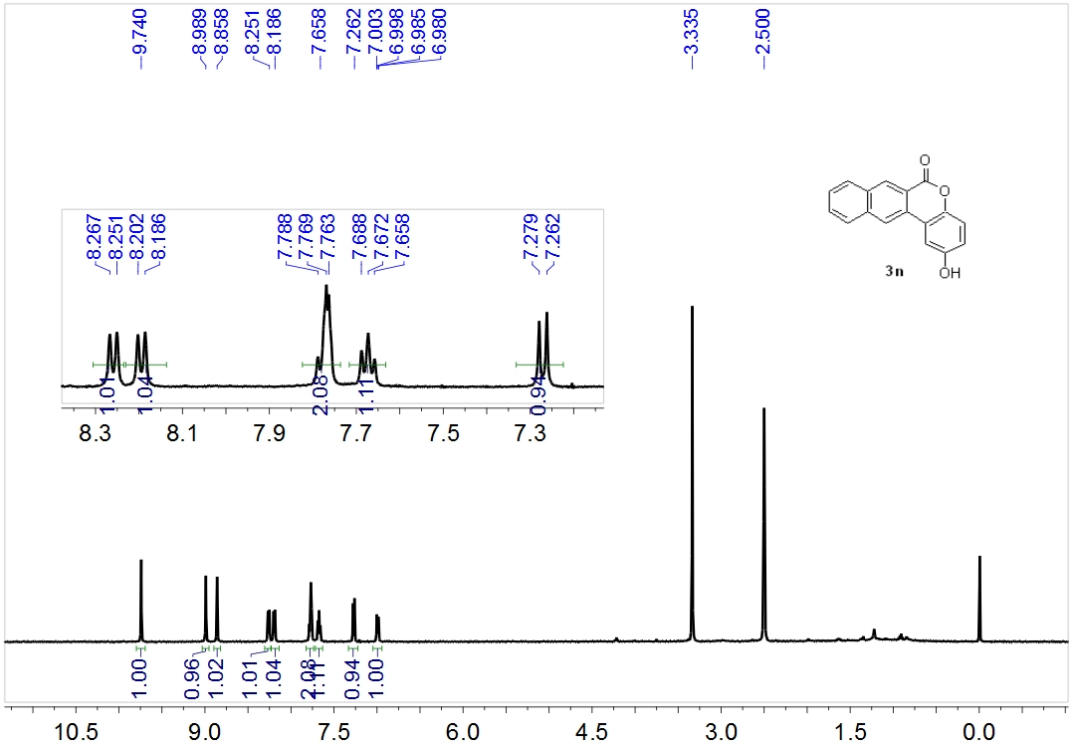
160
140
120
100
80
60
40
20
0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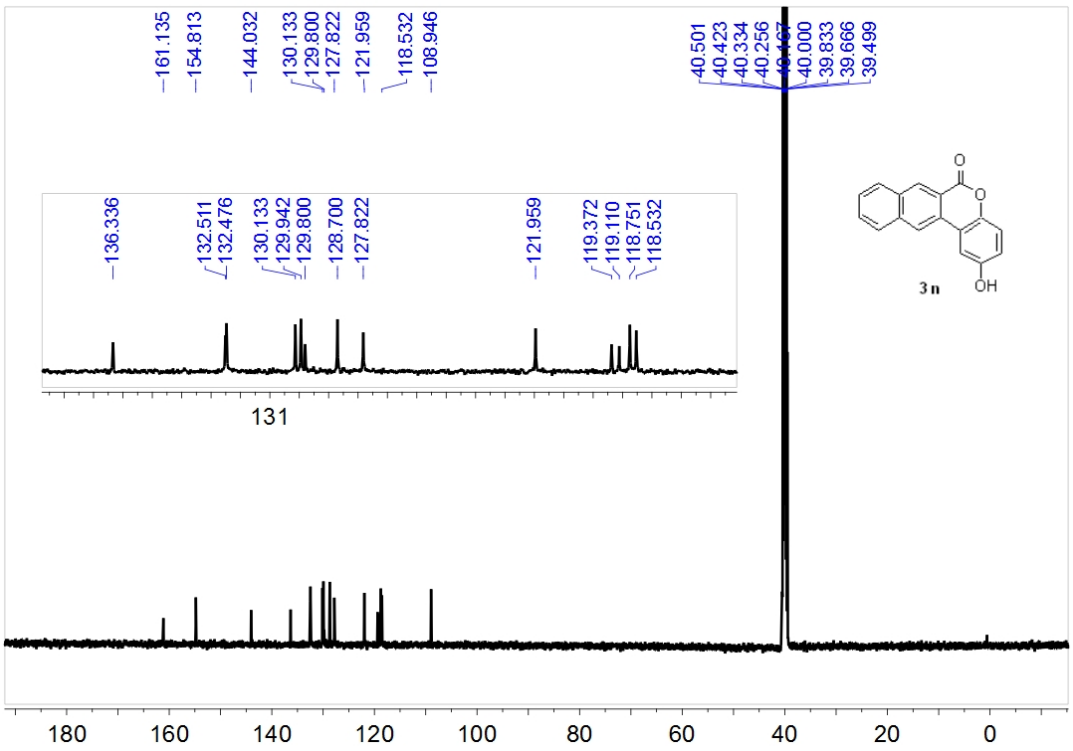
7.658
7.262
7.003
6.998
6.985
6.980
3.335
2.500
8.267
8.251
8.202
8.186
7.788
7.769
7.763
7.688
7.672
7.658
7.279
7.262
3n
OH
1.00
0.96
1.02
1.01
1.04
2.08
1.11
0.94
1.00
10.5
9.0
7.5
6.0
4.5
3.0
1.5
0.0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129.800
127.822
121.959
118.532
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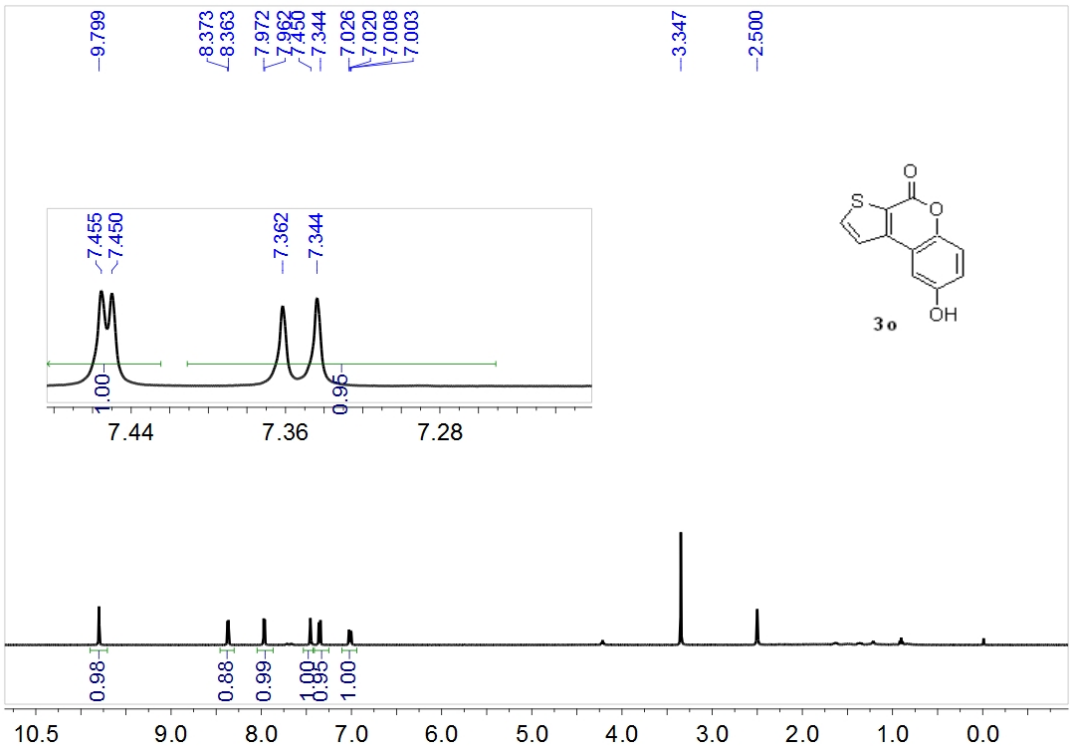
40.423
40.334
40.256
40.167
40.000
39.833
39.666
39.499
136.336
132.511
132.476
130.133
129.942
129.800
128.700
127.822
121.959
119.372
119.110
118.751
118.532
3n
OH
131
180
160
140
120
100
80
60
40
20
0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7.362
7.344
7.026
7.020
7.008
7.003
3.347
2.500
O
S
O
OH
3o
1.00
0.96
7.44
7.36
7.28
0.98
0.88
0.99
1.00
0.95
1.00
10.5
9.0
8.0
7.0
6.0
5.0
4.0
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2.0
1.0
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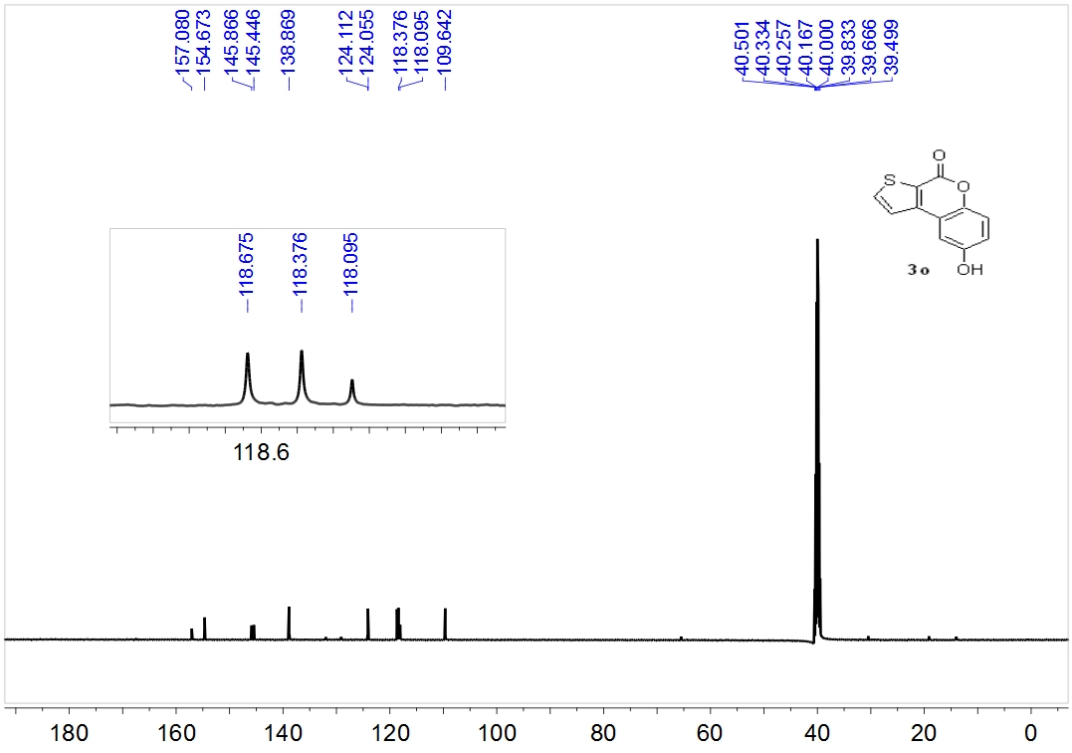
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145.446
138.869
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124.055
118.376
118.095
109.642
40.501
40.334
40.257
40.167
40.000
39.833
39.666
39.499
O
S
O
OH
3o
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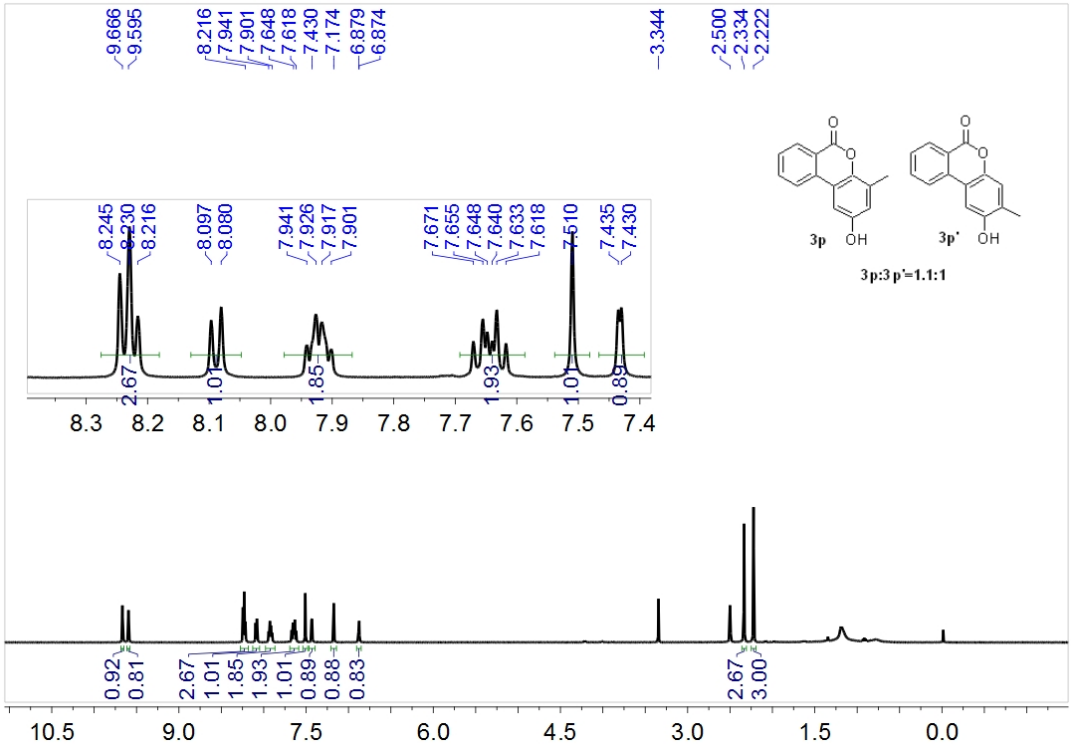
118.376
118.095
118.6
180
160
140
120
100
80
60
40
20
0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8.216
7.941
7.901
7.648
7.618
7.430
7.174
6.879
6.874
3.344
2.500
2.334
2.222
3p
3p'
OH
3p:3p'=1.1:1
8.245
8.230
8.216
8.097
8.080
7.941
7.926
7.917
7.901
7.671
7.655
7.648
7.640
7.633
7.618
7.510
7.435
7.430
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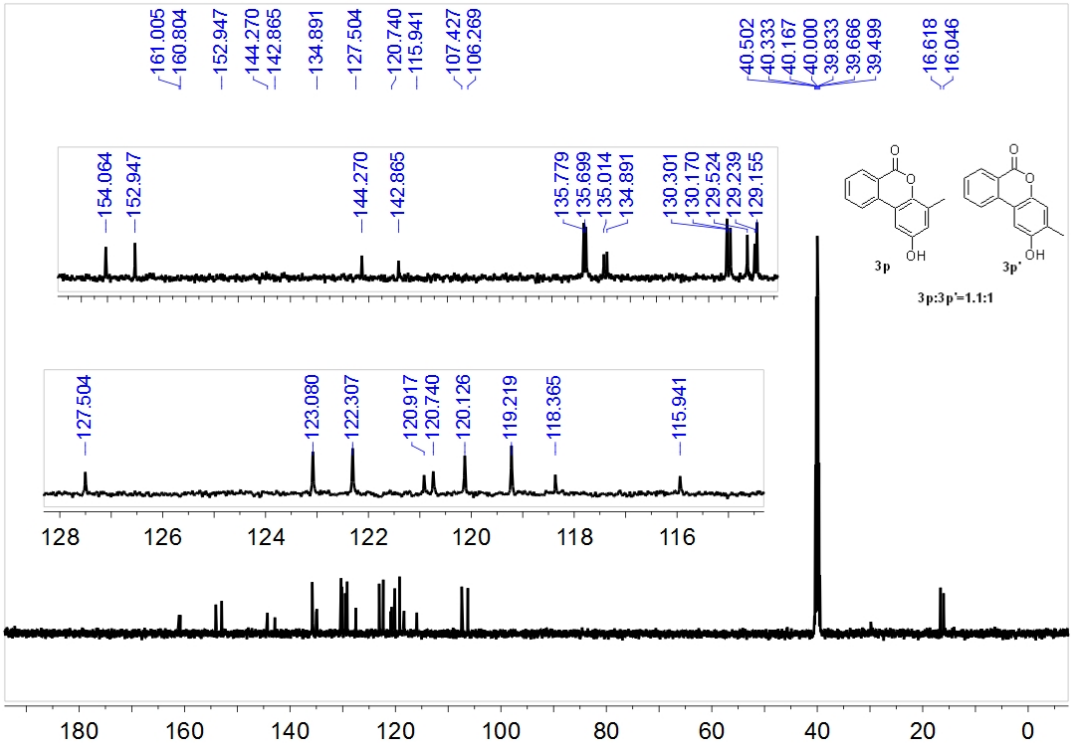
1.85
1.93
1.01
0.89
0.92
0.81
0.88
0.83
2.67
3.00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120.740
115.941
107.427
106.269
40.502
40.333
40.167
40.000
39.833
39.666
39.499
16.618
16.046
154.064
152.947
144.270
142.865
135.779
135.699
135.014
134.891
130.301
130.170
129.524
129.239
129.155
127.504
123.080
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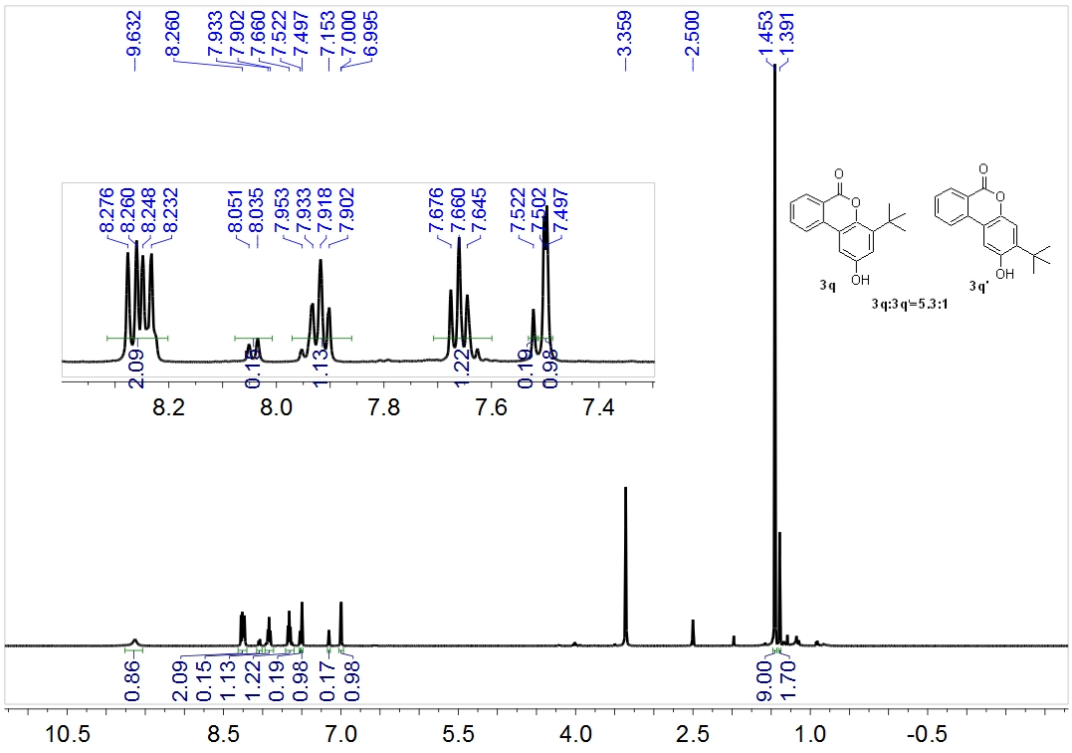
120.126
119.219
118.365
115.941
3p
3p'
OH
3p:3p'=1.1:1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7.902
7.660
7.522
7.497
7.153
7.000
6.995
3.359
2.500
1.453
1.391
8.276
8.260
8.248
8.232
8.051
8.035
7.953
7.933
7.918
7.902
7.676
7.660
7.645
7.522
7.502
7.497
2.09
0.15
1.13
1.22
0.19
0.98
3q
3q'
3q:3q'=5.3:1
0.86
2.09
0.15
1.13
1.22
0.19
0.98
0.17
0.98
9.00
1.70
10.5
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4.0
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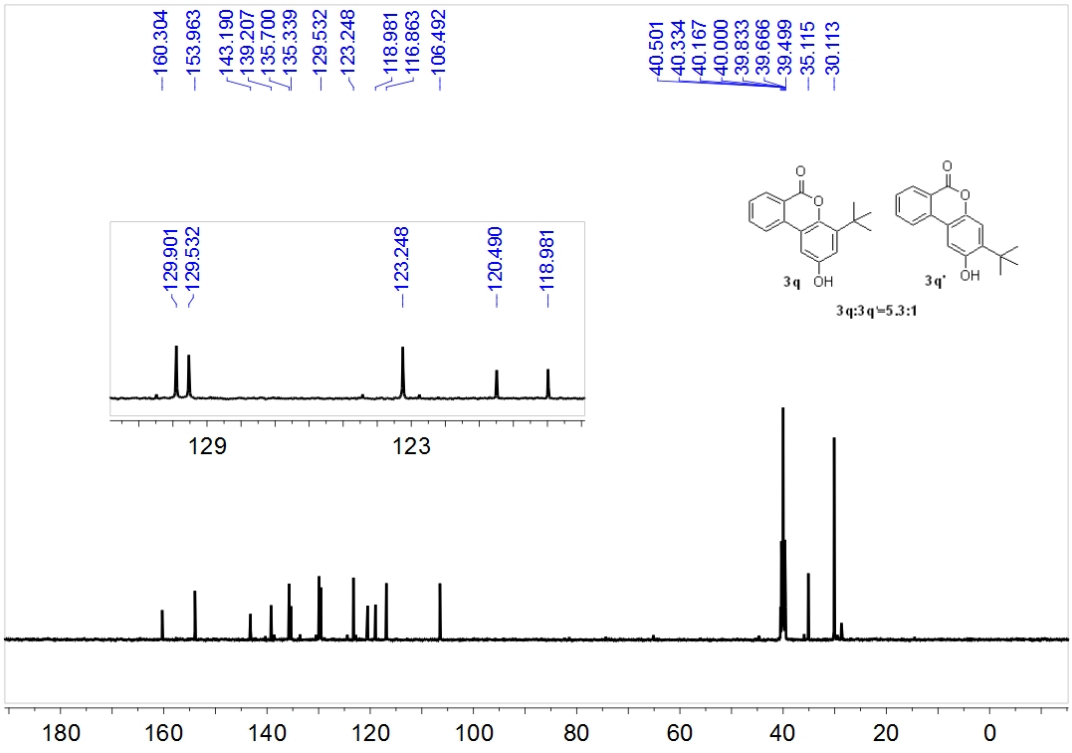
1.0
-0.5
8.2
8.0
7.8
7.6
7.4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135.339
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123.248
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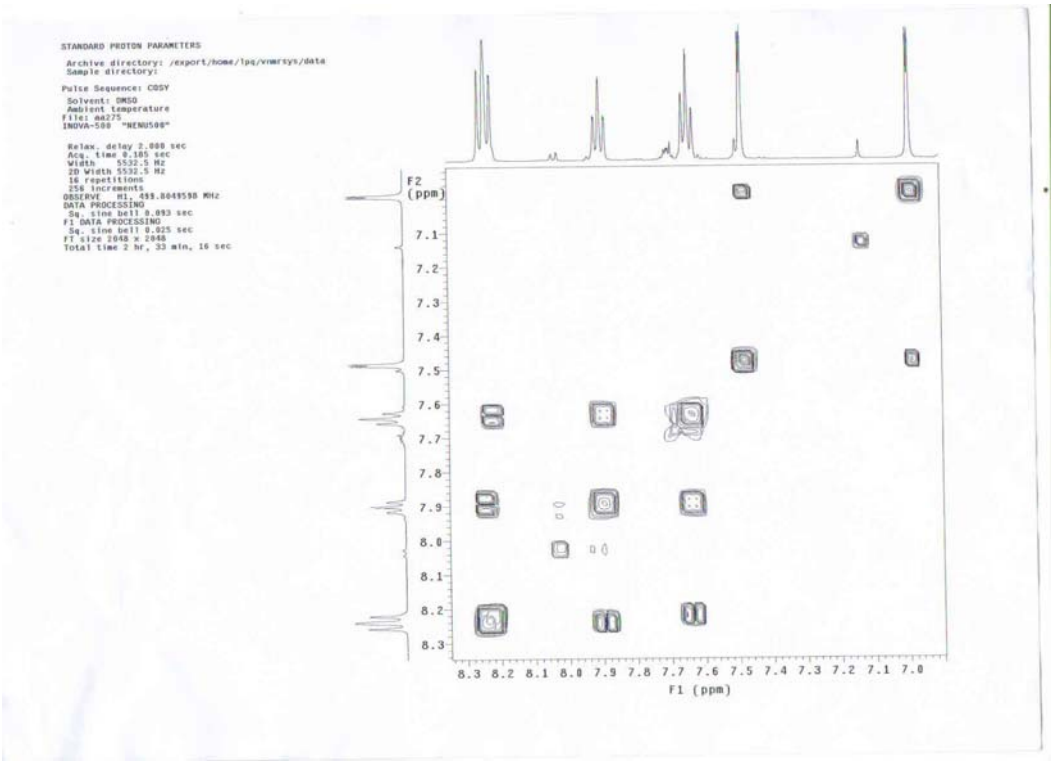
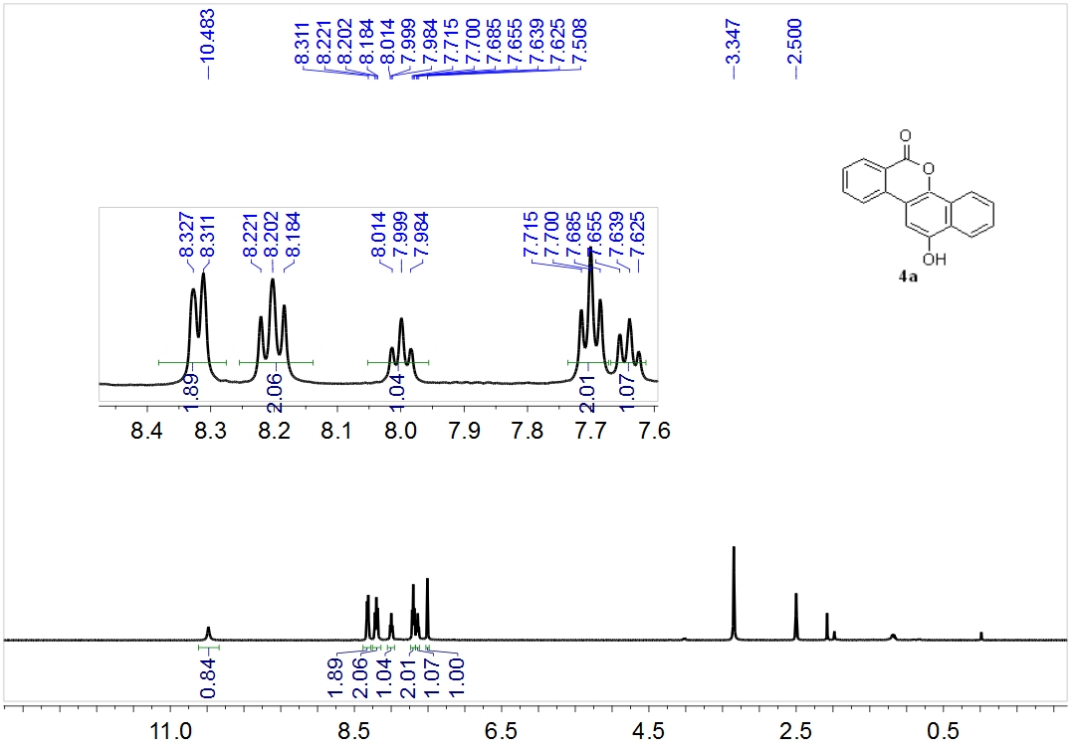
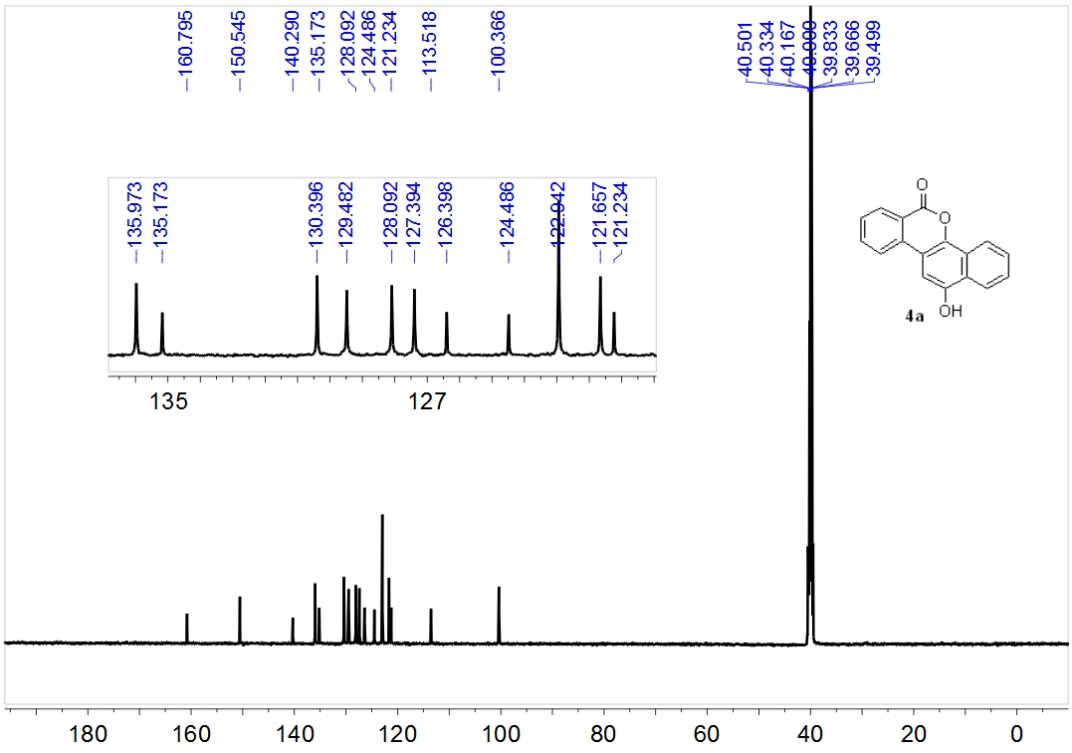
106.492
40.501
40.334
40.167
40.000
39.833
39.666
39.499
35.115
30.113
129.901
129.532
123.248
120.490
118.981
3q
3q'
3q:3q'=5.3:1
129
123
180
160
140
120
100
80
60
40
20
0



The H-H Cosy data demonstrates **3q** is the main product.

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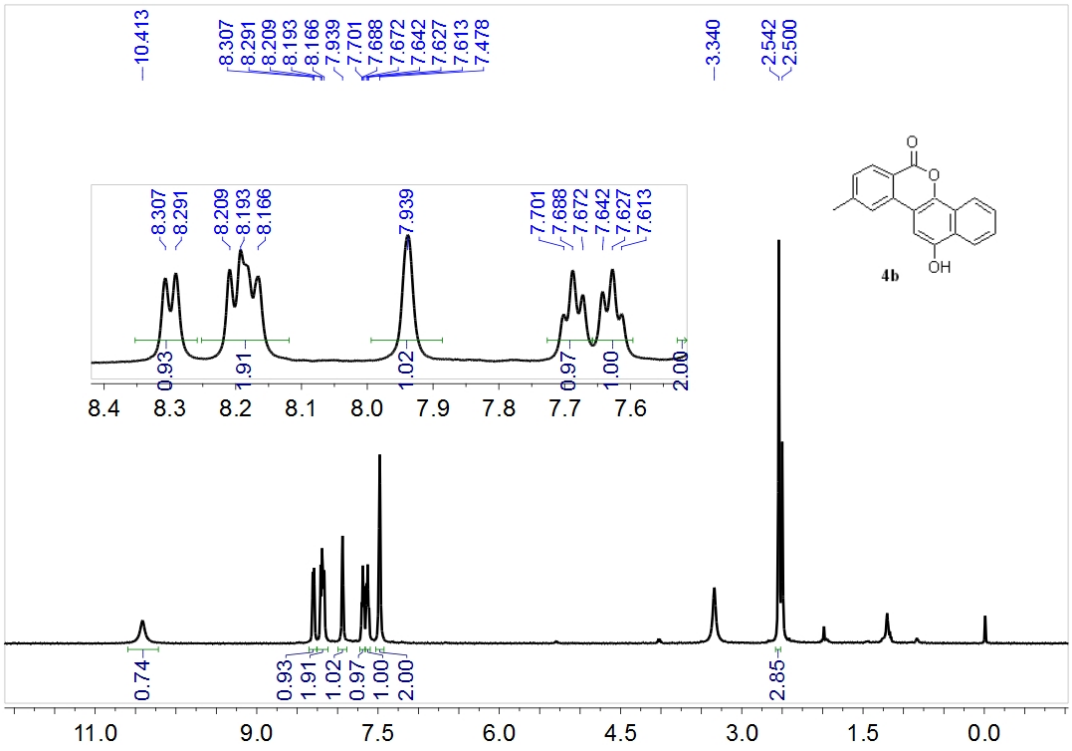
121.234
113.518
100.366
40.501
40.334
40.167
40.000
39.833
39.666
39.499
135.973
135.173
130.396
129.482
128.092
127.394
126.398
124.486
122.042
121.657
121.234
135
127
4a
OH
180
160
140
120
100
80
60
40
20
0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7.701
7.688
7.672
7.642
7.627
7.613
7.478
3.340
2.542
2.500
0.93
1.91
1.02
0.97
1.00
2.00
4b
OH
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
0.74
2.85
11.0
9.0
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6.0
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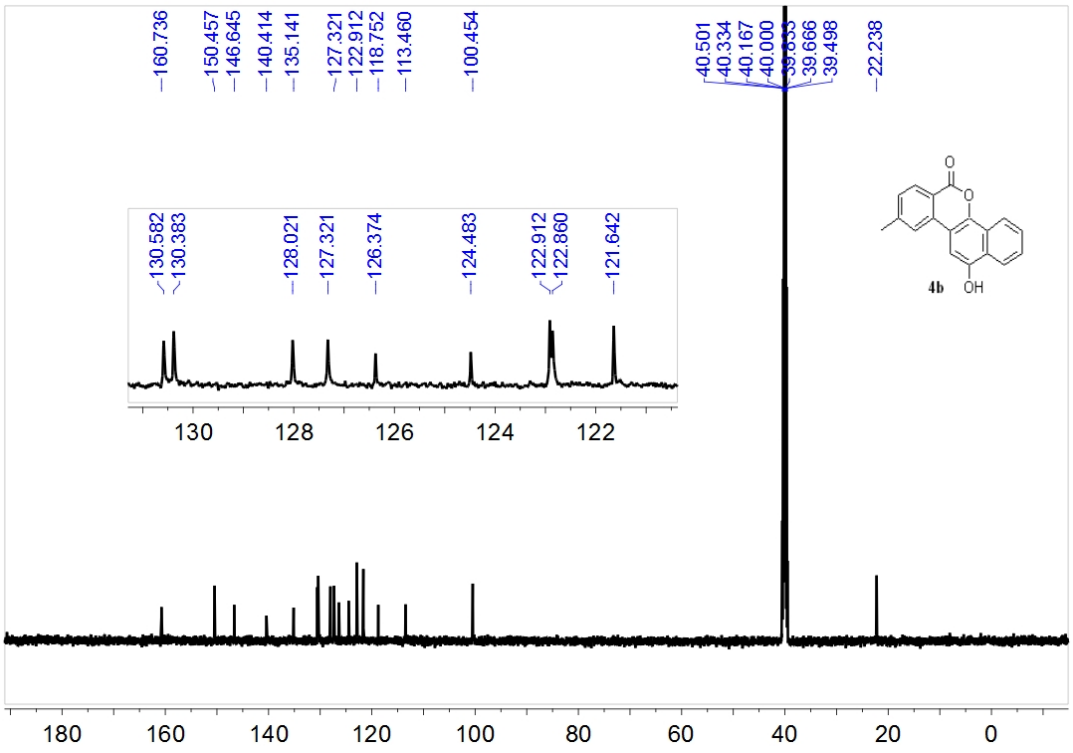
1.5
0.0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39.666
39.498
22.238
130.582
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128.021
127.321
126.374
124.483
122.912
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128
126
124
122
4b
OH
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140
120
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20
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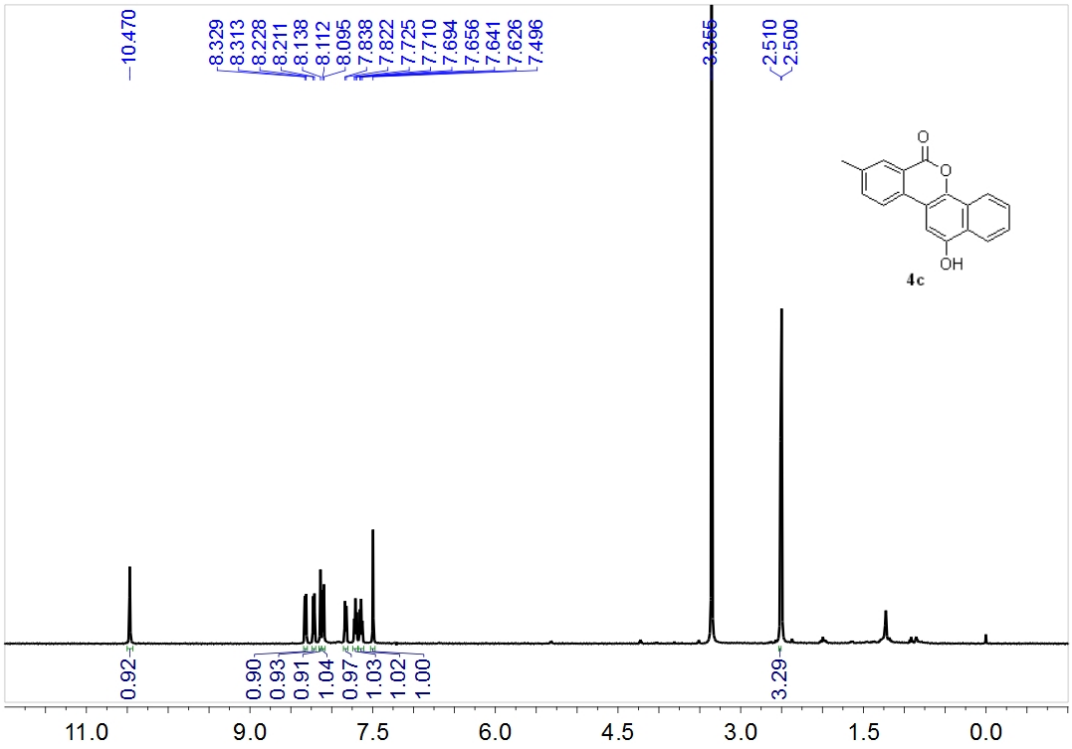
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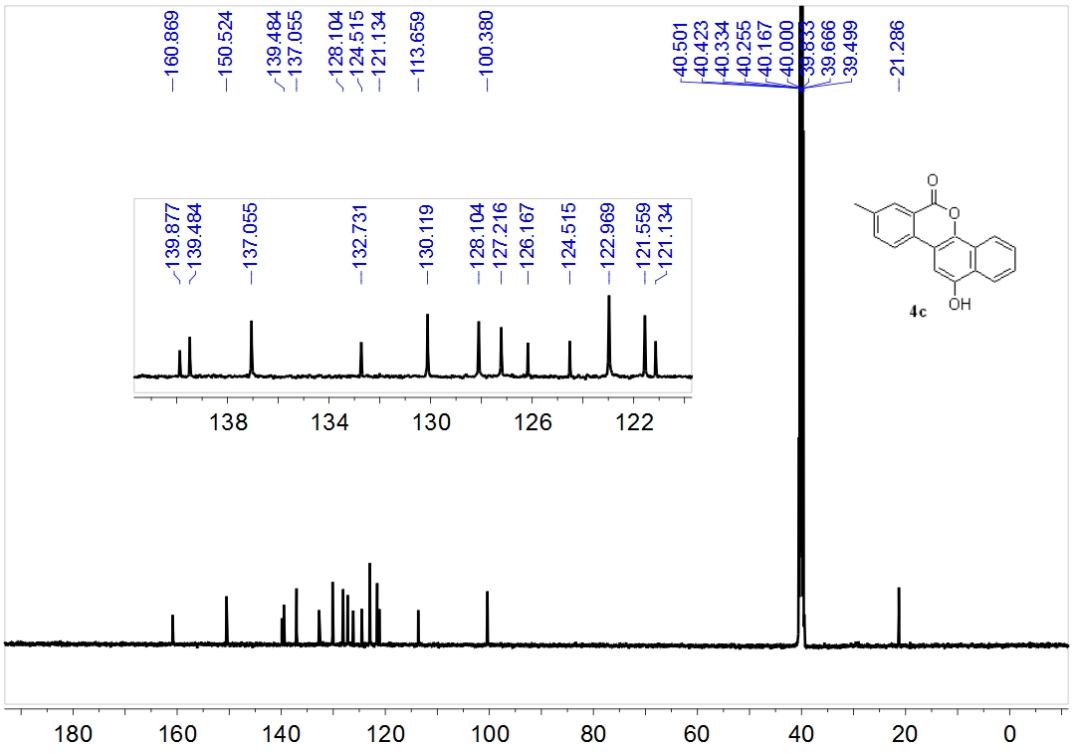
8.228
8.211
8.138
8.112
8.095
7.838
7.822
7.725
7.710
7.694
7.656
7.641
7.626
7.496
3.356
2.510
2.500
0.92
0.90
0.93
0.91
1.04
0.97
1.03
1.02
1.00
3.29
4c
OH
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0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40.423
40.334
40.255
40.167
40.000
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39.666
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130.119
128.104
127.216
126.167
124.515
122.969
121.559
121.134
138
134
130
126
122
O
O
OH
4c
180
160
140
120
100
80
60
40
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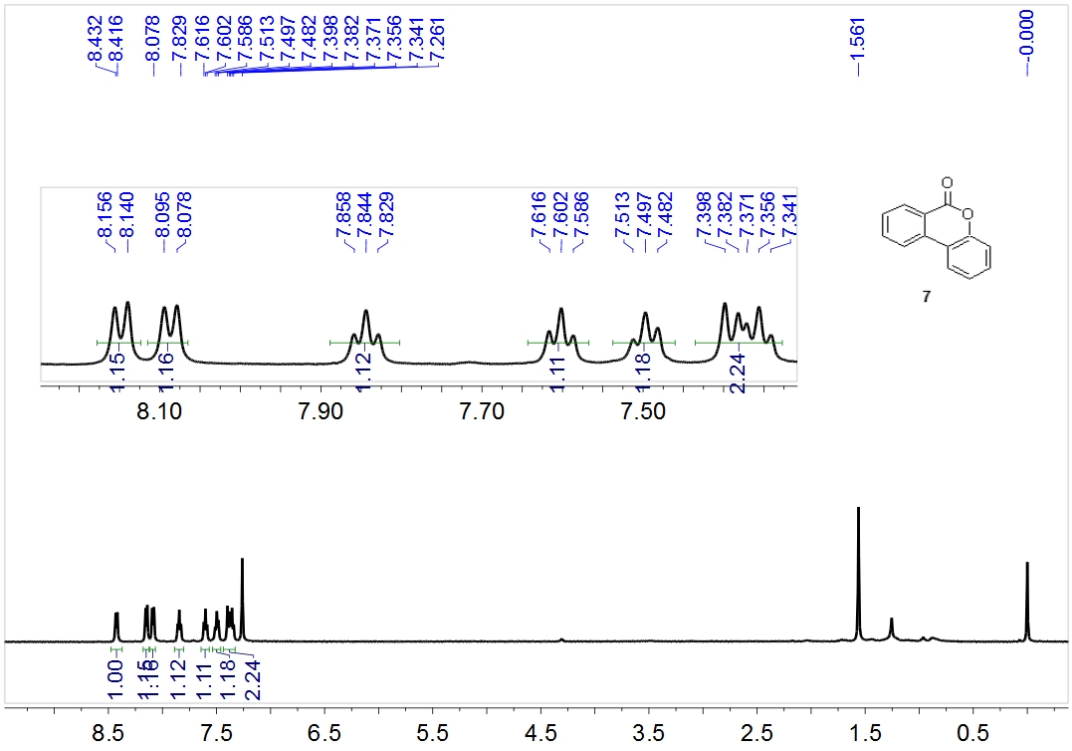
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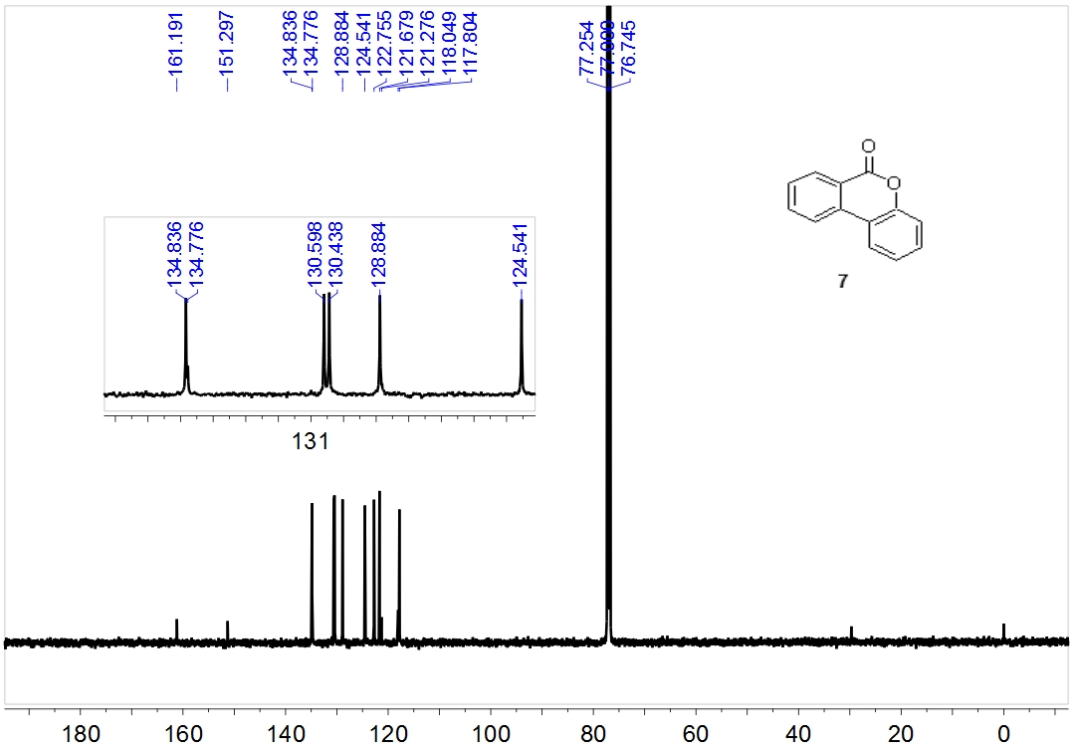
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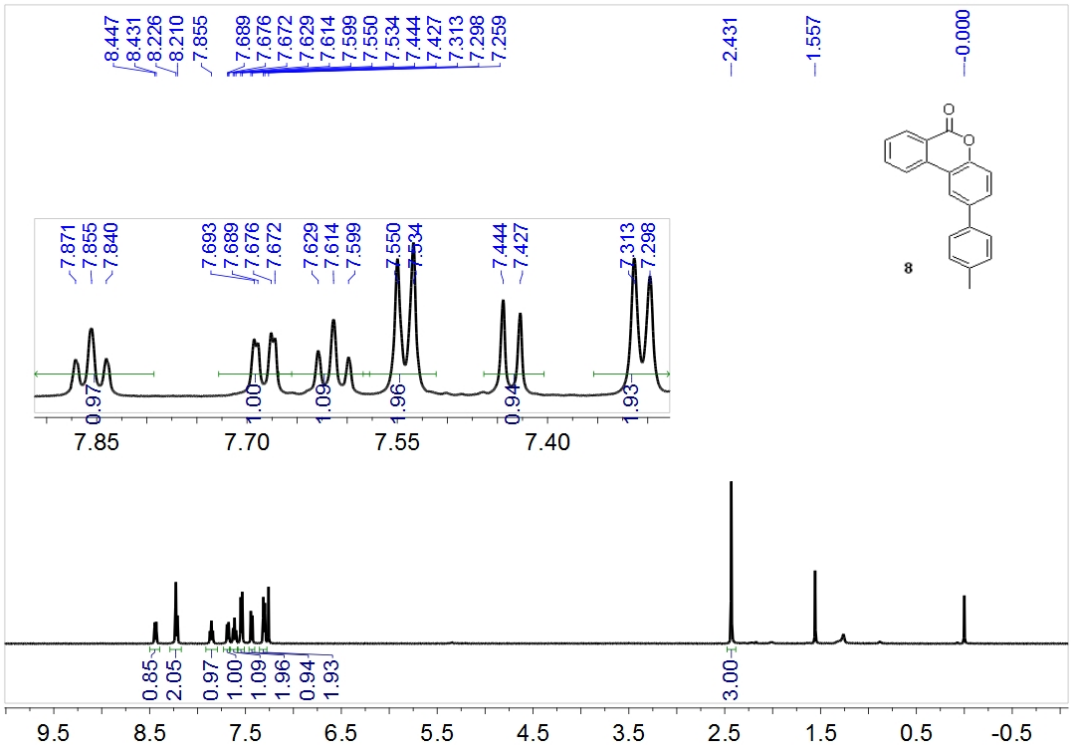
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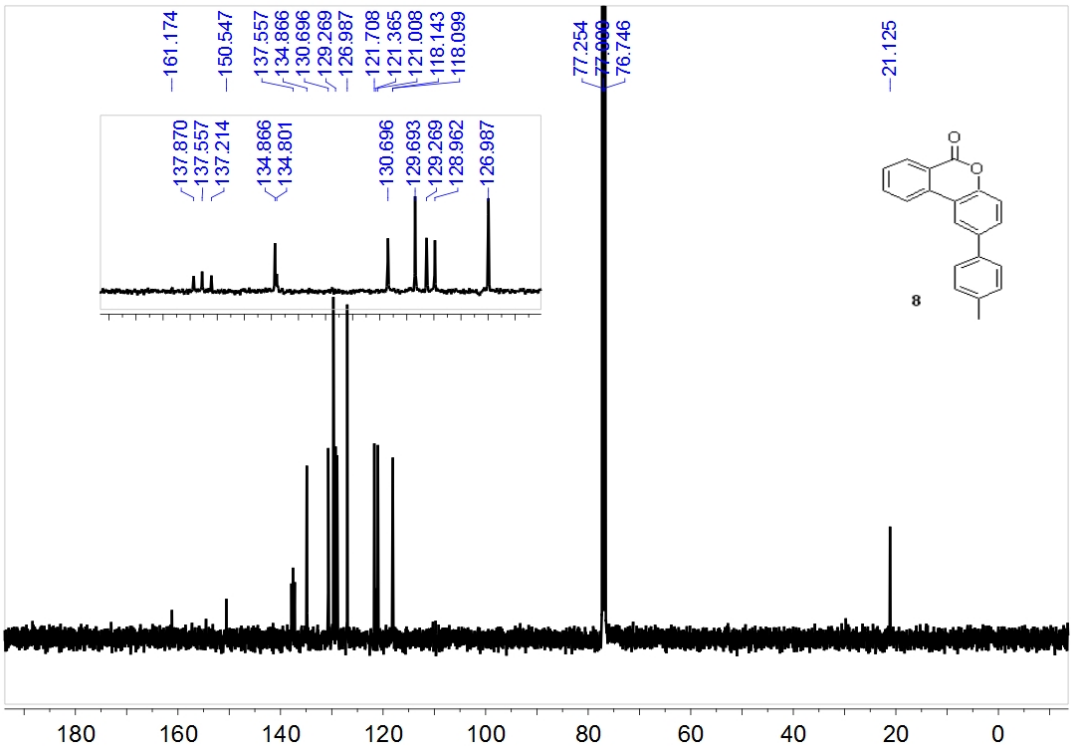
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