

Supporting Information

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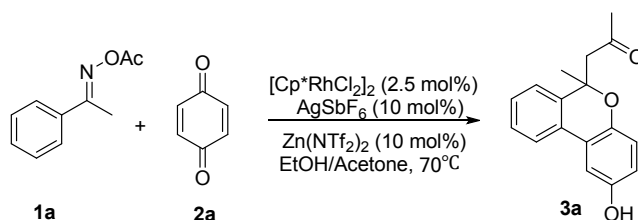
I. General Information

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 uncorrected. NMR spectra were obtained on a Varian Inova 400, 500 and 600 spectrometer (400, 500 and 600 MHz for ^1H NMR; 100, 125 and 150 MHz for ^{13}C NMR), with TMS as the internal standard. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

The starting materials were prepared according to the literature procedures.¹

II. Typical Procedures and Analytical Data of 3a-3u

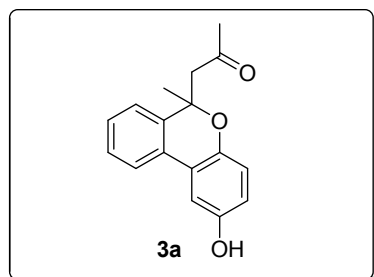


a) General Procedures for Synthesis of 3a-3u (3a as an example):

Without any particular precautions to extrude oxygen or moisture, to a schlenk tube (15 mL) equipped with a stirring bar was added **1a** (35.4 mg, 0.2 mmol), **2a** (32.4 mg, 0.3 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), AgSbF_6 (6.9 mg, 0.02 mmol) and $\text{Zn}(\text{NTf}_2)_2$ (12.5 mg, 0.02 mmol). Acetone (1.0 mL) and EtOH (1.0 mL) were then added. The reaction vessel was sealed and stirred at 70 °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 saturated Na_2CO_3 solution (10 mL), then extracted with EtOAc (10 mL $\times$ 2). The organic phase was combined. 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** (75% yield).

b) Analytical Data of Compounds 3a-3u

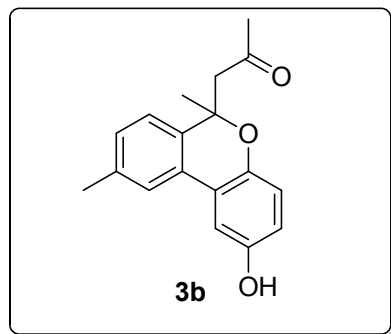
1-(2-hydroxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one (3a)



White solid, 75% yield, m.p. 101-102 °C. ^1H NMR (500 MHz, CDCl_3): δ 1.78 (s, 3H), 2.06 (s, 3H), 2.79 (d, J = 14.0 Hz, 1H), 3.06 (d, J = 13.5 Hz, 1H), 5.05 (s, 1H), 6.76 (d, J = 6.0 Hz, 1H),

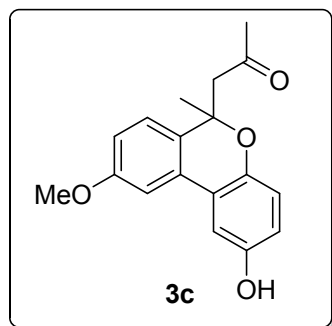
6.85 (d, $J = 8.5$ Hz, 1H), 7.21-7.26 (m, 2H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 25.2, 31.9, 52.2, 77.9, 109.3, 116.6, 118.9, 122.4, 122.9, 124.0, 128.2, 128.4, 137.5, 145.4, 150.6, 207.4. HRMS (ESI-TOF) Calcd for $(\text{C}_{17}\text{H}_{16}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 291.0992. Found 291.0999.

1-(2-hydroxy-6,9-dimethyl-6*H*-benzo[*c*]chromen-6-yl)propan-2-one (3b)



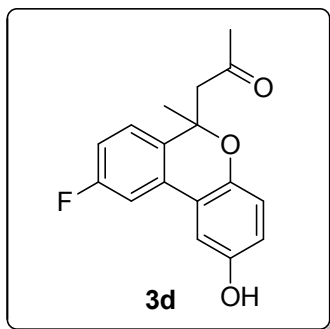
Yellowish solid, 70% yield, m.p. 140-141 °C. ^1H NMR (500 MHz, CDCl_3): δ 1.76 (s, 3H), 2.07 (s, 3H), 2.37 (s, 3H), 2.77 (d, $J = 13.5$ Hz, 1H), 3.05 (d, $J = 13.5$ Hz, 1H), 5.53 (s, 1H), 6.75 (dd, $J = 2.5, 8.5$ Hz, 1H), 6.84 (d, $J = 9.0$ Hz, 1H), 7.10 (s, 2H), 7.24 (d, $J = 2.5$ Hz, 1H), 7.45 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 21.3, 25.4, 31.9, 52.4, 77.9, 109.4, 116.6, 118.8, 122.9, 123.0, 123.9, 128.0, 129.1, 134.7, 137.8, 145.5, 150.7, 207.9. HRMS (ESI-TOF) Calcd for $(\text{C}_{18}\text{H}_{18}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 305.1148. Found 305.1157.

1-(2-hydroxy-9-methoxy-6-methyl-6*H*-benzo[*c*]chromen-6-yl)propan-2-one (3c)



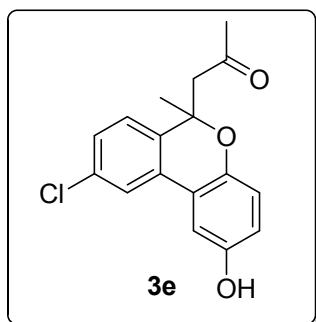
White solid, 50% yield, m.p. 165-166 °C. ^1H NMR (500 MHz, CDCl_3): δ 1.76 (s, 3H), 2.04 (s, 3H), 2.78 (d, $J = 14.0$ Hz, 1H), 3.01 (d, $J = 14.0$ Hz, 1H), 3.86 (s, 3H), 4.79 (s, 1H), 6.76 (dd, $J = 3.0, 8.5$ Hz, 1H), 6.84 (d, $J = 2.5$ Hz, 1H), 6.86 (d, $J = 2.5$ Hz, 1H), 7.14-7.16 (m, 2H), 7.20 (d, $J = 3.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 25.5, 31.9, 52.5, 55.4, 77.9, 107.7, 109.5, 113.7, 116.8, 119.0, 122.9, 125.4, 129.6, 130.1, 145.9, 150.4, 159.4, 207.2. HRMS (ESI-TOF) Calcd for $(\text{C}_{18}\text{H}_{18}\text{NaO}_4)^+ [\text{M}+\text{Na}]^+$ 321.1097. Found 321.1105.

1-(9-fluoro-2-hydroxy-6-methyl-6*H*-benzo[*c*]chromen-6-yl)propan-2-one (3d)



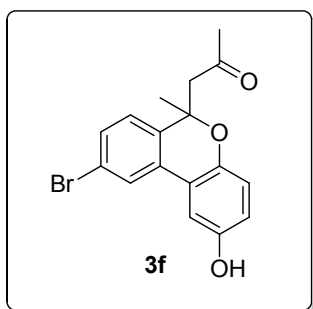
Colourless liquid, 55% yield. **¹H NMR** (500 MHz, CDCl₃): δ 1.77 (s, 3H), 2.07 (s, 3H), 2.81 (d, *J* = 14.0 Hz, 1H), 3.04 (d, *J* = 14.0 Hz, 1H), 5.47 (s, 1H), 6.79 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.98 (dd, *J* = 6.5, 8.5 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 5.5, 8.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H). **¹³C NMR** (150 MHz, CDCl₃): δ 25.5, 31.9, 52.2, 77.9, 109.2, 109.6, 115.0 (d, *J* = 21.5 Hz), 117.5, 119.1, 122.1, 126.1 (d, *J* = 8.4 Hz), 130.7 (d, *J* = 8.1 Hz), 133.2, 145.7, 150.7, 162.7 (d, *J* = 244.5 Hz), 207.2. **HRMS** (ESI-TOF) Calcd for (C₁₇H₁₅FN₃O₃⁺ [M+Na]⁺) 309.0897. Found 309.0890.

1-(9-chloro-2-hydroxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one (3e)



White solid, 71% yield, m.p. 159-160 °C. **¹H NMR** (500 MHz, CDCl₃): δ 1.76 (s, 3H), 2.07 (s, 3H), 2.80 (d, *J* = 14.0 Hz, 1H), 3.03 (d, *J* = 14.0 Hz, 1H), 5.17 (s, 1H), 6.79 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 7.16-7.18 (m, 2H), 7.26 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H). **¹³C NMR** (125 MHz, CDCl₃): δ 25.3, 31.9, 52.0, 77.8, 109.5, 117.5, 119.1, 121.8, 122.5, 125.8, 128.1, 130.2, 134.2, 135.7, 145.7, 150.7, 206.8. **HRMS** (ESI-TOF) Calcd for (C₁₇H₁₅ClNaO₃⁺ [M+Na]⁺) 325.0602. Found 325.0609.

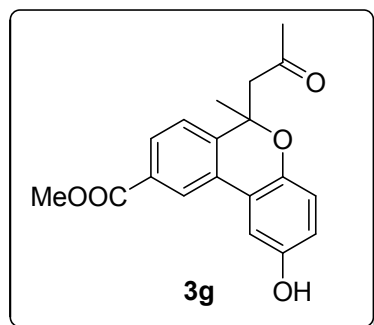
1-(9-bromo-2-hydroxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one (3f)



Yellowish solid, 57% yield, m.p. 176-177 °C. **¹H NMR** (500 MHz, CDCl₃): δ 1.75 (s, 3H), 2.07 (s,

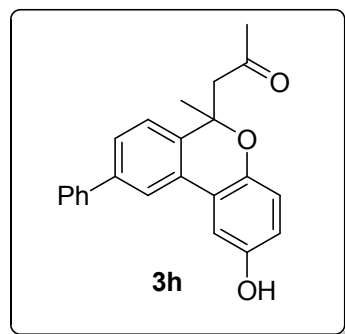
3H), 2.80 (d, $J = 14.5$ Hz, 1H). 3.02 (d, $J = 14.5$ Hz, 1H), 4.96 (s, 1H), 6.78 (dd, $J = 2.5, 8.5$ Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 1H), 7.11 (d, $J = 8.0$ Hz, 1H), 7.17 (d, $J = 3.0$ Hz, 1H), 7.41 (dd, $J = 2.0, 8.5$ Hz, 1H), 7.76 (d, $J = 2.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 25.2, 31.9, 51.9, 77.8, 109.5, 117.6, 119.1, 121.6, 122.3, 125.4, 126.0, 130.5, 131.0, 136.2, 145.6, 150.8, 207.0. HRMS (ESI-TOF) Calcd for $(\text{C}_{17}\text{H}_{15}\text{BrNaO}_3)^+ [\text{M}+\text{Na}]^+$ 369.0097. Found 369.0079.

methyl 2-hydroxy-6-methyl-6-(2-oxopropyl)-6H-benzo[c]chromene-9-carboxylate (3g)



White solid, 28% yield, m.p. 170-171 °C. ^1H NMR (500 MHz, CDCl_3): δ 1.79 (s, 3H), 2.07 (s, 3H), 2.83 (d, $J = 14.0$ Hz, 1H). 3.07 (d, $J = 14.5$ Hz, 1H), 3.95 (s, 3H), 5.50 (s, 1H), 6.81 (dd, $J = 2.5, 9.0$ Hz, 1H), 6.86 (d, $J = 8.5$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 2.5$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 8.34 (s, 1H). ^{13}C NMR (150 MHz, CDCl_3): δ 25.2, 31.9, 51.8, 52.4, 77.9, 109.7, 117.4, 119.0, 122.0, 123.7, 124.4, 128.8, 129.2, 130.0, 141.9, 145.5, 150.9, 166.8, 206.5. HRMS (ESI-TOF) Calcd for $(\text{C}_{19}\text{H}_{18}\text{BrNaO}_5)^+ [\text{M}+\text{Na}]^+$ 349.1046. Found 349.1066.

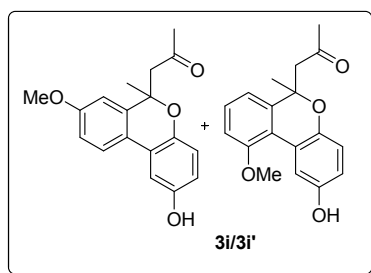
1-(2-hydroxy-6-methyl-9-phenyl-6H-benzo[c]chromen-6-yl)propan-2-one (3h)



White solid, 35% yield, m.p. 97-98 °C. ^1H NMR (500 MHz, CDCl_3): δ 1.81 (s, 3H), 2.09 (s, 3H), 2.83 (d, $J = 14.0$ Hz, 1H). 3.10 (d, $J = 14.0$ Hz, 1H), 4.82 (s, 1H), 6.78 (dd, $J = 3.0, 8.5$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 1H), 7.30 (d, $J = 14.0$ Hz, 1H), 7.32 (d, $J = 3.0$ Hz, 1H), 7.38 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.52 (dd, $J = 1.5, 8.0$ Hz, 1H), 7.62 (d, $J = 7.0$ Hz, 2H), 7.86 (d, $J = 1.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 25.3, 32.0, 52.2, 78.0, 109.5, 116.8, 119.0, 121.2, 122.9, 124.6, 127.1, 127.1, 127.6, 128.6, 128.9, 136.5, 140.5, 141.2, 145.8, 150.6, 207.1. HRMS (ESI-TOF) Calcd for $(\text{C}_{23}\text{H}_{20}\text{NaO}_5)^+ [\text{M}+\text{Na}]^+$ 367.1305. Found 367.1314.

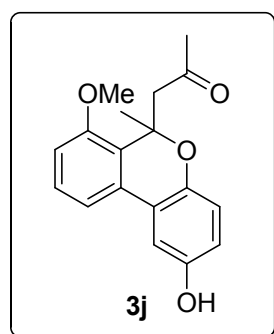
1-(2-hydroxy-8-methoxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one

1-(2-hydroxy-10-methoxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one (3i and 3i')



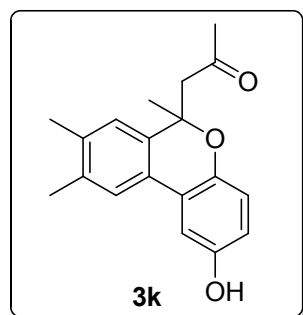
White solid, 99% yield. **¹H NMR** (500 MHz, CDCl₃): δ 1.75 (s, 6.81H), 1.78 (s, 1.75H), 2.04 (s, 4.24H), 2.08 (s, 3H), 2.75 (d, *J* = 14.0 Hz, 2.28H), 3.01 (d, *J* = 14.0 Hz, 1.38H), 3.05 (d, *J* = 14.0 Hz, 0.89H), 3.82 (s, 3H), 3.91 (s, 4.37H), 5.24 (s, 1.04H), 5.45 (s, 0.64H), 6.70 (d, *J* = 8.5 Hz, 1.01H), 6.75-6.75 (m, 2.35H), 6.81-6.88 (m, 4.87H), 6.93 (d, *J* = 8.0 Hz, 1.43H), 7.16 (s, 0.91H), 7.26 (t, *J* = 8.0 Hz, 2.14H), 7.56 (d, *J* = 8.5 Hz, 0.92H), 8.02 (s, 1.32H). **¹³C NMR** (125 MHz, CDCl₃): δ 25.2, 31.9, 51.8, 52.2, 55.4, 55.6, 77.7, 77.9, 108.9, 109.8, 111.2, 113.4, 115.2, 115.6, 115.6, 116.3, 117.3, 118.3, 118.7, 121.2, 122.0, 123.0, 123.5, 123.9, 129.0, 139.2, 140.5, 144.6, 145.6, 149.9, 150.8, 156.7, 159.8, 207.4, 207.6. **HRMS** (ESI-TOF) Calcd for (C₁₈H₁₈NaO₄⁺ [M+Na]⁺) 321.1097. Found 321.1105.

1-(2-hydroxy-7-methoxy-6-methyl-6*H*-benzo[*c*]chromen-6-yl)propan-2-one (3j)



White solid, 46% yield, m.p. 159-160 °C. **¹H NMR** (600 MHz, CDCl₃): δ 1.64 (s, 3H), 2.10 (s, 3H), 2.96 (d, *J* = 14.4 Hz, 1H), 3.52 (d, *J* = 15.0 Hz, 1H), 3.81 (s, 3H), 5.31 (s, 1H), 6.69 (dd, *J* = 3.0, 9.0 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.82 (t, *J* = 4.8 Hz, 1H), 7.13 (d, *J* = 2.4 Hz, 1H), 7.27 (d, *J* = 4.8 Hz, 2H). **¹³C NMR** (125 MHz, CDCl₃): δ 25.8, 31.3, 53.4, 55.3, 78.2, 110.0, 110.8, 115.1, 116.6, 118.6, 122.3, 126.0, 128.8, 130.2, 145.6, 150.4, 155.0, 207.9. **HRMS** (ESI-TOF) Calcd for (C₁₈H₁₈NaO₄⁺ [M+Na]⁺) 321.1097. Found 321.1110.

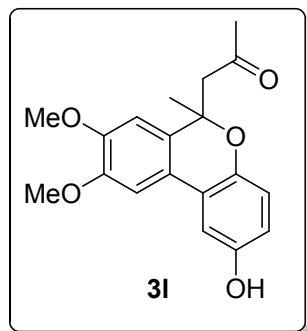
1-(2-hydroxy-6,8,9-trimethyl-6*H*-benzo[*c*]chromen-6-yl)propan-2-one (3k)



Yellow solid, 35% yield, m.p. 161-162 °C. **¹H NMR** (500 MHz, CDCl₃): δ 1.78 (s, 3H), 2.13 (s,

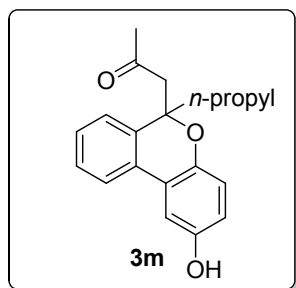
3H), 2.33 (s, 3H), 2.40 (s, 3H), 2.75 (d, $J = 14.0$ Hz, 1H), 3.24 (d, $J = 13.5$ Hz, 1H), 4.99 (s, 1H), 6.73 (dd, $J = 3.0, 9.0$ Hz, 1H), 6.81 (d, $J = 8.5$ Hz, 1H), 6.93 (s, 1H), 7.16 (d, $J = 3.0$ Hz, 1H), 7.35 (s, 1H). **^{13}C NMR** (150 MHz, CDCl_3): δ 20.9, 23.2, 26.1, 31.7, 52.3, 79.5, 110.0, 116.2, 118.6, 121.7, 123.6, 129.1, 133.1, 133.6, 134.4, 137.4, 145.2, 150.6, 207.6. **HRMS** (ESI-TOF) Calcd for $(\text{C}_{19}\text{H}_{20}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 319.1305. Found 319.1314.

1-(2-hydroxy-8,9-dimethoxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one (3l)



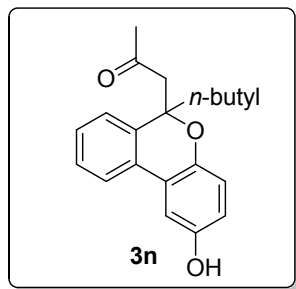
White solid, 60% yield, m.p. 157-158 °C. **^1H NMR** (500 MHz, d_6 -DMSO): δ 1.62 (s, 3H), 2.00 (s, 3H), 2.71 (d, $J = 14.0$ Hz, 1H), 3.06 (d, $J = 14.0$ Hz, 1H), 3.79 (s, 3H), 3.85 (s, 3H), 6.63 (dd, $J = 3.0, 8.5$ Hz, 1H), 6.72 (d, $J = 8.5$ Hz, 1H), 6.86 (s, 1H), 7.20 (d, $J = 2.5$ Hz, 1H), 7.22 (s, 1H), 9.06 (s, 1H). **^{13}C NMR** (125 MHz, d_6 -DMSO): δ 25.9, 32.2, 52.1, 56.2, 56.3, 77.9, 106.2, 108.6, 109.5, 115.9, 118.5, 121.3, 122.9, 131.0, 143.9, 149.1, 149.3, 152.6, 206.6. **HRMS** (ESI-TOF) Calcd for $(\text{C}_{19}\text{H}_{20}\text{NaO}_5)^+ [\text{M}+\text{Na}]^+$ 351.1203. Found 351.1204.

1-(2-hydroxy-6-propyl-6H-benzo[c]chromen-6-yl)propan-2-one (3m)



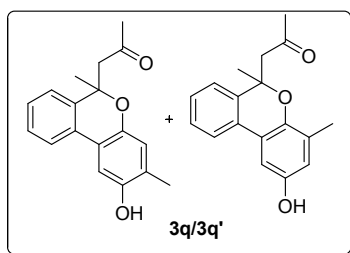
Colourless liquid, 25% yield. **^1H NMR** (400 MHz, CDCl_3): δ 0.87 (t, $J = 7.2$ Hz, 3H), 1.35-1.43 (m, 2H), 1.86-1.94 (m, 1H), 2.03 (s, 3H), 2.06-2.12 (m, 1H), 2.91 (d, $J = 14.0$ Hz, 1H), 3.05 (d, $J = 14.0$ Hz, 1H), 5.05 (s, 1H), 6.74 (dd, $J = 2.8, 8.8$ Hz, 1H), 6.83 (d, $J = 8.8$ Hz, 1H), 7.14 (d, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 2.8$ Hz, 1H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 1H). **^{13}C NMR** (100 MHz, CDCl_3): δ 14.2, 17.1, 31.9, 40.4, 52.0, 80.5, 109.3, 116.7, 118.7, 122.3, 122.4, 124.8, 128.0, 128.1, 128.7, 135.8, 145.7, 150.4, 207.6. **HRMS** (ESI-TOF) Calcd for $(\text{C}_{19}\text{H}_{20}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 319.1305. Found 319.1312.

1-(6-butyl-2-hydroxy-6H-benzo[c]chromen-6-yl)propan-2-one (3n)



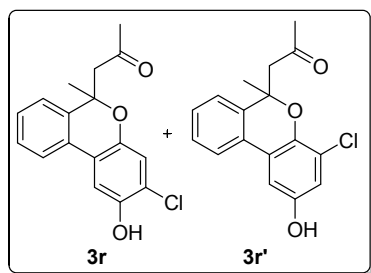
Colourless liquid, 35% yield. **¹H NMR** (400 MHz, CDCl₃): δ 0.84 (t, *J* = 7.2 Hz, 3H), 1.25-1.34 (m, 4H), 1.87-1.94 (m, 1H), 2.03 (s, 3H), 2.08-2.15 (m, 1H), 2.91 (d, *J* = 14.0 Hz, 1H), 3.05 (d, *J* = 14.0 Hz, 1H), 5.10 (s, 1H), 6.74 (dd, *J* = 2.8, 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃): δ 14.0, 22.8, 25.9, 31.9, 37.8, 51.9, 80.5, 109.4, 116.7, 118.8, 122.3, 122.4, 124.8, 128.0, 128.1, 128.7, 135.9, 145.7, 150.4, 207.7. **HRMS** (ESI-TOF) Calcd for (C₂₀H₂₂NaO₃⁺ [M+Na]⁺) 333.1461. Found 333.1465.

1-(2-hydroxy-3,6-dimethyl-6H-benzo[c]chromen-6-yl)propan-2-one
1-(2-hydroxy-4,6-dimethyl-6H-benzo[c]chromen-6-yl)propan-2-one
(3q and 3q')



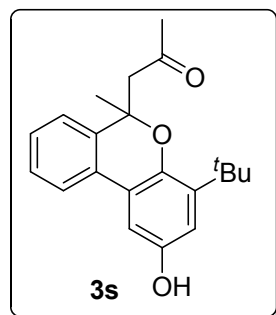
Purple solid, 76% yield. **¹H NMR** (600 MHz, CDCl₃): δ 1.75 (s, 3.09H), 1.76 (s, 4.73H), 2.03 (s, 3.01H), 2.05 (s, 4.35H), 2.21 (s, 3H), 2.26 (s, 4.60H), 2.79 (d, *J* = 13.8 Hz, 1.54H), 2.94 (d, *J* = 13.8 Hz, 1.08H), 3.03 (d, *J* = 6.6 Hz, 1.46H), 3.06 (d, *J* = 6.6 Hz, 1.09H), 4.66 (s, 1.44H), 4.69 (s, 0.93H), 6.64 (d, *J* = 2.4 Hz, 0.99H), 6.75 (s, 1.44H), 7.07 (d, *J* = 2.4 Hz, 1.07H), 7.16 (s, 1.51H), 7.19-7.21 (m, 2.53H), 7.27-7.30 (m, 2.32H), 7.32-7.35 (m, 2.62H), 7.61 (d, *J* = 7.8 Hz, 1.50H), 7.64 (d, *J* = 7.8 Hz, 1.05H). **¹³C NMR** (150 MHz, CDCl₃): δ 15.9, 15.9, 25.3, 25.5, 31.9, 32.2, 52.0, 52.3, 77.9, 78.0, 106.8, 108.9, 118.1, 120.1, 120.5, 122.0, 122.4, 122.6, 123.9, 124.0, 126.0, 127.9, 128.1, 128.1, 128.4, 128.5, 128.7, 137.2, 137.6, 143.9, 145.4, 148.9, 149.8, 207.0, 207.2. **HRMS** (ESI-TOF) Calcd for (C₁₈H₁₈NaO₃⁺ [M+Na]⁺) 305.1148. Found 305.1151.

1-(3-chloro-2-hydroxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one (3r)
1-(4-chloro-2-hydroxy-6-methyl-6H-benzo[c]chromen-6-yl)propan-2-one (3r')



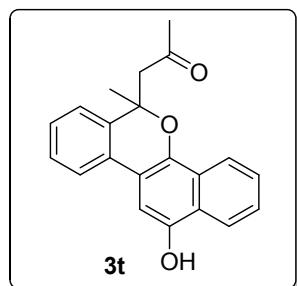
Yellowish solid, 35% yield. **¹H NMR** (500 MHz, CDCl₃): δ 1.76 (s, 3.19H), 1.77 (s, 0.47H), 2.05 (s, 2.70H), 2.15 (s, 0.40H), 2.84 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 13.5 Hz, 0.14H), 3.04 (d, *J* = 14.0 Hz, 1H), 3.11 (d, *J* = 14.0 Hz, 0.13H), 5.41 (s, 1H), 6.87 (d, *J* = 3.0 Hz, 0.14H), 6.97 (s, 0.84H), 7.15 (d, *J* = 2.5 Hz, 0.16H), 7.22 (d, *J* = 8.0 Hz, 1.07H), 7.25 (s, 0.13H), 7.32 (t, *J* = 7.5 Hz, 1.16H), 7.36 (t, *J* = 7.5 Hz, 1.21H), 7.40 (s, 0.95H), 7.62 (s, 0.12H), 7.65 (d, *J* = 7.5 Hz, 1.03H). **¹³C NMR** (150 MHz, CDCl₃): δ 25.4, 31.9, 32.2, 52.2, 78.5, 108.3, 109.9, 117.2, 118.2, 120.1, 122.4, 122.5, 122.7, 124.0, 124.1, 127.5, 128.3, 128.3, 128.7, 128.9, 137.3, 145.6, 146.6, 206.6. **HRMS** (ESI-TOF) Calcd for (C₁₇H₁₅ClNaO₃⁺ [M+Na]⁺) 325.0602. Found 325.0603.

1-(4-(*tert*-butyl)-2-hydroxy-6-methyl-6H-benzo[*c*]chromen-6-yl)propan-2-one (**3s**)



Purple liquid, 72% yield. **¹H NMR** (500 MHz, CDCl₃): δ 1.39 (s, 9H), 1.77 (s, 3H), 1.88 (s, 3H), 2.97 (d, *J* = 14.0 Hz, 1H), 3.30 (d, *J* = 14.0 Hz, 1H), 5.60 (s, 1H), 6.84 (d, *J* = 3.0 Hz, 1H), 7.13 (d, *J* = 3.0 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.25 (t, *J* = 7.0 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H). **¹³C NMR** (150 MHz, CDCl₃): δ 25.8, 29.9, 32.0, 34.7, 52.0, 78.1, 107.3, 114.9, 123.0, 123.3, 123.8, 127.9, 128.2, 129.1, 136.7, 140.7, 144.3, 149.8, 207.5. **HRMS** (ESI-TOF) Calcd for (C₂₁H₂₄NaO₃⁺ [M+Na]⁺) 347.1618. Found 347.1629.

1-(12-hydroxy-6-methyl-6H-dibenzo[*c,h*]chromen-6-yl)propan-2-one (**3t**)

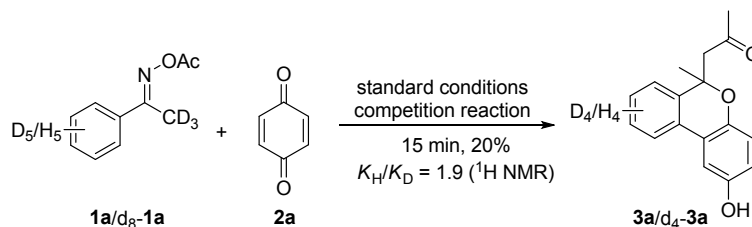


Brown solid, 62% yield, m.p. 135-136 °C. **¹H NMR** (500 MHz, CDCl₃): δ 1.87 (s, 3H), 1.99 (s, 3H), 2.94 (d, *J* = 14.0 Hz, 1H), 3.14 (d, *J* = 14.0 Hz, 1H), 6.39 (s, 1H), 7.21-7.29 (m, 4H), 7.48-7.51 (m, 2H), 7.56 (d, *J* = 7.0 Hz, 1H), 8.15-8.19 (m, 2H). **¹³C NMR** (125 MHz, CDCl₃): δ 25.3,

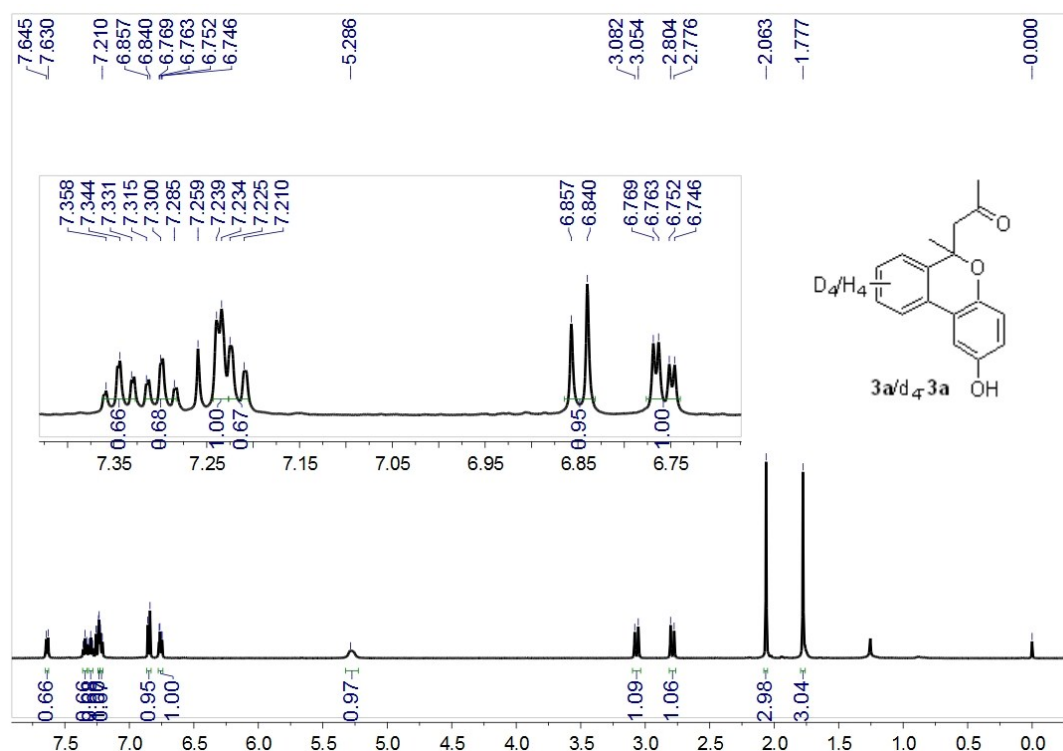
32.3, 51.8, 78.6, 102.9, 115.8, 121.8, 122.0, 122.2, 123.9, 126.0, 126.4, 127.8, 128.2, 128.7, 136.9, 140.9, 146.5, 207.7. **HRMS** (ESI-TOF) Calcd for (C₂₁H₁₈NaO₃⁺ [M+Na]⁺) 341.1148. Found 341.1155.

III. Kinetic Isotope Effect Experiments

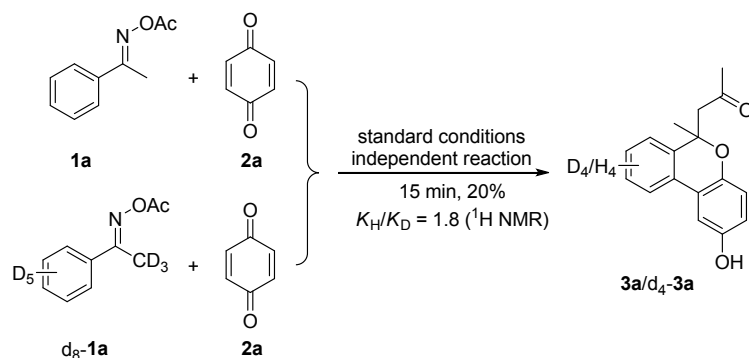
a) The Competition Reaction



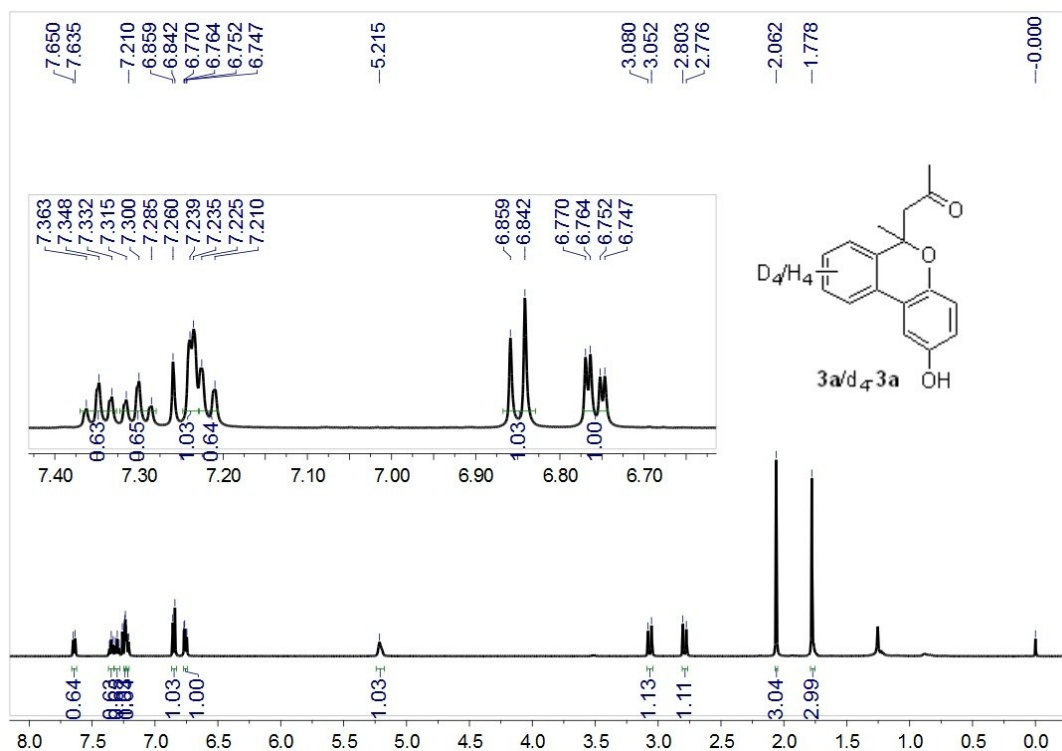
According to the general procedure, to a schlenk tube (15 mL) equipped with a stirring bar was added **1a** (35.4 mg, 0.2 mmol), **d₈-1a** (37.0 mg, 0.2 mmol), **2a** (32.4 mg, 0.3 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol), AgSbF₆ (6.9 mg, 0.02 mmol) and Zn(NTf₂)₂ (12.5 mg, 0.02 mmol). Acetone (1.0 mL) and EtOH (1.0 mL) were then added. The reaction vessel was sealed and stirred at 70 °C for 15 min. The reaction mixture was quenched with saturated Na₂CO₃ solution (10 mL) at 0 °C and extracted with EtOAc (2 × 10 mL). The organic phase was combined. After dried over Na₂SO₄, the organic phase was concentrated in vacuo. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1, v/v) to afford the desired product **3a** and **d₄-3a**. **KIE=1.9**.



b) The Independent Reaction



According to the general procedure, to a schlenk tube (15 mL) equipped with a stirring bar was added **1a** (35.4 mg, 0.2 mmol), **2a** (32.4 mg, 0.3 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), AgSbF_6 (6.9 mg, 0.02 mmol) and $\text{Zn}(\text{NTf}_2)_2$ (12.5 mg, 0.02 mmol). Acetone (1.0 mL) and EtOH (1.0 mL) were then added. In another sealed tube was added **d₈-1a** (37.0 mg, 0.2 mmol), **2a** (32.4 mg, 0.3 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 0.005 mmol), AgSbF_6 (6.9 mg, 0.02 mmol), $\text{Zn}(\text{NTf}_2)_2$ (12.5 mg, 0.02 mmol), acetone (1.0 mL) and EtOH (1.0 mL). These two reaction mixtures were stirred side-by-side at 70 °C for 15 min. These two mixtures were rapidly combined and the combined mixture was quenched with saturated Na_2CO_3 solution (10 mL) at 0 °C and extracted with EtOAc (2×10 mL). The organic phase was combined. 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 desired product **3a** and **d₄-3a**. **KIE=1.8**.

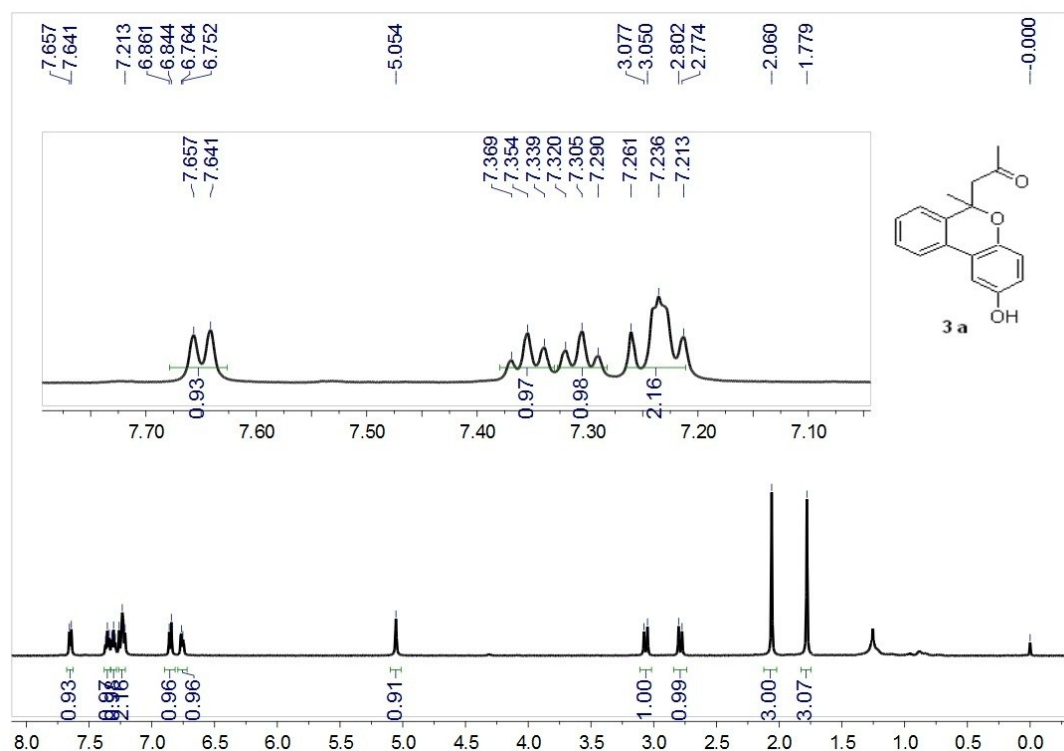


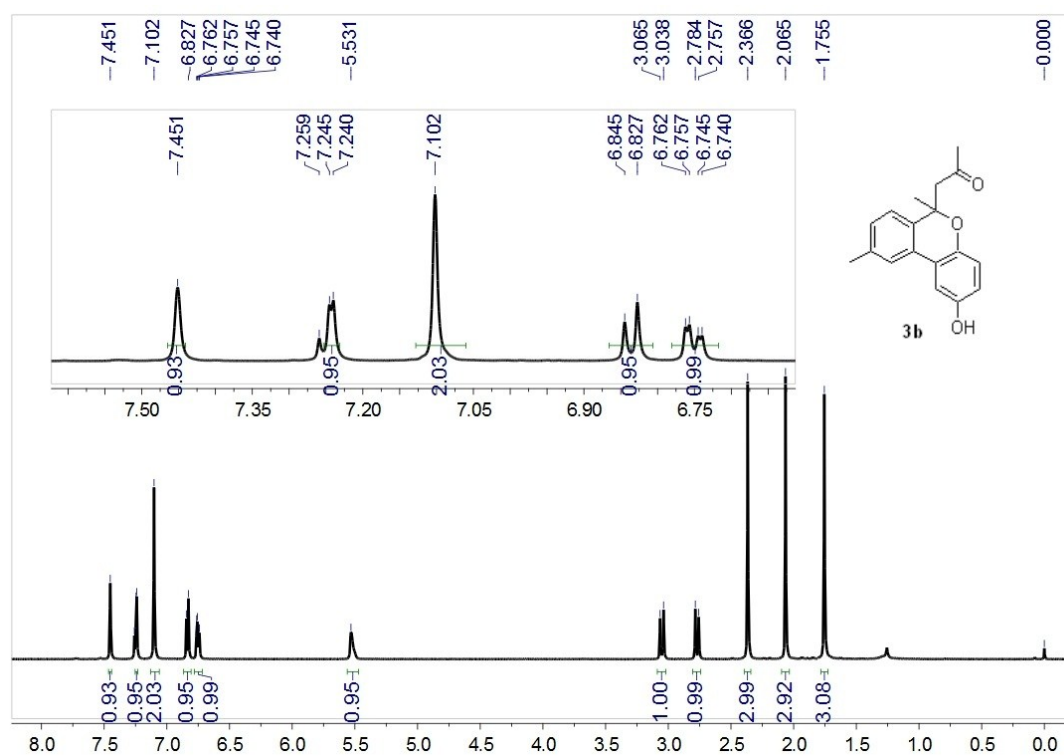
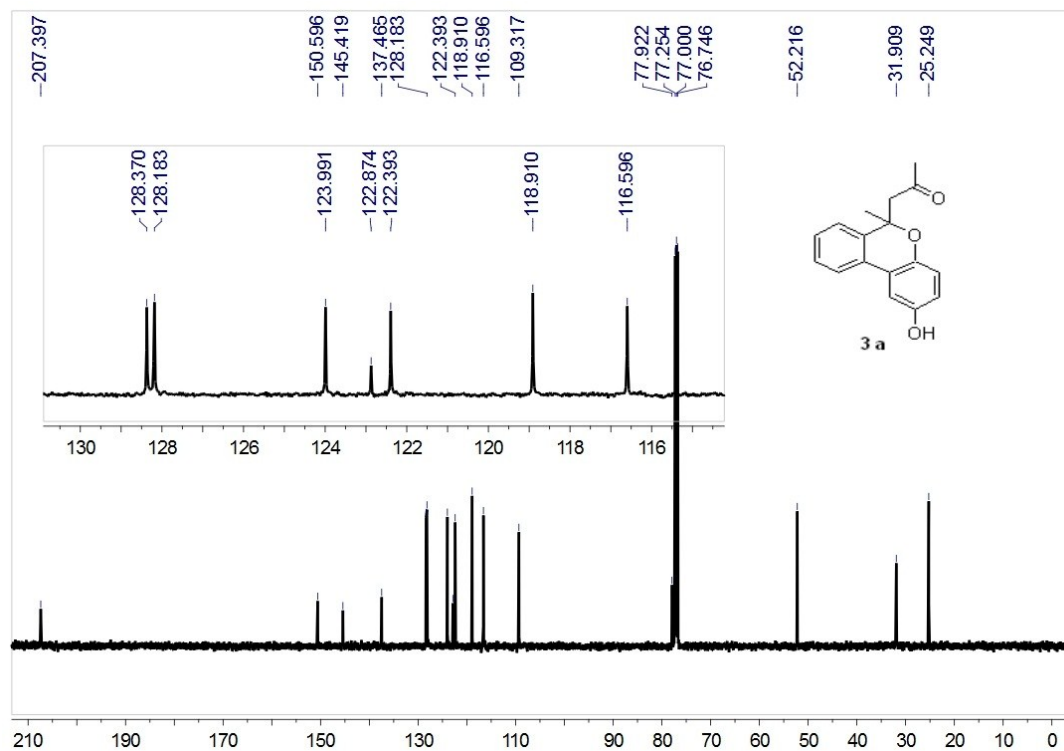
IV. Antibacterial Assay²

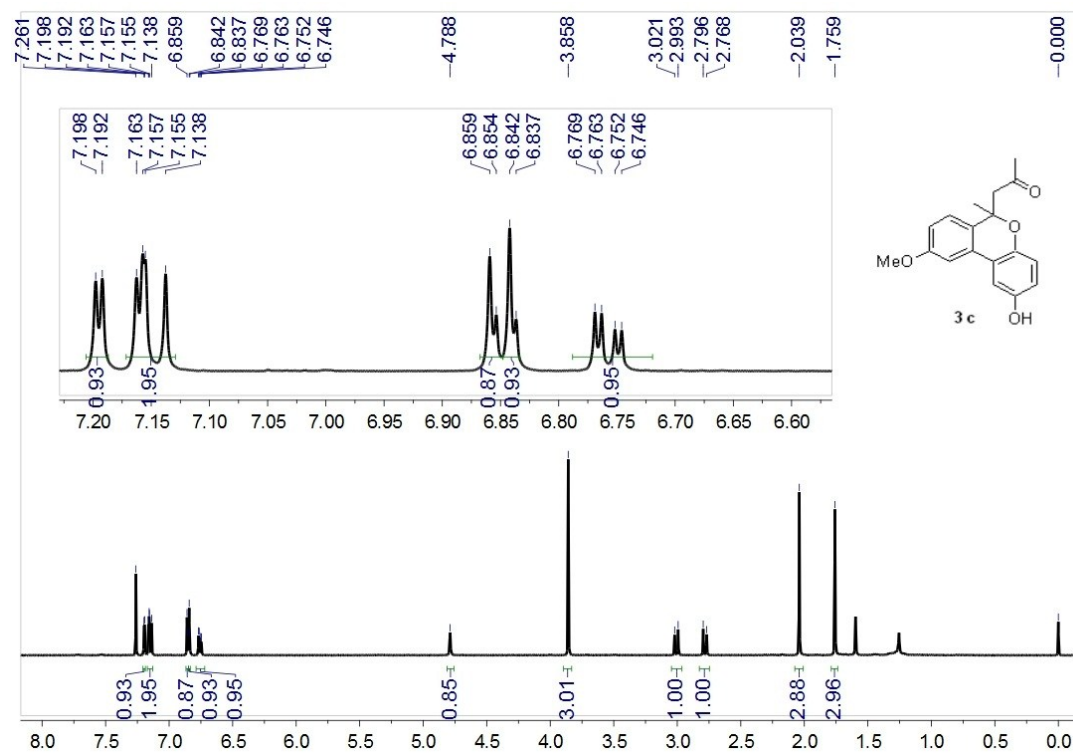
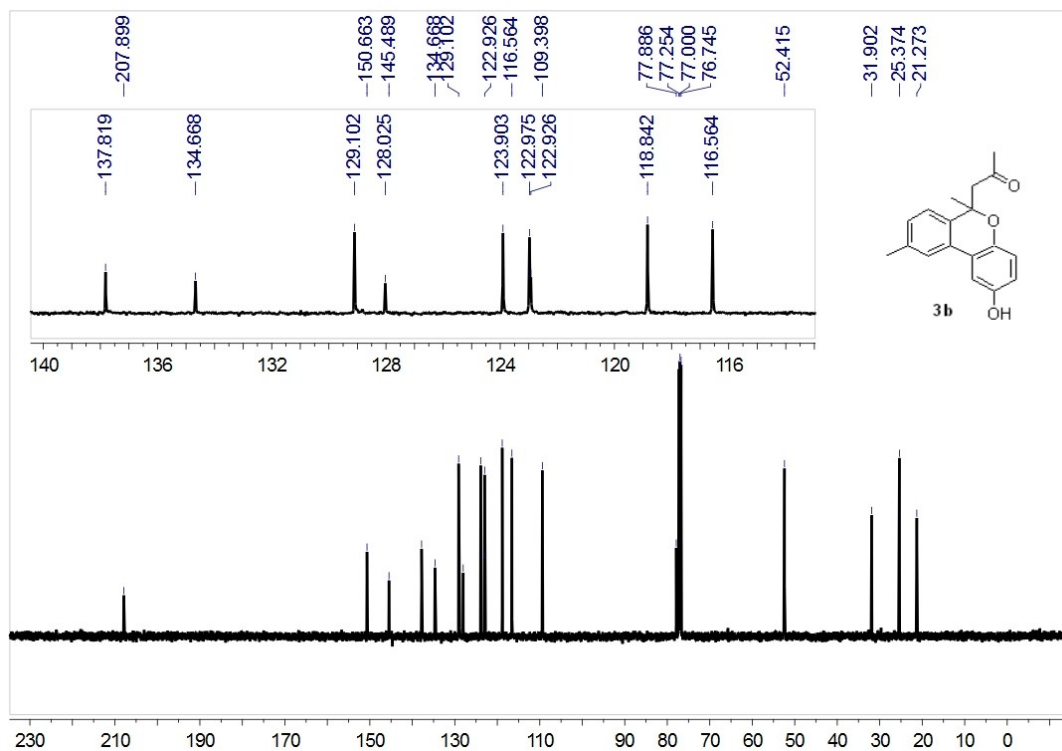
The technique used was based on a method published by the National Committee of Laboratory Safety and Standards (NCLSS) in 1997.³ Products dissolved in DMSO (not exceeding 5%, total volume) were incubated with two bacterial strains (China General Microbiological Culture

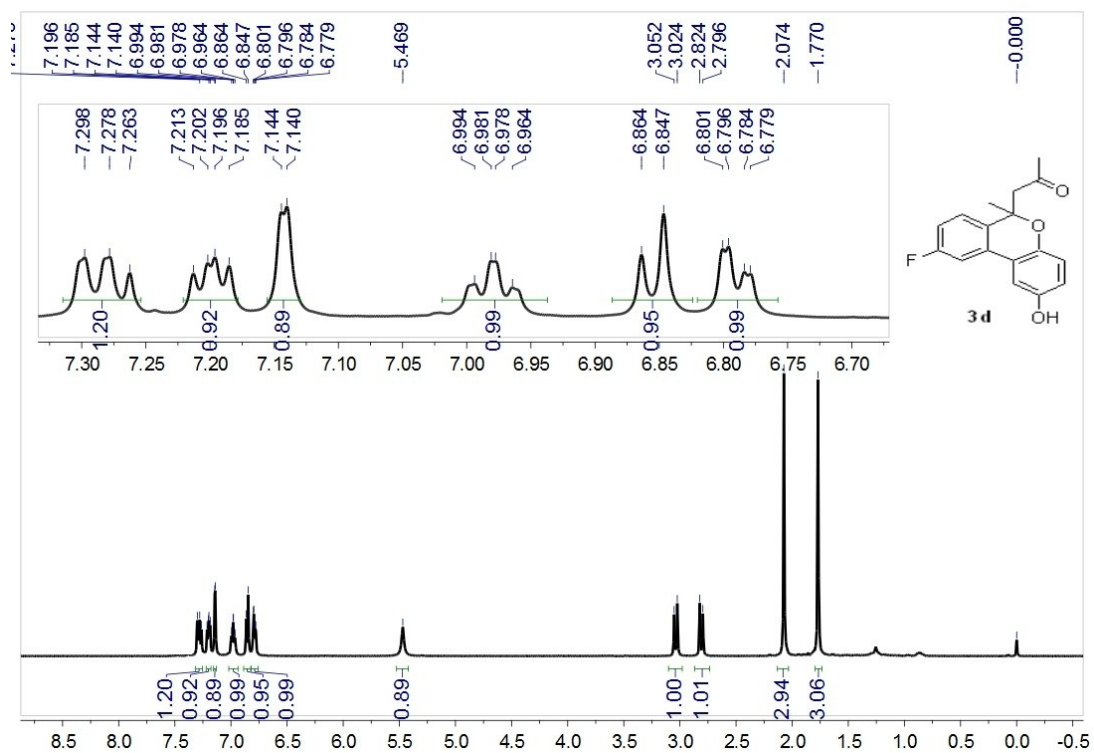
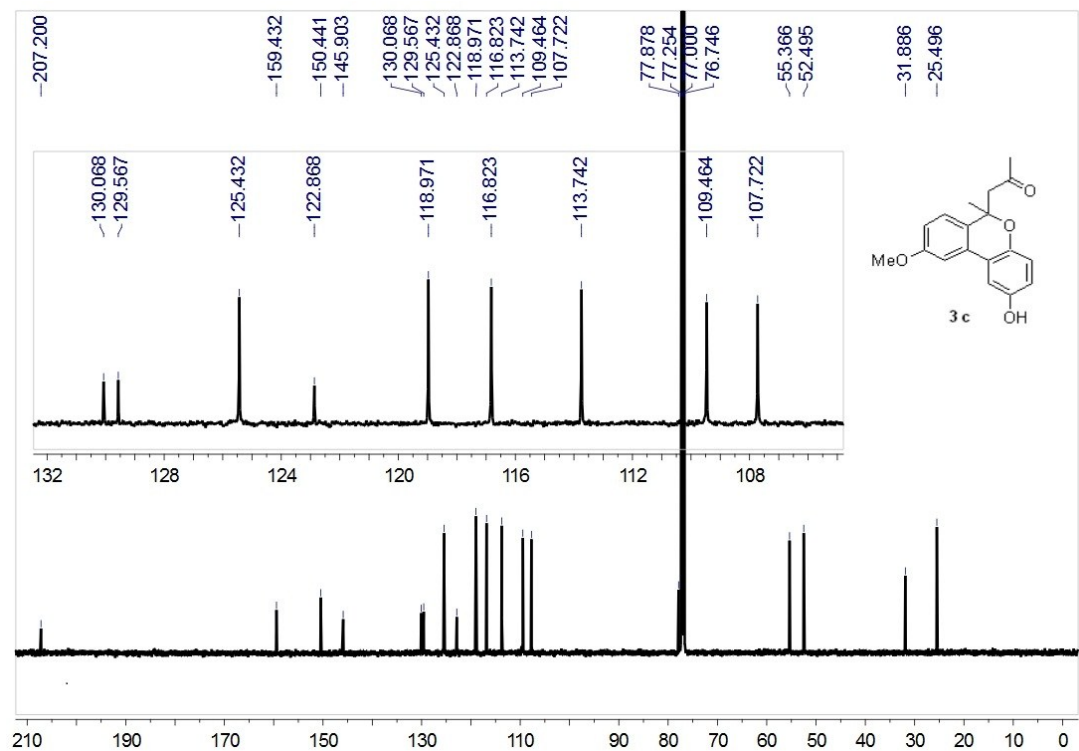
Collection Center), a Gram-positive (*Micrococcus luteus*) and a Gram-negative (*Escherichia coli*), in 96-well plates (MERCK) in PB medium, at 37 °C during 24 h, under stirring. Assays were carried out in triplicate and the results averaged. Growth was evaluated by reading optical density (630 nm). When an activity was detected (absence of growth), a sample of media was taken on rich solid medium (Petri dishes) to establish the effect (bacteriostatical or bactericidal effect).

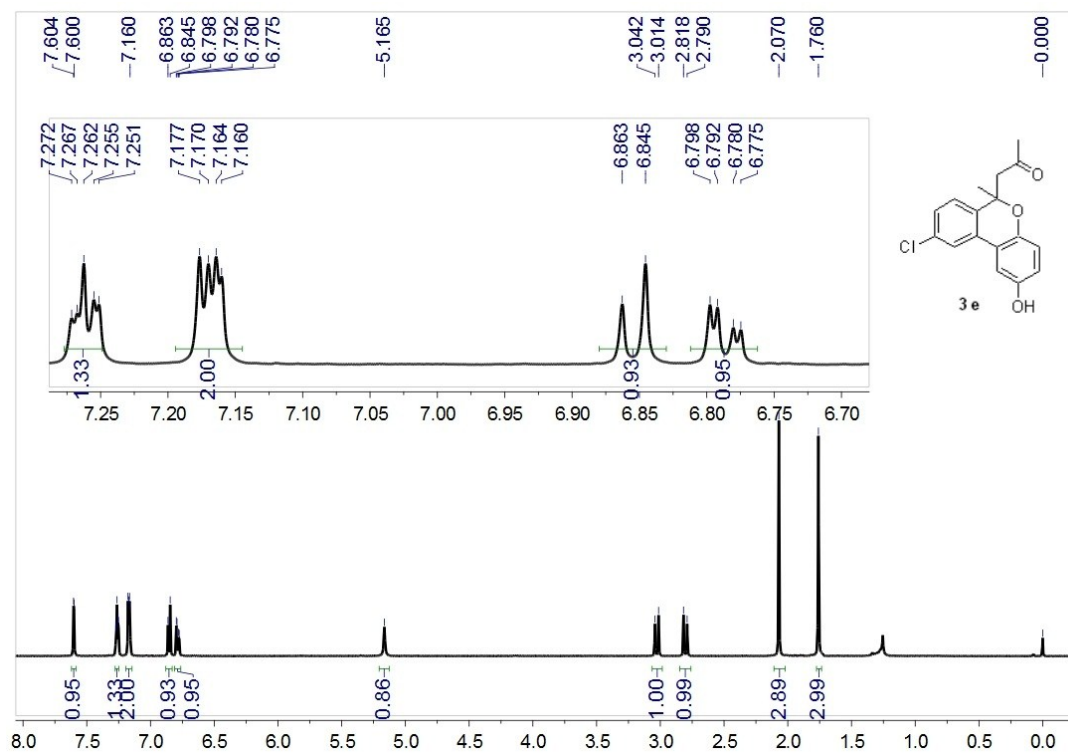
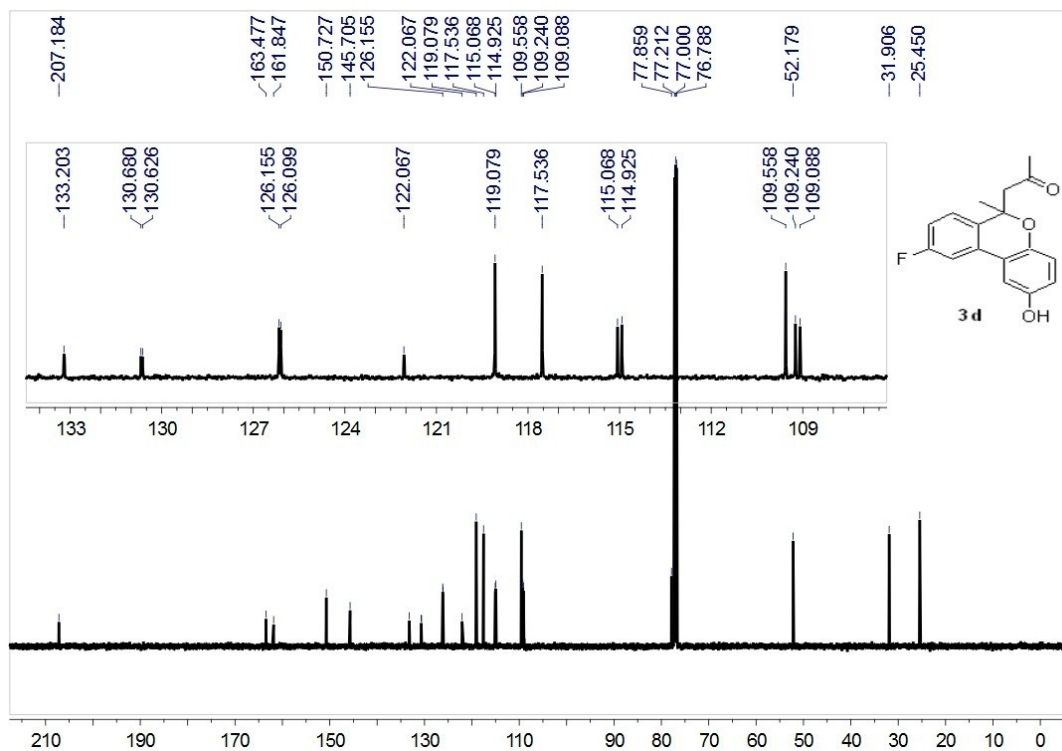
V. Copies of ^1H NMR and ^{13}C NMR Spectra

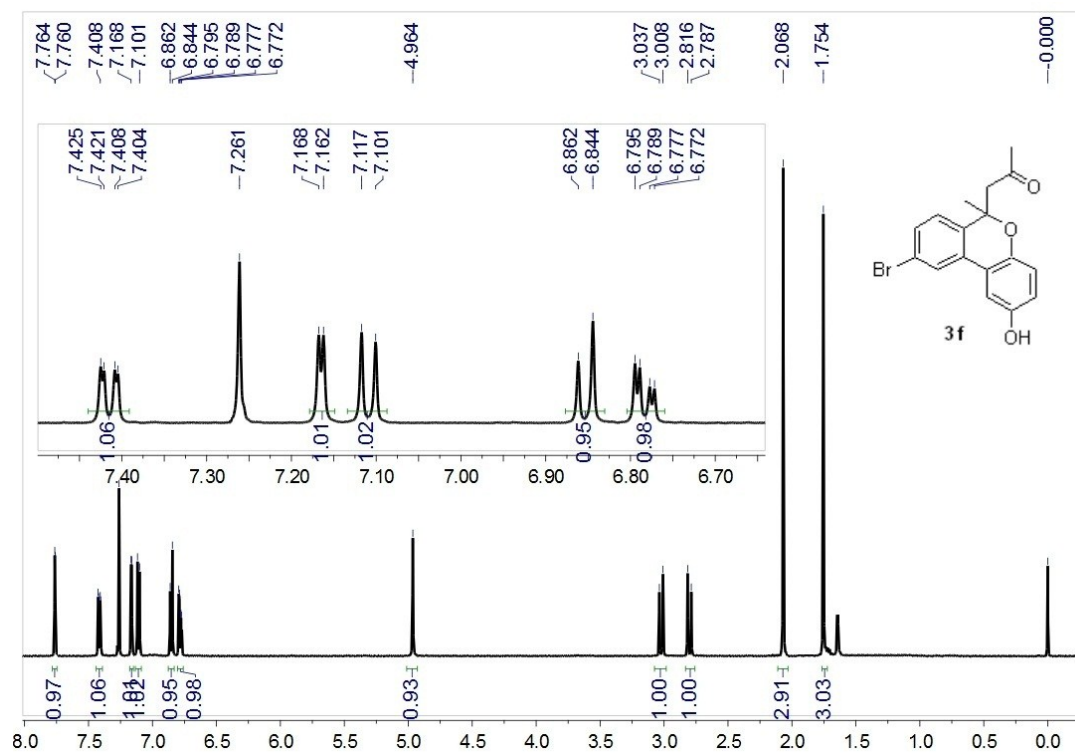
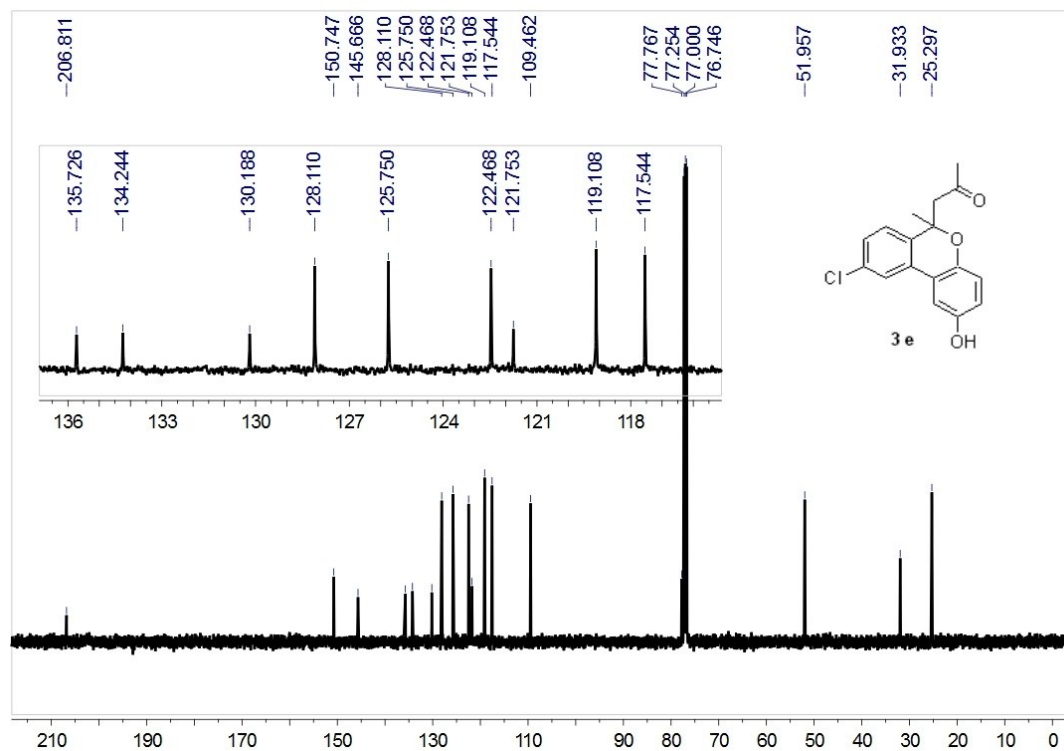


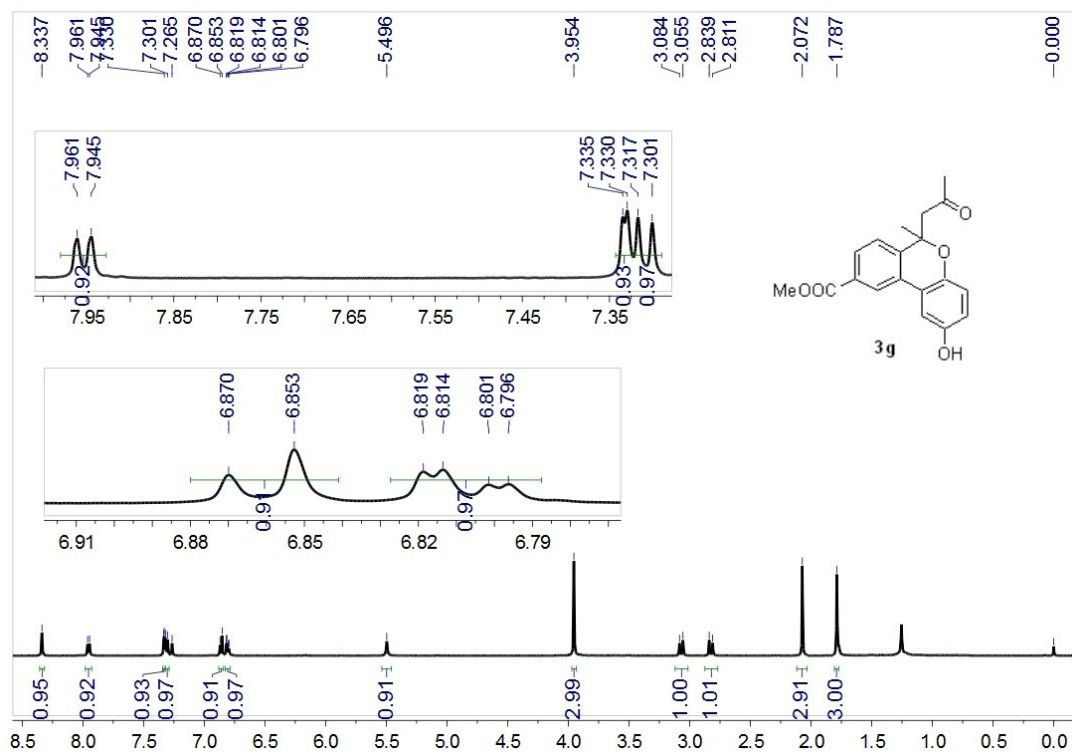
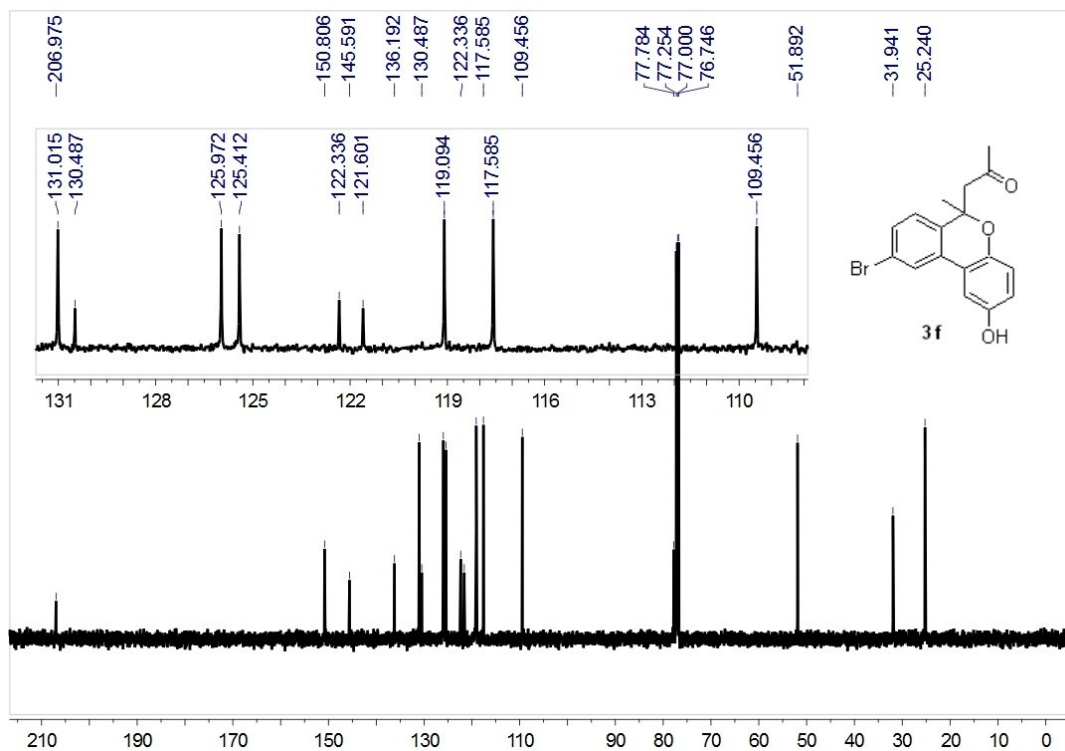


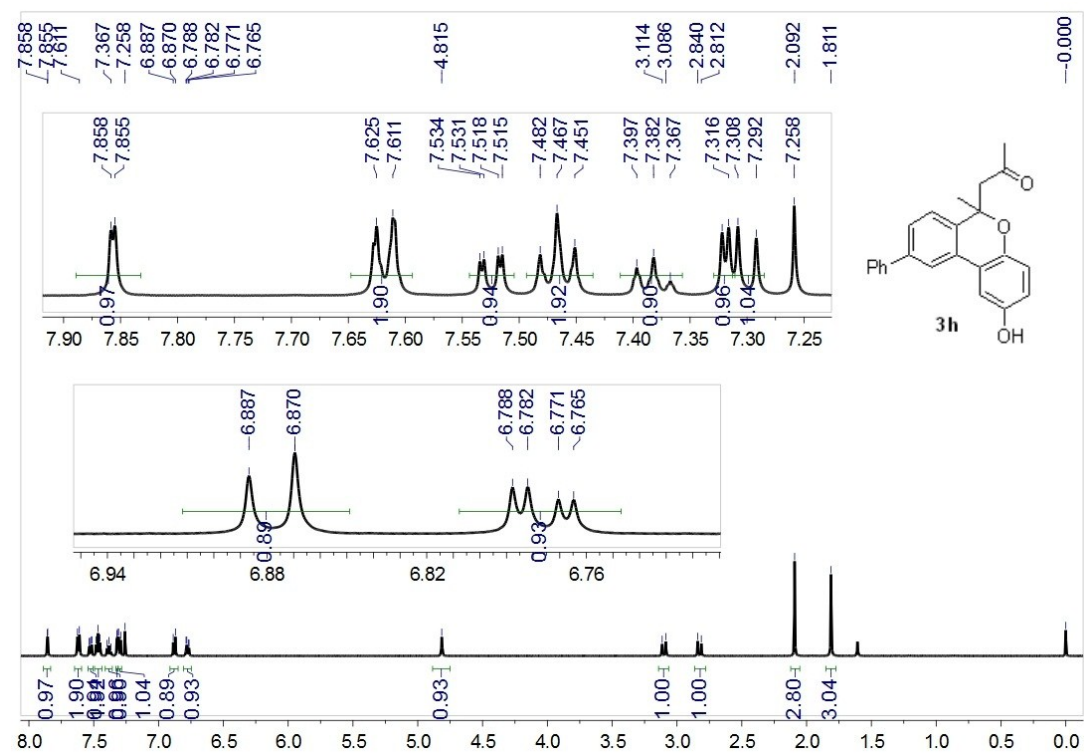
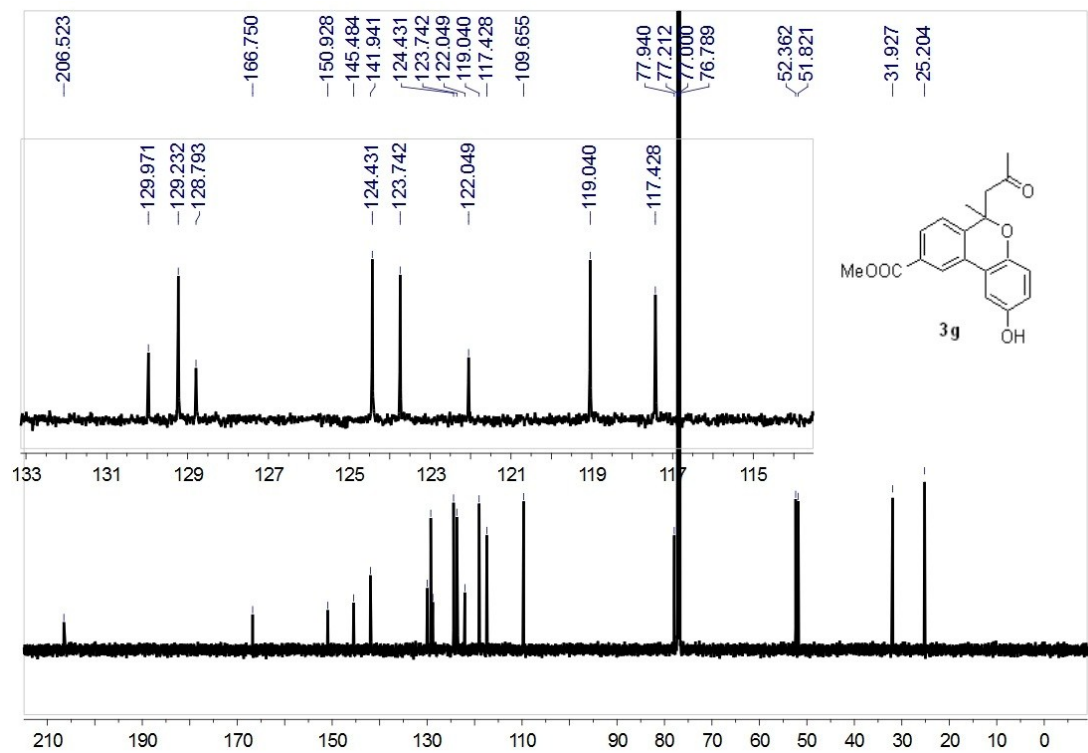


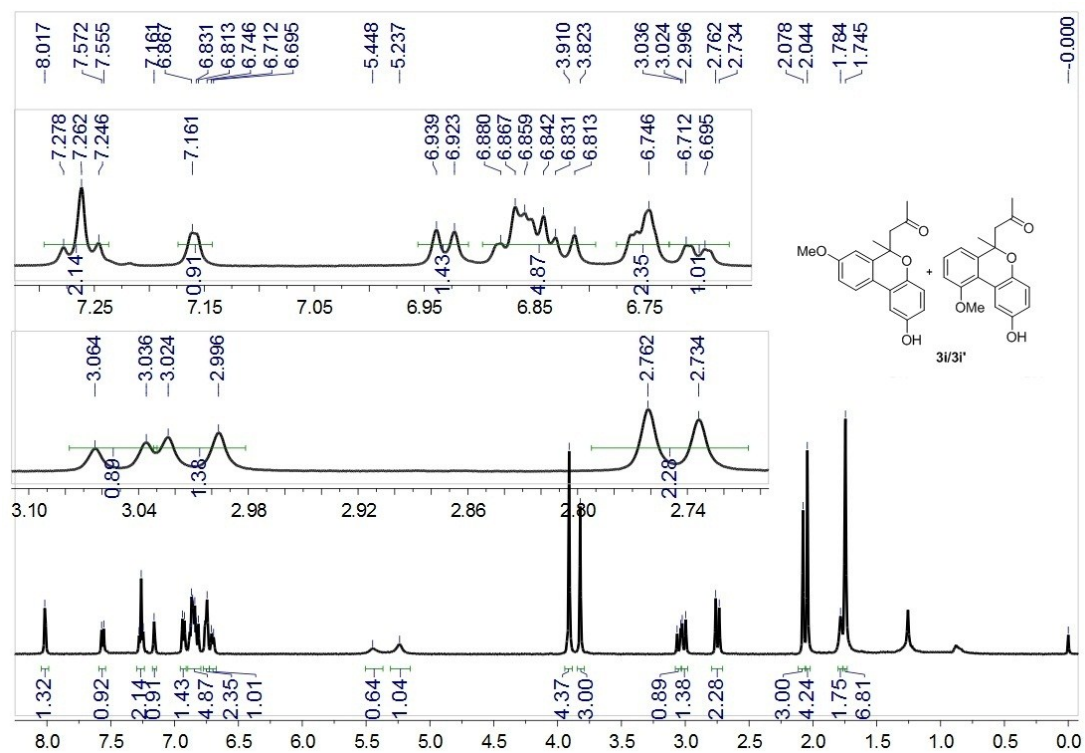
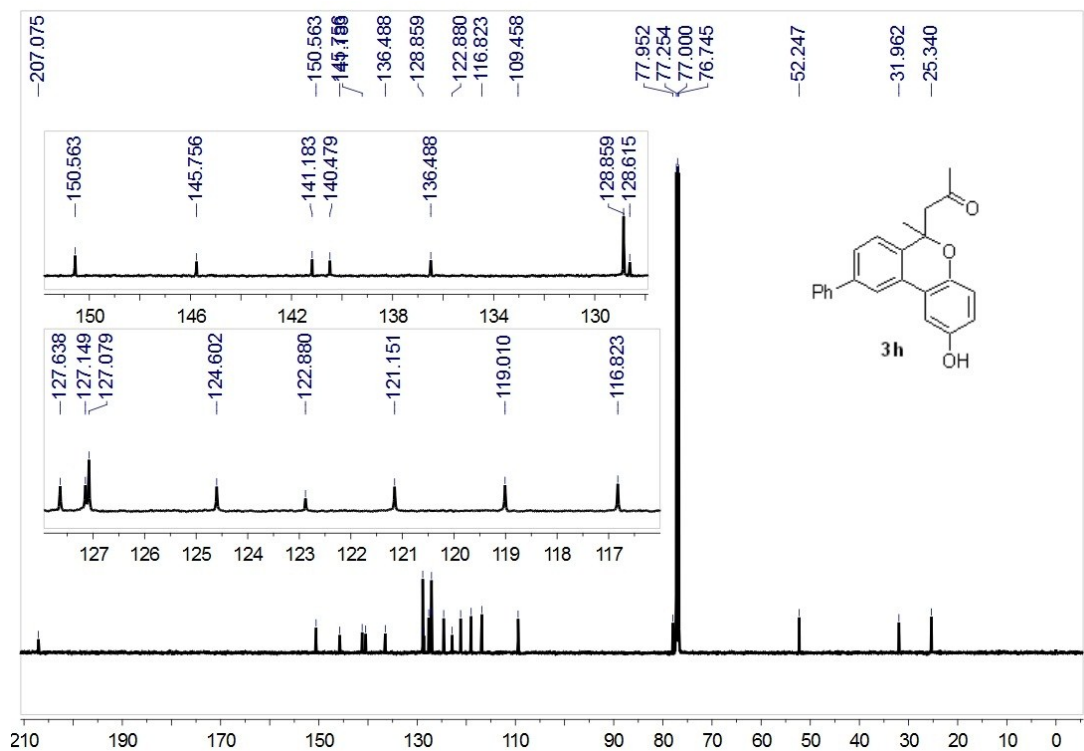


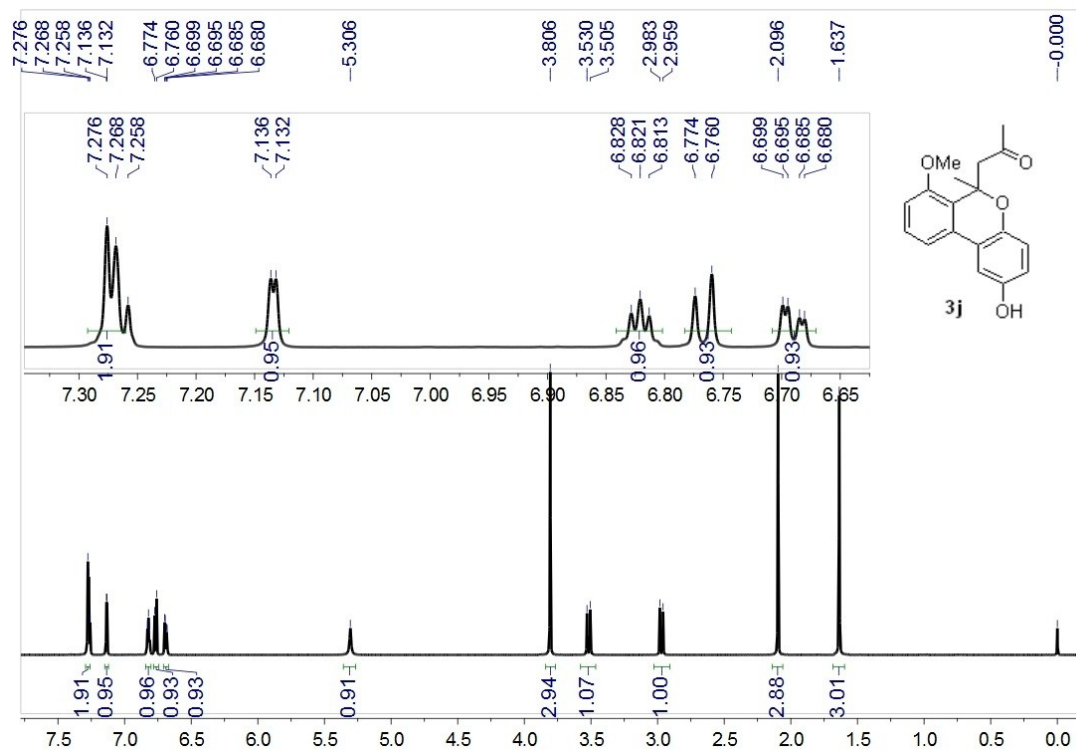
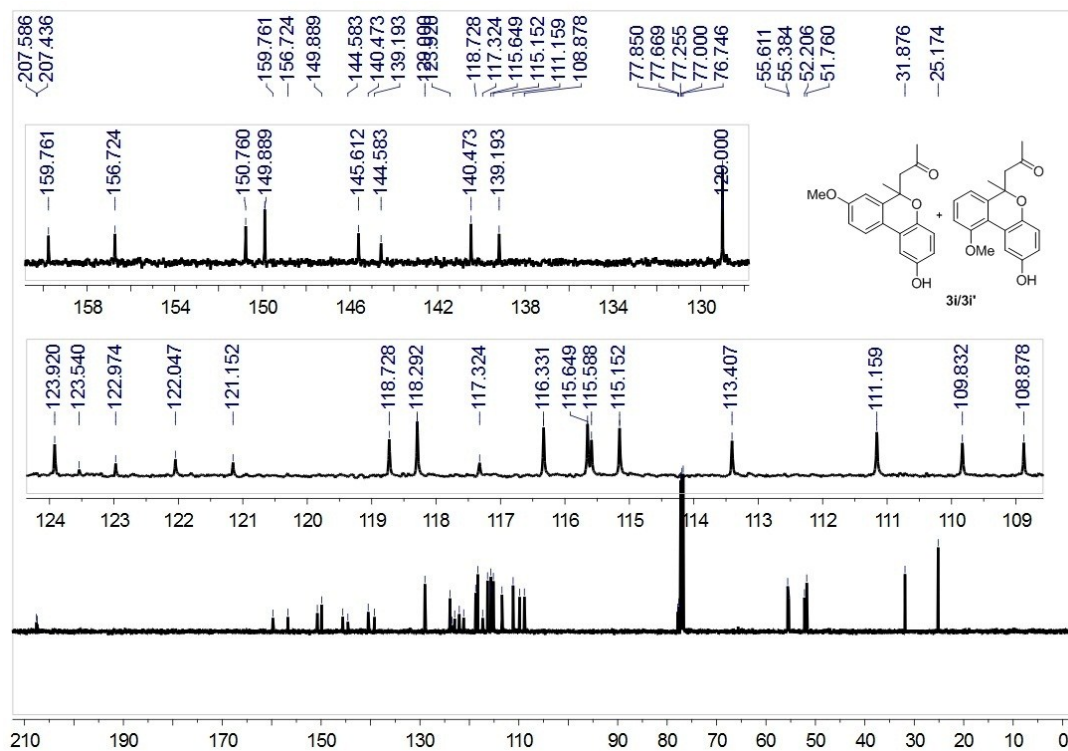


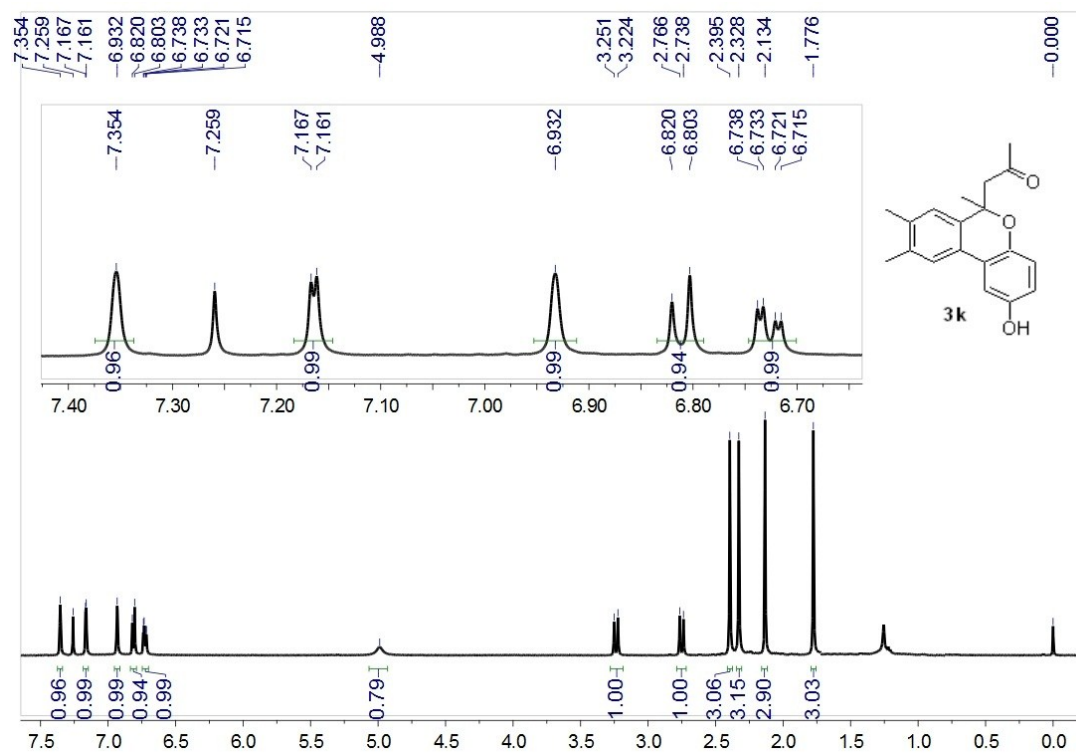
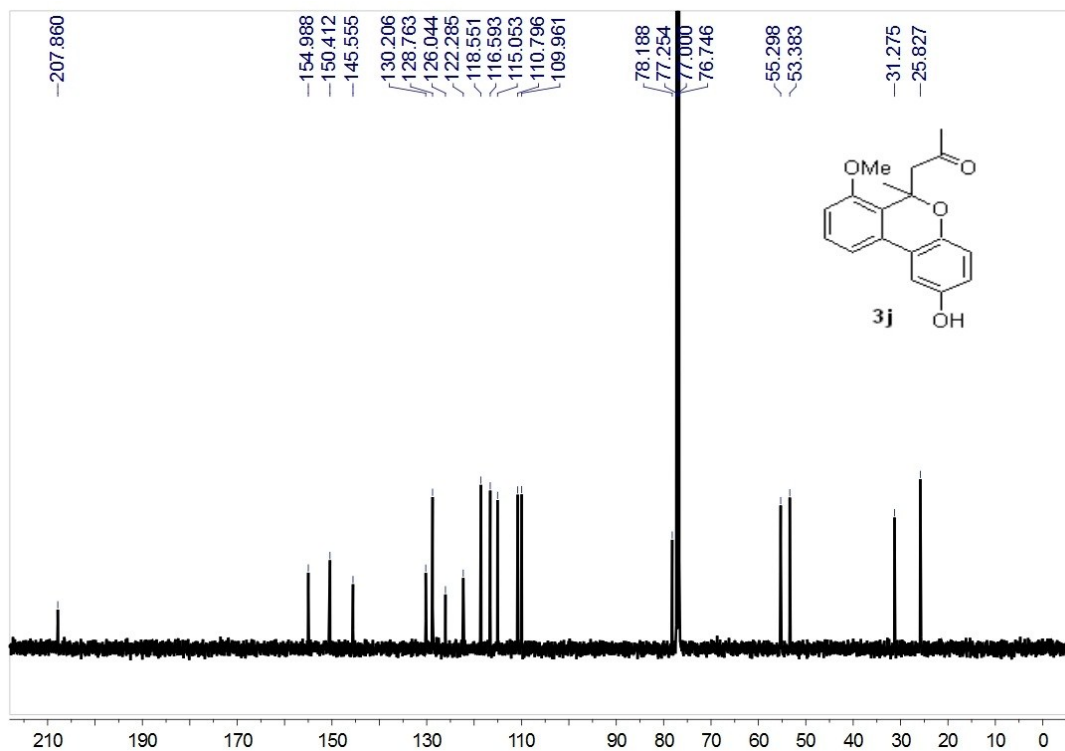


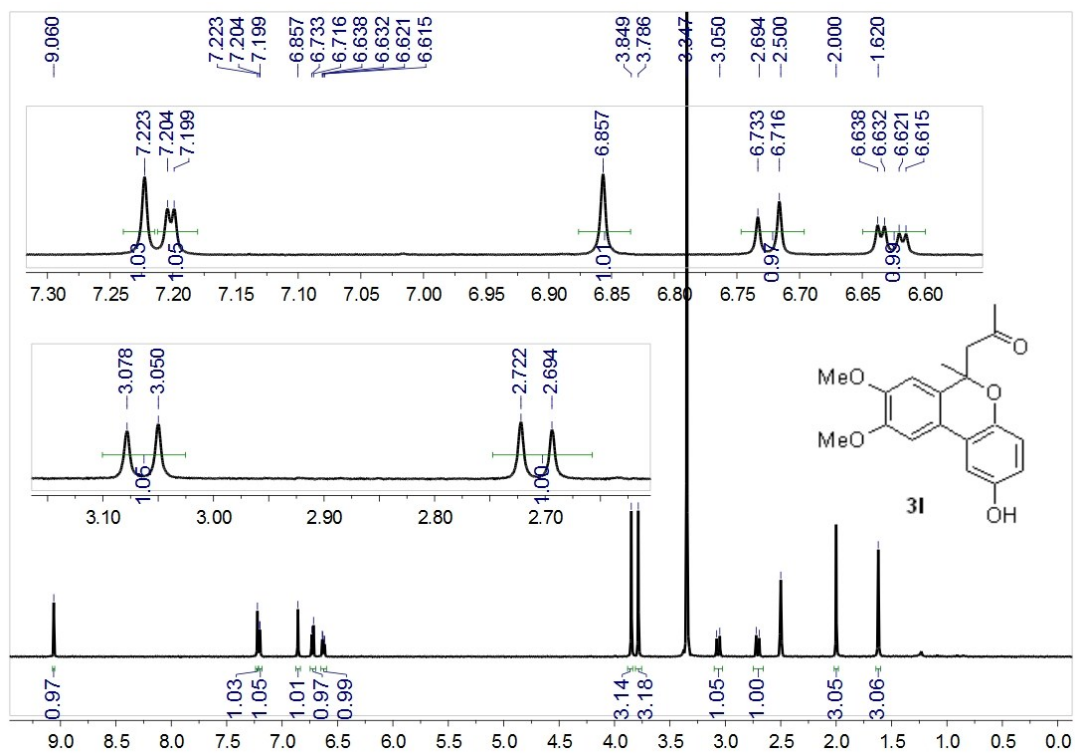
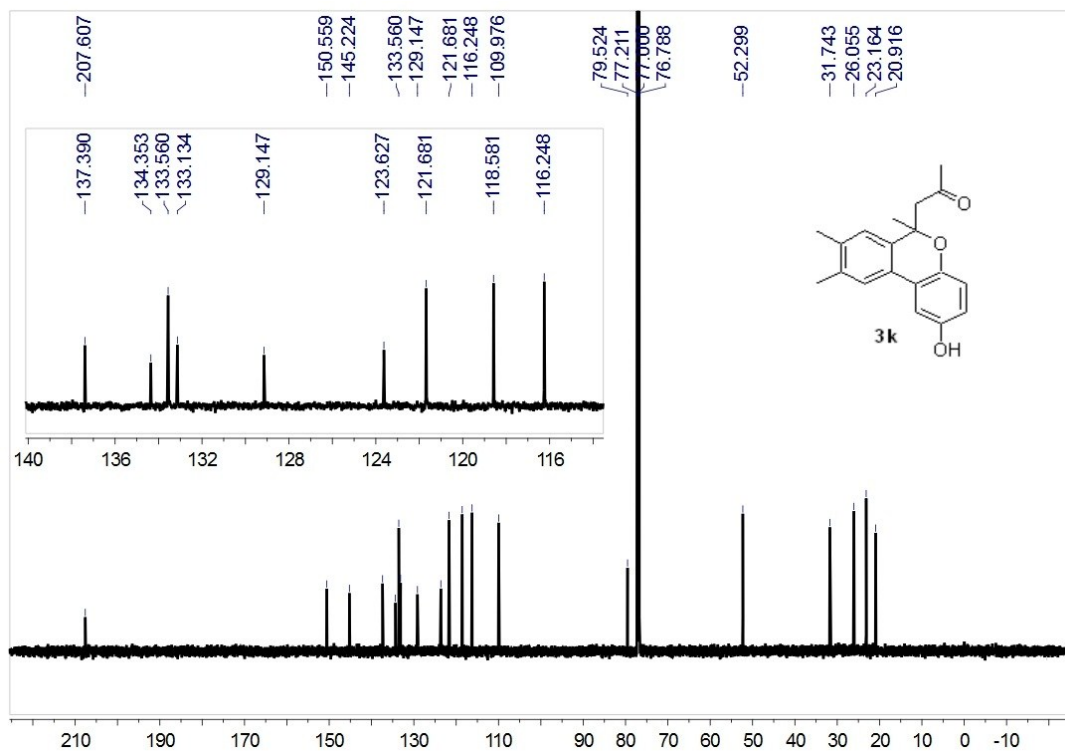


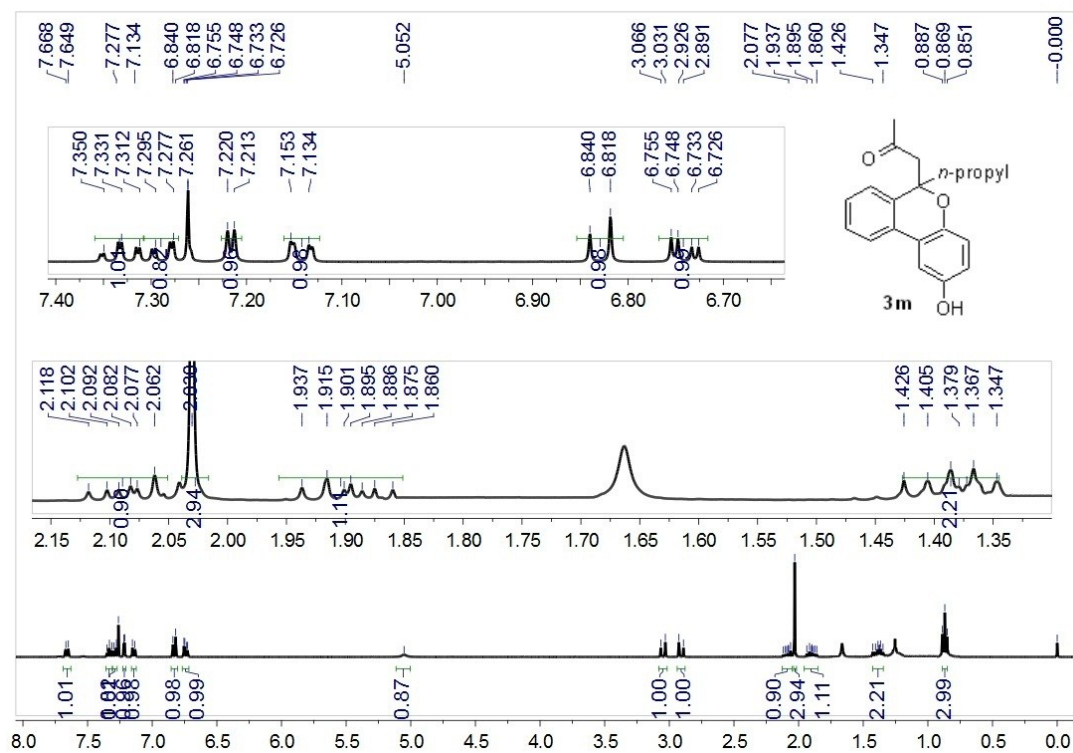
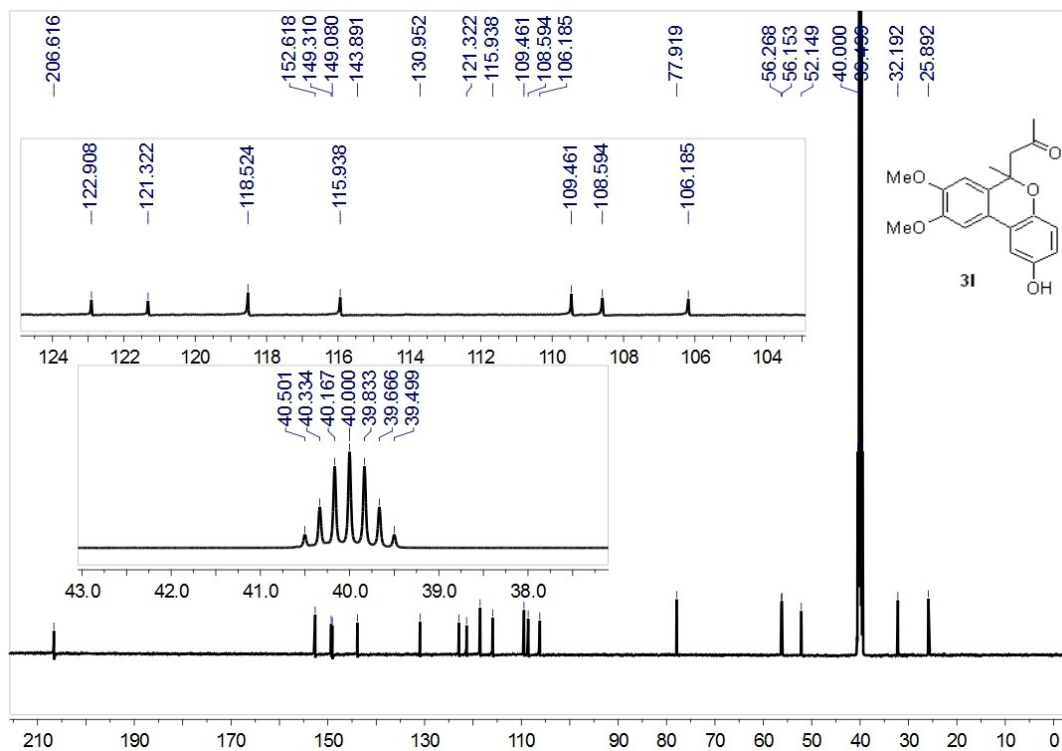


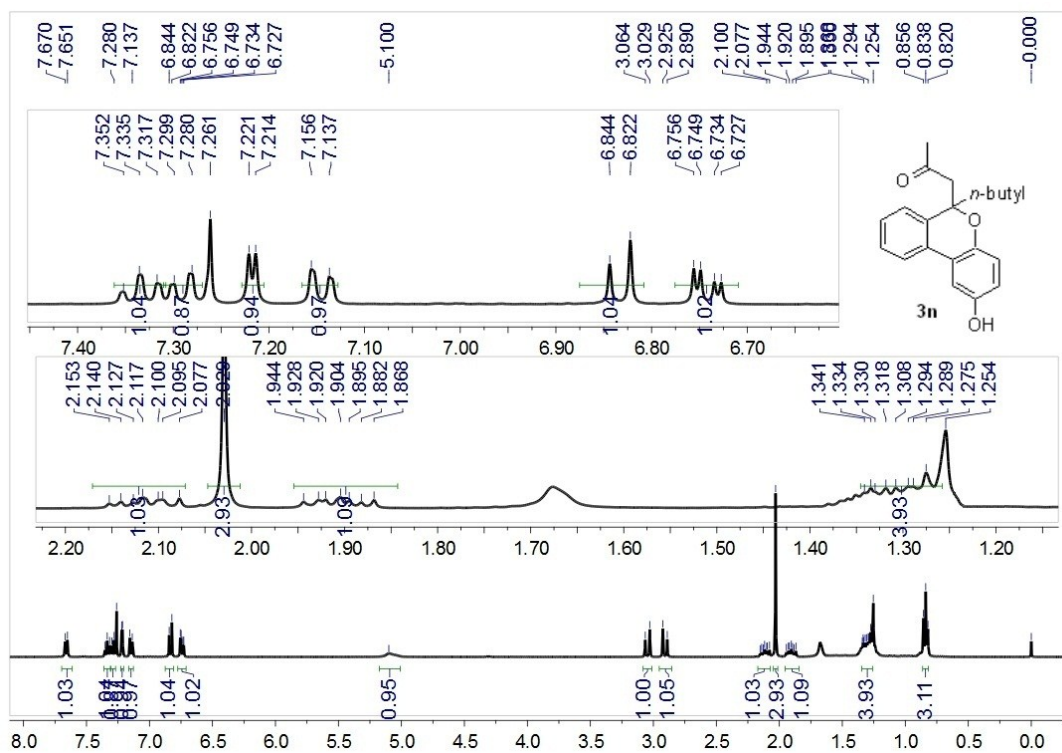
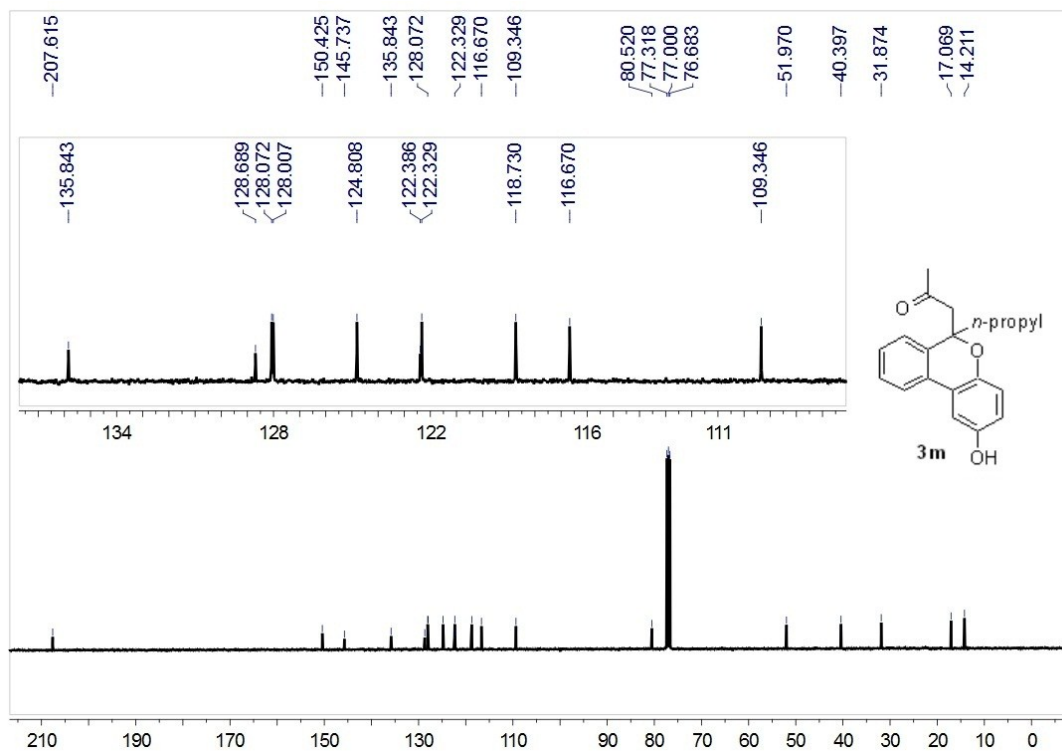


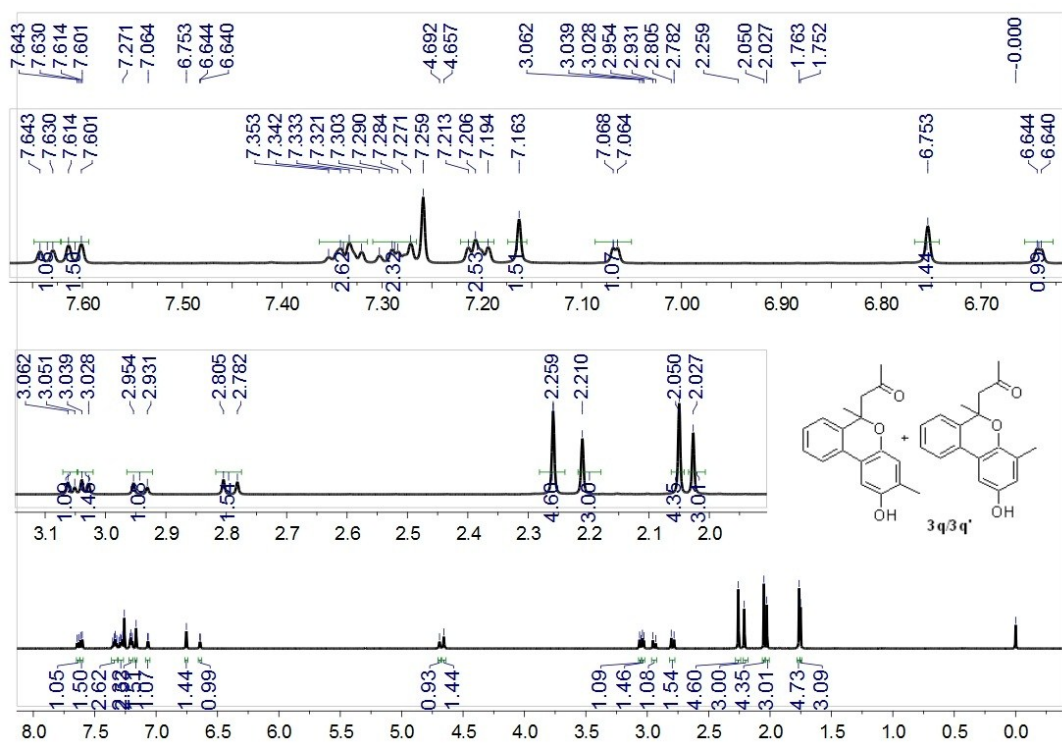
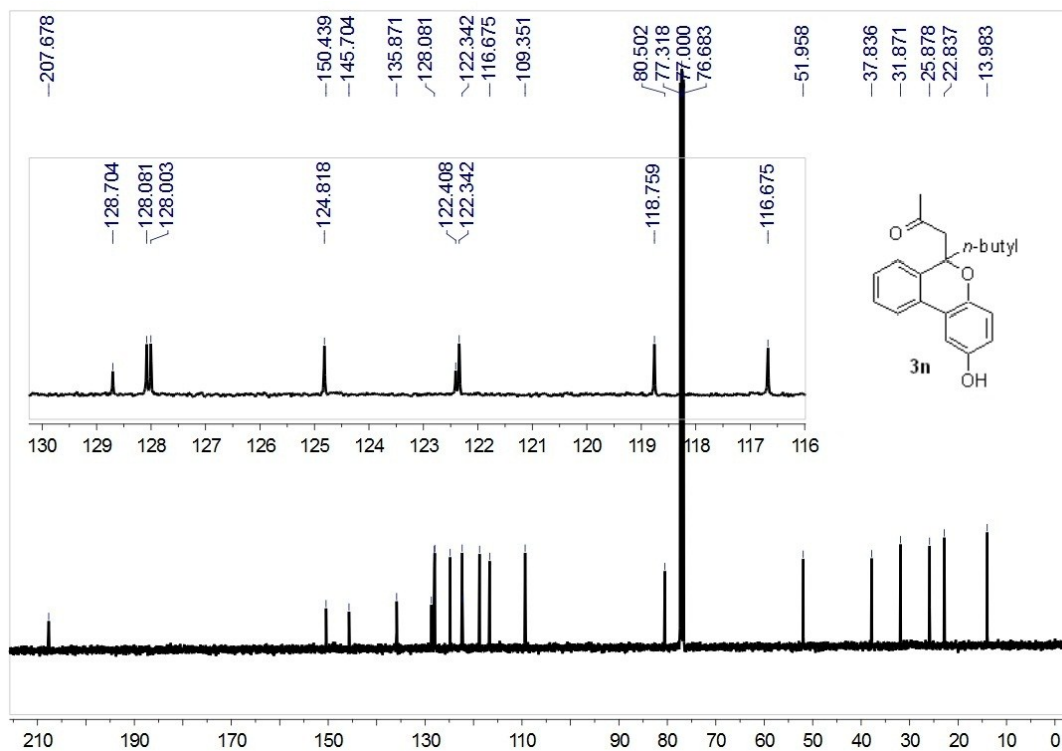


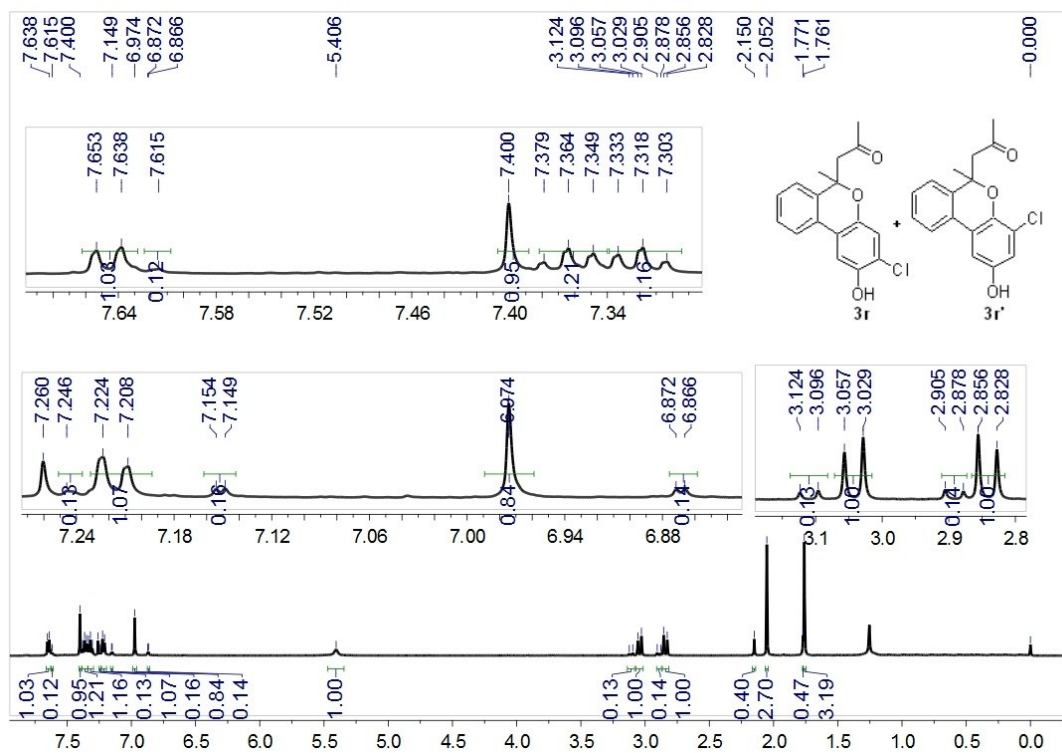
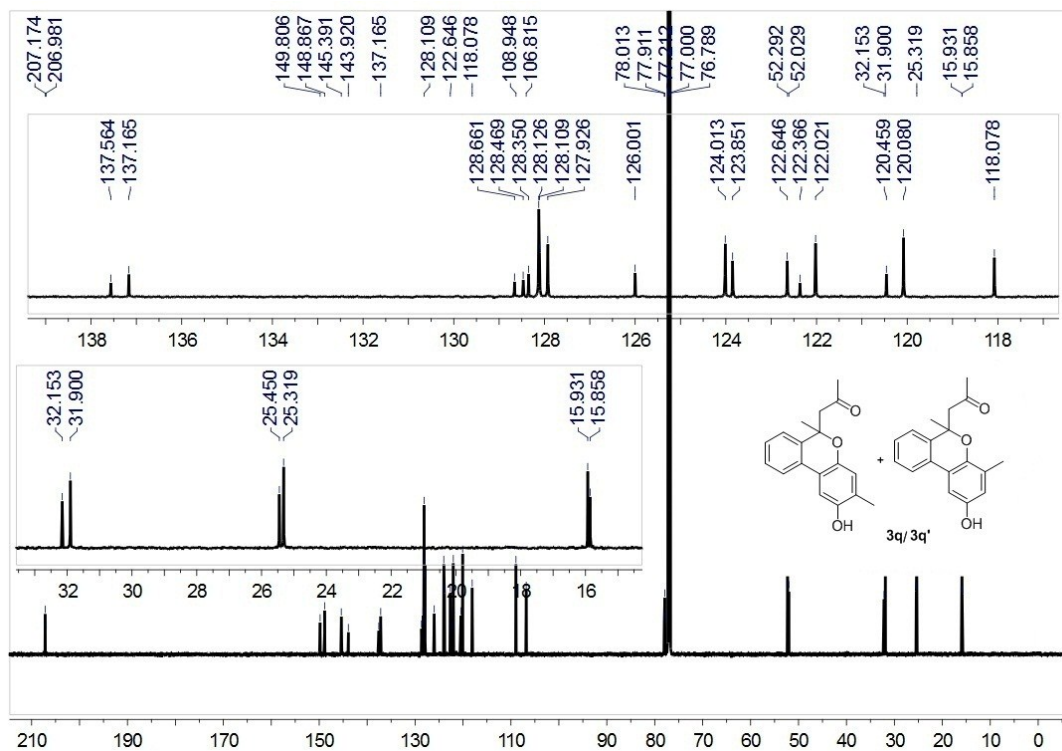


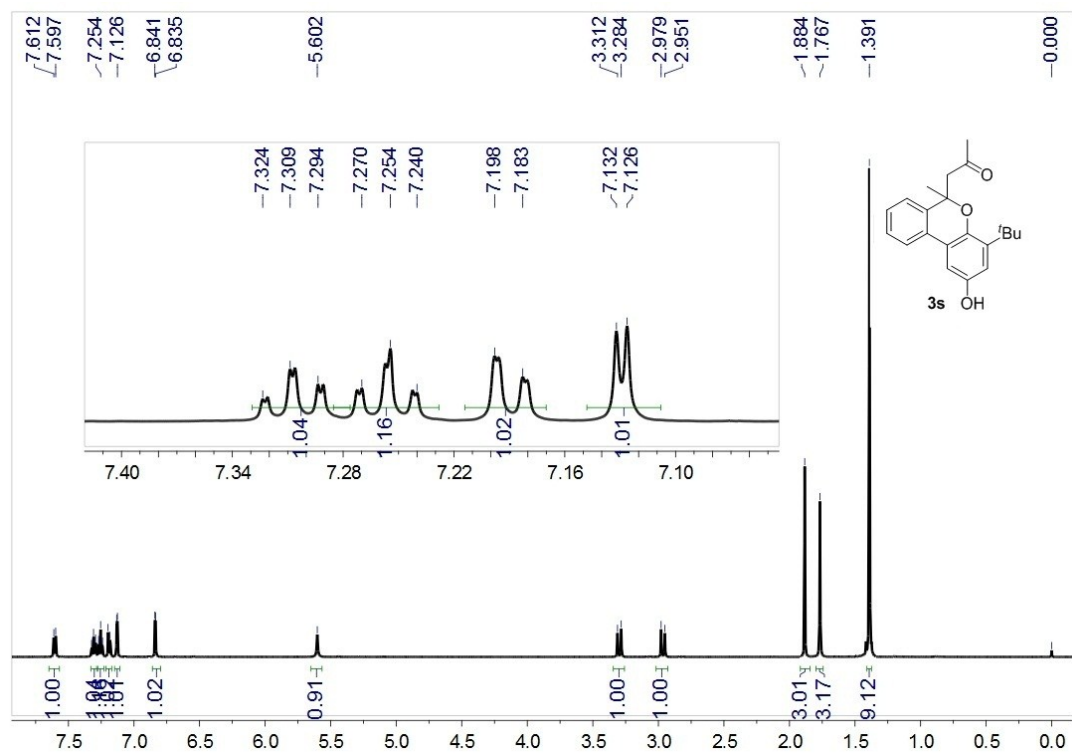
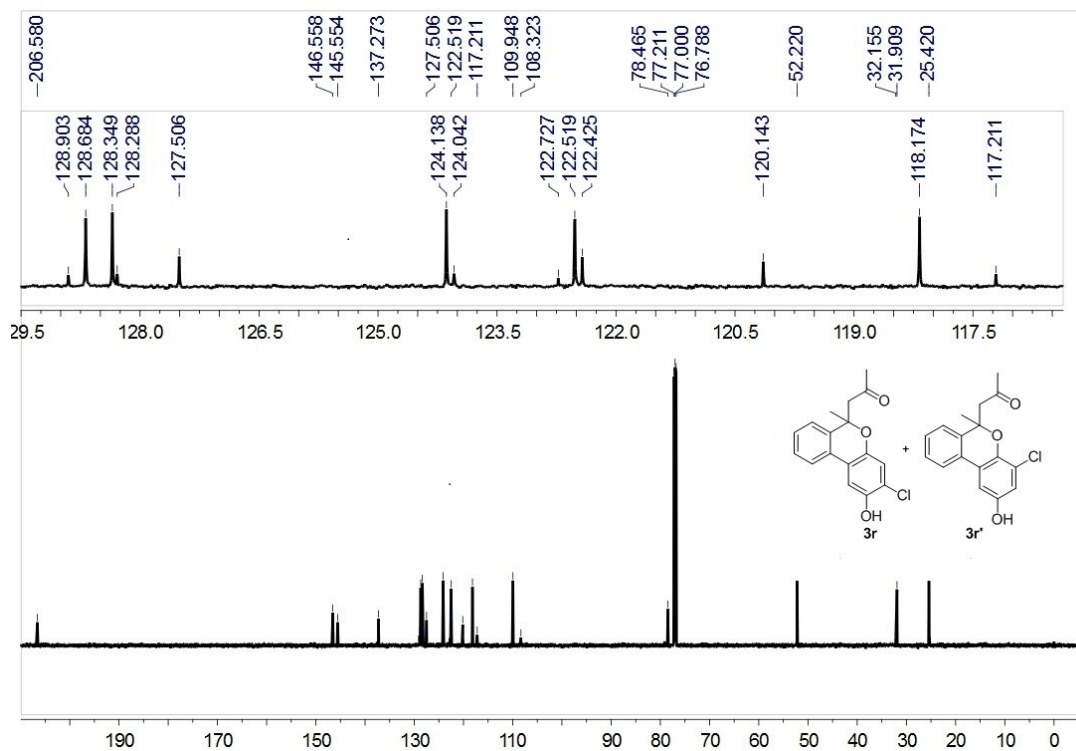


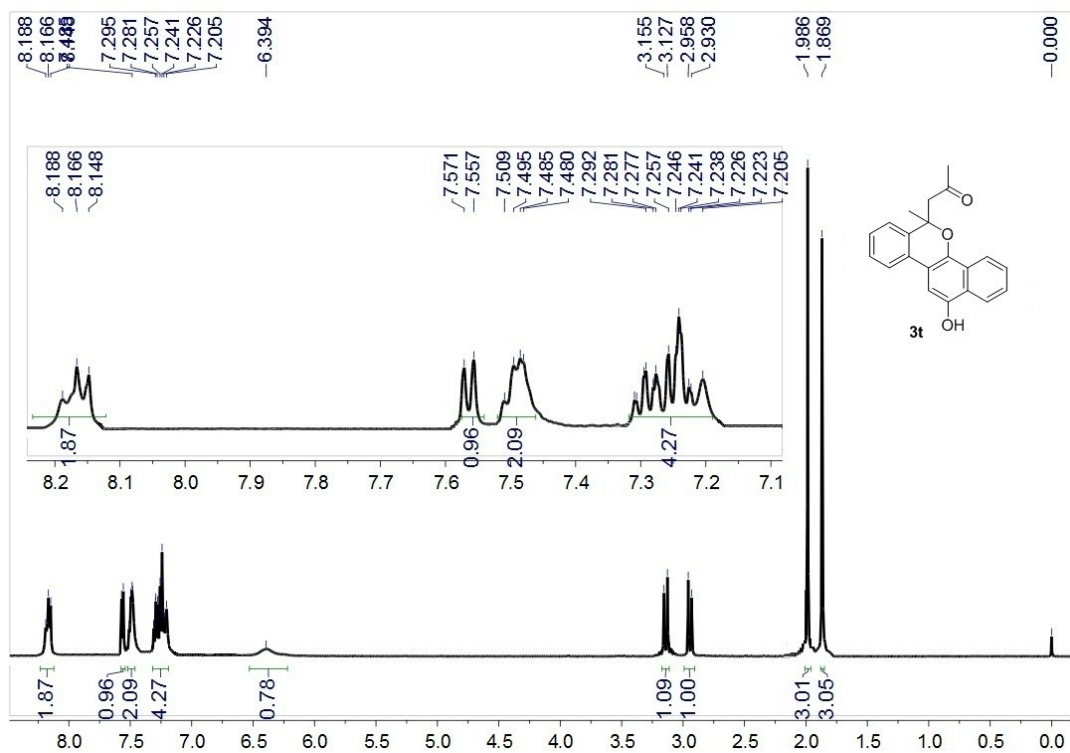
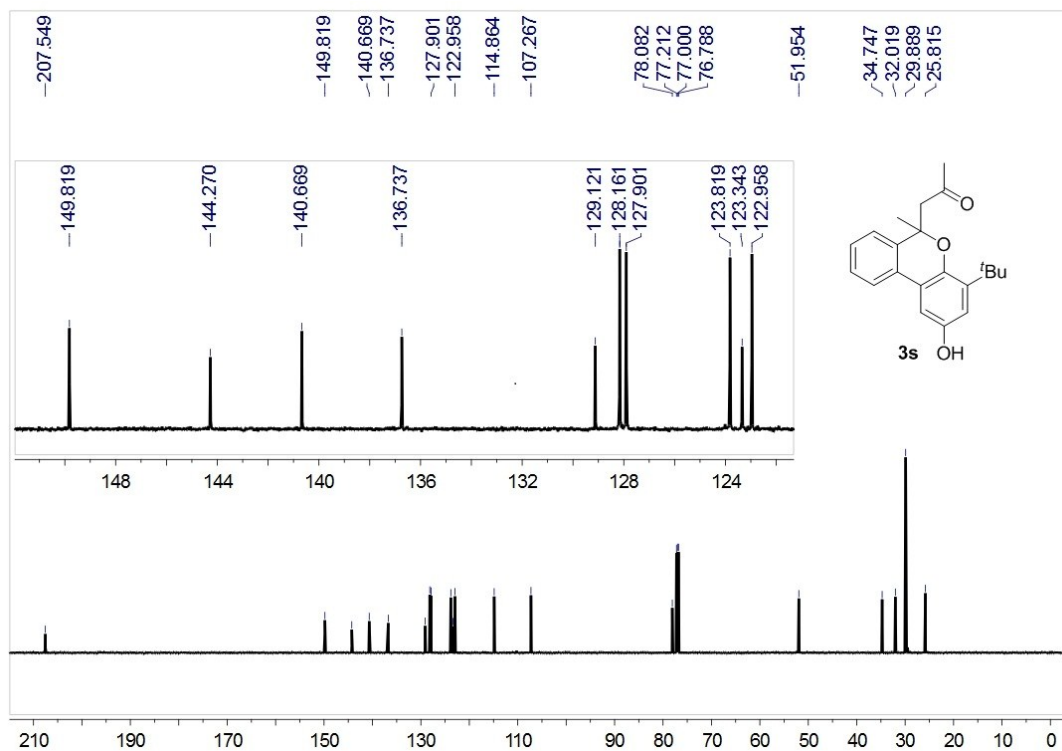


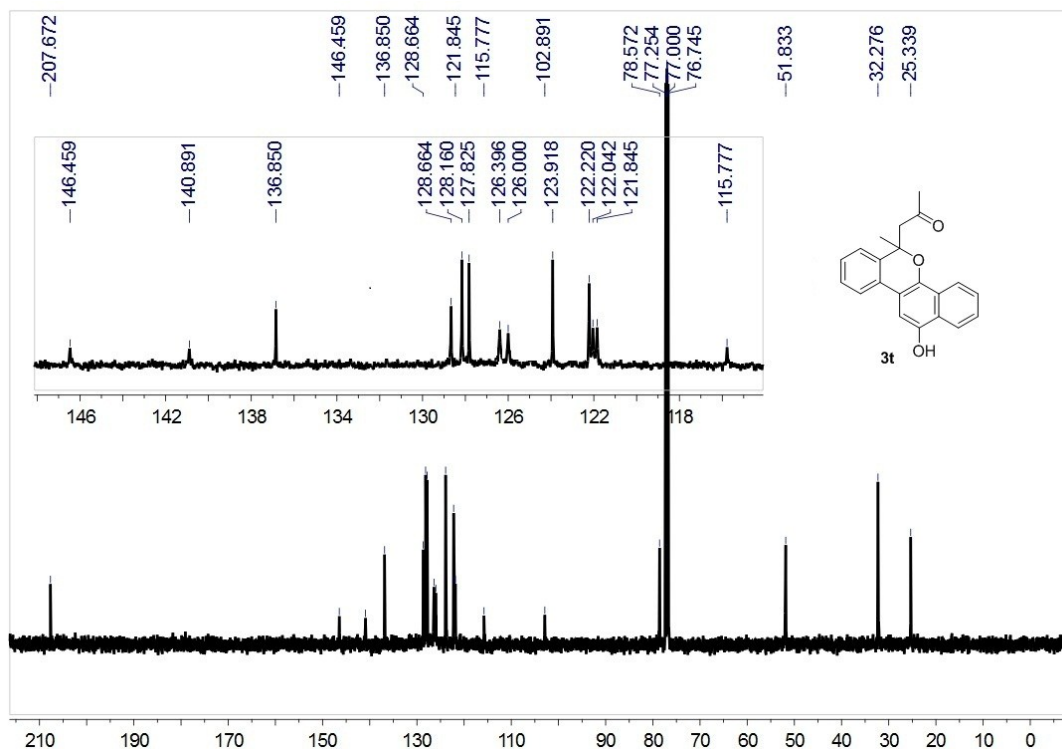




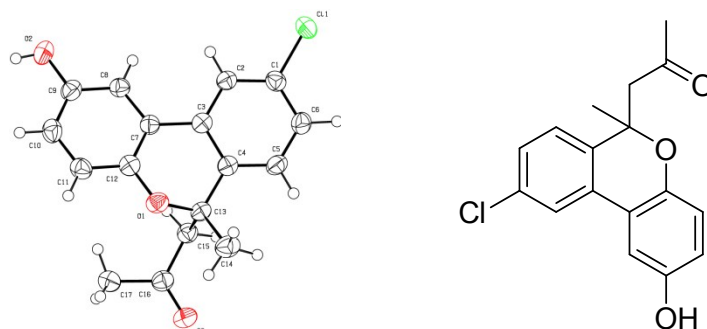








VI. Crystal Structure of **3e**



Single-crystal X-ray diffraction data for **3e** was collected on an X-ray diffractometer operated using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å) and Bruker APEX CCD area-detector in the range $1.70^\circ < \theta < 26.07^\circ$ at room temperature. Crystallographic data for compound **3e** is given in Table S1.

Table S1. Crystal data and structure refinements for **3e**.

Compound	3e
Empirical formular	C ₁₇ H ₁₅ ClO ₃
Formular weight	302.74
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
	$a = 7.2405(7)$ Å $\alpha = 90$
	$b = 16.1028(16)$ Å $\beta = 91.275(2)$
	$c = 12.0426(12)$ Å $\gamma = 90$

Volume /Å ³	1403.7(2)
ρ _{calc} /cm ³	1.433
Z	4
μ (mm ⁻¹)	0.279
F (000)	632.0
Crystal size (mm ³)	0.2×0.15×0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.224 to 52.07
Index ranges	-8 ≤ h ≤ 7, -19 ≤ k ≤ 19, -11 ≤ l ≤ 14
Reflections collected	7273
Independent reflections	2742 [R _{int} = 0.0402, R _{sigma} = 0.0486]
Data/restraints/parameters	2742/445/193
Goodness-of-fit on F ²	1.028
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0547, wR ₂ = 0.1337
Final R indexes [all data]	R ₁ = 0.0850, wR ₂ = 0.1571
Largest diff. peak/hole / e Å ⁻³	0.38/-0.33

REFERENCE

1. P. C. Too, Y. F. Wang and S. Chiba, *Org. Lett.*, 2010, **12**, 5688.
2. A. Simon-Levert, A. Arrault, N. Bontemps-Subielos, C. Canal and B. Banaigs, *J. Nat. Prod.*, 2005, **68**, 1412.
3. E. Nurnberg, *Dtsch. Apotheker-Ztg.*, 1961, **101**, 268.