

Supporting Information

Rh(III)-Catalyzed synthesis of dibenzo[*b,d*]pyran-6-ones from aryl ketone
O-acetyl oximes and quinones via C–H activation and C–C bond cleavage

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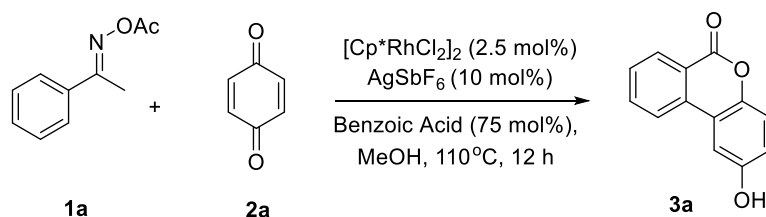
I. General Information

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 and 500 spectrometer (400 and 500MHz for ¹H NMR; 100 and 125 MHz for ¹³C 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). GC-MS spectra were obtained on a GCMS-QP2010 spectrometer.

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

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

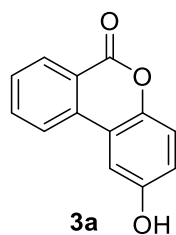


a) General procedure for the synthesis of 3a-3u (3a as an example)

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 benzoic acid (18.3 mg, 0.15 mmol). MeOH (1 mL) was then added. The reaction vessel was sealed and stirred at 110 °C for 12 h and 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 = 10/4, v/v) to afford the product **3a** (70% yield).

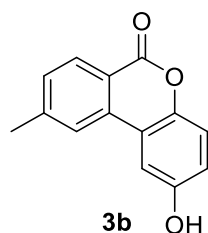
b) Analytical Data of Compounds 3a-3u

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



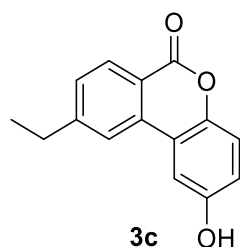
White solid, m.p. 161–162 °C. $^1\text{H NMR}$ (400 MHz, DMSO): δ 9.72 (s, 1H), 8.23 (t, $J = 8.0$ Hz, 2H), 7.91 (t, $J = 6.8$ Hz, 1H), 7.65 (t, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 2.4$ Hz, 1H), 7.25 (d, $J = 8.8$ Hz, 1H), 6.99 (dd, $J = 9.2, 2.8$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 160.9, 154.7, 144.4, 135.7, 134.7, 130.2, 129.6, 122.9, 121.1, 118.9, 118.7, 118.6, 108.6. Calcd for $(\text{C}_{13}\text{H}_8\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 235.0366. Found 235.0367.

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



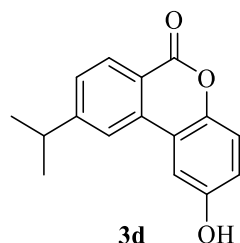
White solid, m.p. 224–225 °C. $^1\text{H NMR}$ (400 MHz, DMSO): δ 9.68 (s, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 8.06 (s, 1H), 7.57 (d, $J = 2.4$ Hz, 1H), 7.46 (d, $J = 8.0$ Hz, 1H), 7.22 (d, $J = 8.8$ Hz, 1H), 6.97 (dd, $J = 8.8, 2.8$ Hz, 1H), 2.49 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 160.9, 154.7, 146.5, 144.6, 134.7, 130.8, 130.2, 122.9, 118.8, 118.7, 118.5, 108.7, 22.1. Calcd for $(\text{C}_{14}\text{H}_{11}\text{O}_3)^+ [\text{M}+\text{H}]^+$ 227.0703. Found 227.0707.

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



White solid, m.p. 135–136 °C. $^1\text{H NMR}$ (400 MHz, DMSO): δ 9.72 (s, 1H), 8.13 (d, $J = 8.0$ Hz, 1H), 8.07 (s, 1H), 7.62 (d, $J = 2.4$ Hz, 1H), 7.50 (d, $J = 8.0$ Hz, 1H), 7.23 (d, $J = 8.8$ Hz, 1H), 6.98 (dd, $J = 8.8, 2.8$ Hz, 1H), 2.81 (q, $J = 7.6$ Hz, 2H), 1.27 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 160.9, 154.7, 152.4, 144.5, 134.8, 130.4, 129.6, 121.8, 118.8, 118.8, 118.7, 118.5, 108.7, 29.1, 15.6. Calcd for $(\text{C}_{15}\text{H}_{12}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 263.0679. Found 263.0675.

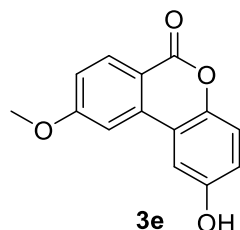
2-hydroxy-9-isopropyl-6H-benzo[c]chromen-6-one (3d)



White liquid. $^1\text{H NMR}$ (400 MHz, DMSO): δ 9.70 (s, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.10 (s, 1H), 7.67 (d, $J = 2.4$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.24 (d, $J = 8.8$ Hz, 1H), 6.98 (dd, $J = 8.8, 2.8$ Hz, 1H), 3.17–3.06 (m, 1H), 1.29 (d, $J = 6.8$ Hz, 6H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 160.8, 156.9, 154.7, 144.5, 134.9, 130.5, 128.2, 120.5, 119.0, 118.9, 118.8, 118.5, 108.8, 34.5, 23.8. Calcd for

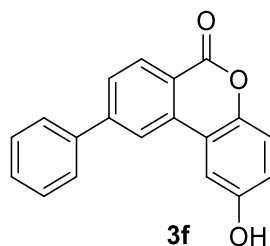
(C₁₆H₁₄NaO₃⁺ [M+Na]⁺) 277.0835. Found 277.0831.

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



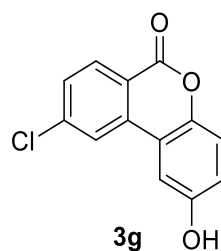
Yellowish solid, m.p. 187–188 °C. ¹H NMR (400 MHz, DMSO): δ 9.69 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 3.2 Hz, 2H), 7.24–7.20 (m, 2H), 7.00 (dd, *J* = 8.8, 2.8 Hz, 1H), 3.99 (s, 3H). ¹³C NMR (100 MHz, DMSO): δ 165.1, 160.6, 154.6, 144.8, 137.2, 132.6, 119.1, 118.7, 118.5, 117.6, 114.0, 109.1, 105.9, 56.5. Calcd for (C₁₄H₁₀NaO₄⁺ [M+Na]⁺) 265.0471. Found 265.0471.

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



Yellowish solid, m.p. 153–154 °C. ¹H NMR (400 MHz, DMSO): δ 8.49 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.91 (s, 1H), 7.84 (d, *J* = 2.8 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 6.8 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.4 Hz, 1H). ¹³C NMR (100 MHz, DMSO): δ 160.8, 154.8, 147.0, 144.6, 139.0, 135.4, 131.0, 129.6, 129.4, 128.1, 128.0, 120.8, 119.9, 119.0, 118.8, 118.5, 109.3. Calcd for (C₁₉H₁₃O₃⁺ [M+H]⁺) 289.0859. Found 289.0870.

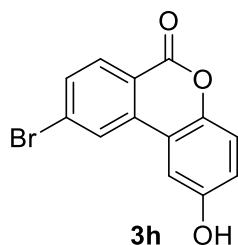
9-chloro-2-hydroxy-6H-benzo[*c*]chromen-6-one (3g)



White solid, m.p. 192–193 °C. ¹H NMR (400 MHz, DMSO): δ 9.81 (s, 1H), 8.36 (d, *J* = 2.0 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.68 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.64 (d, *J* = 2.8 Hz, 1H), 7.26 (d, *J* =

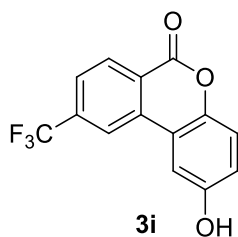
8.8 Hz, 1H), 7.03 (dd, $J = 8.8, 2.8$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ 160.3, 154.9, 144.8, 141.1, 136.7, 132.4, 129.8, 122.9, 119.9, 119.7, 118.6, 117.8, 109.3. Calcd for $(\text{C}_{13}\text{H}_8\text{ClO}_3^+ [\text{M}+\text{H}]^+)$ 247.0156. Found 247.0166.

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



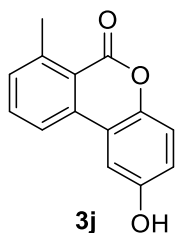
Yellowish solid, m.p. 191–192 °C. ^1H NMR (400 MHz, DMSO): δ 9.77 (s, 1H), 8.53 (d, $J = 2.0$ Hz, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.84 (dd, $J = 8.4, 1.6$ Hz, 1H), 7.66 (d, $J = 2.8$ Hz, 1H), 7.27 (d, $J = 8.8$ Hz, 1H), 7.03 (dd, $J = 8.8, 2.8$ Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ 160.5, 154.8, 144.8, 136.7, 132.7, 132.3, 130.4, 125.9, 120.2, 119.6, 118.7, 117.7, 109.2. Calcd for $(\text{C}_{13}\text{H}_8\text{BrO}_3^+ [\text{M}+\text{H}]^+)$ 290.9651. Found 290.9638.

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



Yellowish solid, m.p. 138–139 °C. ^1H NMR (400 MHz, DMSO): δ 9.81 (s, 1H), 8.61 (s, 1H), 8.41 (d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 2.4$ Hz, 1H), 7.29 (d, $J = 8.8$ Hz, 1H), 7.05 (dd, $J = 8.8, 2.4$ Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ 160.0, 154.9, 144.6, 135.7, 135.0 (q, $^2J_{\text{C-F}} = 32.0$ Hz), 131.6, 125.6 (q, $^3J_{\text{C-F}} = 3.4$ Hz), 124.2, 124.0 (q, $^1J_{\text{C-F}} = 271.9$ Hz), 120.4 (q, $^3J_{\text{C-F}} = 3.5$ Hz), 119.8, 118.7, 117.9, 109.3. Calcd for $(\text{C}_{14}\text{H}_8\text{FO}_3^+ [\text{M}+\text{H}]^+)$ 281.0420. Found 281.0409.

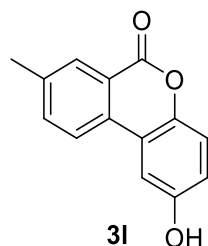
2-hydroxy-7-methyl-6H-benzo[*c*]chromen-6-one (3j)



Yellowish solid, m.p. 160–161 °C. ^1H NMR (400 MHz, DMSO): δ 9.72 (s, 1H), 8.11 (d, $J = 8.0$ Hz,

1H), 7.76 (t, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 2.4$ Hz, 1H), 7.48 (d, $J = 7.6$ Hz, 1H), 7.21 (d, $J = 8.8$ Hz, 1H), 6.97 (dd, $J = 8.8, 2.4$ Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 160.3, 154.6, 144.5, 143.7, 136.2, 135.0, 132.9, 121.1, 119.5, 119.0, 118.9, 118.2, 108.9, 23.9. Calcd for $(\text{C}_{14}\text{H}_{10}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 249.0522. Found 249.0504.

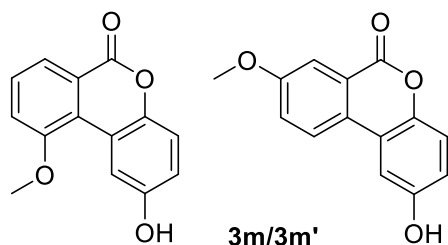
2-hydroxy-8-methyl-6H-benzo[*c*]chromen-6-one (3l)



Yellow solid, m.p. 162–163 °C. ^1H NMR (400 MHz, DMSO): δ 9.68 (s, 1H), 8.15 (d, $J = 8.4$ Hz, 1H), 8.03 (s, 1H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 2.8$ Hz, 1H), 7.24 (d, $J = 8.8$ Hz, 1H), 6.96 (dd, $J = 8.8, 2.4$ Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 160.9, 154.7, 144.1, 139.6, 136.7, 132.2, 129.9, 122.9, 120.9, 118.8, 118.5, 118.4, 108.4, 21.2. Calcd for $(\text{C}_{14}\text{H}_{10}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 249.0522. Found 249.0518.

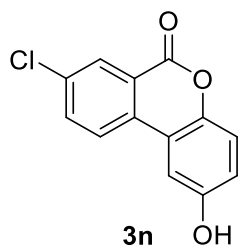
2-hydroxy-10-methoxy-6H-benzo[*c*]chromen-6-one

2-hydroxy-8-methoxy-6H-benzo[*c*]chromen-6-one (3m/3m')



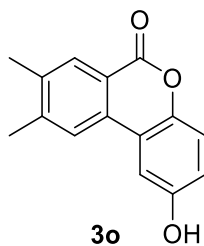
Yellowish solid. ^1H NMR (400 MHz, DMSO): δ 9.67 (s, 1.13H), 8.39 (s, 0.39H), 8.18 (d, $J = 8.8$ Hz, 0.90H), 7.90 (d, $J = 7.6$ Hz, 0.37H), 7.63–7.60 (m, 1.63H), 7.51–7.48 (m, 1.81H), 7.22 (d, $J = 8.8$ Hz, 1.34H), 6.96–6.91 (m, 1.33H), 4.05 (s, 1.19H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO): δ 160.8, 160.1, 154.8, 154.1, 143.6, 130.2, 128.0, 124.9, 124.1, 122.4, 122.2, 118.8, 118.4, 118.3, 117.9, 117.8, 117.6, 114.1, 111.8, 108.2, 56.8, 56.2. Calcd for $(\text{C}_{14}\text{H}_{10}\text{NaO}_4)^+ [\text{M}+\text{Na}]^+$ 265.0471. Found 265.0464.

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



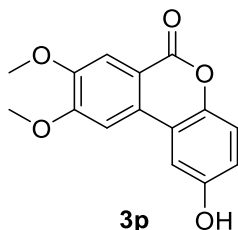
Yellowish solid, m.p. 140–141 °C. $^1\text{H NMR}$ (400 MHz, DMSO): δ 9.79 (s, 1H), 8.31 (d, $J = 8.8$ Hz, 1H), 8.17 (d, $J = 2.4$ Hz, 1H), 7.96 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.59 (d, $J = 2.8$ Hz, 1H), 7.28 (d, $J = 8.8$ Hz, 1H), 7.02 (dd, $J = 8.8, 2.4$ Hz, 1H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 159.9, 154.9, 144.3, 135.6, 134.1, 133.7, 129.2, 125.5, 122.8, 119.3, 118.7, 118.0, 108.8. Calcd for $(\text{C}_{13}\text{H}_8\text{ClO}_3)^+ [\text{M}+\text{H}]^+$ 247.0156. Found 247.0140.

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



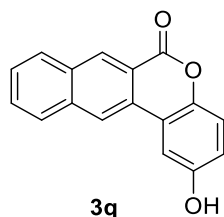
Yellowish solid, m.p. 176–177 °C. $^1\text{H NMR}$ (400 MHz, DMSO): δ 9.61 (s, 1H), 7.82 (d, $J = 11.2$ Hz, 2H), 7.44 (d, $J = 2.8$ Hz, 1H), 7.15 (d, $J = 8.8$ Hz, 1H), 6.92 (dd, $J = 8.8, 2.4$ Hz, 1H), 2.32 (s, 3H), 2.25 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 160.7, 154.5, 145.4, 144.3, 138.6, 132.4, 130.1, 123.2, 118.7, 118.6, 118.3, 118.1, 108.3, 20.4, 19.6. Calcd for $(\text{C}_{15}\text{H}_{12}\text{NaO}_3)^+ [\text{M}+\text{Na}]^+$ 263.0679. Found 263.0667.

2-hydroxy-8,9-dimethoxy-6H-benzo[c]chromen-6-one (3p)



Yellowish solid, m.p. 110–111 °C. $^1\text{H NMR}$ (400 MHz, DMSO): δ 10.98 (s, 1H), 8.61 (s, 2H), 7.26 (d, $J = 1.6$ Hz, 1H), 7.15 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 1H), 3.76 (s, 6H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 167.8, 152.9, 150.2, 149.9, 149.0, 133.3, 130.1, 129.7, 129.0, 119.0, 116.2, 111.8, 109.0, 56.0, 55.8. Calcd for $(\text{C}_{15}\text{H}_{12}\text{NaO}_5)^+ [\text{M}+\text{Na}]^+$ 295.0577. Found 295.0573.

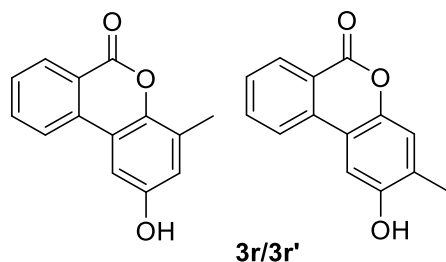
2-hydroxy-6H-naphtho[2,3-c]chromen-6-one (3q)



Yellow solid, m.p. 164–165 °C. $^1\text{H NMR}$ (500 MHz, DMSO): δ 9.73 (s, 1H), 8.97 (s, 1H), 8.84 (s, 1H), 8.24 (d, $J = 8.5$ Hz, 1H), 8.18 (d, $J = 9.0$ Hz, 1H), 7.78–7.75 (m, 2H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.26 (d, $J = 8.5$ Hz, 1H), 6.98 (dd, $J = 8.5, 2.0$ Hz, 1H). $^{13}\text{C NMR}$ (125 MHz, DMSO): δ 161.1, 154.6, 143.9, 136.2, 132.4, 132.3, 130.0, 129.8, 129.6, 128.5, 127.7, 121.8, 119.2, 119.0, 118.6, 118.4, 108.8. Calcd for $(\text{C}_{17}\text{H}_{11}\text{O}_3)^+ [\text{M}+\text{H}]^+$ 263.0703. Found 263.0710.

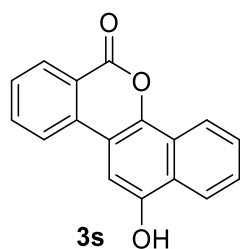
2-hydroxy-4-methyl-6H-benzo[*c*]chromen-6-one

2-hydroxy-3-methyl-6H-benzo[*c*]chromen-6-one (3r/3r')



Yellowish solid. $^1\text{H NMR}$ (400 MHz, DMSO): δ 9.68 (s, 1.16H), 9.61 (s, 0.81H), 8.24 (t, $J = 7.6$ Hz, 2.79H), 8.10 (d, $J = 8.0$ Hz, 1.27H), 7.95–7.90 (m, 2.06H), 7.68–7.62 (m, 2.15H), 7.52 (s, 1.17H), 7.44 (d, $J = 2.8$ Hz, 0.85H), 7.19 (s, 1.16H), 6.88 (d, $J = 2.4$ Hz, 0.91H), 2.34 (s, 2.56H), 2.23 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, DMSO): δ 161.0, 160.8, 154.1, 153.0, 144.3, 142.9, 135.8, 135.7, 135.0, 134.9, 130.3, 130.2, 129.5, 129.3, 129.2, 127.5, 123.1, 122.3, 120.9, 120.7, 120.2, 119.2, 118.4, 116.0, 107.5, 106.3, 16.6, 16.0. Calcd for $(\text{C}_{14}\text{H}_{11}\text{O}_3)^+ [\text{M}+\text{H}]^+$ 227.0703. Found 227.0704.

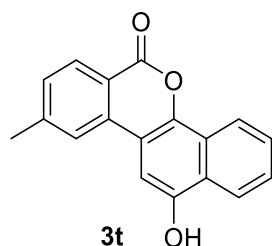
12-hydroxy-6H-dibenzo[*c,h*]chromen-6-one (3s)



Brown solid, m.p. 194–195 °C. $^1\text{H NMR}$ (400 MHz, DMSO): δ 10.48 (s, 1H), 8.34 (d, $J = 8.0$ Hz, 2H), 8.23 (dd, $J = 8.0, 4.0$ Hz, 2H), 8.02 (t, $J = 8.0$ Hz, 1H), 7.72 (t, $J = 8.0$ Hz, 2H), 7.66 (t, $J = 7.2$

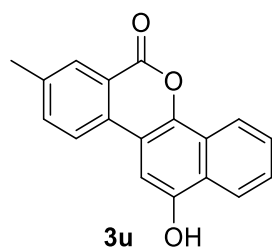
Hz, 1H), 7.53 (s, 1H). ^{13}C NMR (100 MHz, DMSO): δ 160.8, 150.6, 140.3, 136.0, 135.2, 130.4, 129.5, 128.2, 127.4, 126.4, 124.5, 123.0, 121.7, 121.3, 113.6, 100.4. Calcd for $(\text{C}_{17}\text{H}_{10}\text{NaO}_3)^+$ $[\text{M}+\text{Na}]^+$ 285.0522. Found 285.0500.

12-hydroxy-9-methyl-6H-dibenzo[*c,h*]chromen-6-one (3t)



Brown solid, m.p. 248–249 °C. ^1H NMR (500 MHz, DMSO): δ 10.41 (s, 1H), 8.28 (d, $J = 7.5$ Hz, 1H), 8.19–8.15 (m, 2H), 7.92 (s, 1H), 7.67 (t, $J = 7.0$ Hz, 1H), 7.61 (t, $J = 8.0$ Hz, 1H), 7.47 (s, 2H), 2.54 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 160.6, 150.3, 146.5, 140.3, 135.0, 130.4, 130.2, 127.9, 127.2, 126.2, 124.3, 122.8, 122.7, 121.5, 118.6, 113.3, 100.3, 22.1. Calcd for $(\text{C}_{18}\text{H}_{13}\text{O}_3)^+$ $[\text{M}+\text{H}]^+$ 277.0859. Found 277.0859.

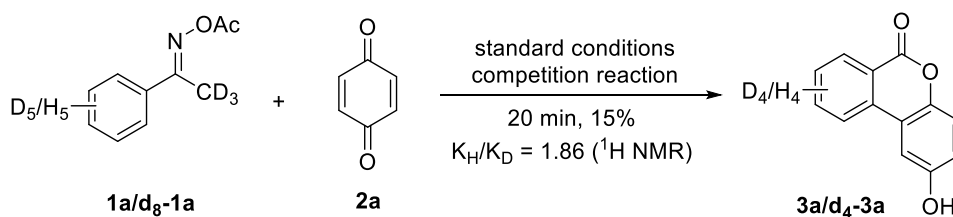
12-hydroxy-8-methyl-6H-dibenzo[*c,h*]chromen-6-one (3u)



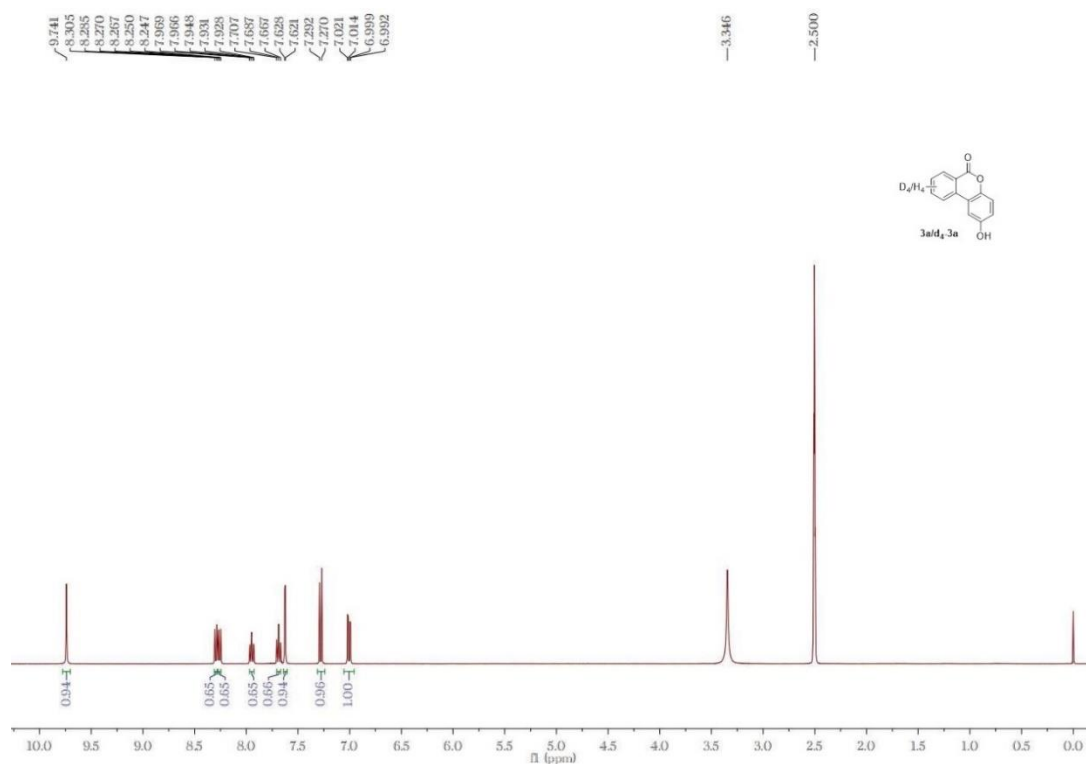
Brown solid, m.p. 237–238 °C. ^1H NMR (500 MHz, DMSO): δ 10.48 (s, 1H), 8.33 (d, $J = 8.5$ Hz, 1H), 8.23 (d, $J = 8.0$ Hz, 1H), 8.14 (s, 1H), 8.11 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.5$ Hz, 1H), 7.72 (t, $J = 8.0$ Hz, 1H), 7.65 (t, $J = 7.5$ Hz, 1H), 7.50 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ 160.7, 150.4, 139.7, 139.3, 136.9, 132.6, 130.0, 128.0, 127.1, 126.0, 124.4, 122.8, 121.4, 121.0, 113.5, 100.2, 21.1. Calcd for $(\text{C}_{18}\text{H}_{12}\text{NaO}_3)^+$ $[\text{M}+\text{Na}]^+$ 299.0679. Found 299.0667.

III. Kinetic Isotope Effect Experiments

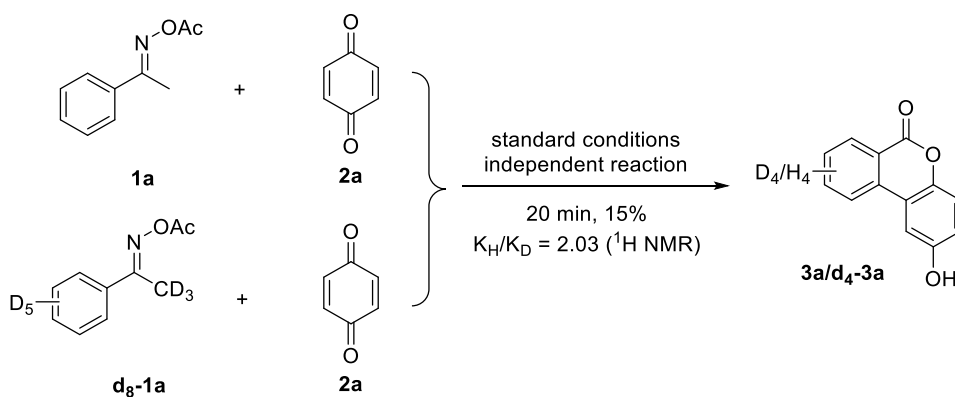
a) The Competition Reaction



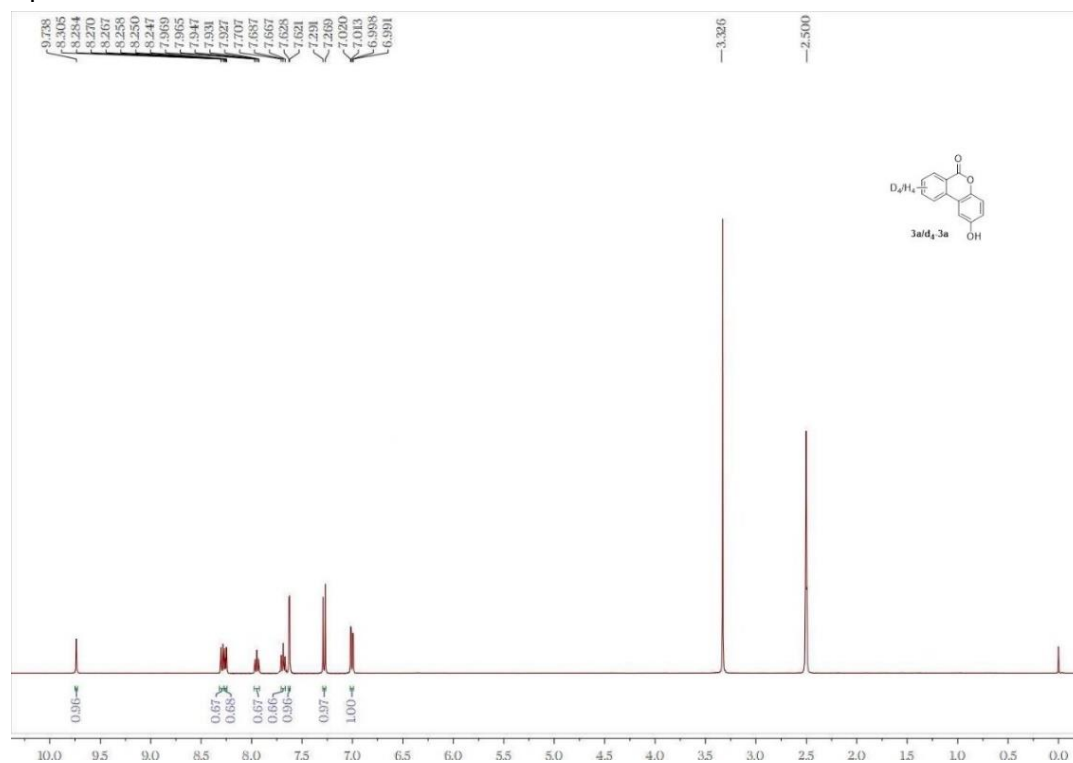
According to the general procedure, to a schlenk tube (15 mL) equipped with a stirring bar was added **1a** (35.4 mg, 0.2 mmol), **d₈-1a** (37.0 mg, 0.2 mmol), **2a** (32.4 mg, 0.3 mmol), [Cp**Rh*Cl₂]₂ (3.1 mg, 0.005 mmol), AgSbF₆ (6.9 mg, 0.02 mmol) and benzoic acid (18.3 mg, 0.15 mmol). MeOH (1 mL) was then added. The reaction vessel was sealed and stirred at 110 °C for 20 min. The reaction mixture was cooled to room temperature and diluted with saturated Na₂CO₃ solution (10 mL), then extracted with EtOAc (10 mL×2). 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 = 10/4, v/v) to afford the desired product **3a** and **d₄-3a**. **KIE=1.86**.



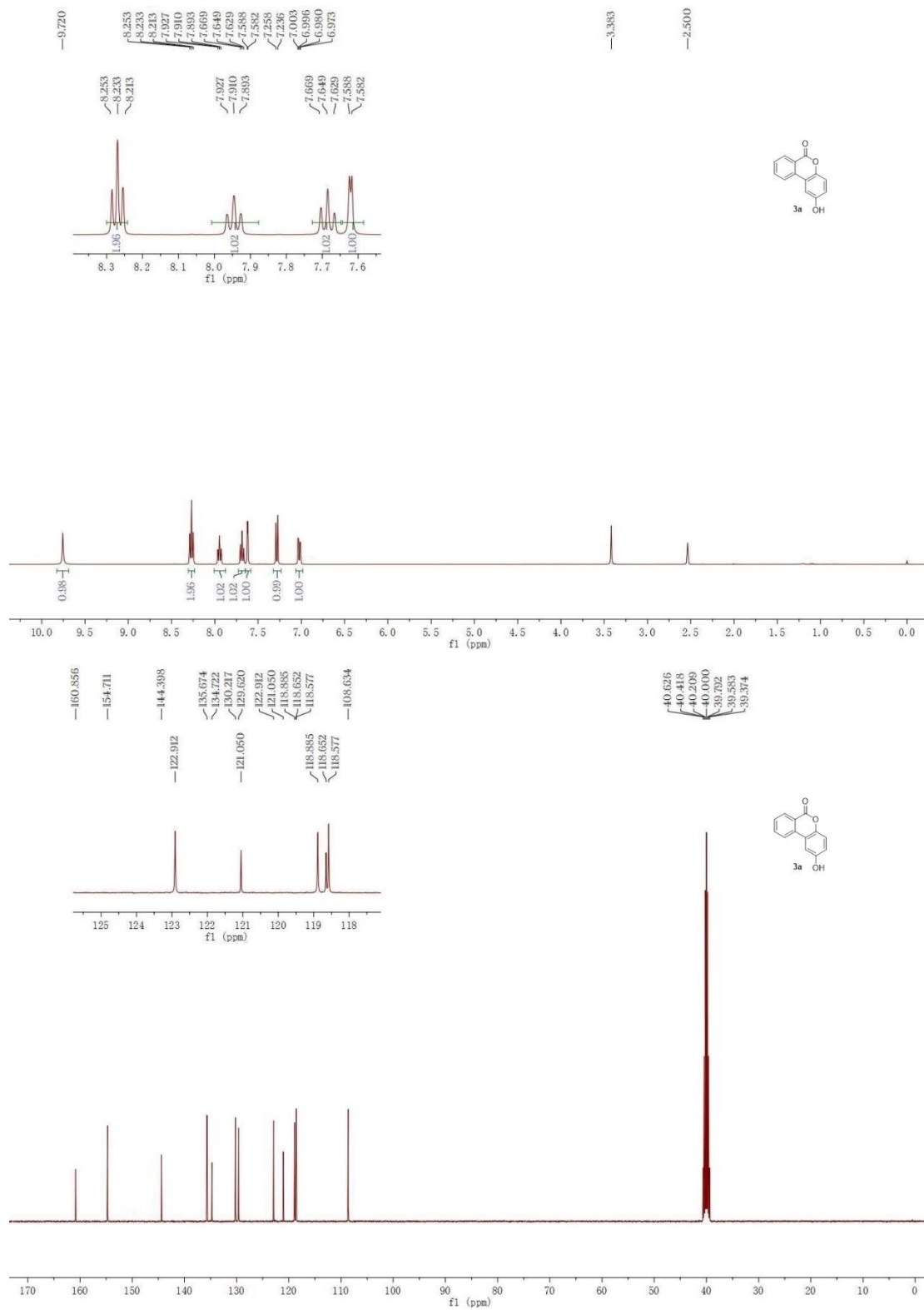
b) The Independent Reaction

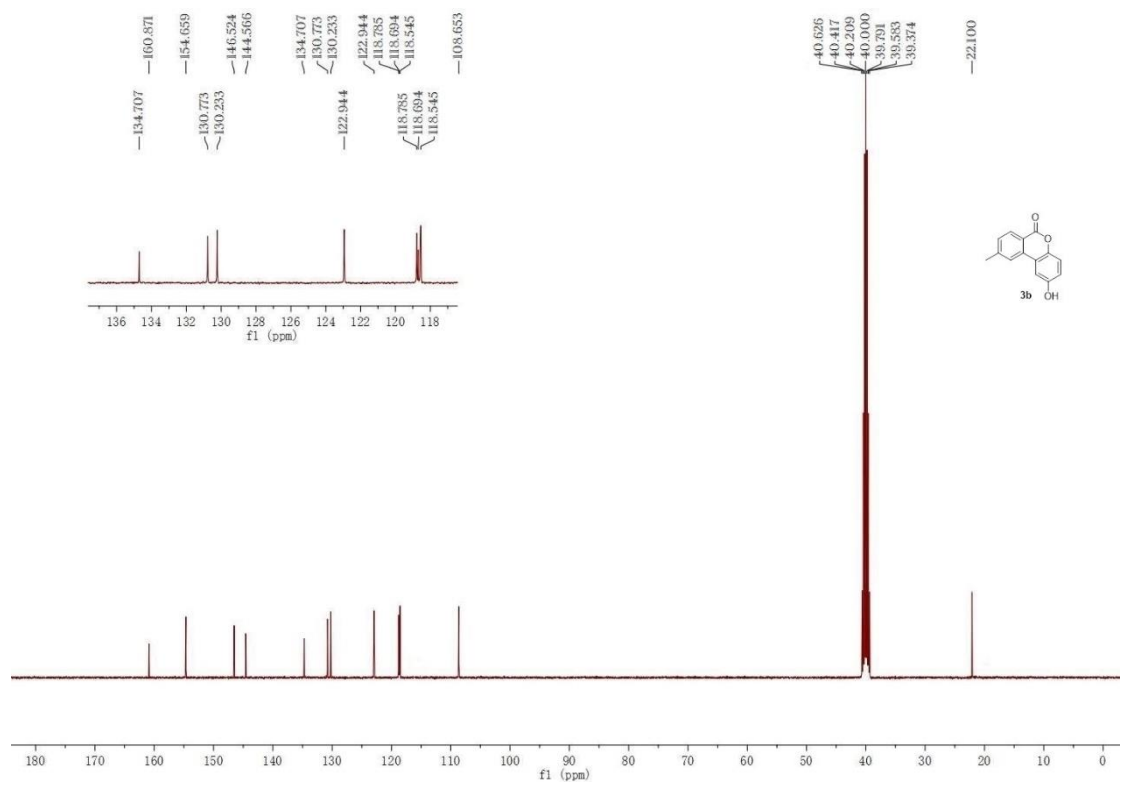
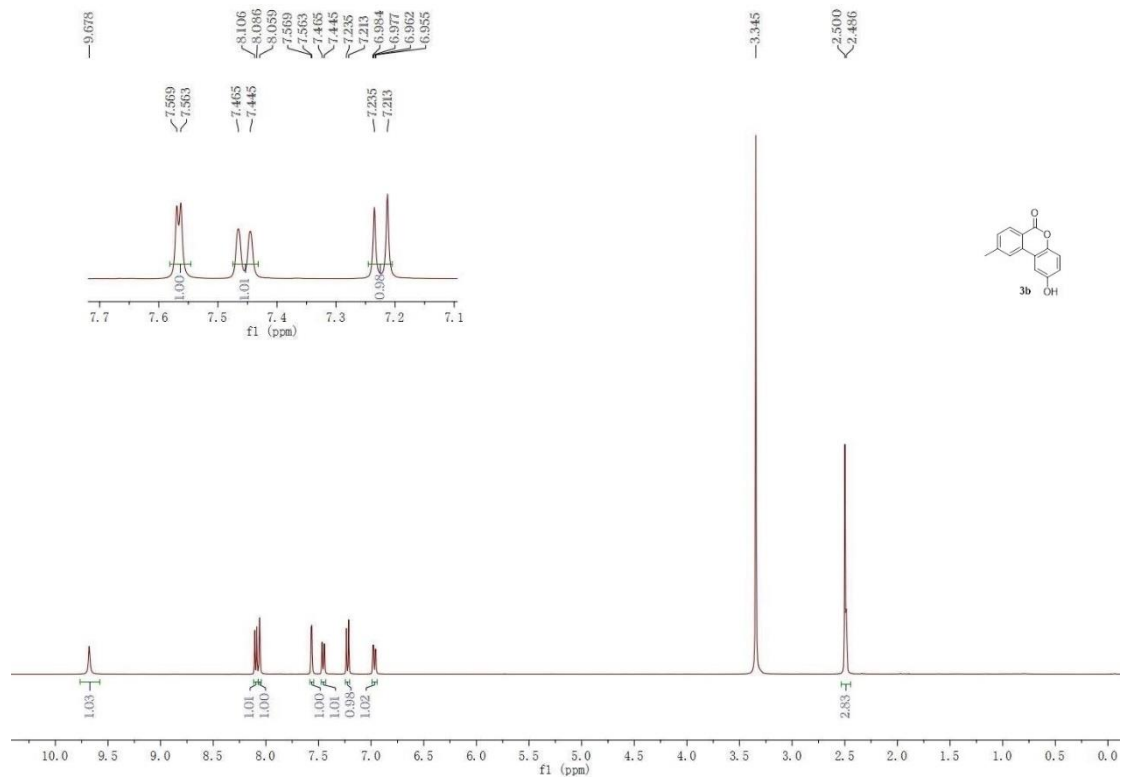


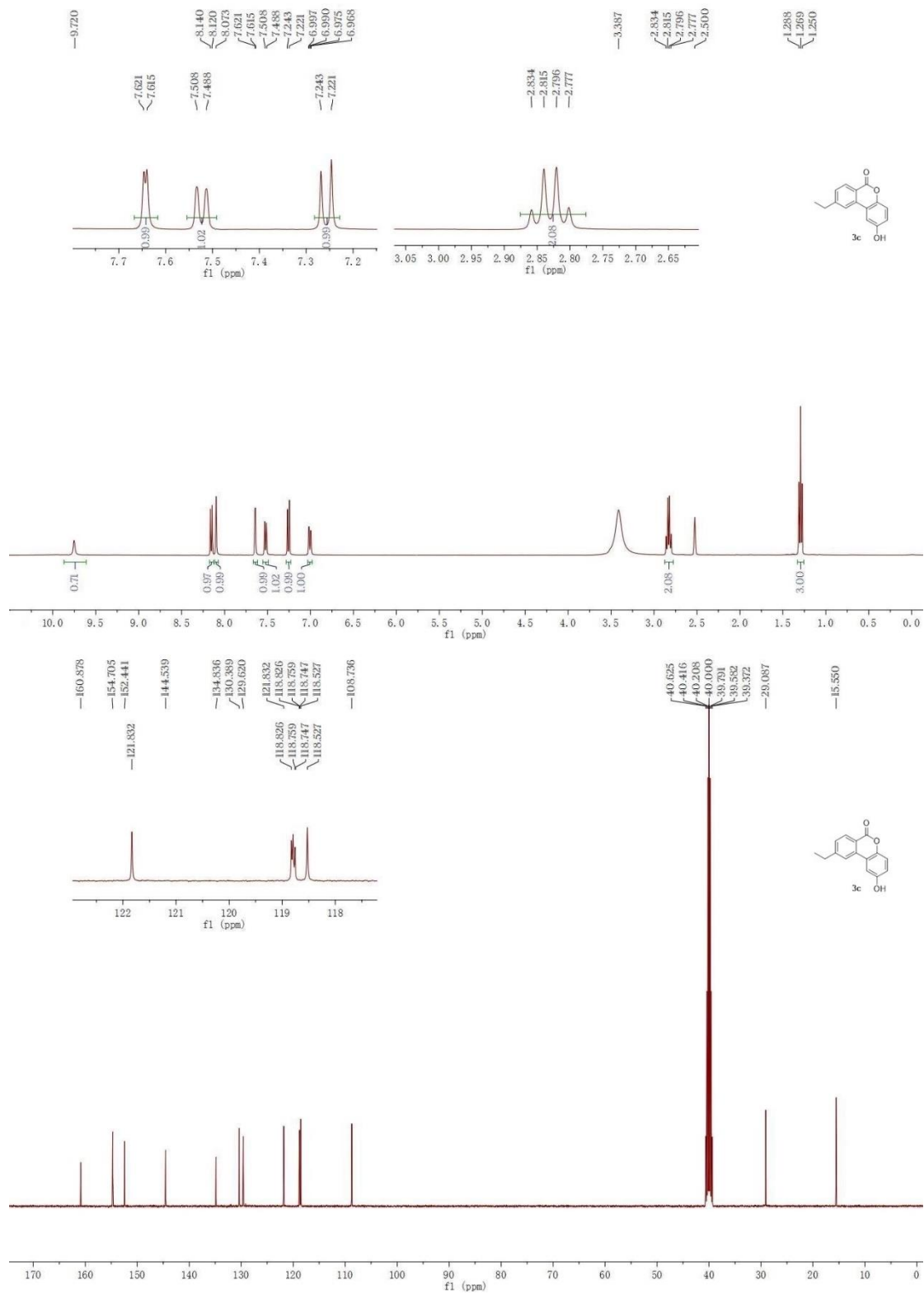
According to the general procedure, to a schlenk tube (15 mL) equipped with a stirring bar was added **1a** (35.4 mg, 0.2 mmol), **2a** (32.4 mg, 0.3 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol), AgSbF₆ (6.9 mg, 0.02 mmol) and benzoic acid (18.3 mg, 0.15 mmol). MeOH (1 mL) was then added. In another sealed tube was added **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), benzoic acid (18.3 mg, 0.15 mmol) and MeOH (1 mL). These two reaction mixtures were stirred side-by-side at 110 °C for 20 min. These two mixtures were rapidly combined and the combined mixture was quenched with saturated Na₂CO₃ solution (10 mL) and extracted with EtOAc (10 mL×2). 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 = 10/4, v/v) to afford the desired product **3a** and **d₄-3a**. KIE=2.03.

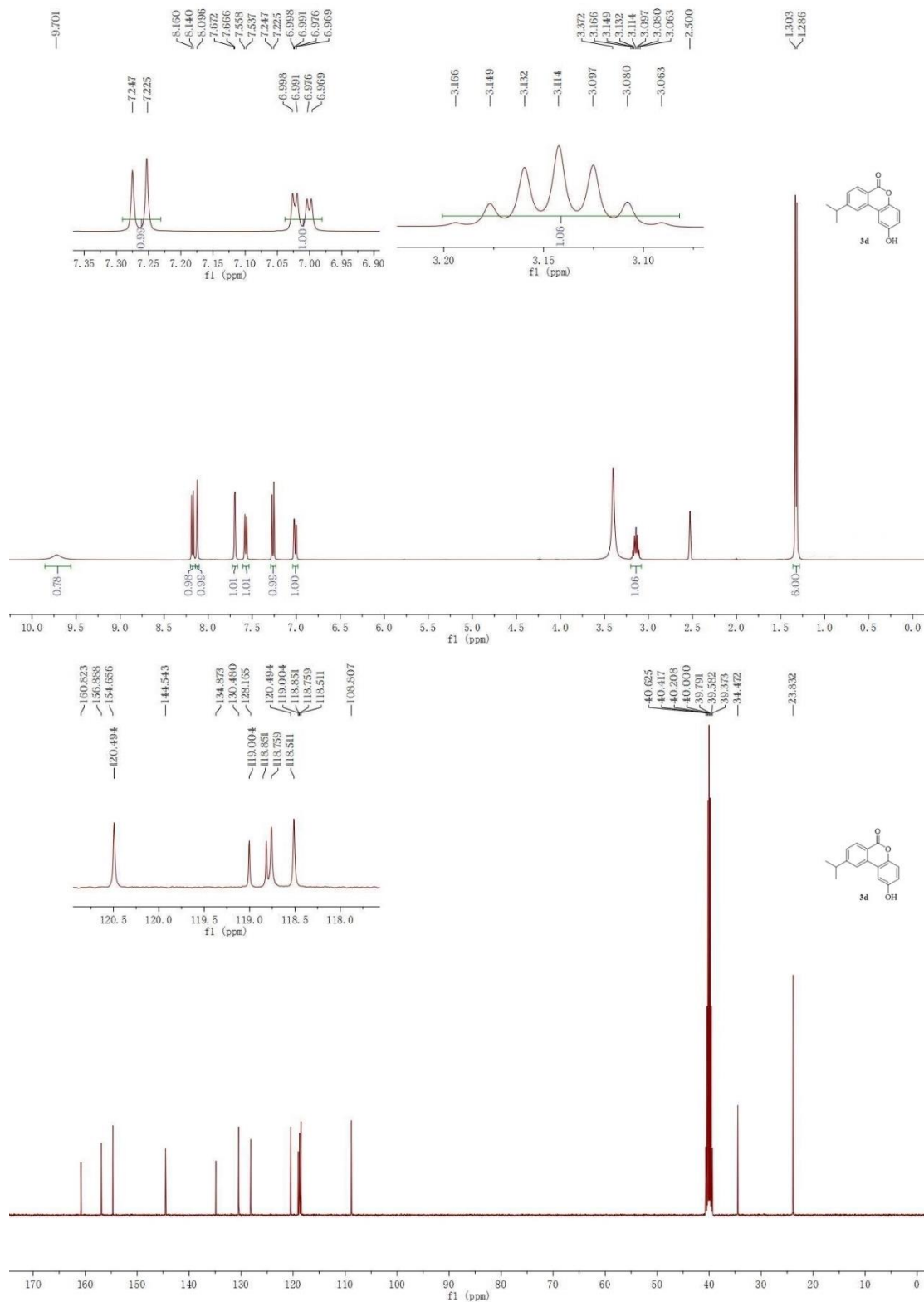


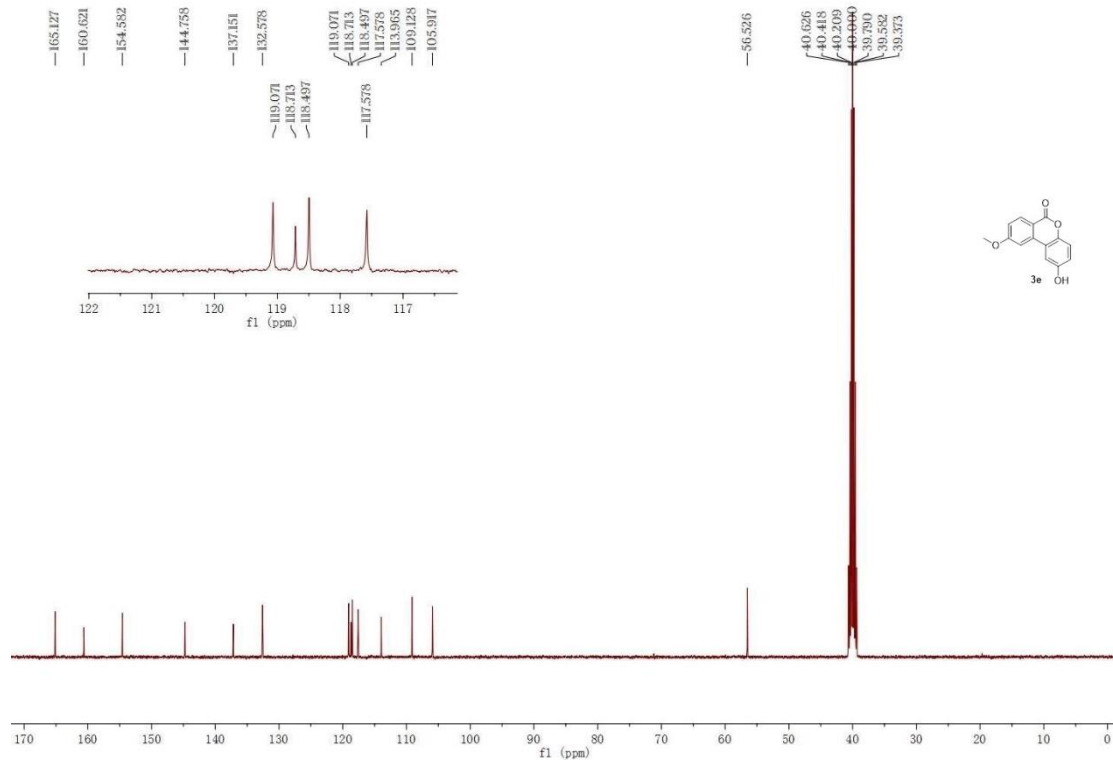
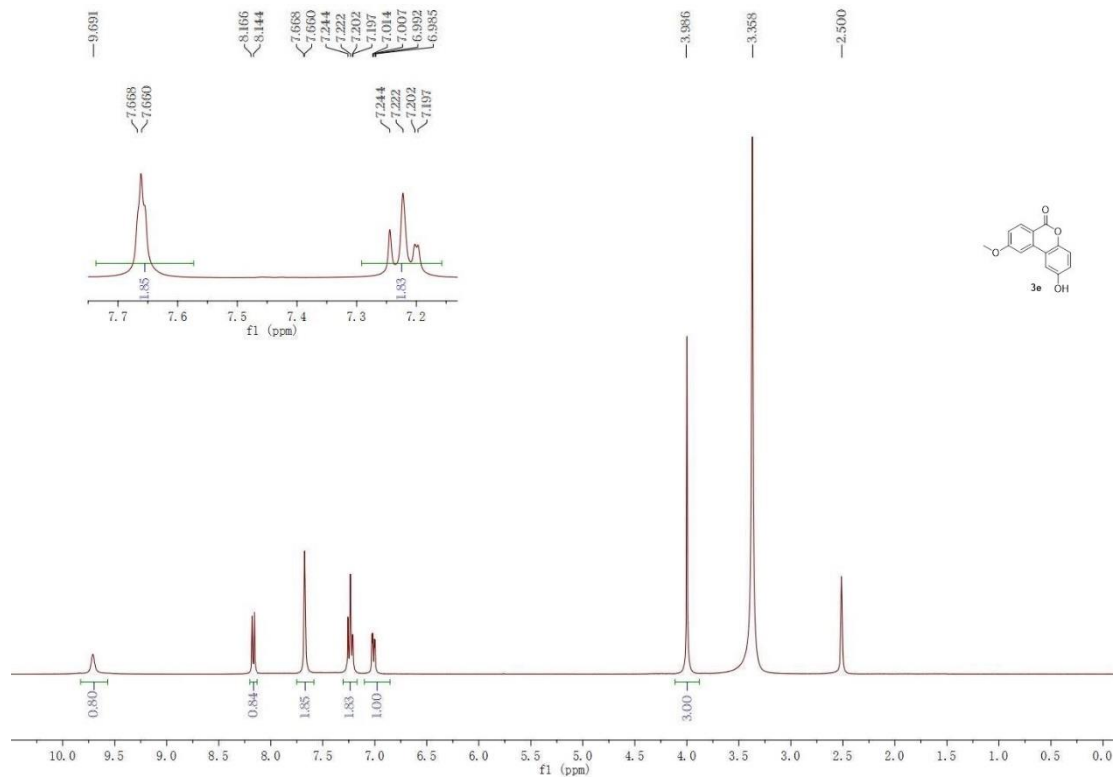
IV. Copies of ^1H NMR and ^{13}C NMR and GC-MS spectra

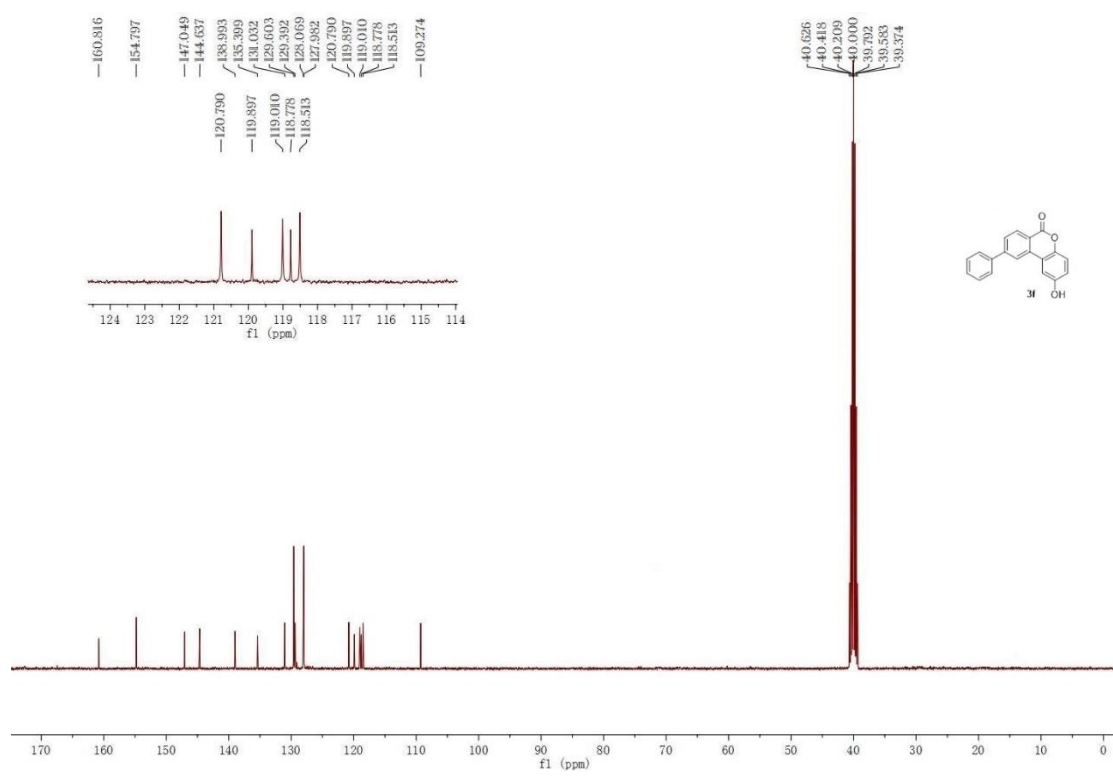
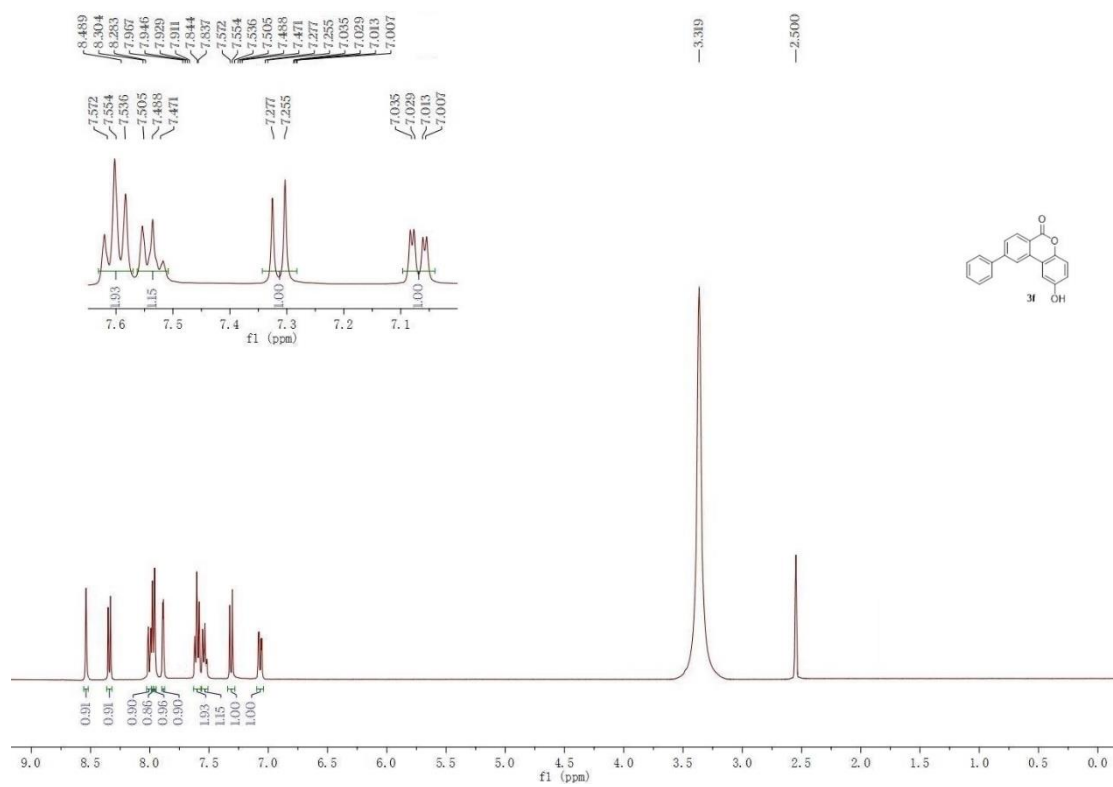


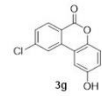
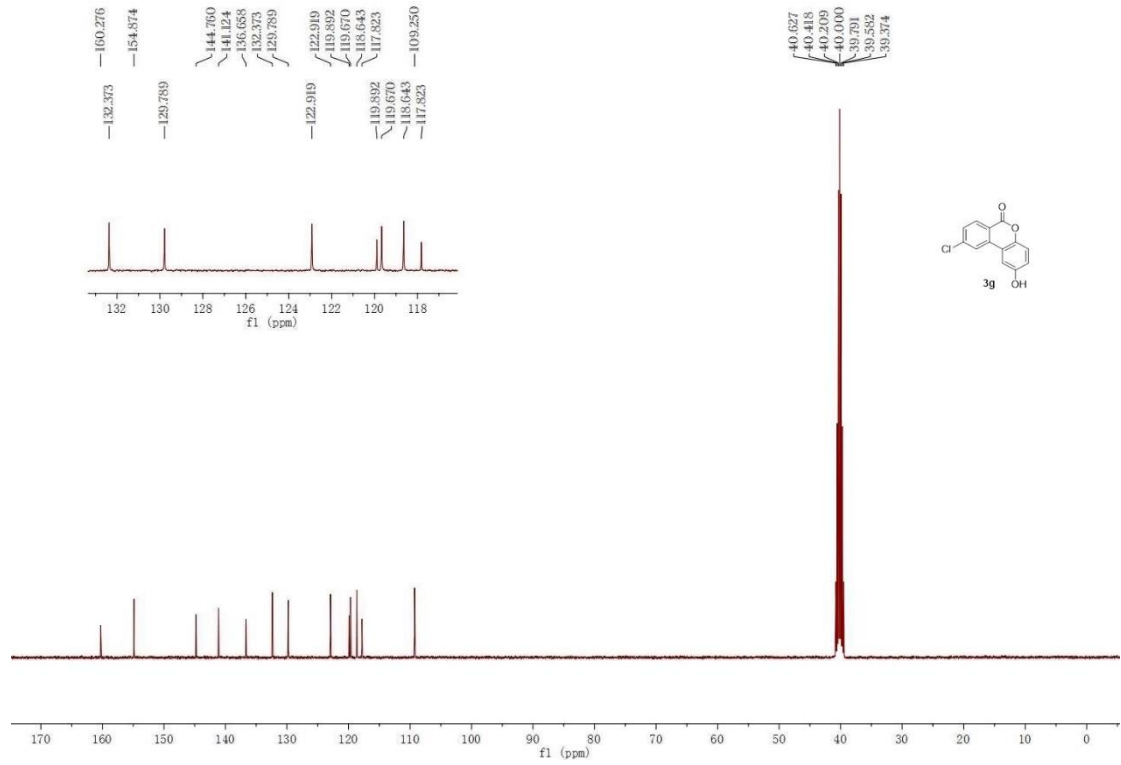
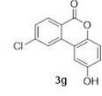
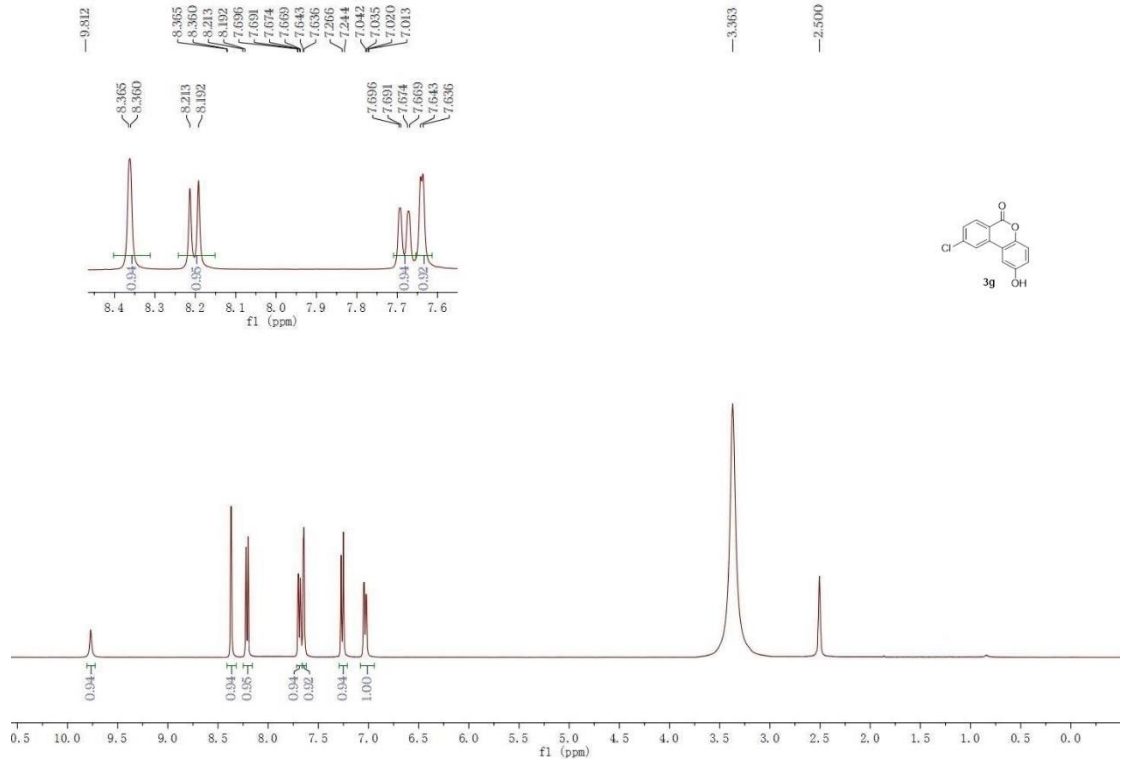


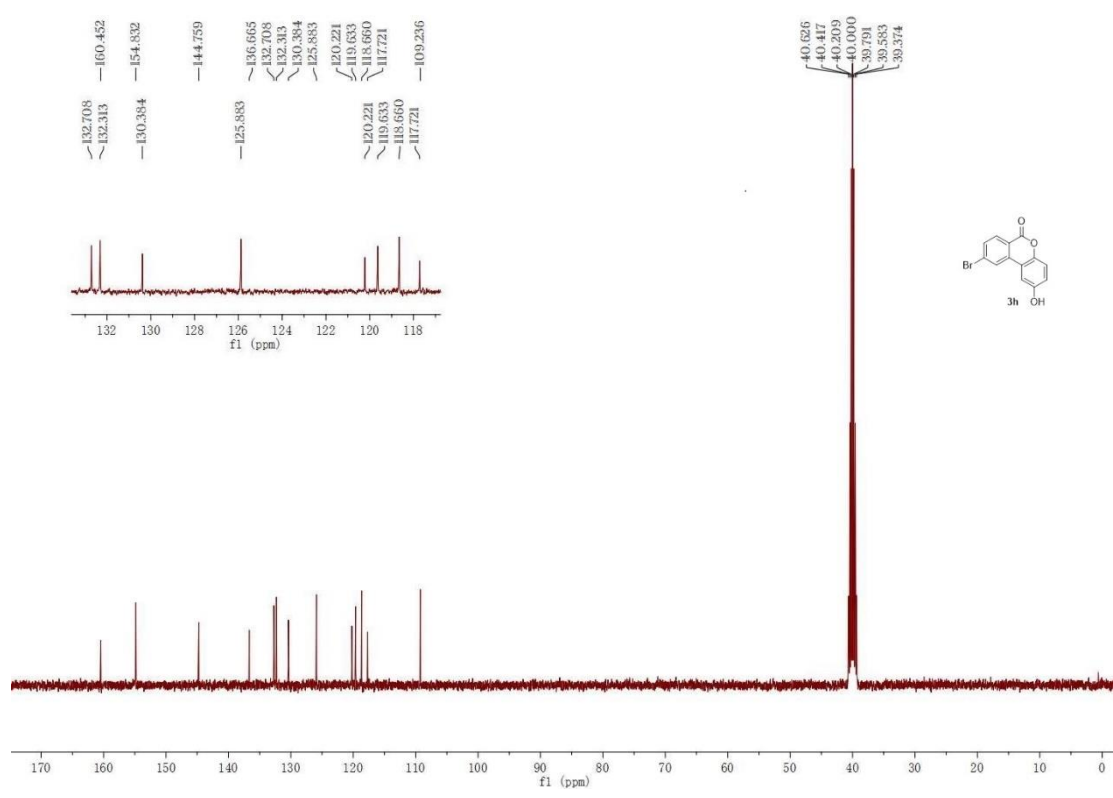
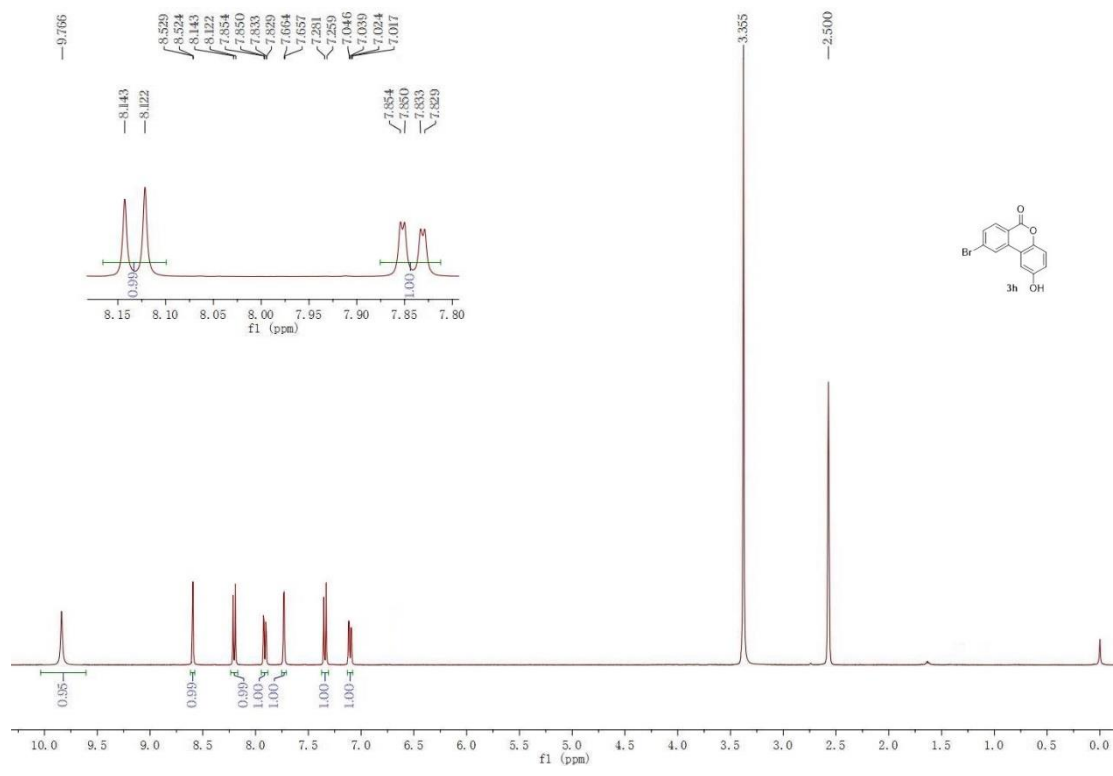


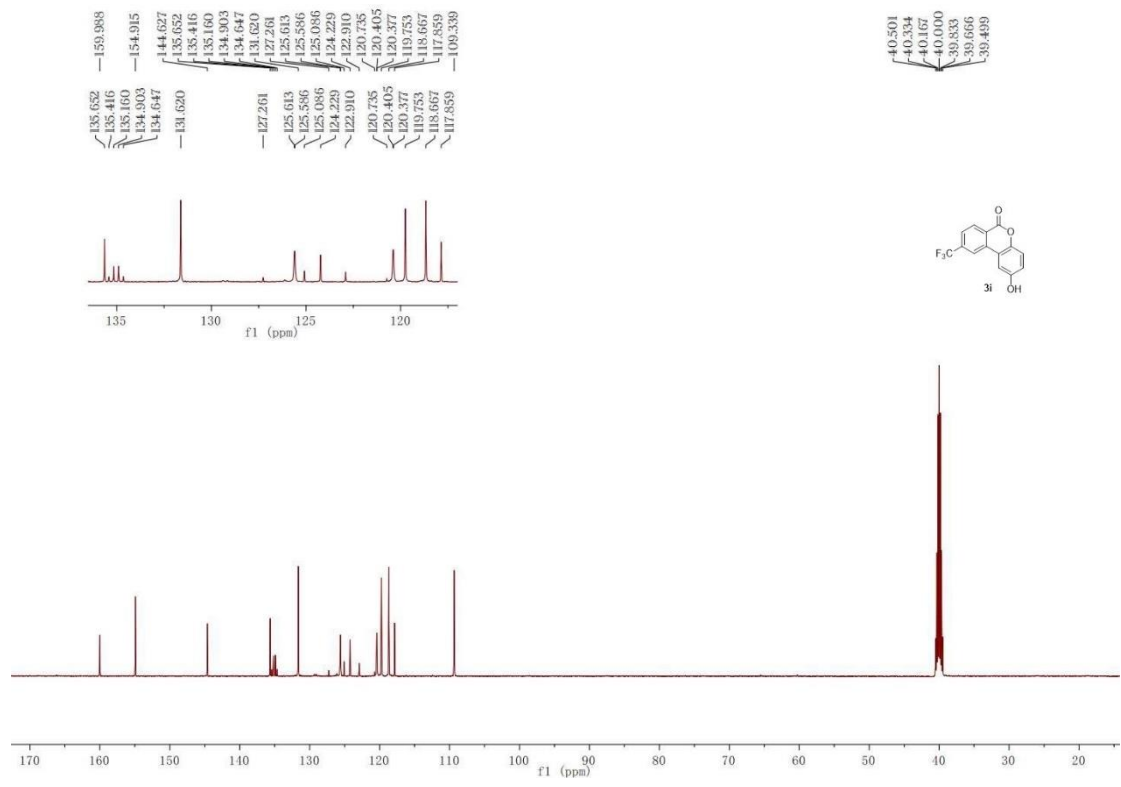
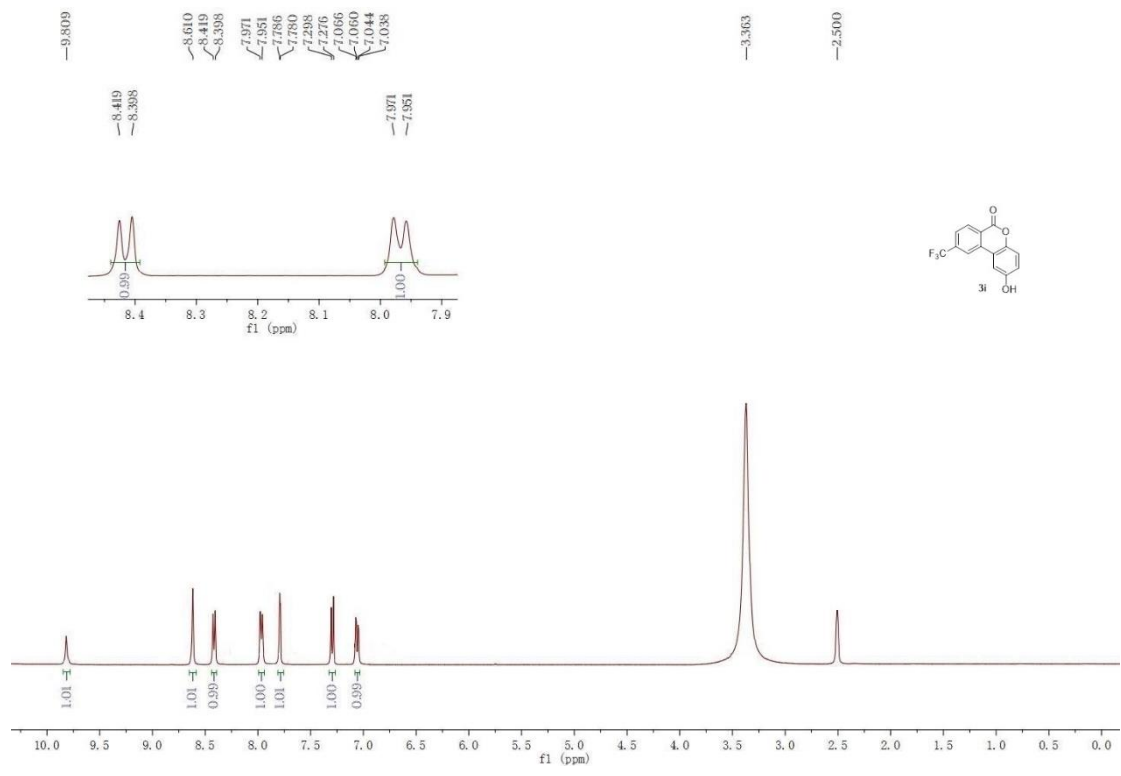


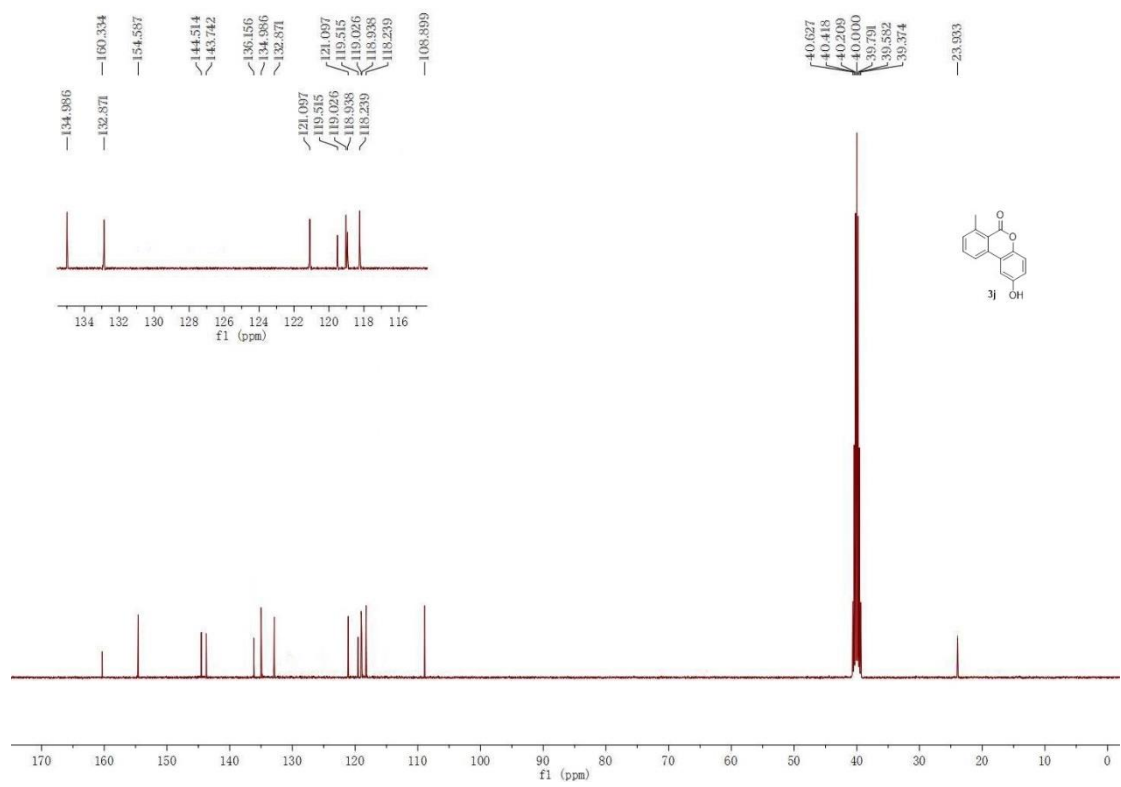
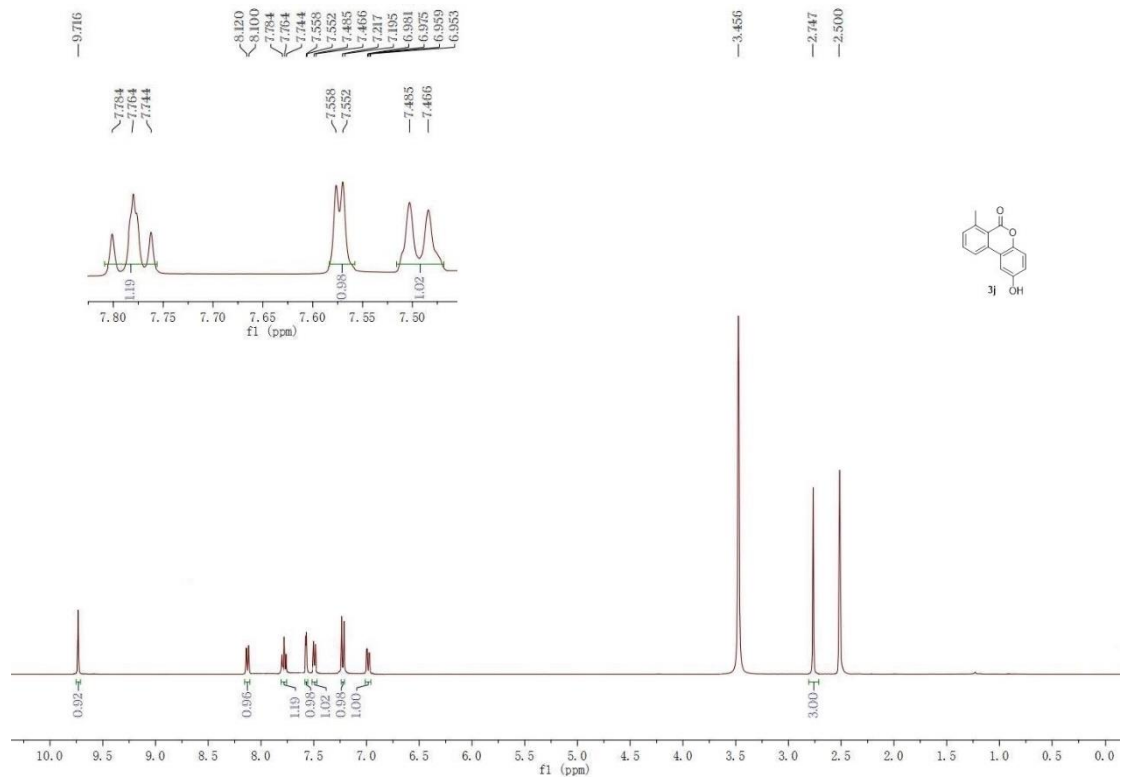


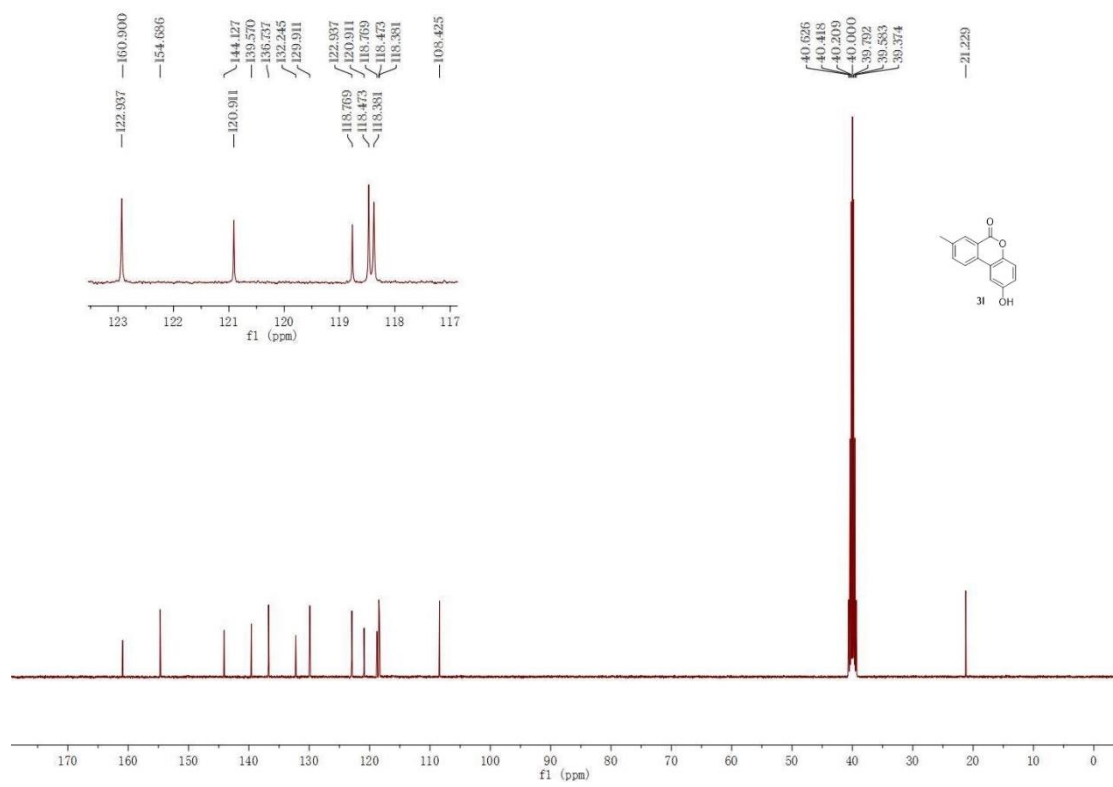
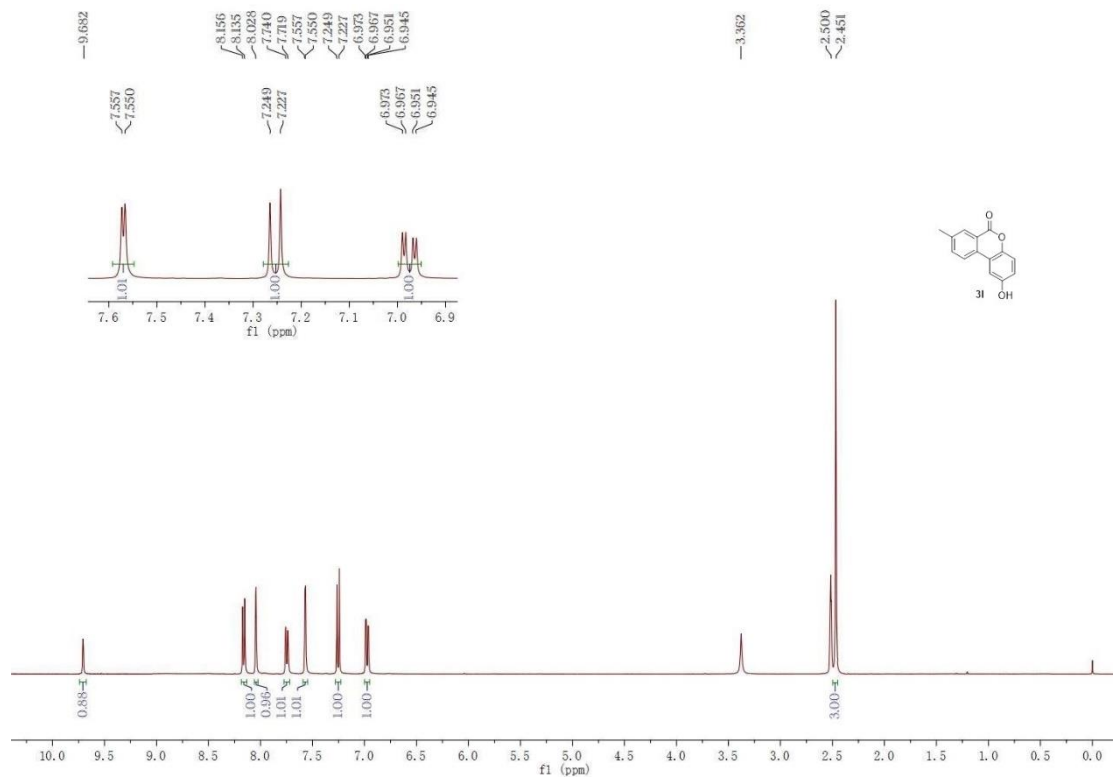


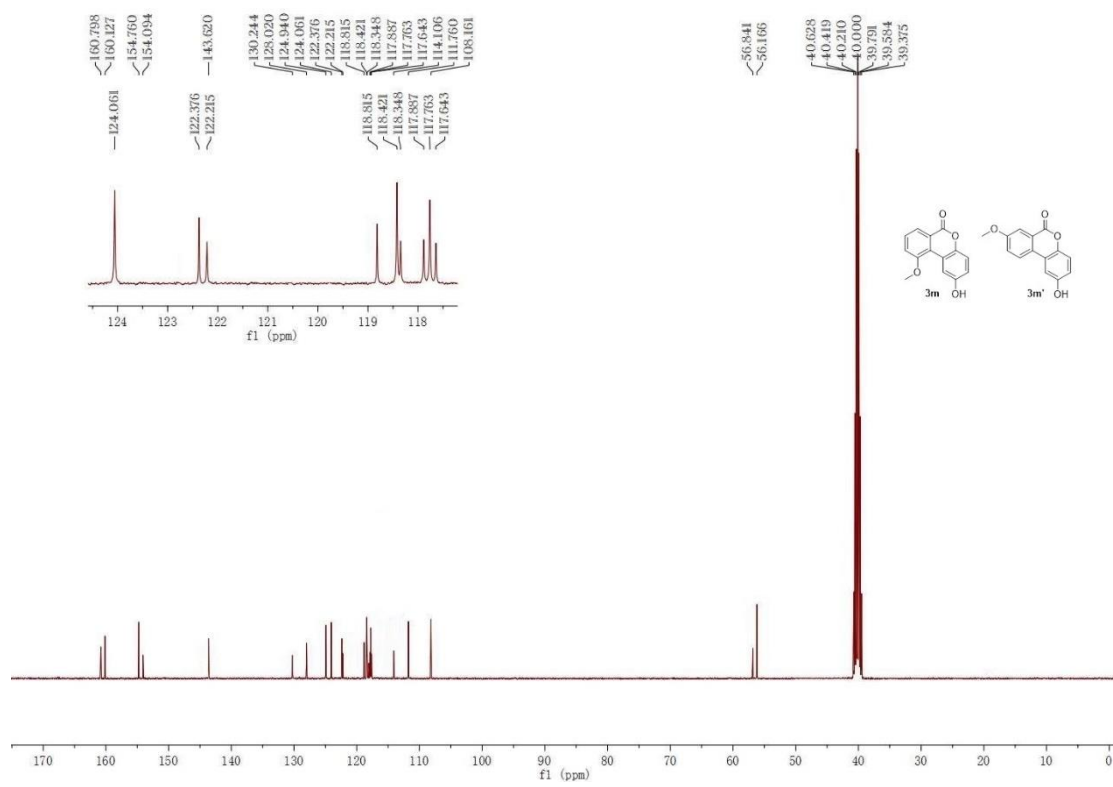
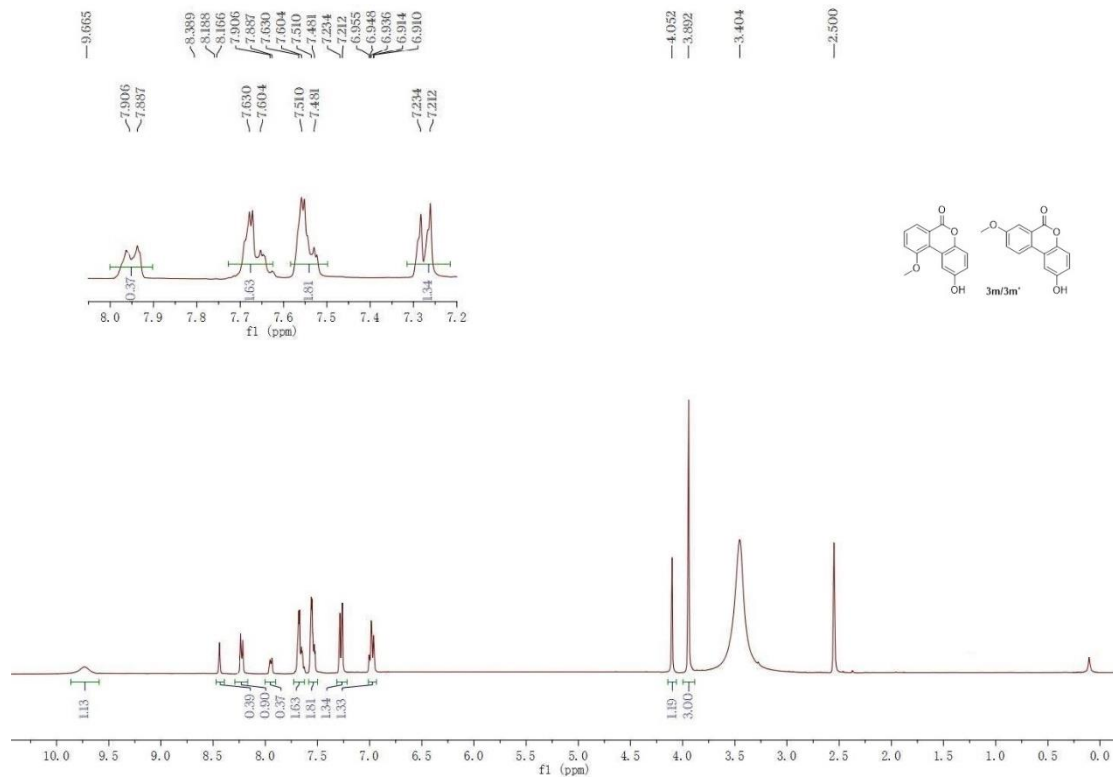


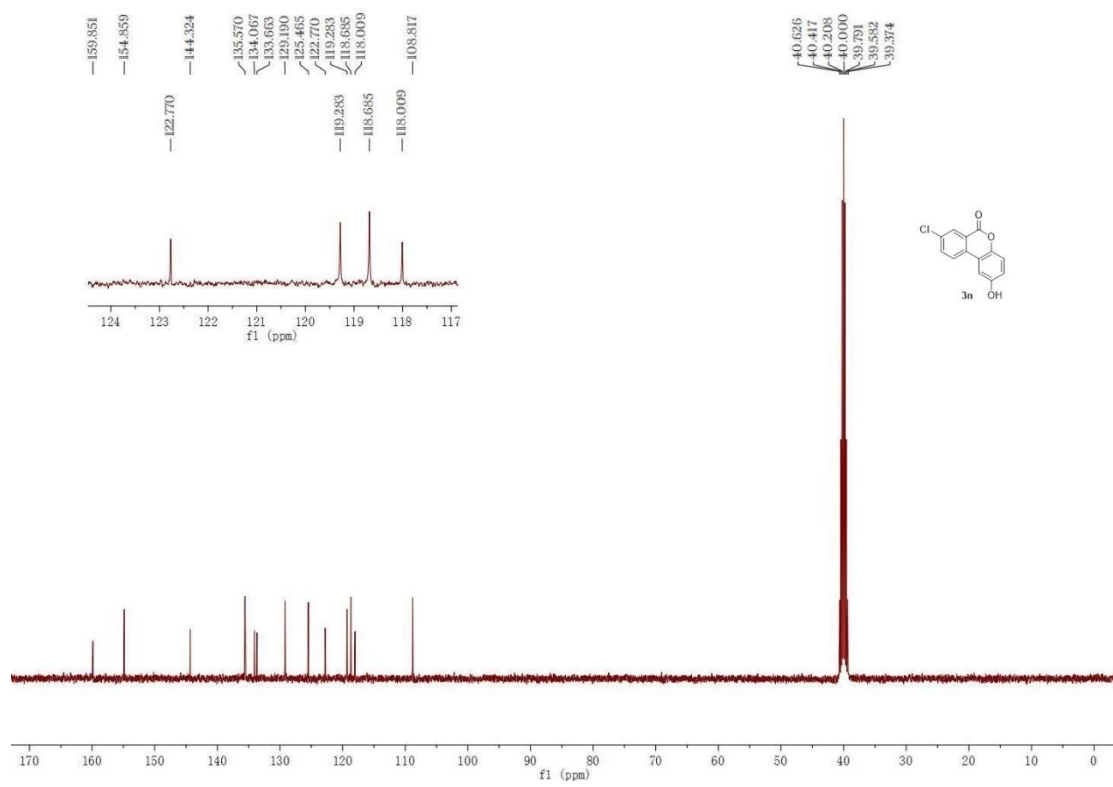
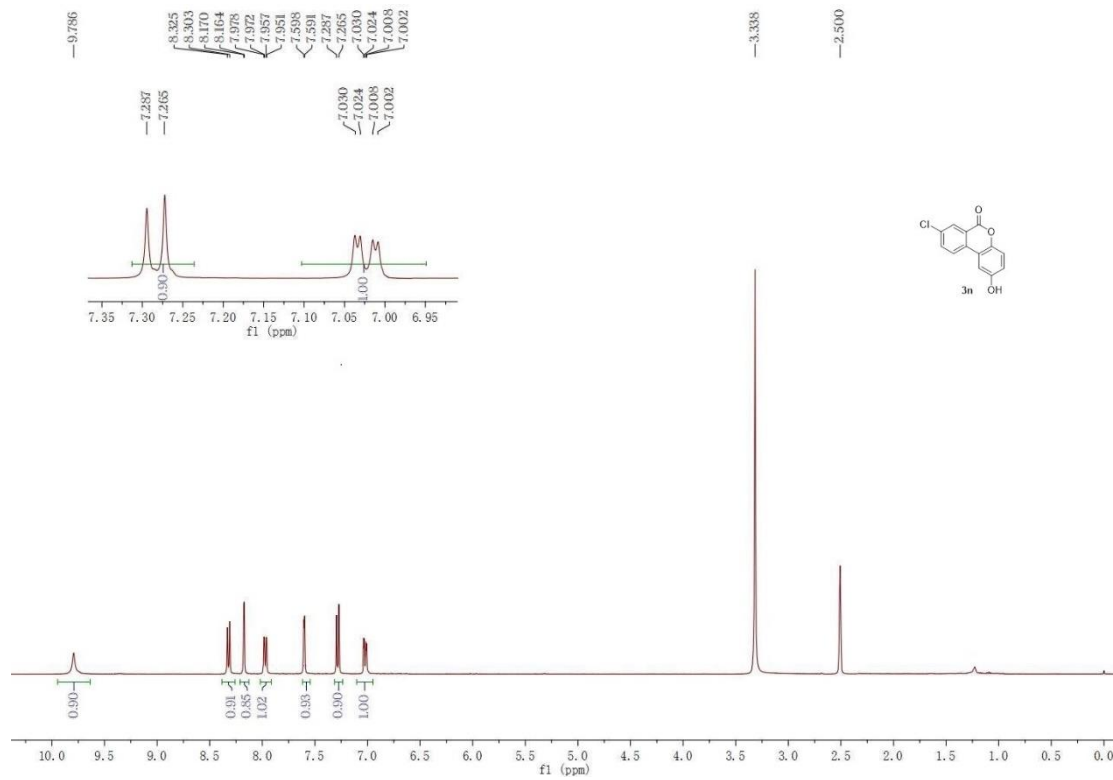


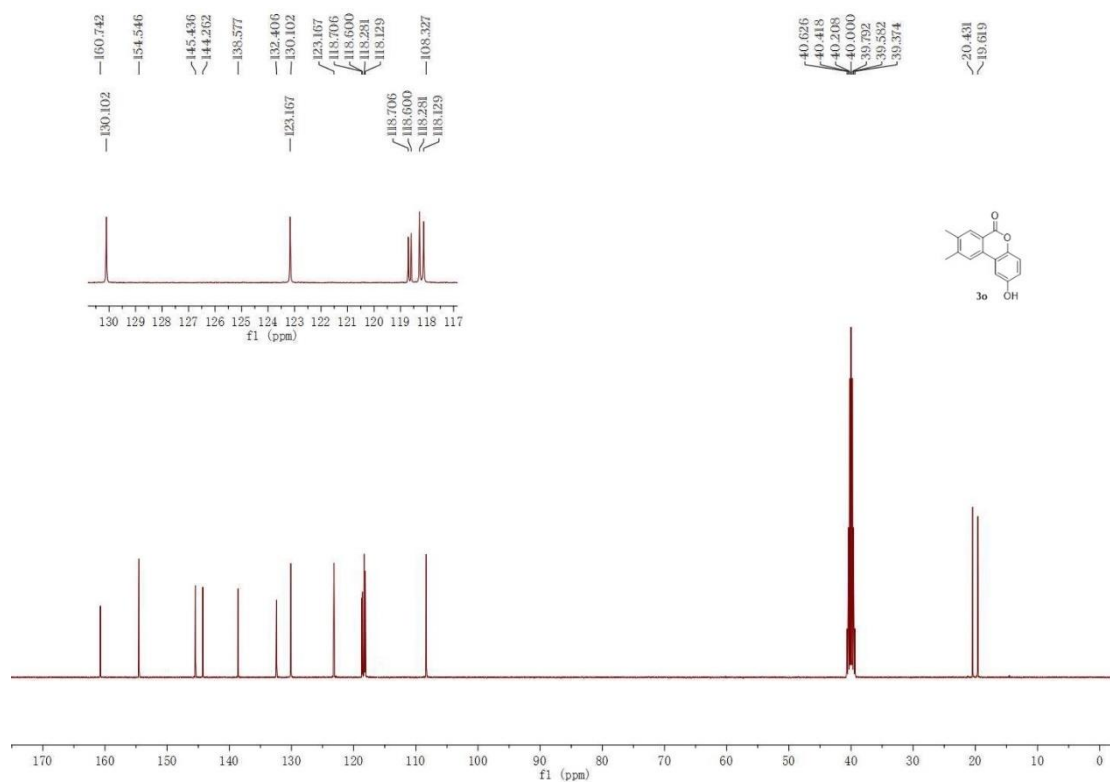
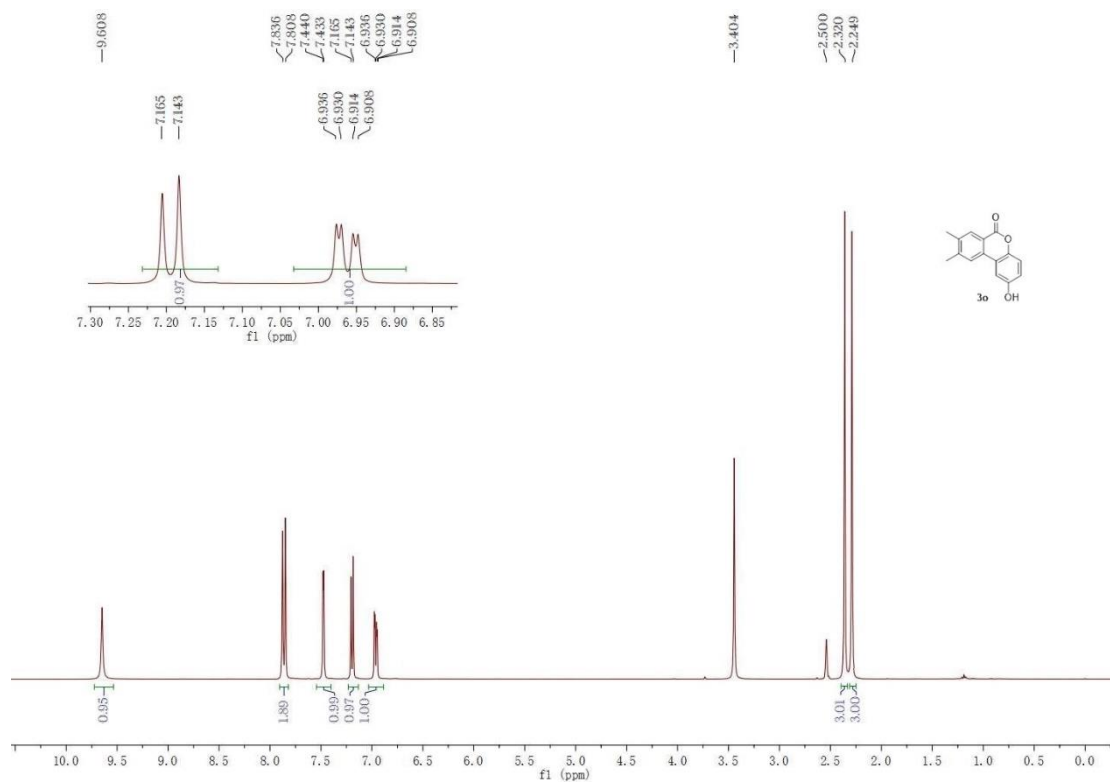


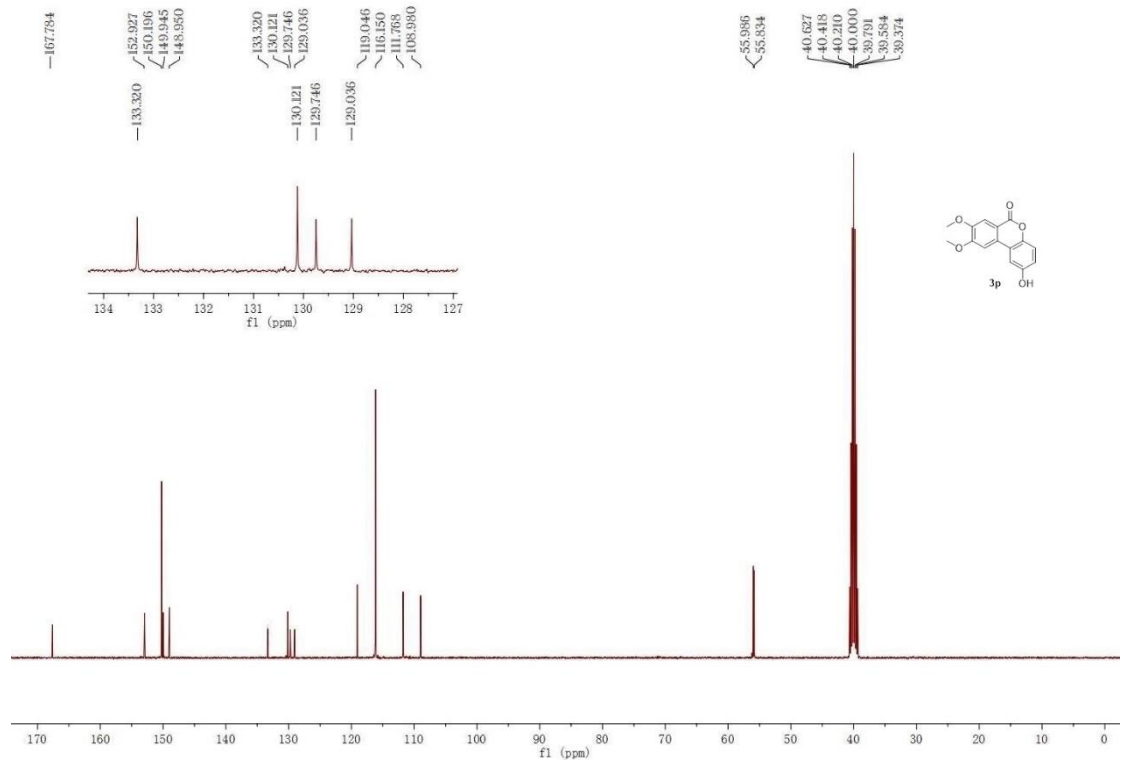
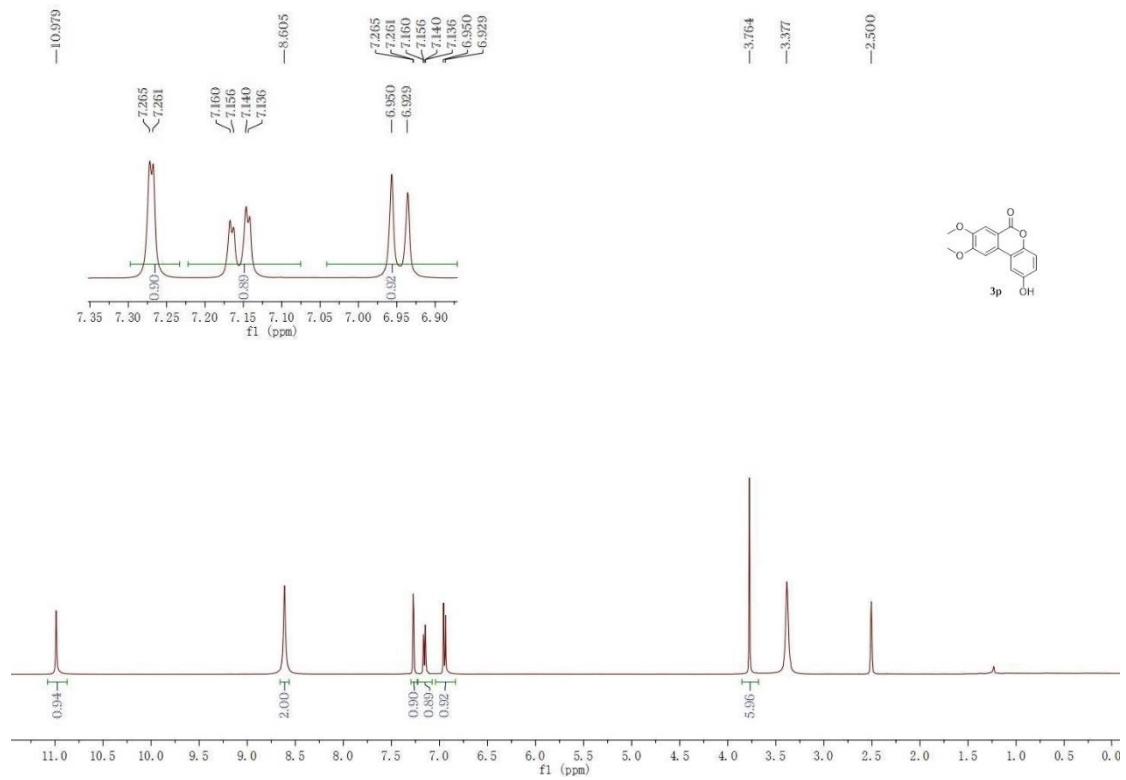


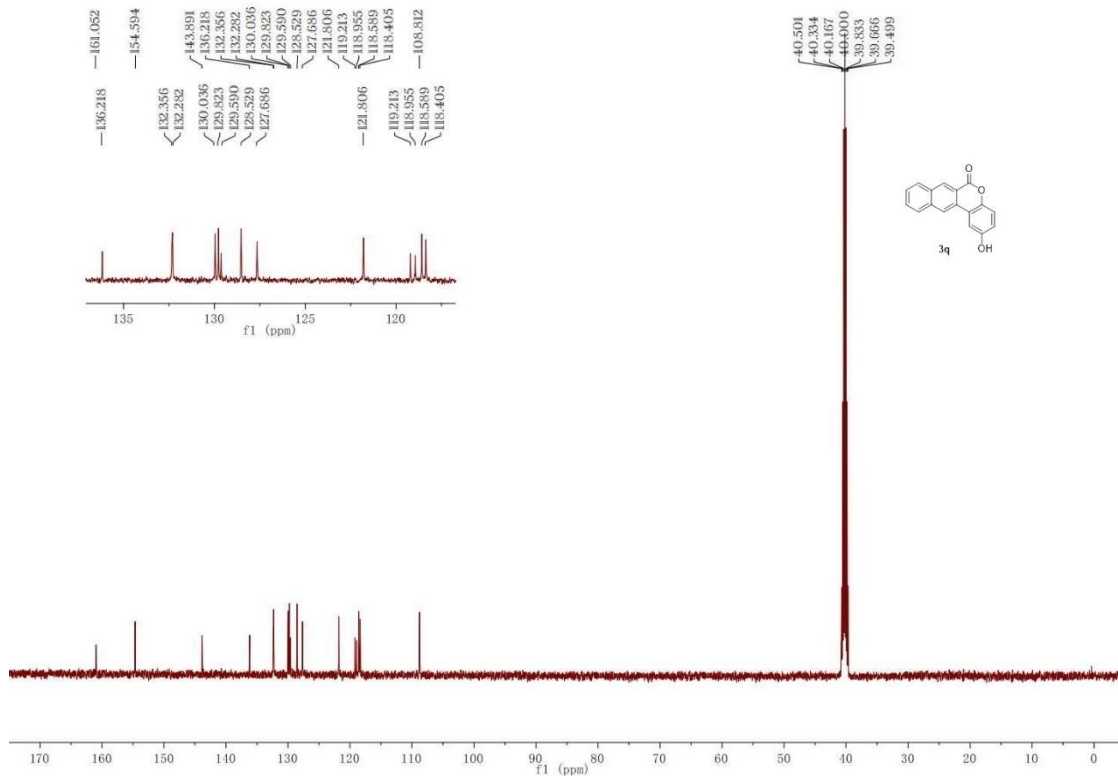
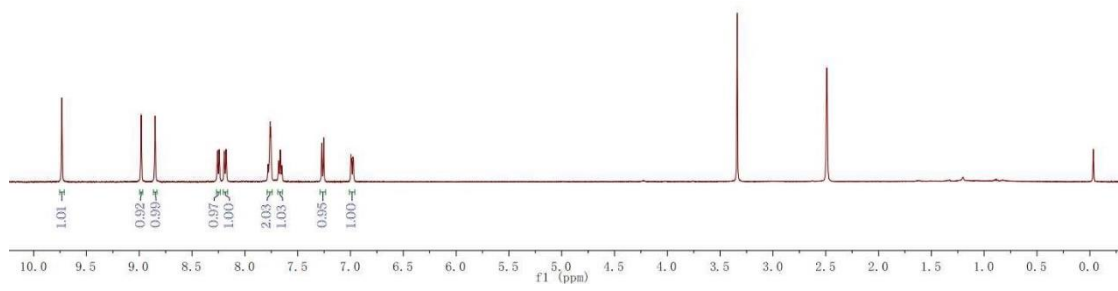
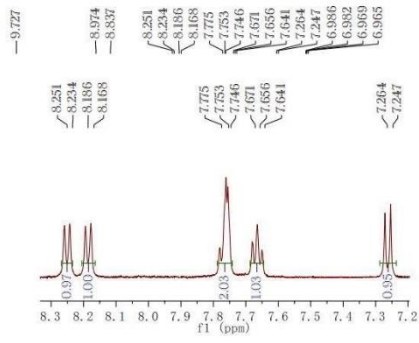


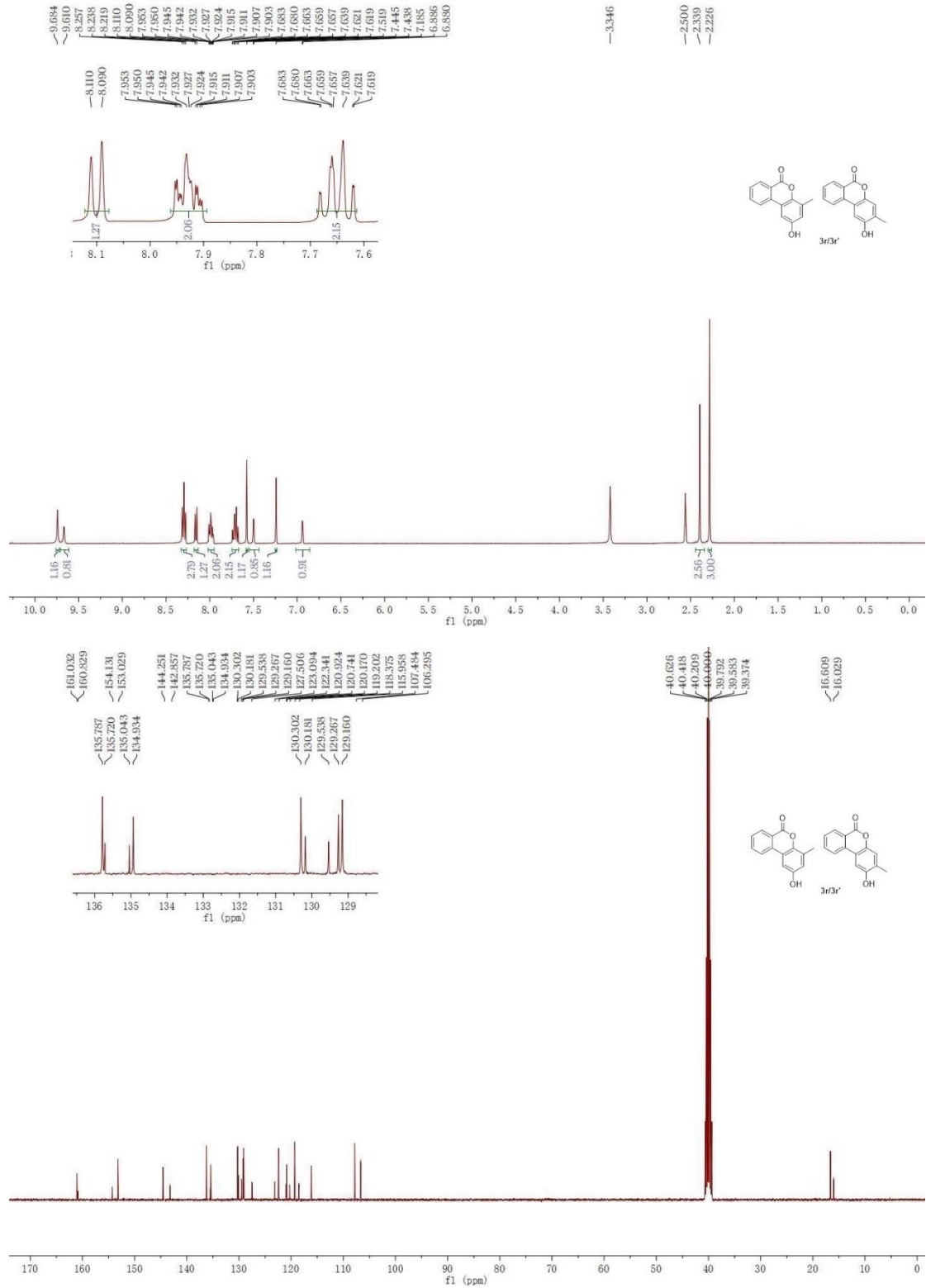


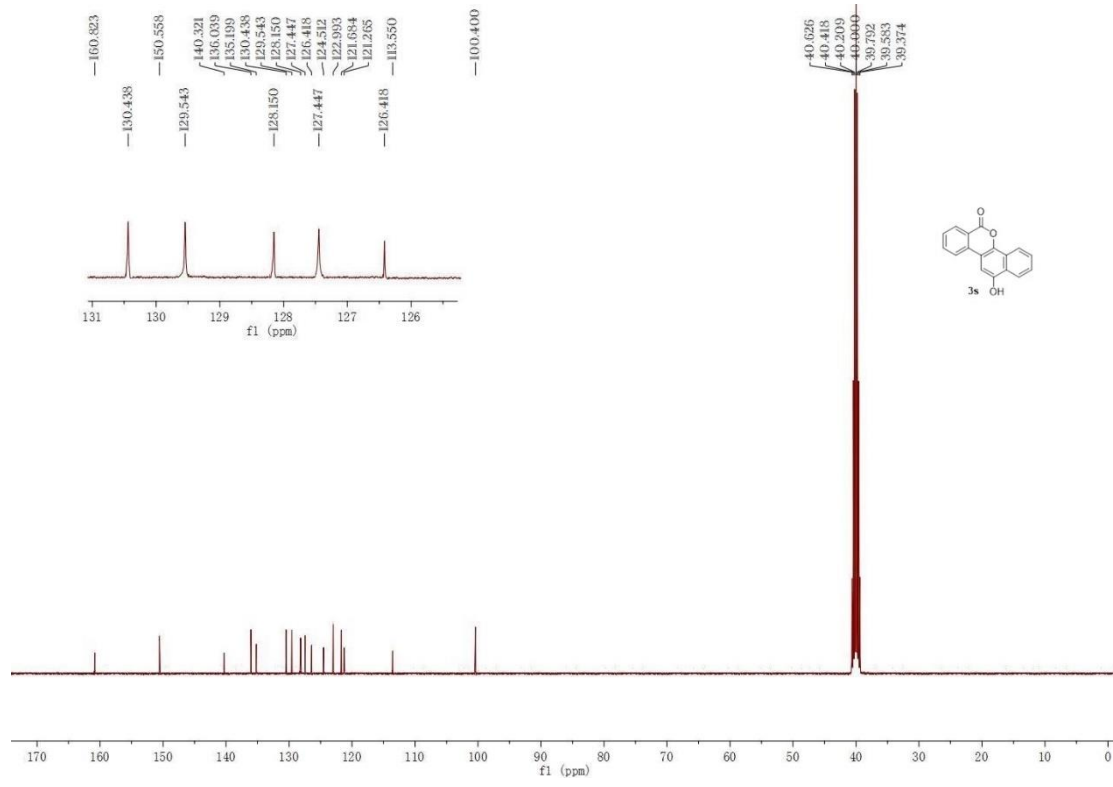
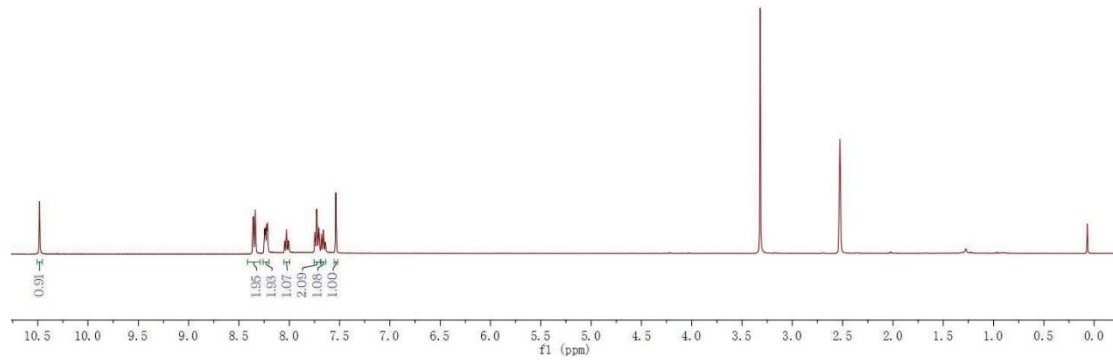
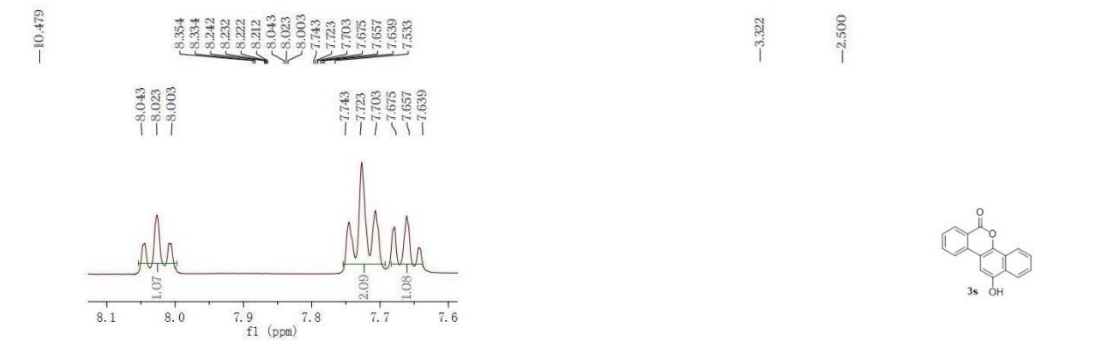


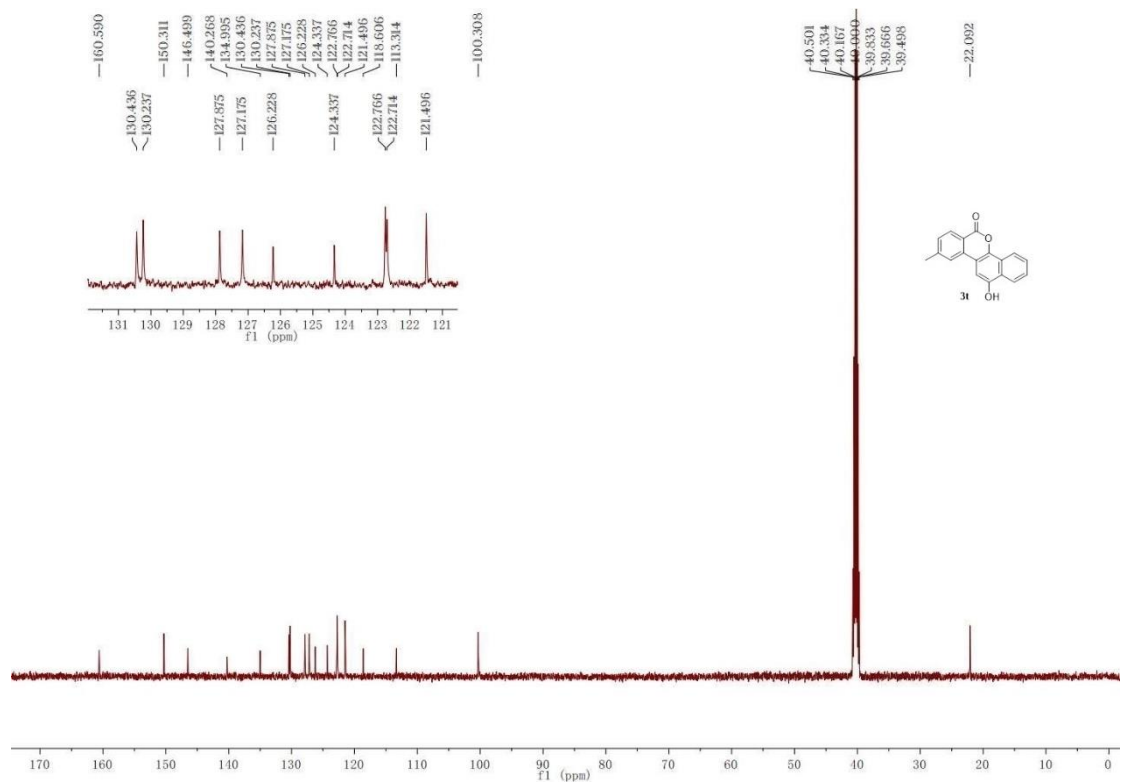
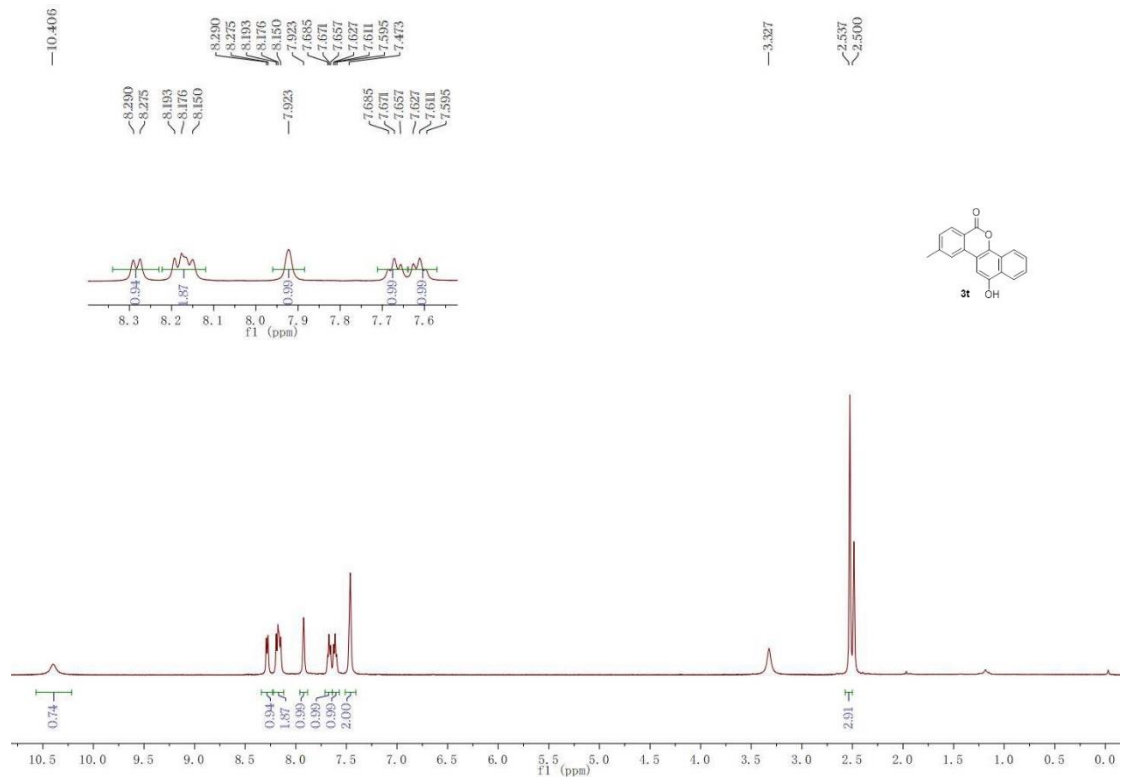


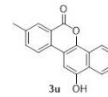
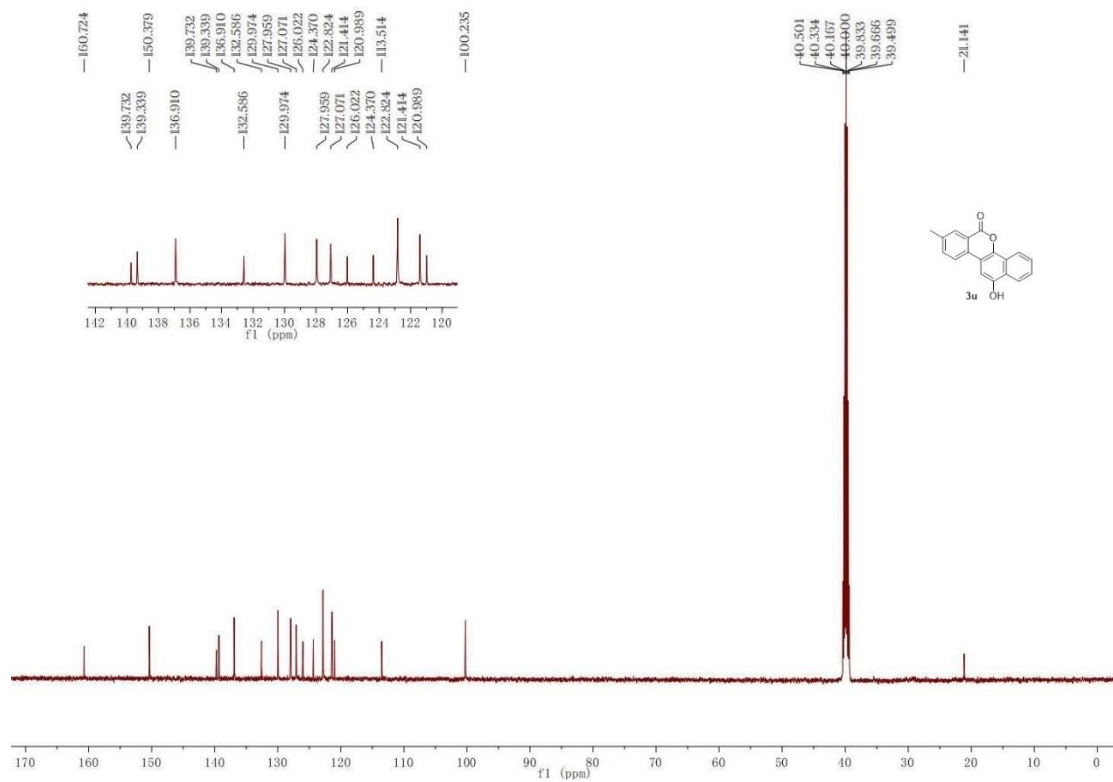
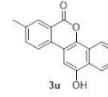
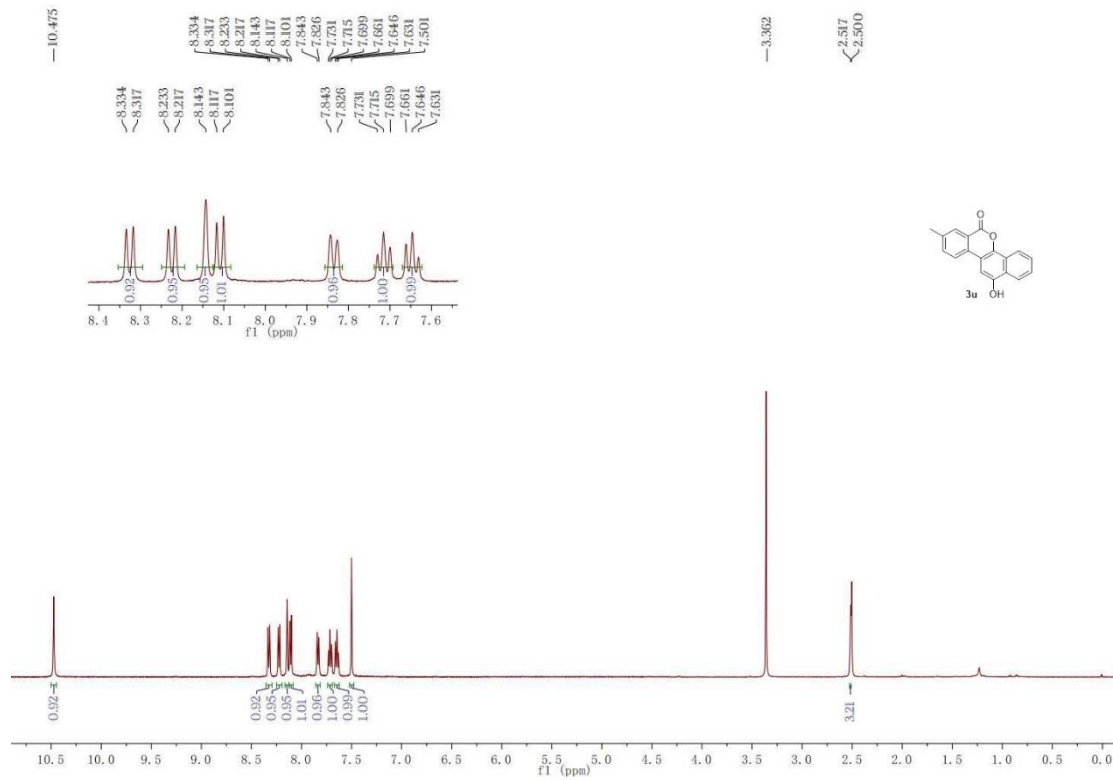








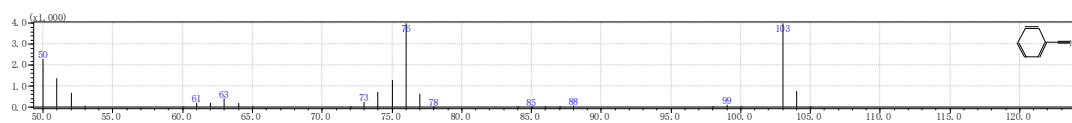




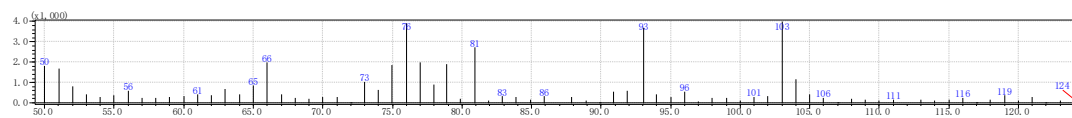
GC-MS of benzonitrile

The reaction mixture was filtered and then tested on a GCMS-QP2010 spectrometer.

Standard sample



Tested sample



REFERENCE

- 1 P. C. Too, Y. F. Wang and S. Chiba, *Org. Lett.*, 2010, **12**, 5688.