Supplementary Information

Rh(III)-catalyzed sequential *ortho*- C–H oxidative arylation/cyclyzation of sulfoxonium ylides with quinones toward 2-hydroxy-dibenzo[*b*,*d*]pyran-6-ones

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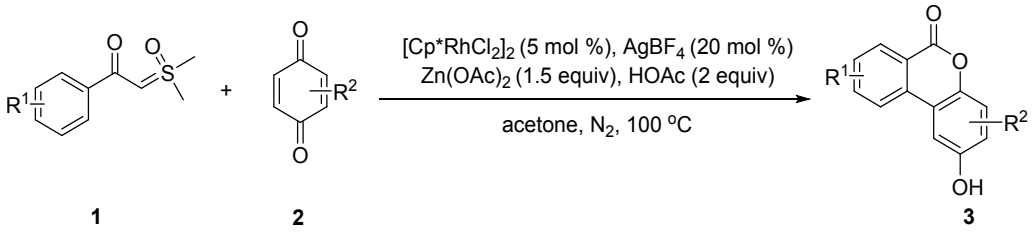
1. General experimental details

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, etc.) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a 300 or 400 MHz NMR spectrometer (75 or 100 MHz for ^{13}C). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) or DMSO-d_6 (δ 2.50 or 39.5 ppm) as the internal standard. The coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh).

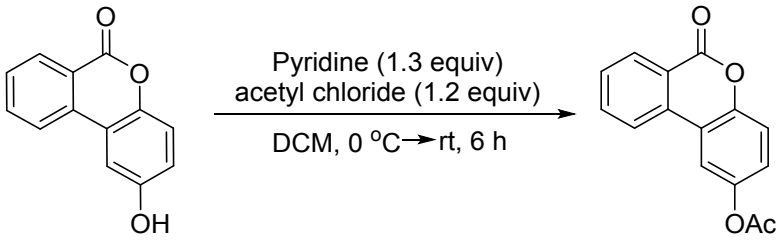
General procedure:



1 **2** **3**

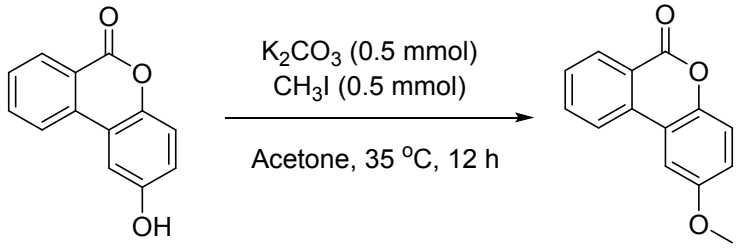
Ylide **1** (0.15 mmol), quinone **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %, 4.7 mg), $AgBF_4$ (20 mol %, 5.8 mg), $Zn(OAc)_2$ (0.23 mmol, 41.1 mg), HOAc (0.3 mmol, 19 μL) and acetone (2 mL) were added into the tube and sealed. The reaction vessel was evacuated and backfilled with N_2 in three times. The reaction mixture was vigorously stirred at 100 °C for 12 h. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1 (v/v) to give the corresponding product **3**.

2. Detail procedures for the further transformation of compound 3a



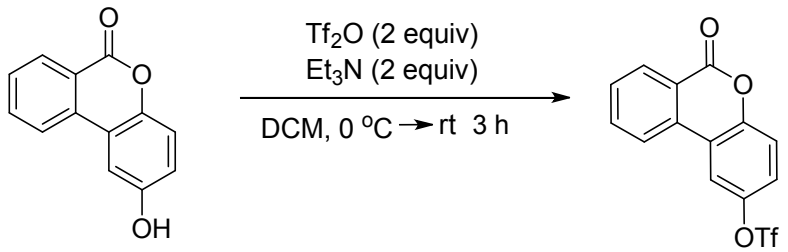
3a **4**

3a (0.1 mmol, 21.2 mg) was dissolved in dichloromethane (1 mL) in a flame-dried flask that was cooled to 0 °C. Pyridine (0.13 mmol, 8 μL) was added to the flask immediately followed by acetyl chloride (0.12 mmol, 9.4 mg). The flask was warmed to room temperature and the reaction mixture stirred until complete as indicated by TLC (approx. 6 hours). The reaction mixture was washed with water, 3 M HCl (aq.), water, $NaHCO_3$ (sat. aq.) and finally dried with Na_2SO_4. The solvent was removed under reduced pressure and pure material was isolated after column chromatography (eluent: petroleum ether/ethyl acetate = 10/1, v/v) to afford the product **4** in 78% yield.



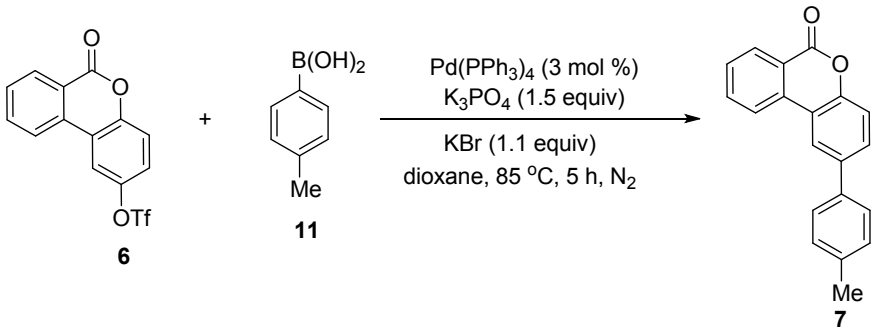
3a **5**

An oven-dried Schlenk tube was charged with **3a** (0.1 mmol, 21.2 mg), methyl iodide (0.5 mmol, 30 μL), K_2CO_3 (0.5 mmol, 69.1 mg), was dissolved in acetone (1 mL). The flask was warmed to 35 °C and the reaction mixture stirred until complete as indicated by TLC (approx. 12 hours). The resulting mixture was washed several times with H_2O. The organic phase was dried with Na_2SO_4 and then evaporated under reduced pressure and pure material was isolated after column chromatography (eluent: petroleum ether/ethyl acetate = 10/1, v/v) to afford the product **5** in 85% yield.



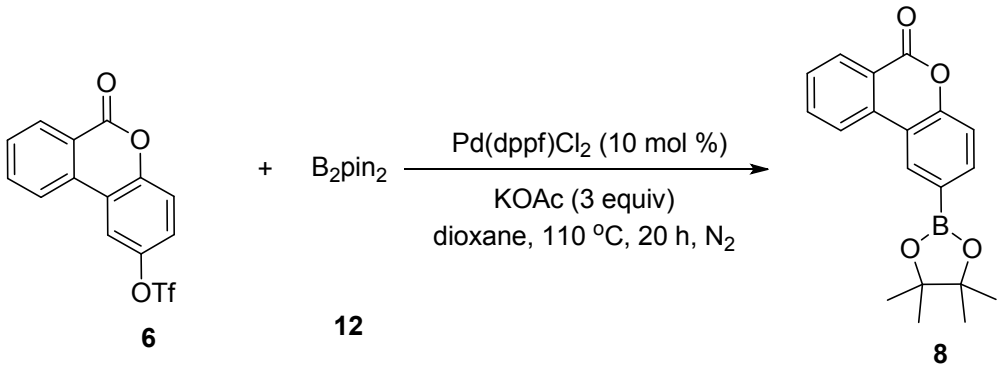
3a **6**

To an ice-bath cooled solution of **3a** (0.1 mmol, 21.2 mg) in DCM (1.0 mL), Et_3N (0.2 mmol, 14 μL) and $(CF_3SO_2)_2O$ (0.2 mmol, 30 μL) were added successively. The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with brine (10 mL) and 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 (eluent: petroleum ether/ethyl acetate = 10/1, v/v) to afford the product **6** in 95% yield.



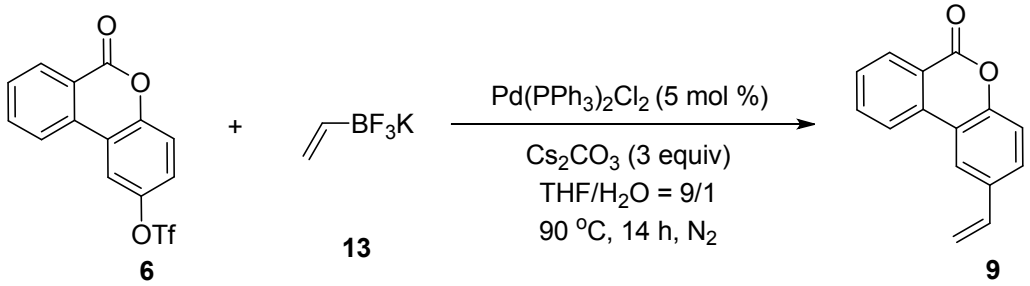
6 **11** **7**

An oven-dried Schlenk tube was charged with **6** (0.1 mmol, 34.3 mg), *p*-tolylboronic acid **11** (0.2 mmol, 27 mg), $Pd(PPh_3)_4$ (0.003 mmol, 3.5 mg), K_3PO_4 (0.15 mmol, 31.8 mg) and KBr (0.11 mmol, 13.1 mg) and was evacuated and refilled with N_2 three times, followed by adding anhydrous 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 (eluent: petroleum ether/Et_2O = 50/1, v/v) to afford the product **7** in 89% yield.



6 **12** **8**

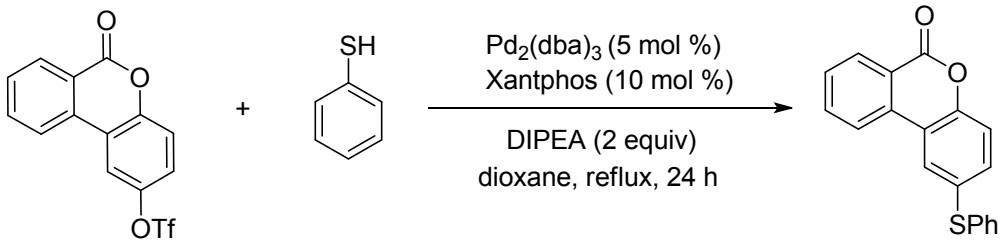
Under N_2, to an oven-dried Schlenk tube were sequentially added bis(pinacolato)diboron **12** (0.2 mmol, 50.8 mg), $Pd(dppf)Cl_2$ (0.01 mmol, 7.3 mg), KOAc (0.3 mmol, 29.4 mg), and a solution of **6** (0.1 mmol, 34.4 mg) in anhydrous dioxane (1 mL). The mixture was heated to reflux (110 °C), and the reaction progress was monitored by TLC. Upon completion (~ 20 h), the reaction was filtered through a short pad of silica gel, which was washed with ethyl acetate (20 mL×3). The filtrate was concentrated, and the residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ ethyl acetate = 9/1, v/v) to afford compound **8** in 51% yield.



6 **13** **9**

Under N_2 at rt, to an oven-dried Schlenk tube were sequentially added $Pd(PPh_3)_2Cl_2$ (5 mol %, 3.5 mg), Cs_2CO_3 (0.3 mmol, 97.7 mg), potassium vinyltrifluoroborate (0.2 mmol, 26.8 mg), a solution of **6** (0.1 mmol, 34.4 mg) in THF (0.9 mL), and H_2O (0.1 mL). The mixture was stirred at 90 °C, and the progress was monitored by TLC. Upon completion (~ 14 h), Na_2SO_4 was added to remove water. The mixture was filtrated through a short pad of silica gel, which was washed with ethyl acetate (20 mL×3). The filtrate was concentrated. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 10/1,

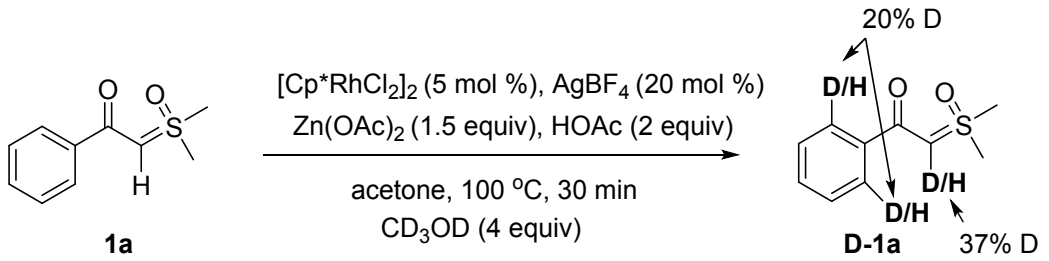
v/v) to afford the product **9** in 68% yield.



6 **14** **10**

Under N_2, to an oven-dried Schlenk tube were sequentially added $Pd_2(dba)_3$ (0.005 mmol, 3 mg), Xantphos (0.01 mmol, 5.8 mg), a solution of **6** (0.1 mmol, 34.4 mg) in anhydrous dioxane (1 mL), PhSH **14** (0.15 mmol, 17 μL), DIPEA (0.2 mmol, 25.8 mg), and anhydrous dioxane (1 mL). The reaction was heated to reflux (110 ^oC), and the reaction progress was monitored by TLC. Upon completion (~ 24 h), the reaction was filtered through a short pad of silica gel, which was washed with ethyl acetate (20 mL×3). The filtrate was concentrated. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 10/1, v/v) to afford **10** in 42% yield.

3. H/D Exchange Experiment



Ylide **1a** (0.15 mmol, 29.7mg), $[Cp^*RhCl_2]_2$ (5 mol %, 4.7 mg), $AgBF_4$ (20 mol %, 5.8 mg), $Zn(OAc)_2$ (0.23 mmol, 41.1 mg), HOAc (0.3 mmol, 18 mg) and acetone (2 mL) and CD_3OD (0.6 mmol, 32 μL) was added into a 20 mL Schlenk tube equipped with a Teflon cap. The reaction mixture was vigorously stirred at 100 °C for 30 min. Then, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the D-**1a** (Figure S1).

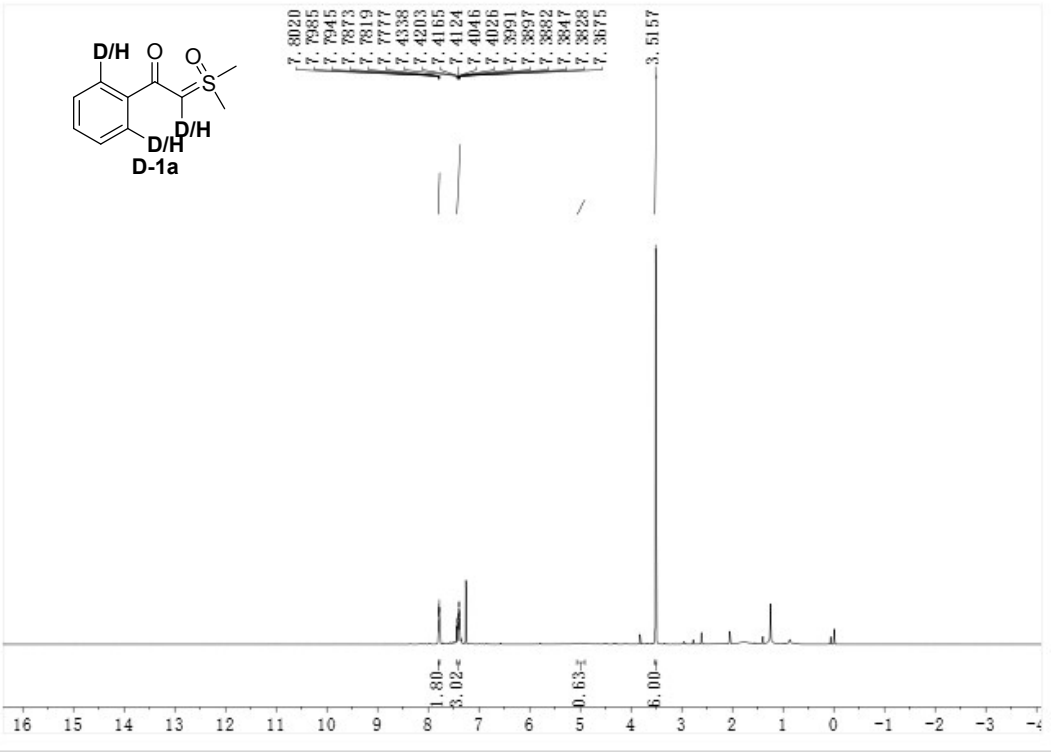
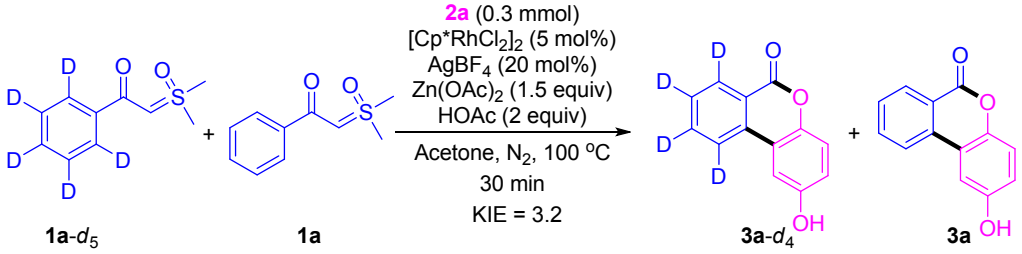


Figure S1

4. Intermolecular KIE experiment



Ylide **1a** (0.075 mmol), **1a**-d_5 (0.075 mmol), quinone **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol %, 4.7 mg), $AgBF_4$ (20 mol %, 5.8 mg), $Zn(OAc)_2$ (0.23 mmol, 41.1 mg), HOAc (0.3 mmol, 18 mg) and acetone (2 mL) were added into the tube and sealed. The reaction vessel was evacuated and backfilled with N_2 in three times. The reaction mixture was vigorously stirred at 100 °C for 30 min. After the reaction was completed as indicated by TLC analysis, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ethyl acetate = 10:1 (v/v) to give the corresponding product **3a** and **3a**-d_4. Upon analyzing the corresponding ^{1}H NMR spectrum, the intermolecular KIE (K_H/K_D) was about 3.2. (Figure S2)

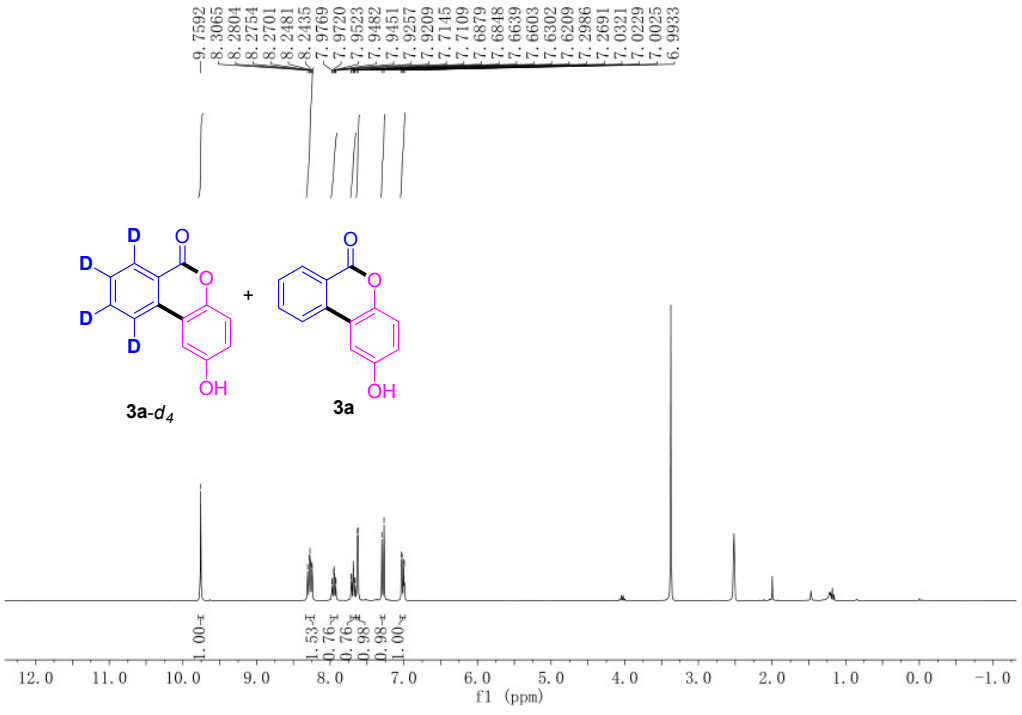
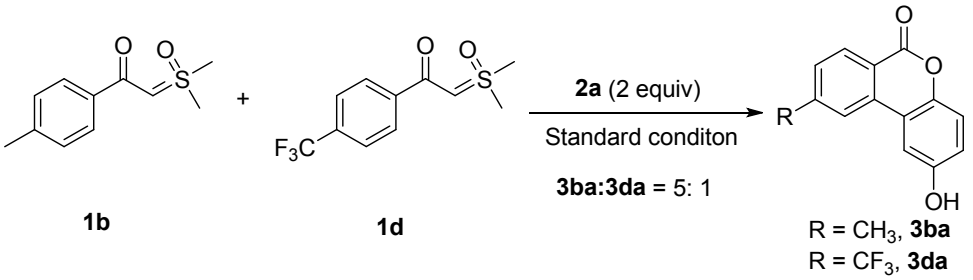


Figure S2

5. Intermolecular competition experiments



Ylide **1b:1d** = 1:1 (0.15 mmol, 35.6 mg), quinone **2a** (0.3 mmol, 32 mg), $[Cp^*RhCl_2]_2$ (5 mol %, 4.7 mg), $AgBF_4$ (20 mol %, 5.8 mg), $Zn(OAc)_2$ (0.23 mmol, 41.1 mg), HOAc (0.3 mmol, 18 mg) and acetone (2 mL) were added into the tube and sealed. The reaction vessel was evacuated and backfilled with N_2 in three times. The reaction mixture was vigorously stirred at 100 ^oC for 12 h. After the reaction was completed as indicated by TLC analysis. The solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent: petroleum ether/ethyl acetate = 10/1, v/v) to afford product **3ba** and **3da**. The mole ratio of **3ba**:**3da** = 5:1 was determined on the basis of ^1H NMR analysis (Figure S3).

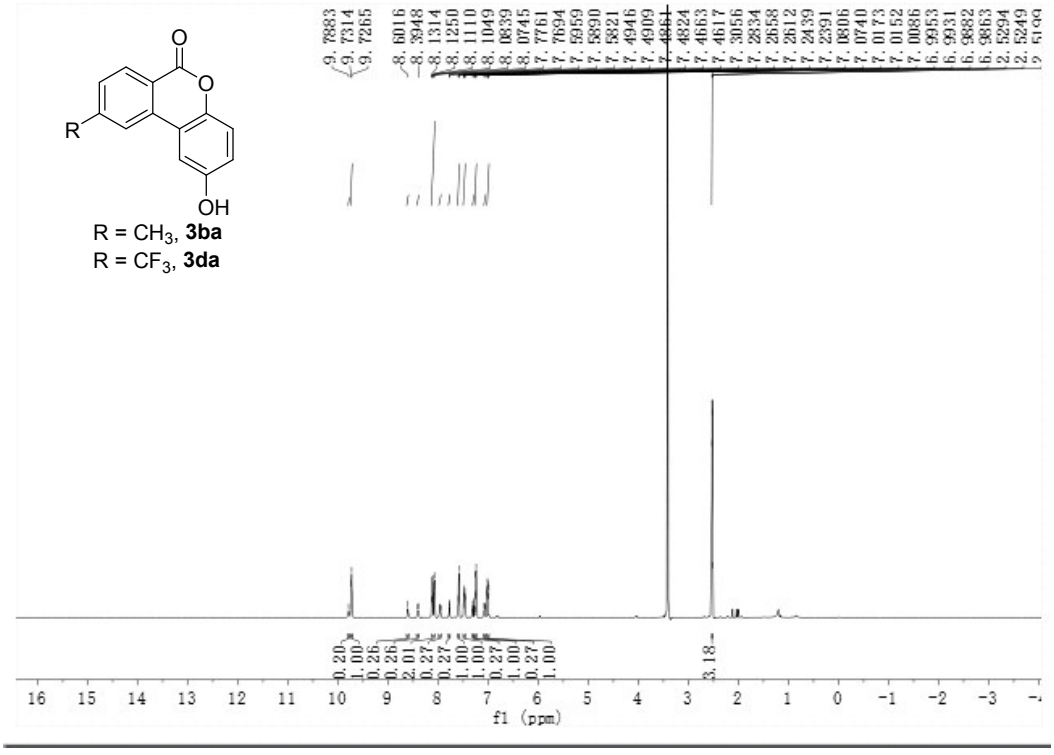
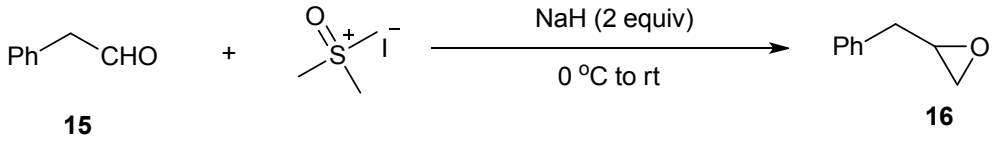


Figure S3

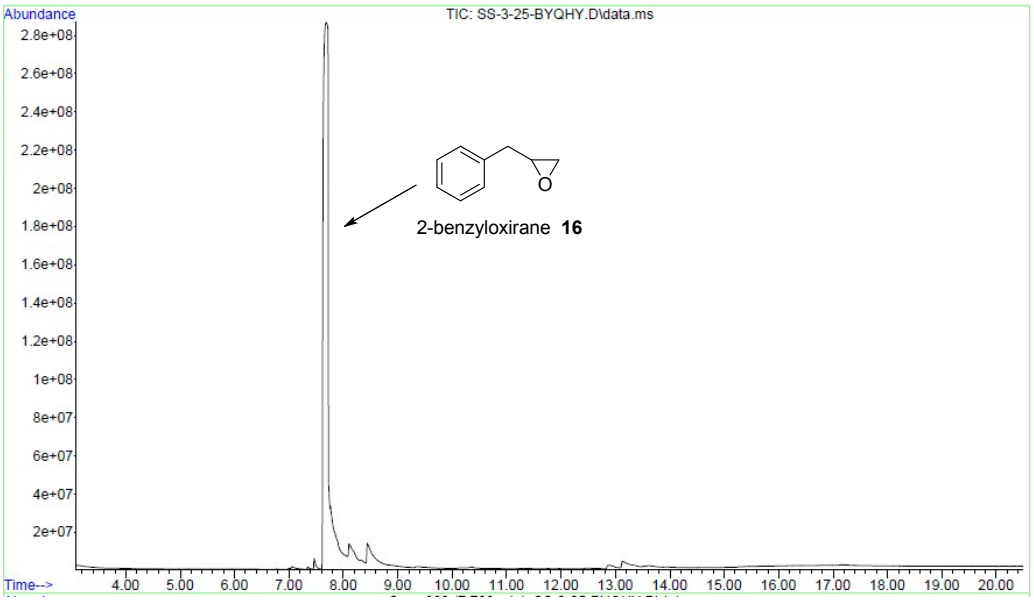
6. Experiment of trapping the Corey's ylide G

6.1 Synthesis of the Corey's yield 16[1]



15 **16**

In a vacuum-dried Schlenk, trimethyl sulfonium iodide (10 mmol, 2.04 g) is added to a slurry of NaH (60% in mineral oil, 10 mmol, 0.4 g) in dry DMSO and THF (1:0.7, 17 mL) and allowed to stir for 30 min at room temperature. The reaction mixture is brought to 0 °C and phenylacetaldehyde **15** (5 mmol, 0.6 g) is added as a solution in dry THF (5 mL). The reaction mixture is maintained at 0 °C for 2 h and allowed to stir at room temperature. After completion of the reaction (TLC monitoring), the reaction mixture is quenched with a saturated NH_4Cl solution (15 mL), and the aqueous phase is extracted with CH_2Cl_2 (3*10 mL). The combined organic layers are washed successively with a saturated solution of $NaHCO_3$, H_2O and brine and dried over Na_2SO_4. Evaporation of the solvents under reduced pressure afforded the crude product. Purification by flash column chromatography on deactivated silica gel with Et_3N (1%) afforded the analytically pure product **16** in good yields. Then it was analyzed by GC-MS (7.768 min with m/z=134.0) (Figure S4).



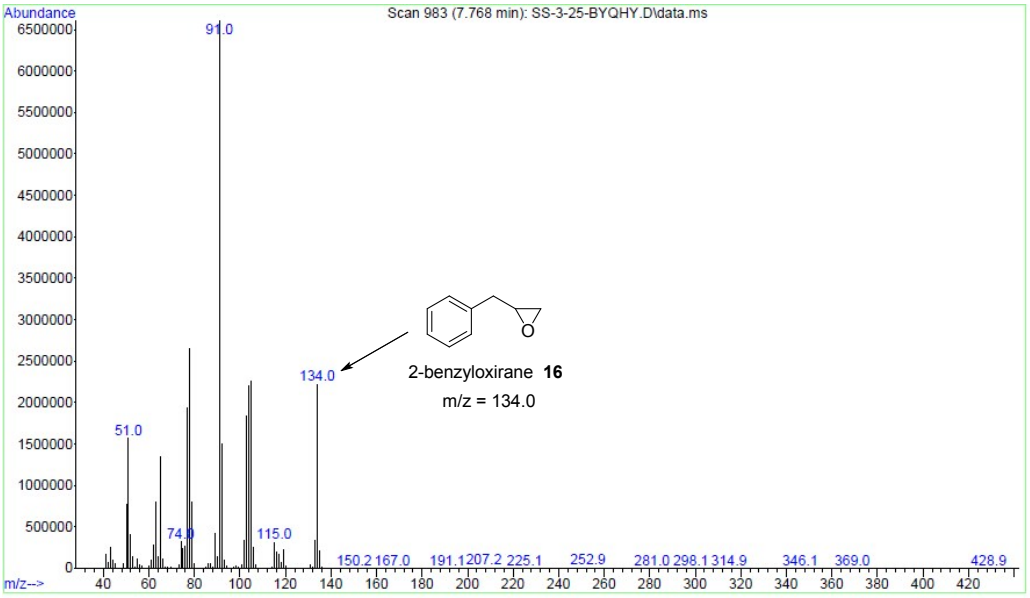
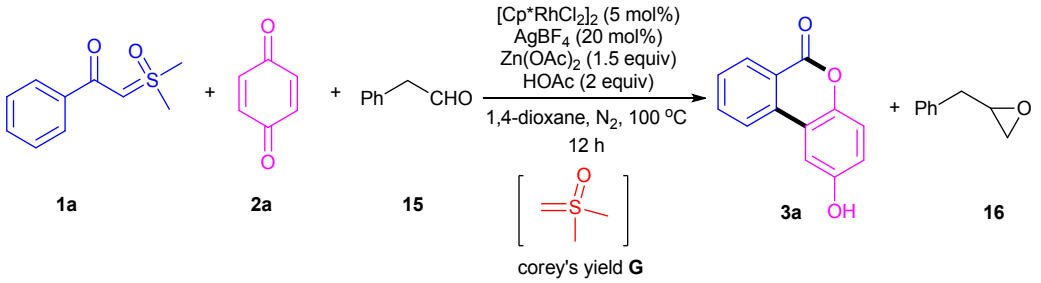


Figure S4 GC-MS spectra of pure compound **16**

6.2 Trapping the Corey's ylide G by phenylacetaldehyde 15



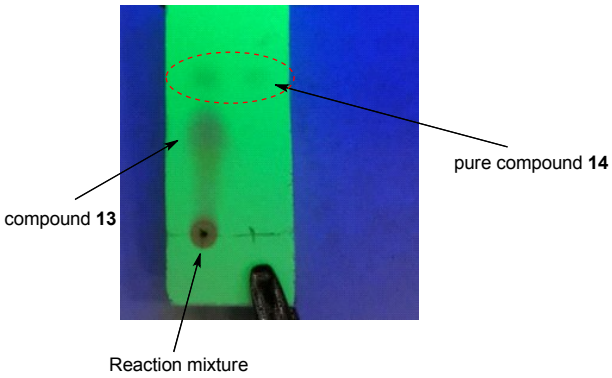


Figure S5 TLC results of the above reaction (hexane: EA = 35: 1)

Ylide **1a** (0.15 mmol, 29.4 mg), quinone **2a** (0.3 mmol, 32.4 mg), $[Cp^*RhCl_2]_2$ (5 mol %, 4.7 mg), $AgBF_4$ (20 mol %, 5.8 mg), $Zn(OAc)_2$ (0.23 mmol, 41.1 mg), HOAc (0.3 mmol, 19 μL), phenylacetaldehyde **15** (0.15 mmol, 18 mg) and 1,4-dioxane (2 mL) were added into the tube and sealed. The reaction vessel was evacuated and

backfilled with N_2 in three times. The reaction mixture was vigorously stirred at 100 ^oC for 12 h. After that, the reaction mixture was analyzed by TLC.

According to the TLC result of the reaction mixture, compound **16** may be generated (Figure S5). When the reaction mixture was analyzed by GC-MS, the GC signal of compound **16** was not detected obviously, which would be overlapped by the strong GC signal of 2-phenylacetaldehyde **15** (Figure S6).

In order to confirm the existence of compound **16** in the reaction mixture, we purified the reaction mixture and the isolated product was analyzed by GC-MS. Delightedly, a component with the molecular weight of 134.0 (7.768 min) was detected, which is consistent with that of pure compound **16** (Figure S4 vs S7).

Based on these results, the Corey's yield **G** may a reaction intermediate in this reaction. The exact reason for the explanation of low amount of intermediate **G** detected was not clear at current stage. It may not exclude the possibility of some corey's yield **G** reacted with quinone **2a** during the reaction.

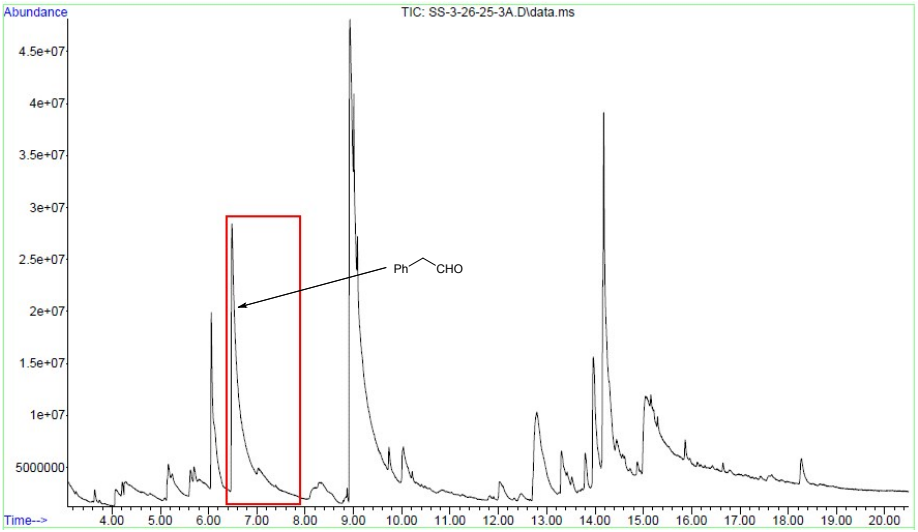


Figure S6 GC spectra of the above reaction mixture

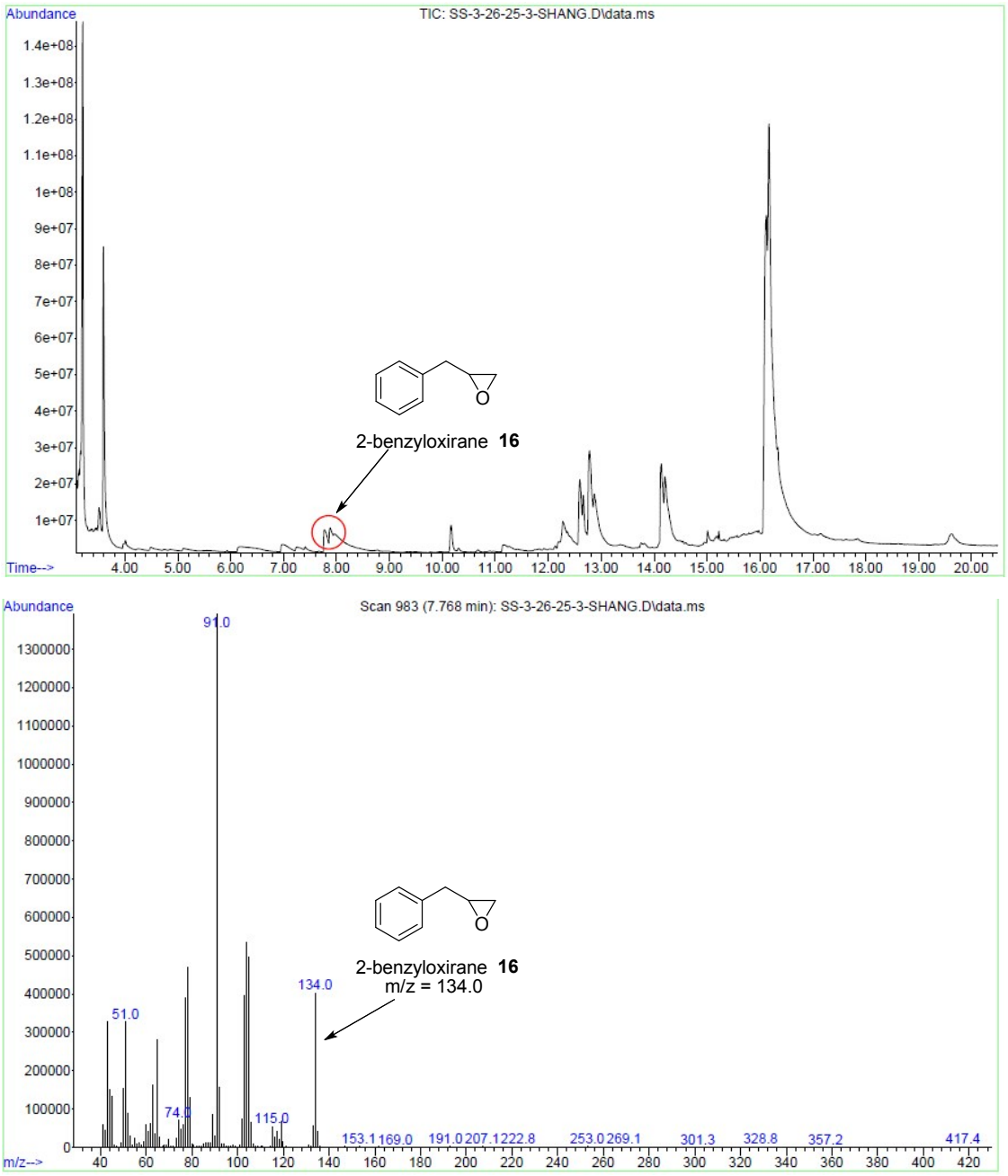
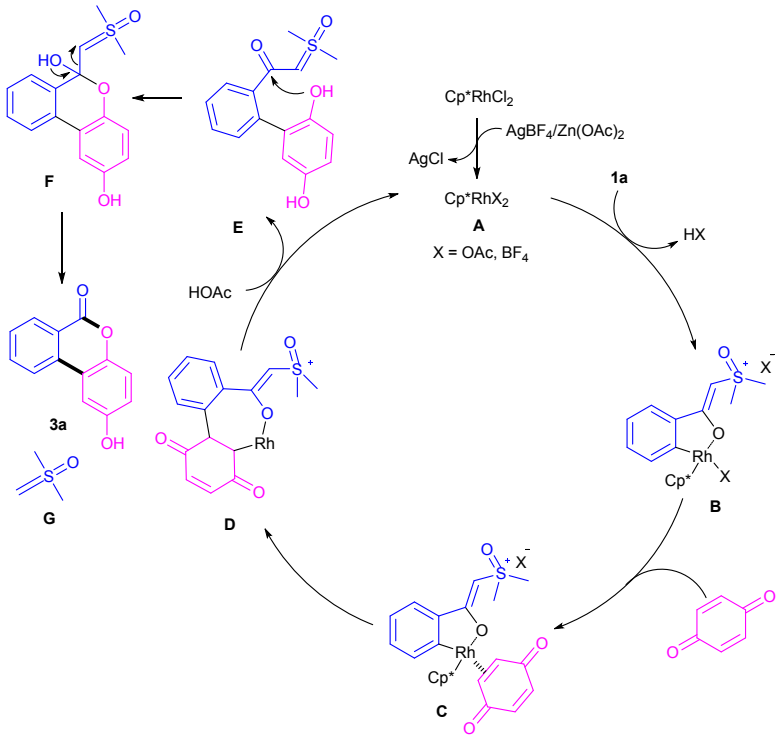


Figure S7 GC-MS spectra of the purified reaction mixture

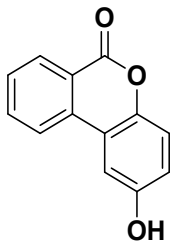
7. Proposed mechanism



Scheme S1

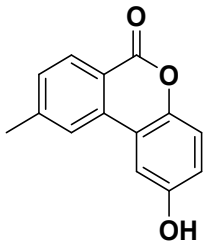
8. Experimental characterization data for compounds

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



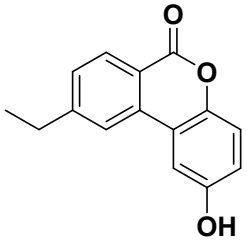
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3a** (88% yield) as a yellowish solid. R_f = 0.4 (ethyl acetate: petroleum ether = 1:3, v/v) ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.79 (s, 1H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.26-8.23 (m, 1H), 7.96-7.91 (m, 1H), 7.69-7.65 (m, 1H), 7.61 (d, *J* = 2.8 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.8 Hz 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.9, 154.7, 144.4, 135.7, 134.7, 130.2, 129.6, 122.9, 121.0, 118.9, 118.6, 118.6, 108.6.

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



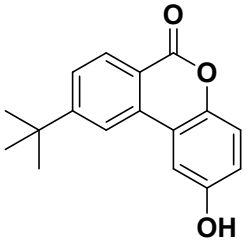
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3b** (79% yield) as a yellowish solid. R_f = 0.5 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.70 (s, 1H), 8.09-8.02 (m, 2H), 7.56-7.54 (m, 1H), 7.45-7.42 (m, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 6.98 (dd, *J* = 8.9, 2.8 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.0, 154.8, 146.6, 144.6, 134.8, 130.8, 130.3, 123.0, 118.9, 118.8, 118.7, 118.6, 108.7, 22.2.

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



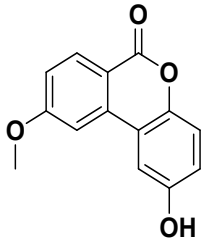
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3c** (75% yield) as a yellowish solid. R_f = 0.5 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.70 (s, 1H), 8.12-8.09 (m, 1H), 8.05-8.03 (s, 1H), 7.60-7.58 (m, 1H), 7.49-7.44 (m, 1H), 7.24-7.20 (m, 1H), 6.98 (dd, *J* = 8.9, 2.7 Hz, 3H), 2.79, (q, *J* = 7.5, 15 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.8, 154.6, 152.3, 152.3, 144.5, 134.8, 130.3, 129.5, 121.7, 118.8, 118.7, 118.5, 108.7, 29.0, 15.5.

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3d** (68% yield) as a yellowish solid. R_f = 0.4 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.70 (s, 1H), 8.20-8.17 (m, 2H), 7.76-7.73 (m, 1H), 7.27 (d, *J* = 8.9 Hz 1H), 7.00 (dd, *J* = 8.9, 2.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.8, 159.0, 154.6, 144.5, 134.5, 130.2, 127.3, 119.1, 118.9, 118.7, 118.7, 118.5, 108.8, 35.9, 31.2.

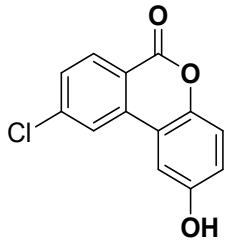
2-hydroxy-9-methoxy-6*H*-benzo[*c*]chromen-6-one (3e)[2]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5)

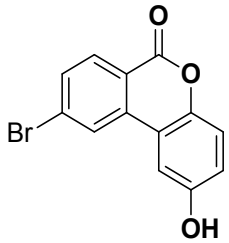
give **3e** (53% yield) as a brown solid. R_f = 0.4 (ethyl acetate: petroleum ether = 1:3, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.70 (s, 1H), 8.17 (d, J = 8.6 Hz, 1H), 7.68 (t, J = 2.2 Hz, 2H), 7.26-7.21 (m, 2H), 7.01 (dd, J = 8.9, 2.8 Hz, 1H), 4.0 (s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 165.1, 160.6, 154.6, 144.8, 137.2, 132.6, 119.1, 118.7, 118.5, 117.6, 114.0, 109.1, 105.9, 56.5.

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



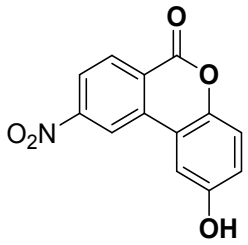
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3f** (35% yield) as a yellowish solid. R_f = 0.4 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.86 (s, 1H), 8.39-8.34 (m, 1H), 8.26-8.19 (m, 1H), 7.72-7.65 (m, 1H), 7.29-7.24 (m, 1H), 7.07 (dd, J = 8.9, 2.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.2, 154.9, 144.7, 141.1, 136.6, 132.3, 129.7, 122.8, 119.8, 119.6, 118.6, 117.7, 109.2.

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



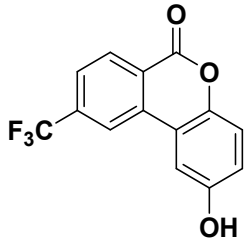
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3g** (40% yield) as a brown solid, m.p. 274-276 ^{o}C. R_f = 0.5 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.75 (s, 1H), 8.49 (s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.83-7.80 (m, 1H), 7.63 (d, J = 2.8 Hz, 1H), 7.25 (d, J = 8.8 Hz 1H), 7.04 (dd, J = 8.9, 2.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.4, 154.8, 144.7, 136.6, 132.6, 132.2, 130.3, 125.8, 120.1, 119.6, 118.6, 117.7, 109.2. Calcd for ($C_{13}H_6BrO_3^-$ [M-H]$^-$) 288.9506 Found: 288.9503.

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3h** (47% yield) as a yellow solid, m.p. 170-172 °C. R_f = 0.45 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.79 (s, 1H), 8.87 (d, *J* = 2.2 Hz, 1H), 8.43-8.40 (m, 1H), 8.35-8.32 (m, 1H), 7.66 (d, *J* = 2.7 Hz, 1H), 7.27 (d, *J* = 8.9, 1H), 7.04 (dd, *J* = 8.9, 2.8 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 159.6, 154.9, 152.0, 144.7, 136.1, 132.4, 125.5, 123.4, 120.1, 118.8, 118.1, 117.6, 109.1. Calcd for ($C_{13}H_6NO_5^-$ [M-H]$^-$) 256.0251 Found: 256.0254.

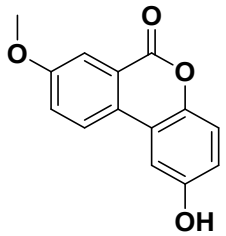
2-hydroxy-9-(trifluoromethyl)-6*H*-benzo[*c*]chromen-6-one (3i)[2]



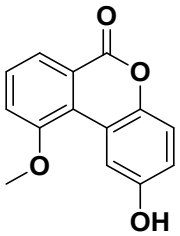
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3** (40% yield) as a yellowish solid. R_f = 0.4 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.75 (s, 1H), 8.59 (s, 1H), 8.39 (d, *J* = 8.3Hz, 1H), 7.97-7.94 (m, 1H), 7.76 (s, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.05 (dd, *J* =8.9, 2.6 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 160.0, 154.9, 144.6, 135.6, 135.3 (q, *J* = 31 Hz),131.6, 125.6 (q, *J* = 3.0 Hz), 124.2, 124.0 (q, *J* = 271.0 Hz), 120.4 (q, *J* = 3.0 Hz), 119.7, 118.7, 117.8, 109.3.

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

2-hydroxy-10-methoxy-6*H*-benzo[*c*]chromen-6-one (3j)[2]



3j'

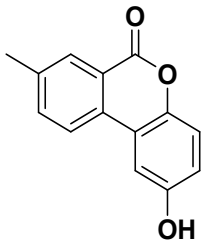


3j

3j':3j=1:1

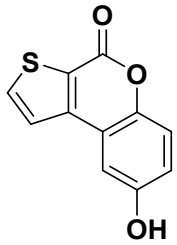
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3j', 3j** (71% yield) as a yellowish solid. R_f = 0.35 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.63 (s, 1H), 9.57(s, 1H) 8.39 (d, *J* = 2.8 Hz, 1H), 8.18 (d, *J* = 8.9 Hz, 1H), 7.90 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.65-7.58 (m, 3H), 7.51-7.47 (m, 2H), 7.23 (d, *J* = 8.9 Hz, 1H), 6.96-6.91 (m, 2H), 4.06 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.8, 160.7, 160.0, 157.5, 154.7, 154.0, 143.8, 143.6, 130.2, 128.0, 124.9, 124.0, 123.3, 122.8, 122.3, 122.1, 118.8, 118.4, 118.2, 118.0, 117.8, 117.68, 117.6, 114.1, 111.7, 108.1, 56.8, 56.1.

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



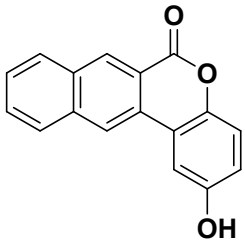
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3k** (47% yield) as a yellowish solid. R_f = 0.5 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.73 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.00 (s, 1H), 7.71-7.68 (m, 1H), 7.53 (d, *J* = 2.9 Hz, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.00 (dd, *J* =8.8, 2.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.0, 154.8, 144.2, 139.6, 136.8, 132.3, 130.0, 123.0, 121.0, 118.9, 118.6, 118.5, 108.5, 21.4.

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



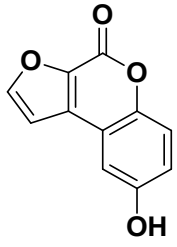
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3l** (63% yield) as a light brown solid. R_f = 0.4 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.81 (s, 1H), 8.37 (d, J = 5.2 Hz, 1H), 7.97 (d, J = 5.3 Hz, 1H), 7.46 (d, J = 2.9 Hz, 1H), 7.36 (d, J = 8.9 Hz, 1H), 7.04 (dd, J = 9.0, 2.9 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 157.1, 154.7, 145.9, 145.4, 138.8, 124.1, 118.6, 118.3, 118.1, 109.6.

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



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3m** (66% yield) as a yellowish solid. R_f = 0.35 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.75 (s, 1H), 8.95 (s, 1H), 8.81 (s, 1H), 8.24-8.15 (m, 2H), 7.79-7.73 (m, 2H), 7.69-7.63 (m, 1H), 7.26 (d, J = 8.8 Hz, 1H), 7.01 (dd, J = 8.8, 2.7 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 161.1, 154.8, 144.0, 136.3, 132.4, 132.4, 130.0, 129.9, 129.7, 128.7, 127.7, 121.9, 119.3, 119.1, 118.7, 118.5, 108.9.

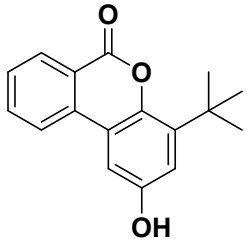
8-hydroxy-4*H*-furo[2,3-*c*]chromen-4-one (3n)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5)

give **3n** (25% yield) as a yellowish solid, m.p. 256-257 °C. R_f = 0.35 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.83 (s, 1H), 8.38 (d, *J* = 2.0 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.38-7.33 (m, 2H), 7.01 (dd, *J* = 9.0, 2.9 Hz, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 154.7, 152.4, 152.4, 145.6, 137.6, 133.7, 118.3, 118.3, 117.0, 109.7, 107.7. Calcd for ($C_{11}H_5O_4^-$ [M-H]$^-$) 201.0193 Found: 201.0199.

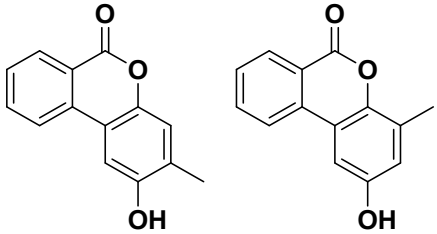
3-(*tert*-butyl)-2-hydroxy-6*H*-benzo[*c*]chromen-6-one(3o)[2]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3o** (65% yield) as a Yellowish solid. R_f = 0.5 (ethyl acetate: petroleum ether = 1:3, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.65 (s, 1H), 8.31-8.25 (m, 2H), 7.97-7.92 (s, 1H), 7.59-7.57 (m, 1H), 7.71-7.66 (m, 1H), 7.52 (s, *J* = 2.7 Hz, 1H), 7.01 (d, *J* = 2.7 Hz, 1H), 1.47 (s, 1H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.3, 154.0, 143.2, 139.2, 135.7, 135.3, 129.9, 129.6, 123.3, 120.5, 119.0, 116.9, 106.5, 35.1, 30.1.

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

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

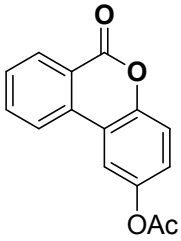


3p : 3p' = 4:1

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give **3p, 3p'** (57% yield) as a yellowish solid. R_f = 0.5 (ethyl acetate: petroleum ether = 1:2, v/v). ^{1}H NMR (DMSO-d_6, 300 MHz): δ 9.68 (s, 1H), 9.61 (s, 1H), 8.26-8.21 (m,

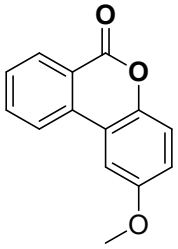
1H), 8.11-8.08 (m, 0.27H), 7.96-7.92 (m, 1H), 7.91-7.89 (m, 0.33H), 7.69-7.63 (m, 1H), 7.62 (d, *J* = 1.1 Hz, 0.06 H), 7.52 (s, 0.27H), 7.44 (d, *J* = 2.8 Hz, 1H), 7.18 (s, 0.25H), 6.89-6.88 (m, 1H), 2.35 (s, 3H), 2.24 (s, 0.75H); ^{13}C NMR (DMSO-d_6, 75 MHz): δ 161.0, 160.8, 154.0, 152.9, 144.3, 142.9, 135.7, 135.7, 135.0, 134.9, 130.3, 130.1, 129.5, 129.2, 129.1, 127.5, 123.0, 122.3, 120.9, 120.7, 120.1, 119.2, 118.3, 115.9, 107.4, 106.2, 16.6, 16.0.

6-oxo-6*H*-benzo[*c*]chromen-2-yl acetate (4)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **4** (78% yield) as a white solid, m.p. 136-138 ^{o}C. R_f = 0.4 (ethyl acetate: petroleum ether = 1:3, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.41-8.38 (m, 1H), 8.03-8.00 (m, 1H), 7.77 (d, *J* = 2.6 Hz, 1H), 7.62-7.58 (m, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.20 (dd, *J* = 9.0, 2.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 169.5, 160.9, 148.7, 147.1, 134.9, 134.1, 130.7, 129.4, 123.9, 121.9, 121.1, 118.8, 118.8, 115.7, 21.1. Calcd for ($C_{15}H_{11}O_4^+$ $[M+H]^+$) 255.0652 Found: 255.0682.

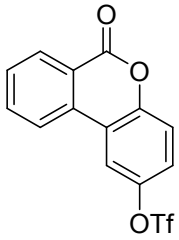
2-methoxy-6*H*-benzo[*c*]chromen-6-one (5)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **5** (85% yield) as a yellowish solid, m.p. 167-169 ^{o}C. R_f = 0.5 (ethyl acetate: petroleum ether = 1:5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.42-8.39 (m, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.85-7.80 (m, 1H), 7.61-7.57 (m, 1H), 7.49 (d, *J* = 2.9 Hz, 1H), 7.30

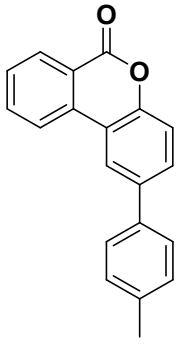
(d, J = 9.0 Hz, 1H), 7.05 (dd, J = 9.0, 2.8 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.3, 156.3, 145.6, 134.8, 134.6, 130.7, 129.0, 121.7, 121.4, 118.7, 118.5, 117.1, 106.4, 55.9. Calcd for ($C_{14}H_{11}O_3^+$ $[M+H]^+$) 227.0703 Found: 227.0739.

6-oxo-6H-benzo[c]chromen-2-yl trifluoromethanesulfonate (6)[2]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **5** (89% yield) as a white solid, m.p. 150-152 °C. R_f = 0.5 (ethyl acetate: petroleum ether = 1:5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40-8.38 (m, 1H), 8.06-8.03 (m, 1H), 7.92 (d, J = 2.8 Hz, 1H), 7.89-7.85 (m, 1H), 7.68-7.64 (m, 1H), 7.43 (d, J = 9.0 Hz, 1H), 7.37 (dd, J = 9.0 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.10, 150.24, 145.66, 135.31, 133.06, 130.81, 130.23, 123.11, 122.01, 121.14, 119.75, 119.72, 118.6 (d, J = 319.0 Hz), 115.91.

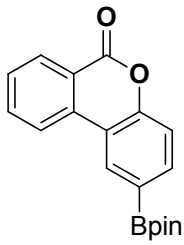
2-(*p*-tolyl)-6*H*-benzo[*c*]chromen-6-one (7)[2]



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **7** (89% yield) as a white solid, m.p. 137−138 °C. R_f = 0.45 (ethyl acetate: petroleum ether = 1:5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43-8.41 (m, 1H), 8.21-8.19 (m, 1H), 7.84 (t, J = 8.0 Hz, 1H), 7.68-7.58 (m, 2H), 7.54-7.52 (m, 2H), 7.41 (d, J = 8.6 Hz, 1H), 7.30 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.2, 150.5, 137.9, 137.6, 137.2, 134.9, 134.8, 130.7, 129.7, 129.3, 129.0, 127.0,

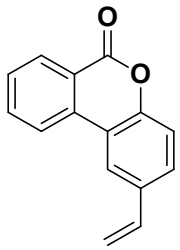
121.7, 121.4, 121.0, 118.2, 118.1, 21.2.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6*H*-benzo[*c*]chromen-6-one (8)



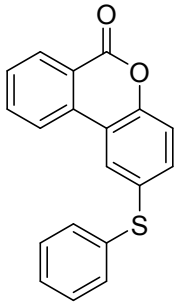
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 9) give **8** (51% yield) as a white solid, m.p. 198-200 ^{o}C. R_f = 0.42 (ethyl acetate: petroleum ether = 1:4, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.53 (d, *J* = 1.4 Hz, 1H), 8.40-8.38 (m, 1H), 8.28-8.26 (m, 1H), 7.90 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.84-7.80 (m, 1H), 7.60-7.55 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 1.38 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.2, 153.5, 136.8, 134.9, 134.8, 130.5, 129.9, 128.8, 122.1, 121.2, 117.5, 117.1, 84.2, 24.9. Calcd for ($C_{19}H_{20}BO_4^+$ $[M+H]^+$) 323.1449 Found: 323.1483.

2-vinyl-6*H*-benzo[*c*]chromen-6-one (9)



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **9** (68% yield) as a white solid, m.p. 129-131 ^{o}C. R_f = 0.45 (ethyl acetate: petroleum ether = 1:5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (dd, *J* = 8.0 1.4, Hz, 1H), 8.15 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.86-7.81 (m, 1H), 7.62-7.54 (m, 2H), 7.33 (d, *J* = 8.6 Hz, 1H), 6.80 (dd, *J* = 17.5, 10.8, Hz, 1H), 5.81 (d, *J* = 17.5 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.1, 150.8, 135.6, 134.9, 134.6, 134.2, 130.7, 129.0, 127.9, 121.7, 121.3, 120.7, 118.9, 117.9, 114.6. Calcd for ($C_{15}H_{11}O_2^+$ $[M+H]^+$) 223.0754 Found: 223.0796.

2-(phenylthio)-6*H*-benzo[*c*]chromen-6-one (10)



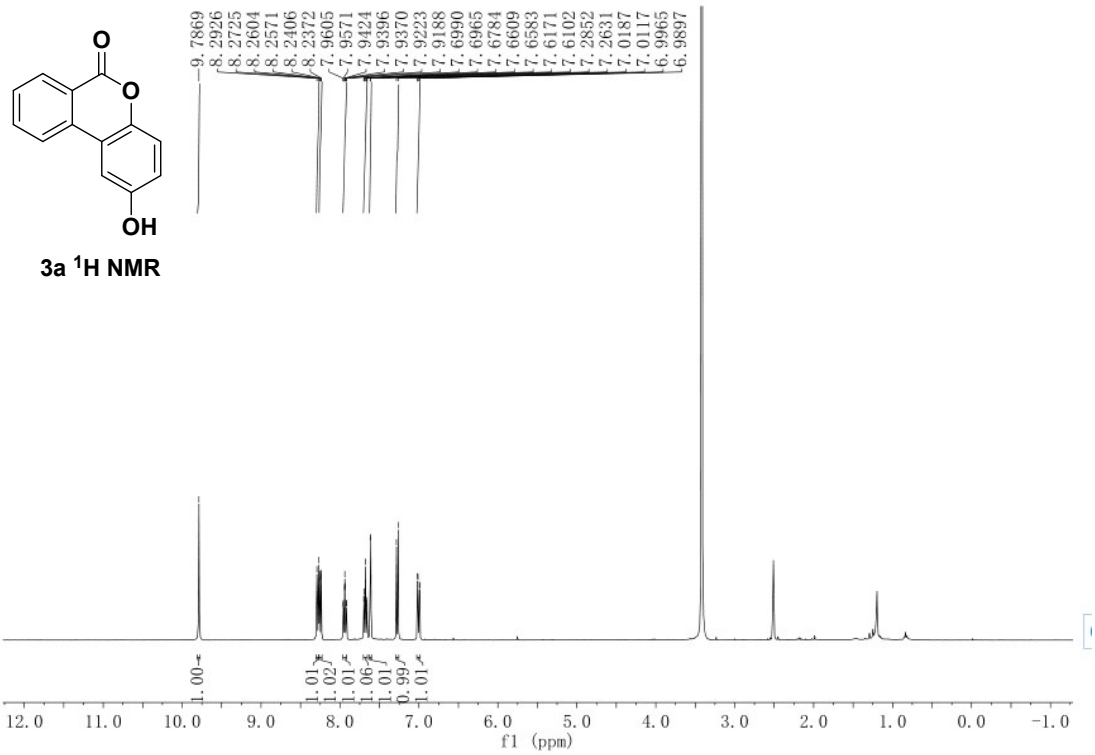
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give **10** (42% yield) as a white solid, m.p 93-95 ^{o}C. R_f = 0.45 (ethyl acetate: petroleum ether = 1:5, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.10 (d, *J* = 2.1 Hz, 1H), 8.03-8.01 (m, 1H), 7.84-7.79 (m, 1H), 7.62-7.58 (m, 1H), 7.46 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.34-7.30 (m, 5H), 7.29-7.27 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.8, 150.6, 135.9, 135.0, 134.0, 133.9, 131.5, 130.7, 130.5, 129.4, 129.3, 127.2, 126.1, 121.8, 121.2, 118.9, 118.9. Calcd for ($C_{19}H_{13}O_2S^+$ $[M+H]^+$) 305.0631 Found: 305.0650.

Reference

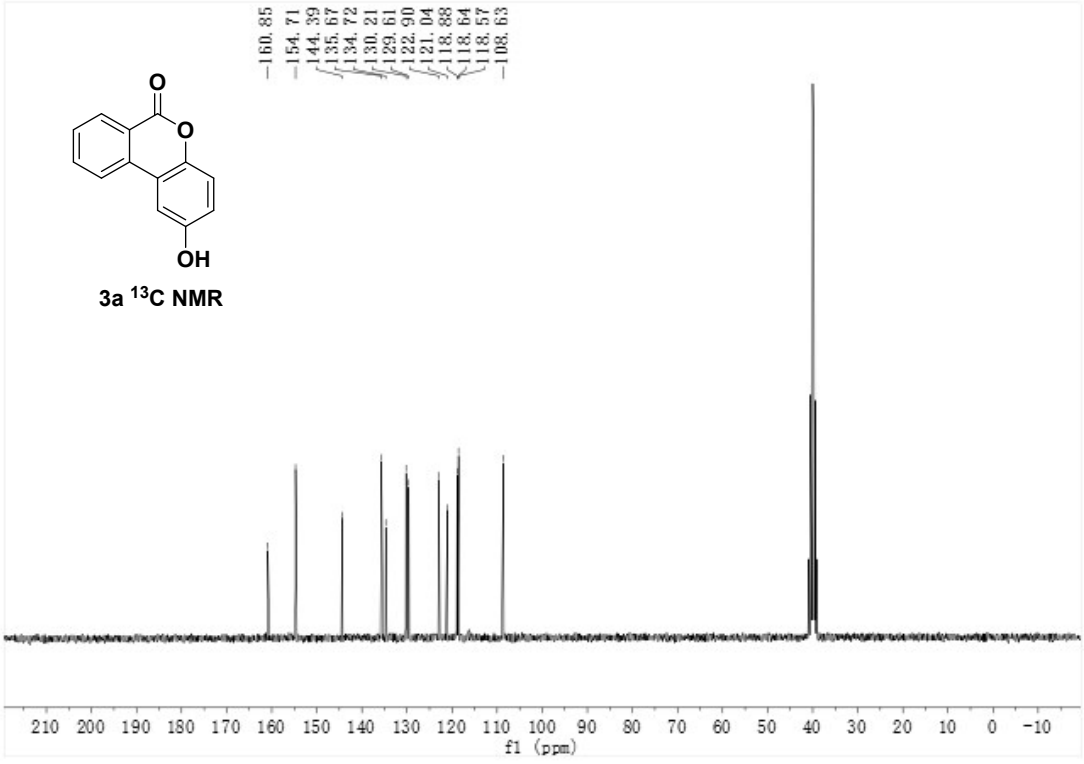
(1) D. J. Vyas, E. Larionov, C. Besnard, L. Guénée, C. Mazet, *J. Am. Chem. Soc.*, 2013, **135**, 6177.

(2) W. Yang, S. Wang, Q. Zhang, Q. Liu and X. Xu, *Chem. Commun.,* 2015, **51**, 661.

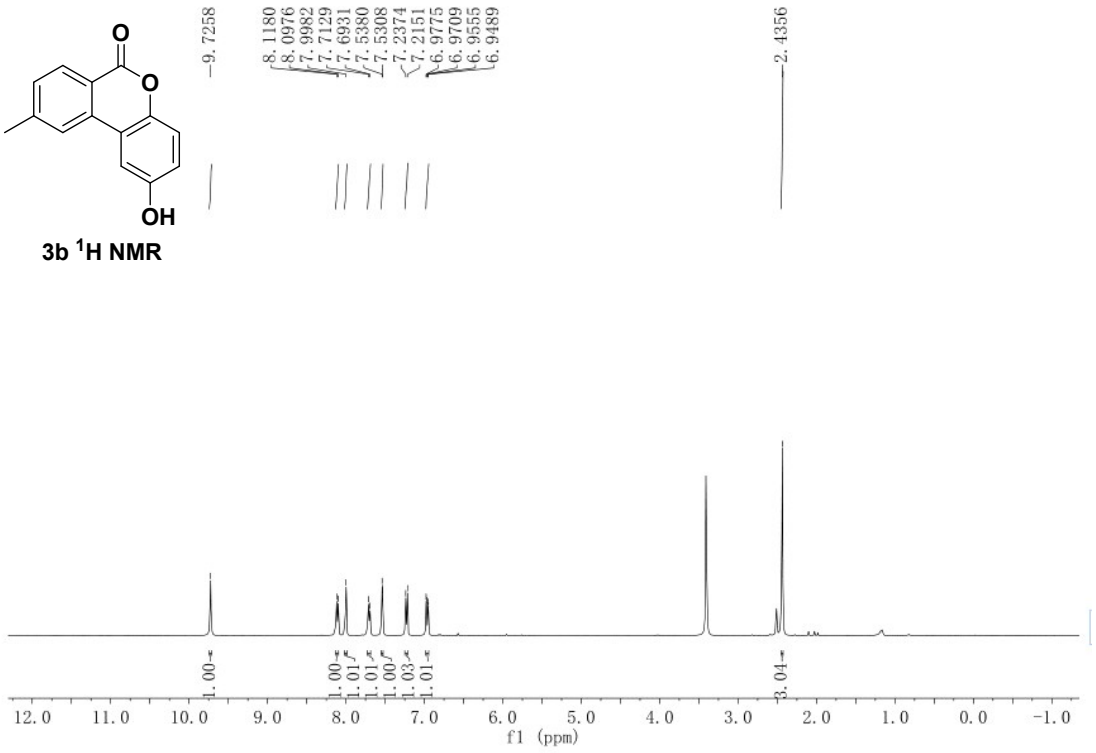
9. Copies of ^{1}H NMR and ^{13}C NMR spectra



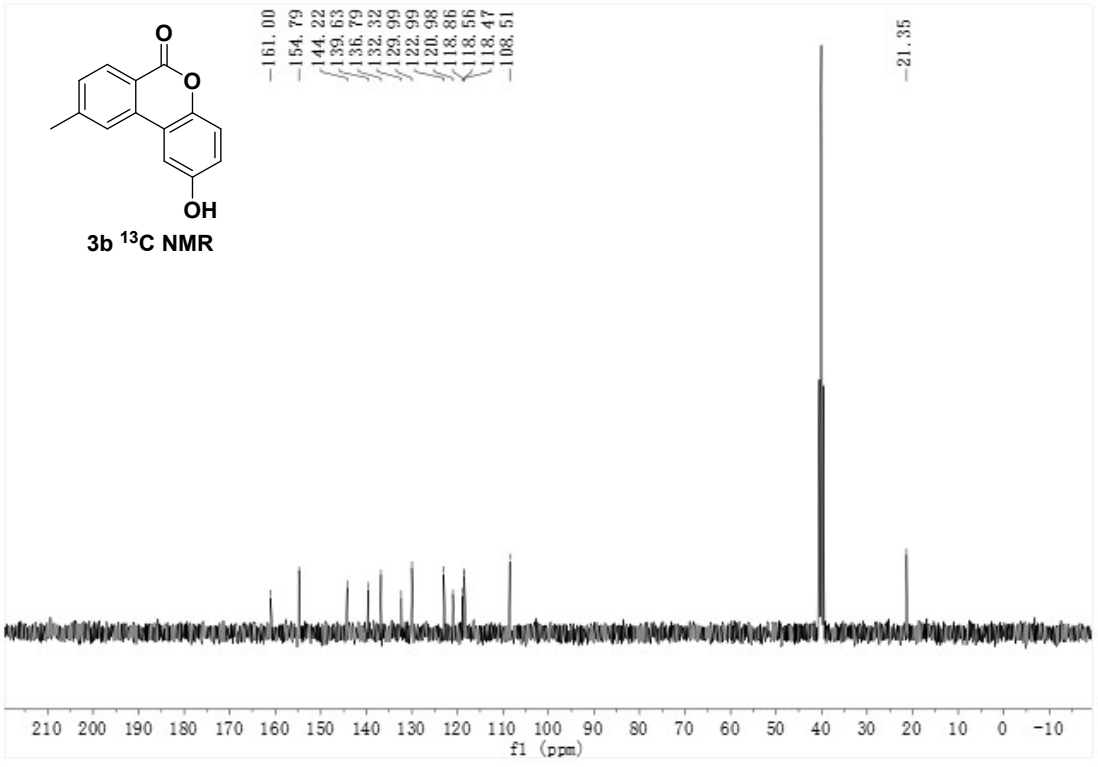
3a ^{1}H NMR



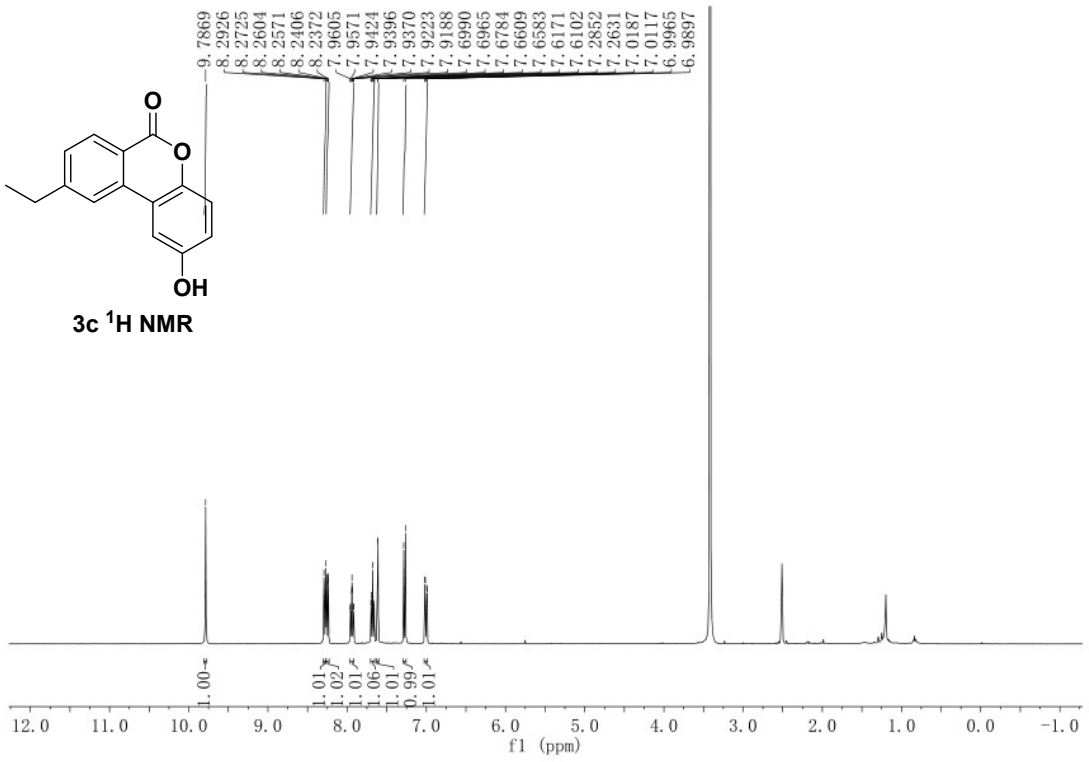
3a ^{13}C NMR



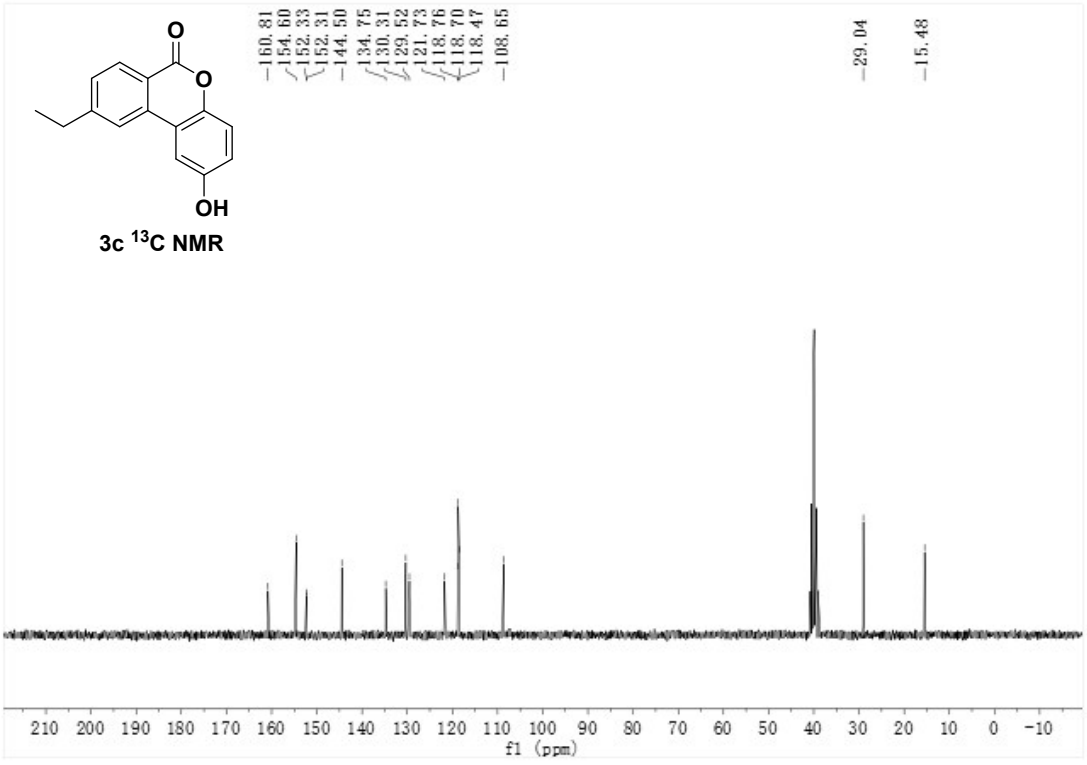
3b ^{1}H NMR



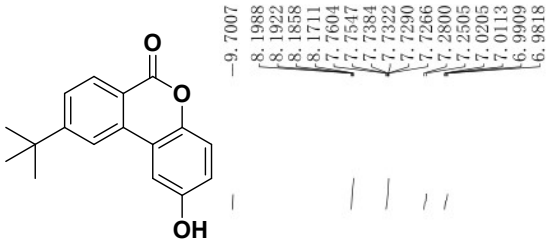
3b ^{13}C NMR



3c ^{1}H NMR



3c ^{13}C NMR



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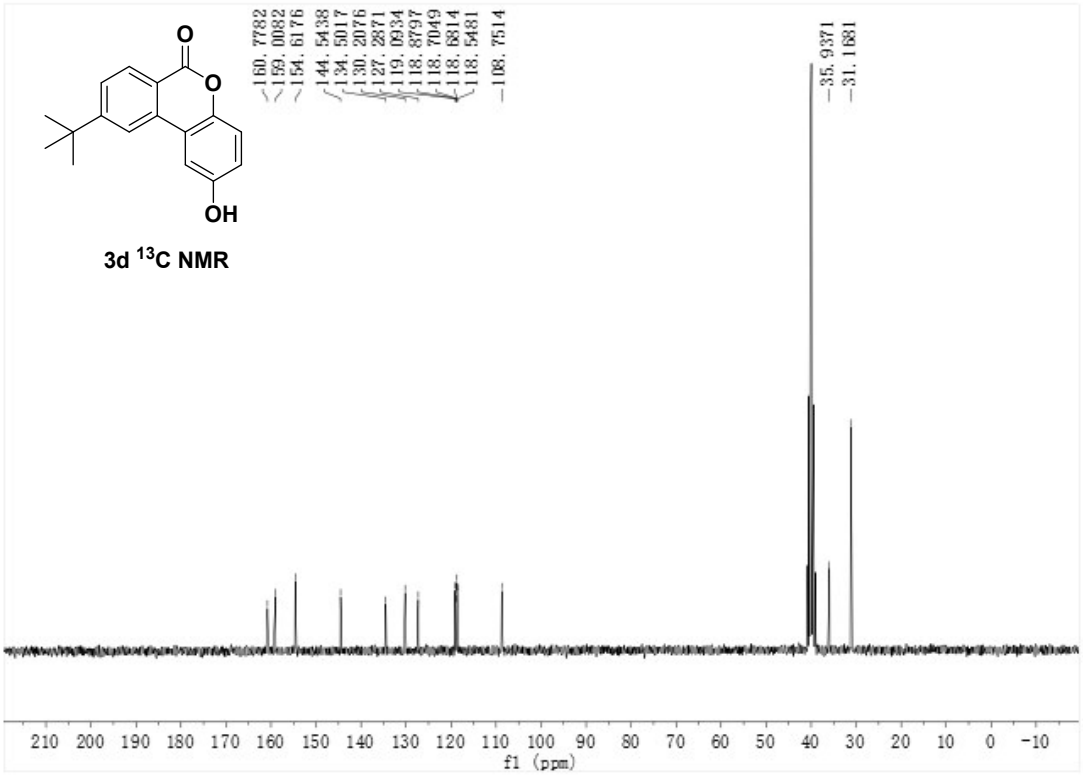
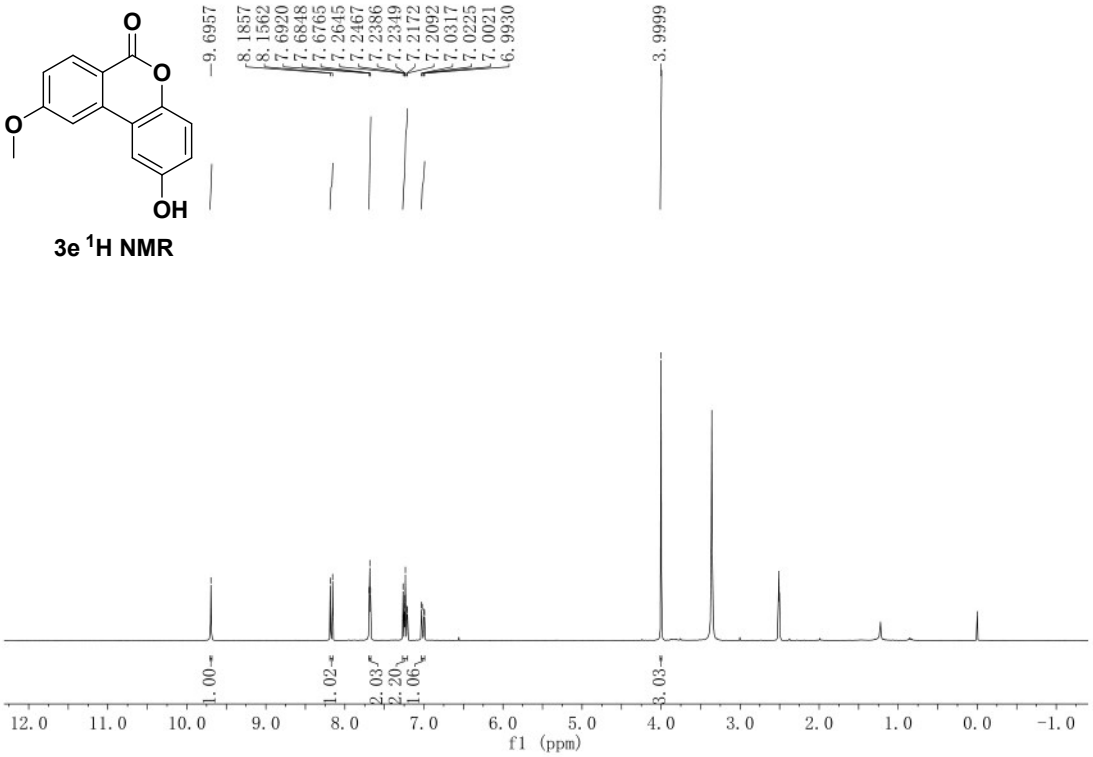
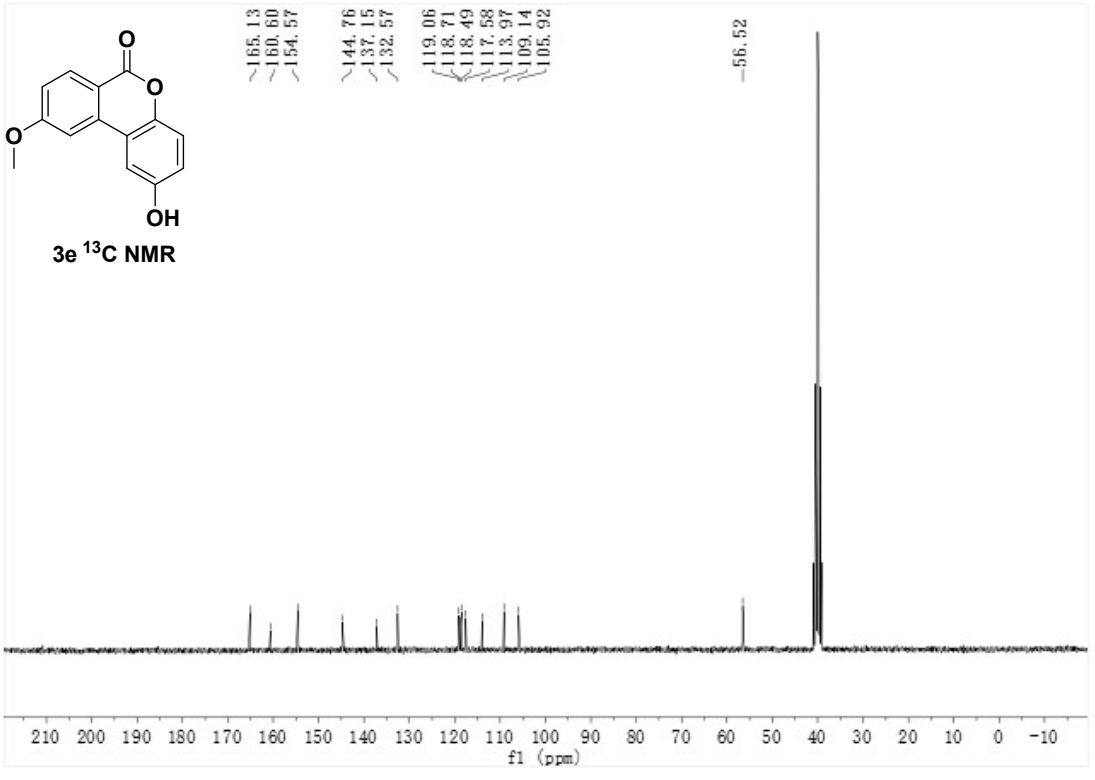


3d ^{13}C NMR



3e ^{1}H NMR



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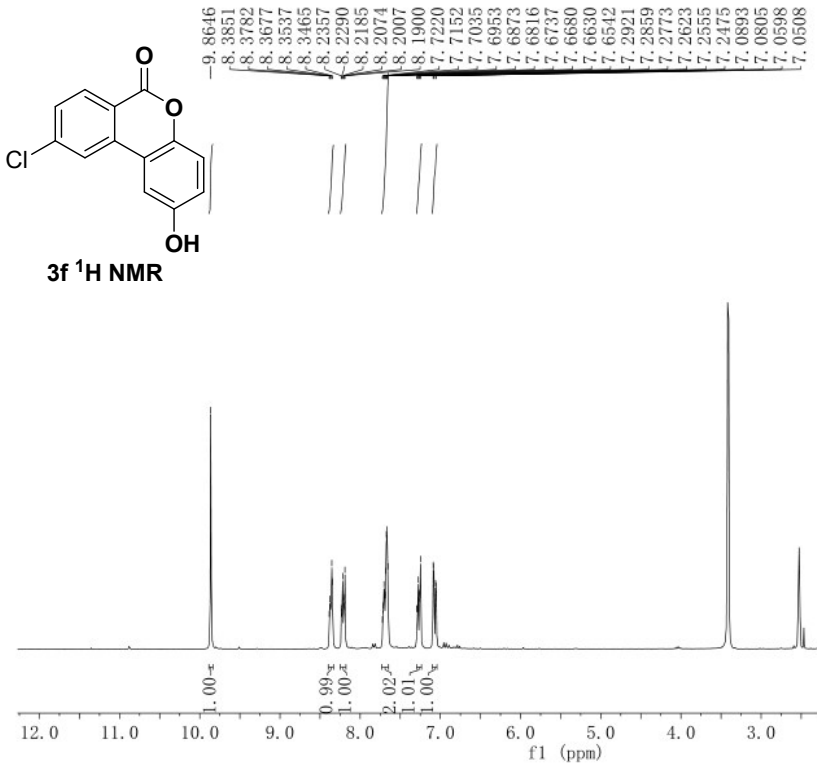
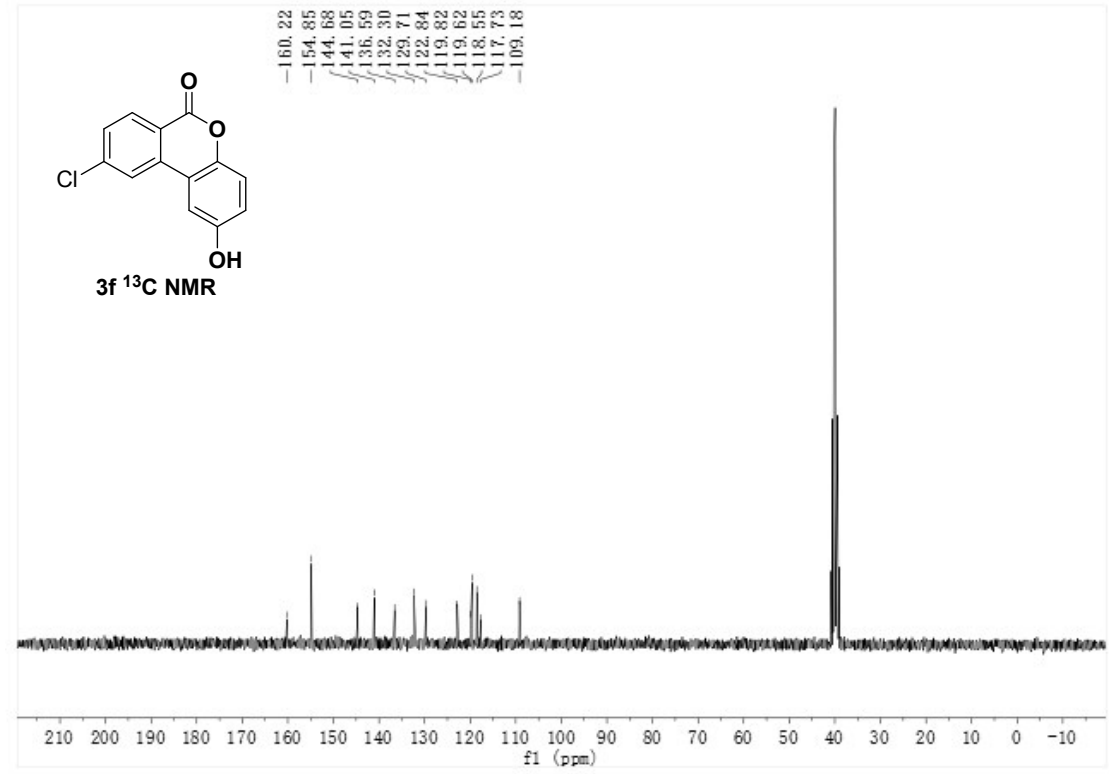
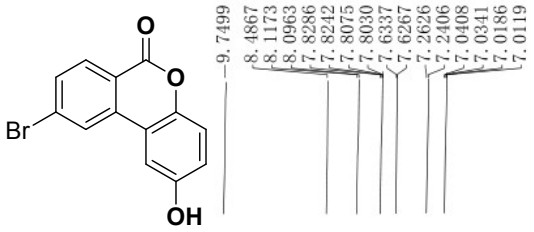


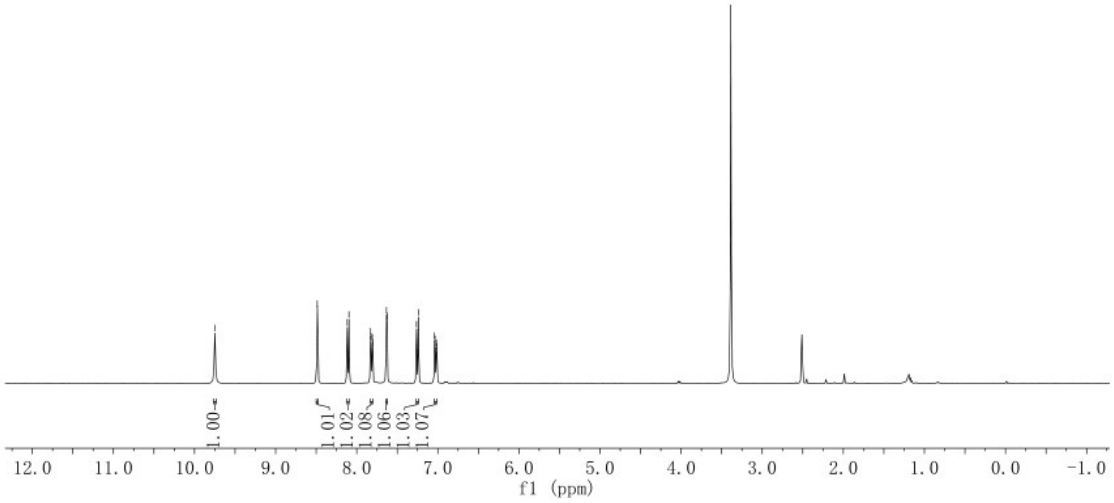
3f ^{1}H NMR

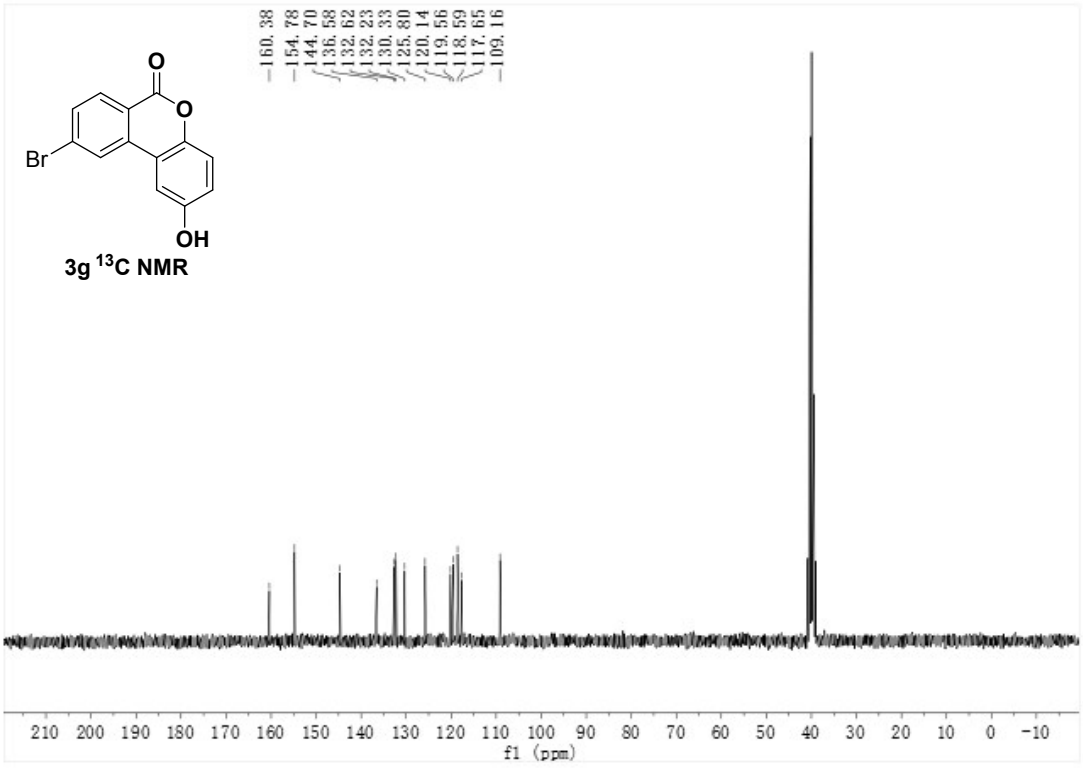


3f ^{13}C NMR

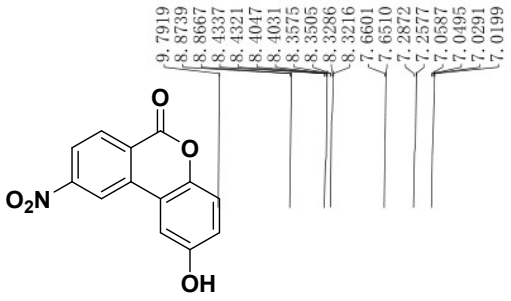


3g ^{1}H NMR

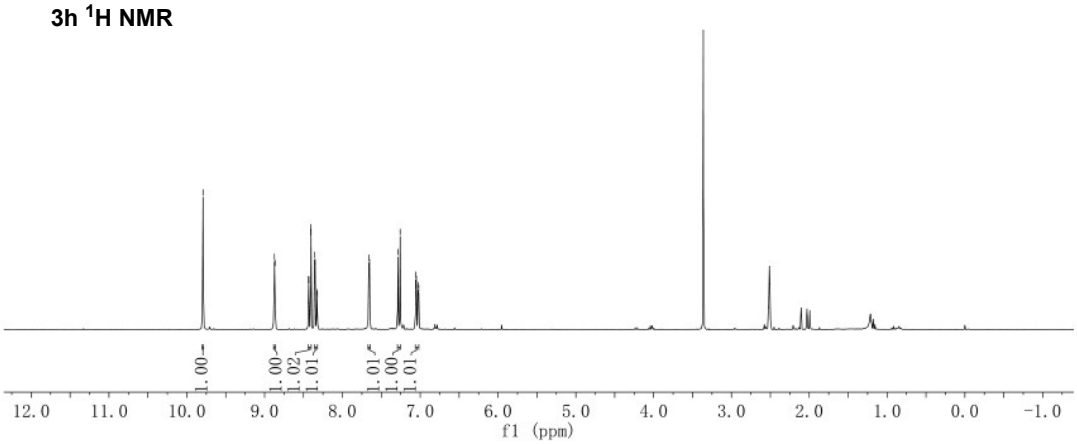


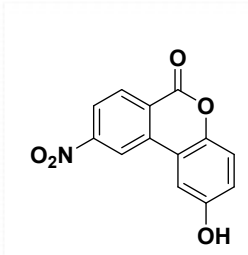


3g ^{13}C NMR



3h ^{1}H NMR





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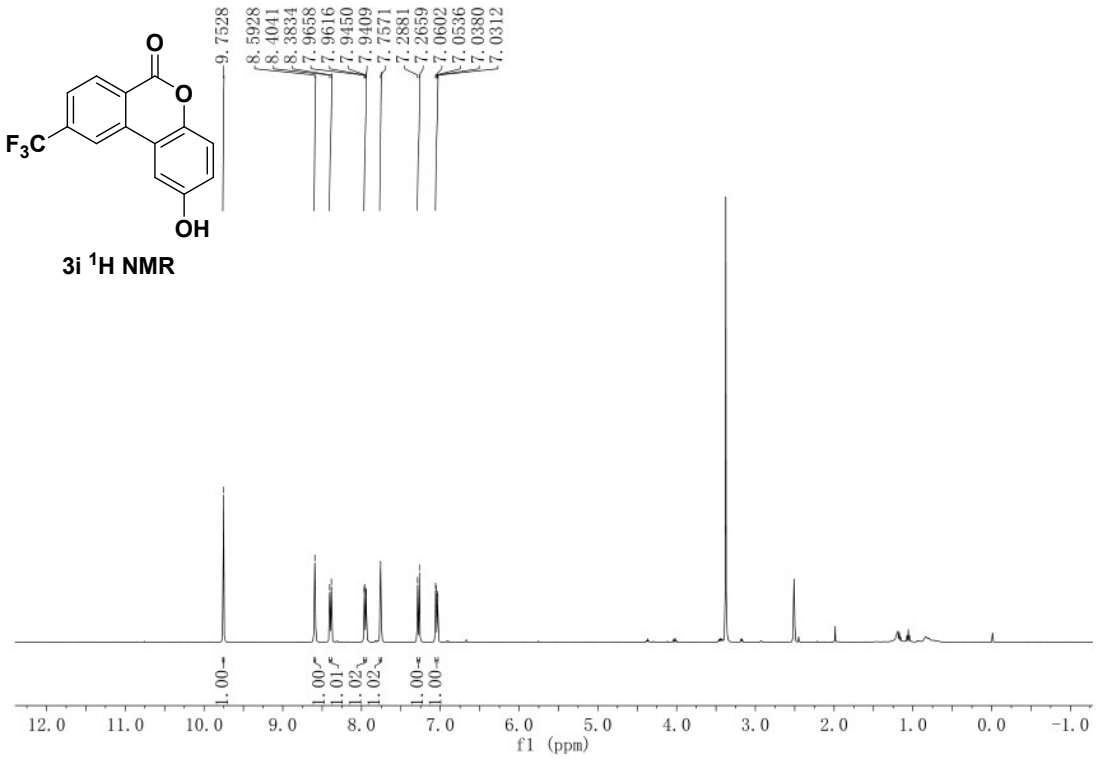

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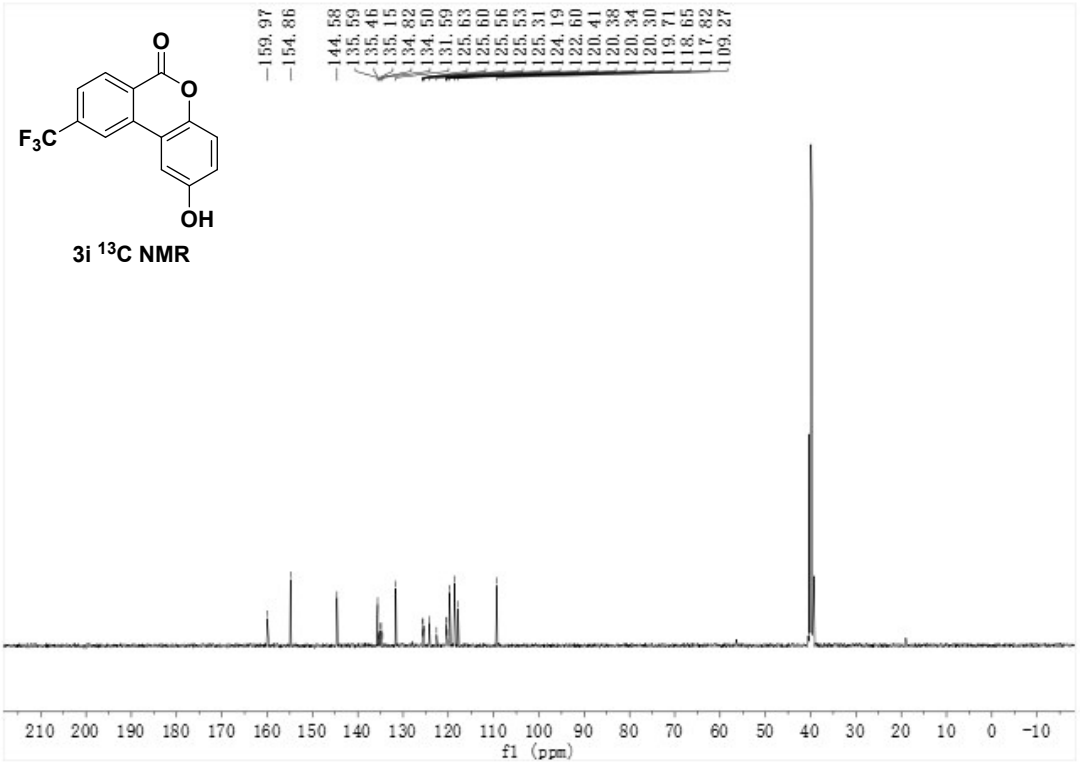

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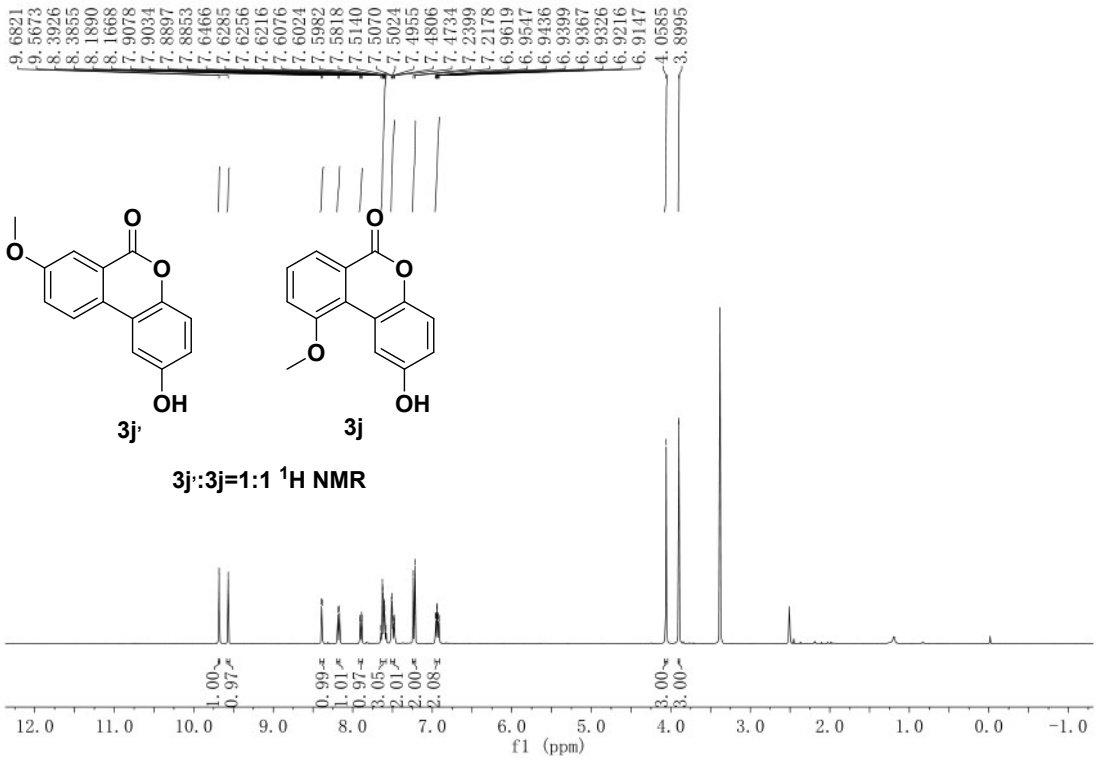
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7.9078
7.9034
7.8897
7.8853
7.6466
7.6285
7.6256
7.6216
7.6076
7.6024
7.5982
7.5818
7.5140
7.5070
7.5024
7.4955
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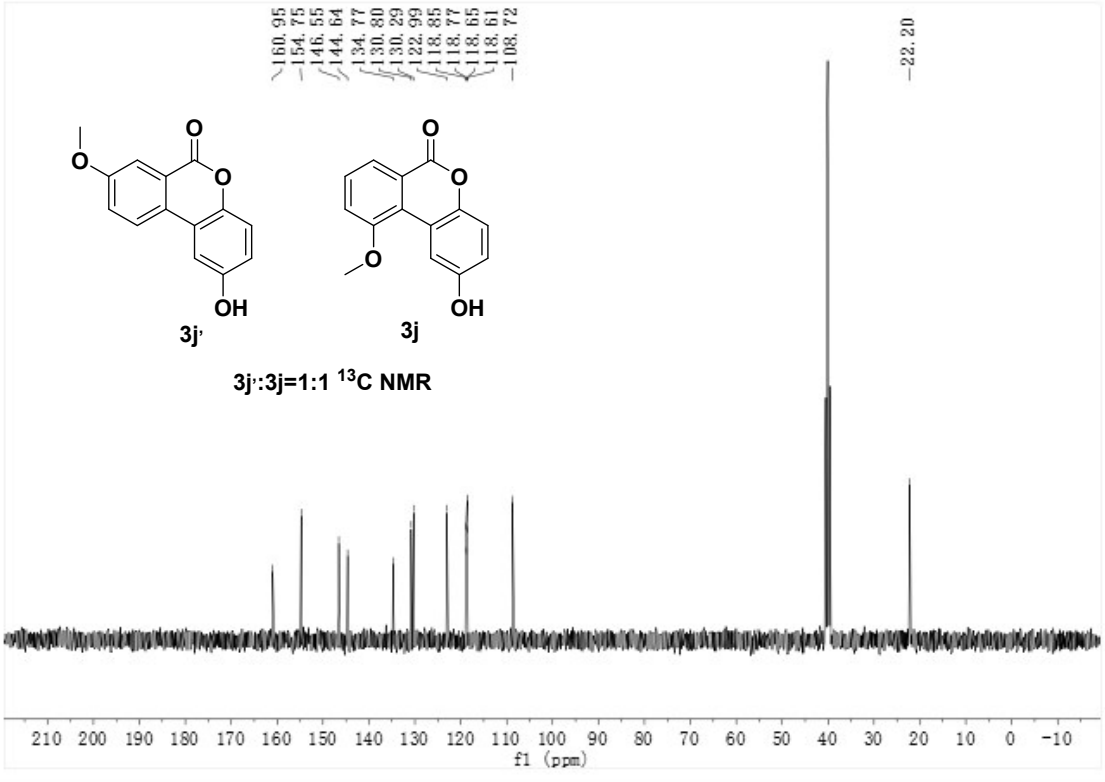
7.4734
7.2399
7.2178
6.9619
6.9547
6.9436
6.9399
6.9367
6.9326
6.9216
6.9147
4.0585
3.8995
O
O
O
OH
3j'
O
O
O
OH
3j
3j':3j=1:1 1H NMR
1.00
0.97
0.99
1.01
0.97
3.05
2.01
2.00
2.08
3.00
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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154.75
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130.29
122.99
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118.77
118.65
118.61
108.72
22.20
O
O
O
OH
3j'
O
O
O
OH
3j
3j':3j=1:1 13C NMR
210
200
190
180
170
160
150
140
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120
110
100
90
80
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60
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40
30
20
10
0
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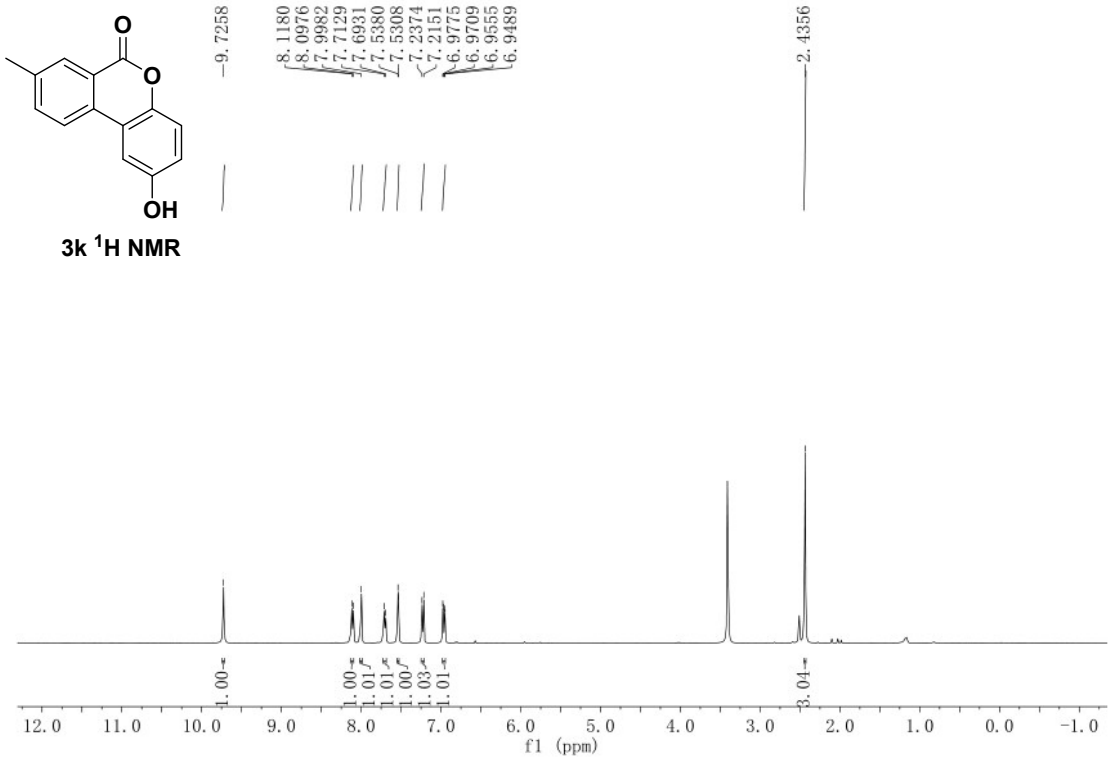
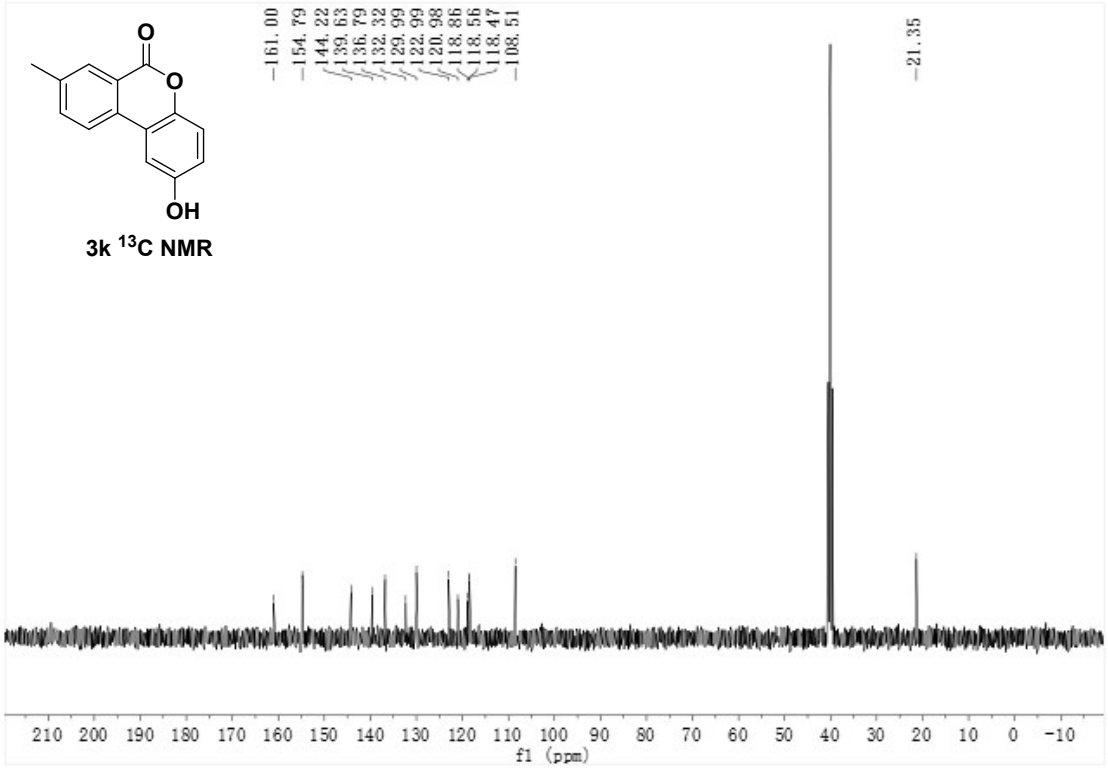
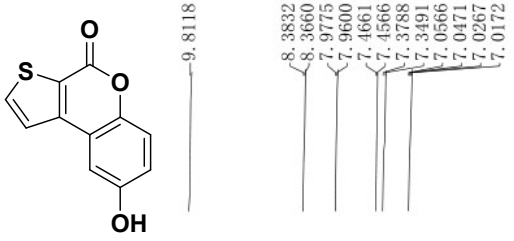
f1 (ppm)



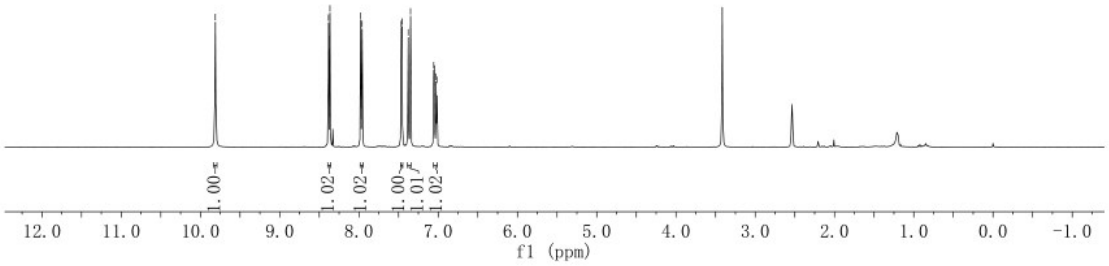
3k ^{1}H NMR

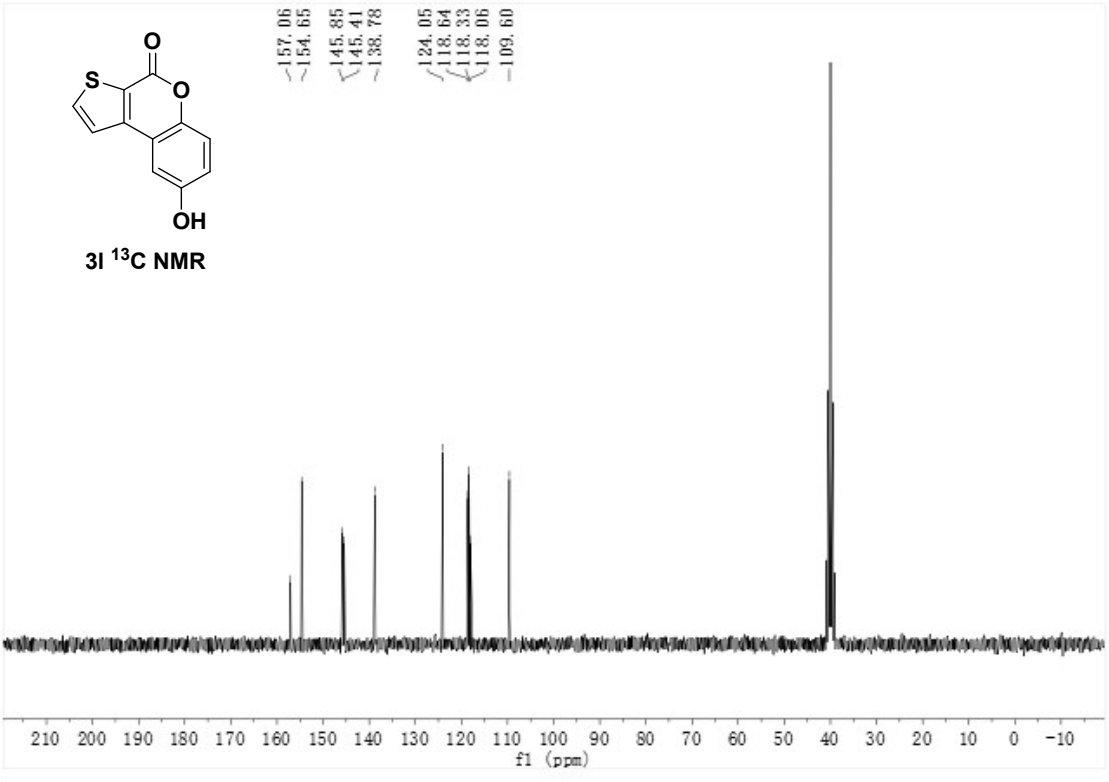


3k ^{13}C NMR

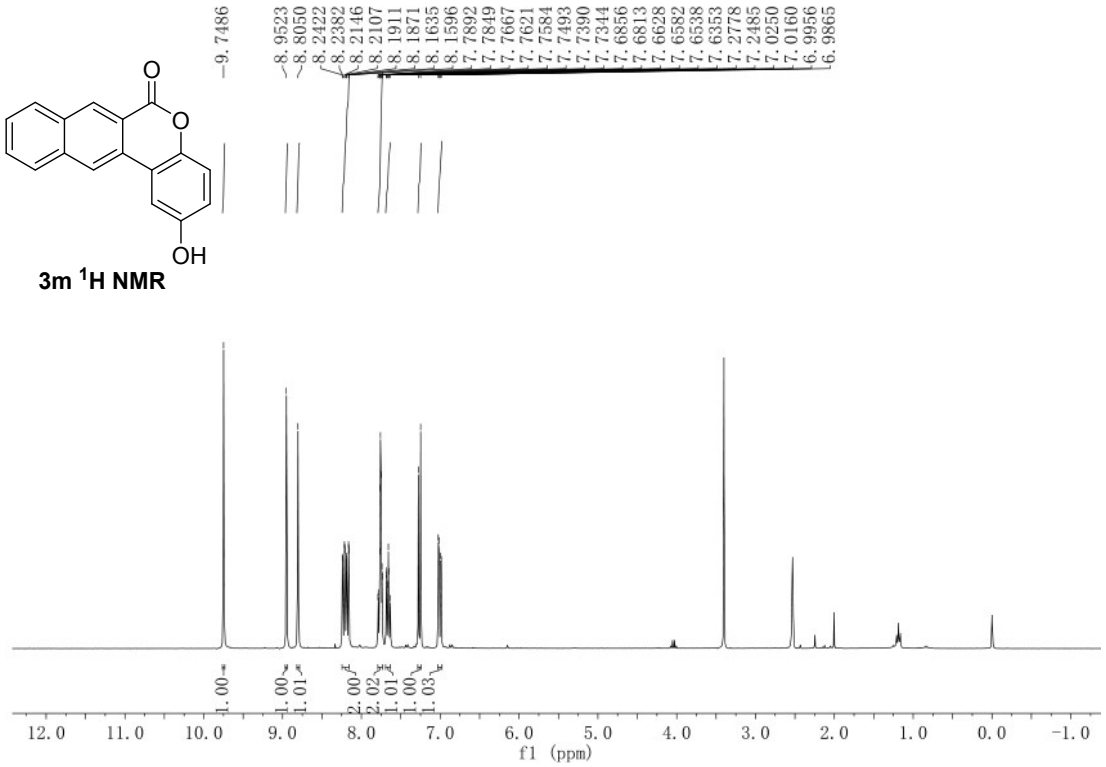


3l ^{1}H NMR

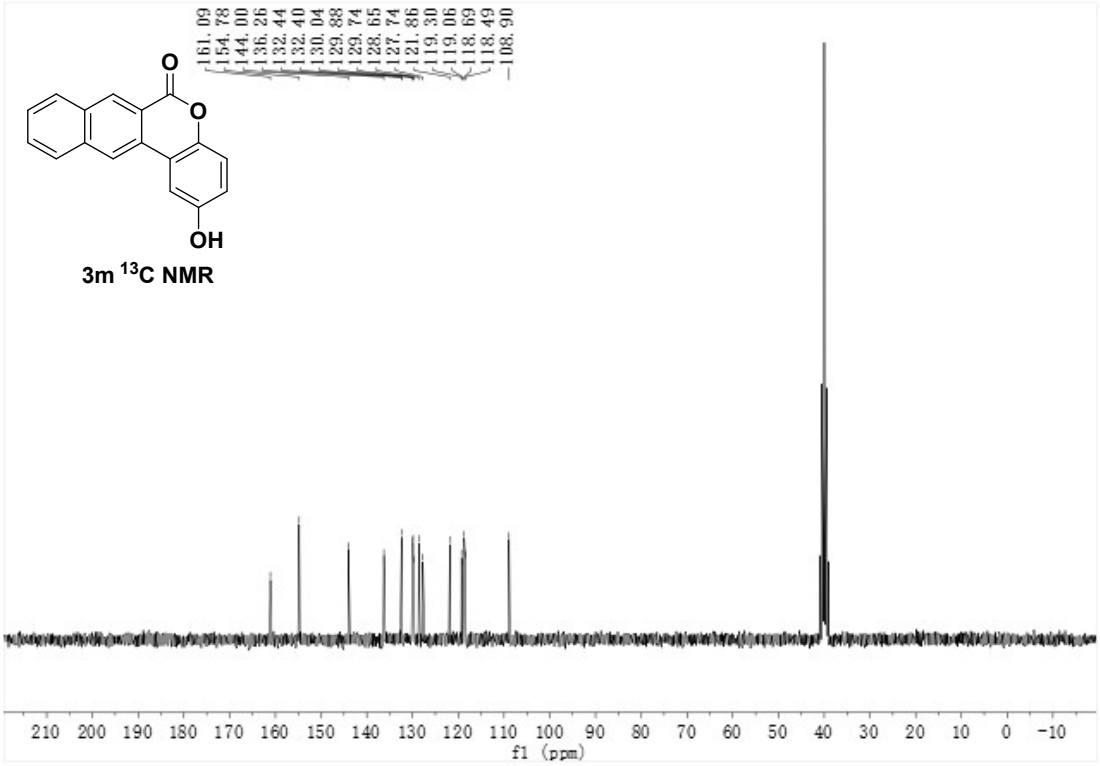




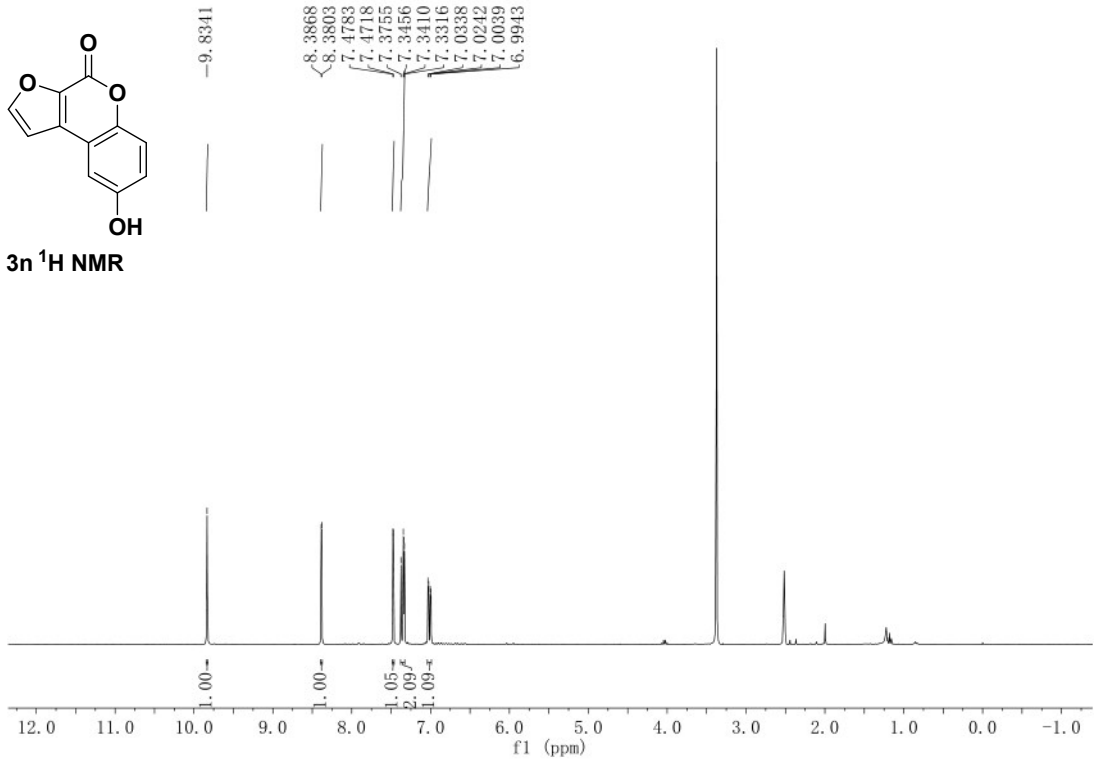
3l ^{13}C NMR



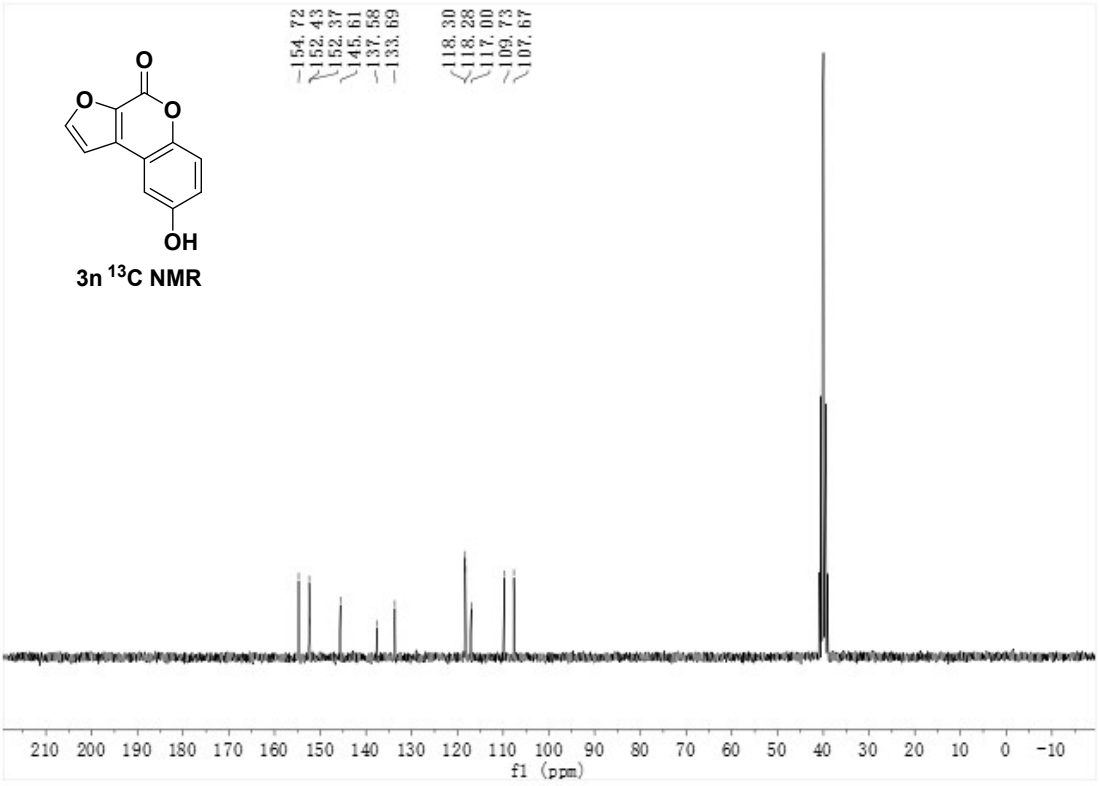
3m ^{1}H NMR



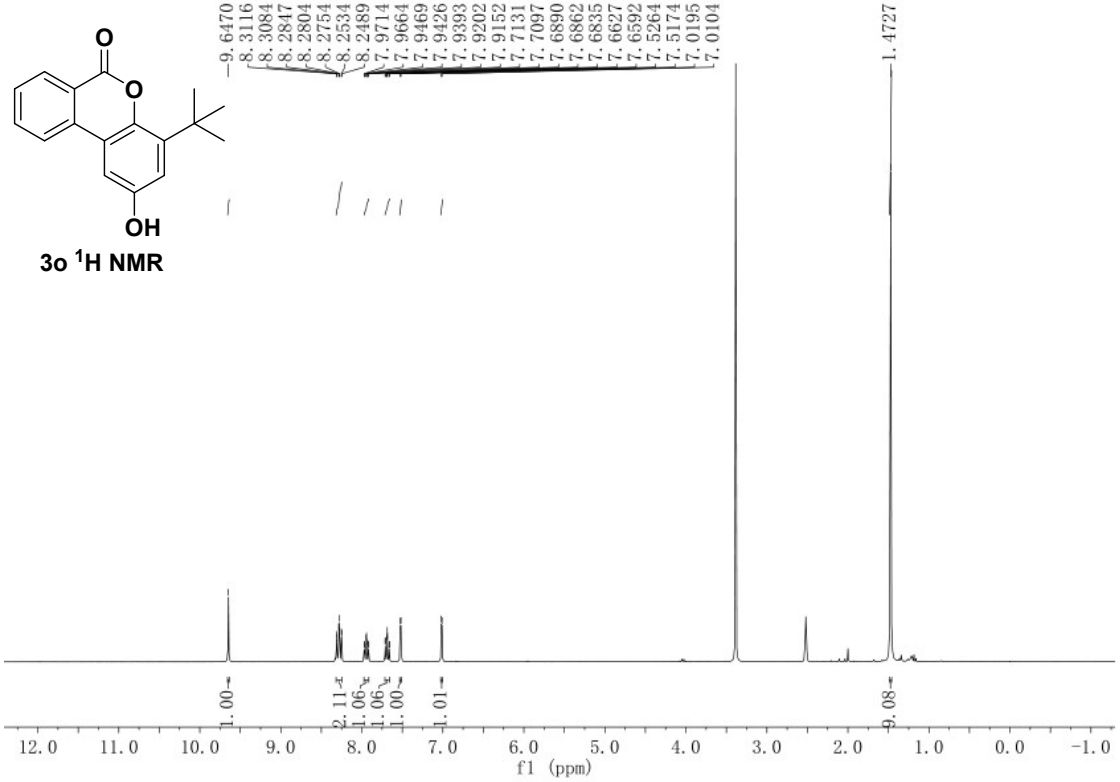
3m ^{13}C NMR



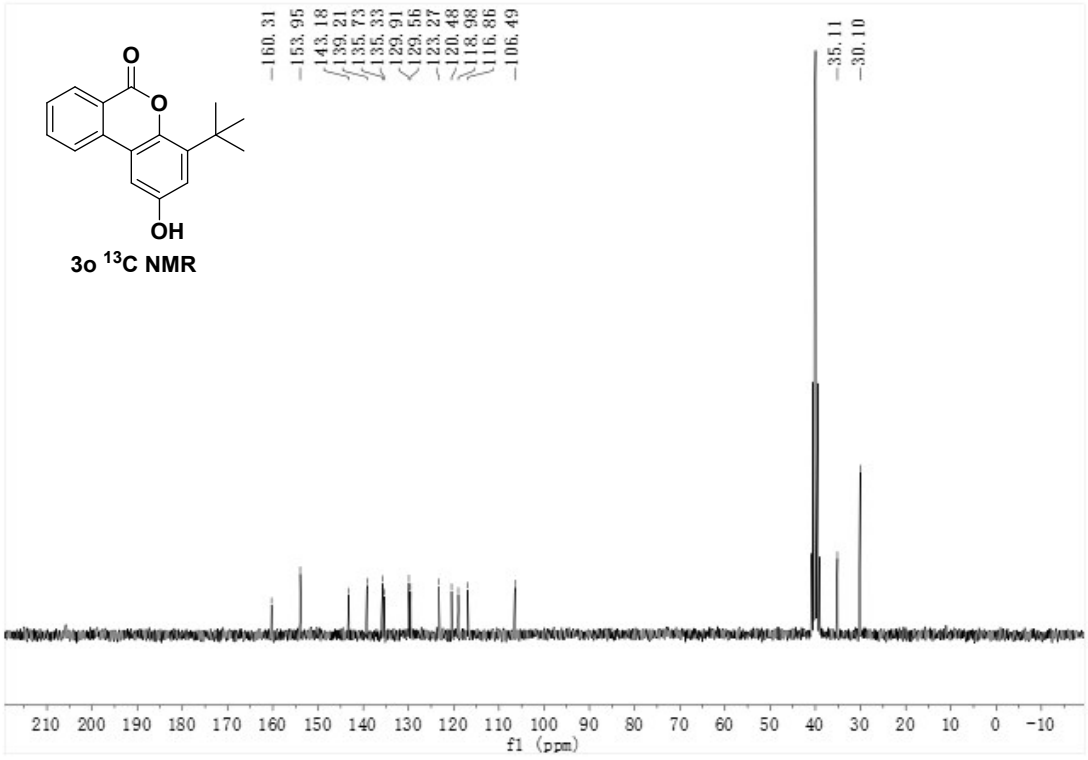
3n ^{1}H NMR



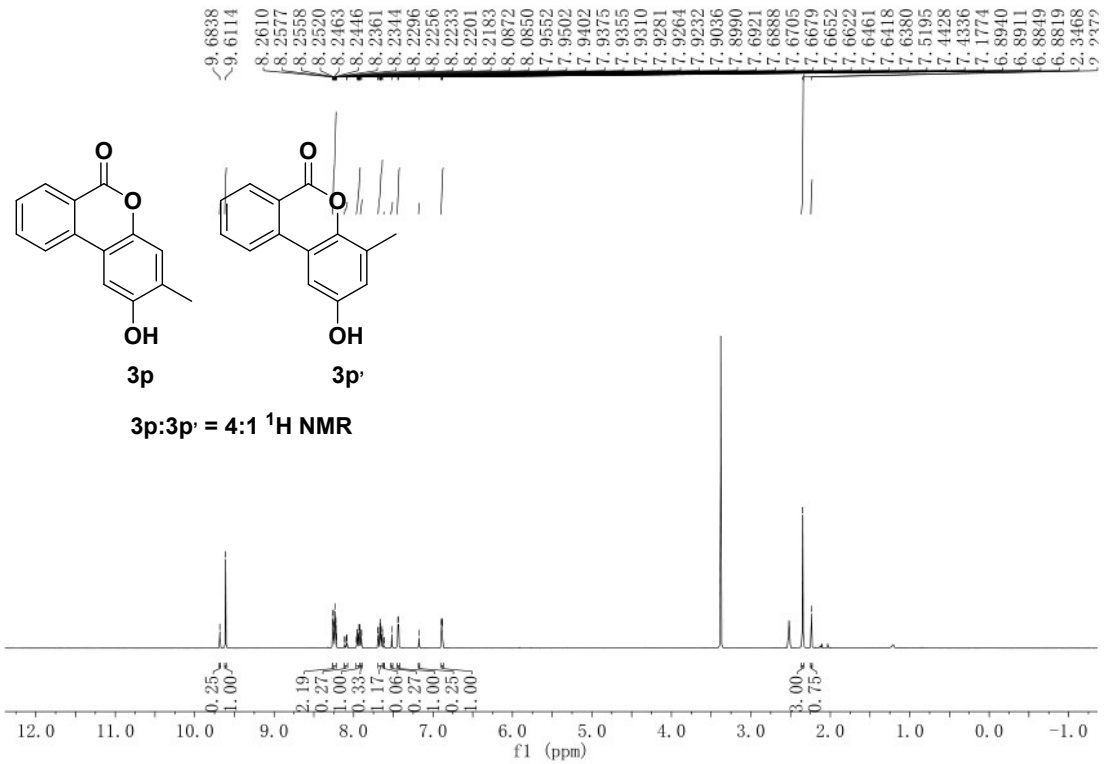
3n ^{13}C NMR



3o ^{1}H NMR



3o ^{13}C NMR


3p
3p'
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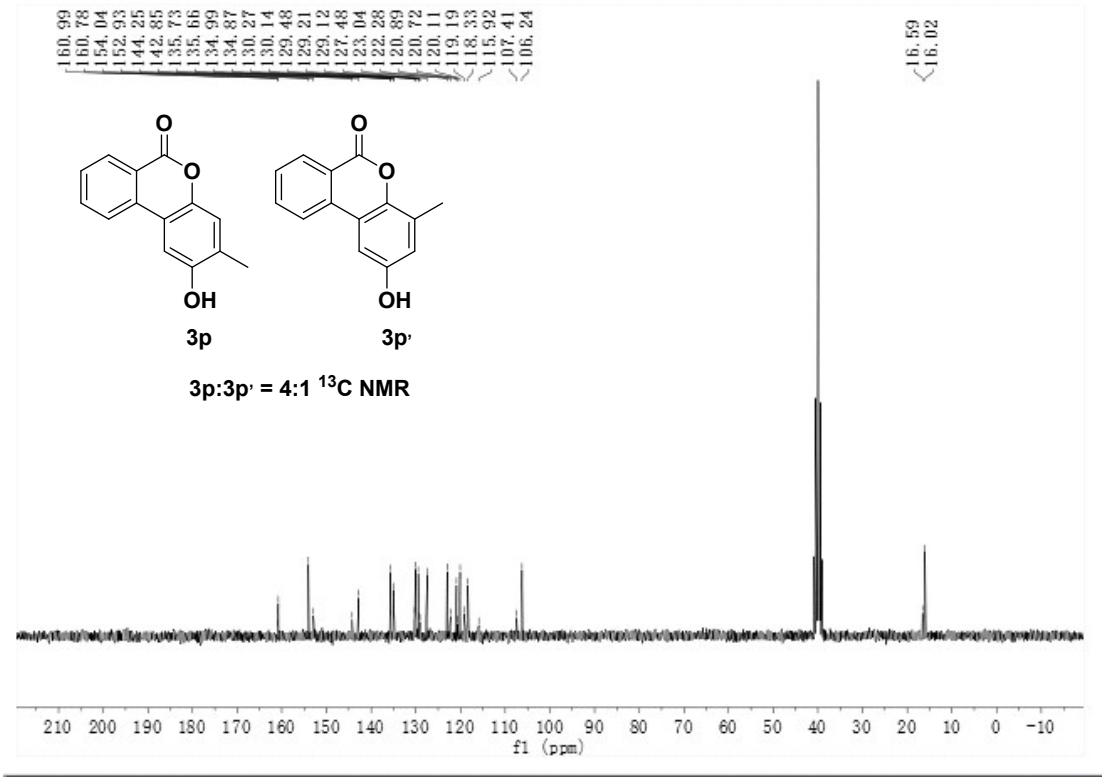
f1 (ppm)


3p
3p'
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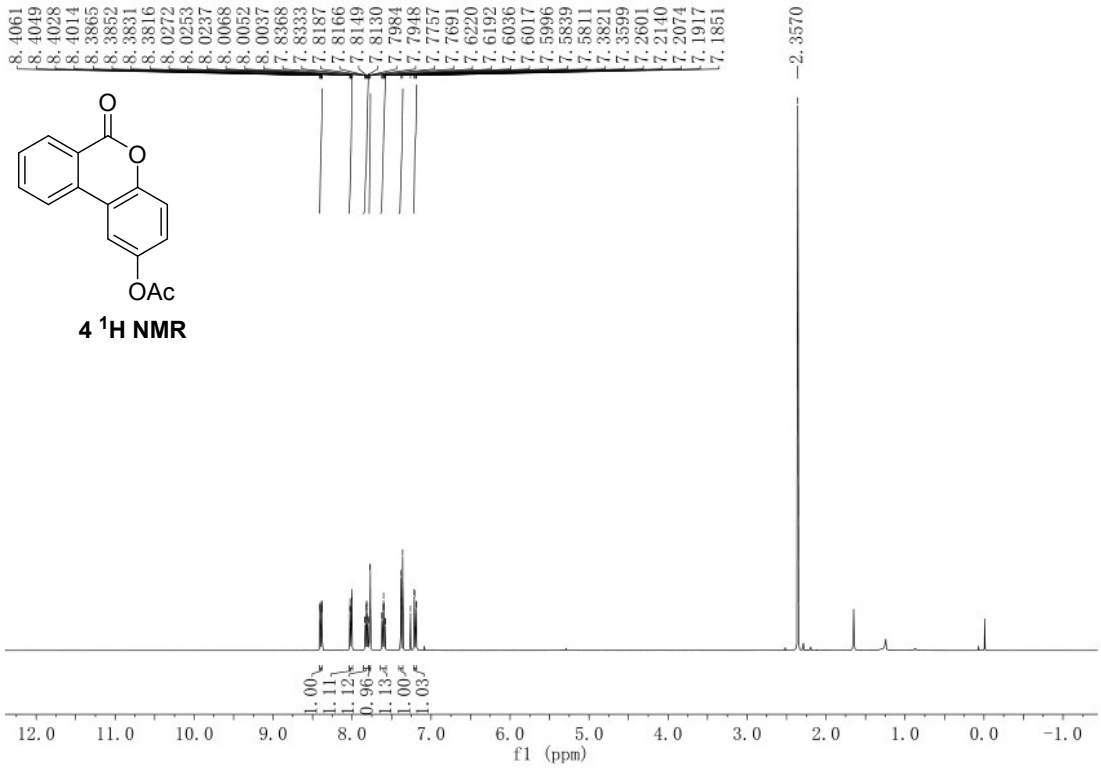
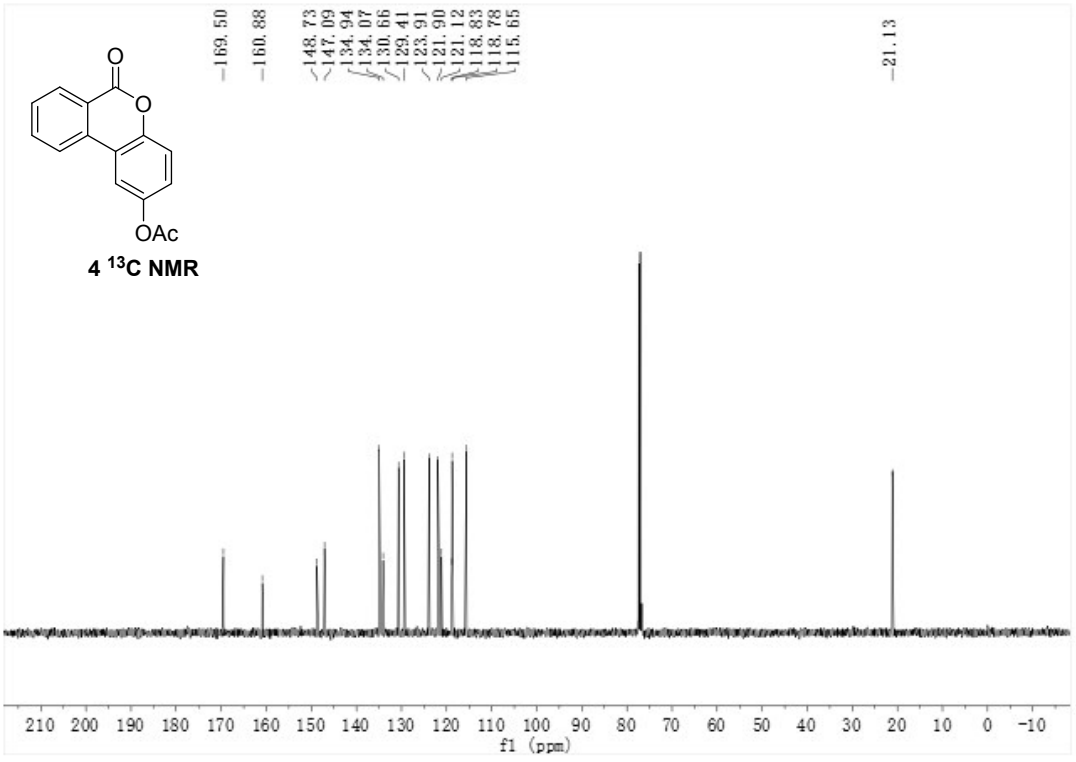
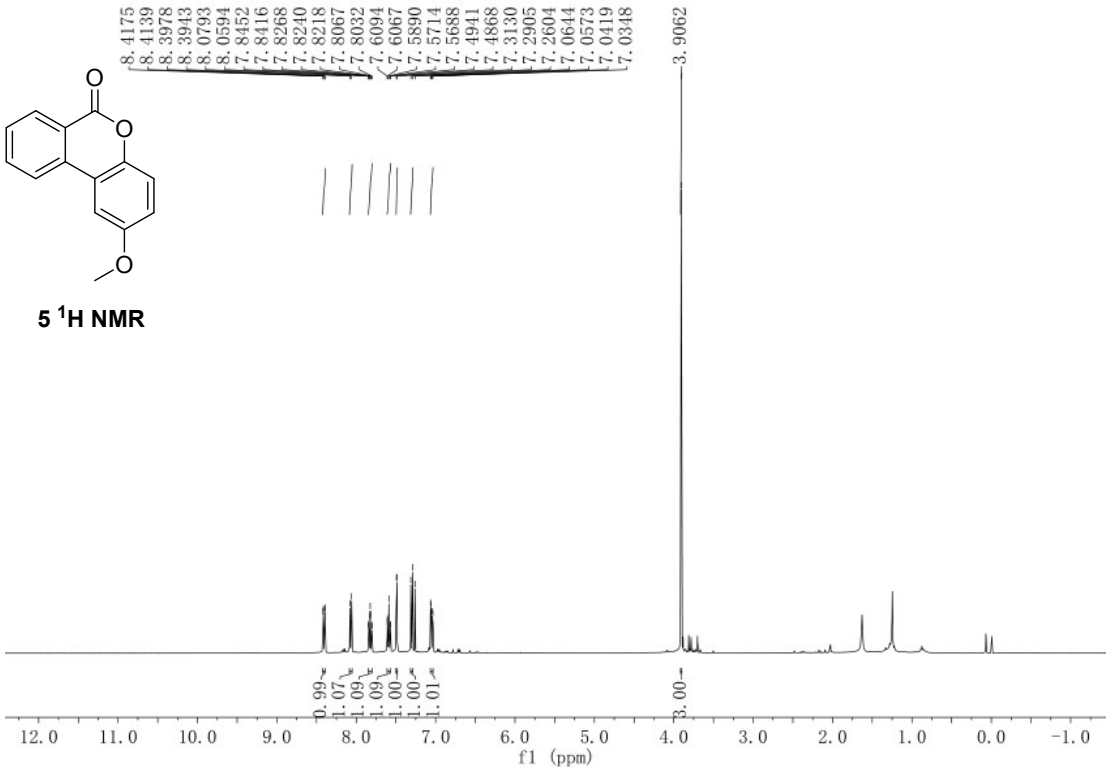
f1 (ppm)



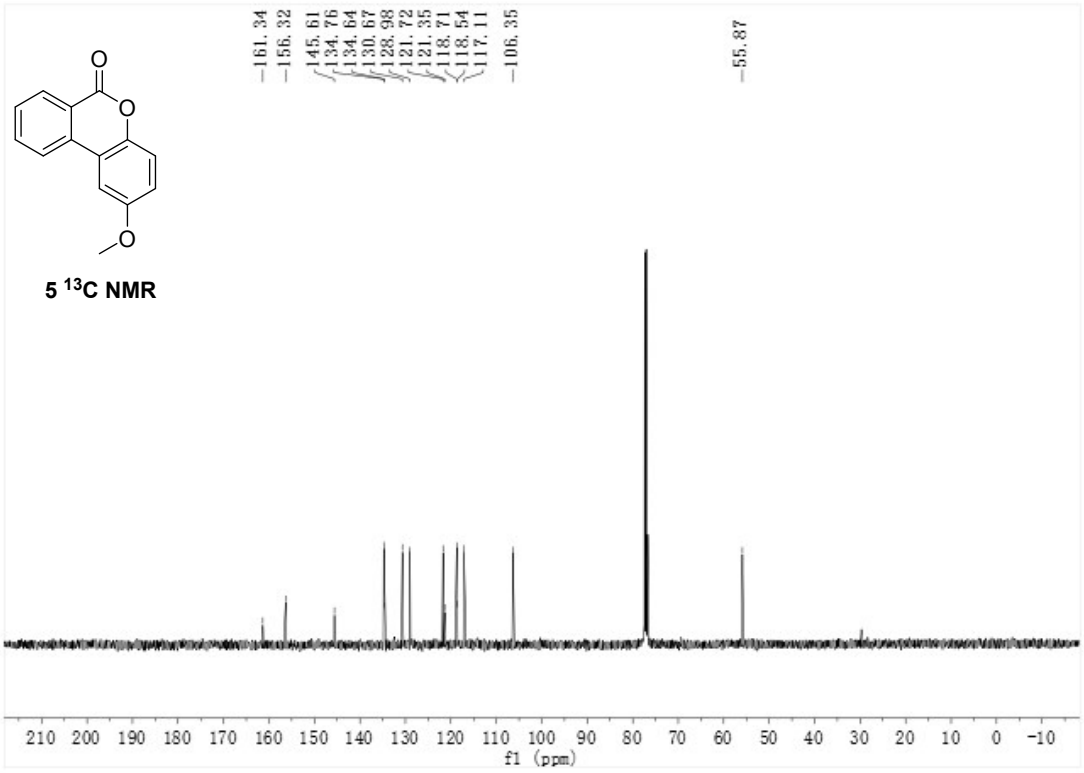
4 ^{1}H NMR



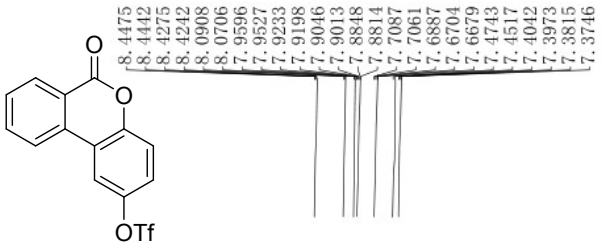
4 ^{13}C NMR



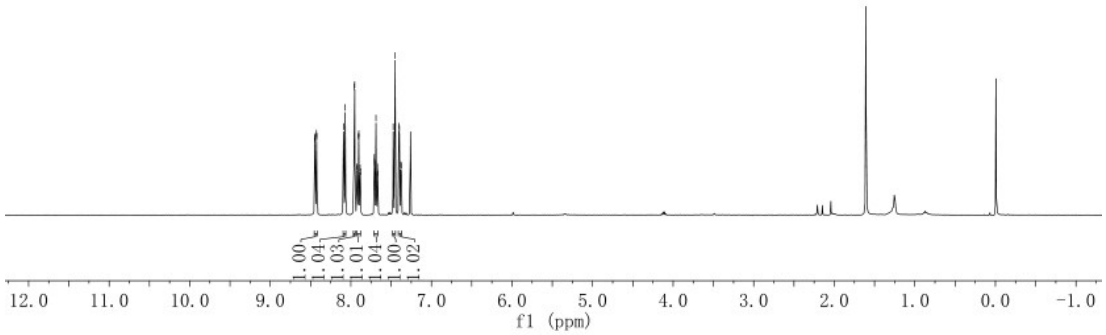
5 ^{1}H NMR

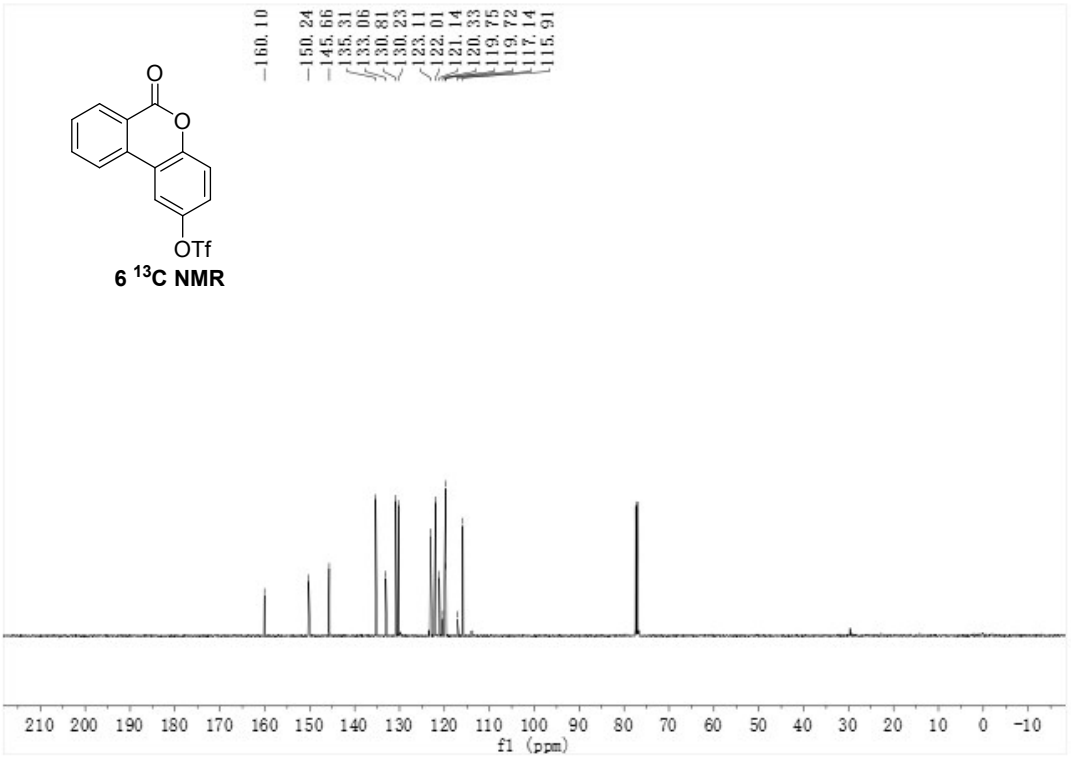


5 ^{13}C NMR

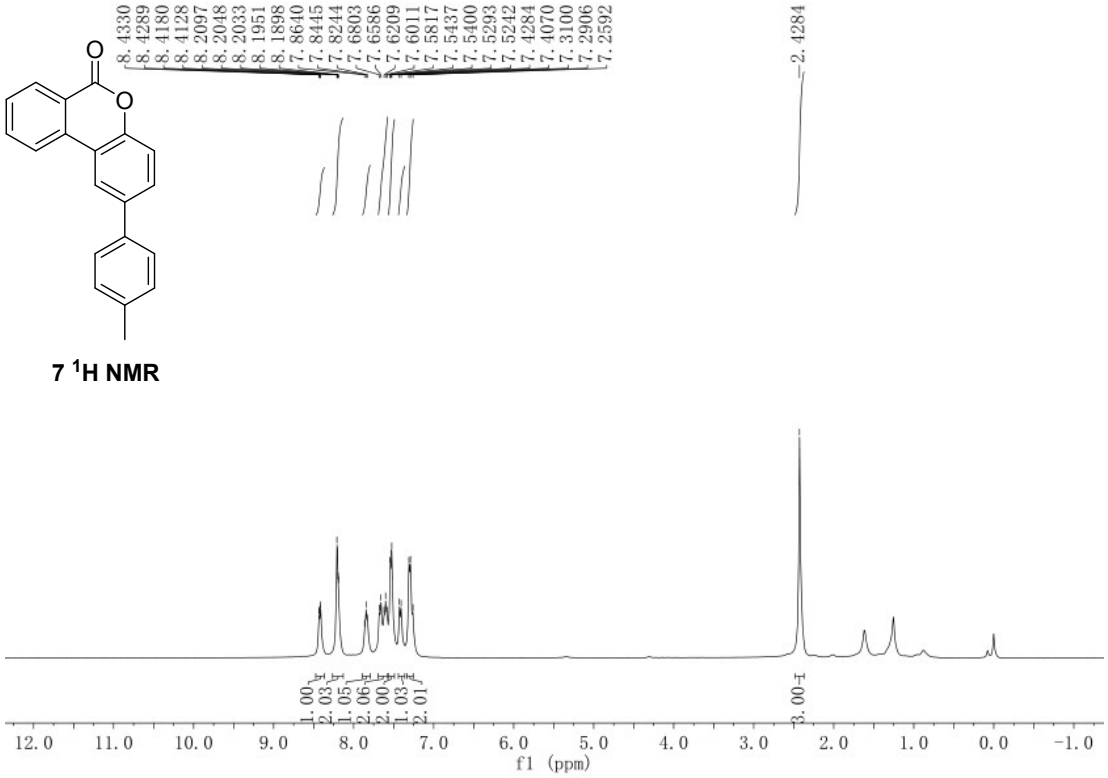


6 ^{1}H NMR

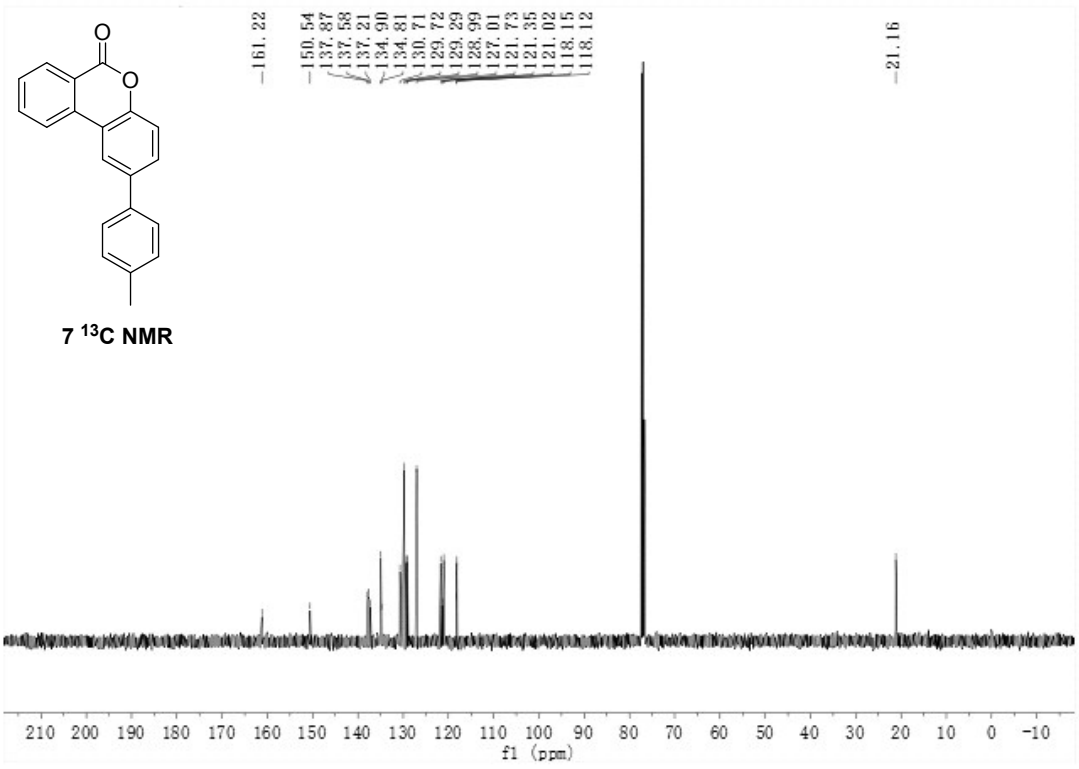




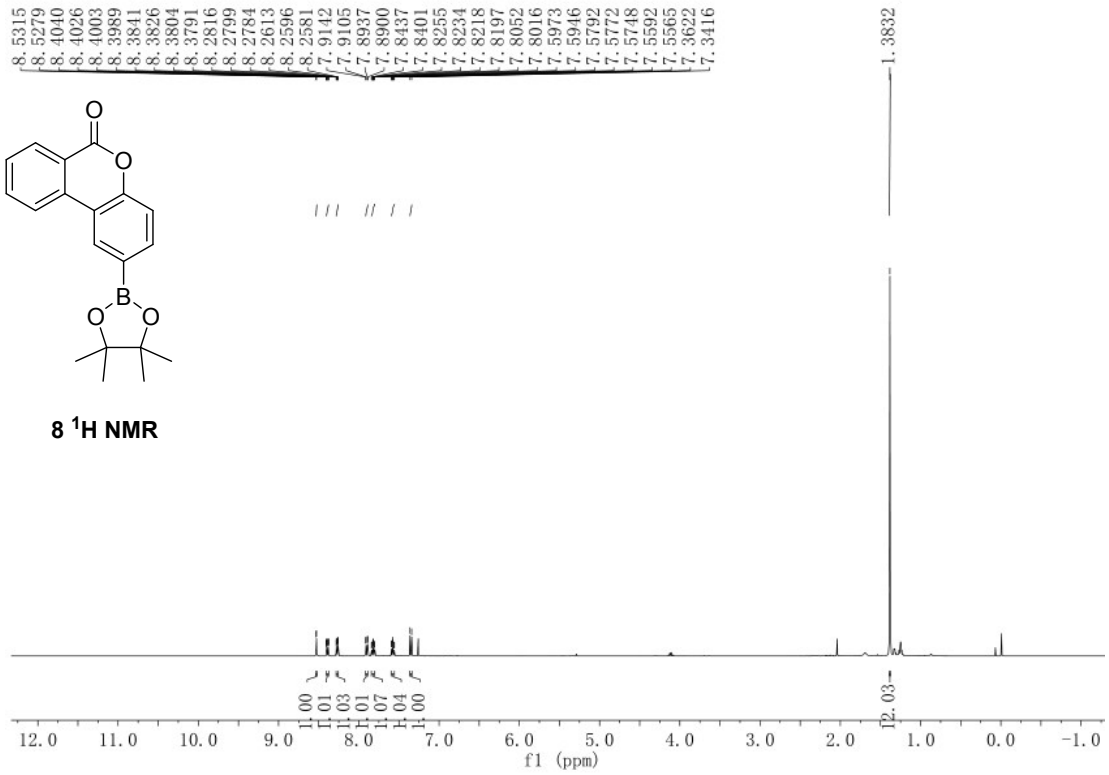
6 ^{13}C NMR



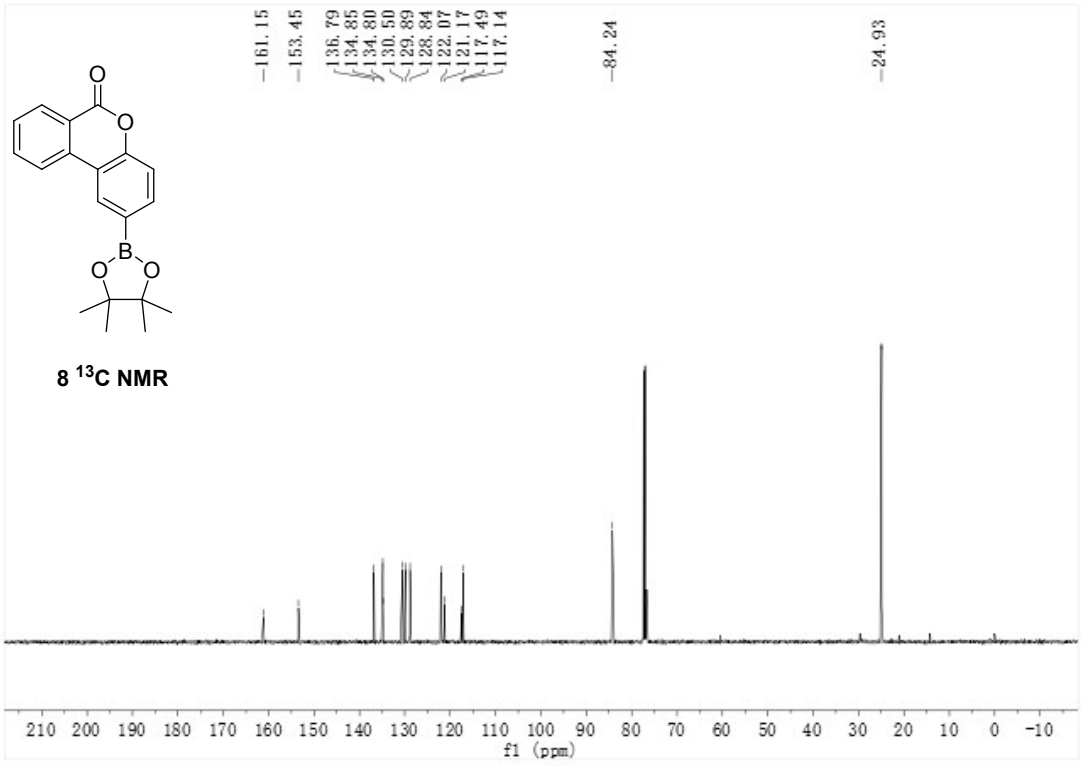
7 ^{1}H NMR



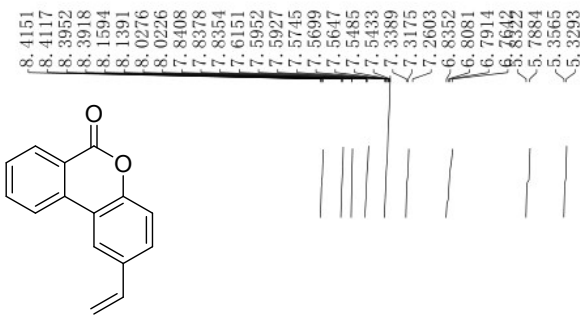
7 ^{13}C NMR



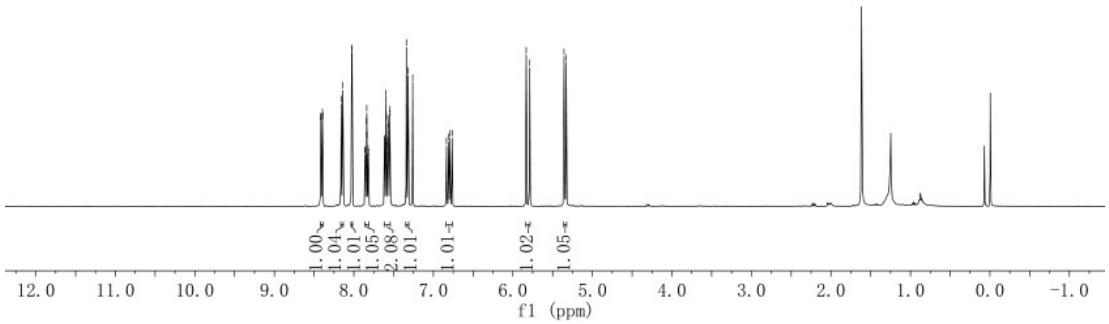
8 ^{1}H NMR

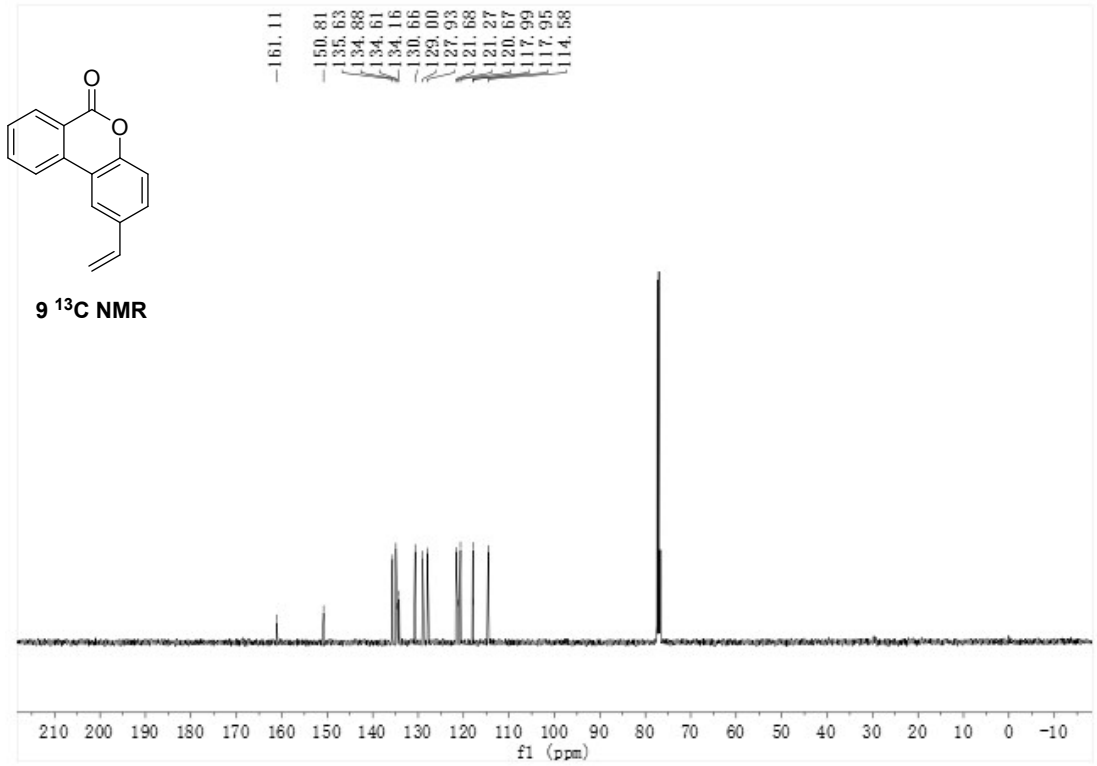


8 ^{13}C NMR

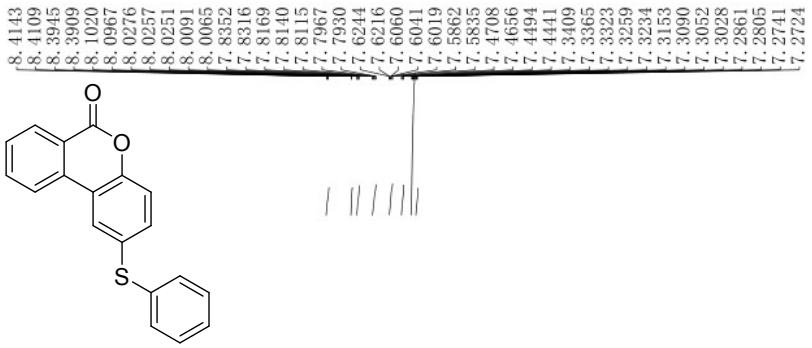


9 ^{1}H NMR

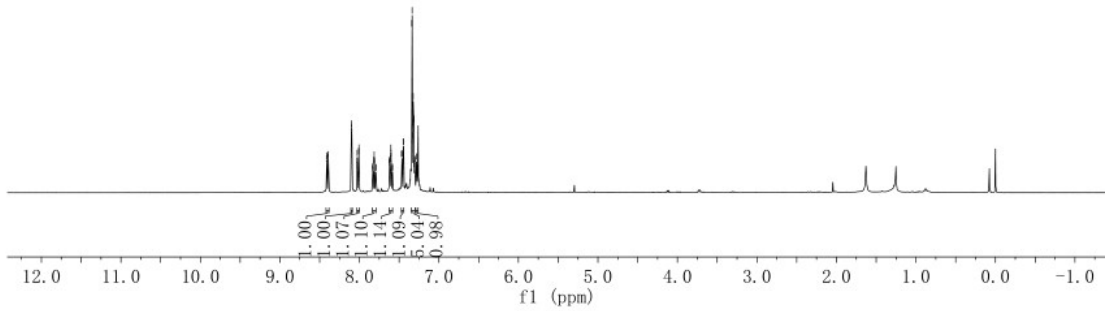


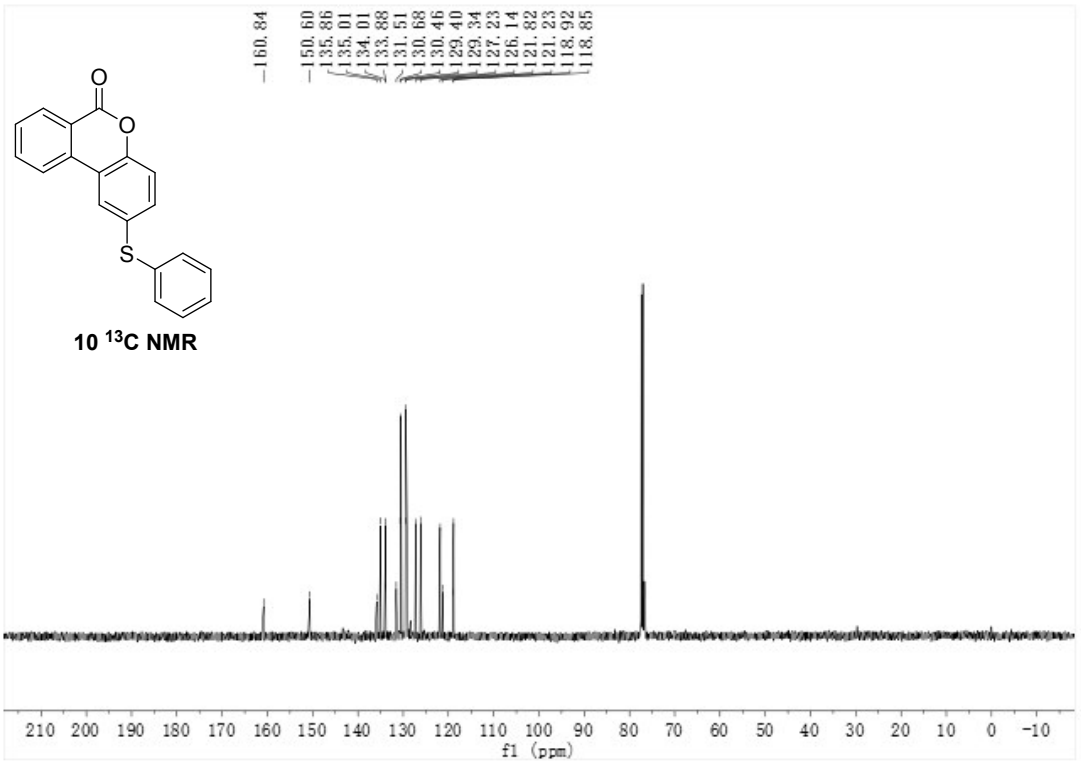


9 ^{13}C NMR



10 ^{1}H NMR





10 ^{13}C NMR