

Supporting Information

Synthesis of Spiropyrans via Ru(II)-Catalyzed Coupling of 3-aryl-2*H*-benzo[*b*][1,4]oxazines with Benzoquinones

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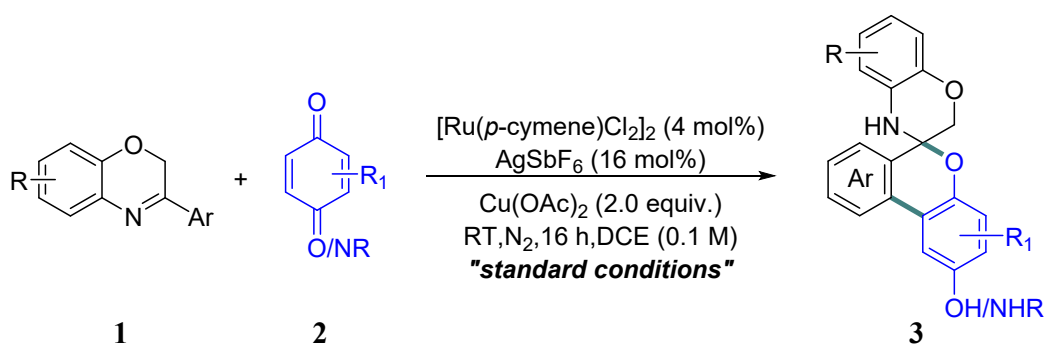
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General information:

Unless otherwise noted, all the reactions were carried out in an nitrogen-filled glove box. Anhydrous solvents were purified and dried by standard procedures. All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Benzoxazines,¹ benzoquinone compounds², N-sulfonyl quinone monoimine³ were prepared by following literature reports. ¹H and ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer (400 MHz for ¹H, 101 MHz for ¹³C). All coupling constants were reported in Hz. The residual solvent signals were used as references for ¹H and ¹³C NMR spectra and the chemical shifts were converted to the TMS scale (CDCl₃: δ ¹H = 7.26 ppm, δ ¹³C = 77.16 ppm. DMSO-*d*₆: δ ¹H = 2.50 ppm, δ ¹³C = 39.52 ppm. CD₃OD: δ ¹H = 3.31 ppm, δ ¹³C = 49.00 ppm). HRMS data were obtained using a TOF mode. Column chromatography was performed on silica gel (200-300 mesh) using ethyl acetate (EA)/petroleum ether (PE)/dichloromethane (DCM). The data of CCDC 2302071, CCDC 2302201, CCDC 2302202 can be obtained free of of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.⁴

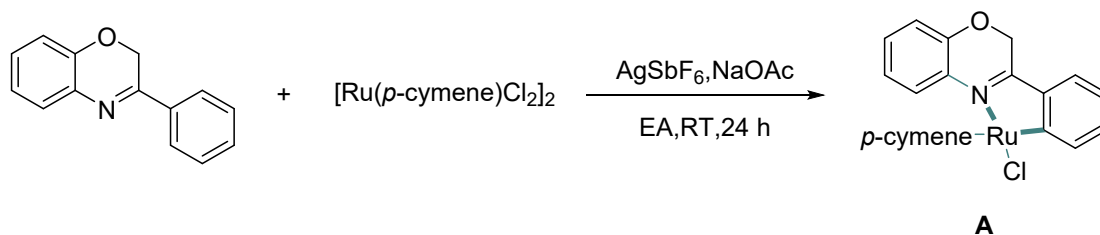
A. Catalytic results:

(a) General Procedure for Synthesis of 3.

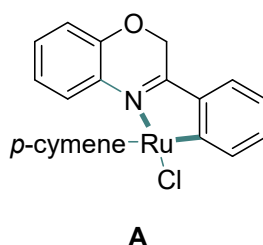


In a glovebox, Benzoxazines **1** (0.20 mmol, 1.0 equiv), benzoquinone compounds **2** (0.44 mmol, 2.2 equiv), [Ru(*p*-cymene)Cl₂]₂ (4 mol%), AgSbF₆ (16 mol%), Cu(OAc)₂ (0.40 mmol, 2.0 equiv) and DCE (2.0 mL) were charged into a pressure tube. The reaction mixture was stirred at room temperature for 16 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (15:1) to afford the desired product **3**.

(b) Synthesis of Ruthenium complexes A.



Benzoxazines **1a** (0.11 mmol), [Ru (*p*-cymene)Cl₂]₂ (0.05 mmol) and NaOAc (0.44 mmol) were weighed into a Schlenk tube equipped with a stir bar. EA (2.0 mL) was added, and the mixture was stirred at room temperature for 24 h under N₂. Afterwards, followed by filtration of any precipitate. The solvent was then removed and the brown product was purified by recrystallization using dichloromethane and diethyl ether to give product complex **A**. Yield of **A**: 10.2 mg (0.023 mmol, 23%).

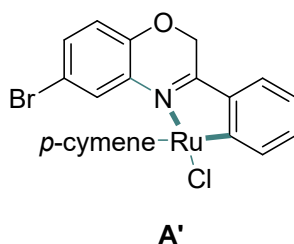


Brown solid 23% (10.2 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.41 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.16 (td, *J* = 7.7, 1.4 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.98 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.50 (d, *J* = 5.7 Hz, 2H), 5.41 (d, *J* = 15.1 Hz, 1H), 5.14 (d, *J* = 6.0 Hz, 1H), 5.11 (d, *J* = 5.9 Hz, 1H), 4.80 (d, *J* = 15.1 Hz, 1H), 2.30 – 2.19 (m, 1H), 2.09 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 191.5, 172.1, 148.0, 142.8, 139.9, 136.9, 130.8, 128.5, 127.0, 126.7, 122.7, 122.6, 115.9, 101.1, 99.9, 92.9, 89.6, 84.4, 83.8, 64.0, 31.0, 22.9, 21.7, 18.8.

HRMS: [M - Cl]⁺ calculated for C₂₄H₂₄NORu⁺: 444.0896, found: 444.0905.

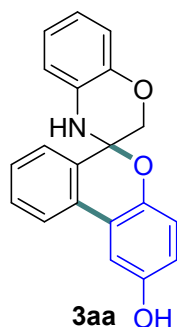


Brown solid 19% (10.6 mg).

¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, *J* = 2.3 Hz, 1H), 8.26 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.21 (td, *J* = 7.4, 1.2 Hz, 1H), 7.02 (t, *J* = 7.1 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 5.55 (t, *J* = 6.1 Hz, 2H), 5.42 (dd, *J* = 15.2, 2.9 Hz, 1H), 5.06 (d, *J* = 5.9 Hz, 1H), 5.02 (d, *J* = 5.9 Hz, 1H), 4.76 (d, *J* = 15.2 Hz, 1H), 2.37 – 2.26 (m, 1H), 2.14 (s, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 192.5, 172.5, 147.1, 142.5, 140.0, 137.9, 131.2, 131.0, 129.5, 127.5, 122.7, 117.5, 114.5, 102.2, 101.4, 94.1, 89.8, 83.4, 82.0, 64.1, 31.1, 23.3, 21.2, 18.8.

HRMS: [M + Na]⁺ calculated for C₂₄H₂₃BrClNNaORu⁺ : 579.9587, found: 579.9588.



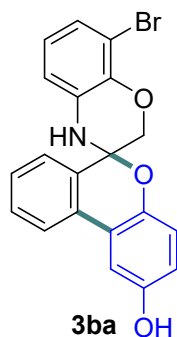
2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3aa)

White solid 83% (52.7 mg), mp: 125 – 126 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.53 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.42 – 7.38 (m, 1H), 7.24 (d, *J* = 2.9 Hz, 1H), 6.95 – 6.86 (m, 3H), 6.83 – 6.79 (m, 1H), 6.77 – 6.72 (m, 2H), 4.79 (s, 1H), 4.75 (s, 1H), 4.40 (dd, *J* = 11.3, 2.5 Hz, 1H), 3.87 (d, *J* = 11.3 Hz, 1H).

¹³C NMR (101 MHz, CD₃OD) δ 153.5, 146.3, 144.4, 133.7, 133.4, 132.2, 130.6, 129.5, 126.5, 123.5, 123.4, 122.7, 120.0, 119.9, 117.8, 117.0, 116.6, 110.1, 84.8, 68.6.

HRMS: [M + H]⁺ calculated for C₂₀H₁₆NO₃⁺ : 318.1125, found: 318.1122.



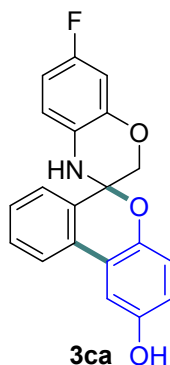
8-bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ba)

White solid 73% (57.8 mg), mp: 133 – 134 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (t, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 6.77 – 6.61 (m, 3H), 5.21 (s, 1H), 4.93 (s, 1H), 4.49 (dd, *J* = 11.3, 2.2 Hz, 1H), 3.87 (d, *J* = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.8, 145.3, 140.3, 132.3, 131.4, 130.6, 130.1, 130.1, 128.8, 125.1, 123.8, 122.8, 122.6, 122.1, 119.6, 117.3, 115.0, 110.6, 109.5, 83.4, 68.2.

HRMS: [M + H]⁺ calculated for C₂₀H₁₅BrNO₃⁺: 396.0230, found: 396.0222.



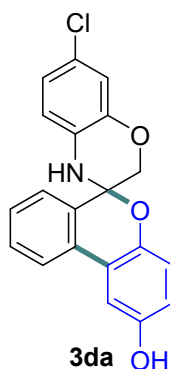
7-fluoro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ca)

White solid 69% (46.2 mg), mp: 207-208 °C.

¹H NMR (400 MHz, CD₃OD) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.43 (m, 1H), 7.37 – 7.34 (m, 1H), 6.86 – 6.65 (m, 3H), 6.63 – 6.44 (m, 2H), 4.28 (d, *J* = 11.2 Hz, 1H), 3.73 (d, *J* = 11.2 Hz, 1H). (two signals were missing).

¹³C NMR (101 MHz, CD₃OD) δ 157.7 (d, *J* = 234.8 Hz), 153.5, 146.2, 144.9 (d, *J* = 11.5 Hz), 133.4, 132.1, 130.6, 129.7 (d, *J* = 2.5 Hz), 129.5, 126.5, 123.4, 123.4, 119.9, 117.8, 116.7 (d, *J* = 9.1 Hz), 110.13, 108.6 (d, *J* = 22.6 Hz), 104.3 (d, *J* = 26.0 Hz), 84.5, 68.7.

HRMS: [M + H]⁺ calculated for C₂₀H₁₅FNO₃⁺: 336.1030, found: 336.1028.



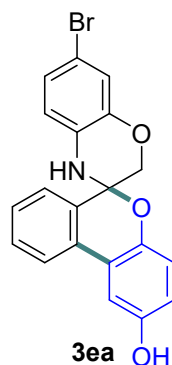
7-chloro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3da)

White solid 81% (56.9 mg), mp: 188 – 189 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.21 (s, 1H), 7.82 (d, *J* = 7.0 Hz, 1H), 7.60 (s, 1H), 7.55 – 7.48 (m, 2H), 7.44 (d, *J* = 6.1 Hz, 1H), 7.26 (s, 1H), 6.95 – 6.81 (m, 2H), 6.81 – 6.72 (m, 2H), 6.72 – 6.65 (m, 1H), 4.27 (d, *J* = 11.0 Hz, 1H), 3.84 (d, *J* = 10.3 Hz, 1H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 152.3, 143.9, 143.1, 131.4, 131.4, 130.2, 129.8, 128.4, 125.5, 122.4, 121.6, 121.3, 121.2, 118.5, 117.0, 116.1, 115.6, 109.3, 82.5, 67.2.

HRMS: [M + H]⁺ calculated for C₂₀H₁₅ClNO₃⁺: 352.0735, found: 352.0729.



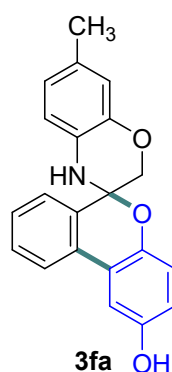
7-bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ea)

White solid 83% (65.5 mg), mp: 208 – 209 °C.

¹H NMR (400 MHz, CD₃OD) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.54 – 7.40 (m, 2H), 7.41 – 7.31 (m, 1H), 7.23 (d, *J* = 2.2 Hz, 1H), 6.99 – 6.81 (m, 2H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.70 – 6.68 (m, 2H), 4.28 (d, *J* = 11.2 Hz, 1H), 3.73 (d, *J* = 11.2 Hz, 1H).

¹³C NMR (101 MHz, CD₃OD) δ 153.5, 146.1, 145.2, 133.2, 132.9, 132.1, 130.7, 129.5, 126.4, 125.3, 123.4, 123.4, 119.9, 119.8, 117.9, 117.7, 110.9, 110.1, 84.3, 68.7.

HRMS: [M + H]⁺ calculated for C₂₀H₁₅BrNO₃⁺: 396.0230, found: 396.0232.



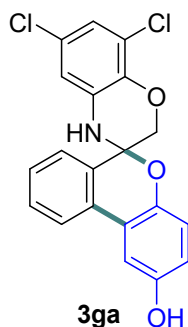
7-methyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3fa)

White solid 78% (51.7 mg), mp: 129 – 130 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.21 – 9.14 (m, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.47 – 7.36 (m, 1H), 7.28 – 7.25 (m, 1H), 7.21 (s, 1H), 6.77 – 6.72 (m, 1H), 6.72 – 6.67 (m, 2H), 6.63 – 6.59 (m, 2H), 4.24 – 4.20 (m, 1H), 3.75 (d, *J* = 11.2 Hz, 1H), 3.41 – 3.37 (m, 2H), 2.18 (s, 3H).

¹³C NMR (101 MHz, CD₃OD) δ 153.4, 146.3, 144.2, 133.8, 132.1, 130.7, 130.5, 129.6, 129.4, 126.5, 123.5, 123.3, 123.2, 119.9, 117.8, 117.5, 116.6, 110.1, 84.9, 68.6, 20.7.

HRMS: [M + H]⁺ calculated for C₂₁H₁₈NO₃⁺: 332.1281, found: 332.1282.



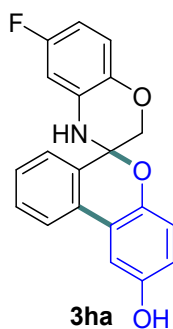
6,8-dichloro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ga)

White solid 37% (28.6 mg), mp: 125 – 126 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 2.5 Hz, 1H), 6.95 – 6.83 (m, 2H), 6.74 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.64 (d, *J* = 2.2 Hz, 1H), 4.95 (s, 1H), 4.72 (s, 1H), 4.51 (dd, *J* = 11.4, 2.1 Hz, 1H), 3.88 (d, *J* = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 151.0, 145.2, 138.3, 133.0, 131.1, 130.3, 129.0, 126.4, 125.0, 122.9, 122.1, 122.0, 120.5, 119.6, 117.3, 114.2, 109.6, 82.9, 68.2.

HRMS: [M + H]⁺ calculated for C₂₀H₁₄Cl₂NO₃⁺: 386.0345, found: 386.0345.



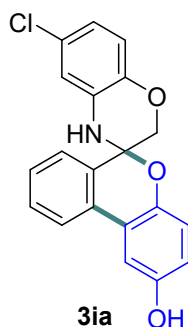
6-fluoro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ha)

White solid 75% (50.3 mg), mp: 196 – 197 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.27 – 9.17 (m, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.70 (d, *J* = 1.6 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.46 – 7.40 (m, 1H), 7.30 – 7.24 (m, 1H), 6.84 – 6.75 (m, 2H), 6.75 – 6.66 (m, 1H), 6.65 – 6.52 (m, 1H), 6.49 – 6.38 (m, 1H), 4.27 – 4.23 (m, 1H), 3.79 (d, *J* = 11.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 157.3 (d, $J = 234.4$ Hz), 152.4, 143.9, 138.6, 133.4 (d, $J = 11.6$ Hz), 131.4, 130.3, 129.8, 128.4, 125.4, 122.4, 121.6, 118.6, 117.0, 116.4 (d, $J = 9.9$ Hz), 109.3, 103.8 (d, $J = 23.3$ Hz), 101.5 (d, $J = 27.0$ Hz), 82.5, 67.1.

HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{15}\text{FNO}_3^+$: 336.1030, found: 336.1033.



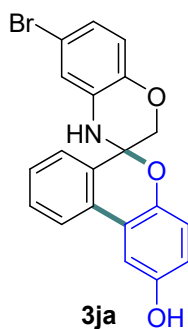
6-chloro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ia)

White solid 84% (59.0 mg), mp: 212 – 213 °C.

^1H NMR (400 MHz, DMSO- d_6) δ 9.21 (s, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 1.2$ Hz, 1H), 7.56 – 7.47 (m, 2H), 7.47 – 7.41 (m, 1H), 7.27 (d, $J = 2.7$ Hz, 1H), 6.84 – 6.78 (m, 2H), 6.76 (d, $J = 8.6$ Hz, 1H), 6.72 – 6.64 (m, 2H), 4.27 (dd, $J = 11.3, 1.8$ Hz, 1H), 3.83 (d, $J = 11.3$ Hz, 1H).

^{13}C NMR (101 MHz, DMSO- d_6) δ 152.4, 143.8, 141.3, 133.7, 131.3, 130.2, 129.8, 128.5, 125.4, 125.1, 122.4, 121.6, 118.6, 117.6, 117.1, 117.0, 114.3, 109.3, 82.4, 67.1.

HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{15}\text{ClNO}_3^+$: 352.0735, found: 352.0740.



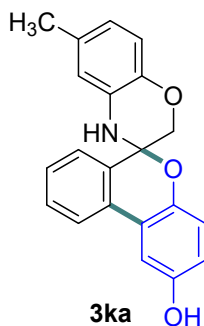
6-bromo-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ja)

White solid 86% (67.9 mg), mp: 229 – 230 °C.

^1H NMR (400 MHz, CD_3OD) δ 7.78 (d, $J = 7.8$ Hz, 1H), 7.52 – 7.46 (m, 2H), 7.41 – 7.37 (m, 1H), 7.26 – 7.23 (m, 1H), 6.95 – 6.93 (m, 1H), 6.84 – 6.74 (m, 2H), 6.74 – 6.64 (m, 2H), 4.31 (d, $J = 11.2$ Hz, 1H), 3.74 (d, $J = 11.2$ Hz, 1H).

^{13}C NMR (101 MHz, CD_3OD) δ 153.6, 146.1, 143.6, 135.2, 133.2, 132.1, 130.7, 130.7, 129.5, 126.4, 123.4, 123.4, 122.4, 119.9, 118.9, 118.4, 117.9, 114.5, 110.1, 84.3, 68.6.

HRMS: $[M + H]^+$ calculated for $C_{20}H_{15}BrNO_3^+$: 396.0230, found: 396.0233



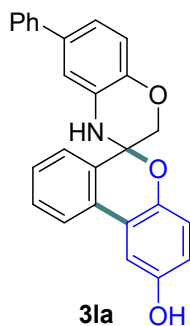
6-methyl-2H,4H-spiro[benzo[b]**[1,4]oxazine-3,6'-benzo**[c]**chromen]-2'-ol (3ka)**

White solid 75% (49.7 mg), mp: 220 – 221 °C.

¹H NMR (400 MHz, CD₃OD) δ 7.74 (d, J = 7.6 Hz, 1H), 7.50 (dd, J = 7.6, 1.1 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.37 – 7.32 (m, 1H), 7.23 (d, J = 2.8 Hz, 1H), 6.78 (d, J = 8.7 Hz, 1H), 6.72 – 6.63 (m, 2H), 6.60 (d, J = 1.4 Hz, 1H), 6.47 (dd, J = 8.1, 1.5 Hz, 1H), 4.25 (d, J = 11.1 Hz, 1H), 3.67 (d, J = 11.2 Hz, 1H), 2.20 (s, 3H).

¹³C NMR (101 MHz, DMSO-*d*₆) δ 153.4, 146.3, 142.2, 133.7, 132.9, 132.2, 130.5, 129.4, 126.5, 123.4, 120.5, 119.9, 117.8, 117.1, 116.7, 110.1, 84.9, 68.6, 20.9. (one signal was missing due to overlap.)

HRMS: $[M + H]^+$ calculated for $C_{21}H_{18}NO_3^+$: 332.1281, found: 332.1283.



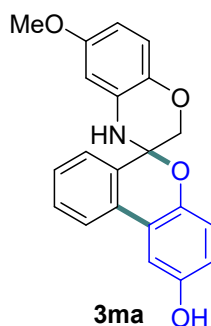
6-phenyl-2H,4H-spiro[benzo[b]**[1,4]oxazine-3,6'-benzo**[c]**chromen]-2'-ol (3la)**

White solid 32% (25.2 mg), mp: 88 – 89 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, J = 6.8 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.49 – 7.35 (m, 4H), 7.33 – 7.28 (m, 1H), 7.22 – 7.20 (m, 1H), 7.05 – 6.97 (m, 2H), 6.96 – 6.93 (m, 1H), 6.91 (dd, J = 8.6, 1.7 Hz, 1H), 6.73 – 6.70 (m, 1H), 5.17 (s, 1H), 4.93 (s, 1H), 4.42 (dd, J = 11.3, 2.1 Hz, 1H), 3.88 (d, J = 11.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.9, 145.5, 143.0, 141.1, 135.4, 132.0, 131.2, 130.7, 130.0, 128.8, 128.8, 126.9, 126.9, 125.3, 122.7, 122.2, 119.5, 119.2, 117.3, 117.0, 114.6, 109.6, 83.7, 67.9.

HRMS: $[M + H]^+$ calculated for $C_{26}H_{20}NO_3^+$: 394.1438, found: 394.1439.



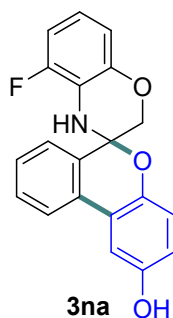
6-methoxy-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ma)

White solid 43% (29.9 mg), mp: 175 – 176 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.45 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.43 – 7.38 (m, 1H), 7.35 – 7.32 (m, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 6.88 – 6.82 (m, 2H), 6.68 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.36 (dd, *J* = 8.7, 2.8 Hz, 1H), 6.31 (d, *J* = 2.8 Hz, 1H), 5.59 (s, 1H), 4.91 (s, 1H), 4.35 (dd, *J* = 11.3, 1.6 Hz, 1H), 3.80 (d, *J* = 11.3 Hz, 1H), 3.73 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 154.8, 150.9, 145.4, 137.4, 132.0, 131.7, 130.6, 129.9, 128.7, 125.1, 122.7, 122.2, 119.4, 117.2, 117.0, 109.6, 105.1, 101.9, 83.7, 67.8, 55.8.

HRMS: [M + H]⁺ calculated for C₂₁H₁₈NO₄⁺ : 348.1230, found: 348.1237.



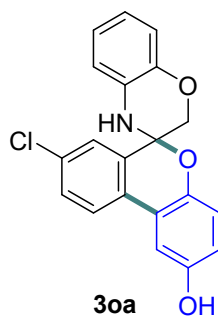
5-fluoro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3na)

White solid 61% (40.9 mg), mp: 166 – 167 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.77 – 6.69 (m, 4H), 4.98 (s, 1H), 4.86 (s, 1H), 4.42 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.86 (d, *J* = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 151.9 (d, *J* = 239.0 Hz), 150.9, 145.5, 144.7 (d, *J* = 5.4 Hz), 131.7, 130.7, 130.1, 128.9, 125.4, 122.7, 122.3, 120.4 (d, *J* = 15.6 Hz), 119.5, 118.7 (d, *J* = 9.0 Hz), 117.3, 112.1 (d, *J* = 2.8 Hz), 109.6, 108.3 (d, *J* = 18.3 Hz), 82.7, 67.8.

HRMS: [M + H]⁺ calculated for C₂₀H₁₅FNO₃⁺ : 336.1030, found: 336.1027.



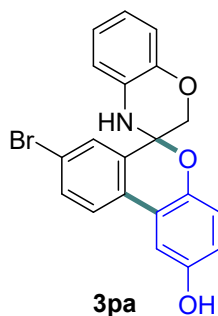
8'-chloro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3oa)

White solid 64% (45.0 mg), mp: 205 – 206 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 1.1 Hz, 1H), 7.43 (dd, J = 8.3, 1.8 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 6.94 – 6.88 (m, 3H), 6.86 – 6.80 (m, 1H), 6.79 – 6.68 (m, 2H), 4.77 (s, 1H), 4.72 (s, 1H), 4.36 (dd, J = 11.3, 2.3 Hz, 1H), 3.81 (d, J = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.9, 145.6, 143.4, 134.7, 133.8, 130.8, 130.1, 129.3, 125.7, 124.2, 122.2, 121.4, 120.6, 119.7, 117.6, 116.8, 116.2, 109.5, 83.5, 67.4.

HRMS [M + H]⁺ calculated for C₂₀H₁₅ClNO₃⁺ = 352.0735, found: 352.0740.



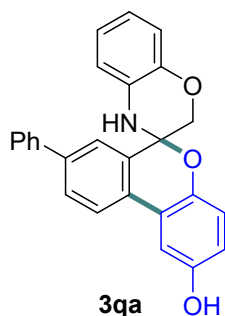
8'-bromo-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3pa)

White solid 69% (54.7 mg), mp: 148 – 149 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 2.0 Hz, 1H), 7.56 (dd, J = 8.4, 2.0 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 2.9 Hz, 1H), 6.95 – 6.85 (m, 3H), 6.84 – 6.80 (m, 1H), 6.78 – 6.70 (m, 2H), 4.91 (s, 1H), 4.79 (d, J = 2.0 Hz, 1H), 4.35 (dd, J = 11.4, 2.5 Hz, 1H), 3.80 (d, J = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.9, 145.5, 143.3, 133.9, 133.0, 130.8, 129.7, 128.6, 124.4, 122.7, 122.2, 121.4, 120.6, 119.7, 117.7, 116.8, 116.2, 109.4, 83.4, 67.4.

HRMS [M + H]⁺ calculated for C₂₀H₁₅BrNO₃⁺ : 396.0230, found: 396.0224.



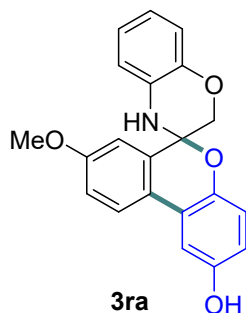
8'-phenyl-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3qa)

White solid 41% (32.3 mg), mp: 194 – 195 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.74 (m, 2H), 7.71 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.25 (d, *J* = 3.0 Hz, 1H), 6.97 – 6.87 (m, 3H), 6.85 – 6.80 (m, 1H), 6.80 – 6.71 (m, 2H), 4.85 (d, *J* = 1.8 Hz, 1H), 4.76 (s, 1H), 4.43 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.91 (d, *J* = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.8, 145.7, 143.5, 141.7, 140.1, 132.7, 131.1, 129.7, 129.1, 128.5, 128.0, 127.1, 124.0, 123.3, 122.1, 120.4, 119.5, 117.2, 116.8, 116.1, 109.5, 83.9, 67.8.

HRMS [M + H]⁺ calculated for C₂₆H₂₀NO₃⁺: 394.1438, found: 394.1447.



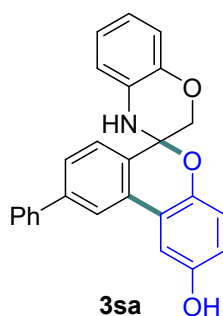
8'-methoxy-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ra)

White solid 68% (47.2 mg), mp: 220 – 221 °C.

¹H NMR (400 MHz, CD₃OD) δ 7.71 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 2.8 Hz, 1H), 7.12 (d, *J* = 2.7 Hz, 1H), 7.04 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.84 – 6.80 (m, 2H), 6.80 – 6.74 (m, 2H), 6.72 – 6.66 (m, 1H), 6.64 (dd, *J* = 8.6, 2.8 Hz, 1H), 4.27 (d, *J* = 11.2 Hz, 1H), 3.85 (s, 3H), 3.72 (d, *J* = 11.2 Hz, 1H). (two signals are missing).

¹³C NMR (101 MHz, CD₃OD) δ 161.6, 153.5, 145.6, 144.4, 135.3, 133.4, 125.0, 124.9, 123.7, 122.7, 120.0, 119.7, 117.0, 116.7, 116.7, 116.3, 111.7, 109.6, 84.8, 68.4, 55.9.

HRMS [M + H]⁺ calculated for C₂₁H₁₈NO₄⁺: 348.1230, found: 348.1230.



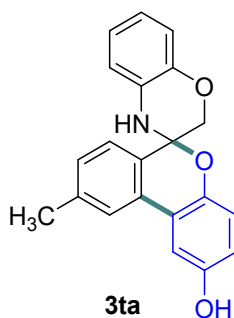
9'-phenyl-2H,4H-spiro[benzo[b]**[1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3sa)**

White solid 65% (51.1 mg), mp: 159 – 160 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.63 (d, *J* = 7.3 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.51 – 7.46 (m, 2H), 7.43 – 7.40 (m, 1H), 7.29 (d, *J* = 2.7 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.88 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.79 – 6.70 (m, 2H), 4.84 (s, 1H), 4.75 (s, 1H), 4.43 (dd, *J* = 11.3, 2.2 Hz, 1H), 3.90 (d, *J* = 11.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.8, 145.9, 143.5, 143.0, 140.5, 131.1, 129.1, 128.1, 127.6, 127.3, 125.9, 122.2, 122.1, 121.5, 120.3, 119.6, 117.4, 116.8, 116.0, 109.6, 83.7, 67.8.

HRMS [M + H]⁺ calculated for C₂₆H₂₀NO₃⁺: 394.1438, found: 394.1438.



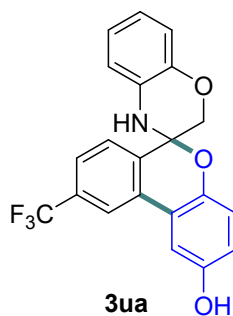
9'-methyl-2H,4H-spiro[benzo[b]**[1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3ta)**

White solid 65% (43.08 mg), mp: 106 – 107 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.49 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.82 – 6.78 (m, 1H), 6.73 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.69 (dd, *J* = 8.6, 2.9 Hz, 1H), 4.86 (s, 1H), 4.79 (s, 1H), 4.37 (dd, *J* = 11.3, 2.3 Hz, 1H), 3.84 (d, *J* = 11.3 Hz, 1H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 150.7, 145.8, 143.4, 139.8, 131.2, 130.5, 129.6, 129.4, 125.2, 123.3, 122.0, 120.2, 119.5, 117.1, 116.7, 115.9, 109.5, 83.7, 67.9, 21.6.

HRMS [M + H]⁺ calculated for C₂₁H₁₈NO₃⁺: 332.1281, found: 332.1280.



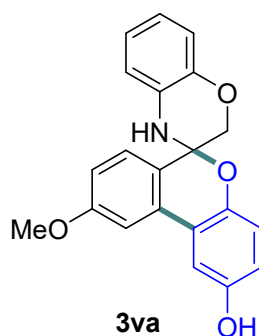
9'-(trifluoromethyl)-2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3ua)

White solid 64% (49.3 mg), mp: 185 – 186 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.69 – 7.59 (m, 2H), 7.24 (d, *J* = 2.8 Hz, 1H), 6.95 – 6.92 (m, 2H), 6.91 – 6.81 (m, 2H), 6.79 – 6.76 (m, 2H), 4.81 (s, 1H), 4.73 (s, 1H), 4.39 (dd, *J* = 11.3, 2.4 Hz, 1H), 3.84 (d, *J* = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 151.0, 145.7, 143.3, 135.3, 132.2 (q, *J* = 32 Hz), 131.6, 130.7, 126.2, 125.2 (q, *J* = 2.5 Hz), 122.6 (q, *J* = 270 Hz), 122.3, 121.0, 120.7, 119.8, 119.61 (q, *J* = 3.7 Hz), 118.3, 116.8, 116.2, 109.6, 83.7, 67.4.

HRMS [M + H]⁺ calculated for C₂₁H₁₅F₃NO₃⁺ : 386.0999, found: 368.1001.



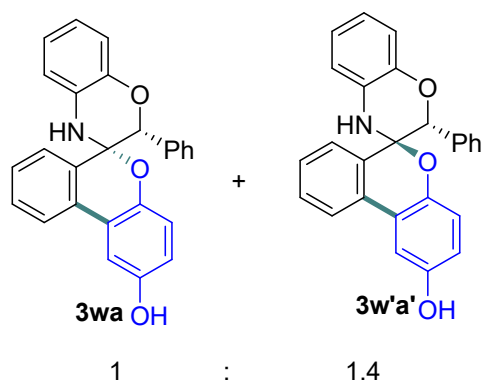
9'-methoxy-2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3va)

White solid 33% (22.9 mg), mp: 207 – 208 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.4 Hz, 1H), 7.20 (s, 1H), 7.18 (s, 1H), 7.04 – 6.84 (m, 4H), 6.82 – 6.78 (m, 1H), 6.75 – 6.71 (m, 2H), 4.35 (d, *J* = 11.3 Hz, 1H), 3.88 (s, 3H), 3.82 (d, *J* = 11.3 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 160.9, 146.0, 143.4, 132.2, 131.2, 126.8, 124.7, 124.7, 122.1, 122.0, 120.2, 119.5, 117.3, 116.7, 115.9, 115.9, 114.2, 108.0, 83.6, 68.0, 55.6.

HRMS [M + H]⁺ calculated for C₂₁H₁₈NO₄⁺ = 348.1230, found: 348.1228.



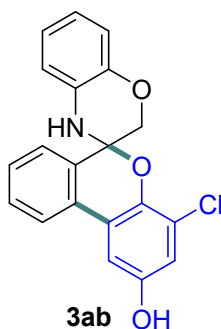
2-phenyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3wa and 3w'a')

White solid 39%, mp: 139 – 140 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.53 (m, 2.4H), 7.40 – 7.32 (m, 3.8H), 7.32 – 7.26 (m, 1H), 7.21 (d, J = 2.9 Hz, 1H), 7.12 – 7.09 (m, 1.4H), 7.07 – 7.02 (dd, J = 7.9, 1.5 Hz, 1.4H), 7.02 – 6.79 (m, 1.8H), 6.75 – 6.65 (m, 8H), 6.52 (dd, J = 8.7, 2.9 Hz, 1.4H), 5.38 (d, J = 1.9 Hz, 1H), 5.09 (s, 1.4H), 4.91 (s, 1.4H), 4.77 (d, J = 2.0 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.8, 149.2, 147.1, 145.7, 143.8, 143.6, 137.4, 134.3, 131.7, 131.0, 130.9, 130.7, 130.6, 130.3, 129.6, 129.4, 128.6, 128.2, 128.0, 127.9, 127.8, 127.5, 127.4, 126.8, 126.7, 126.6, 122.6, 122.1, 122.0, 121.4, 121.0, 119.9, 119.6, 119.4, 117.7, 117.1, 116.7, 116.2, 116.0, 115.3, 109.5, 108.5, 86.1, 84.9, 82.7. (two signals are missing due to overlap).

HRMS [M + H]⁺ calculated for C₂₆H₂₀NO₃⁺: 394.1438, found: 394.1450.



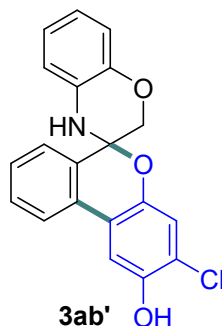
4'-chloro-2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3ab)

White solid 20% (14.1 mg), mp : 197 – 198 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, J = 7.5 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.45 – 7.36 (m, 2H), 7.04 (s, 1H), 6.96 – 6.87 (m, 2H), 6.85 – 6.81 (m, 1H), 6.76 (dd, J = 7.7, 1.6 Hz, 1H), 5.34 (s, 1H), 4.79 (d, J = 1.7, 1H), 4.38 (dd, J = 11.4, 2.5 Hz, 1H), 3.86 (d, J = 11.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 145.6, 143.3, 131.9, 130.8, 130.1, 130.0, 129.1, 125.4, 122.8, 122.1, 121.8, 120.7, 120.5, 118.8, 116.8, 116.0, 110.0, 84.1, 67.7.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{15}\text{ClNO}_3^+$: 352.0735, found: 352.0752.



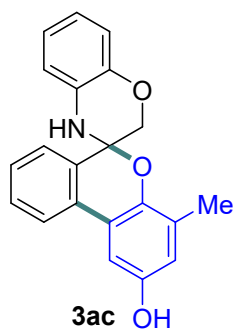
3'-chloro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ab')

White solid 19% (13.4 mg), mp: 148 – 149 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.7$ Hz, 1H), 7.55 (d, $J = 7.2$ Hz, 1H), 7.51 – 7.48 (m, 1H), 7.44 – 7.40 (m, 1H), 7.15 (d, $J = 2.7$ Hz, 1H), 6.95 (d, $J = 7.4$ Hz, 1H), 6.91 – 6.80 (m, 3H), 6.77 (dd, 1H), 4.85 (s, 1H), 4.81 (s, 1H), 4.35 (dd, $J = 11.4, 2.4$ Hz, 1H), 3.86 (d, $J = 11.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.4, 143.7, 142.0, 132.4, 130.8, 130.2, 130.1, 129.4, 125.3, 124.3, 123.8, 123.1, 121.9, 120.5, 117.7, 116.7, 116.2, 108.5, 84.7, 67.6.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{20}\text{H}_{15}\text{ClNO}_3^+$: 352.0735, found: 352.0752.



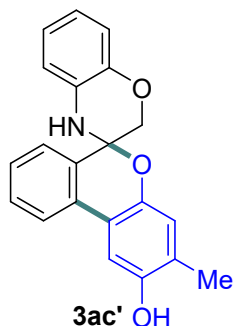
4'-methyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ac)

White solid 23% (15.2 mg), mp: 220 – 221 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.7$ Hz, 1H), 7.51 (d, $J = 7.6$ Hz, 1H), 7.47 – 7.43 (m, 1H), 7.37 – 7.34 (m, 1H), 7.15 (s, 1H), 6.94 (d, $J = 7.8$ Hz, 1H), 6.91 – 6.87 (m, 1H), 6.83 – 6.79 (m, 2H), 6.75 (d, $J = 7.6$ Hz, 1H), 4.79 (s, 1H), 4.61 (s, 1H), 4.40 (dd, $J = 11.3, 2.2$ Hz, 1H), 3.85 (d, $J = 11.3$ Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.1, 145.5, 143.5, 131.9, 131.2, 130.9, 129.9, 128.3, 126.5, 125.3, 122.3, 122.0, 120.6, 120.2, 119.9, 116.7, 116.0, 109.1, 83.6, 67.8, 16.1.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{18}\text{NO}_3^+$ = 332.1281, found: 332.1283.



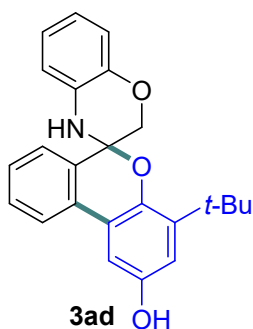
3'-methyl-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ac')

White solid 23% (15.2 mg), mp: 125 – 126 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.38 – 7.35 (m, 1H), 7.04 (d, J = 2.5 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 6.89 – 6.85 (m, 1H), 6.83 – 6.79 (m, 1H), 6.75 (d, J = 7.6 Hz, 1H), 6.61 (d, J = 2.2 Hz, 1H), 4.80 (s, 1H), 4.67 (s, 1H), 4.34 (dd, J = 11.2, 2.2 Hz, 1H), 3.85 (d, J = 11.2 Hz, 1H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.1, 143.8, 143.6, 132.4, 131.3, 131.1, 129.8, 128.6, 125.0, 122.9, 122.1, 121.8, 120.3, 118.4, 116.5, 116.2, 107.0, 83.6, 67.6, 15.8. (one signal was missing due to overlap).

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{18}\text{NO}_3^+$: 332.1281, found: 332.1283.



4'-(tert-butyl)-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ad)

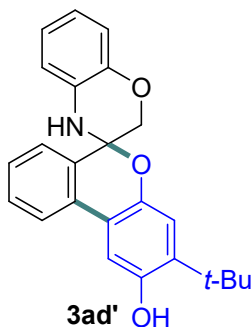
White solid 23% (17.2 mg), mp: 124 – 125 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.37 – 7.33 (m, 1H), 7.03 (s, 1H), 6.96 – 6.93 (m, 2H), 6.91 – 6.87 (m, 1H), 6.84 – 6.80 (m, 1H), 6.76

(dd, $J = 7.6, 1.4$ Hz, 1H), 4.80 (s, 1H), 4.75 (s, 1H), 4.43 (dd, $J = 11.3, 2.2$ Hz, 1H), 3.86 (d, $J = 11.3$ Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.4, 145.4, 143.3, 139.3, 131.7, 131.2, 130.5, 129.8, 128.3, 125.4, 122.1, 122.1, 120.2, 119.1, 117.3, 116.8, 115.9, 110.3, 83.7, 68.0, 34.9, 29.6.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{24}\text{NO}_3^+$: 374.1751, found: 374.1758.



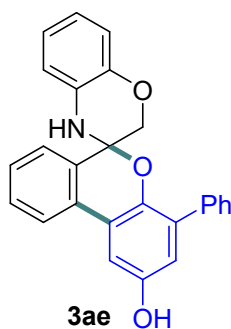
3'-(tert-butyl)-2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3ad')

White solid 23% (17.2 mg), mp: 118 – 119 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.6$ Hz, 1H), 7.54 – 7.43 (m, 2H), 7.40 – 7.36 (m, 1H), 7.13 (d, $J = 2.6$ Hz, 1H), 6.93 – 6.75 (m, 4H), 6.70 (d, $J = 7.4$ Hz, 1H), 4.78 (s, 1H), 4.56 (s, 1H), 4.48 (dd, $J = 11.2, 1.8$ Hz, 1H), 4.04 (d, $J = 11.2$ Hz, 1H), 1.24 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.7, 144.4, 143.2, 141.7, 131.8, 131.3, 131.0, 129.8, 128.5, 124.5, 123.2, 122.3, 121.8, 120.2, 116.7, 115.6, 115.6, 107.1, 83.1, 68.0, 35.0, 29.8.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{24}\text{NO}_3^+$: 374.1751, found: 374.1758.



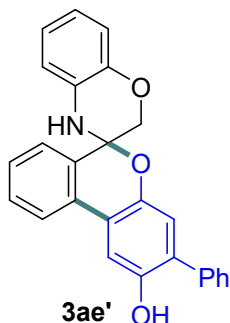
4'-phenyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3ae)

White solid 14 % (11.0 mg), mp: 101 – 102 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 7.7$ Hz, 1H), 7.54 (d, $J = 7.6$ Hz, 1H), 7.52 – 7.44 (m, 5H), 7.43 – 7.37 (m, 3H), 6.97 (s, 1H), 6.94 – 6.85 (m, 2H), 6.82 – 6.78 (m, 1H), 6.76 (dd, $J = 7.6, 1.4$ Hz, 1H), 5.10 (s, 1H), 4.81 (s, 1H), 4.46 (dd, $J = 11.3, 2.0$ Hz, 1H), 3.90 (d, $J = 11.3$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 147.7, 145.6, 143.4, 136.5, 132.2, 131.1, 130.6, 130.0, 129.9, 129.5, 129.0, 128.8, 128.3, 125.4, 122.8, 122.0, 121.9, 120.3, 119.7, 116.7, 116.0, 110.0, 83.7, 67.9.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{20}\text{NO}_3^+$: 394.1438, found: 394.1451.



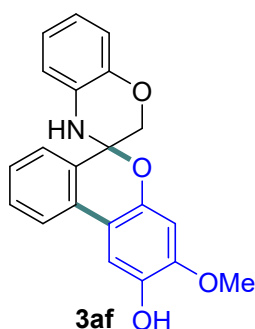
3'-phenyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3ae')

White solid 13% (10.2 mg), mp : 120-121 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.6$ Hz, 1H), 7.60 – 7.52 (m, 2H), 7.50 – 7.43 (m, 2H), 7.35 (t, $J = 7.5$ Hz, 1H), 7.22 (d, $J = 2.9$ Hz, 1H), 7.19 – 7.10 (m, 3H), 6.97 (dd, $J = 7.8, 1.2$ Hz, 1H), 6.87 – 6.75 (m, 3H), 6.50 (dd, $J = 7.6, 1.5$ Hz, 1H), 4.76 (d, 1H), 4.68 (s, 1H), 4.55 (dd, $J = 11.3, 2.5$ Hz, 1H), 3.97 (d, $J = 11.3$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.4, 143.3, 142.6, 136.9, 133.1, 131.8, 131.1, 130.7, 129.8, 129.6, 128.8, 128.1, 127.3, 124.9, 123.1, 123.0, 121.9, 120.4, 118.3, 116.4, 116.4, 108.8, 83.6, 67.8.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{20}\text{NO}_3^+$: 394.1438, found: 394.1451.



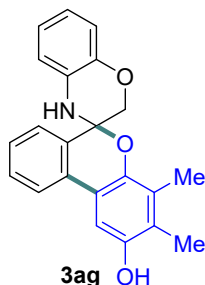
3'-methoxy-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (3af)

White solid 61% (42.4 mg), mp: 163 – 164 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 7.7$ Hz, 1H), 7.53 – 7.40 (m, 2H), 7.35 – 7.28 (m, 2H), 6.94 (dd, $J = 7.8, 1.5$ Hz, 1H), 6.90 – 6.86 (m, 1H), 6.83 – 6.80 (m, 1H), 6.75 (dd, $J = 7.7, 1.5$ Hz, 1H), 6.58 (s, 1H), 5.36 (s, 1H), 4.82 (s, 1H), 4.44 (dd, $J = 11.3, 2.3$ Hz, 1H), 3.87 (d, $J = 11.4$ Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.1, 145.6, 143.4, 141.1, 131.1, 131.0, 130.9, 129.9, 127.7, 125.1, 122.1, 122.0, 120.2, 116.7, 115.9, 113.9, 108.3, 101.7, 83.9, 67.8, 56.2.

HRMS $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{18}\text{NO}_4^+$: 348.1230, found: 348.1230.



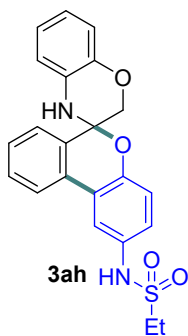
3',4'-dimethyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-ol (3ag)

White solid 45% (31.1 mg), mp: 185 – 186 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 7.7$ Hz, 1H), 7.54 – 7.48 (m, 1H), 7.47 – 7.43 (m, 1H), 7.37 – 7.33 (m, 1H), 7.04 (s, 1H), 6.95 – 6.84 (m, 2H), 6.84 – 6.72 (m, 2H), 4.77 (s, 1H), 4.53 (s, 1H), 4.35 (dd, $J = 11.2, 2.5$ Hz, 1H), 3.85 (d, $J = 11.2$ Hz, 1H), 2.18 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.7, 143.7, 143.7, 132.3, 131.4, 131.4, 129.8, 128.3, 128.2, 125.2, 125.0, 122.6, 121.8, 120.3, 119.4, 116.5, 116.2, 106.5, 83.6, 67.6, 12.3, 12.1.

HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{22}\text{H}_{20}\text{NO}_3^+$: 346.1438, found: 346.1441.



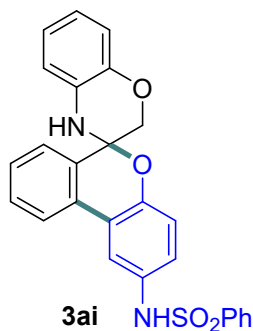
N-(2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-yl)ethanesulfonamide (3ah)

White solid 32% (26.1 mg), mp: 172 – 173 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 2.4$ Hz, 1H), 7.56 – 7.48 (m, 2H), 7.44 – 7.40 (m, 1H), 7.06 (dd, $J = 8.6, 2.5$ Hz, 1H), 6.99 (d, $J = 8.6$ Hz, 1H), 6.95 – 6.87 (m, 2H), 6.85 – 6.80 (m, 1H), 6.77 (dd, $J = 7.6, 1.4$ Hz, 1H), 6.61 (s, 1H), 4.84 (d, $J = 1.6$ Hz, 1H), 4.37 (dd, $J = 11.4, 2.4$ Hz, 1H), 3.87 (d, $J = 11.4$ Hz, 1H), 3.12 (q, $J = 7.4$ Hz, 2H), 1.41 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.9, 143.3, 131.7, 130.9, 130.8, 130.2, 130.0, 129.3, 125.4, 124.4, 122.9, 122.4, 122.1, 120.4, 119.6, 117.8, 116.8, 116.0, 84.2, 68.0, 45.8, 8.4.

HRMS $[M + Na]^+$ calculated for $C_{22}H_{20}N_2NaO_4S^+$: 431.1036, found: 431.1042.



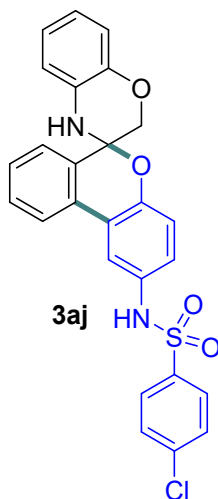
***N*-(2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-yl)benzenesulfonamide (3ai)**

White solid 21% (19.2 mg), mp: 153 – 154 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.66 (d, $J = 7.7$ Hz, 1H), 7.58 – 7.37 (m, 7H), 6.94 – 6.77 (m, 5H), 6.75 (dd, $J = 7.7, 1.4$ Hz, 1H), 6.68 (s, 1H), 4.81 (d, $J = 1.7$ Hz, 1H), 4.31 (dd, $J = 11.4, 2.4$ Hz, 1H), 3.84 (d, $J = 11.4$ Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 143.3, 139.0, 133.2, 131.6, 130.9, 130.4, 130.1, 130.0, 129.2, 127.4, 125.6, 125.4, 122.8, 122.1, 122.1, 120.4, 119.3, 119.1, 116.7, 115.9, 84.1, 68.0.

HRMS: $[M + Na]^+$ calculated for $C_{26}H_{20}N_2NaO_4S^+$: 479.1036, found: 479.1043.



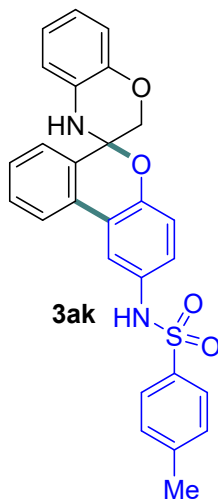
4-chloro-*N*-(2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-yl)benzenesulfonamide (3aj)

White solid 16% (15.7 mg), mp: 125 – 126 °C.

1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 3H), 7.56 (d, $J = 2.4$ Hz, 1H), 7.55 – 7.46 (m, 2H), 7.45 – 7.38 (m, 3H), 6.94 – 6.85 (m, 3H), 6.85 – 6.78 (m, 2H), 6.76 (dd, $J = 7.6, 1.3$ Hz, 1H), 6.71 (s, 1H), 4.82 (d, $J = 2.1$ Hz, 1H), 4.32 (dd, $J = 11.4, 2.4$ Hz, 1H), 3.85 (d, $J = 11.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.3, 143.3, 139.8, 137.5, 131.6, 130.8, 130.2, 130.0, 129.9, 129.5, 129.3, 128.9, 125.6, 125.5, 122.8, 122.2, 122.2, 120.4, 119.5, 119.2, 116.8, 115.9, 84.2, 68.0.

HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{20}\text{ClN}_2\text{O}_4\text{S}^+$: 491.0827, found: 491.0826.



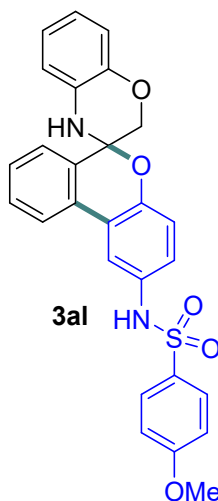
4-methyl-N-(2H,4H-spiro[benzo[b][1,4]oxazine-3,6'-benzo[c]chromen]-2'-yl)benzenesulfonamide (3ak)

White solid 22% (20.7 mg), mp: 88–89 °C.

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.67 – 7.62 (m, 3H), 7.58 – 7.49 (m, 3H), 7.49 – 7.43 (m, 2H), 7.34 (d, $J = 8.2$ Hz, 2H), 6.91 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.81 (s, 1H), 6.80 – 6.76 (m, 3H), 6.67 – 6.62 (m, 1H), 4.18 (dd, $J = 11.3, 1.9$ Hz, 1H), 3.80 (d, $J = 11.3$ Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 148.6, 143.3, 142.4, 136.7, 132.0, 131.8, 131.4, 130.0, 129.7, 129.4, 128.9, 126.9, 125.8, 123.6, 122.1, 121.7, 121.3, 118.6, 118.5, 116.6, 115.9, 115.3, 83.6, 67.3, 21.0.

HRMS: $[\text{M} + \text{H}]^+$ calculated for $\text{C}_{27}\text{H}_{23}\text{N}_2\text{O}_4\text{S}^+$: 471.1373, found: 471.1382.



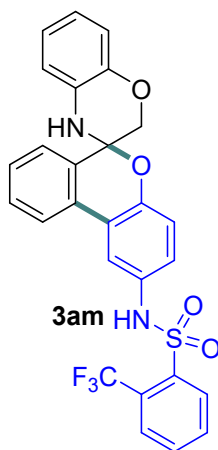
4-methoxy-*N*-(2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-yl)benzenesulfonamide (3al)

White solid 37% (36.0 mg), mp: 180 – 181 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.66 (m, 3H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.41 (t, *J* = 7.5 Hz, 1H), 6.94 – 6.84 (m, 5H), 6.84 – 6.73 (m, 3H), 6.52 (s, 1H), 4.80 (d, *J* = 2.0 Hz, 1H), 4.32 (dd, *J* = 11.4, 2.3 Hz, 1H), 3.85 (d, *J* = 11.5 Hz, 1H), 3.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 163.3, 150.0, 143.3, 131.6, 130.9, 130.7, 130.6, 130.1, 130.1, 129.6, 129.2, 125.5, 125.4, 122.9, 122.1, 122.0, 120.4, 119.3, 119.0, 116.7, 115.9, 114.3, 84.1, 68.0, 55.7.

HRMS: [M + Na]⁺ calculated for C₂₇H₂₂N₂NaO₅S⁺ : 509.1142, found: 509.1140.



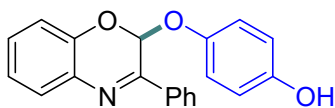
***N*-(2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-yl)-2-(trifluoromethyl)benzenesulfonamide (3am)**

White solid 26%(27.3 mg), mp: 149 – 150 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.58 – 7.52 (m, 2H), 7.52 – 7.44 (m, 2H), 7.41 – 7.37 (m, 1H), 6.92 – 6.84 (m, 2H), 6.83 – 6.74 (m, 3H), 6.73 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.69 (s, 1H), 4.80 (d, *J* = 1.7 Hz, 1H), 4.26 (dd, *J* = 11.4, 2.3 Hz, 1H), 3.81 (d, *J* = 11.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 150.4, 143.2, 137.4, 133.2, 132.6, 132.4, 131.5, 130.8, 130.2, 129.8, 129.7, 129.3, 128.6 (q, *J* = 6.3 Hz), 127.7 (d, *J* = 32.9 Hz), 125.5, 125.5, 123.2 (d, *J* = 273.9 Hz), 122.8, 122.2, 122.1, 120.4, 119.3, 119.3, 116.7, 115.9, 84.2, 68.0.

HRMS: [M + Na]⁺ calculated for C₂₇H₁₉F₃N₂NaO₄S⁺ : 547.0910, found: 547.0917.



4aa

4-((3-phenyl-2H-benzo[*b*][1,4]oxazin-2-yl)oxy)phenol (4aa)

Pale yellow solid 50% (31.7 mg), mp: 155 – 156 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.93 (m, 2H), 7.63 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 – 7.48 (m, 3H), 7.31 – 7.22 (m, 2H), 7.17 – 7.13 (m, 1H), 7.12 – 7.05 (m, 3H), 6.86 – 6.74 (m, 2H), 6.50 (s, 1H), 5.08 (s, 1H).

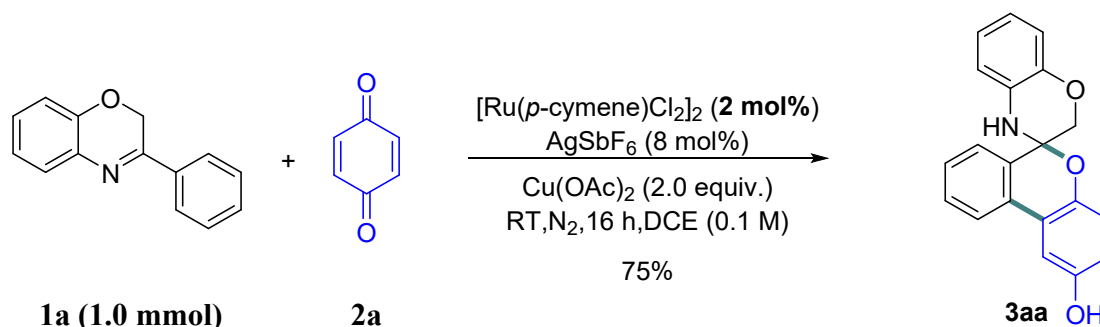
¹³C NMR (101 MHz, CDCl₃) δ 153.9, 152.0, 150.4, 143.2, 135.2, 132.9, 131.3, 129.2, 129.0, 128.3, 127.2, 123.2, 119.6, 116.8, 116.4, 90.5.

HRMS: [M + H]⁺ calculated for C₂₀H₁₆NO₃⁺ : 318.1125, found: 318.1137.

References

1. Sabitha, M. G.; Rao, A. S. *Synth. Commun.* **1987**, *17*, 341.
2. Pelter, A.; Elgendy, S. *Tetrahedron lett.* **1988**, *29*, 677-680
3. (a)Leduc, A. B.; Kerr, M. A. *Eur. J. Org. Chem.* **2007**, *2*, 237-240. (b) Chen, K.; Liu, S.; Wang, D.; Hao, W. J.; Zhou, P.; Tu, S. J.; Jiang, B. *J. Org. Chem.* **2017**, *82*, 11524-11530.
4. Experimental Crystal Structure Determination: (a) CCDC 2302071: 2023, DOI: 10.5517/ccdc.csd.cc2h8hcn. (b) CCDC: 2302201: DOI: 2023, 10.5517/ccdc.csd.cc2h8mkz. (c) CCDC: 2302202, 2023, DOI: 10.5517/ccdc.csd.cc2h8ml0.

B. Scale-up Reaction.

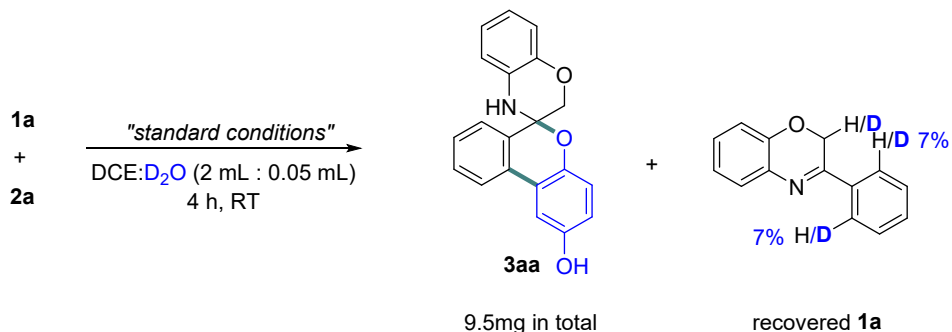


3-phenyl-2H-benzo[*b*][1,4]oxazine (1.0 mmol), benzoquinone (2.2 mmol), [Ru(*p*-cymene)Cl₂] (2 mol%), AgSbF₆ (8 mol %), Cu(OAc)₂ (2.0 mmol) and DCE (10 mL) were charged into a pressure tube. The reaction mixture was stirred at room temperature for 16 h. After completion of the reaction, the solvent was removed under reduced pressure and the crude reaction mixture was directly purified

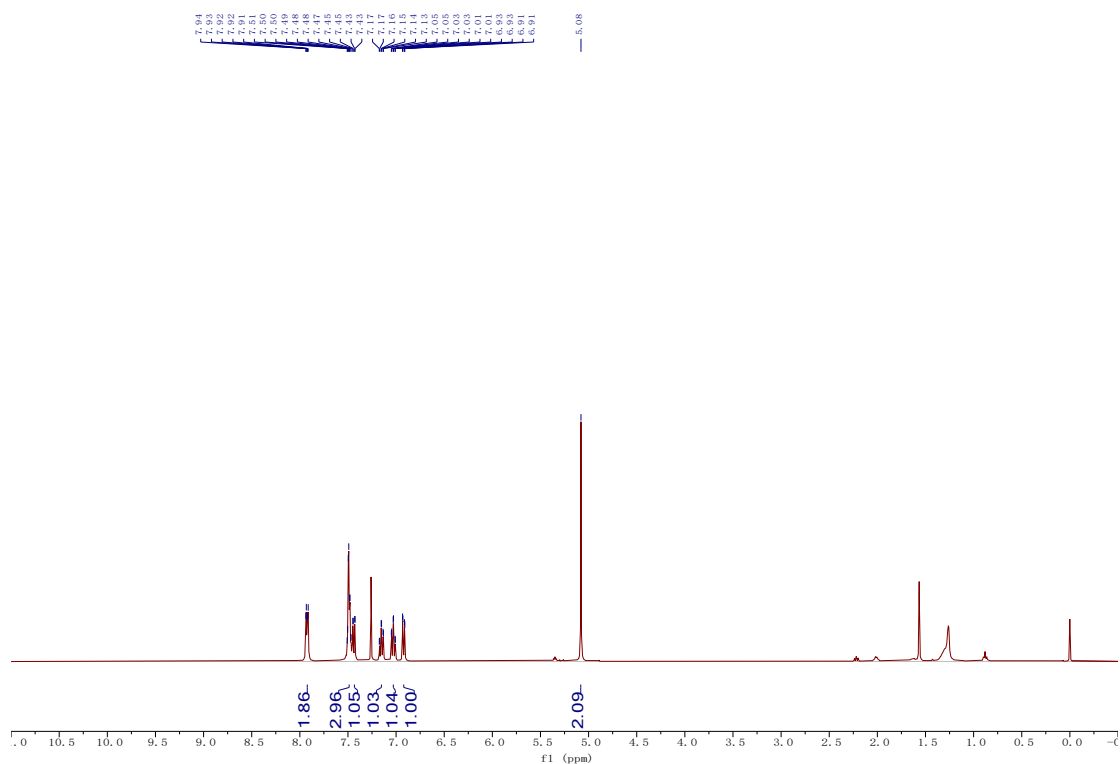
through column chromatography on silica gel using PE/EA (15:1) as eluent to obtain 2*H*,4*H*-spiro[benzo[*b*]-[1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol (**3aa**) in 75% yield (0.24 g).

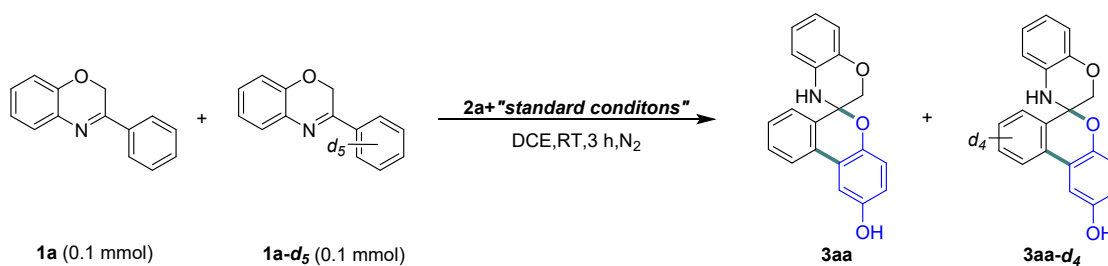
C. Mechanistic studies :

(a) H/D exchange.

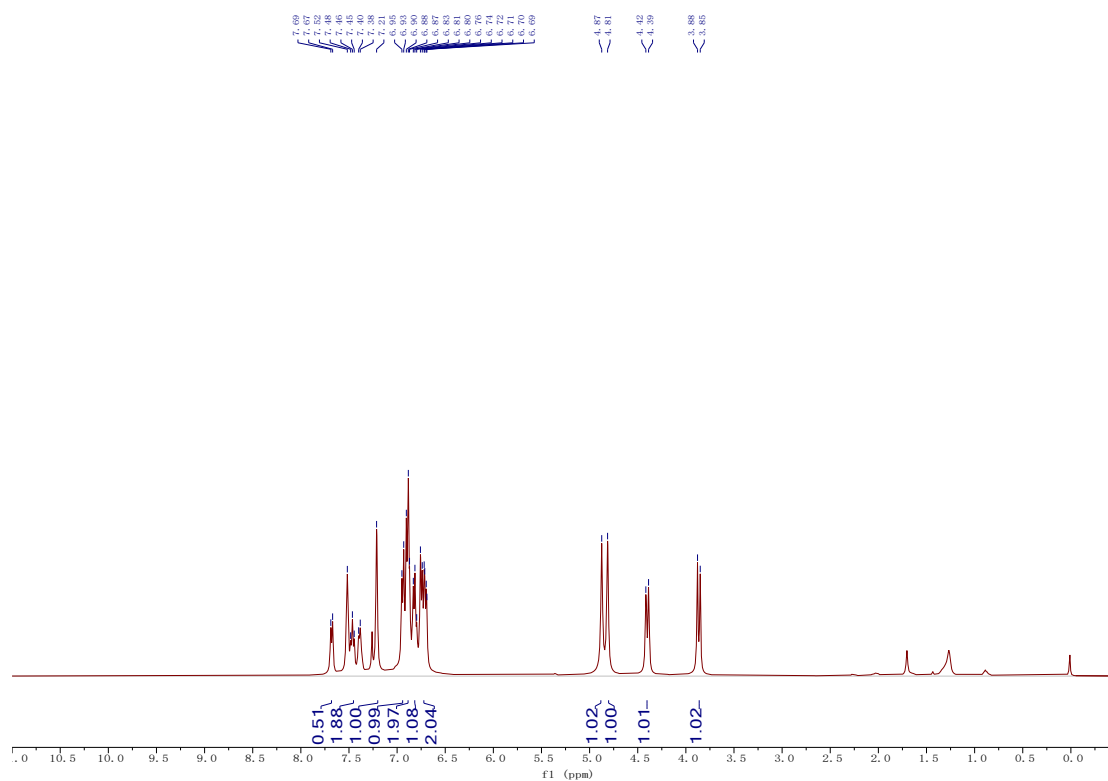


1a (0.10 mmol), **2a** (0.22 mmol), [Ru (*p*-cymene)Cl₂]₂ (4 mol%), AgSbF₆ (16 mol%), Cu(OAc)₂ (0.20 mmol), 50 μL D₂O and DCE (2.0 mL) were charged into a pressure tube, and the mixture was stirred at room temperature for 4 h. 7% H/D exchange was observed on the basis of ¹H NMR analysis, indicating that the C-H activation was largely irreversible in the catalytic system.

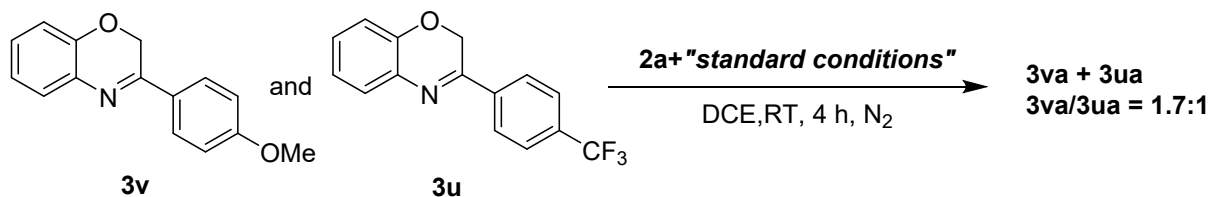




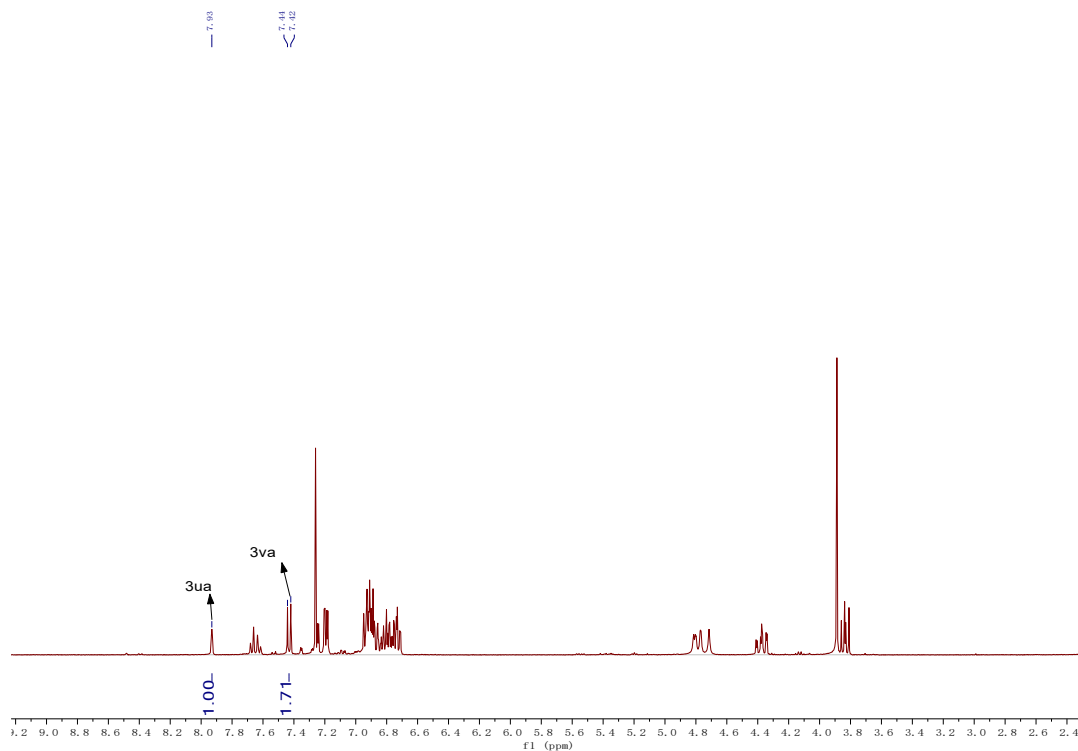
Suspensions of 3-phenyl-2*H*-benzo[*b*][1,4]oxazine $1\mathbf{a}$ (0.1 mmol) and $1\mathbf{a-d}_5$ (0.1 mmol), $2\mathbf{a}$ (0.44 mmol), $[\text{RuCl}_2(p\text{-cymene})]_2$ (4 mol%), AgSbF_6 (16 mol%), $\text{Cu}(\text{OAc})_2$ (0.40 mmol) and DCE (2.0 mL) were stirred side-by-side at room temperature for 3 h under N_2 . The reaction were removed under reduced pressure. The residue was purified by silica gel chromatography with 26.3 mg of $3\mathbf{aa}$ and $3\mathbf{aa-d}_4$ were recovered. KIE value ($k_{\text{H}}/k_{\text{D}} = 1.5:1$) was determined on the basis of ^1H NMR analysis of $3\mathbf{aa}$ and $3\mathbf{aa-d}_4$.



(c) Procedure for competitive experiment between Benzoquinone

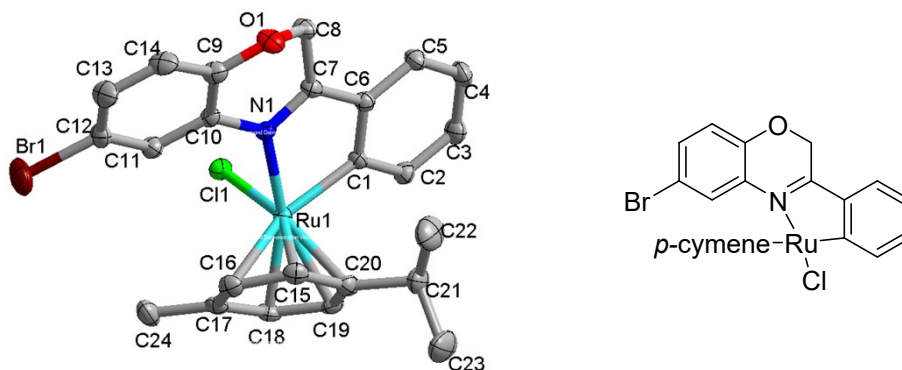


Suspensions of 3-(4-methoxyphenyl)-2*H*-benzo[*b*][1,4]oxazine **3v** (0.1 mmol) and 3-(4-(trifluoromethyl)phenyl)-2*H*-benzo[*b*][1,4]oxazine **3u** (0.1 mmol), **2a** (0.44 mmol), [RuCl₂(*p*-cymene)]₂ (4 mol%), AgSbF₆ (16 mol%), Cu(OAc)₂ (0.40 mmol) and DCE (2.0 mL) were stirred side-by-side at room temperature for 4 h under N₂. The reaction were removed under reduced pressure. The residue was purified by silica gel chromatography. The ratio of 3va and 3ua (1 : 0.6) was determined on the basis of ¹H NMR analysis of **3va** and **3ua**.



D. Crystal structure.

(a) Crystal structure of complex **A'**, CCDC Number = 2302201



(b) Crystal structure of 3ag, CCDC Number = 2302071

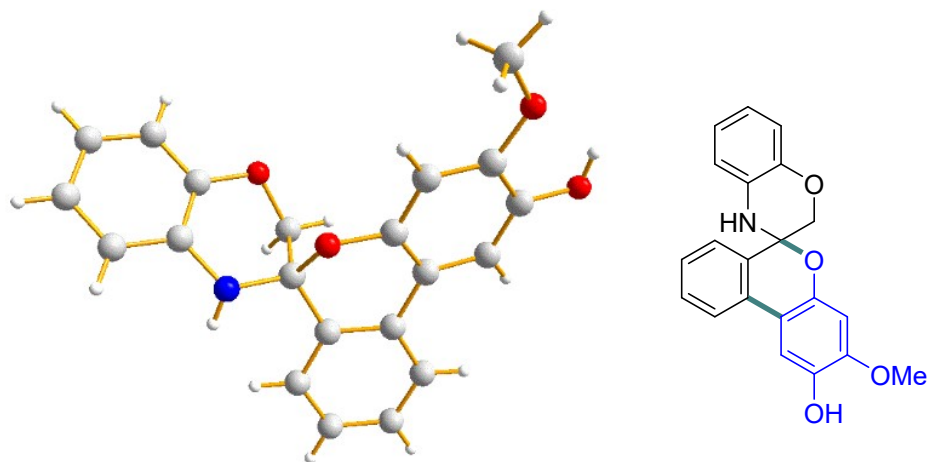


Figure S2 Crystal structure of 3db with thermal ellipsoids at 50% probability.

no syntax errors found. [View dictionary](#) [Interpreting this report](#)

Datablock: exp_11188

Bond precision:	C-C = 0.0050 Å	Wavelength=0.71073	
Cell:	a=6.8063 (9) alpha=90	b=14.985 (2) beta=90	c=17.161 (3) gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1750.3 (4)	1750.4 (4)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C21 H17 N O4	C21 H17 N O4	
Sum formula	C21 H17 N O4	C21 H17 N O4	
Mr	347.36	347.36	
Dx, g cm ⁻³	1.318	1.318	
Z	4	4	
Mu (mm ⁻¹)	0.092	0.092	
F000	728.0	728.0	
F000'	728.37		
h, k, lmax	9, 20, 23	9, 20, 23	
Nref	4869	4126	
Tmin, Tmax	0.957, 0.973	0.966, 1.000	
Tmin'	0.929		
Correction method=	# Reported T Limits: Tmin=0.966 Tmax=1.000		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.847	Theta(max)=	29.468
R(reflections)=	0.0759(1969)	WR2(reflections)=	0.2049(4126)
S =	1.038	Npar=	237

(c) Crystal structure of 3ah, CCDC Number = 2302202

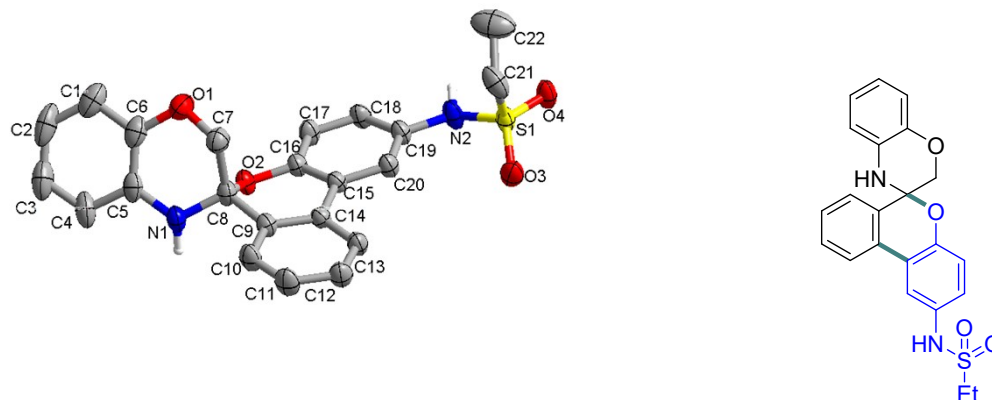
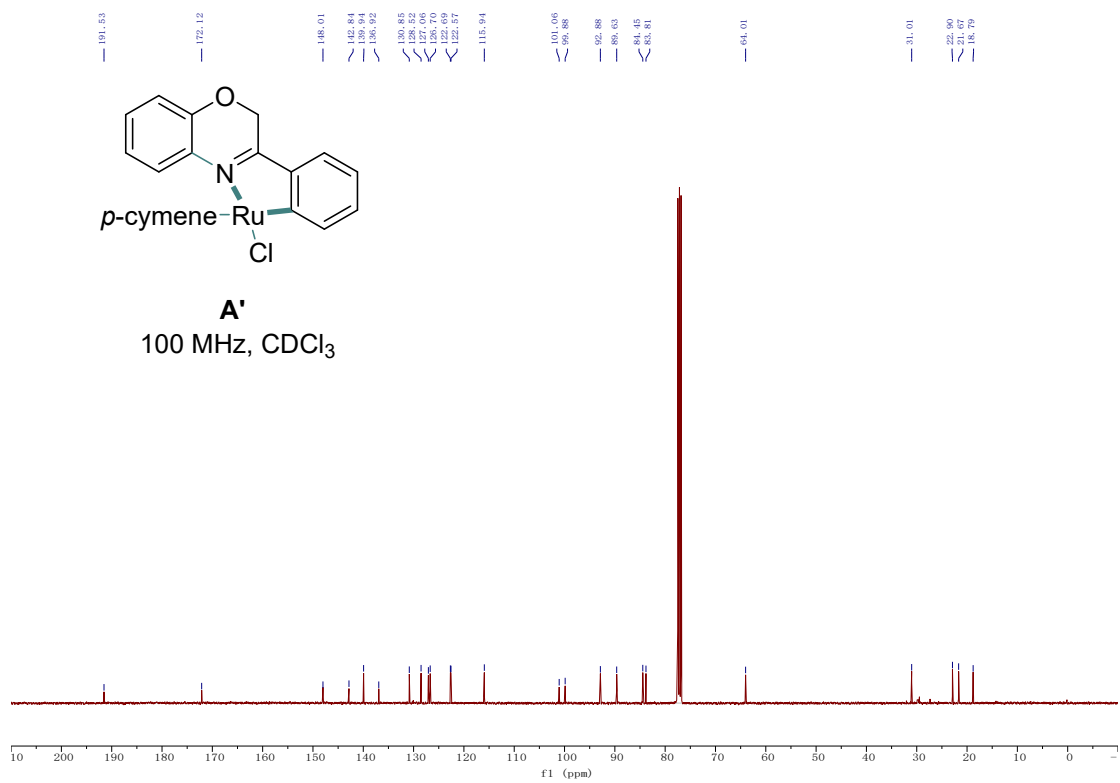
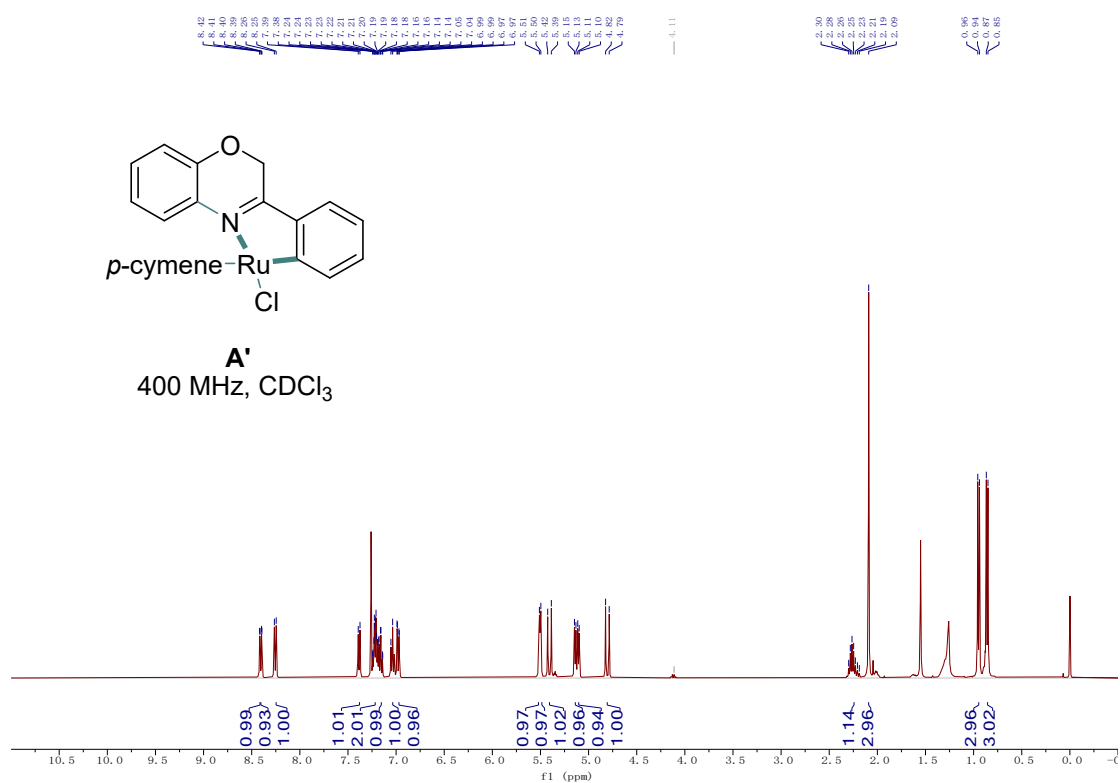


Figure S3 Crystal structure of 3db with thermal ellipsoids at 50% probability.

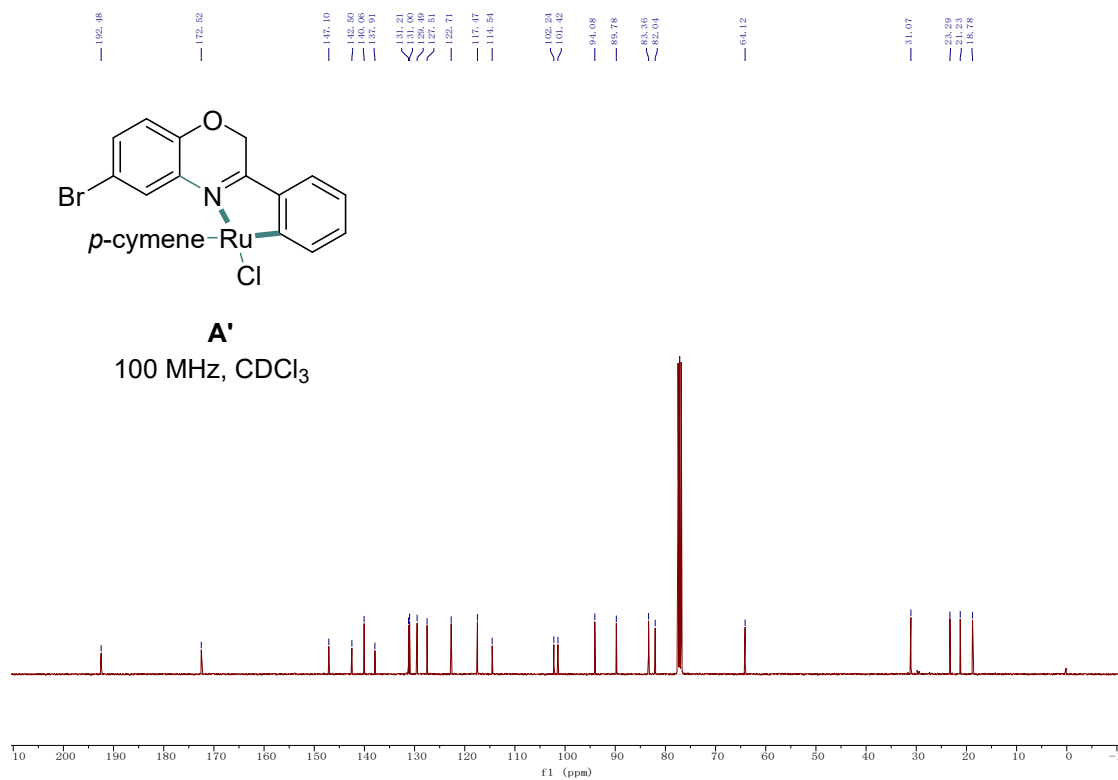
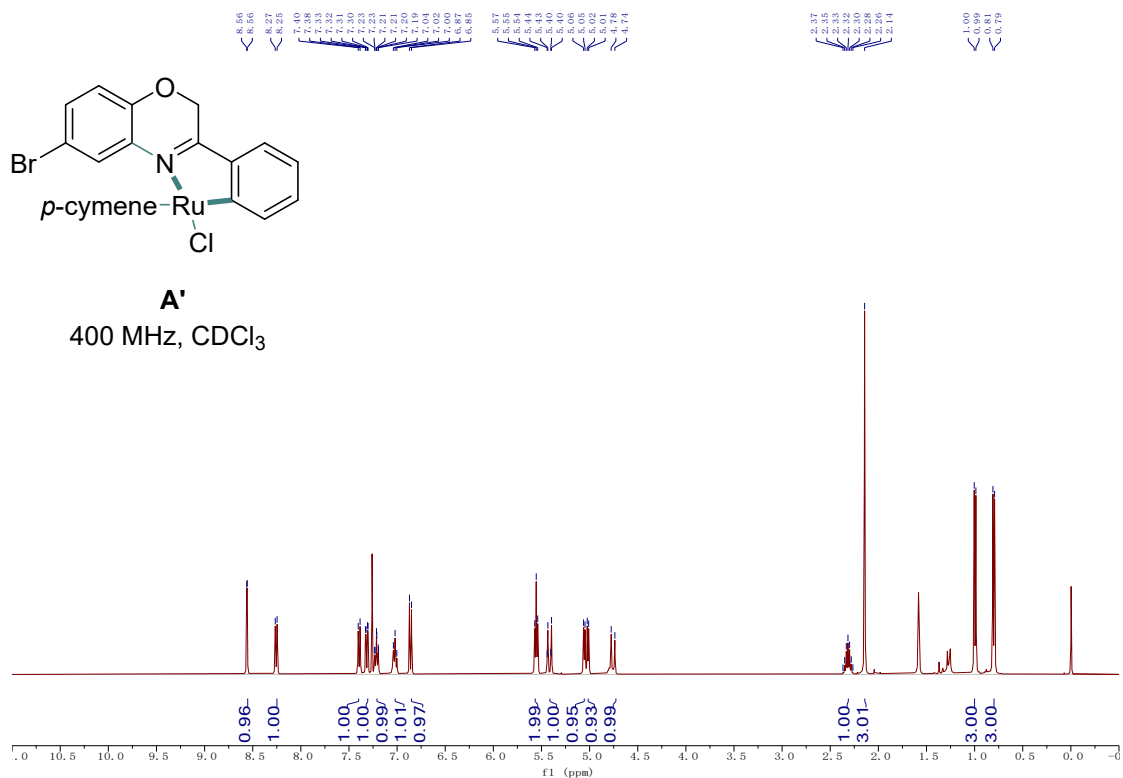
Bond precision:	C-C = 0.0054 Å	Wavelength=1.54184	
Cell:	a=9.6568 (6) alpha=87.571 (6)	b=10.2090 (6) beta=71.911 (7)	c=13.0889 (11) gamma=80.248 (5)
Temperature:	293 K		
	Calculated	Reported	
Volume	1208.81 (15)	1208.82 (16)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C22 H20 N2 O4 S [+ solvent]	C22 H20 N2 O4 S	
Sum formula	C22 H20 N2 O4 S [+ solvent]	C22 H20 N2 O4 S	
Mr	408.46	408.46	
Dx, g cm ⁻³	1.122	1.122	
Z	2	2	
Mu (mm ⁻¹)	1.410	1.410	
F000	428.0	428.0	
F000'	429.92		
h, k, lmax	11, 12, 15	11, 12, 15	
Nref	4321	4320	
Tmin, Tmax	0.803, 0.868	0.924, 1.000	
Tmin'	0.787		
Correction method= #	Reported T Limits: Tmin=0.924 Tmax=1.000		
AbsCorr = MULTI-SCAN			
Data completeness= 1.000	Theta(max)= 67.075		
R(reflections)= 0.0587(2985)		wR2(reflections)= 0.1920(4320)	
S = 0.992	Npar= 271		

E. NMR spectra :

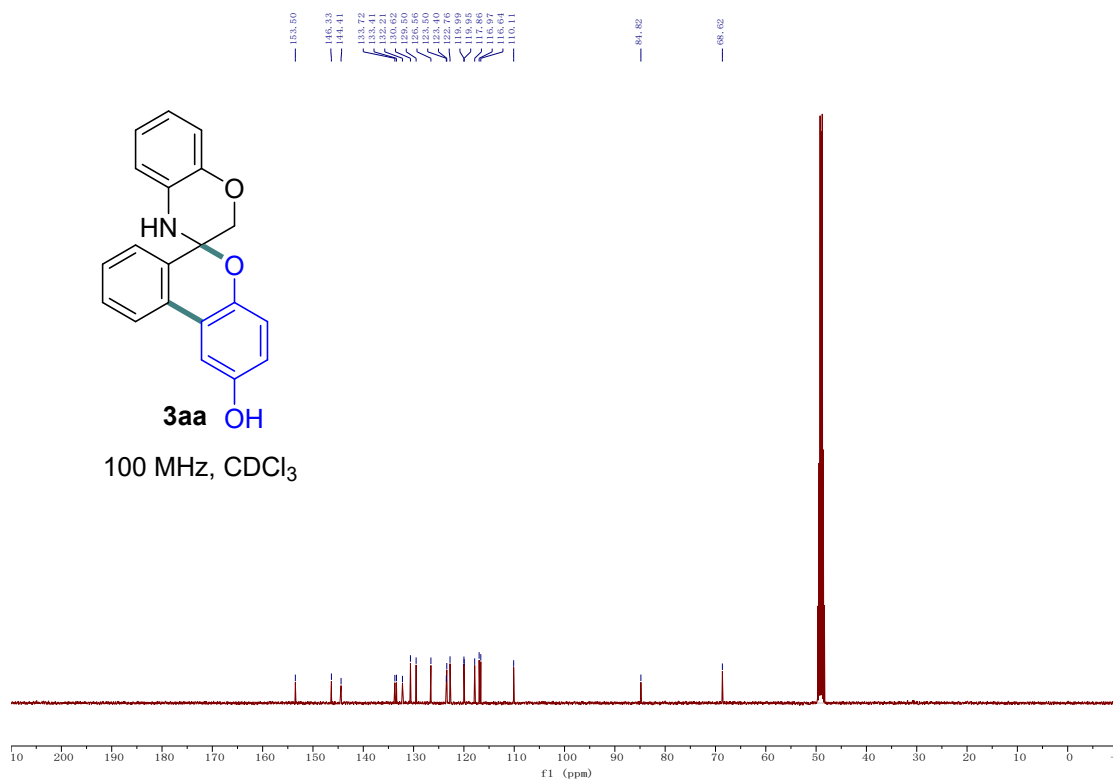
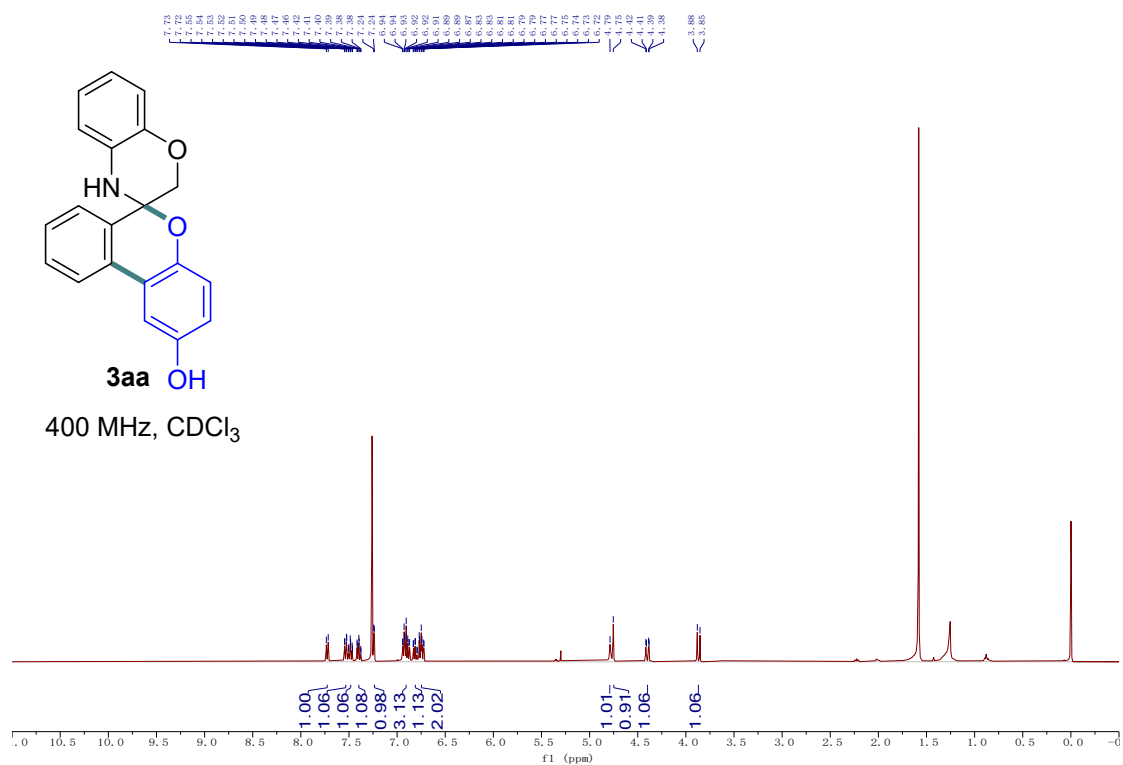
¹H and ¹³C NMR Spectra of compound A



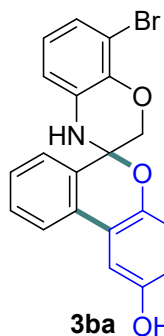
¹H and ¹³C NMR Spectra of compound B



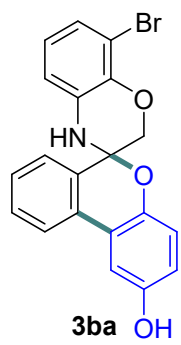
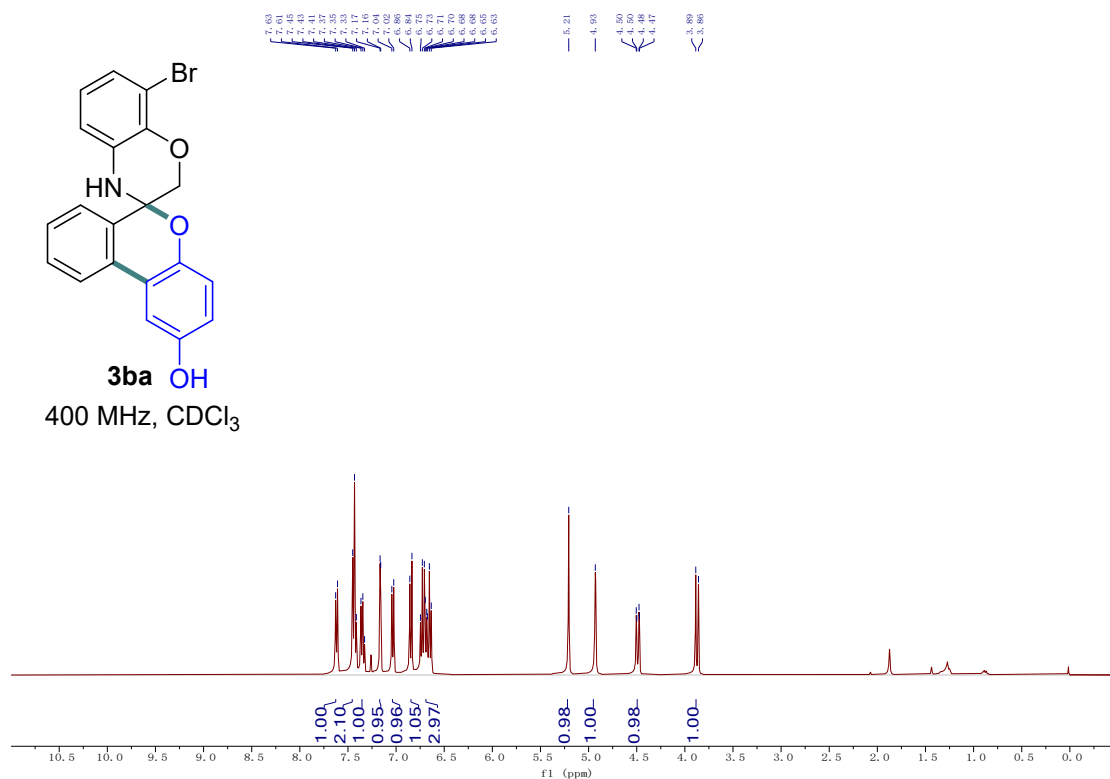
¹H and ¹³C NMR Spectra of 3aa



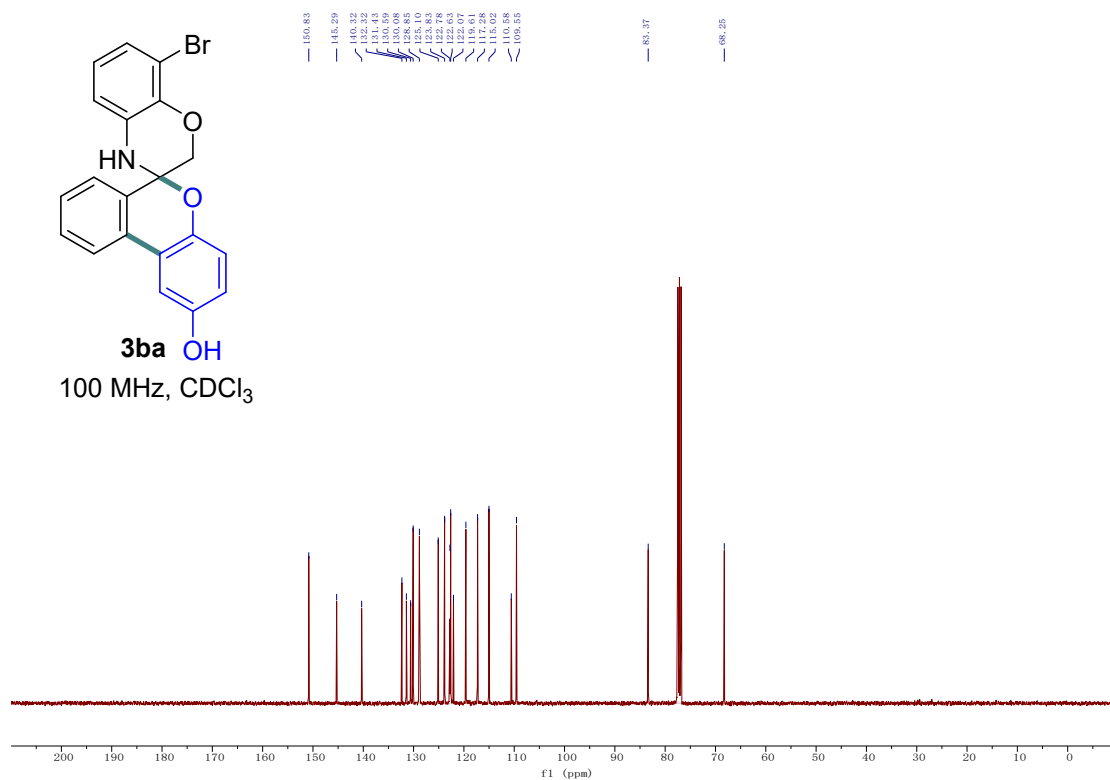
¹H and ¹³C NMR Spectra of 3ba



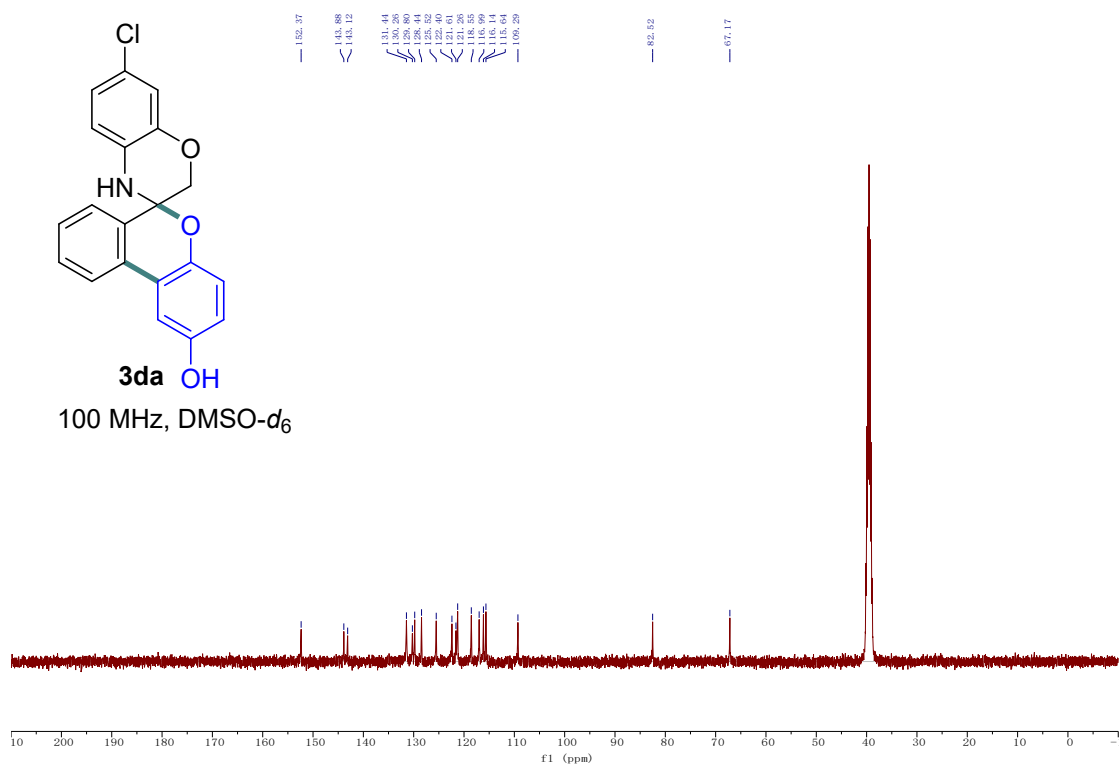
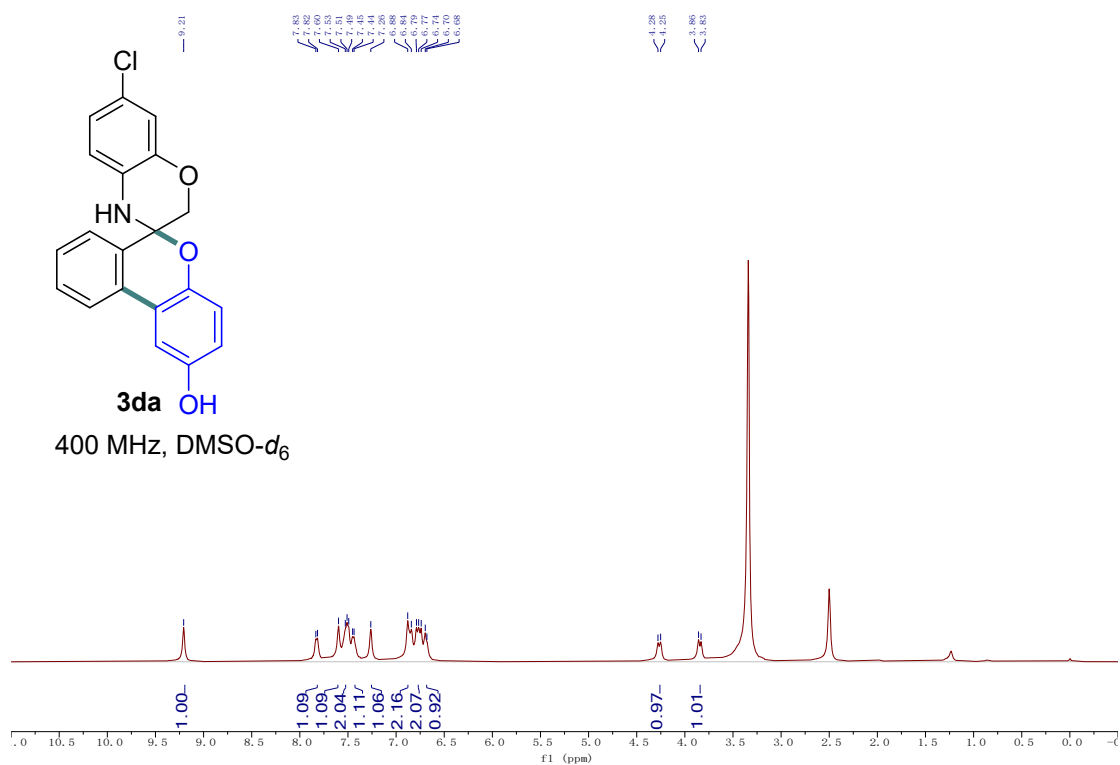
400 MHz, CDCl₃



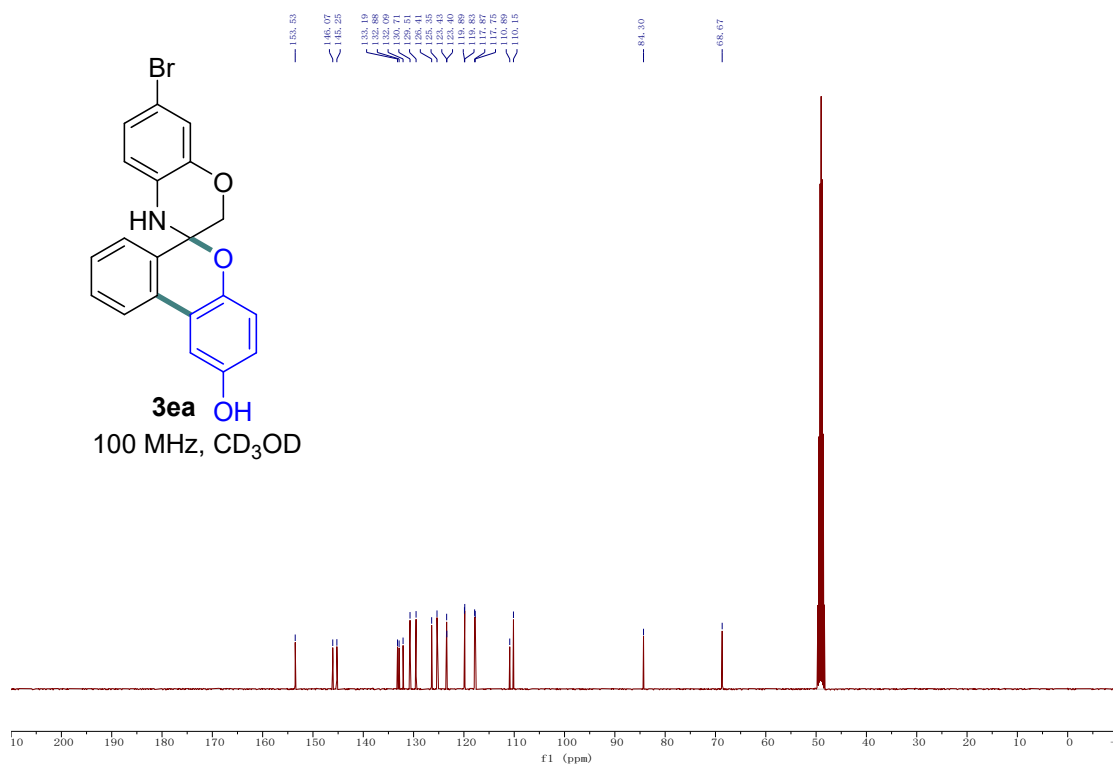
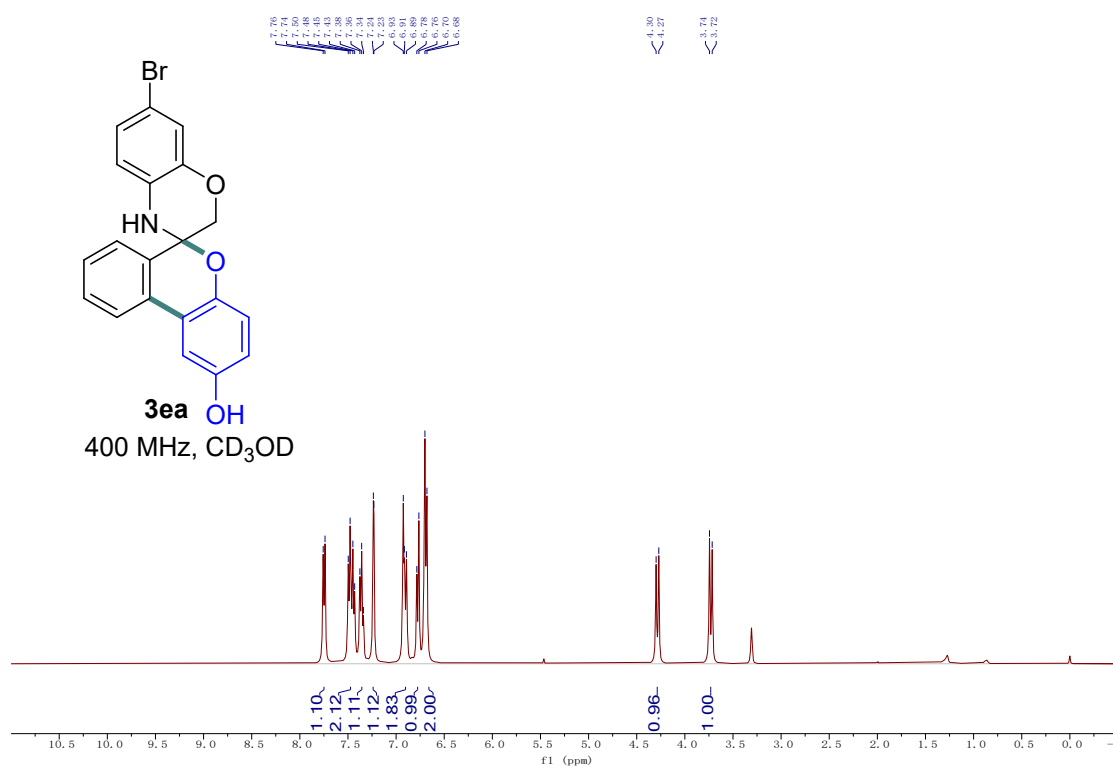
100 MHz, CDCl₃



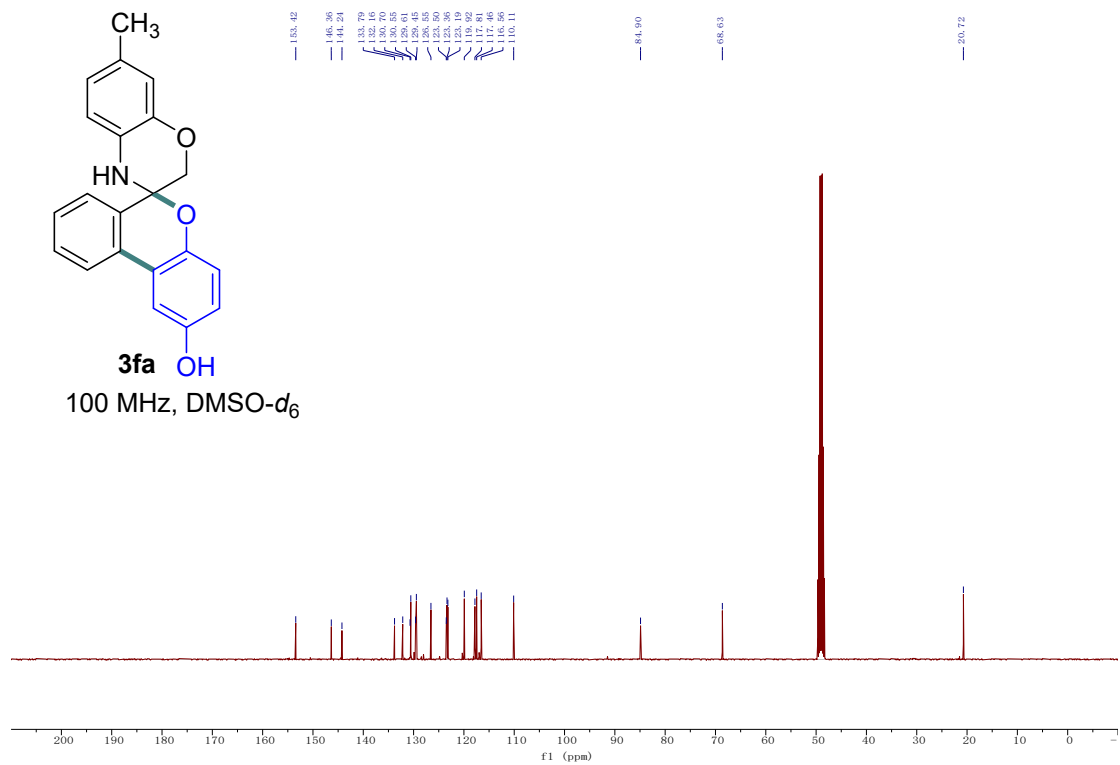
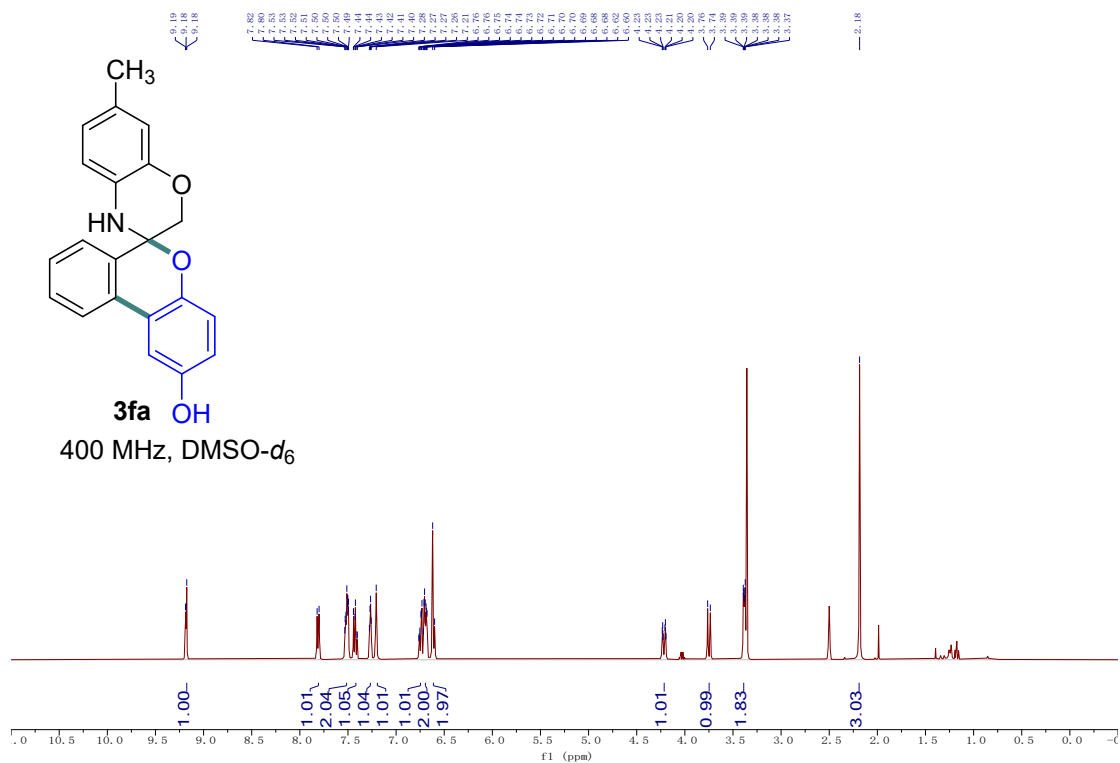
¹H and ¹³C NMR Spectra of 3da



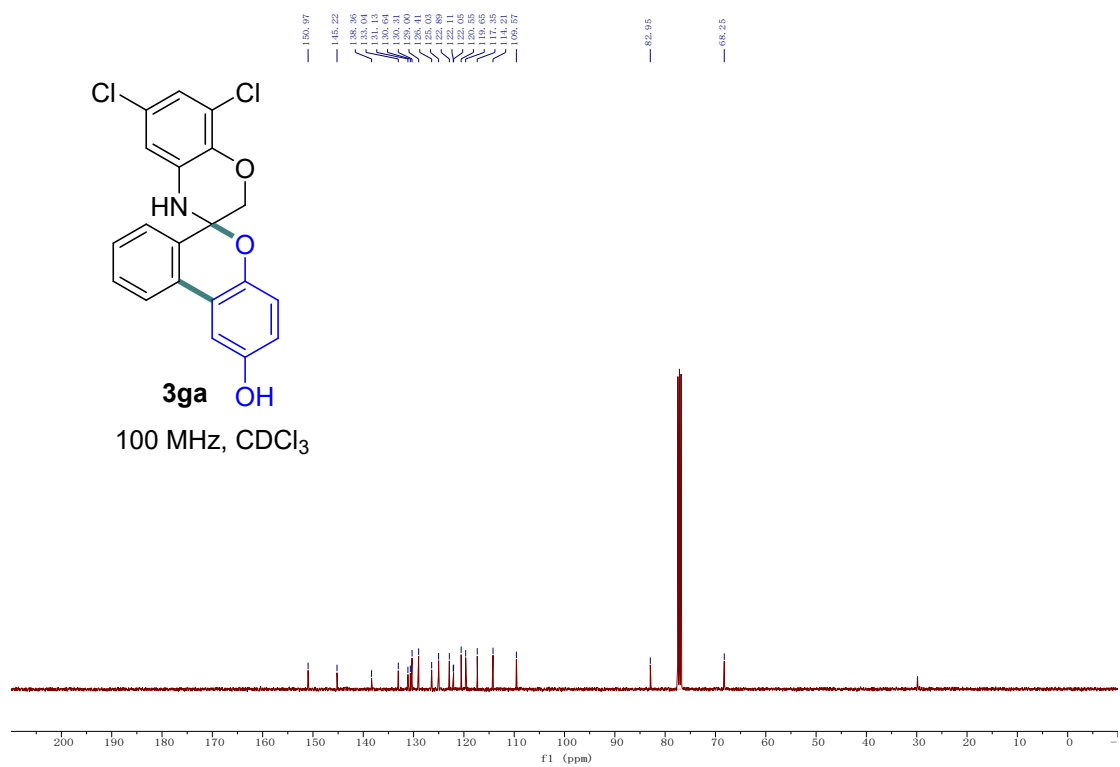
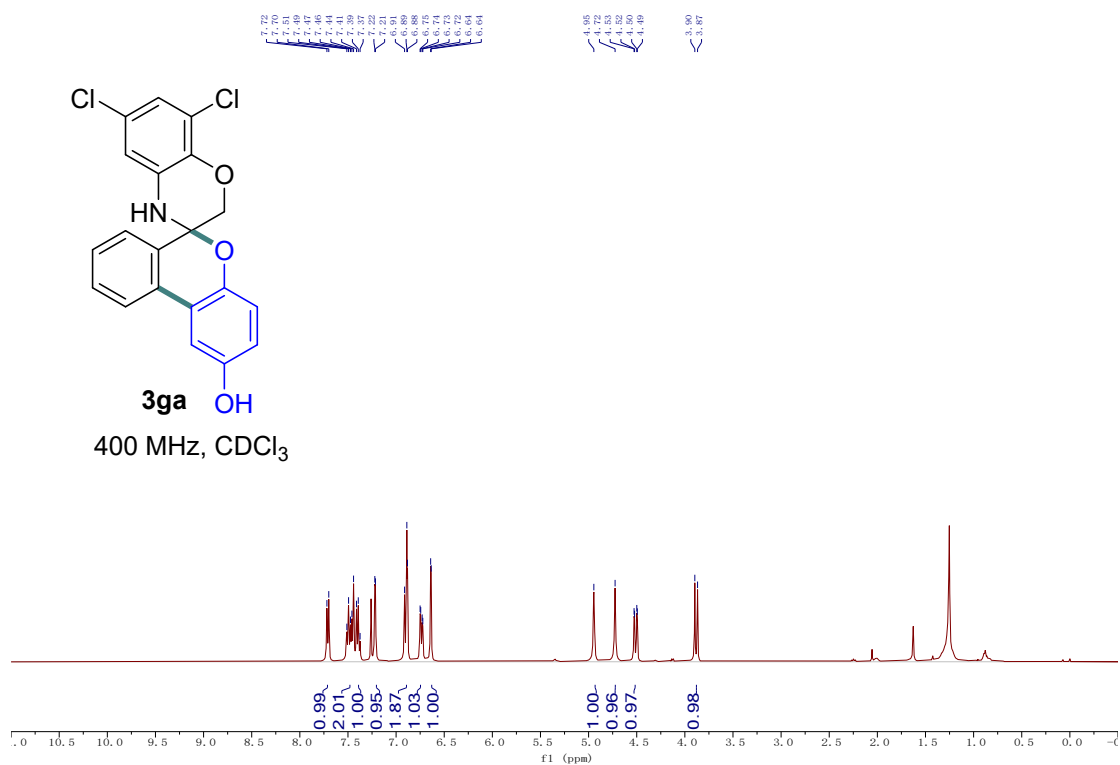
¹H and ¹³C NMR Spectra of 3ea



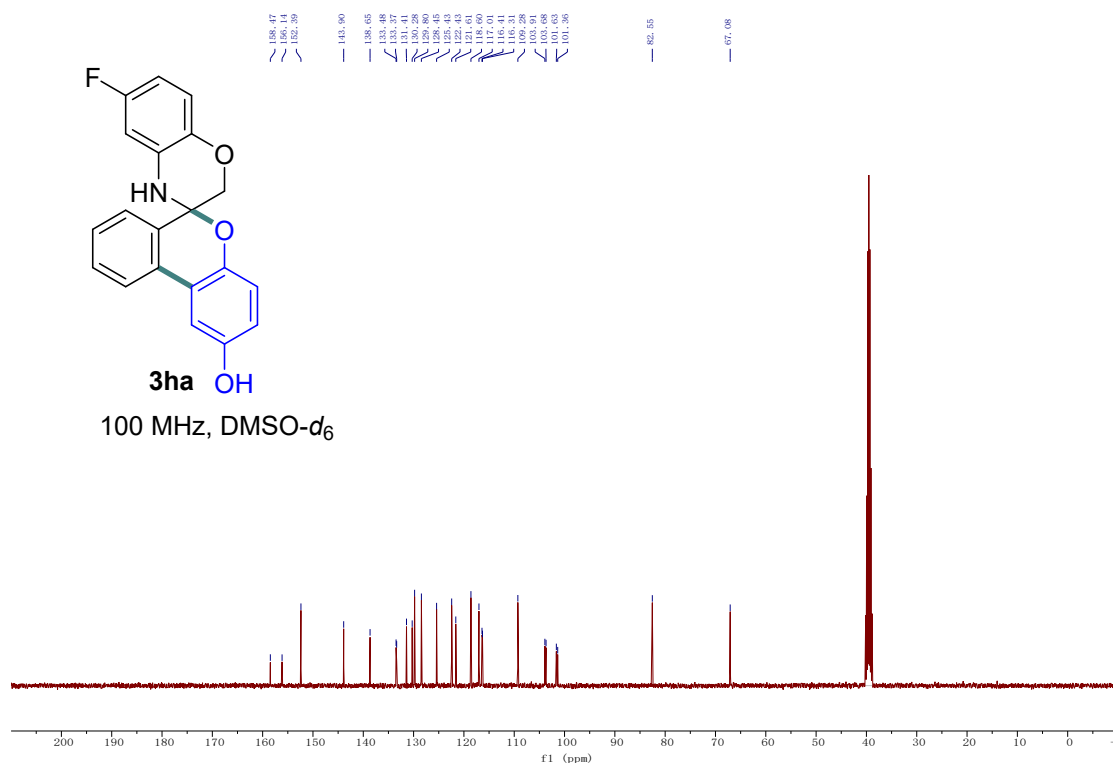
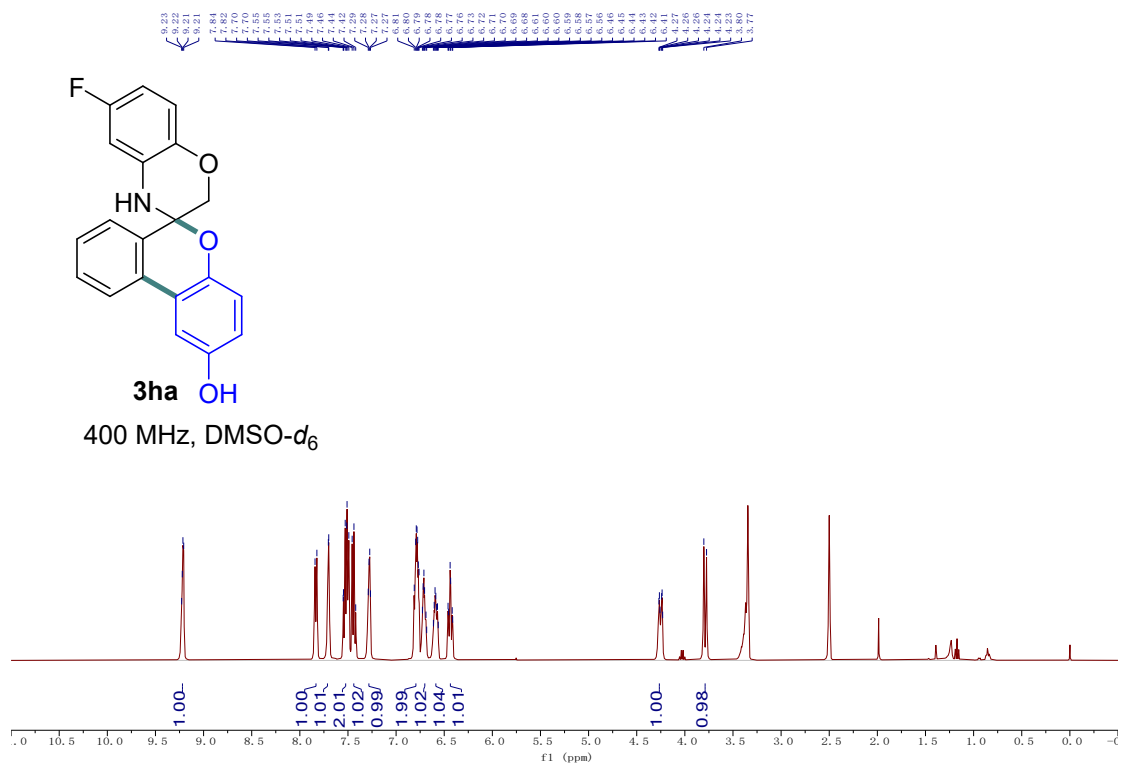
¹H and ¹³C NMR Spectra of 3fa



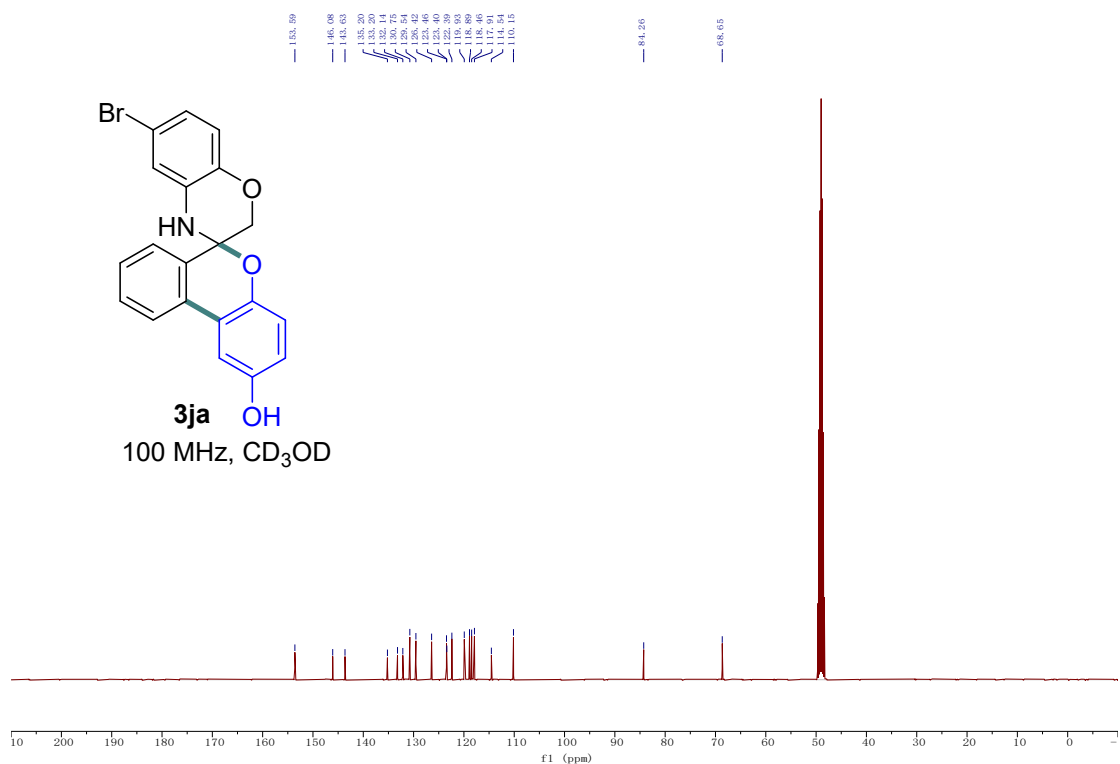
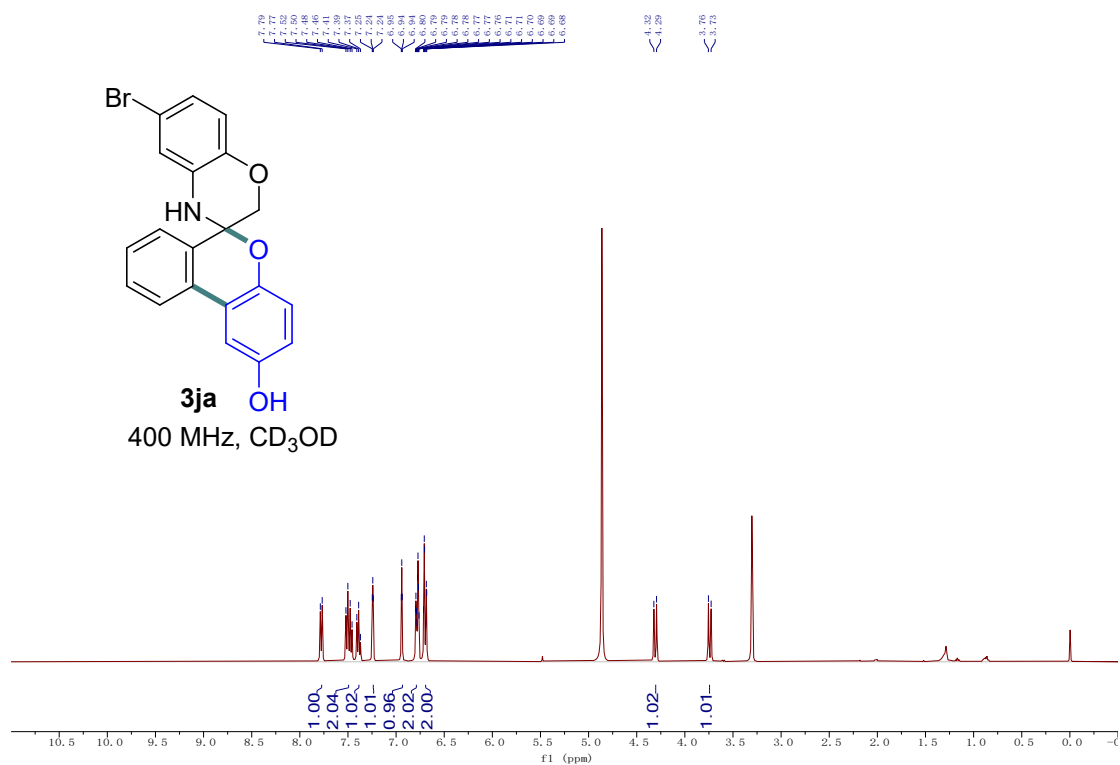
¹H and ¹³C NMR Spectra of 3ga



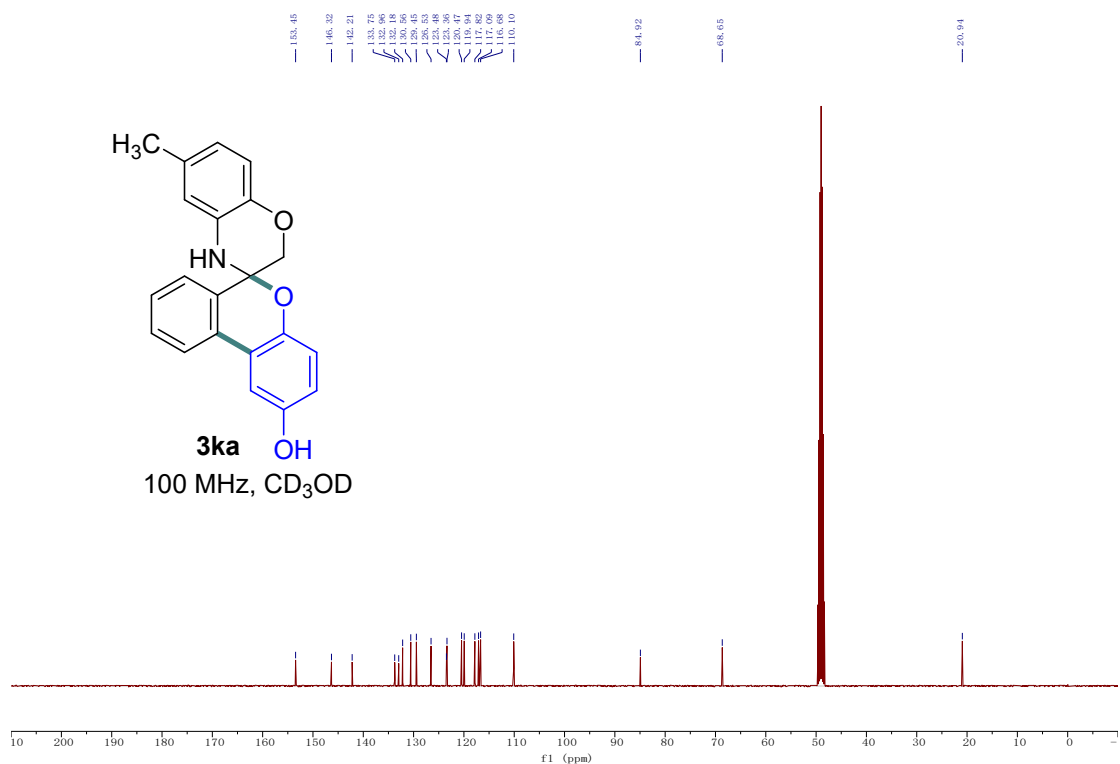
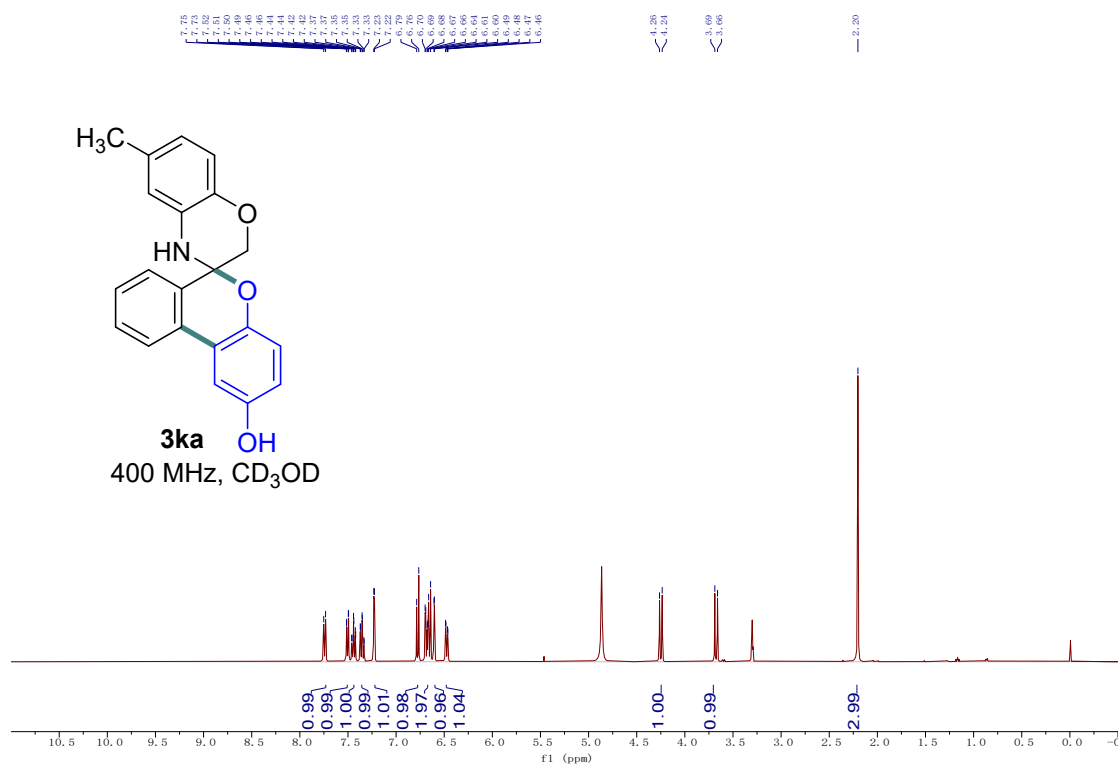
¹H and ¹³C NMR Spectra of 3ha



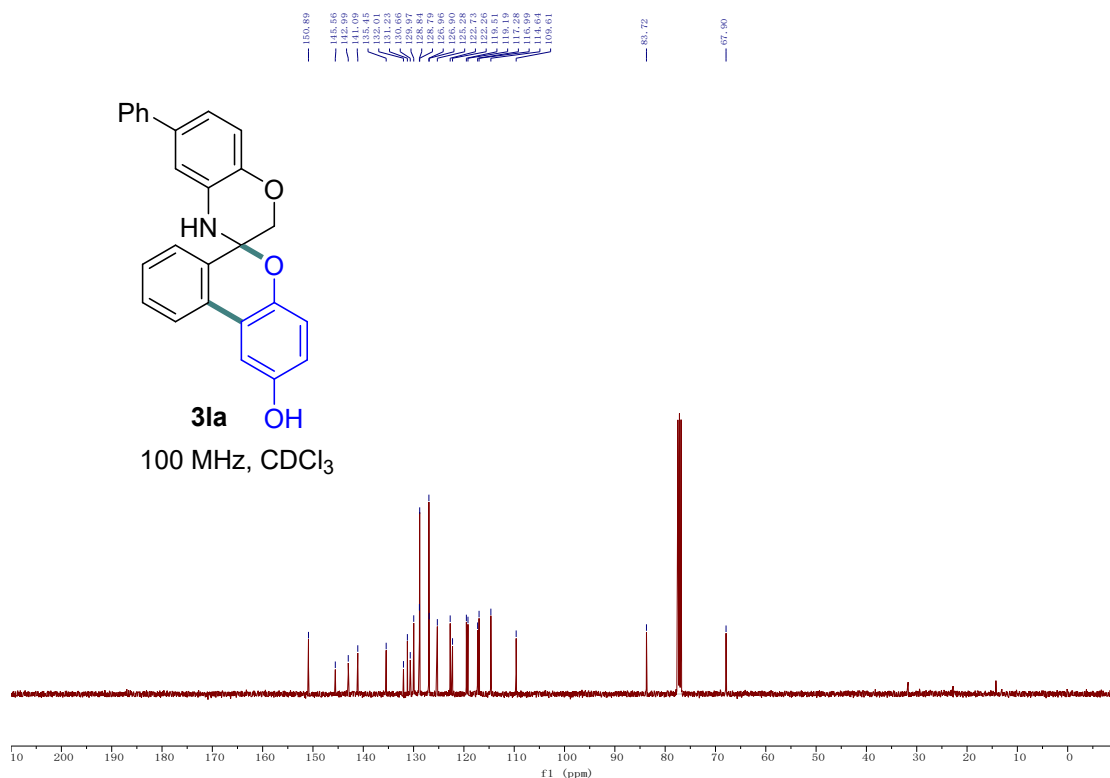
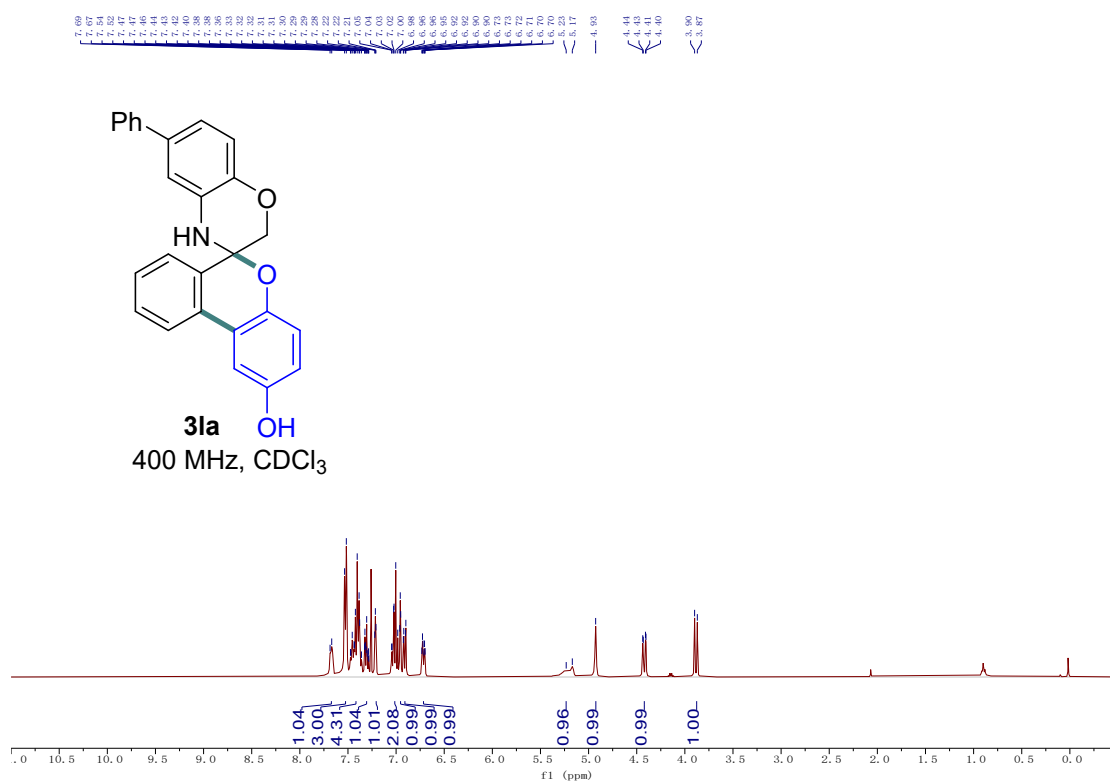
¹H and ¹³C NMR Spectra of 3ja



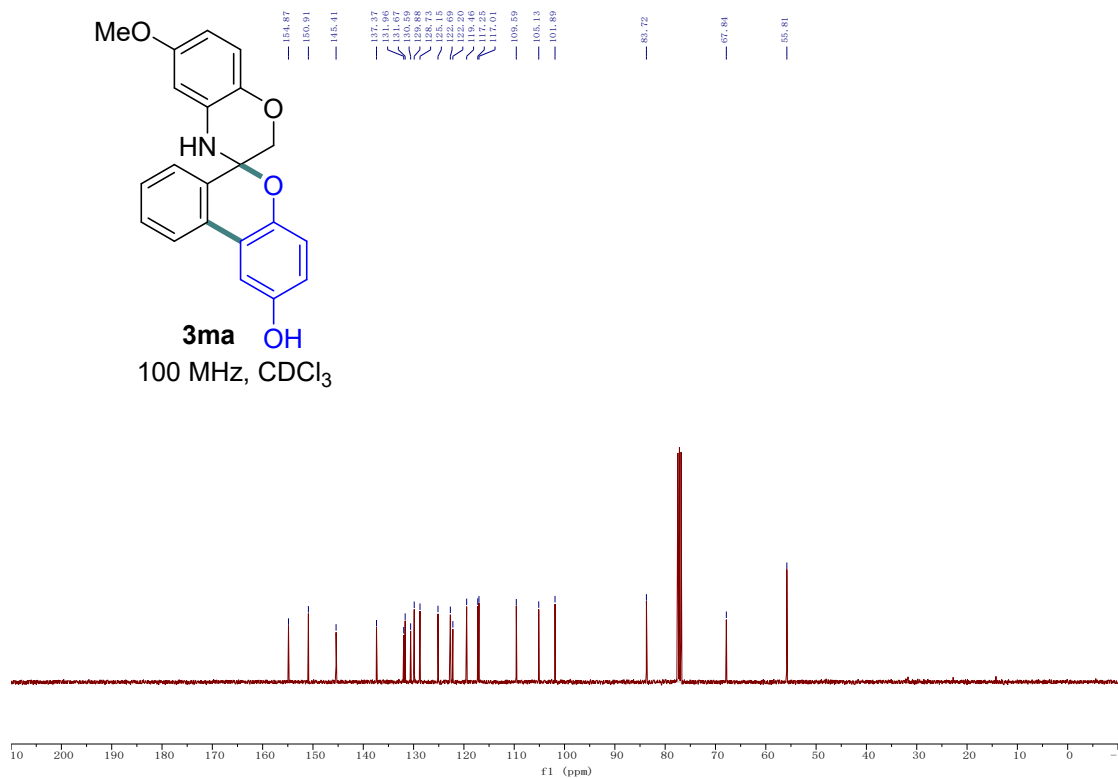
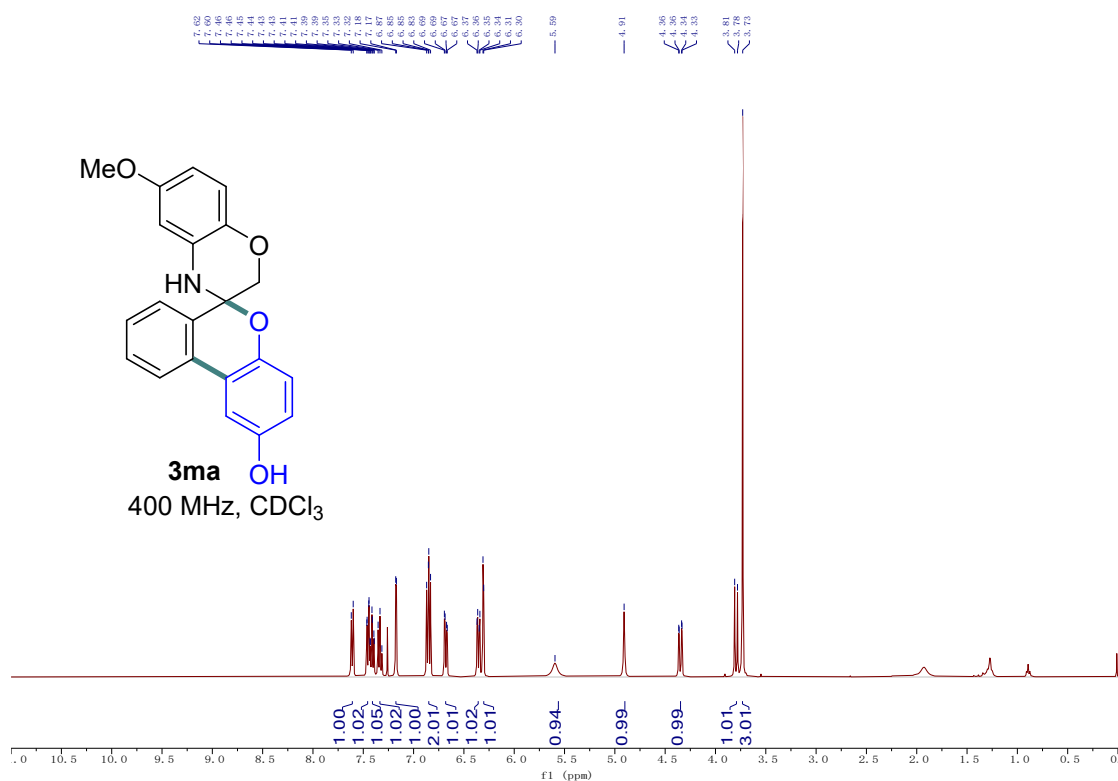
¹H and ¹³C NMR Spectra of 3ka



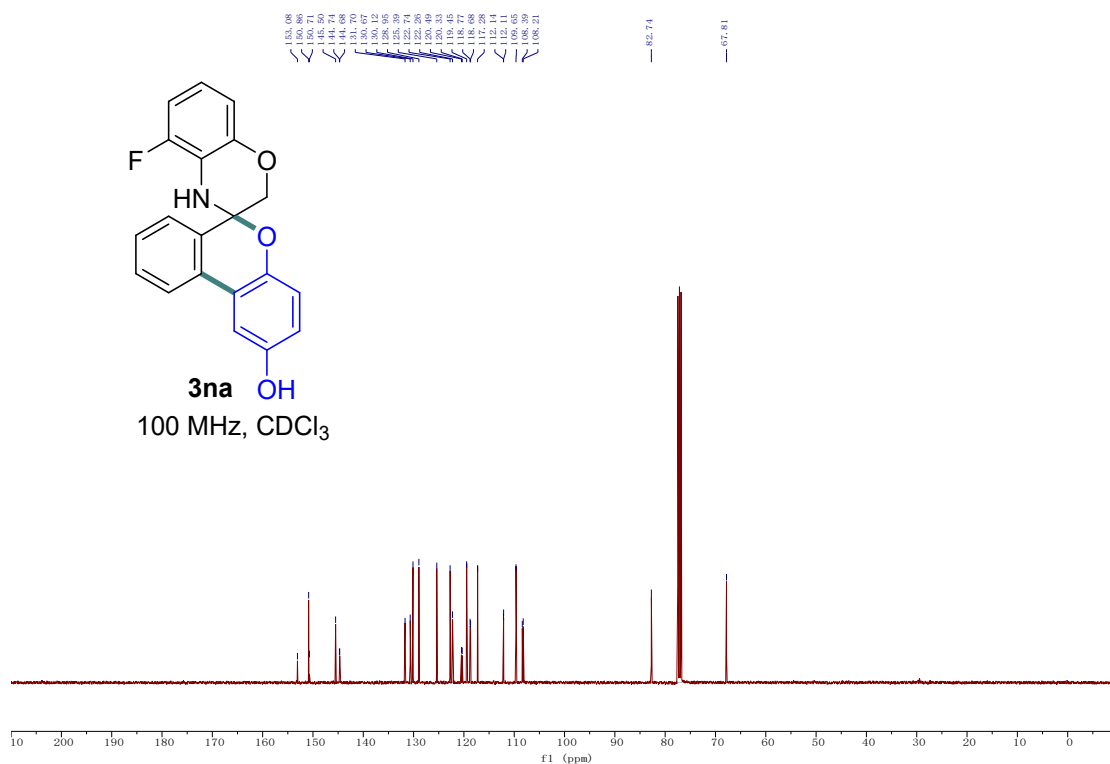
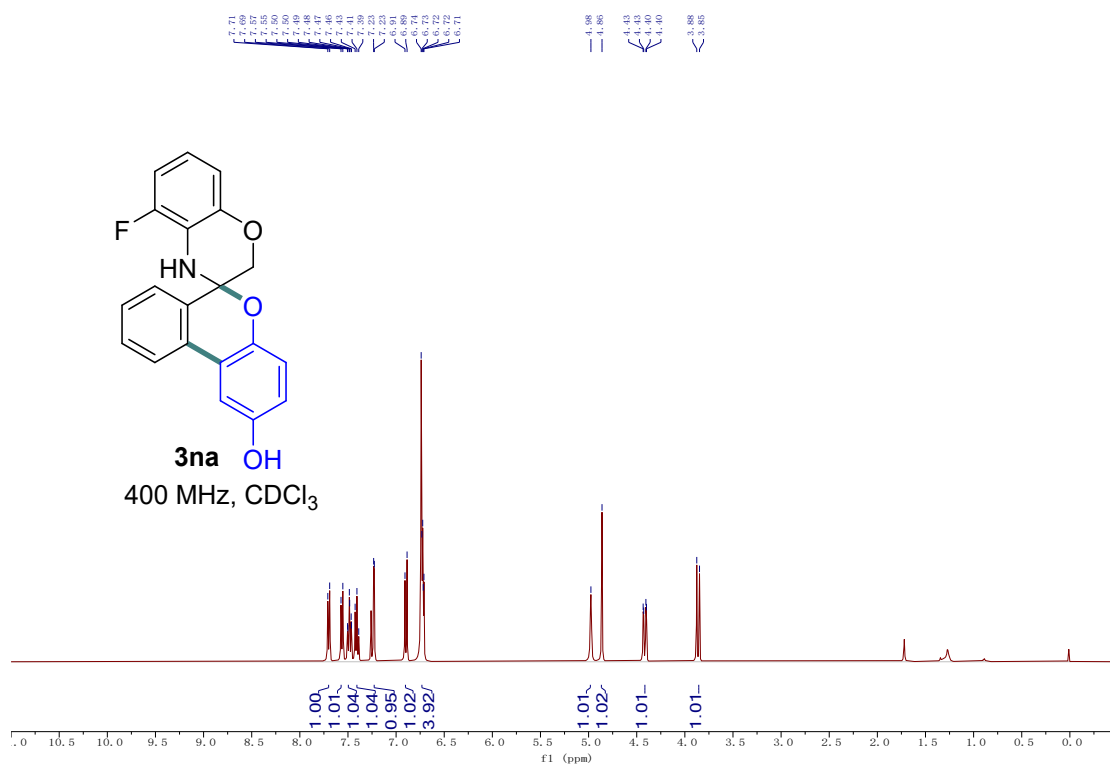
¹H and ¹³C NMR Spectra of 3la



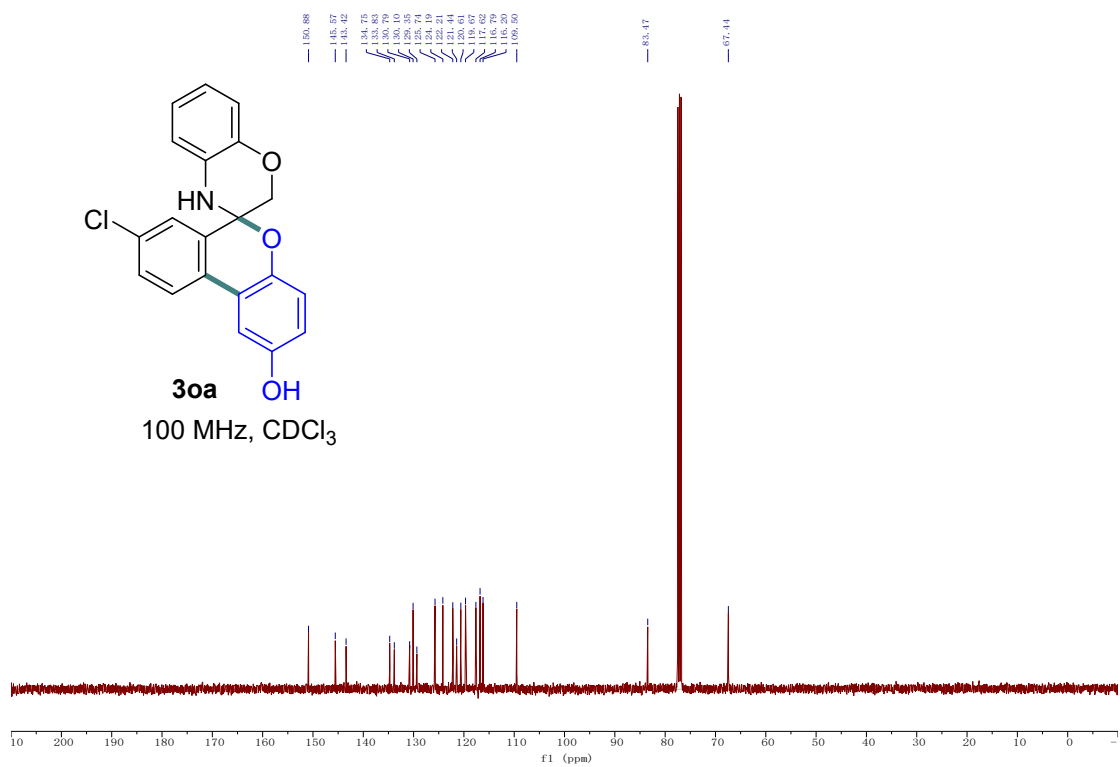
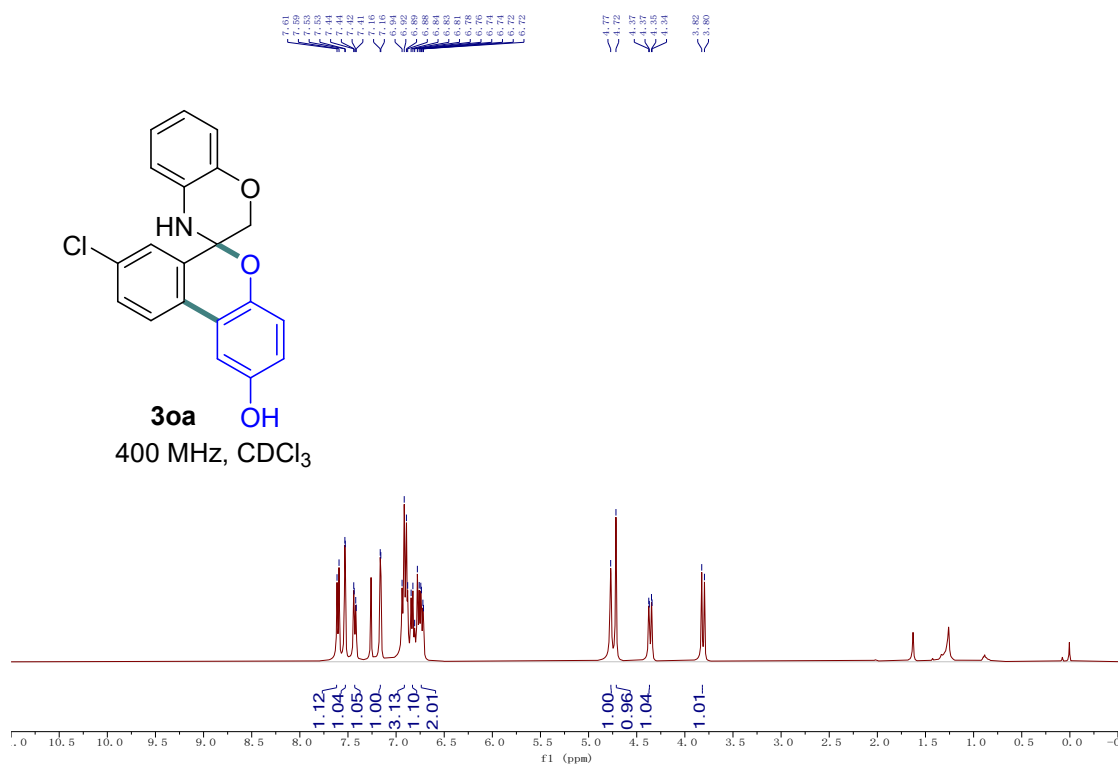
¹H and ¹³C NMR Spectra of **3ma**



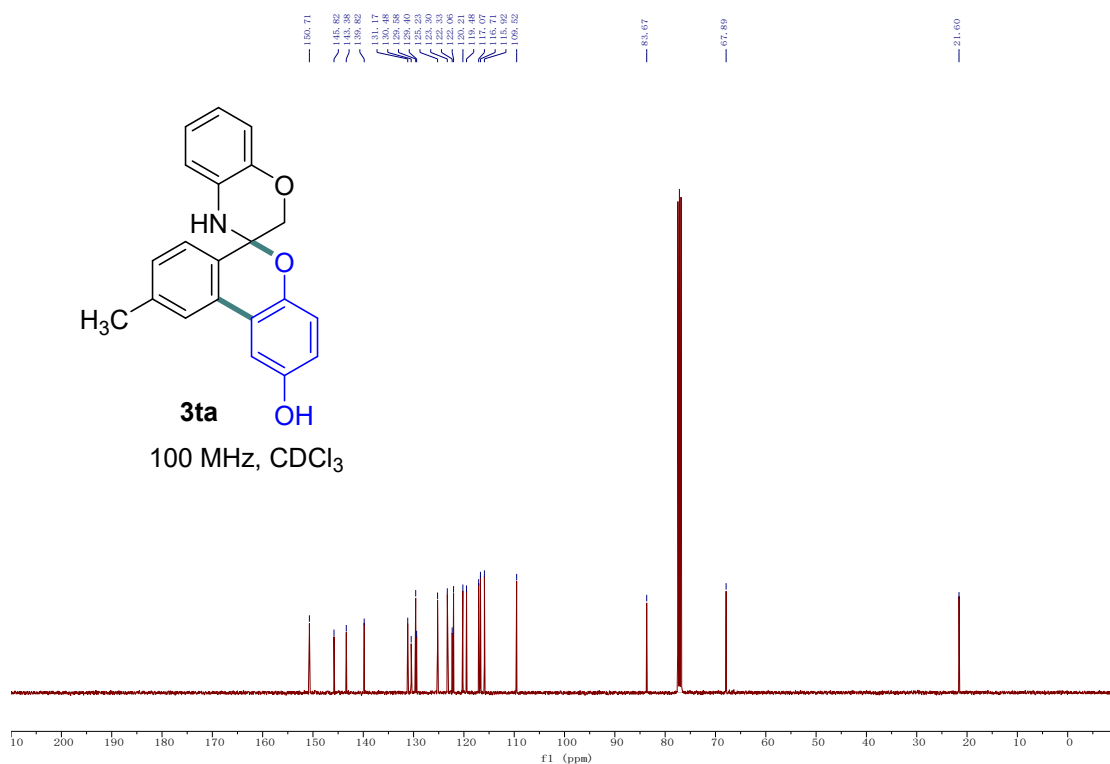
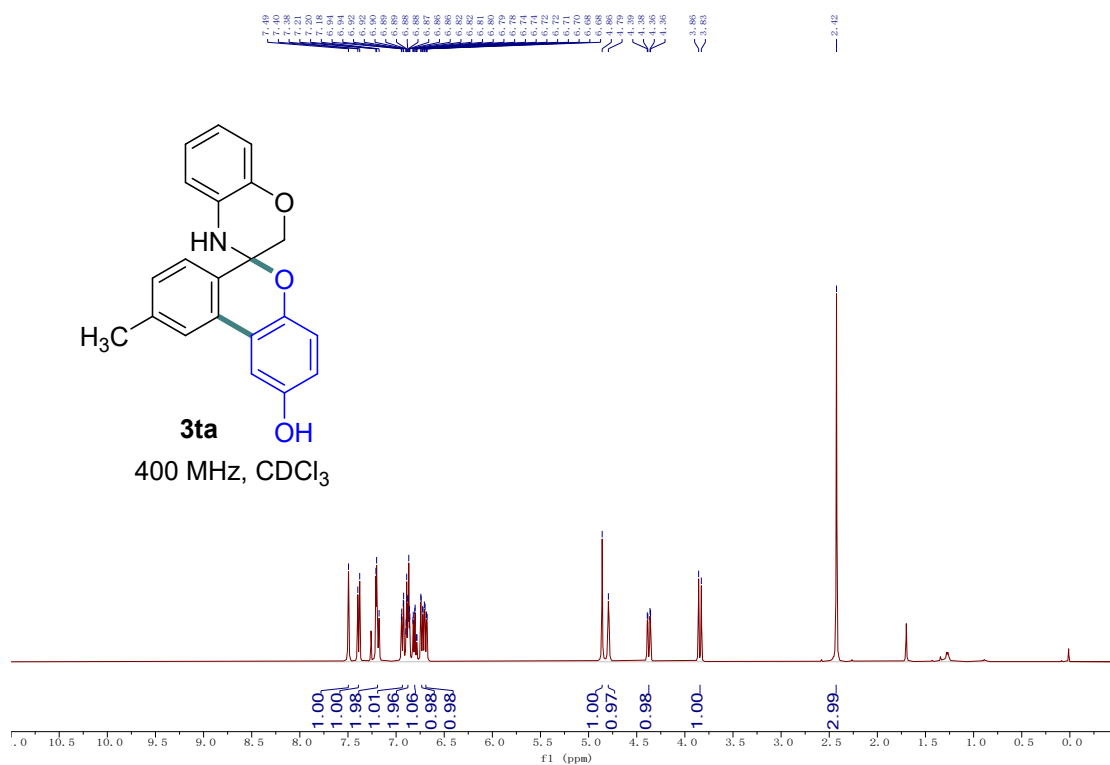
¹H and ¹³C NMR Spectra of 3na



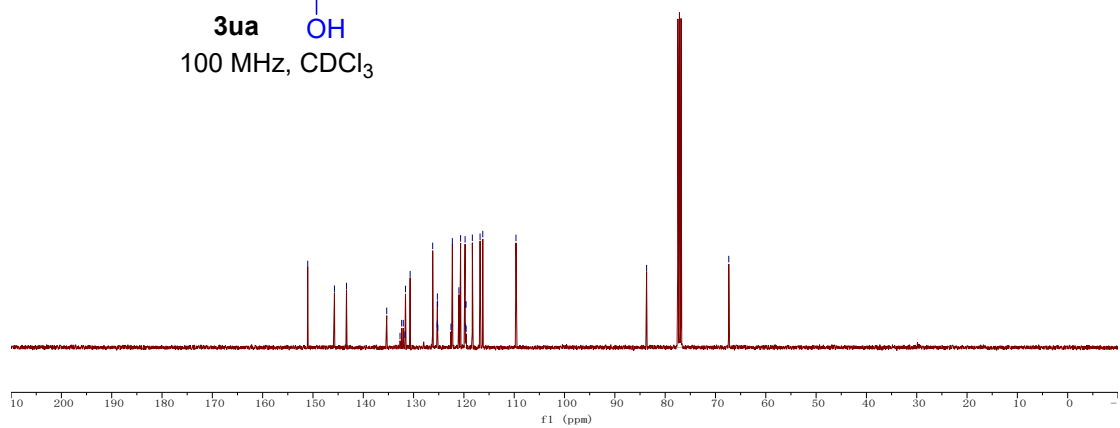
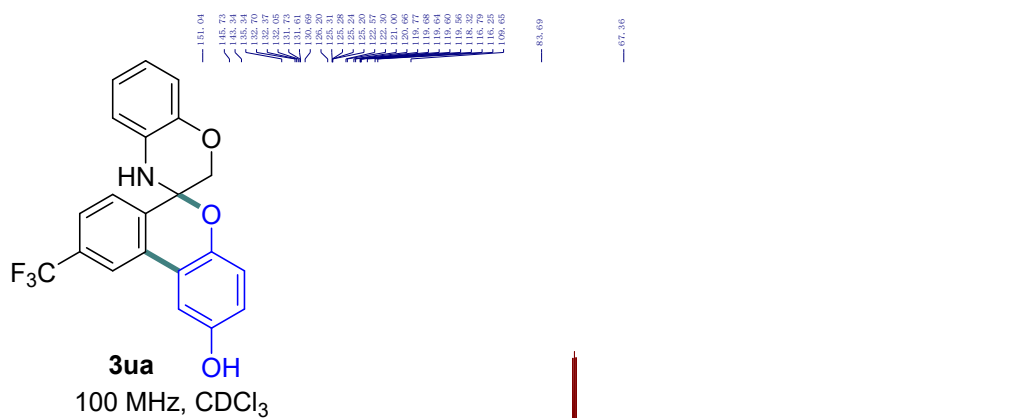
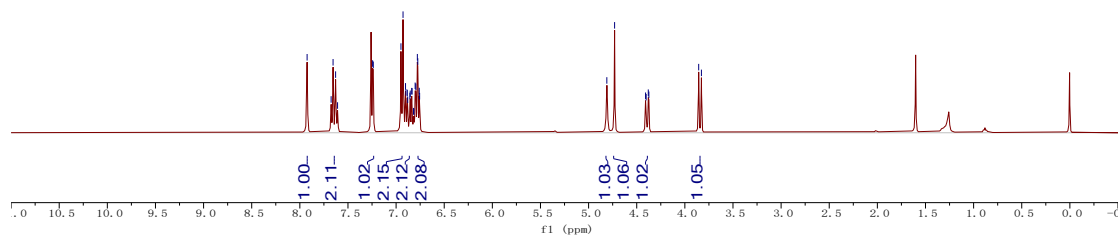
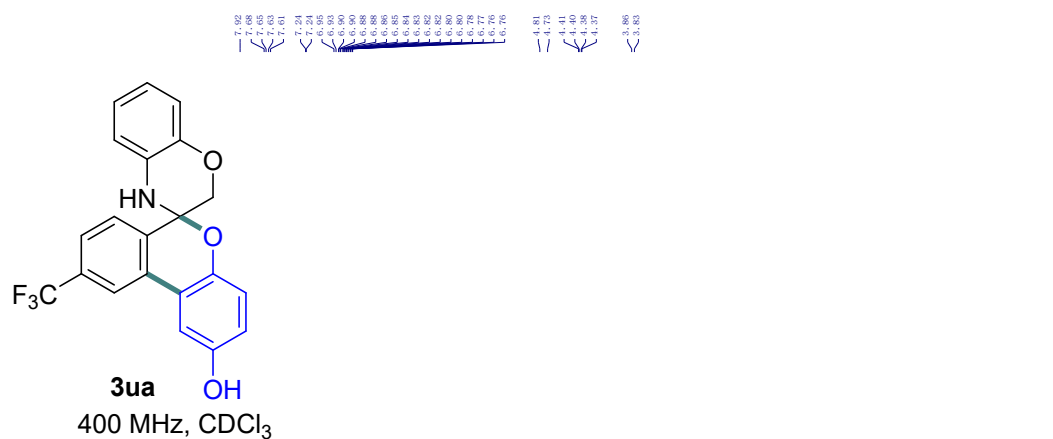
¹H and ¹³C NMR Spectra of 3oa



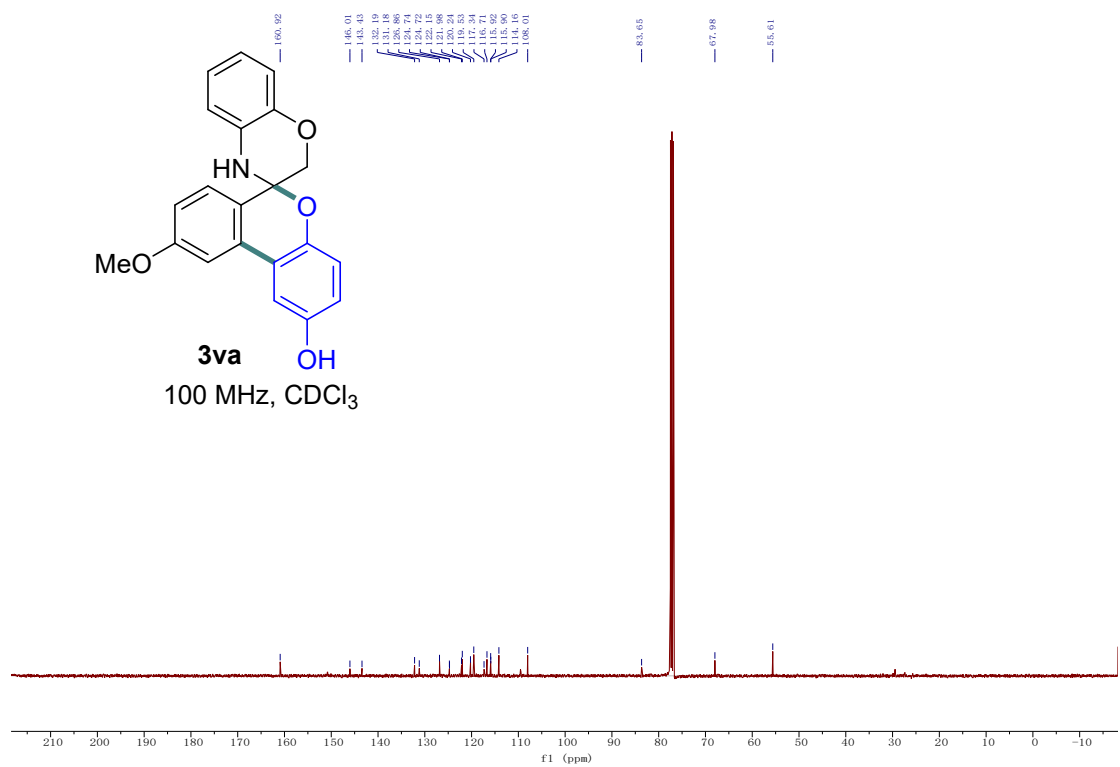
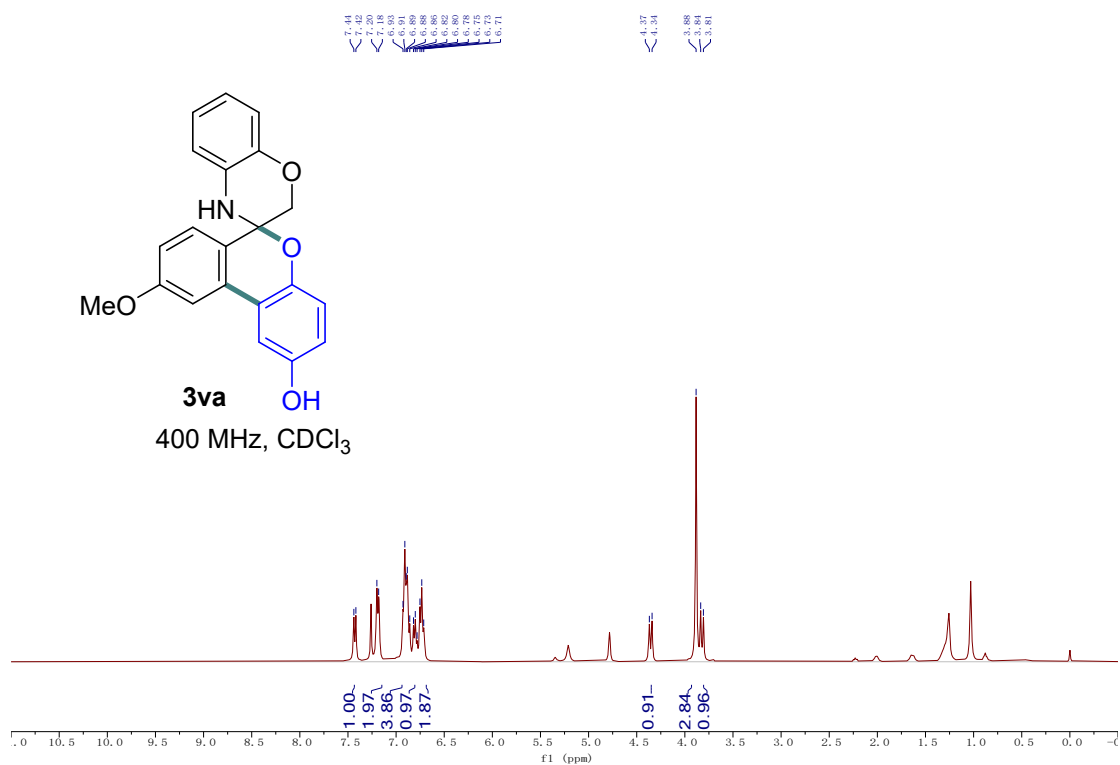
¹H and ¹³C NMR Spectra of 3ta



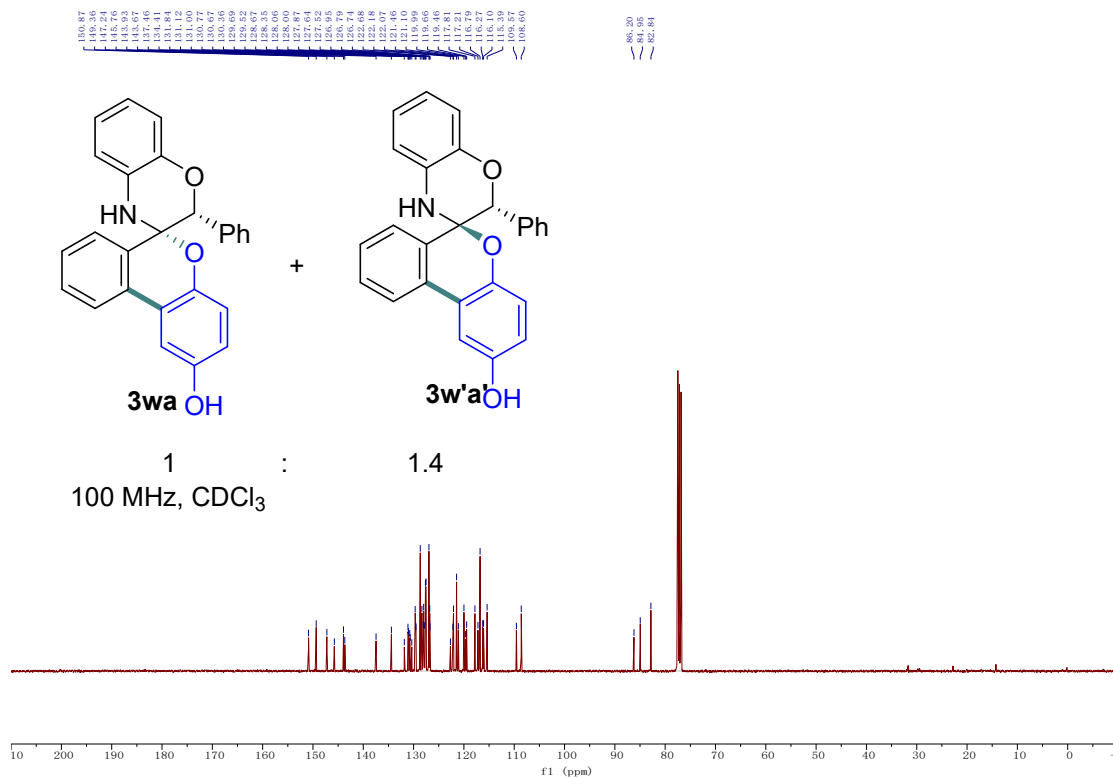
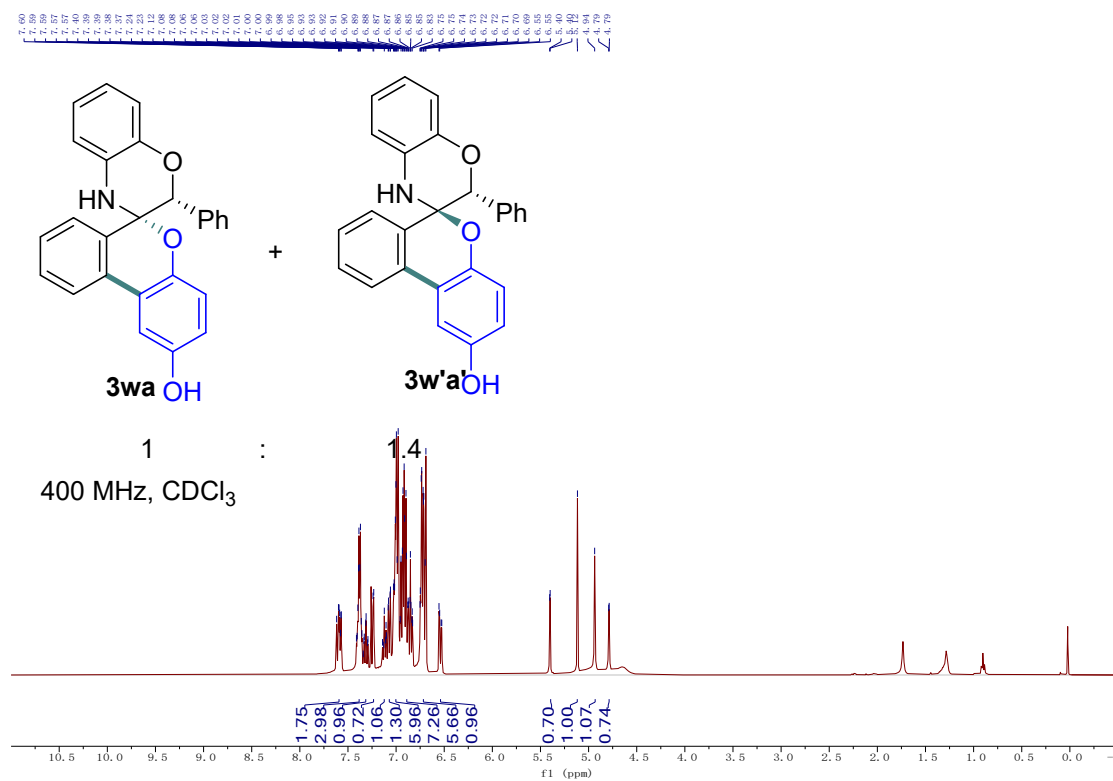
¹H and ¹³C NMR Spectra of 3ua



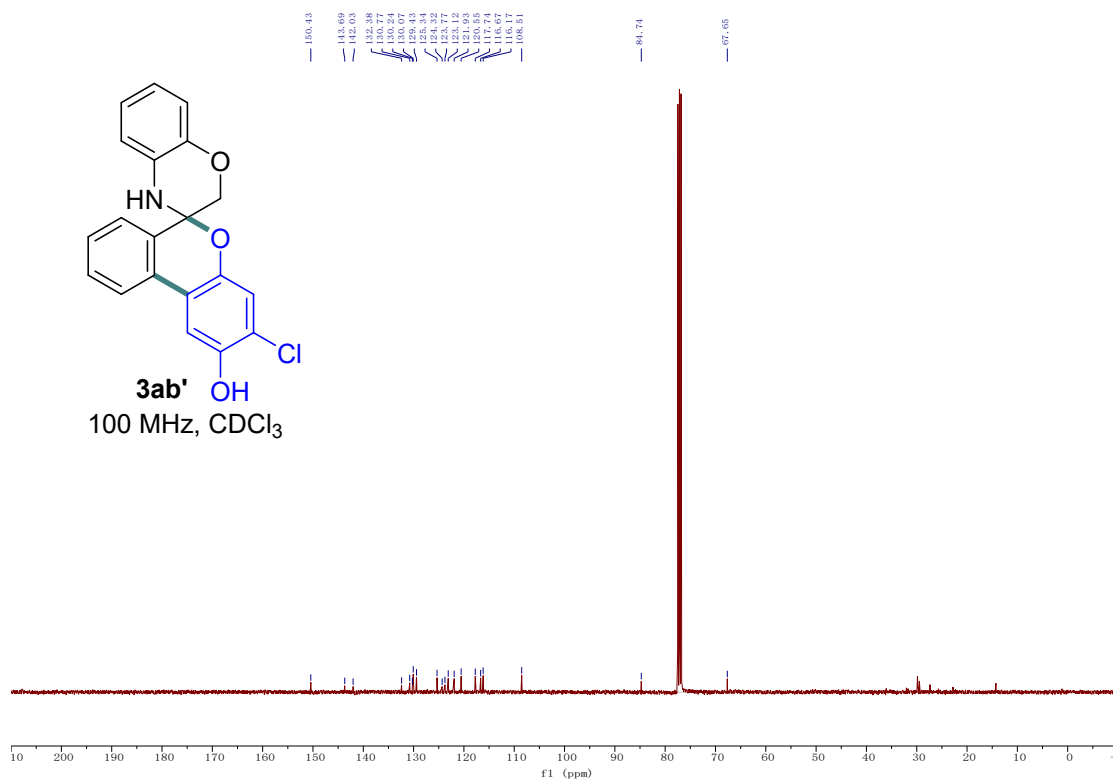
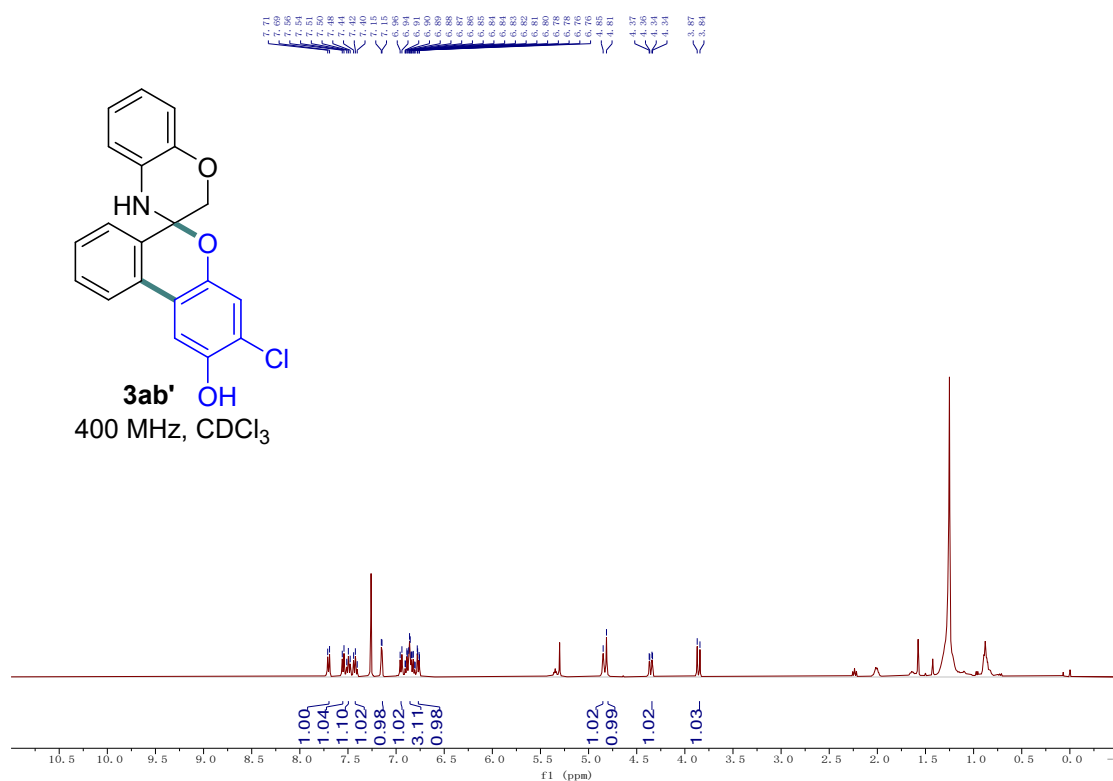
¹H and ¹³C NMR Spectra of 3va



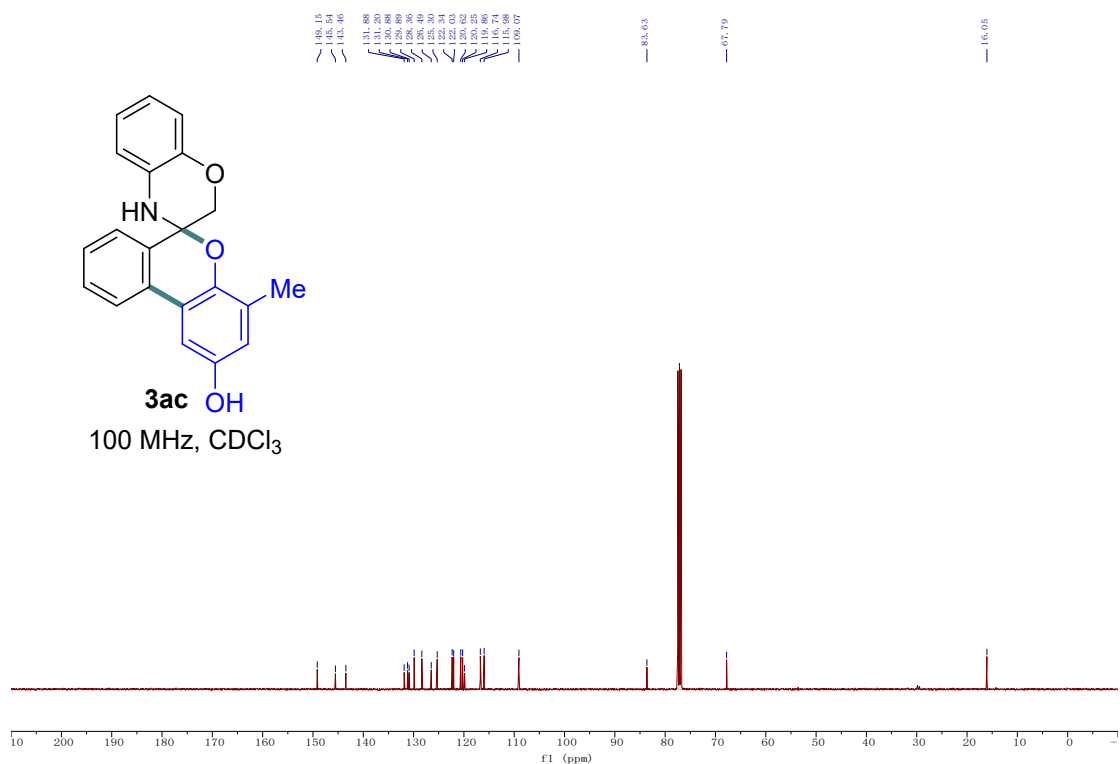
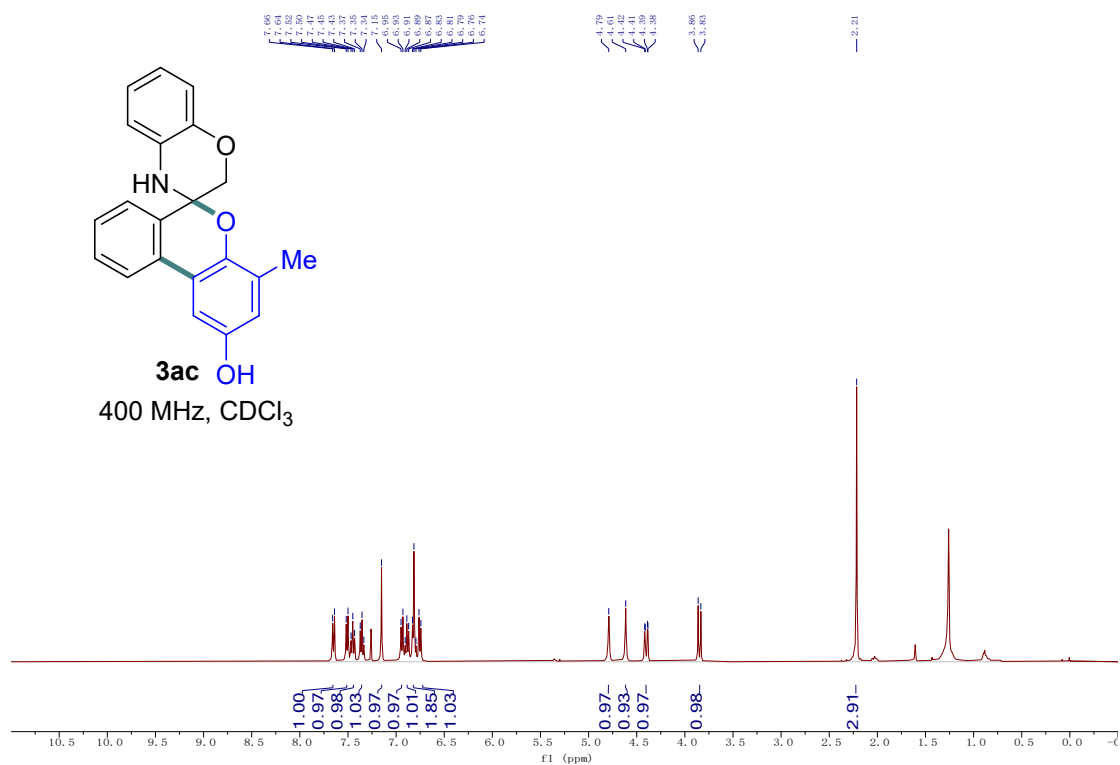
¹H and ¹³C NMR Spectra of 3wa and 3w'a'



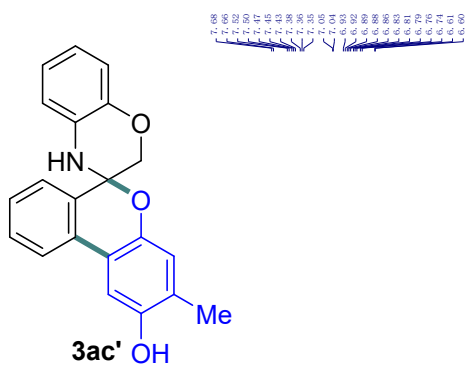
¹H and ¹³C NMR Spectra of 3ab'



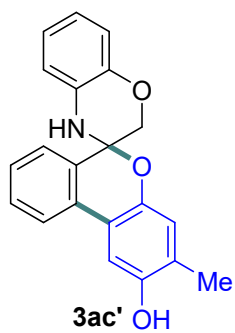
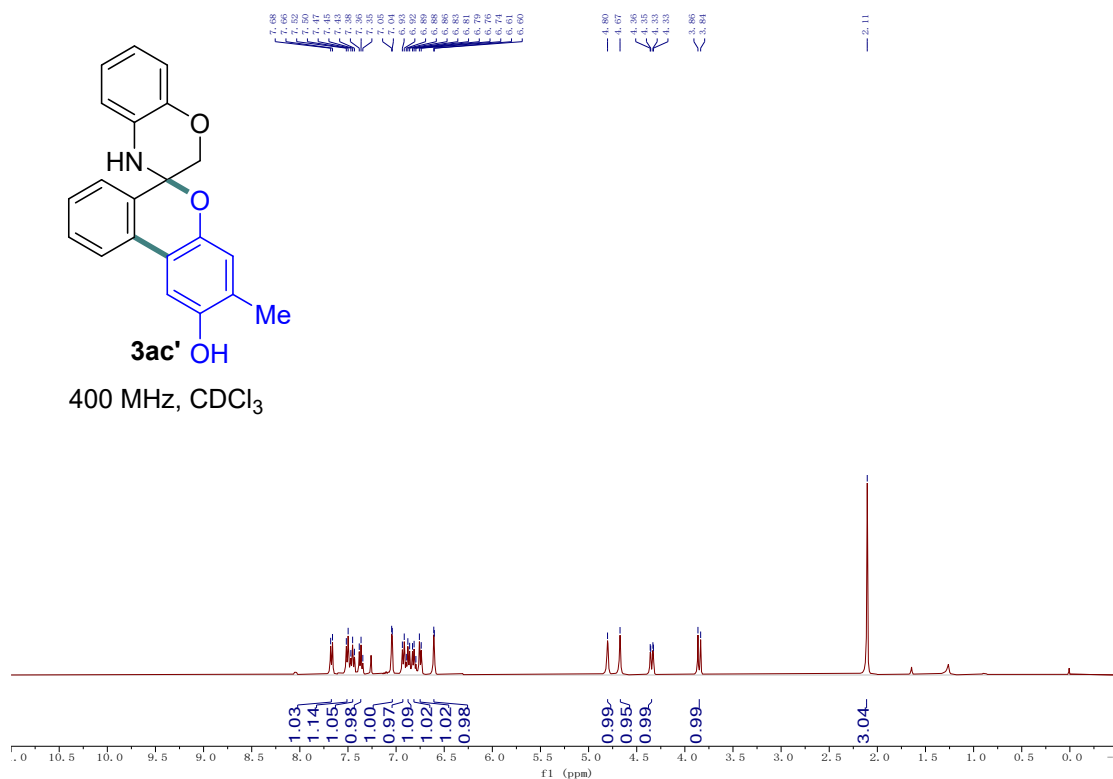
¹H and ¹³C NMR Spectra of 3ac



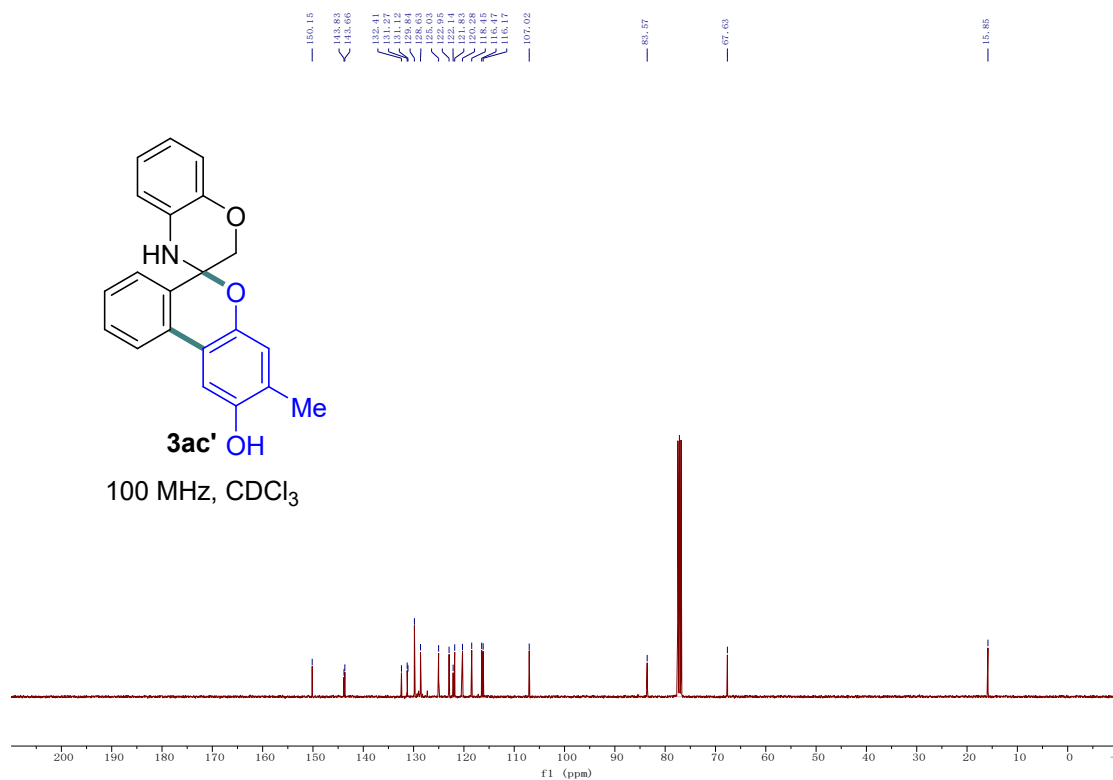
¹H and ¹³C NMR Spectra of 3ac'



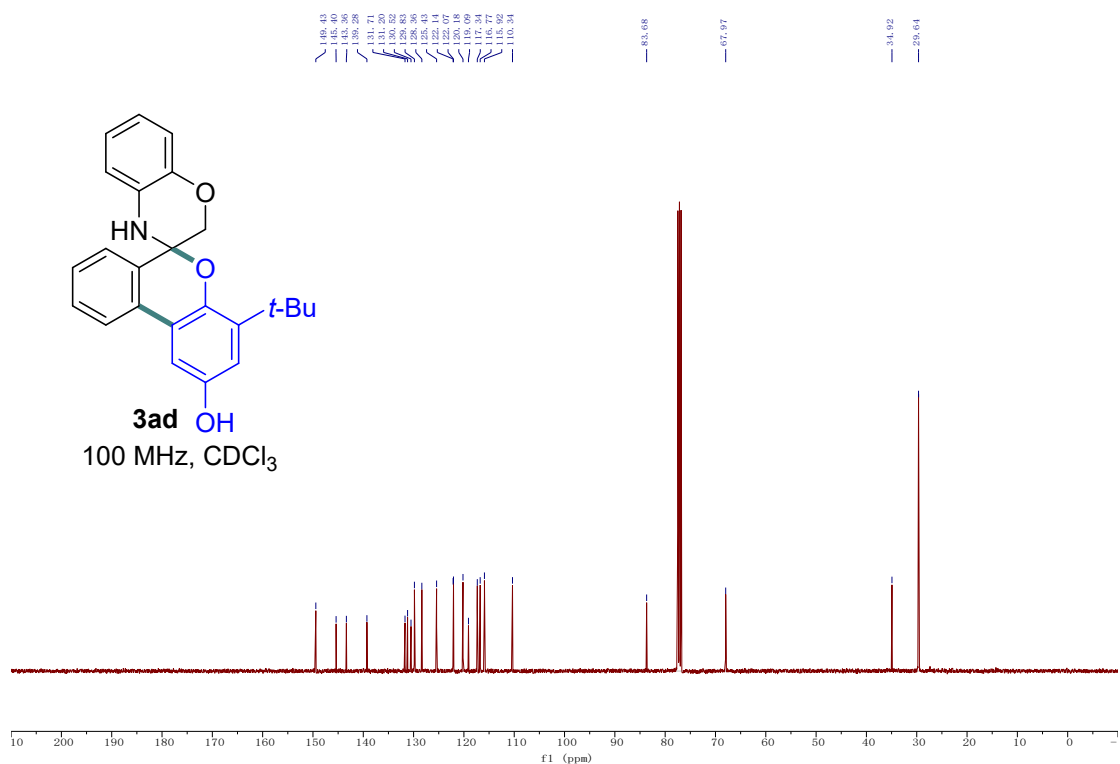
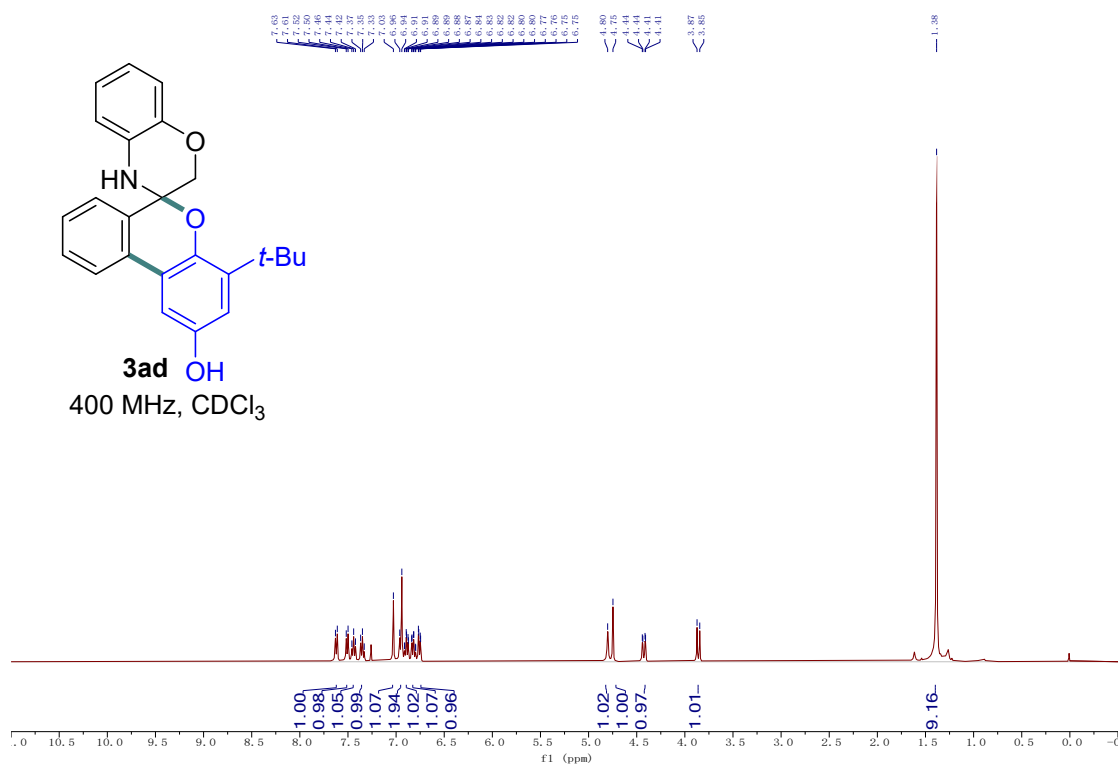
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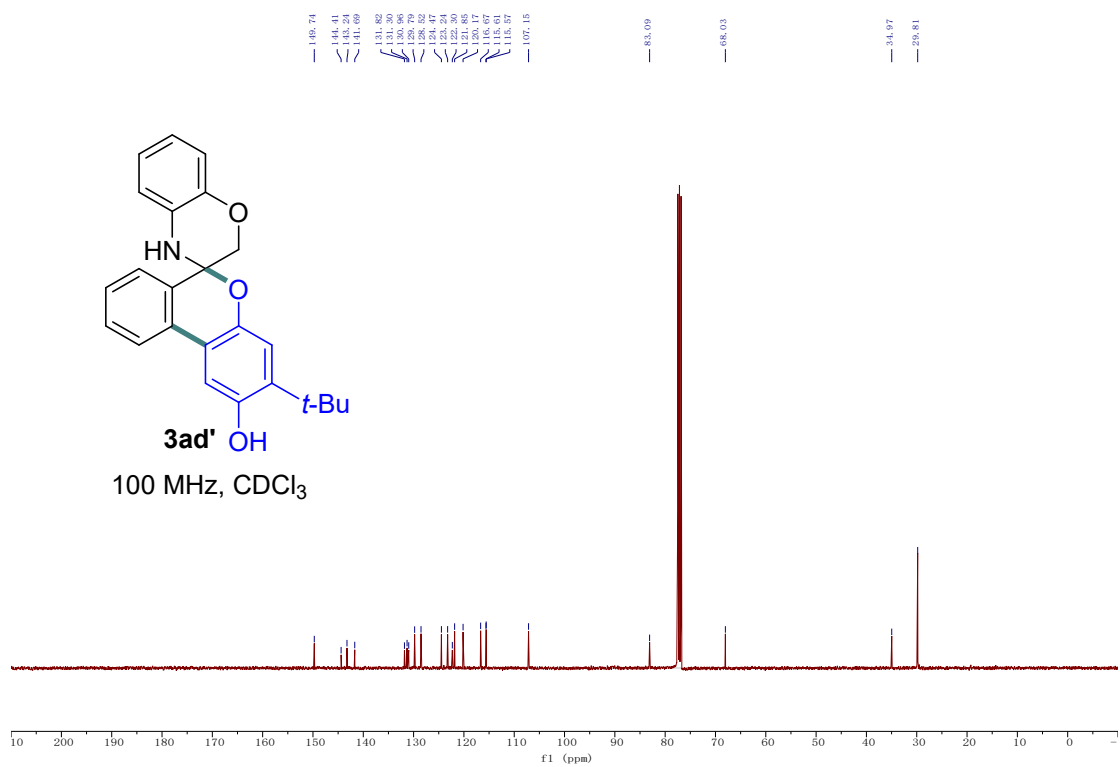
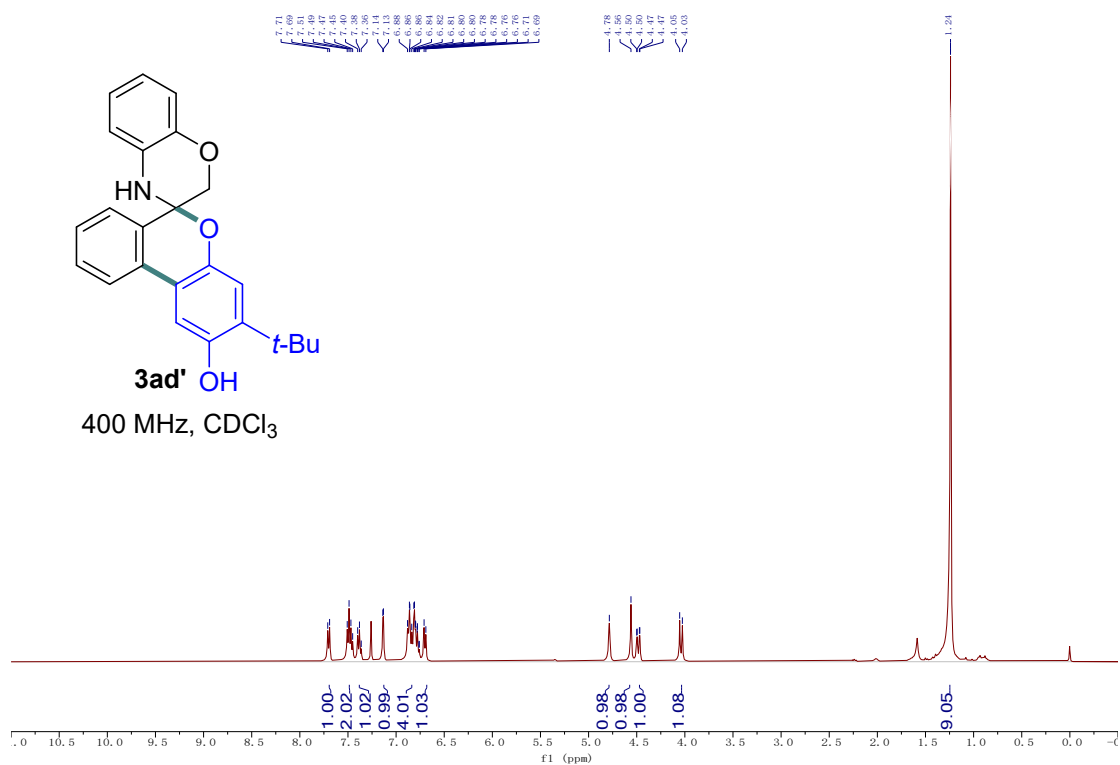
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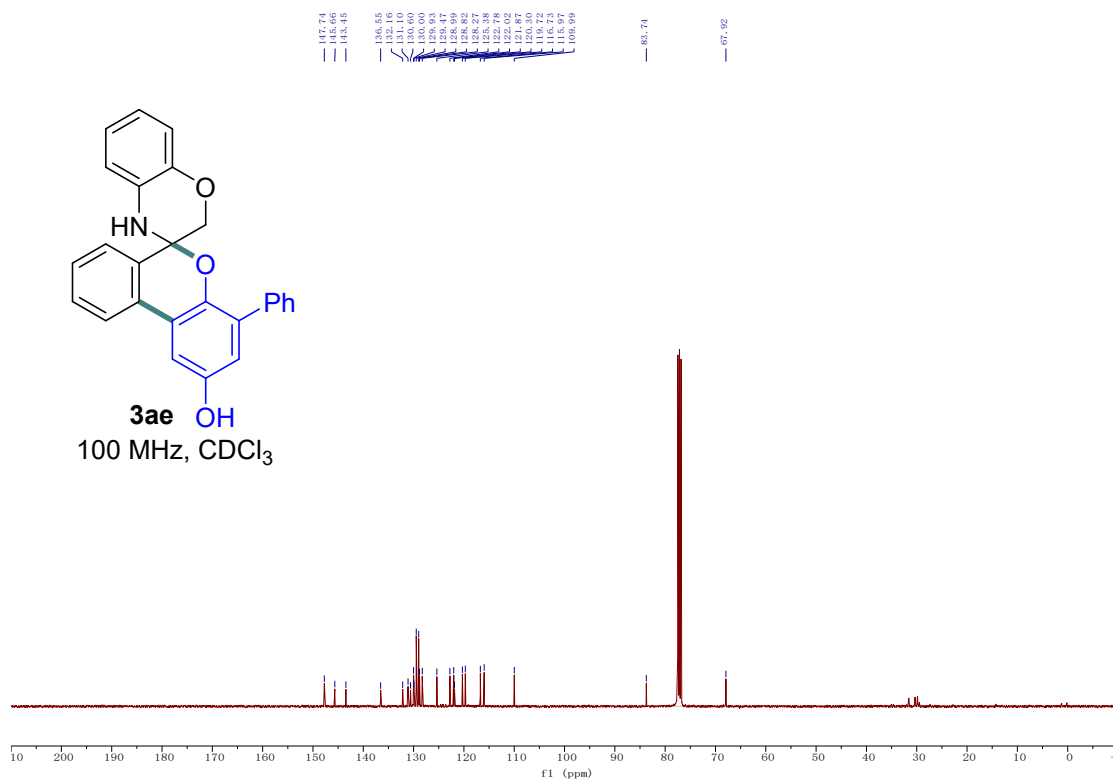
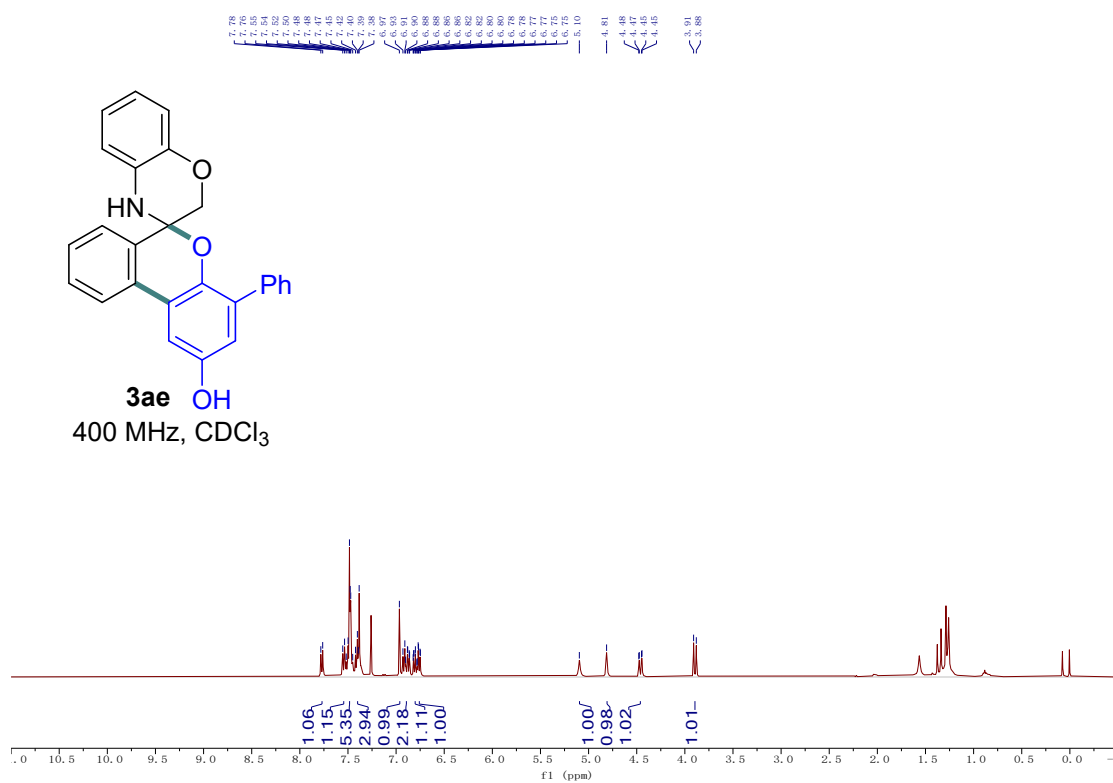
¹H and ¹³C NMR Spectra of 3ad



¹H and ¹³C NMR Spectra of 3ad'

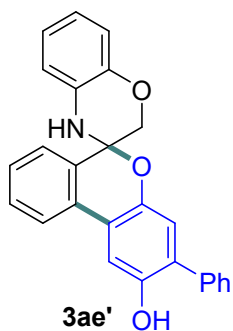


¹H and ¹³C NMR Spectra of 3ae

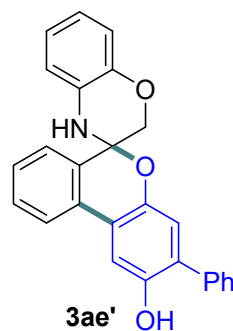
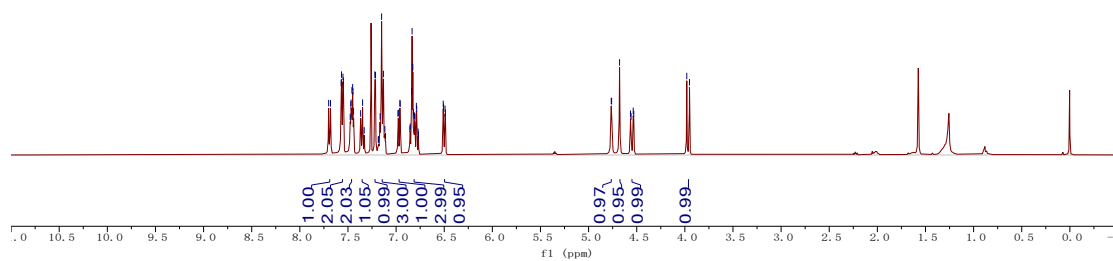


¹H and ¹³C NMR Spectra of 3ae'

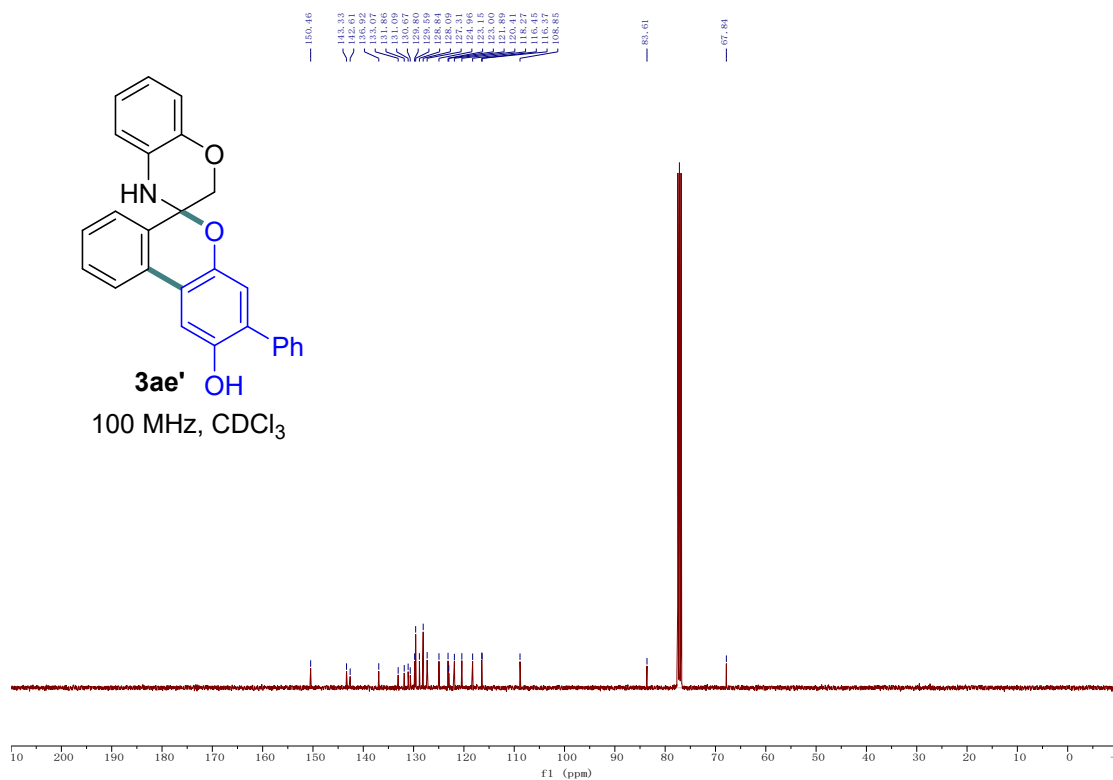
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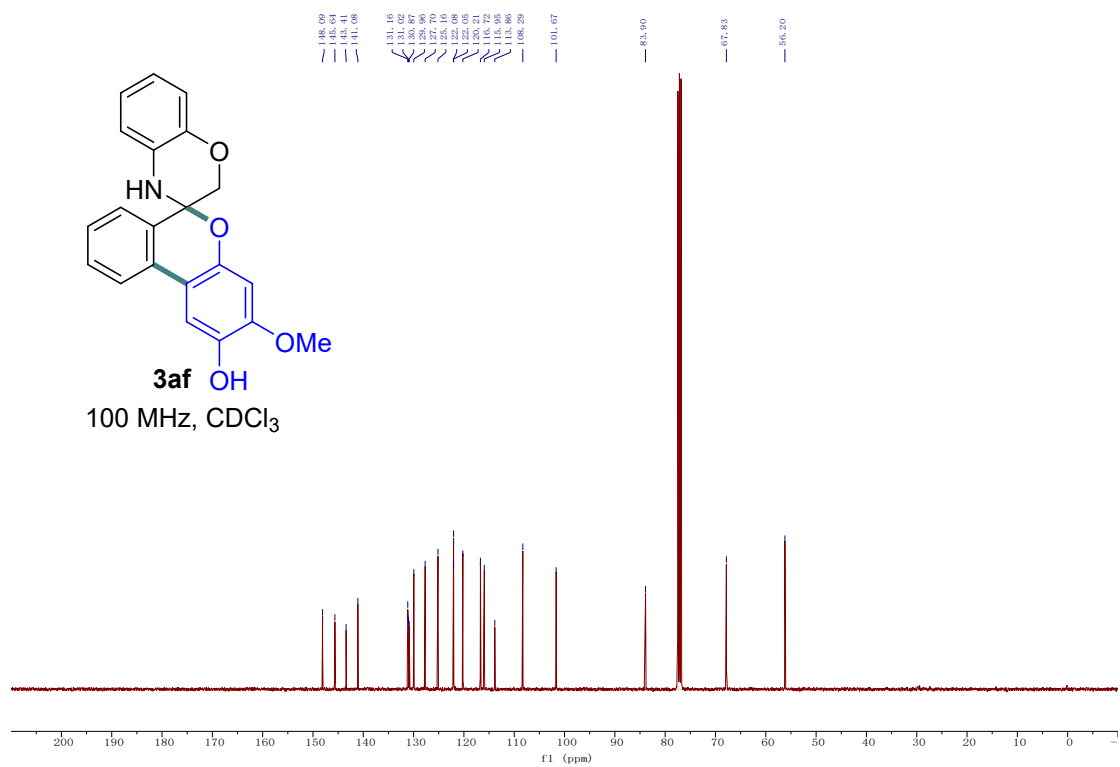
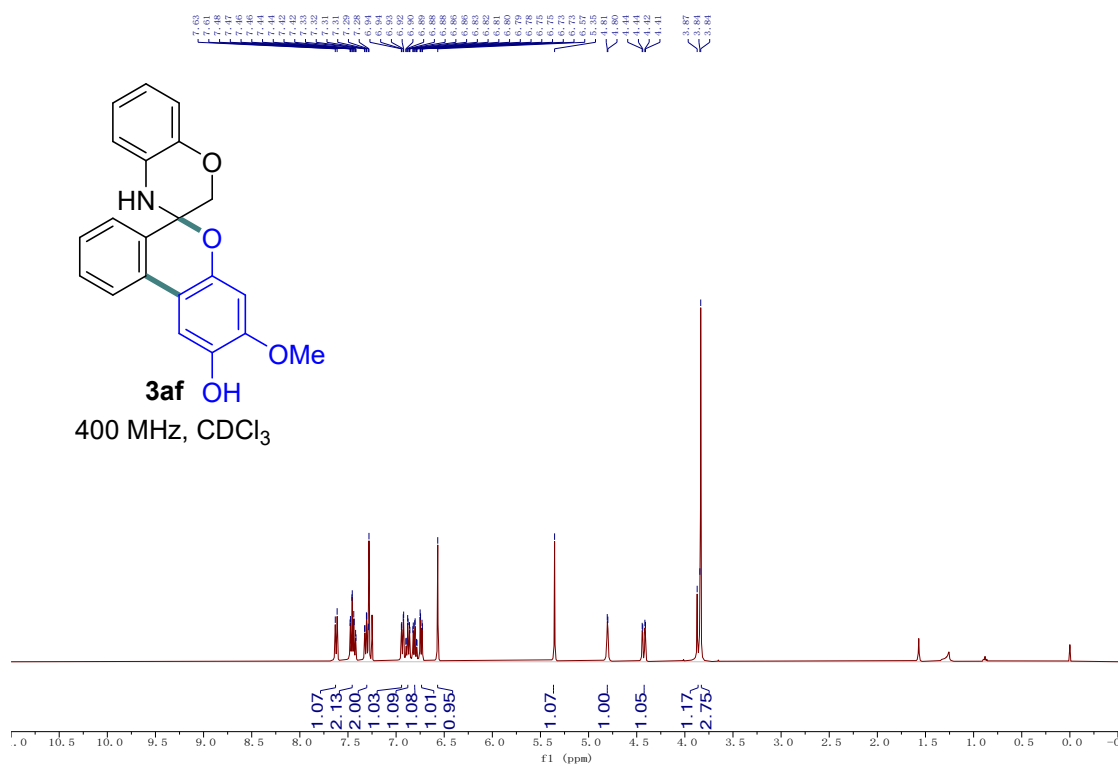
3ae'
400 MHz, CDCl₃



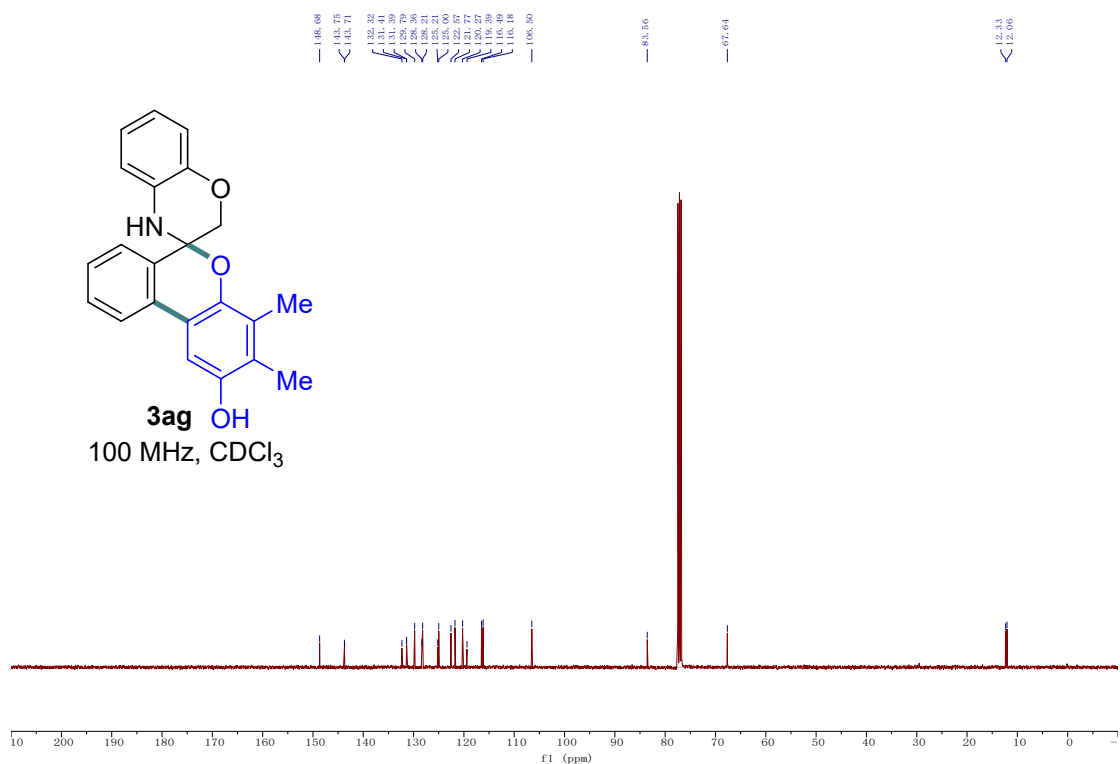
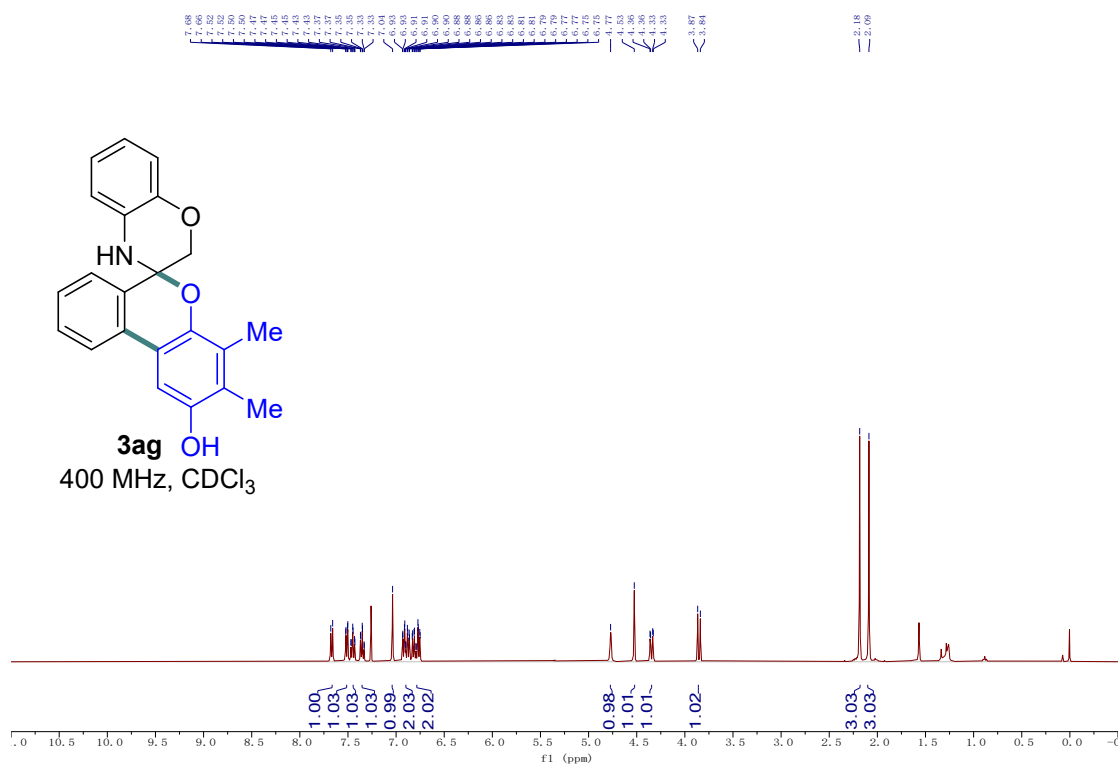
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100 MHz, CDCl₃



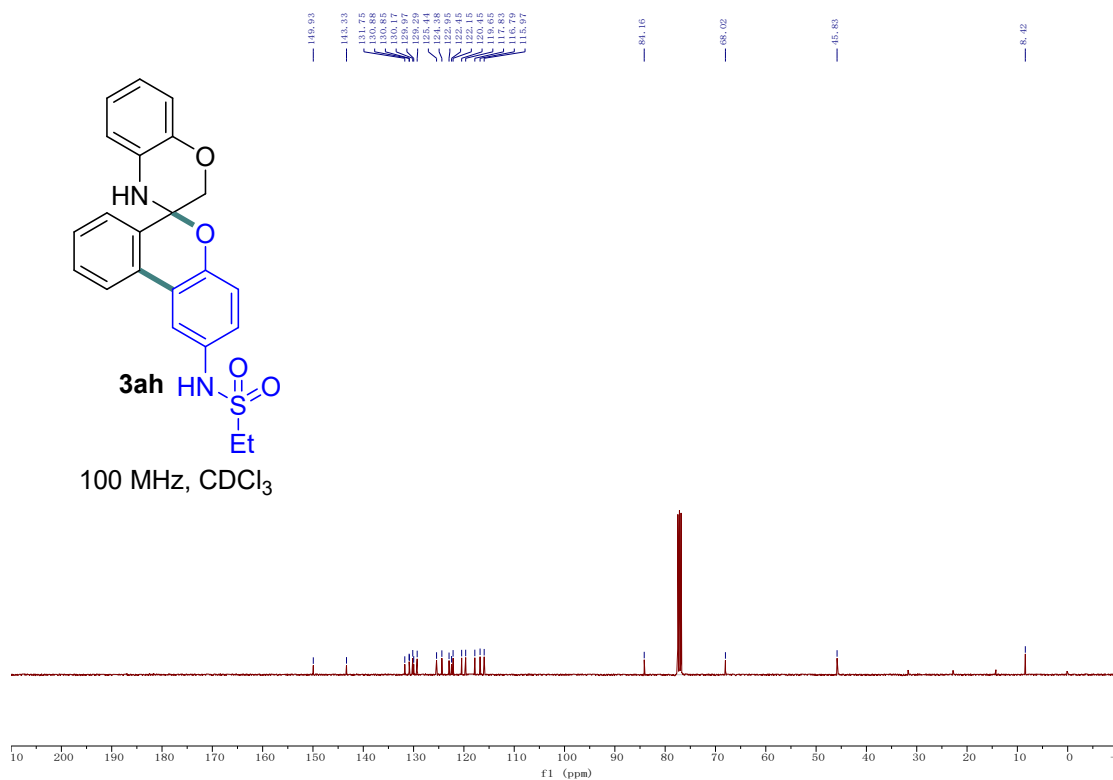
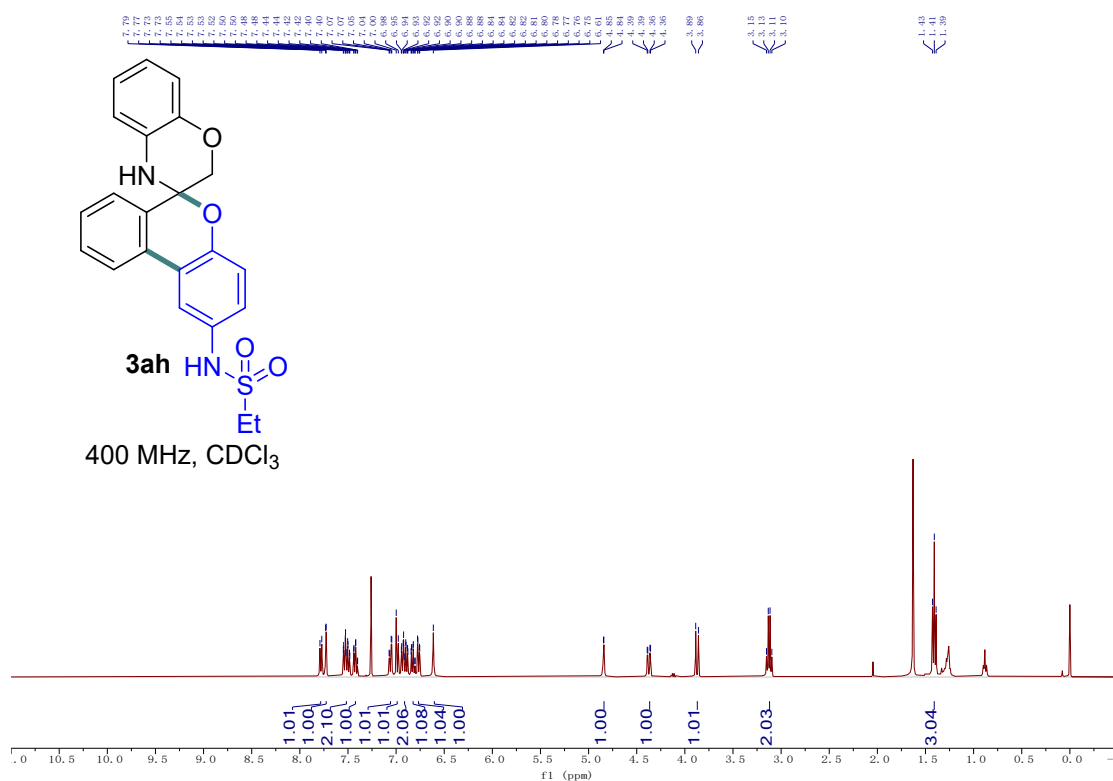
¹H and ¹³C NMR Spectra of 3af



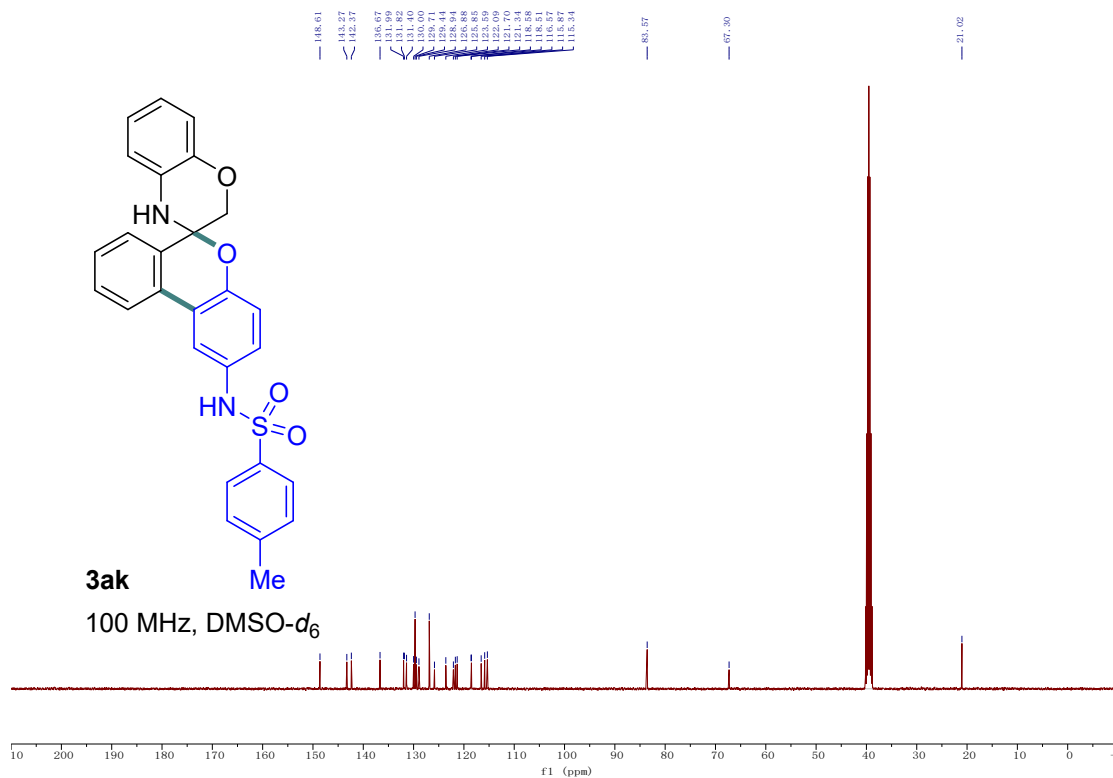
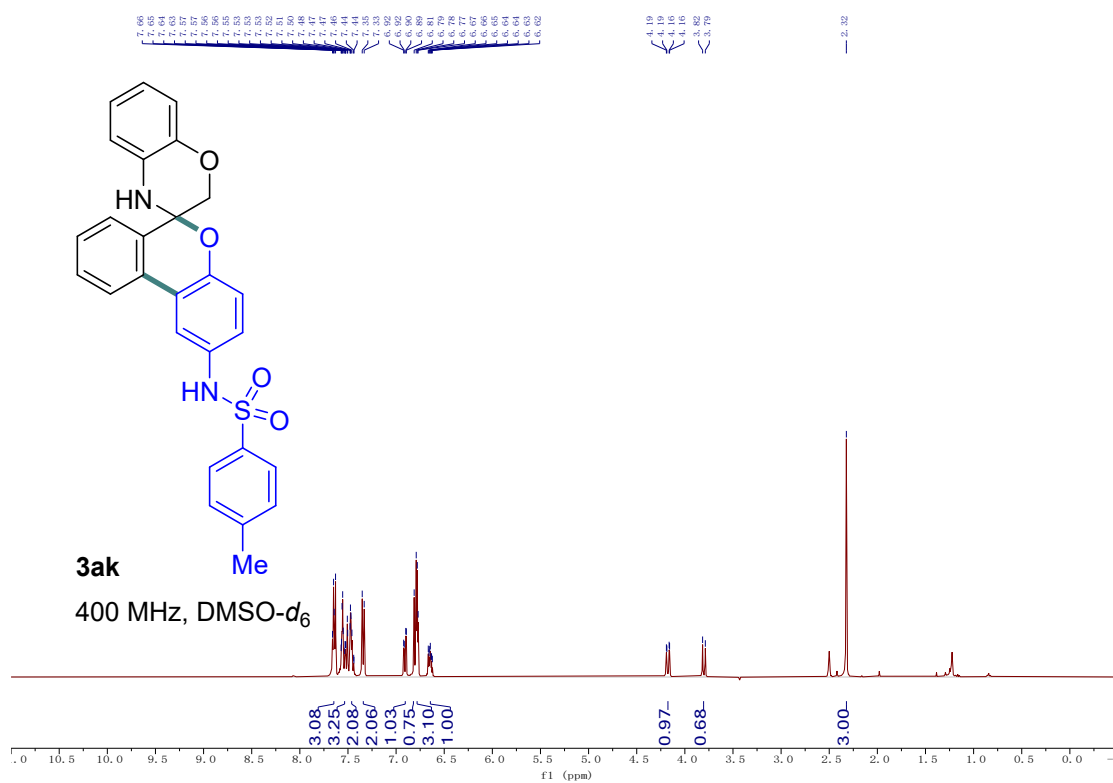
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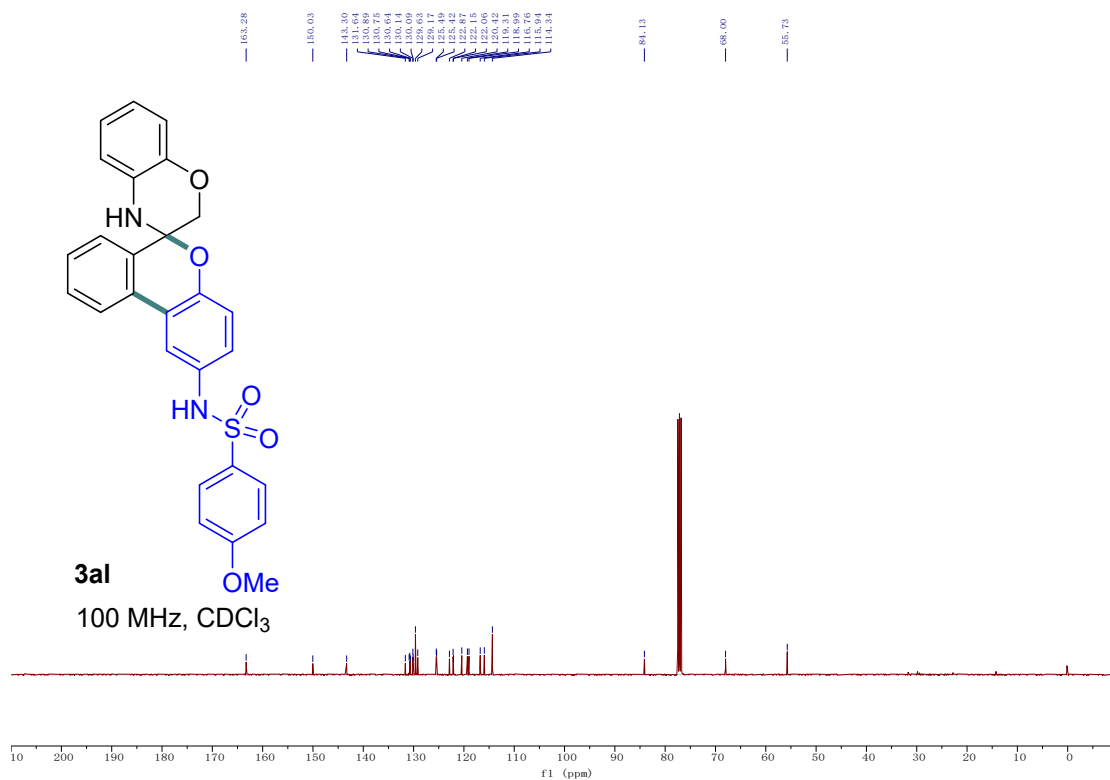
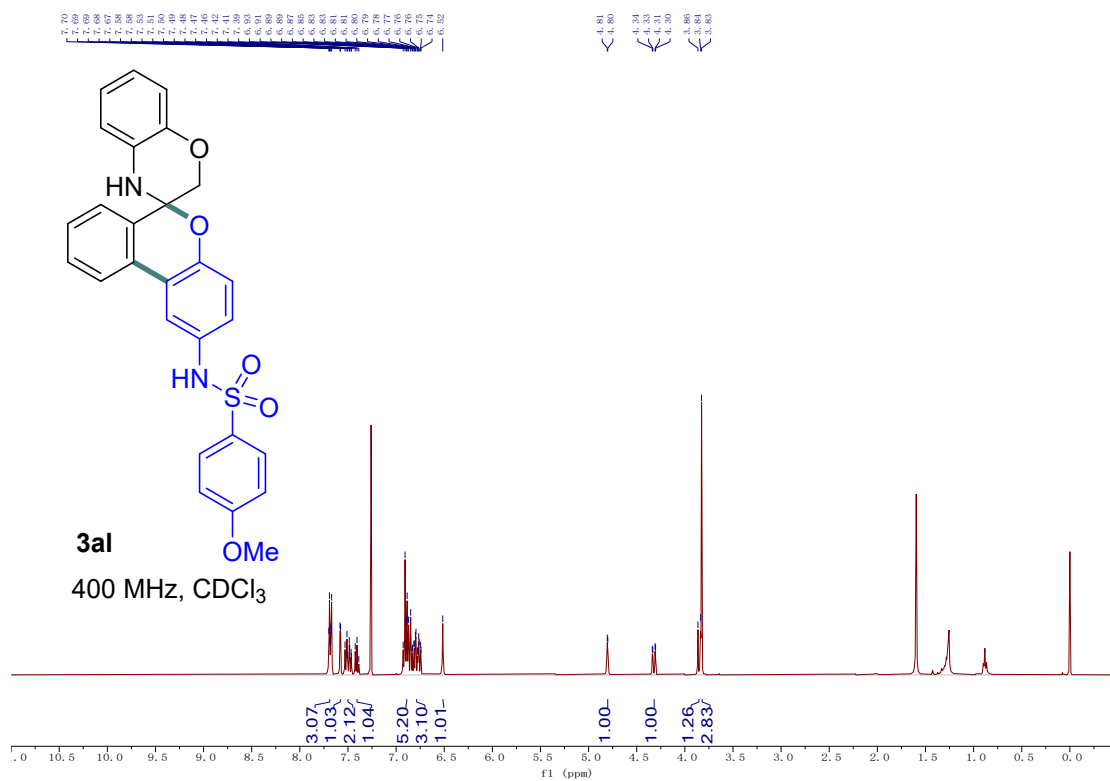
¹H and ¹³C NMR Spectra of 3ah



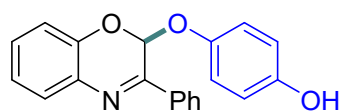
¹H and ¹³C NMR Spectra of 3ak



¹H and ¹³C NMR Spectra of 3al



¹H and ¹³C NMR Spectra of 4aa



4aa
400 MHz, CDCl₃

