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Supporting Information

Catalyst-controlled divergent synthesis of 2,8-dioxabicyclo[3.3.1]nonanes and benzo[*c*]chromen-6-ones

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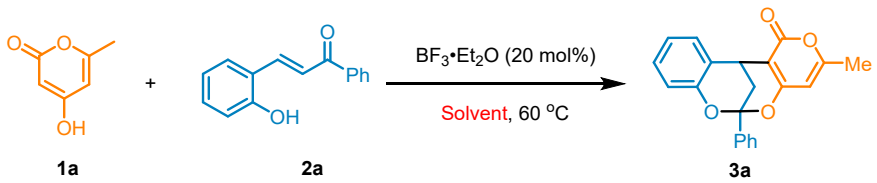
1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification. *ortho*-Hydroxychalcones [1] were prepared according to literature reports.

2. Optimization of conditions for the synthesis of 3a

Table S1. Optimization of solvents[a]

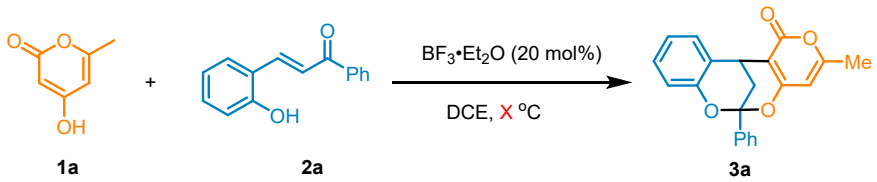


1a 2a 3a

entry	Solvent	Time (h)	Yield (%)[b]
1	$CHCl_3$	36	83
2	EtOH	42	74
3	EtOAc	36	53
4	**DCE**	**36**	**90**
5	MeOH	42	81
6	CH_3CN	36	67
7	toluene	42	80
8	THF	72	0

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.20 mmol), $BF_3{\cdot}OEt_2$ (0.04 mmol) in specified solvent (1.0 mL) at 60 °C. [b] Isolated yields determined by silica gel column chromatography. DCE = 1,2 - Dichloroethane.

Table S2. Optimization of temperatures[a]



1a 2a 3a

entry	X °C	Time (h)	Yield (%)[b]
1	35	72	trace
2	50	72	trace
3	60	36	90
4	70	24	84
5	**80**	**22**	**91**
6	90	12	85

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.20 mmol), $BF_3.Et_2O$ (0.04 mmol) in DCE (1.0 mL)

at specified temperature. [b] Isolated yields determined by silica gel column chromatography. DCE = 1,2 - Dichloroethane.

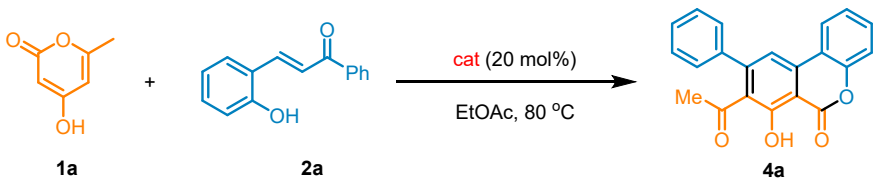
Table S3. Optimization of catalysts[a]

entry	Catalyst (0.2 equiv)	Time (h)	Yield (%)[b]
1	$Cu(OTf)_2$	72	59 (12)[c]
2	$Fe(OTf)_3$	48	69 (8)[c]
3	$Sc(OTf)_3$	48	73 (10)[c]
4	$In(OTf)_3$	48	64 (15)[c]
5	$Bi(OTf)_3$	72	50 (22)[c]
6	TfOH	24	63 (10)[c]
7	TFA	24	77 (20)[c]
8	*p*-TSA	24	79 (8)[c]

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.20 mmol), catalyst (0.04 mmol) in DCE (1.0 mL) at 80 °C. [b] Isolated yields determined by silica gel column chromatography. DCE = 1,2 - Dichloroethane. [c] The data in the parentheses corresponded to the isolated yields of **4a**.

3. Optimization of conditions for the synthesis of 4a

Table S4. Optimization of catalysts[a]

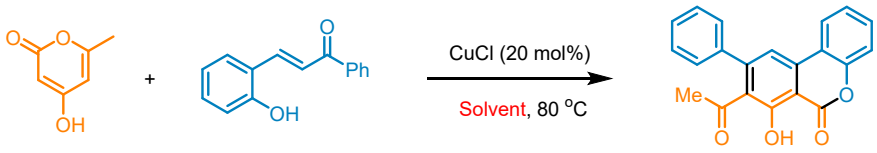


entry	Catalyst (0.2 equiv)	Time (h)	Yield (%)[b]
1	$Cu(OTf)_2$	72	23 (56)[c]
2	$In(OTf)_3$	72	17 (60)[c]
3	$Bi(OTf)_3$	72	36 (40)[c]
4	**CuCl**	**72**	**42** (20)[c]
5	CuI	72	39 (15)[c]

6	CuBr	72	38 (19)[c]
7	HOAc	72	34 (50)[c]
8	TFA	72	35 (30)[c]
9	TfOH	72	21 (35)[c]
10	$MeSO_3H$	72	0 (20)[c]

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.20 mmol), catalyst (0.04 mmol) in EtOAc (1.0 mL) at 80 °C. [b] ^{1}HNMR yields with 1,3,5-trimethoxybenzene (0.2 mmol) as the internal standard. [c] The data in the parentheses corresponded to the ^{1}HNMR yields of the respective 2,8-dioxabicyclo[3.3.1]nonanes **3a**. $MeSO_3H$ = methanesulfonic acid.

Table S5. Optimization of solvents[a]

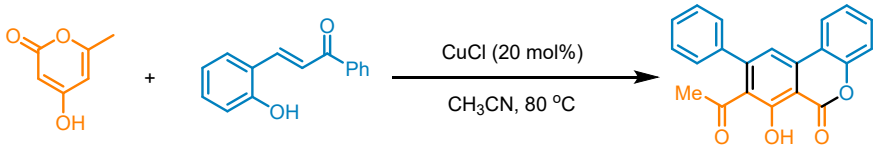


1a **2a** **4a**

entry	Solvent	Time (h)	Yield (%)[b]
1	EtOAc	72	42 (20)[c]
2	$CHCl_3$	72	41 (15)[c]
3	**CH_3CN**	**72**	**55** (10)[c]
4	DCE	72	47 (15)[c]
5	DMF	72	0 (5)[c]
6	toluene	72	44 (19)[c]

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.20 mmol), CuCl (0.04 mmol) in specified solvent (1.0 mL) at 80 °C. [b] ^{1}HNMR yields with 1,3,5-trimethoxybenzene (0.2 mmol) as the internal standard. [c] The data in the parentheses corresponded to the ^{1}HNMR yields of the respective 2,8-dioxabicyclo[3.3.1]nonanes **3a**. DCE = 1,2 – Dichloroethane; EtOAc = Ethyl acetate; DMF = *N*,*N*-Dimethylformamide.

Table S6. Optimization of Ratios[a]

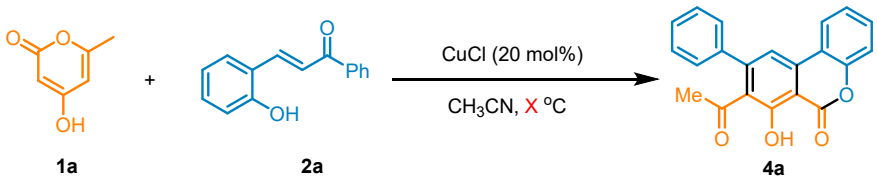


1a **2a** **4a**

entry	Ratio (**1a**:**2a**)	Time (h)	Yield (%)[b]
1	1.2 : 1.0	72	53 (12)[c]
2	1.5 : 1.0	72	65 (15)[c]
3	1.8 : 1.0	72	59 (15)[c]
4	1.0 : 1.0	72	55 (15)[c]
5	1.0 : 1.2	72	70 (10)[c]
6	1.0 : 1.5	72	53 (12)[c]
7	1.0 : 1.8	72	58 (18)[c]

[a] Reaction conditions: **1a** (specified equiv), **2a** (specified equiv), CuCl (0.04 mmol) in CH_3CN (1.0 mL) at 80 °C. [b] ^{1}HNMR yields with 1,3,5-trimethoxybenzene (0.2 mmol) as the internal standard. [c] The data in the parentheses corresponded to the ^{1}HNMR yields of the respective 2,8-dioxabicyclo[3.3.1]nonanes **3a**.

Table S7. Optimization of temperatures[a]

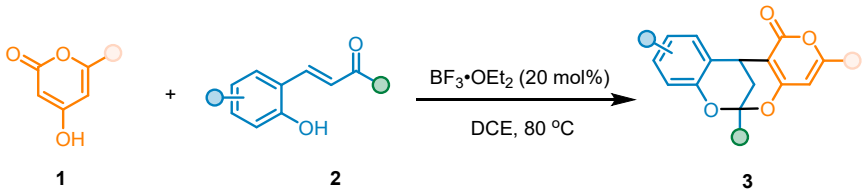


1a **2a** **4a**

entry	X °C	Time (h)	Yield (%)[b]
1	50	72	0
2	60	72	0
3	70	72	0
4	**80**	**72**	**70** (59)[c,d]
5	90	72	66 (18)[e]
6	100	72	67 (15)[e]

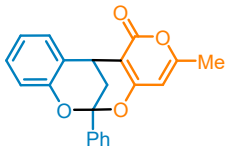
[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), CuCl (0.04 mmol) in CH_3CN (1.0 mL) at 80 °C. [b] ^{1}HNMR yields with 1,3,5-trimeth0xybenzene (0.2 mmol) as the internal standard. [c] The data in the parentheses corresponded to the isolated yields determined by silica gel column chromatography. [d] The isolated yield of **3a** was 10%. [e] The data in the parentheses corresponded to the ^{1}HNMR yields of the respective 2,8-dioxabicyclo[3.3.1]nonanes **3a**.

4. Experimental data for the formation of 3



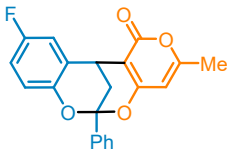
1 2 3

General procedure: To a 5.0 mL vial were successively added 4-hydroxy-6-methyl-2-pyrone **1** (0.20 mmol), *ortho*-hydroxychalcones **2** (0.20 mmol), BF_3•Et_2O (0.04 mmol) and 1.0 mL of DCE. The resulting mixture was stirred at 80 °C until almost full consumption of **1** as monitored by TLC. The reaction mixture was concentrated in vacuo and the residue was purified by silica-gel column chromatography (using petroleum ether/ethyl acetate as the eluent) to produce compounds **3**.



3-Methyl-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3a**)

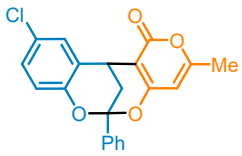
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20 : 1 to 15:1); 60.2 mg, 91% yield; reaction time = 22 h; mp 151.6-152.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.66 (m, 2H), 7.50 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.48-7.43 (m, 3H), 7.21-7.17 (m, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.99-6.95 (m, 1H), 5.91 (s, 1H), 4.22 (t, J = 4.0 Hz, 1H), 2.37-2.29 (m, 2H), 2.16(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 162.7, 160.8, 151.2, 139.5, 129.1, 128.3, 128.0, 127.9, 125.4, 125.4, 121.8, 116.1, 103.1, 99.9, 99.7, 32.6, 26.5, 19.7. IR (KBr) ν 3442, 1709, 1587, 1238, 1114, 1008, 756 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{17}O_4$ $[M+H]^+$: 333.1121, found: 333.1116.



10-Fluoro-3-methyl-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3b**)

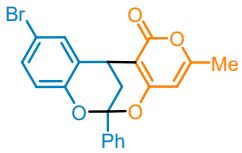
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 65.6 mg, 94% yield; reaction time = 20 h; mp 169.4-170.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.62 (m, 2H), 7.49-7.42 (m, 3H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.7 (dd, J_1 = 8.0

Hz, J_2 = 4.0 Hz, 1H), 6.89-6.84 (m, 1H), 5.93 (s, 1H), 4.17 (s, 1H), 2.33 (d, J = 4.0 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 163.0, 161.2, 157.4 (d, J = 240.0 Hz, 1C), 147.2, 139.3, 129.3, 128.5, 126.7 (d, J = 7.0 Hz, 1C), 125.4, 117.0 (d, J = 8.0 Hz, 1C), 114.6 (d, J = 24.0 Hz, 1C), 114.3 (d, J = 24.0 Hz, 1C), 102.7, 100.0, 99.7, 32.4, 26.7, 19.8. IR (KBr) ν 3435, 3082, 1709, 1584, 1487, 1007, 873, 754 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}FO_4$ $[M+H]^+$: 351.1027, found: 351.1029.



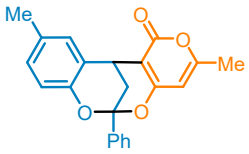
10-Chloro-3-methyl-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3c**)

Orange-red solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 60.4 mg, 82% yield; reaction time = 16 h; mp 177.8-178.6°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.63 (m, 2H), 7.48-7.43 (m, 4H), 7.12 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 5.92 (s, 1H), 4.17 (t, J = 4.0 Hz, 1H), 2.32 (d, J = 4.0 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 162.8, 161.2, 149.9, 139.1, 129.4, 128.5, 128.0, 127.5, 127.0, 126.7, 125.4, 117.4, 102.6, 99.9, 99.6, 32.3, 26.5, 19.8. IR (KBr) ν 3412, 3070, 1712, 1586, 1007, 826 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}ClO_4$ $[M+H]^+$: 367.0732, found: 367.0735.



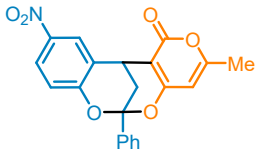
10-Bromo-3-methyl-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3d**)

Orange-red solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 71.1 mg, 86% yield; reaction time = 23 h; mp 176.4-177.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.60 (m, 3H), 7.48-7.44 (m, 3H), 7.27 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.92 (s, 1H) 4.17 (t, J = 4.0 Hz, 1H), 2.32 (d, J = 4.0 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 162.8, 161.3, 150.5, 139.1, 131.0, 130.4, 129.4, 128.5, 127.5, 125.4, 117.9, 114.1, 102.6, 99.9, 99.7, 32.4, 26.4, 19.9. IR (KBr) ν 23448, 1712, 1643, 755 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}BrO_4$ $[M+H]^+$: 411.0226, found: 411.0225.



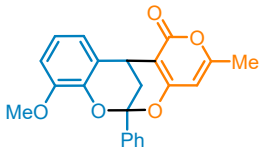
3,10-Dimethyl-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3e**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 60.5 mg, 87% yield; reaction time = 16 h; mp 171.1-171.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.49-7.41 (m, 3H), 7.31 (s, 1H), 7.00 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 5.91 (s, 1H), 4.18 (t, J = 4.0 Hz, 1H), 2.36-2.27 (m, 5H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.8, 160.7, 149.0, 139.7, 131.3, 129.1, 128.6, 128.3, 128.2, 125.4, 125.1, 115.8, 103.2, 99.9, 99.7, 32.8, 26.5, 20.4, 19.7. IR (KBr) ν 3411, 2920, 1708, 1585, 757 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{19}O_4$ $[M+H]^+$: 347.1278, found: 347.1281.



3-Methyl-10-nitro-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3f**)

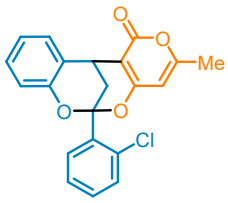
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 8:1); 30.6 mg, 41% yield; reaction time = 18 h; mp 237.6-238.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 4.0 Hz, 1H), 8.10 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.67-7.64 (m, 2H), 7.50-7.48 (m, 3H), 7.11 (d, J = 12.0 Hz, 1H), 5.96 (s, 1H), 4.32 (t, J = 4.0 Hz, 1H), 2.47-2.35 (m, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.5, 161.8, 156.7, 142.3, 138.4, 129.8, 128.7, 126.5, 125.4, 124.3, 123.8, 116.8, 102.3, 100.3, 99.5, 32.1, 26.6, 20.0. IR (KBr) ν 3451, 2358, 1712, 1587, 1338, 752 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}NO_6$ $[M+H]^+$: 378.0972, found: 378.0982.



8-Methoxy-3-methyl-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3g**)

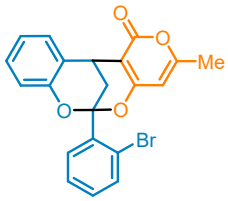
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 51.3 mg, 71% yield; reaction time = 16 h; mp 107.8-108.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$)

δ 7.72-7.69 (m, 2H), 7.48-7.43 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.92 (t, *J* = 12.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 1H), 4.22-4.21 (m, 1H), 3.87 (s, 3H), 2.32-2.31 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.9, 160.8, 148.0, 140.6, 139.6, 129.1, 128.4, 126.6, 125.7, 121.7, 119.8, 110.7, 103.0, 99.9, 99.8, 56.0, 32.8, 26.6, 19.8. IR (KBr) ν 3427, 2950, 1716, 1588, 1256, 1013, 763 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{19}O_5$ $[M+H]^+$: 363.1227, found: 363.1233.



6-(2-Chlorophenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3h**)

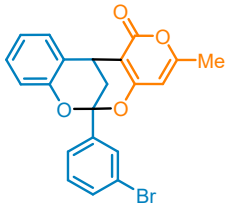
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 68.9 mg, 94% yield; reaction time = 16 h; mp 167.4-168.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 1H), 7.50-7.46 (m, 2H), 7.41-7.35 (m, 2H), 7.22-7.18 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 7.00-6.96 (m, 1H), 5.92 (s, 1H), 4.24 (t, *J* = 4.0 Hz, 1H), 2.64 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.45 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.4, 161.0, 150.8, 135.9, 132.4, 131.7, 130.6, 128.3, 128.2, 128.0, 126.9, 125.6, 122.0, 116.4, 103.5, 99.7, 99.6, 29.1, 26.1, 19.9. IR (KBr) ν 3446, 2953, 1714, 1590, 756 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}ClO_4$ $[M+H]^+$: 367.0732, found: 367.0729.



6-(2-Bromophenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3i**)

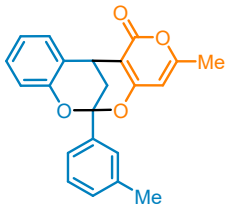
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 78.9 mg, 96% yield; reaction time = 15 h; mp 172.4-172.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 5.92 (s, 1H), 4.23 (t, *J* = 4.0 Hz, 1H), 2.68 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 2.46 (dd, J_1 = 16.0 Hz, J_2 = 4.0

Hz, 1H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.4, 160.9, 150.8, 137.3, 135.3, 130.7, 128.6, 128.2, 127.9, 127.5, 125.6, 122.0, 121.0, 116.4, 103.5, 99.9, 99.8, 29.1, 26.0, 19.9. IR (KBr) ν 3412, 2951, 1715, 1588, 1120, 753 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}BrO_4$ $[M+H]^+$: 411.0226, found: 411.0226.



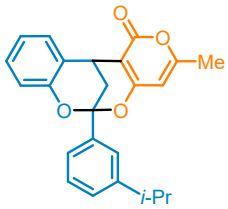
6-(3-Bromophenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3j**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 68.0 mg, 83% yield; reaction time = 15 h; mp 166.7-167.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.21-7.17 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 5.91 (s, 1H), 4.22 (t, *J* = 4.0 Hz, 1H), 2.35-2.26 (m, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 162.6, 161.1, 151.1, 138.8, 131.7, 128.2, 128.0, 127.4, 125.4, 123.6, 122.1, 116.2, 103.3, 99.7, 99.6, 32.7, 26.5, 19.9, two carbons missing in the aromatic region. IR (KBr) ν 3446, 2924, 1714, 1646, 1591, 757 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}BrO_4$ $[M+H]^+$: 411.0226, found: 411.0225.



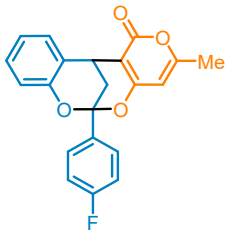
3-Methyl-6-(*m*-tolyl)-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3k**)

Orange-red solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 68.6 mg, 99% yield; reaction time = 15 h; mp 136.8-137.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 3H), 7.36-7.32 (m, 1H), 7.24-7.23 (m, 1H), 7.20-7.16 (m, 1H), 7.04 (d, *J* = 4.0 Hz,1H), 6.98-6.94 (m, 1H), 5.92 (s, 1H), 4.21 (t, *J* = 4.0 Hz, 1H), 2.42 (s, 3H), 2.38-2.28 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.8, 160.8, 151.3, 139.5, 138.2, 130.0, 128.4, 128.1, 127.9, 126.1, 125.5, 122.5, 121.9, 116.2, 103.2, 100.0, 99.8, 32.7, 26.6, 21.5, 19.8. IR (KBr) ν 3437, 2927, 1712, 1587, 1025, 754 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{19}O_4$ $[M+H]^+$: 347.1278, found: 347.1273.



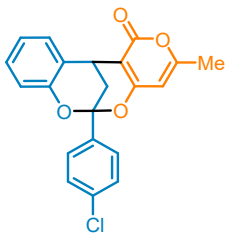
6-(3-Isopropylphenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3l**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 56.0 mg, 75% yield; reaction time = 14 h; mp 189.8-190.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.21-7.16 (m, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.99-6.95 (m, 1H), 5.92 (s, 1H), 4.23 (t, *J* = 4.0 Hz, 1H), 3.01-2.94 (m, 1H), 2.39-2.30 (m, 2H), 2.17 (s, 3H), 1.29 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.8, 160.8, 151.3, 150.1, 137.0, 128.0, 127.9, 126.5, 125.5, 125.4, 121.8, 116.2, 103.2, 100.0, 99.8, 33.8, 32.6, 26.6, 23.8, 19.8, two carbons missing in the aromatic region. IR (KBr) ν 3441, 2955, 1715, 1588, 1239, 763 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{23}O_4$ $[M+H]^+$: 375.1591, found: 375.1590.



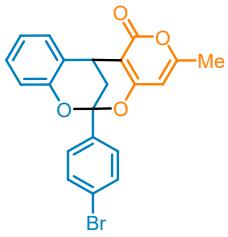
6-(4-Fluorophenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3m**)

Green solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 60.9 mg, 87% yield; reaction time = 18 h; mp 193.4-194.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.63 (m, 2H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.21-7.11 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 5.90 (s, 1H), 4.22 (t, *J* = 4.0 Hz, 1H), 2.36-2.27 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 247.0 Hz, 1C), 162.8 (d, *J* = 48.0 Hz, 1C), 161.0, 151.1, 135.6 (d, *J* = 3.0 Hz, 1C), 128.1 (d, *J* = 19.0 Hz, 1C), 127.6, 127.6, 125.4, 122.0, 116.1, 115.4, 115.2, 103.2, 99.7, 99.6, 32.8, 26.6, 19.8. IR (KBr) ν 3144, 2948, 1715, 1588,761 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}FO_4$ $[M+H]^+$: 351.1027, found: 351.1033.



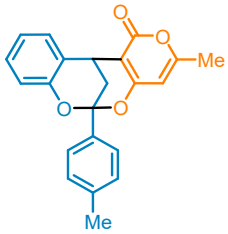
6-(4-Chlorophenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3n**)

Pale yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 64.6 mg, 88% yield; reaction time = 16 h; mp 171.5-172.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.44-7.42 (m, 2H), 7.21-7.17 (m, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.97 (t, J = 8.0 Hz, 1H), 5.90 (s, 1H), 4.22 (t, J = 4.0 Hz, 1H), 2.35-2.26 (m, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 162.5, 161.0, 151.1, 138.2, 135.3, 128.6, 128.2, 128.0, 127.1, 125.4, 122.1, 116.1, 103.2, 99.6, 99.6, 32.7, 26.5, 19.8. IR (KBr) ν 3421, 2946, 1711, 1008, 764 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}ClO_4$ $[M+H]^+$: 367.0732, found: 367.0733.



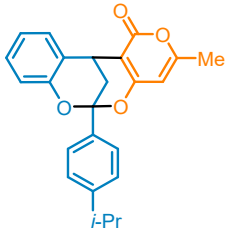
6-(4-Bromophenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3o**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 73.8mg, 90% yield; reaction time = 15 h; mp 175.1-176.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.61 (m, 3H), 7.50-7.45 (m, 3H), 7.28 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 5.93 (s, 1H), 4.18 (t, J = 4.0 Hz, 1H), 2.36-2.30 (m, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 162.9, 161.3, 150.5, 139.2, 131.1, 130.5, 129.5, 128.6, 127.6, 125.5, 118.0, 114.2, 102.7, 100.0, 99.7, 32.5, 26.5, 19.9. IR (KBr) ν 3436, 2924, 1713, 1588,753 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{16}BrO_4$ $[M+H]^+$: 411.0226, found: 411.0224.



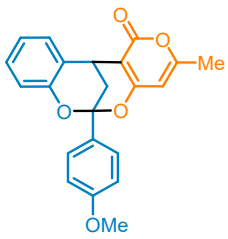
3-Methyl-6-(*p*-tolyl)-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3p**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 56.2 mg, 81% yield; reaction time = 18 h; mp 165.7-166.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.28-7.26 (m, 2H), 7.20-7.16 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.98-6.94 (m, 1H), 5.92 (s, 1H), 4.21 (t, J = 4.0 Hz, 1H), 2.40 (s, 3H), 2.37-2.28 (m, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.9, 160.9, 151.4, 139.2, 136.8, 129.1, 128.1, 128.0, 125.6, 125.4, 121.9, 116.2, 103.3, 100.1, 99.9, 32.8, 26.7, 21.2, 19.9. IR (KBr) ν 3437, 2923, 1708, 1584, 1239, 757 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{19}O_4$ $[M+H]^+$: 347.1278, found: 347.1272.



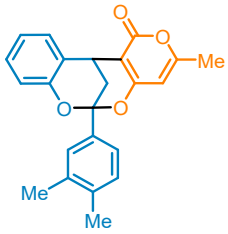
6-(4-Isopropylphenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3q**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 15:1); 49.4 mg, 66% yield; reaction time = 14 h; mp 192.5-193.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.21-7.16 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.99-6.95 (m, 1H), 5.92 (s, 1H), 4.23 (t, J = 4.0 Hz, 1H), 3.01-2.94 (m, 1H), 2.40-2.30 (m, 2H), 2.17 (s, 3H), 1.29 (d, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.8, 160.8, 151.3, 150.1, 137.0, 128.1, 127.9, 126.5, 125.5, 125.5, 121.8, 116.2, 103.2, 100.0, 99.8, 33.8, 32.6, 26.6, 23.8, 19.8. IR (KBr) ν 3438, 2957, 1715, 1589, 763 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{23}O_4$ $[M+H]^+$: 375.1591, found: 375.1585.



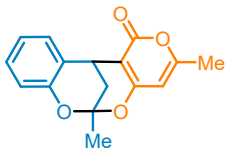
6-(4-Methoxyphenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3r**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 10:1); 37.8 mg, 52% yield; reaction time = 23 h; mp 150.6-151.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.57 (m, 2H), 7.48 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.98-6.94 (m, 3H), 5.90 (s, 1H), 4.21 (t, J = 4.0 Hz, 1H), 3.84 (s, 3H), 2.36-2.28 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.8, 160.8, 160.2, 151.3, 131.8, 128.0, 127.9, 126.8, 125.5, 121.8, 116.1, 113.7, 103.2, 99.9, 99.8, 55.3, 32.7, 26.6, 19.8. IR (KBr) ν 3452, 29481713, 1587, 1246, 1112 759 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{19}O_5$ $[M+H]^+$: 363.1227, found: 363.1225.



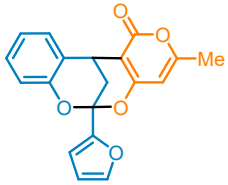
6-(3,4-Dimethylphenyl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3s**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 52.7 mg, 73% yield; reaction time = 18 h; mp 145.0-146.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.47 (d, J = 8.0 Hz, 1H), 7. 39 (d, J = 12.0 Hz, 2H), 7.25-7.15 (m, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.95 (t, J = 8.0 Hz, 1H), 5.92 (s, 1H), 4.20 (t, J = 4.0 Hz, 1H), 2.38-2.29 (m, 8H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.9, 160.7, 151.3, 137.8, 137.1, 136.7, 129.6, 128.0, 127.9, 126.6, 125.6, 122.8, 121.8, 116.2, 103.2, 100.0, 99.8, 32.7, 26.6, 19.9, 19.8, 19.5. IR (KBr) ν 3441, 2934, 1713, 1583, 1235, 1756 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{21}O_4$ $[M+H]^+$: 361.1434, found: 361.1427.



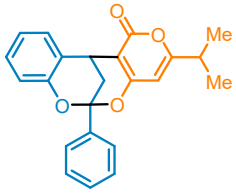
3,6-Dimethyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3t**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 29.6 mg, 55% yield; reaction time = 16 h; mp 174.5-175.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7. 39 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.11-7.07 (m, 1H), 6.89-6.83 (m, 2H), 5.75 (s, 1H), 4.10 (t, J = 4.0 Hz, 1H), 2.20-2.06 (m, 5H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 162.6, 160.5, 151.0, 127.8, 127.8, 125.3, 121.4, 115.9, 103.0, 99.6, 99.3, 30.7, 26.5, 26.1, 19.7. IR (KBr) ν 3406, 2987, 1713, 1585, 1133, 757 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{15}O_4$ $[M+H]^+$: 2710965, found: 271.0963.



6-(Furan-2-yl)-3-methyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3u**)

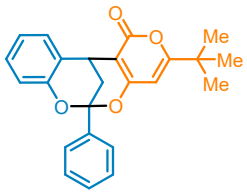
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 55.8 mg, 87% yield; reaction time = 16 h; mp 198.6-199.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 2H), 7.15 (t, J = 8.0 Hz, 1H), 6.98-6.93 (m, 2H), 6.72 (d, J = 4.0 Hz, 1H), 6.46 (s, 1H), 5.87 (s, 1H), 4.23 (t, J = 4.0 Hz, 1H), 2.47 (d, J = 4.0 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 162.2, 160.9, 150.9, 150.6, 143.2, 128.1, 128.0, 125.3, 122.0, 116.2, 110.5, 108.1, 103.2, 99.6, 96.3, 29.4, 25.7, 19.8. IR (KBr) ν 3445, 2952, 1704, 1588, 757 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{15}O_5$ $[M+H]^+$: 323.0914, found: 323.0909.



3-Isopropyl-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3v**)

Pink solid obtained by column chromatography (petroleum ether/ethyl acetate = 30:1 to 20:1); 55.5 mg, 77% yield; reaction time = 18 h; mp 69.2-70.1 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ

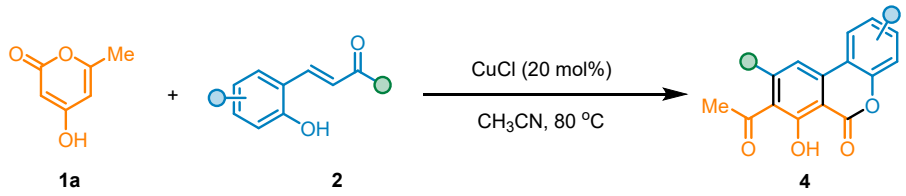
7.70-7.68 (m, 2H), 7.52-7.43 (m, 4H), 7.22-7.19 (m, 1H), 7.06 (d, *J* = 10.0 Hz, 1H), 7.00-6.97 (m, 1H), 5.93 (s, 1H), 4.24 (t, *J* = 5.0 Hz, 1H), 2.73-2.64 (m, 1H), 2.38-2.31 (m, 2H), 1.22-1.20 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.3, 163.2, 162.8, 151.3, 139.6, 129.2, 128.5, 128.1, 128.0, 125.5, 125.5, 121.9, 116.2, 103.3, 99.9, 97.0, 32.8, 32.5, 26.6, 19.9. IR (KBr) ν 3375, 2967, 1712, 1587, 1239, 1016, 756 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{21}O_4$ $[M+H]^+$: 361.1440, found: 361.1440.



3-(*tert*-Butyl)-6-phenyl-1*H*,12*H*-6,12-methanobenzo[*d*]pyrano[3,4-*g*][1,3]dioxocin-1-one (**3w**)

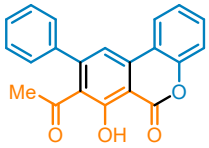
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 60.2 mg, 81% yield; reaction time = 18 h; mp 167.3-168.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.53-7.43 (m, 4H), 7.23-7.19 (m, 1H), 7.06 (d, *J* = 10.0 Hz, 1H), 7.01-6.97 (m, 1H), 5.99 (s, 1H), 4.24 (t, *J* = 5.0 Hz, 1H), 2.38-2.32 (m, 2H), 1.24 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 163.2, 162.8, 151.3, 139.7, 129.2, 128.5, 128.1, 128.0, 125.5, 125.5, 121.9, 116.2, 103.2, 99.9, 96.1, 36.0, 32.8, 27.7, 26.6. IR (KBr) ν 3088, 2967, 1702, 1581, 753 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{23}O_4$ $[M+H]^+$: 375.1596, found: 375.1593.

5. Experimental data for the formation of 4



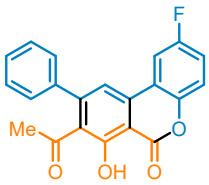
1a **2** **4**

General procedure: To a 5.0 mL vial were successively added 4-hydroxy-6-methyl-2-pyrone **1a** (0.20 mmol), *ortho*-hydroxychalcones **2** (0.24 mmol), CuCl (0.04 mmol) and 1.0 mL of CH_3CN. The resulting mixture was stirred at 80 °C until almost full consumption of **1a** as monitored by TLC. The reaction mixture was concentrated in vacuo and the residue was purified by silica-gel column chromatography using petroleum ether/ethyl acetate as the eluent to produce compounds **4**.



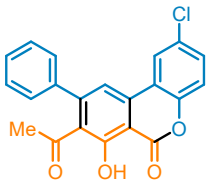
8-Acetyl-7-hydroxy-9-phenyl-6*H*-benzo[*c*]chromen-6-one (**4a**)

Pale yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 38.8 mg, 59% yield; reaction time = 72 h; mp 189.6-190.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.55-7.34 (m, 9H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 165.1, 159.0, 150.8, 148.3, 138.9, 135.4, 131.3, 129.3, 128.8, 128.8, 128.5, 125.4, 123.5, 117.8, 117.6, 113.8, 105.0, 32.2. IR (KBr) ν 3387, 2938, 1673, 1612, 750 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{15}O_4$ $[M+H]^+$: 331.0965, found: 331.0961.



8-Acetyl-2-fluoro-7-hydroxy-9-phenyl-6*H*-benzo[*c*]chromen-6-one (**4b**)

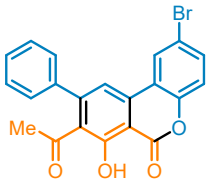
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 27.5 mg, 40% yield; reaction time = 72 h; mp 172.7-173.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (s, 1H), 7.70 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.47-7.46 (m, 4H), 7.41-7.37 (m, 3H), 7.28-7.23 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.1, 164.8, 159.7 (d, *J* = 244.0 Hz, 1C), 159.1, 148.4, 147.0, 138.6, 134.5 (d, *J* = 3.0 Hz, 1C), 130.0, 129.0, 128.9, 128.5, 119.5 (d, *J* = 8.0 Hz, 1C), 119.0 (d, *J* = 8.0 Hz, 1C), 118.6 (d, *J* = 24.0 Hz, 1C), 114.1, 109.5 (d, *J* = 24.0 Hz, 1C), 104.9, 32.2. IR (KBr) ν 3430, 3096, 1699, 1617, 1252, 1117, 741 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}FO_4$ $[M+H]^+$: 349.0871, found: 349.0867.



8-Acetyl-2-chloro-7-hydroxy-9-phenyl-6*H*-benzo[*c*]chromen-6-one (**4c**)

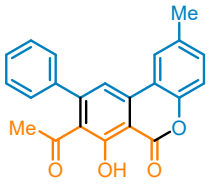
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 20.6 mg, 28% yield; reaction time = 72 h; mp 200.5-201.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.70 (s, 1H), 8.01 (d, *J* = 4.0 Hz, 1H), 7.51-7.46 (m, 5H), 7.42-7.40 (m, 2H), 7.36 (d, *J* = 8.0

Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 164.7, 159.1, 149.3, 148.6, 138.6, 134.2, 131.3, 131.1, 130.1, 129.0, 128.9, 128.5, 123.3, 119.3, 119.1, 114.0, 105.0, 32.2. IR (KBr) ν 3428, 3092, 1698, 1619, 1207, 1100, 752 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}ClO_4$ $[M+H]^+$: 365.0575, found: 365.0566.



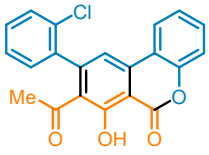
8-Acetyl-2-bromo-7-hydroxy-9-phenyl-6*H*-benzo[*c*]chromen-6-one (**4d**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 14.9 mg, 18% yield; reaction time = 72 h; mp 201.1-201.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.69 (s, 1H), 8.16 (d, J = 4.0 Hz, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.51-7.40 (m, 6H), 7.30 (d, J = 8.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 164.6, 159.1, 149.8, 148.6, 138.6, 134.1, 134.1, 130.1, 129.0, 128.9, 128.5, 126.3, 119.6, 119.5, 118.5, 114.0, 105.0, 32.2. IR (KBr) ν 3430, 3084, 1698, 1615, 1207, 745 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}BrO_4$ $[M+H]^+$: 409.0070, found: 409.0066.



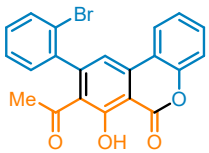
8-Acetyl-7-hydroxy-2-methyl-9-phenyl-6*H*-benzo[*c*]chromen-6-one (**4e**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 19.4 mg, 28% yield; reaction time = 72 h; mp 188.5-189.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82-11.81 (m, 1H), 7.76 (s, 1H), 7.50-7.39 (m, 6H), 7.31-7.29 (m, 1H), 7.23-7.20 (m, 1H), 2.43 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 165.2, 159.0, 148.9, 148.1, 138.9, 135.4, 135.1, 132.2, 129.0, 128.8, 128.7, 128.5, 123.3, 117.4, 117.1, 113.7, 104.9, 32.2, 21.0. IR (KBr) ν 3394, 3067, 1701, 1670, 1130, 746 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{17}O_4$ $[M+H]^+$: 345.1121, found: 345.1122.



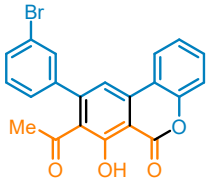
8-Acetyl-9-(2-chlorophenyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4f**)

Green solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 24.7 mg, 34% yield; reaction time = 72 h; mp 170.8-171.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.96 (s, 1H), 8.00 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.57-7.53 (m, 1H), 7.48-7.45 (m, 2H), 7.42-7.30 (m, 5H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.7, 165.1, 159.7, 150.9, 146.4, 138.0, 135.8, 131.8, 131.5, 130.8, 129.7, 129.6, 129.2, 126.8, 125.4, 123.7, 117.8, 117.6, 114.6, 105.7, 31.5. IR (KBr) ν 3386, 3018, 2970, 1672, 1615, 750 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}ClO_4$ $[M+H]^+$: 365.0575, found: 365.0574.



8-Acetyl-9-(2-bromophenyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4g**)

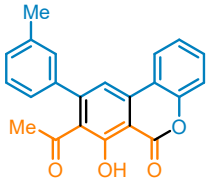
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 19.2 mg, 24% yield; reaction time = 72 h; mp 206.3-206.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.97 (s, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.49-7.46 (m, 1H), 7.43-7.35 (m, 3H), 7.32-7.26 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 165.2, 159.8, 151.0, 147.9, 139.9, 135.8, 132.8, 131.5, 130.8, 129.9, 129.1, 127.3, 125.5, 123.7, 121.8, 117.9, 117.6, 114.6, 105.8, 31.7. IR (KBr) ν 3379, 3019, 2970, 1693, 1615, 747 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}BrO_4$ $[M+H]^+$: 409.0070, found: 409.0058.



8-Acetyl-9-(3-bromophenyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4h**)

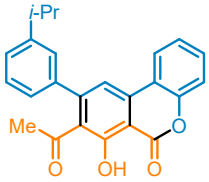
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 21.0 mg, 26% yield; reaction time = 72 h; mp 198.1-198.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.80 (s, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.59-7.56 (m, 2H), 7.54-7.52 (m, 1H),7.50 (s, 1H), 7.39-7.36 (m, 2H), 7.29-7.26 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 165.0, 159.2, 150.8, 147.0, 137.8, 135.6, 131.9, 131.5, 130.1, 129.1, 125.4, 123.4, 123.3, 117.8, 117.4, 113.6, 105.2, 32.3, two carbons missing in the aromatic region. IR (KBr) ν 3372, 3064, 1688, 1610, 1270, 760 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}BrO_4$ $[M+H]^+$: 409.0070, found:

409.0077.



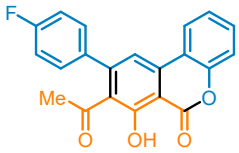
8-Acetyl-7-hydroxy-9-(*m*-tolyl)-6*H*-benzo[*c*]chromen-6-one (**4i**)

Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 27.2 mg, 40% yield; reaction time = 72 h; mp 193.1-193.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 2H), 7.38-7.32 (m, 3H), 7.26-7.23 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 2.42 (s, 3H) 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 165.1, 158.9, 150.8, 148.5, 138.9, 138.6, 135.3, 131.3, 129.6, 129.2, 129.1, 128.6, 125.6, 125.3, 123.5, 117.8, 117.7, 113.8, 104.9, 32.2, 21.4. IR (KBr) ν 3361, 3052, 1699, 1612, 751 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{17}O_4$ $[M+H]^+$: 345.1121, found: 345.1117.



8-Acetyl-7-hydroxy-9-(3-isopropylphenyl)-6*H*-benzo[*c*]chromen-6-one (**4j**)

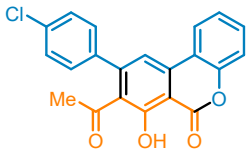
Green solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 12.6 mg, 17% yield; reaction time = 72 h; mp 158.7-159.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.05 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.58 (s, 1H), 7.56-7.52 (m, 1H), 7.42-7.31 (m, 6H), 3.01-2.94 (m, 1H), 2.31 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 165.2, 159.0, 150.9, 149.9, 148.4, 136.3, 135.4, 131.3, 129.3, 128.6, 126.9, 125.4, 123.5, 117.9, 117.8, 113.9, 104.9, 33.9, 32.3, 23.9, two carbons missing in the aromatic region. IR (KBr) ν 3404, 2961, 1676, 1616, 751 cm^{-1}. HRMS (ESI) calcd for $C_{24}H_{21}O_4$ $[M+H]^+$: 373.1434, found: 373.1430.



8-Acetyl-9-(4-fluorophenyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4k**)

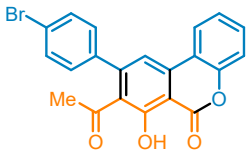
Light yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1

to 20:1); 10.3 mg, 15% yield; reaction time = 72 h; mp 171.5-172.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.80 (s, 1H), 8.05 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.57-7.53 (m, 2H), 7.42-7.37 (m, 4H), 7.18-7.13 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 165.1, 159.1, 150.9, 147.2, 135.6, 134.9 (d, J = 5.0 Hz, 1C), 131.5, 130.4 (d, J = 11.0 Hz, 1C), 129.3, 125.4, 123.5, 117.9, 117.6, 116.0, 115.7, 113.8, 105.2, 32.3. IR (KBr) ν 3375, 2929, 1686, 1611, 753 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}FO_4$ $[M+H]^+$: 349.0871, found: 349.0870.



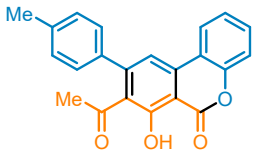
8-Acetyl-9-(4-chlorophenyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4l**)

Green solid obtained by column chromatography(petroleum ether/ethyl acetate = 25:1 to 20:1); 23.6 mg, 32% yield; reaction time = 72 h; mp 175.1-176.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.80 (s, 1H), 8.01 (d, J = 4.0 Hz, 1H), 7.54 (t, J = 4.0 Hz, 1H), 7.50 (s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 165.0, 159.1, 150.58, 147.0, 137.3, 135.6, 135.1, 131.5, 129.8, 129.1, 129.0, 125.4, 123.4, 117.8, 117.5, 113.7, 105.2, 32.3. IR (KBr) ν 3433, 3058, 1673, 1612, 757 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}ClO_4$ $[M+H]^+$: 365.0575, found: 365.0577.



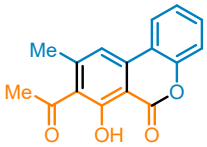
8-Acetyl-9-(4-bromophenyl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4m**)

Green solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 27.2 mg, 33% yield; reaction time = 72 h; mp 202.6-203.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.60-7.51 (m, 4H), 7.41-7.37 (m, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 165.0, 159.2, 150.9, 147.1, 137.8, 135.7, 132.0, 131.5, 130.1, 129.1, 125.5, 123.5, 123.3, 117.9, 117.5, 113.7, 105.3, 32.4. IR (KBr) ν 3434, 3066, 1680, 1613, 760 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{14}BrO_4$ $[M+H]^+$: 409.0070, found: 409.0066.



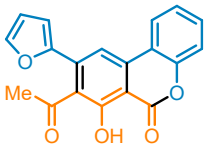
8-Acetyl-7-hydroxy-9-(*p*-tolyl)-6*H*-benzo[*c*]chromen-6-one (**4n**)

Green solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 10:1); 28.7 mg, 42% yield; reaction time = 72 h; mp 194.6-195.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.05 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.55-7.51 (m, 2H), 7.40-7.32 (m, 3H), 7.27-7.23 (m, 2H), 7.19 (d, J = 8.0 Hz, 1H), 2.43 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 165.1, 159.0, 150.9, 148.5, 138.9, 138.6, 135.4, 131.3, 129.6, 129.1, 128.7, 125.7, 125.4, 123.5, 117.8, 113.8, 105.0, 32.2, 21.4. IR (KBr) ν 3397, 3052, 1695, 1614, 751 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{17}O_4$ $[M+H]^+$: 345.1121, found: 345.1122.



8-Acetyl-7-hydroxy-9-methyl-6*H*-benzo[*c*]chromen-6-one (**4o**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 25:1 to 20:1); 10.8 mg, 20% yield; reaction time = 72 h; mp 162.1-162.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.72 (s, 1H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.51-7.46 (m, 1H), 7.35-7.30 (m, 3H), 2.61 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 165.0, 159.7, 150.8, 146.0, 135.4, 131.1, 128.9, 125.2, 123.3, 117.7, 117.5, 114.3, 104.1, 32.0, 20.9. IR (KBr) ν 3431, 3067, 1678, 1613, 1266, 759 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{13}O_4$ $[M+H]^+$: 269.0732, found: 269.0730.

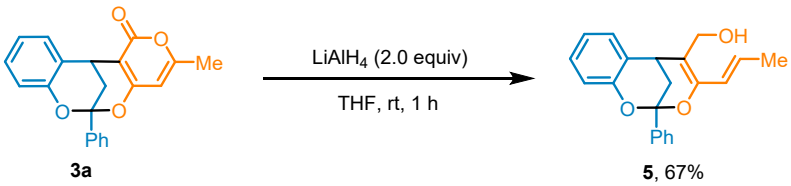


8-Acetyl-9-(furan-2-yl)-7-hydroxy-6*H*-benzo[*c*]chromen-6-one (**4p**)

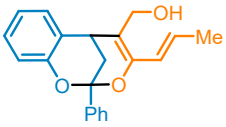
White solid obtained by column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1); 30.2 mg, 47% yield; reaction time = 72 h; mp 160.6-161.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 8.06-8.03 (m, 1H), 7.80 (s, 1H), 7.58-7.50 (m, 2H), 7.39-7.34 (m, 2H), 6.82 (d, J = 4.0 Hz, 1H), 6.54-6.53 (m, 1H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 164.8, 158.9, 150.8, 150.2, 144.4, 135.3, 134.5, 131.2, 126.2, 125.3, 123.4, 117.8, 117.6, 112.5, 111.8, 109.4, 104.6, 31.8. IR (KBr) ν 3437, 2925, 1663, 1617, 754 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{13}O_5$

[M+H]$^+$: 321.0757, found: 321.0755.

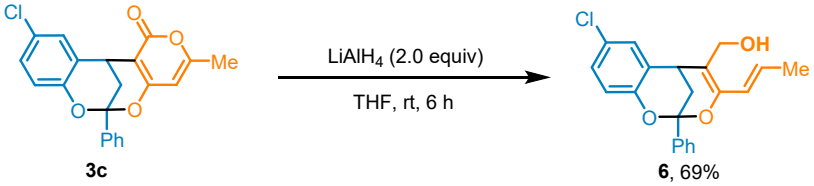
6. Experimental data for the chemical conversion of 5 and 6



General procedure for the formation of 5: Under nitrogen atmosphere, to a solution of **3a** (99.7 mg, 0.30 mmol) in dry THF (1.5 mL) was added $LiAlH_4$ by syringe (2.4 M in hexane, 0.25 mL) successively. The resulting reaction mixture was stirred at room temperature for 60 min. Then saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2 for three times. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to obtain **5** in 67% yield (64.4 mg).

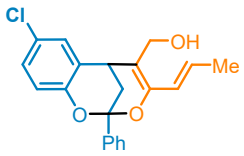


(*E*)-(2-Phenyl-4-(prop-1-en-1-yl)-6*H*-2,6-methanobenzo[*d*][1,3]dioxocin-5-yl)methanol (**5**)
Yellow solid obtained by column chromatography (petroleum ether/ethyl acetate = 3:1); 64.4 mg, 67% yield; reaction time = 1 h; mp 167.9-168.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 2H), 7.42-7.37 (m, 3H), 7.20 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.17-7.12 (m, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.91-6.87 (m, 1H), 6.37-6.28 (m, 1H), 6.24-6.20 (m, 1H), 4.41 (d, J = 12.0 Hz, 1H), 4.14 (d, J = 12.0 Hz, 1H), 3.71 (t, J = 4.0 Hz, 1H), 2.25-2.17 (m, 2H), 1.79 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 3H), one hydrogen for OH was missing; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 145.9, 141.6, 128.6, 128.5, 128.2, 127.7, 126.8, 126.7, 125.7, 120.9, 120.8, 116.2, 112.9, 97.9, 60.3, 33.7, 31.3, 18.3. IR (KBr) ν 2930, 1633, 1453, 757 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{21}O_3$ [M+H]$^+$: 321.1491, found: 321.1493.



General procedure for the formation of 6: Under nitrogen atmosphere, to a solution of

3c (110.0 mg, 0.30 mmol) in dry THF (2.0 mL) was added $LiAlH_4$ by syringe (2.4 M in hexane, 0.25 mL) successively. The resulting reaction mixture was stirred at room temperature for 6.0 h. Then saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2 for three times. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography (petroleum ether/ ethyl acetate = 10:1 to 5:1) to obtain **6** in 69% yield (73.1 mg).



(*E*)-(8-Chloro-2-phenyl-4-(prop-1-en-1-yl)-6*H*-2,6-methanobenzo[*d*][1,3]dioxocin-5-yl)methanol (**6**)

White solid obtained by column chromatography (petroleum ether/ethyl acetate = 10:1 to 5:1); 73.1 mg, 69% yield; reaction time = 6 h; mp 156.4-157.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66-7.63 (m, 2H), 7.49-7.41 (m, 3H), 7.36 (d, *J* = 4.0 Hz, 1H), 7.19-7.16 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.15-6.06 (m, 1H), 4.93 (t, *J* = 4.0 Hz, 1H), 4.28-4.23 (m, 1H), 3.94-3.90 (m, 1H), 3.74 (s, 1H), 2.27-2.23 (m, 1H), 2.15-2.11 (m, 1H), 1.78 (d, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.1, 143.5, 141.2, 128.8, 128.7, 128.3, 127.1, 126.8, 126.6, 125.5, 124.2, 121.5, 117.3, 114.4, 97.7, 57.3, 32.0, 29.5, 18.0. IR (KBr) ν 3320, 3050, 2927, 1478, 1247, 1001 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{20}ClO_3$ $[M+H]^+$: 355.1096, found: 355.1094.

7. Crystal structures

7.1 Crystal structure of 3a

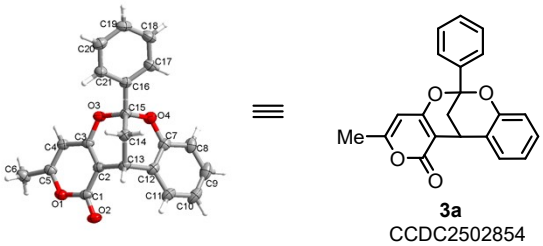


Table S7. Crystal data and structure refinement for **3a**

Identification code	**3a**
Empirical formula	$C_{21}H_{16}O_4$
Formula weight	332.34

Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.8673(6)
b/Å	11.3115(6)
c/Å	13.3163(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1636.92(17)
Z	4
ρ_{calc}g/cm^3	1.349
μ/mm^{-1}	0.761
F(000)	696.0
Crystal size/mm^3	0.2 × 0.16 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.26 to 134.156
Index ranges	-12 ≤ h ≤ 7, -13 ≤ k ≤ 13, -14 ≤ l ≤ 15
Reflections collected	6198
Independent reflections	2921 [R_{int} = 0.0342, R_{sigma} = 0.0450]
Data/restraints/parameters	2921/0/228
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.1073
Final R indexes [all data]	R_1 = 0.0491, wR_2 = 0.1158
Largest diff. peak/hole / e Å^{-3}	0.13/-0.17

7.2 Crystal structure of 4a

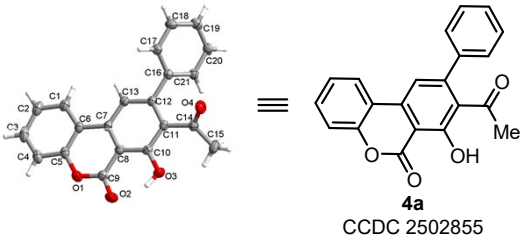


Table S8. Crystal data and structure refinement for **4a**

Identification code	**4a**
Empirical formula	$C_{21}H_{14}O_4$
Formula weight	330.32
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$

a/Å	9.4615(3)
b/Å	7.4413(3)
c/Å	22.9597(7)
α/°	90
β/°	97.165(3)
γ/°	90
Volume/Å^3	1603.87(10)
Z	4
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	0.776
F(000)	688.0
Crystal size/mm^3	0.17 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.762 to 141.562
Index ranges	-11 ≤ h ≤ 7, -8 ≤ k ≤ 8, -27 ≤ l ≤ 28
Reflections collected	6385
Independent reflections	3019 [R_{int} = 0.0263, R_{sigma} = 0.0330]
Data/restraints/parameters	3019/0/228
Goodness-of-fit on F^2	1.025
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1253
Final R indexes [all data]	R_1 = 0.0609, wR_2 = 0.1411
Largest diff. peak/hole / e Å^{-3}	0.20/-0.26

7.3 Crystal structure of 6

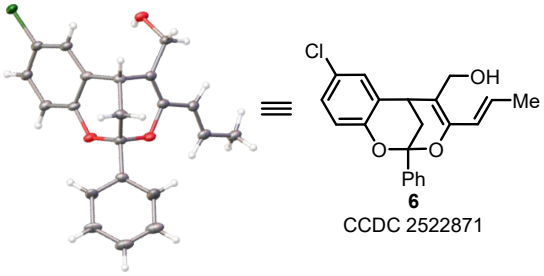


Table S9. Crystal data and structure refinement for **6**

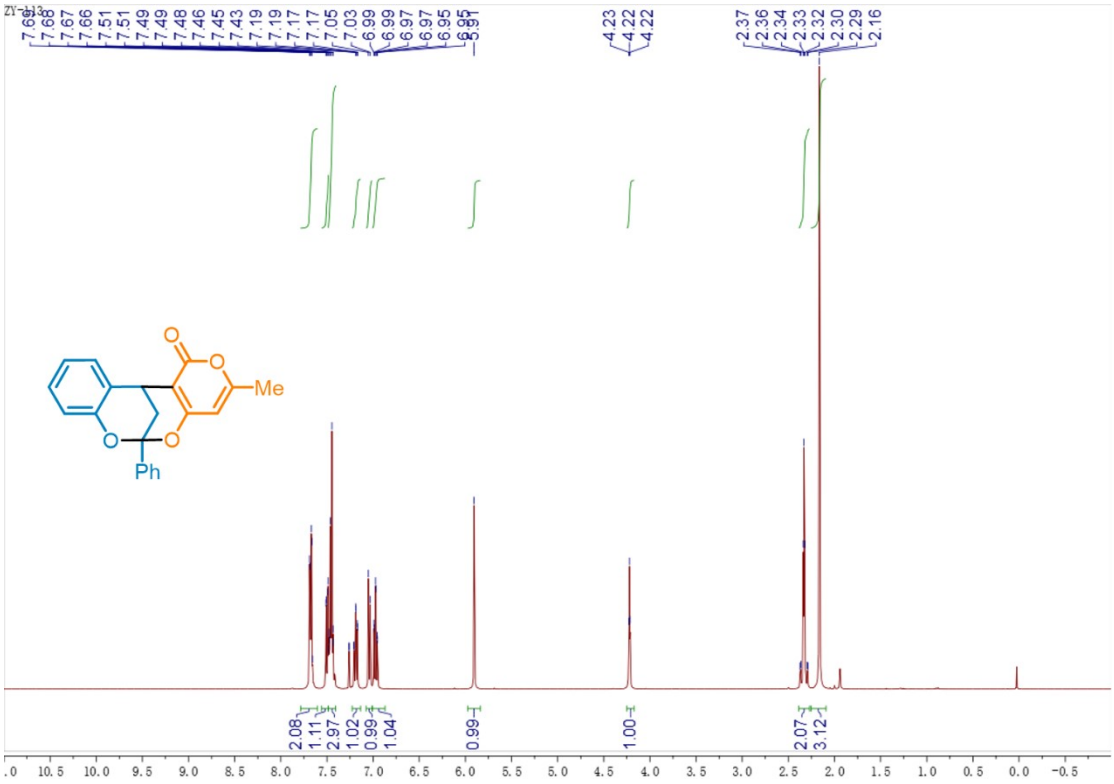
Identification code	**6**
Formula weight	354.81
Temperature/K	100.08(14)
Crystal system	monoclinic
Space group	I2
a/Å	11.2354(5)
b/Å	5.1466(2)
c/Å	30.3740(12)
α/°	90
β/°	97.699(4)
γ/°	90
Volume/Å^3	1740.52(12)
Z	4
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	2.080
F(000)	744.0
Crystal size/mm^3	0.15 × 0.14 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.09 to 133.202
Index ranges	-13 ≤ h ≤ 13, -4 ≤ k ≤ 5, -35 ≤ l ≤ 36
Reflections collected	8907
Independent reflections	2560 [R_{int} = 0.0709, R_{sigma} = 0.0385]
Data/restraints/parameters	2560/247/254
Goodness-of-fit on F^2	1.658
Final R indexes [I>=2σ (I)]	R_1 = 0.1242, wR_2 = 0.3376
Final R indexes [all data]	R_1 = 0.1275, wR_2 = 0.3428
Largest diff. peak/hole / e Å^{-3}	0.95/-0.53

8. REFERENCE

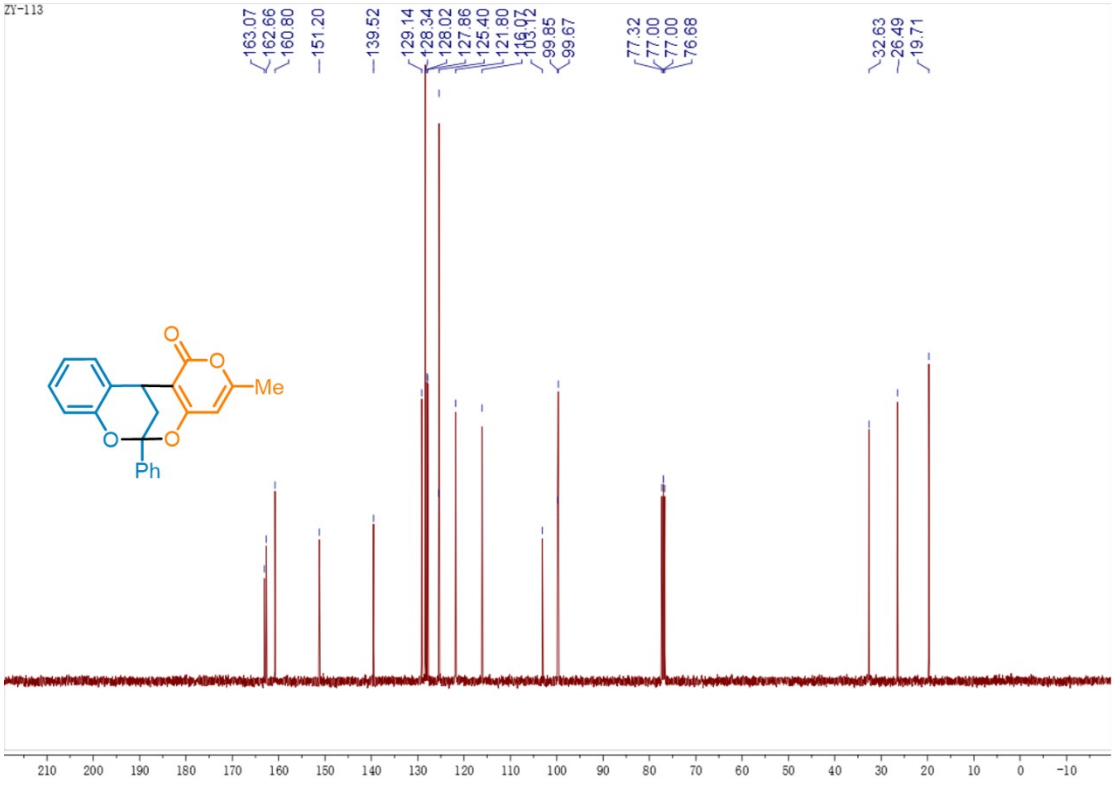
1. (a) Zhu, Y.- S.; Guo, J.; Jin, S.-J.; Guo, J.-M.; Bai, X.-G.; Wang, Q.-L.; Bu, Z.-W. Construction of bridged cyclic *N*,*O*-ketal spirooxindoles through a Michael addition/*N*,*O*-ketalization sequence. *Org. Biomol. Chem.*, **2018**, *16*, 1751-1759. (b) Guo, J.-M.; Bai, X.-G.; Wang, Q.-L.; Bu, Z.-W. Diastereoselective Construction of Indole-Bridged Chroman Spirooxindoles through a TfOH-Catalyzed Michael Addition-Inspired Cascade Reaction. *J. Org. Chem.*, **2018**, *83*, 3679-3687. (c) Wang, W.-B.; Bai, X.-G.; Jin, S.-J.; Guo, J.-M.; Zhao, Y.; Miao, H.-J.; Zhu, Y.-S.; Wang, Q.-L.; Bu, Z.-W. An unexpected $FeCl_3$-catalyzed cascade reaction of indoles and o-hydroxychalcones for the assembly of chromane-bridged polycyclic indoles. *Org. Lett.*, **2018**, *20*, 3451-3454. (d) Jin, S.-J.; Guo, J.; Fang, D.-M.; Huang, Y.-W.; Wang, Q.-L.; Bu, Z.-W. A Brønsted Acid-Catalyzed Michael Addition/Cyclization Sequence for the Diastereoselective Assembly of Chroman-Bridged Polycyclic Isoindolinones. *Adv. Synth. Catal.,* **2019**, *361*, 456-461. (e) Guo, J.-M.; Miao, H.-J.; Zhao, Y.; Bai, X.-G.; Zhu, Y.-S.; Wang, Q.-L.; Bu, Z.-W. An unexpected multi-component one-pot cascade reaction to access furanobenzodihydropyran-fused polycyclic heterocycles. *Chem. Commun.,* **2019**, *55*, 5207-5210. (f) Jin, Z.-C.; Yang, R.-J.; Du, Y.; Tiwari, B.; Ganguly, R.; Chi, Y.-G, R. Enantioselective Intramolecular Formal [2+4] Annulation of Acrylates and *r,β*-Unsaturated Imines Catalyzed by Amino Acid Derived Phosphines. *Org. Lett.*, **2012**, *14*, 3226-3229.

9. NMR spectra

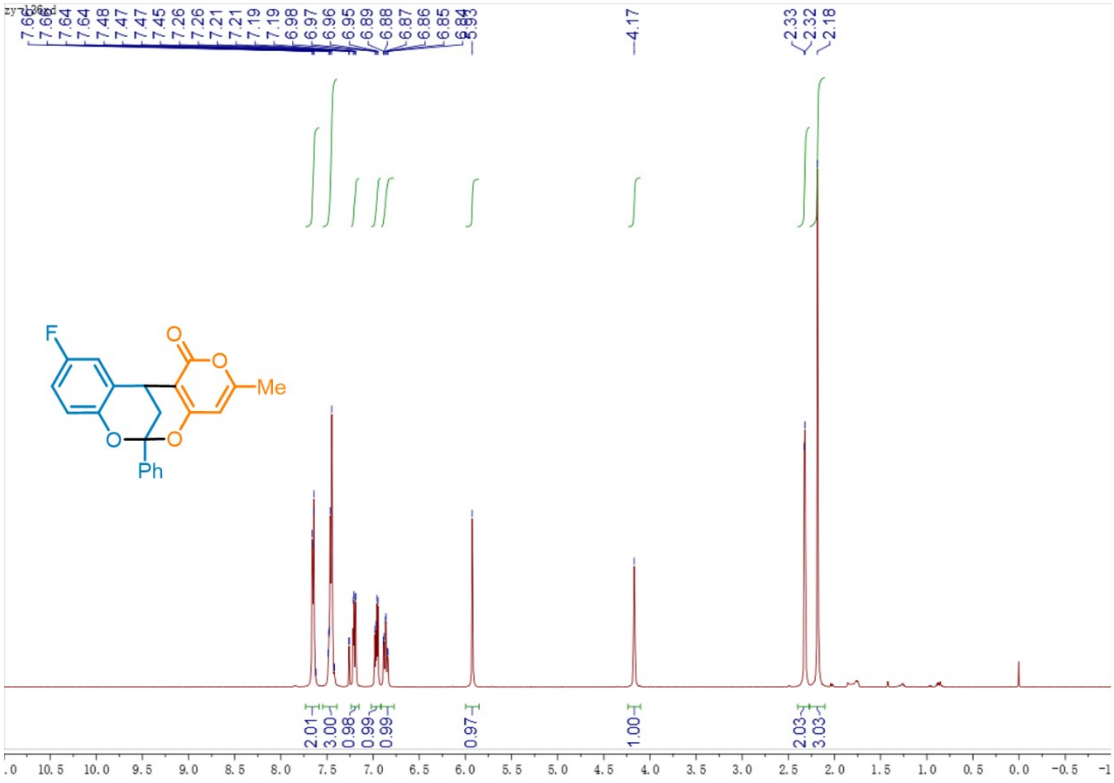
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



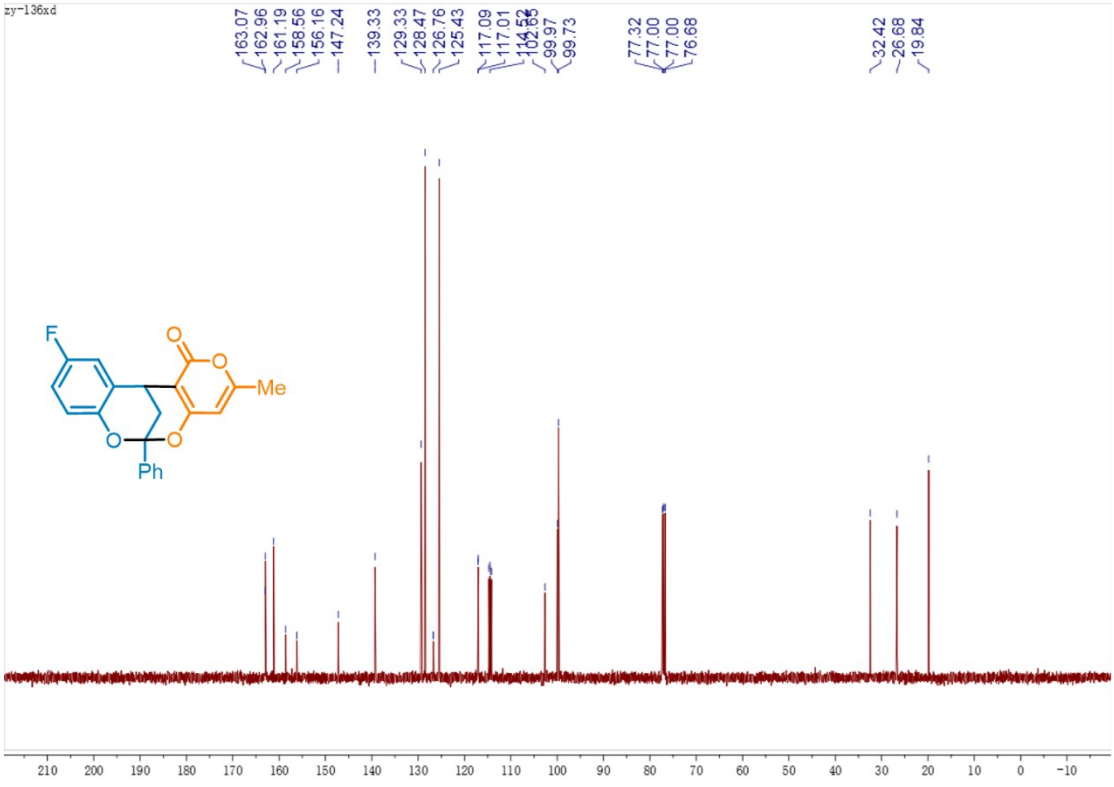
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



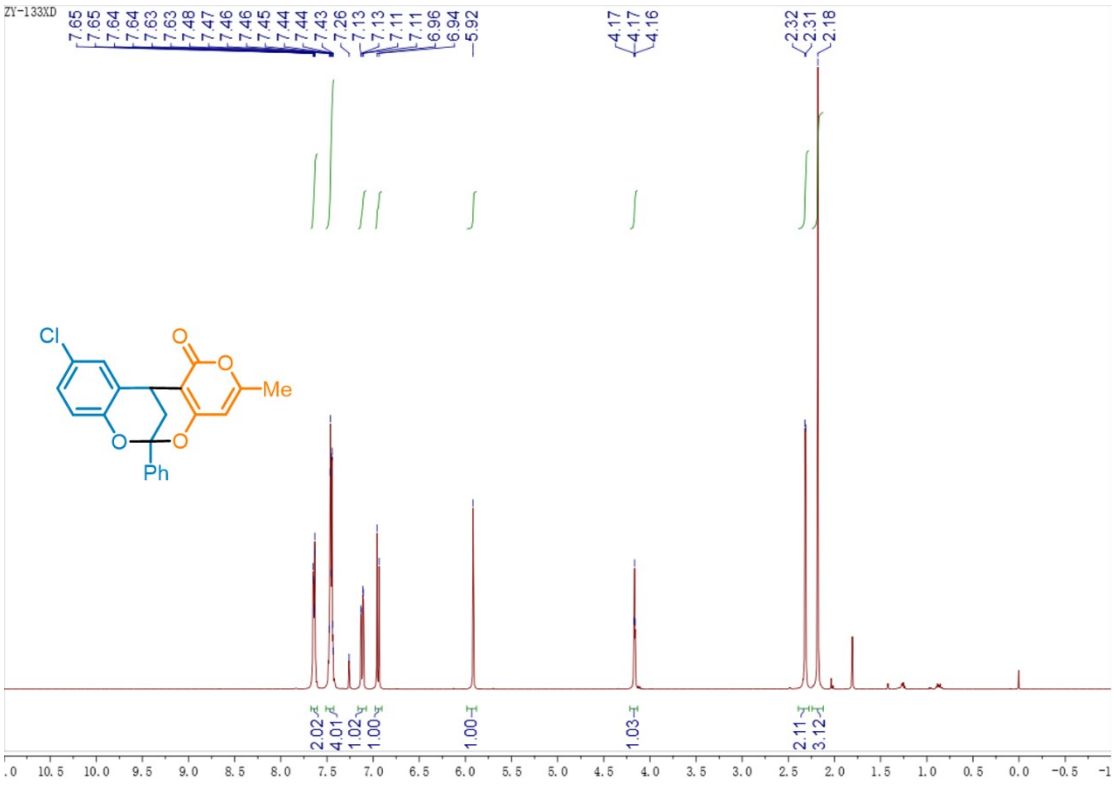
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



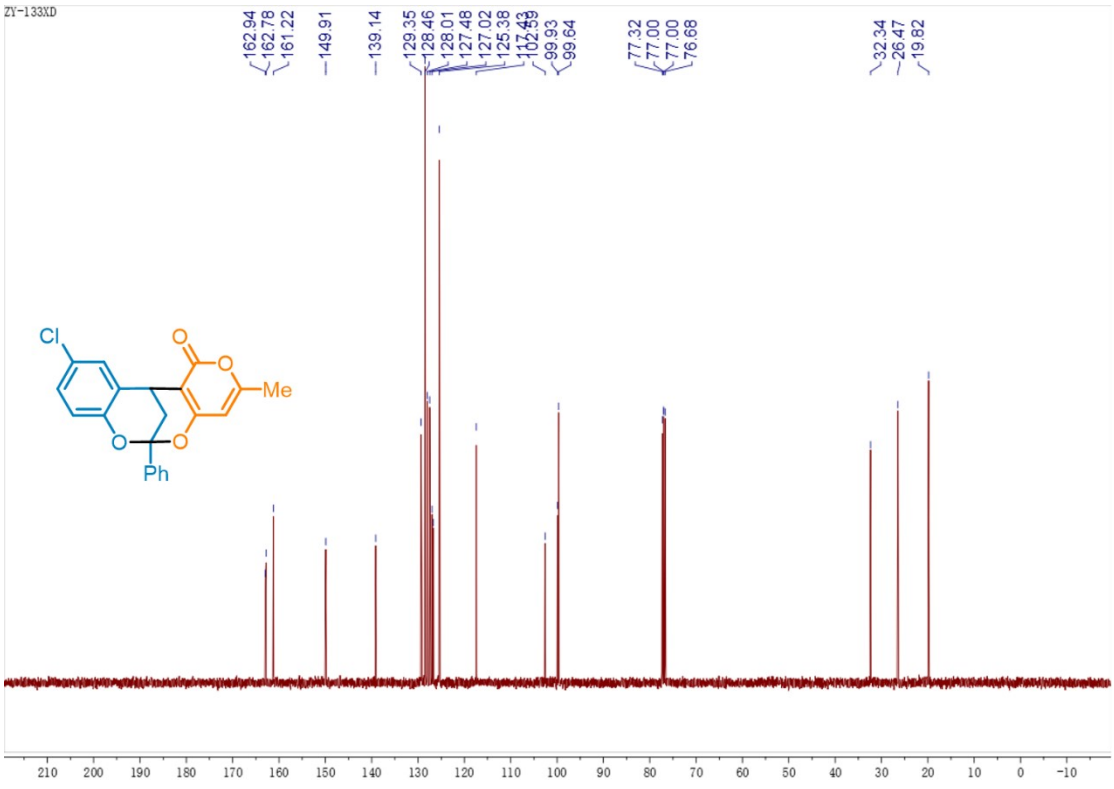
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



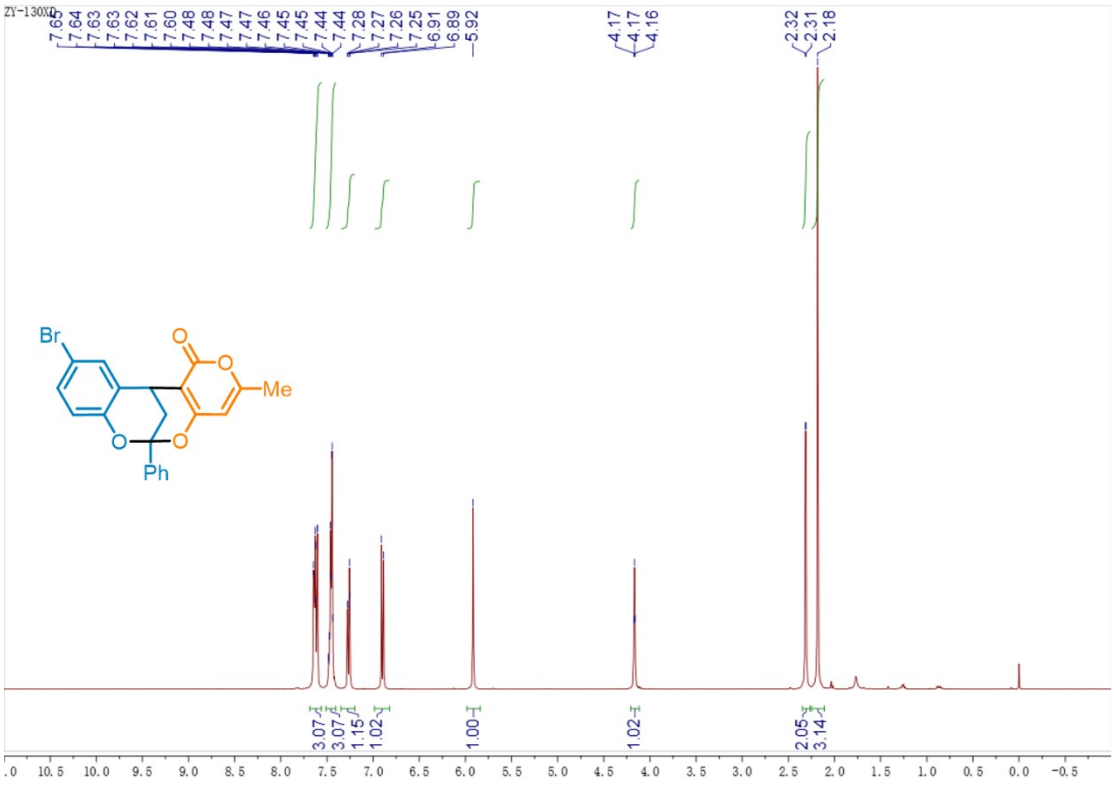
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



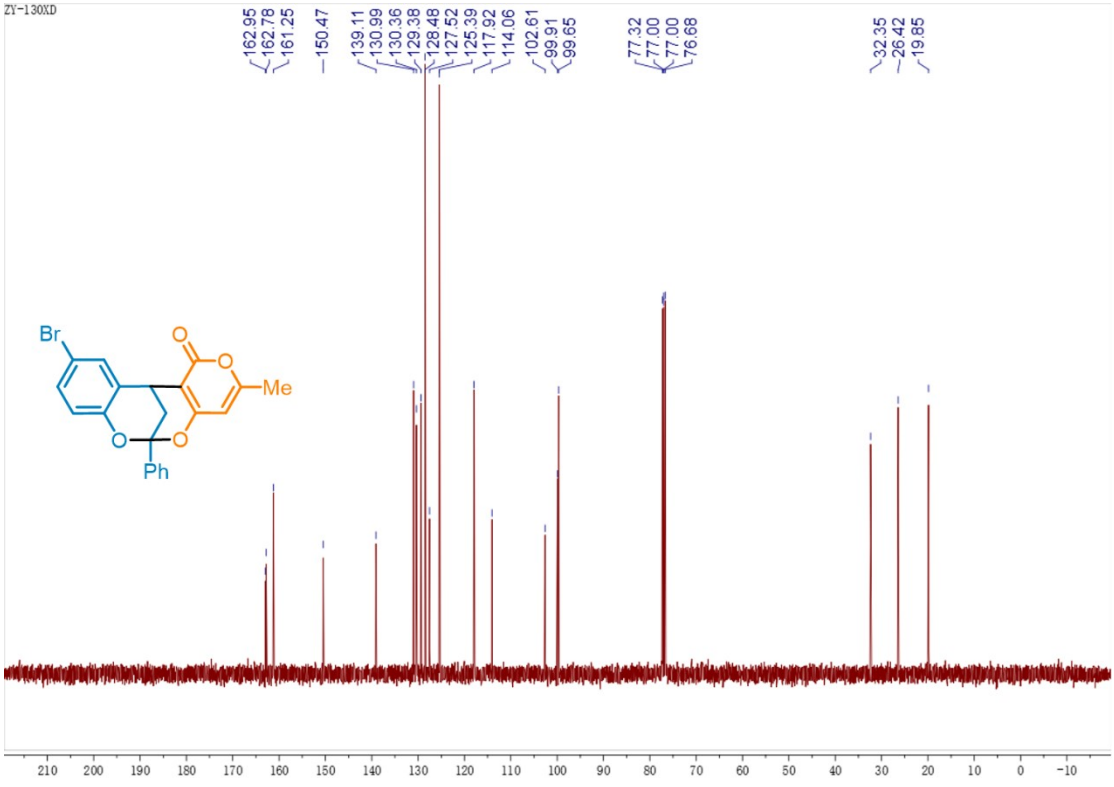
^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)



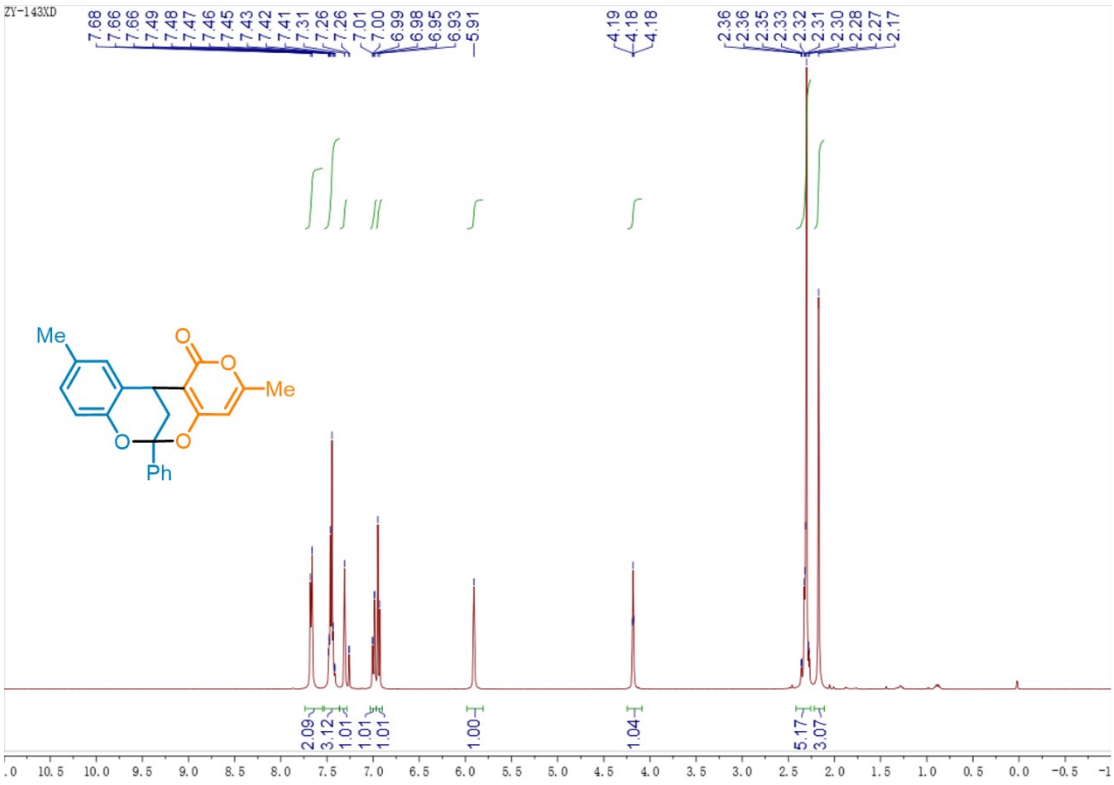
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



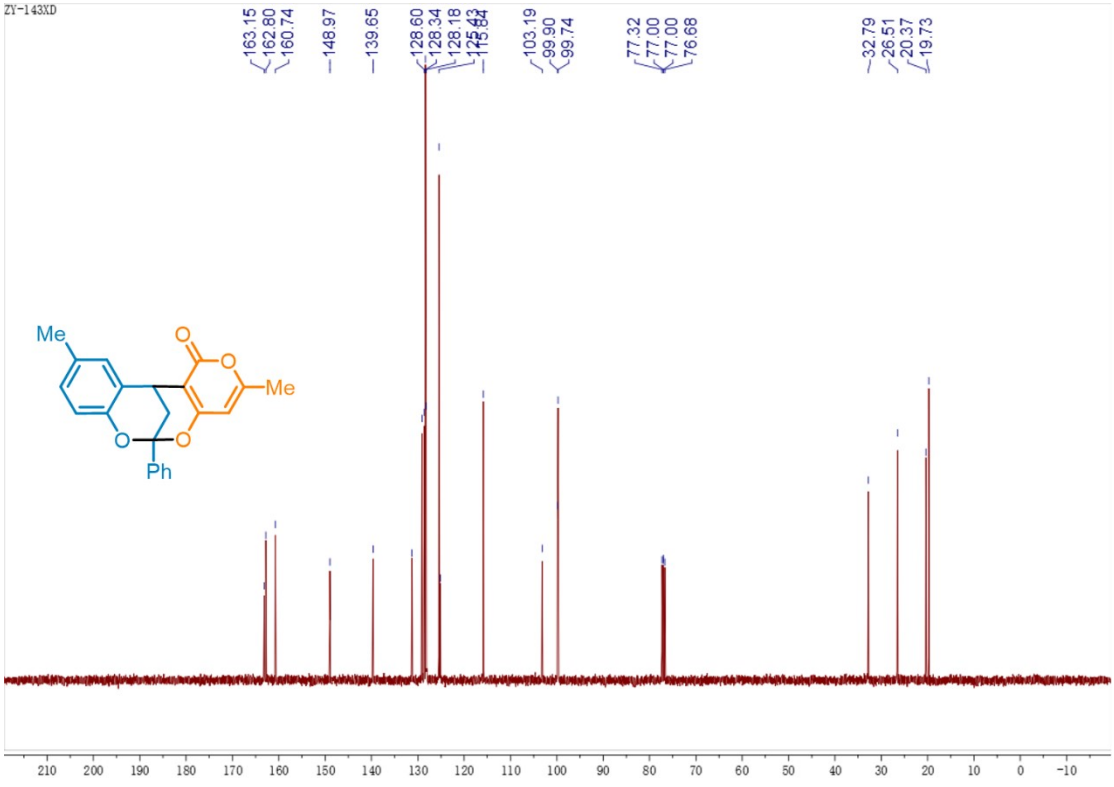
^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$)



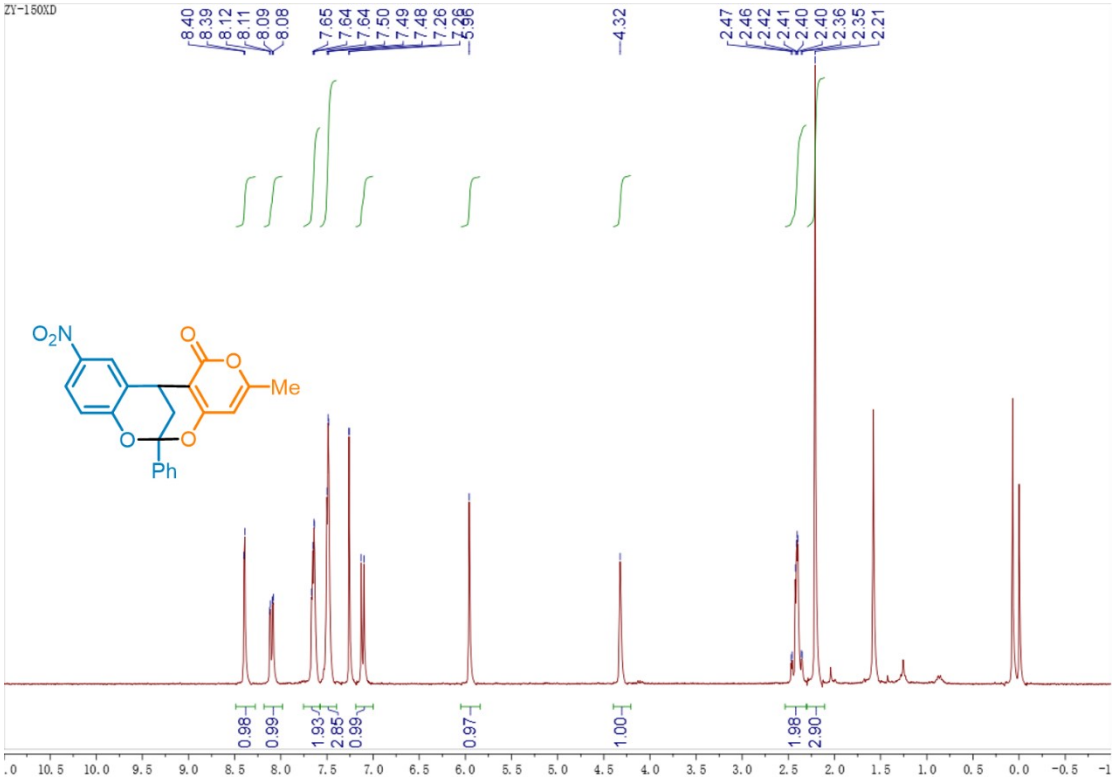
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



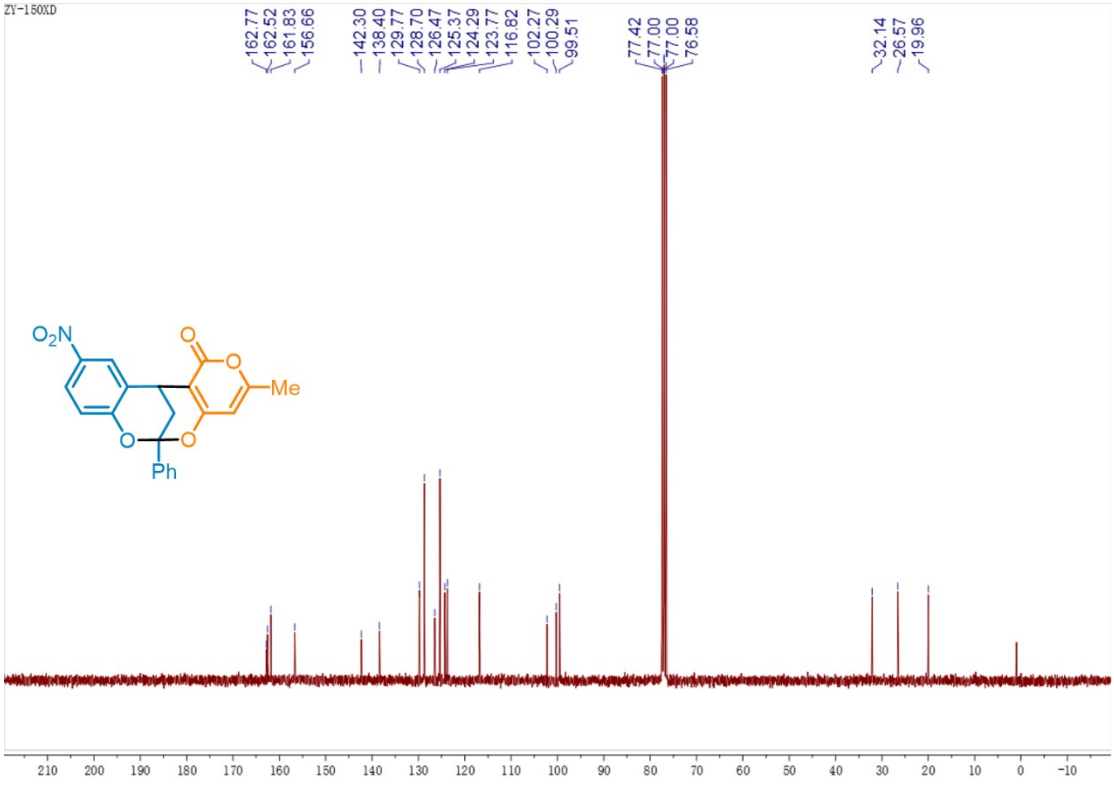
^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)



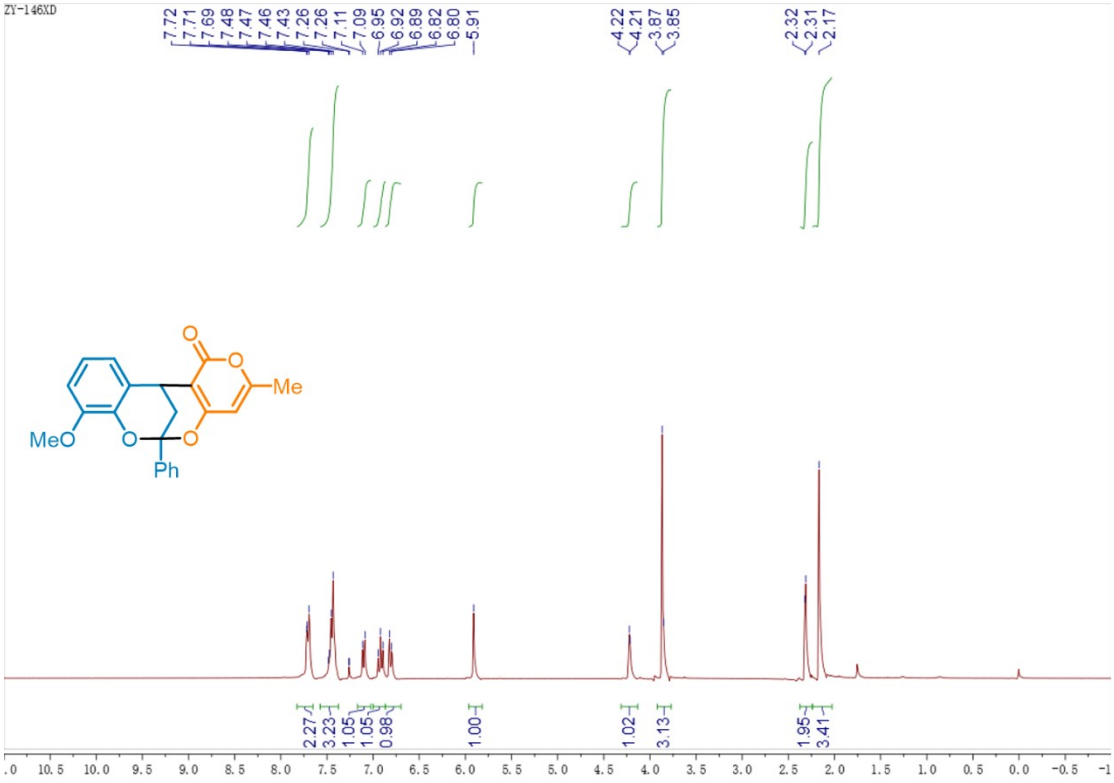
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



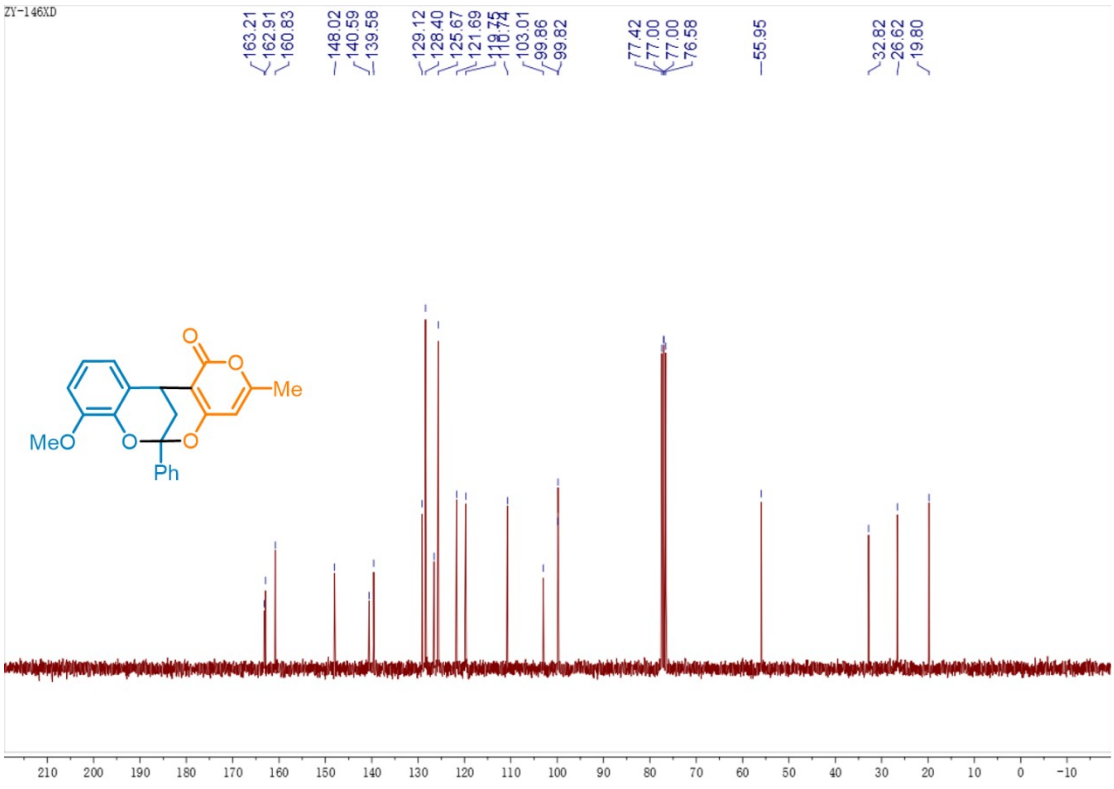
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



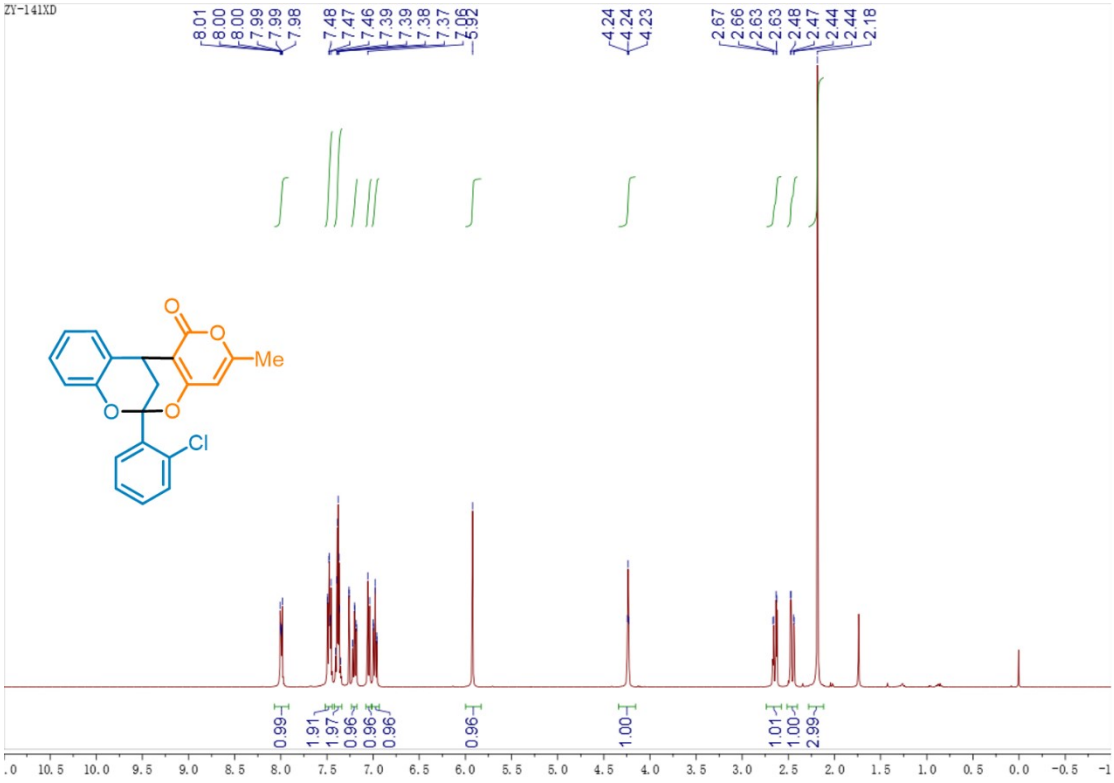
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



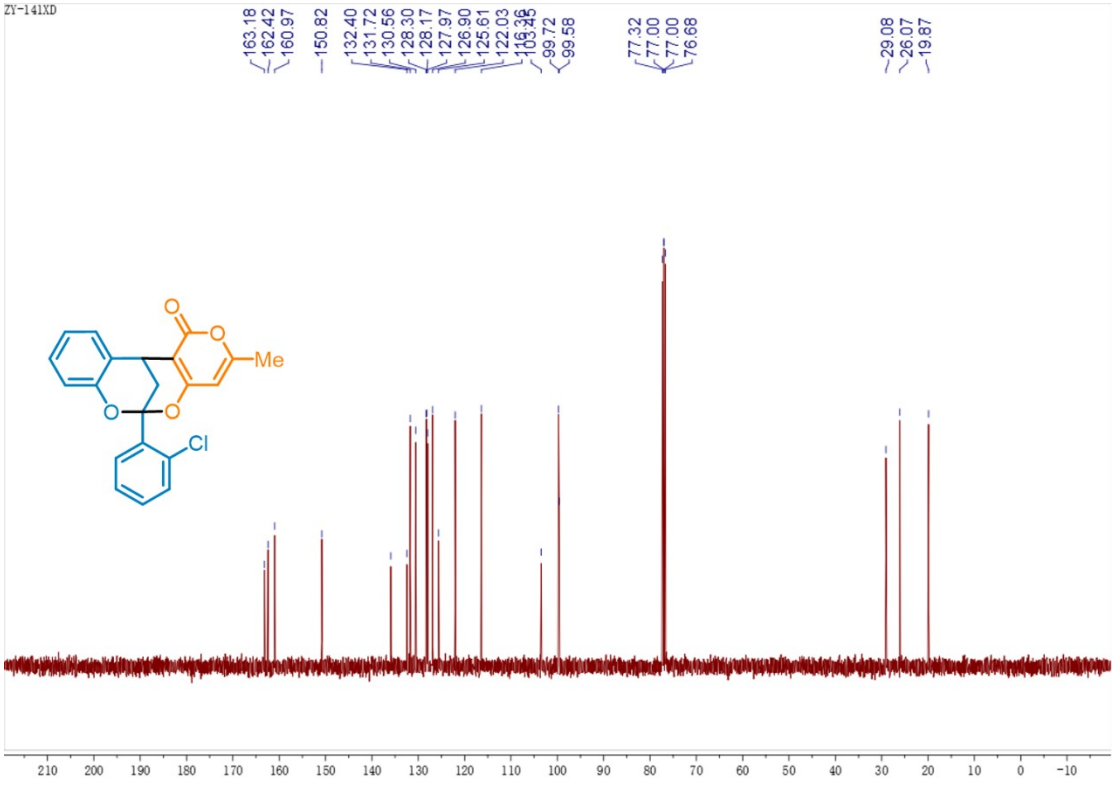
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



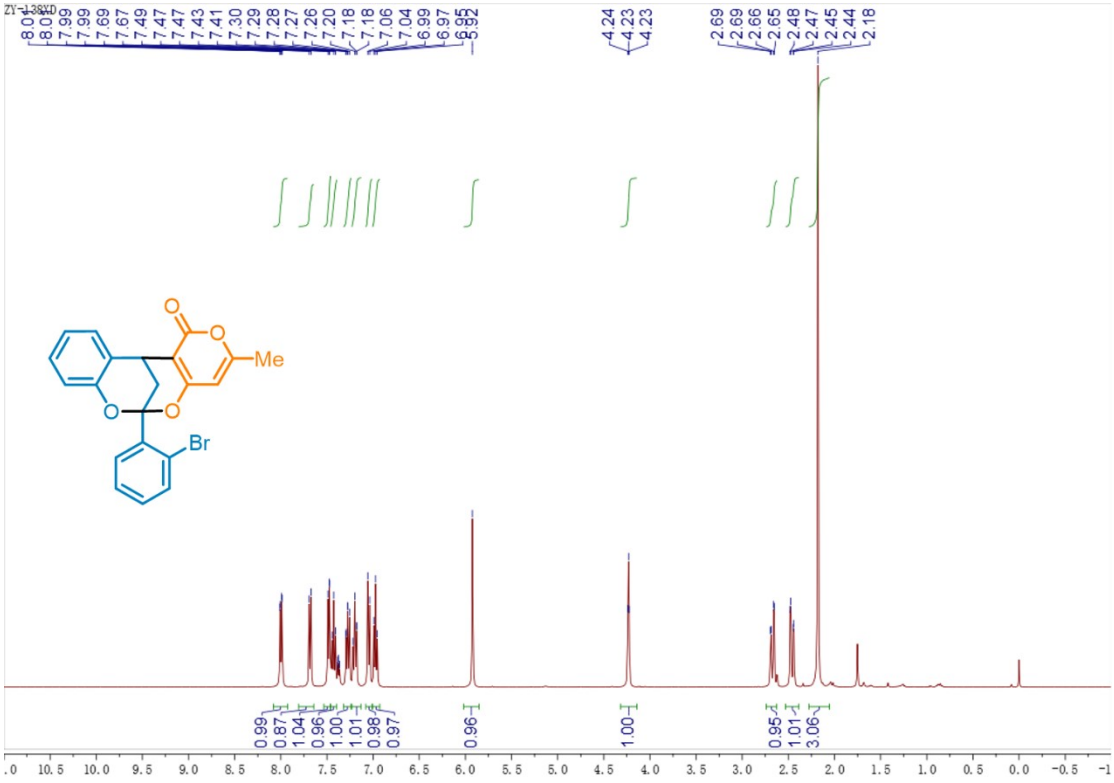
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



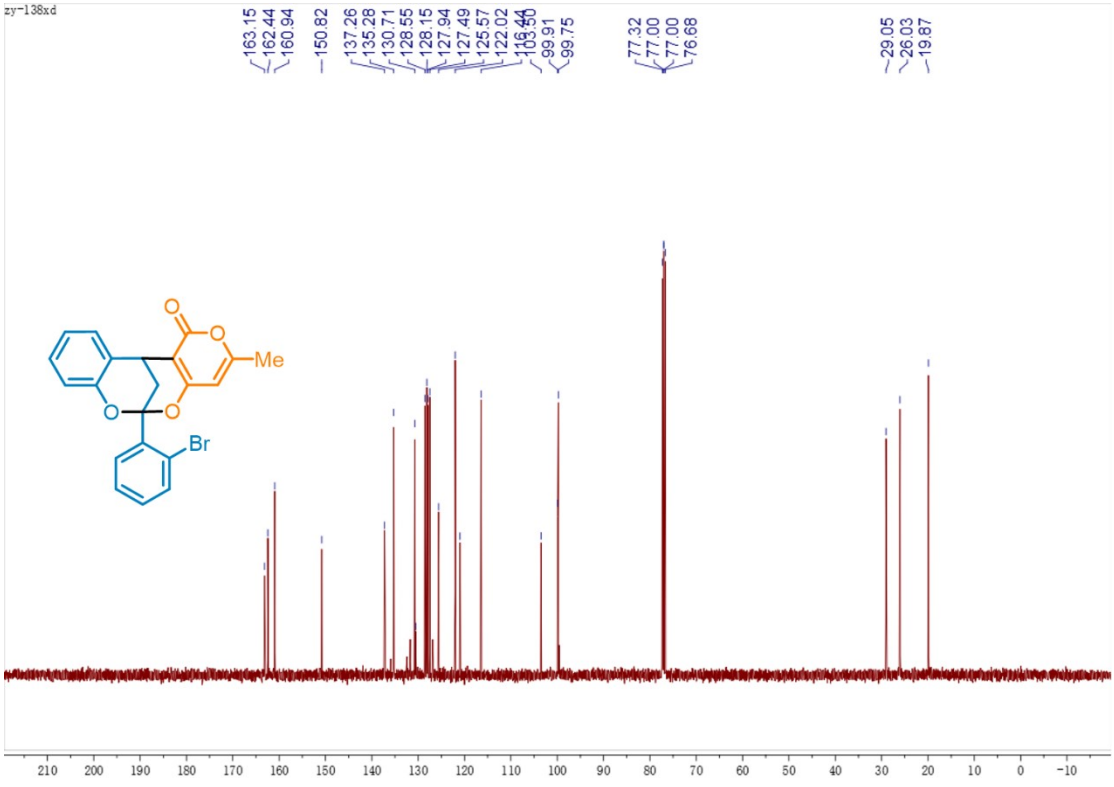
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



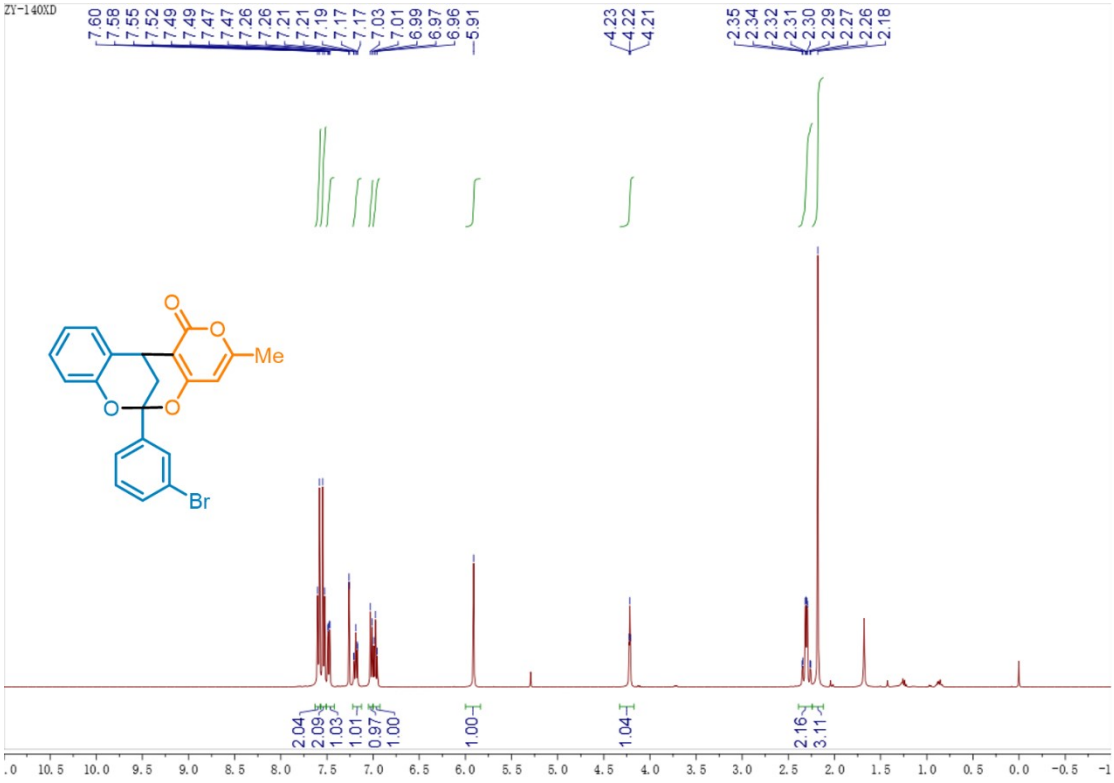
^{1}H NMR spectrum of **3i** (400 MHz, $CDCl_3$)



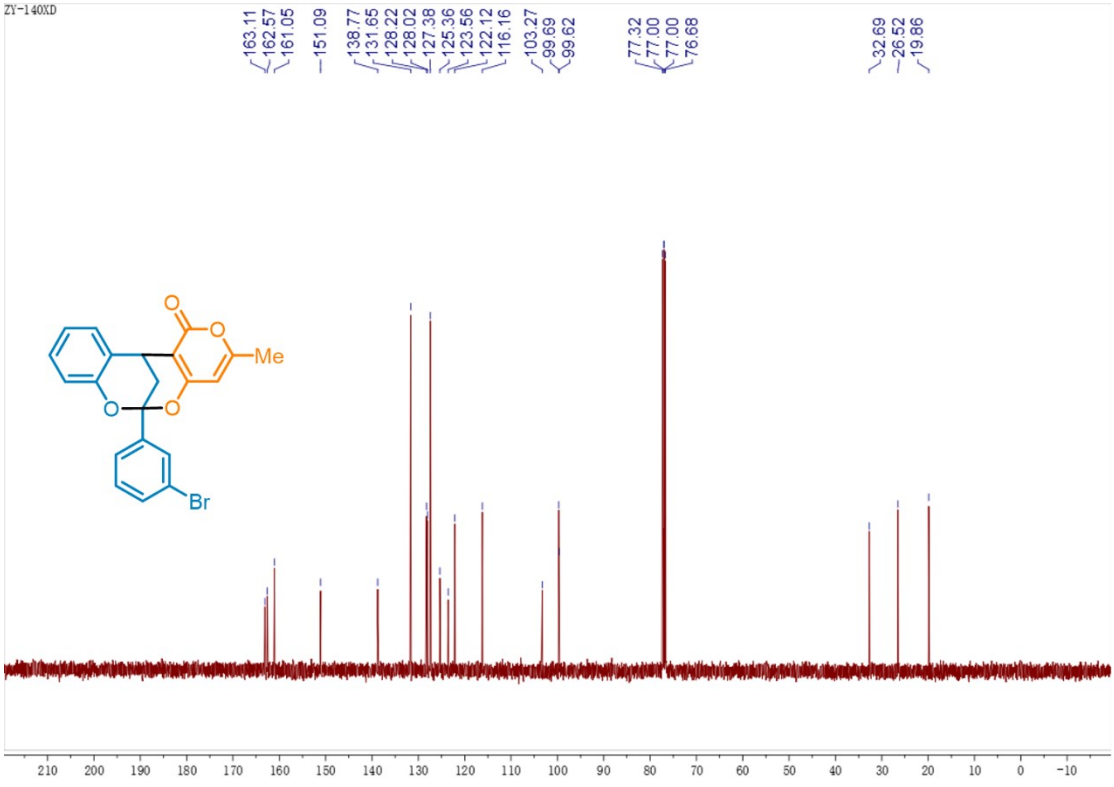
^{13}C NMR spectrum of **3i** (100 MHz, $CDCl_3$)



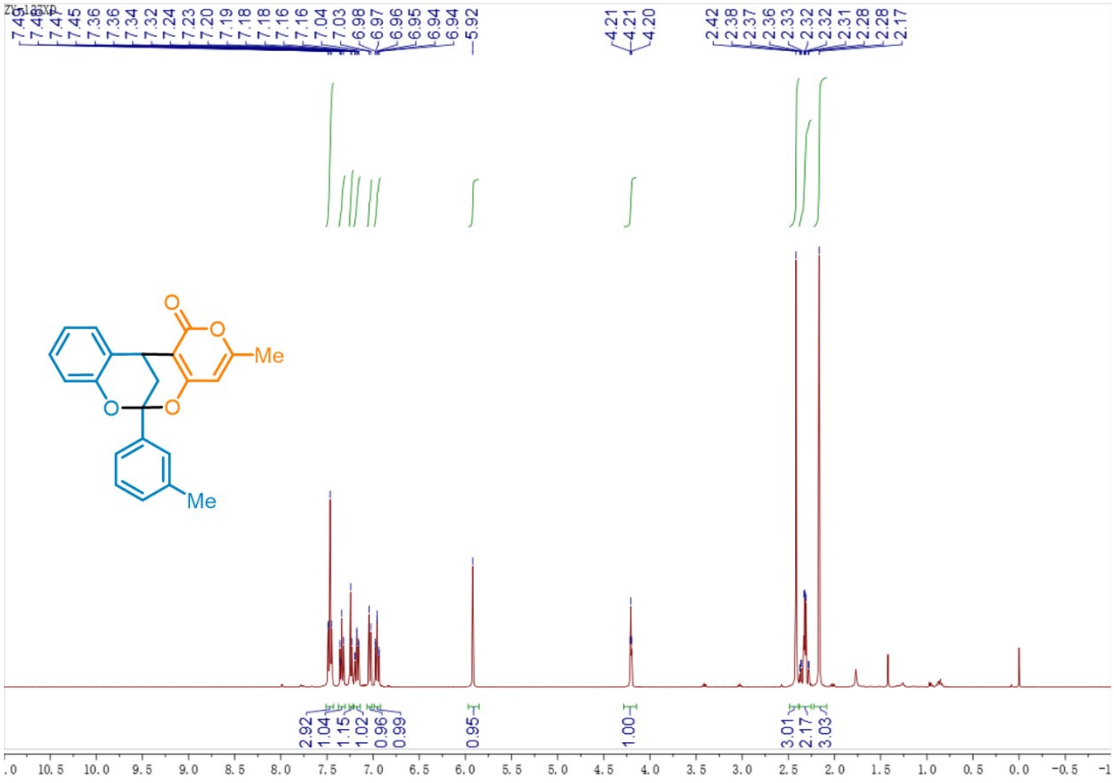
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



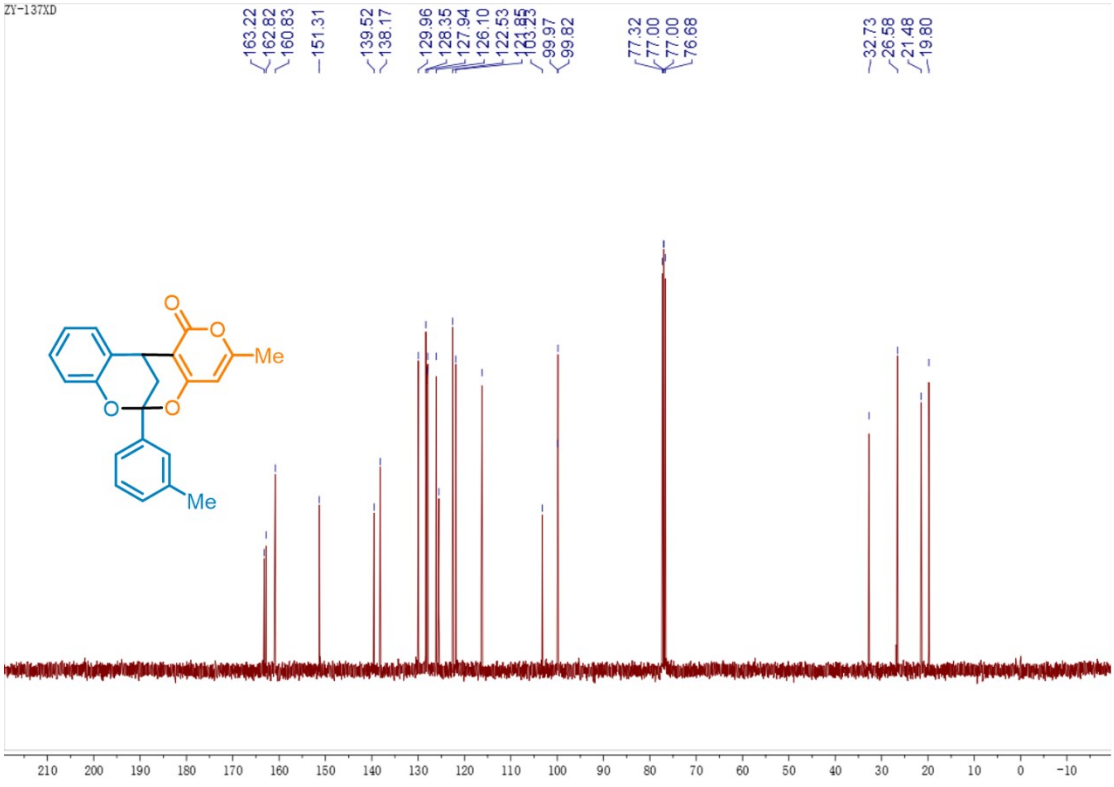
^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$)



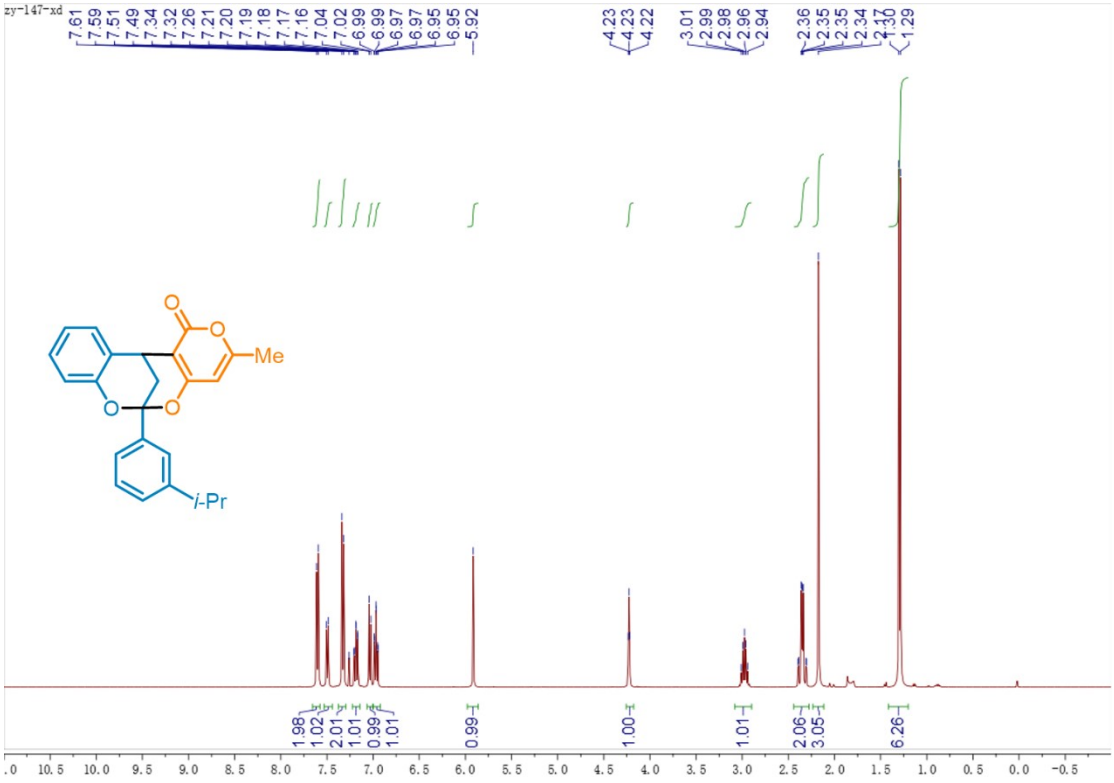
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



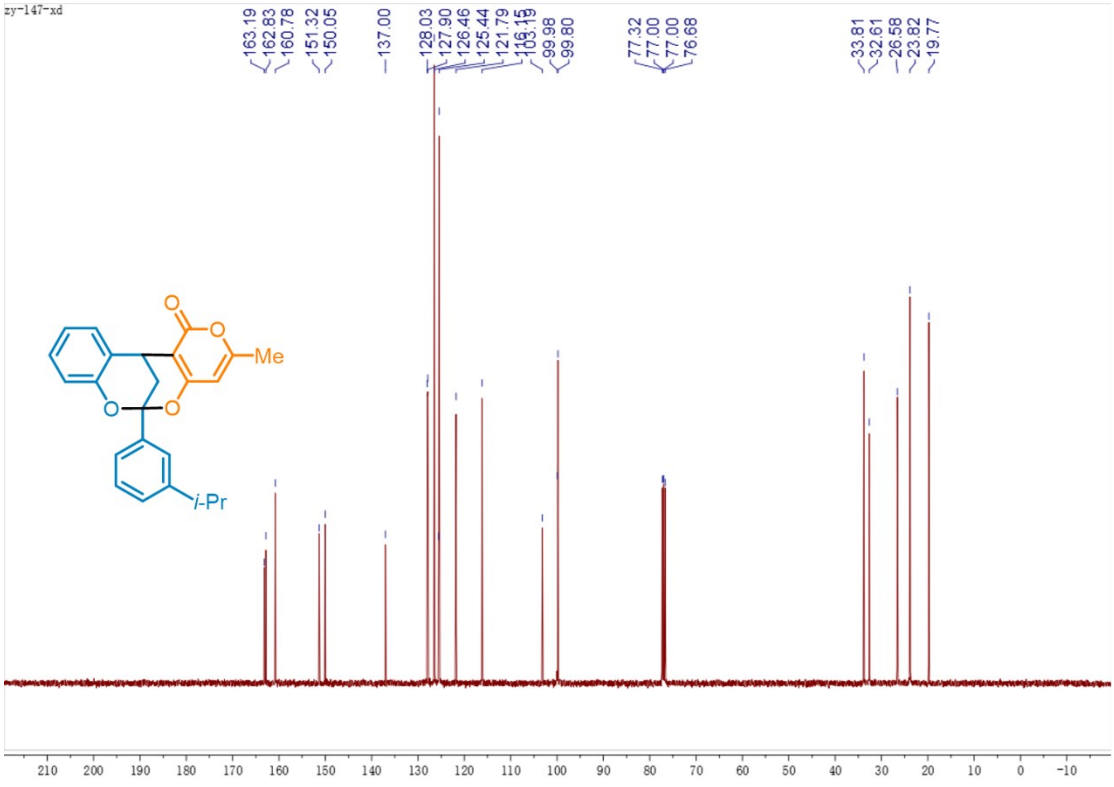
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



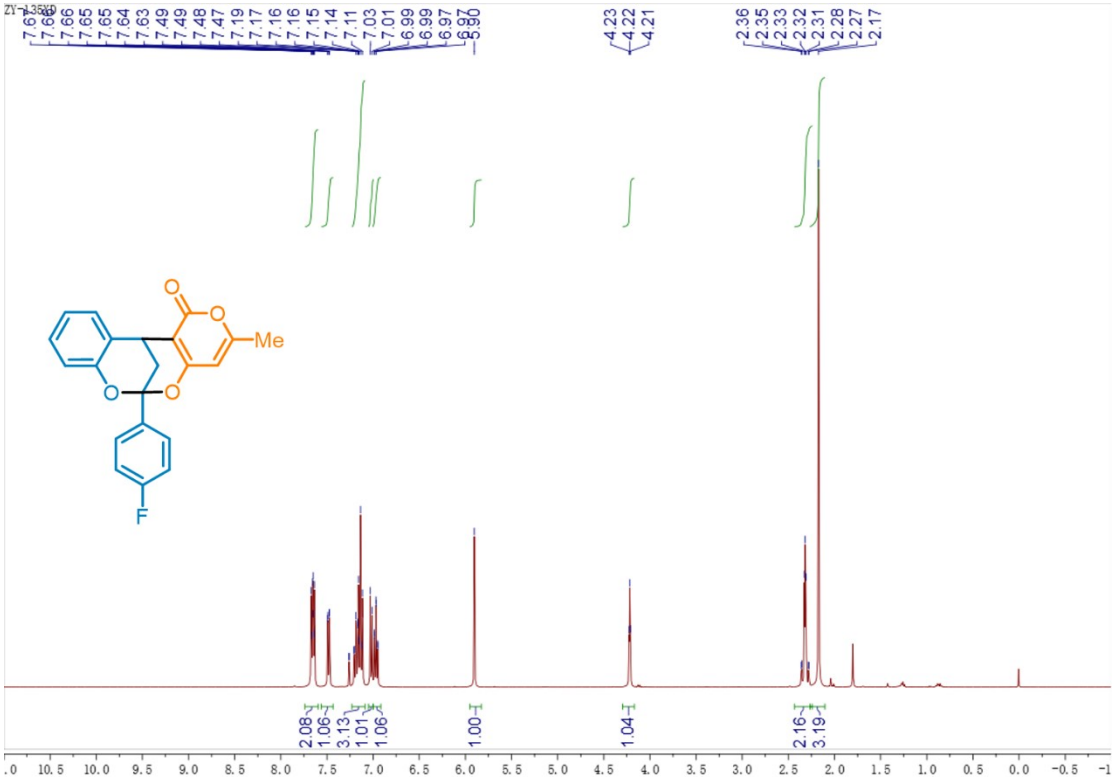
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



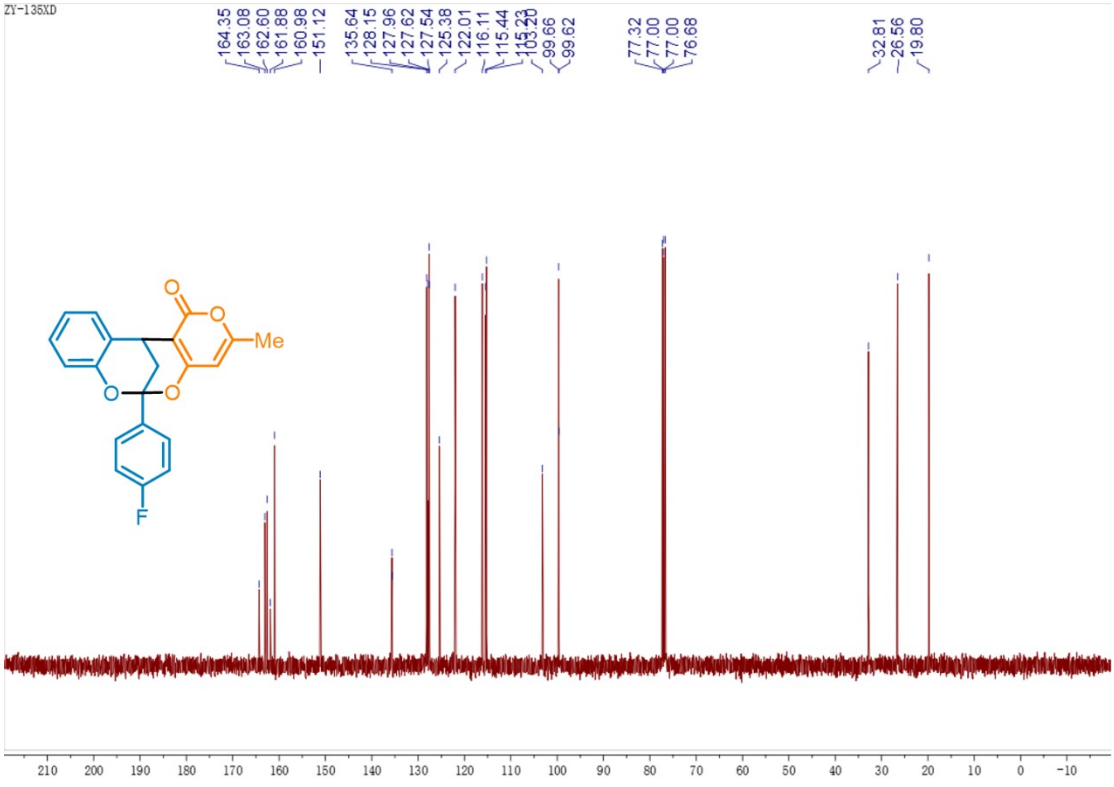
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



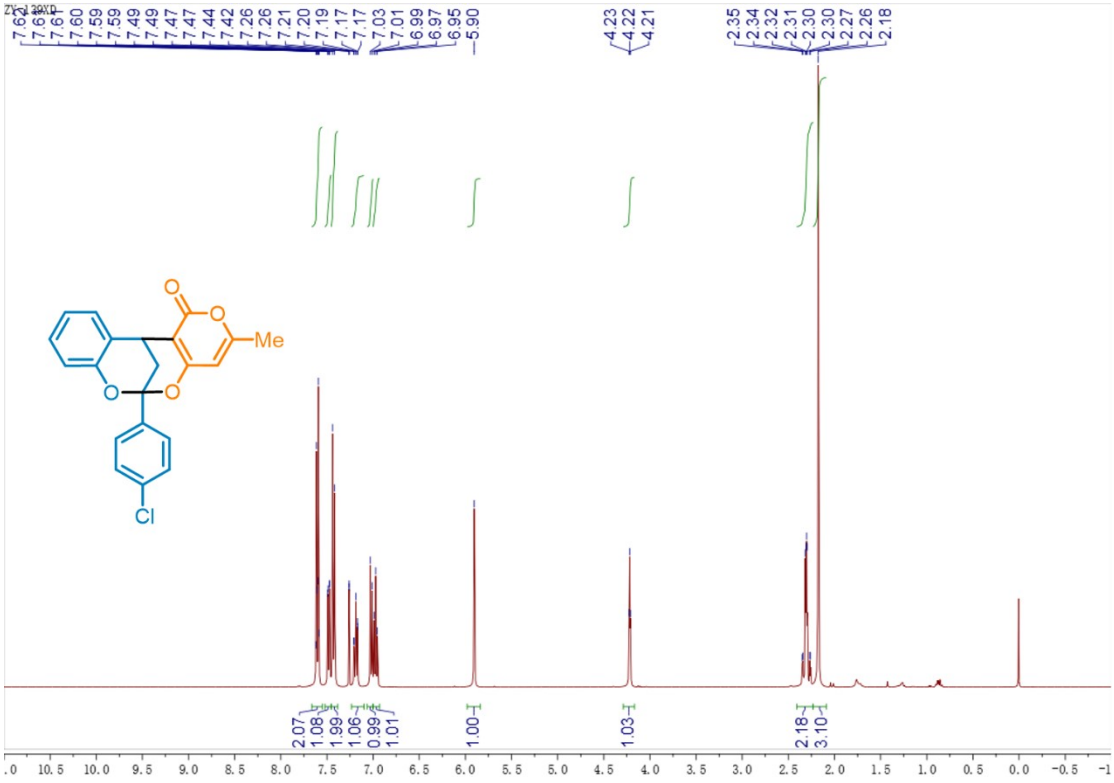
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



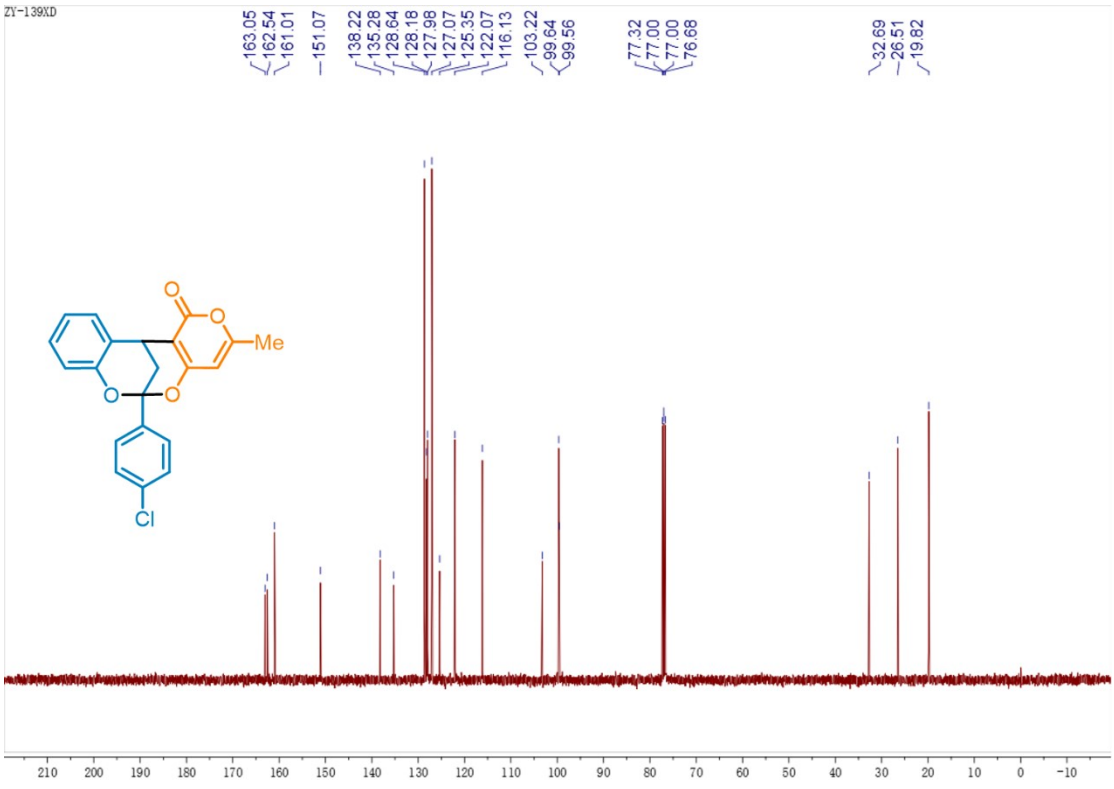
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



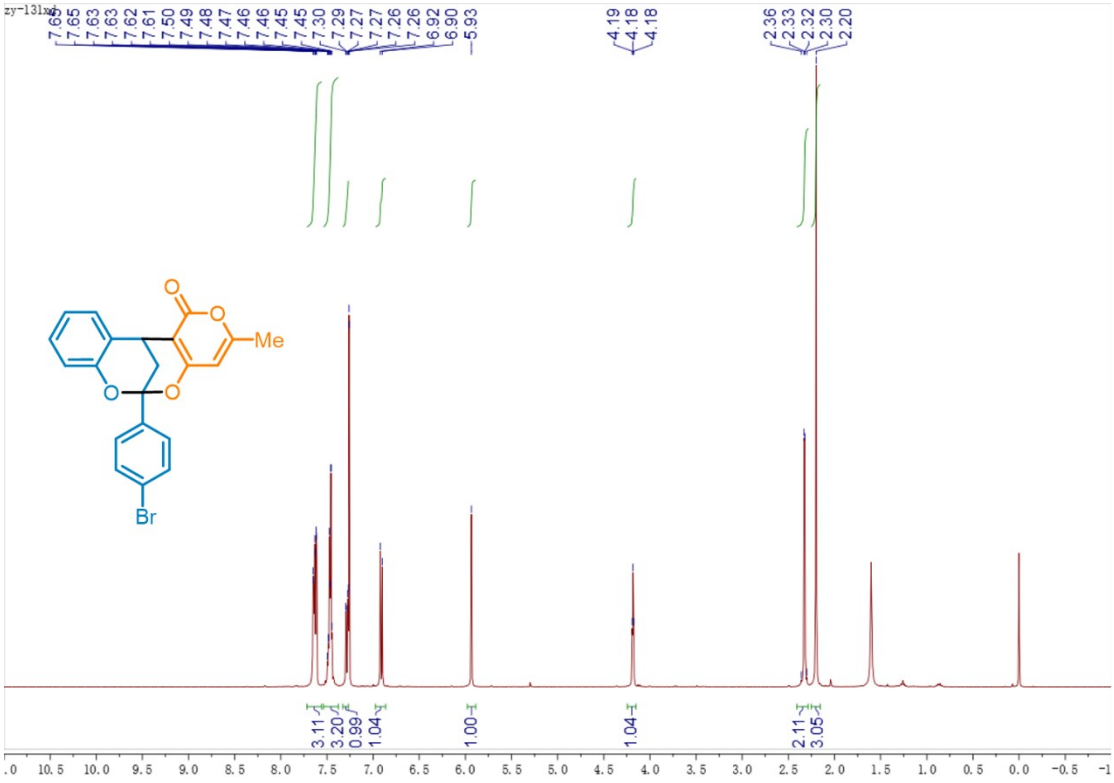
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



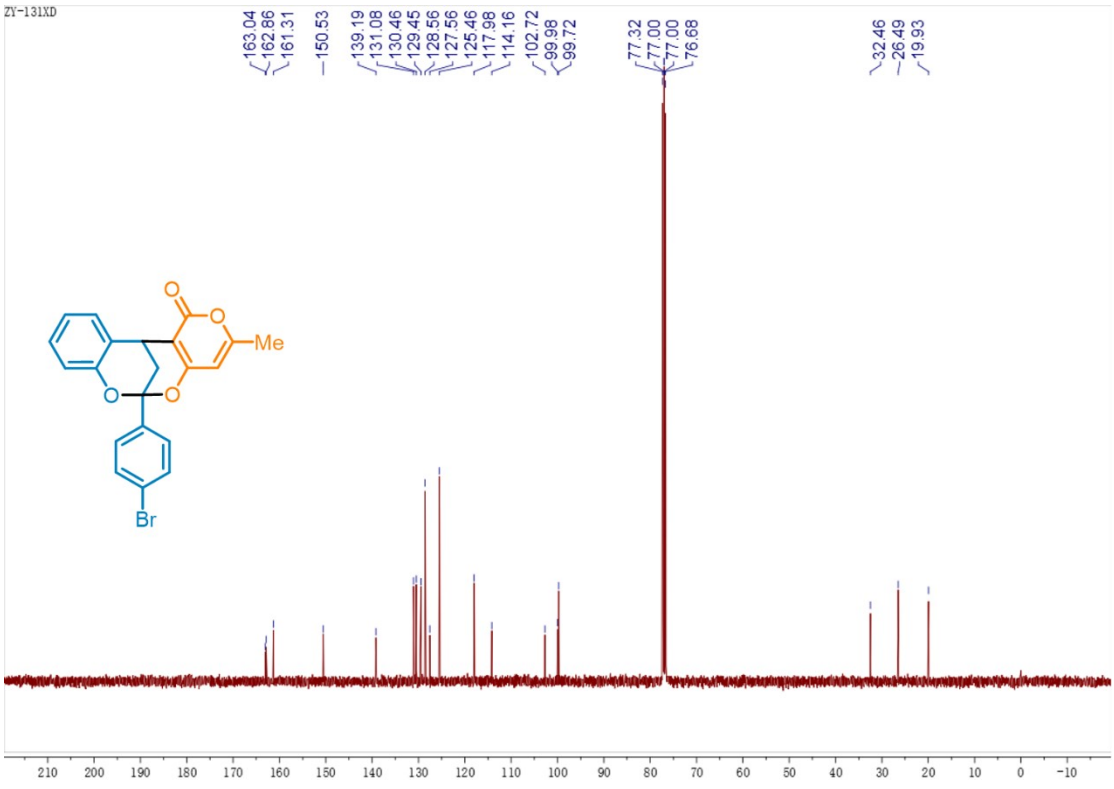
^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$)



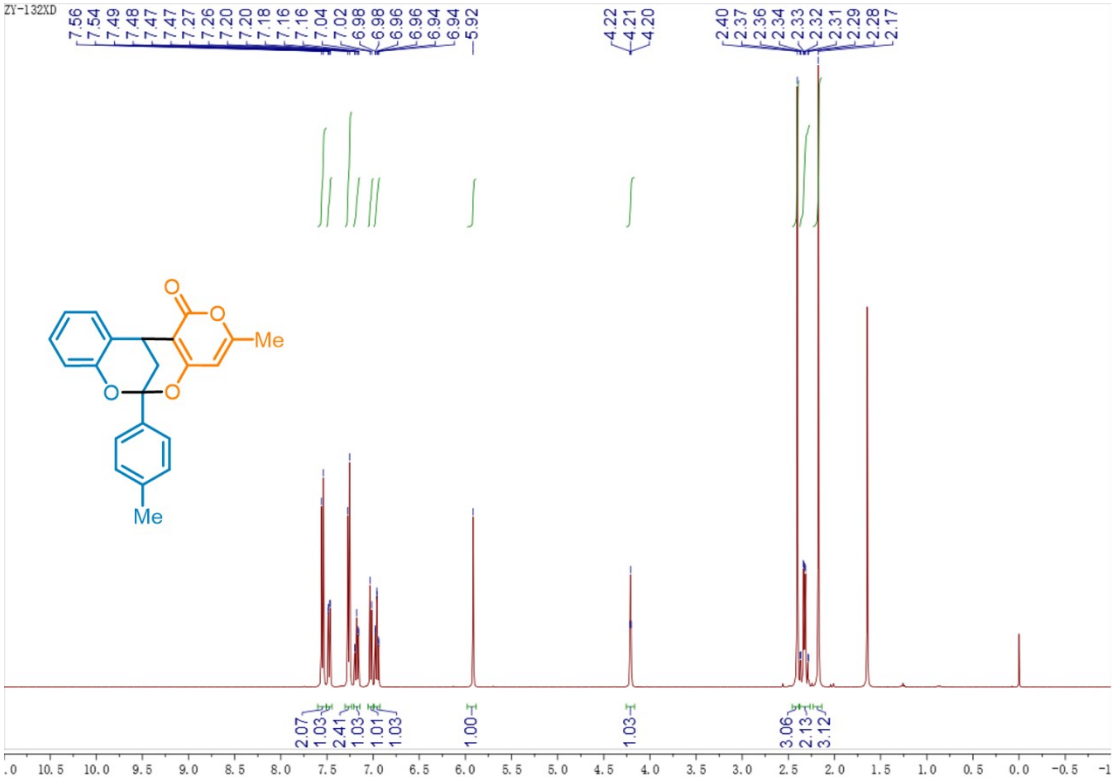
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



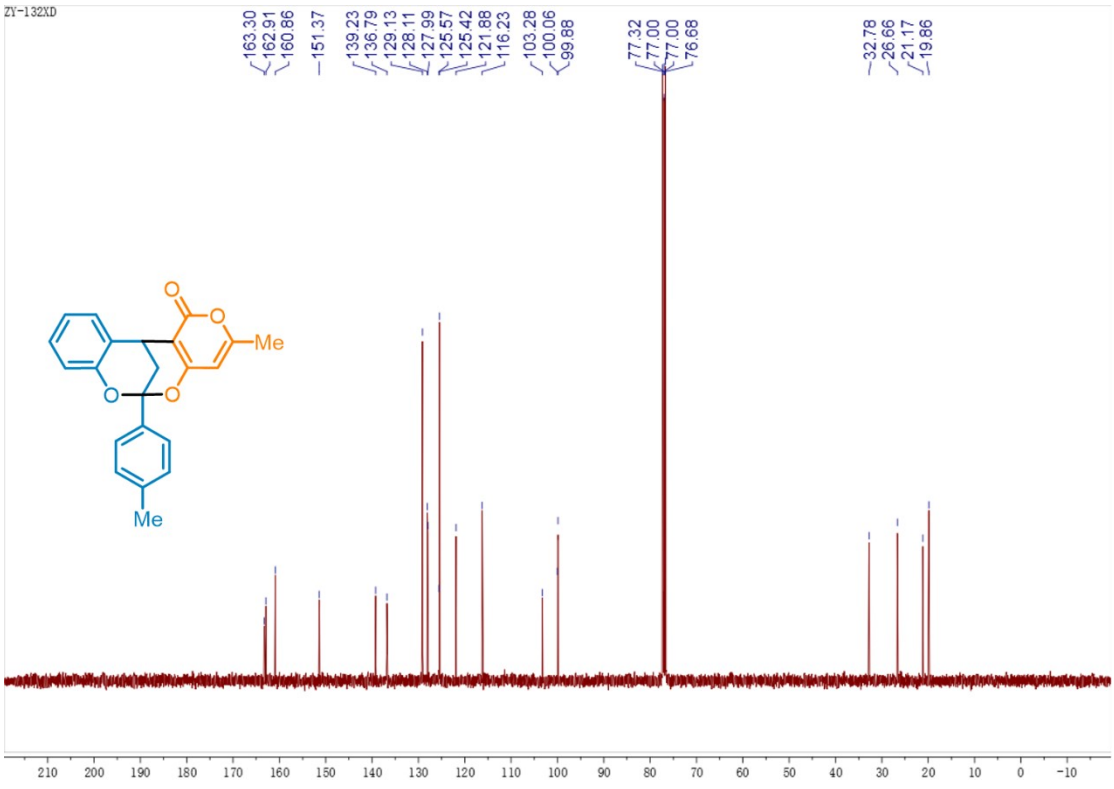
^{13}C NMR spectrum of **3o** (100 MHz, $CDCl_3$)



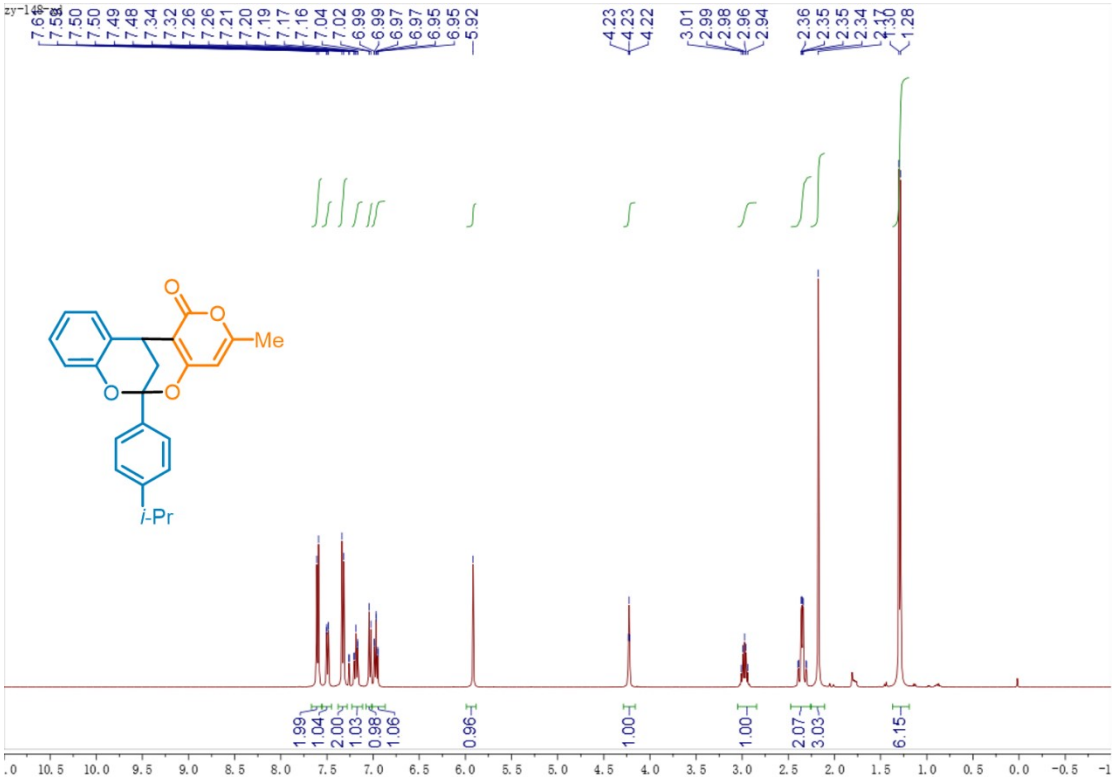
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



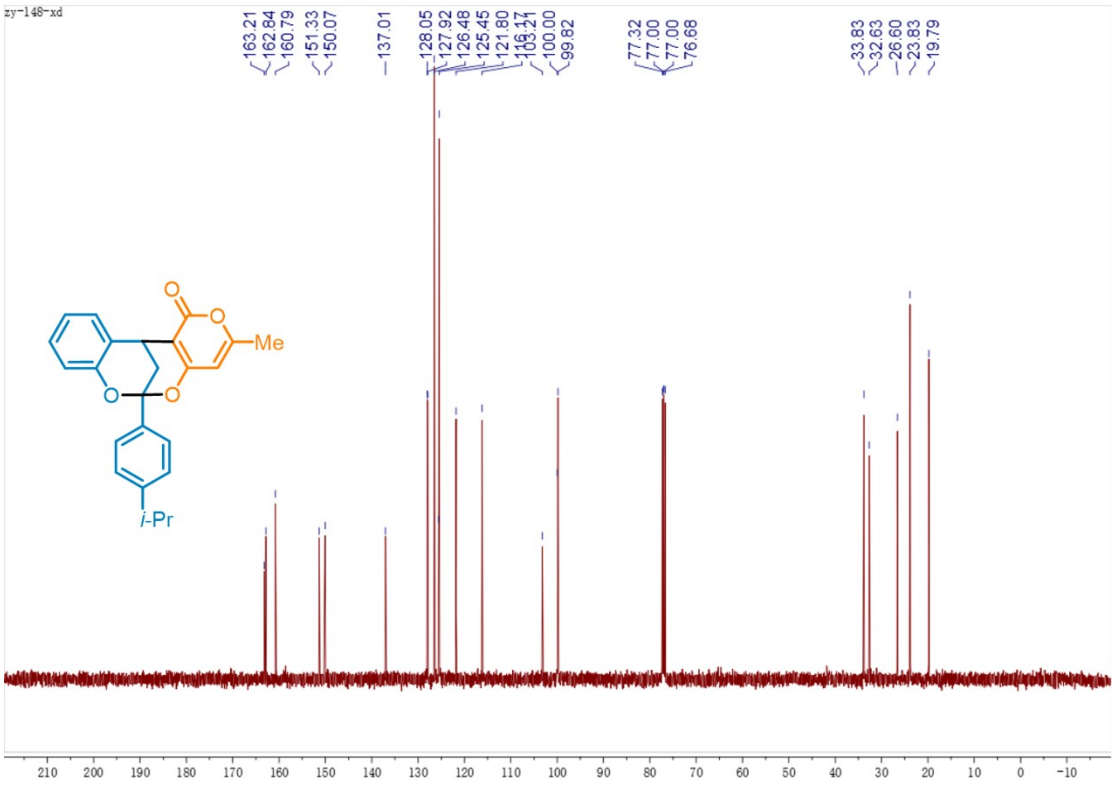
^{13}C NMR spectrum of **3p** (100 MHz, $CDCl_3$)



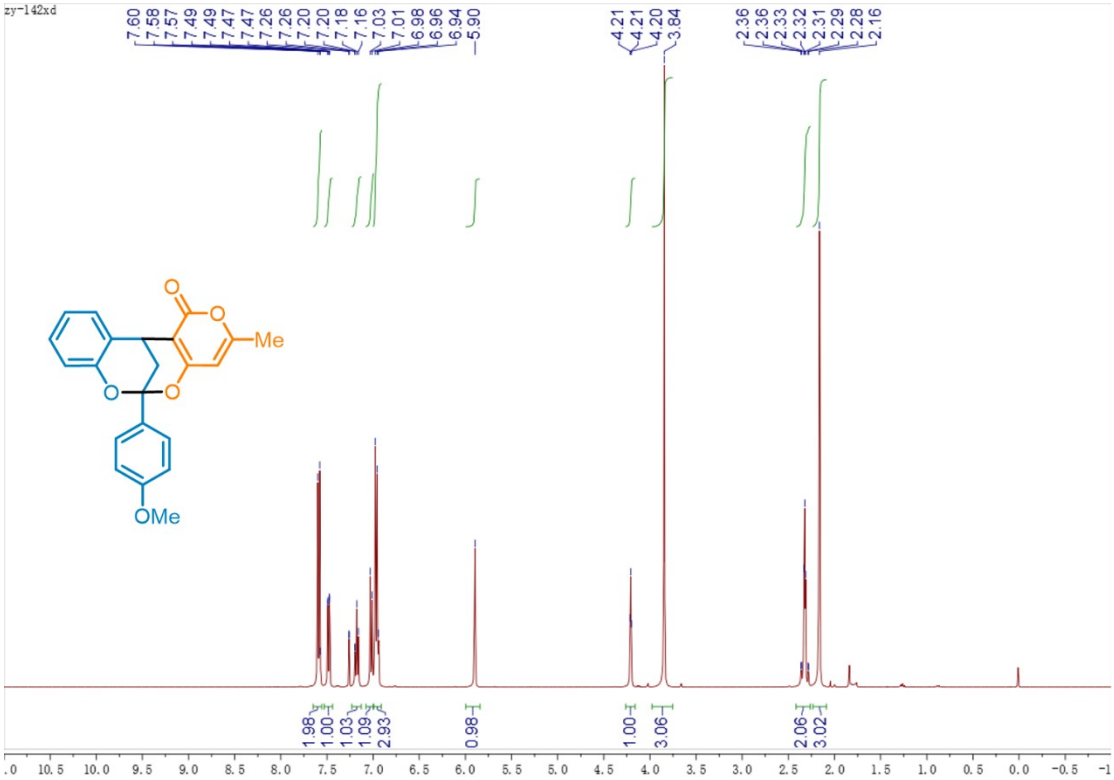
^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



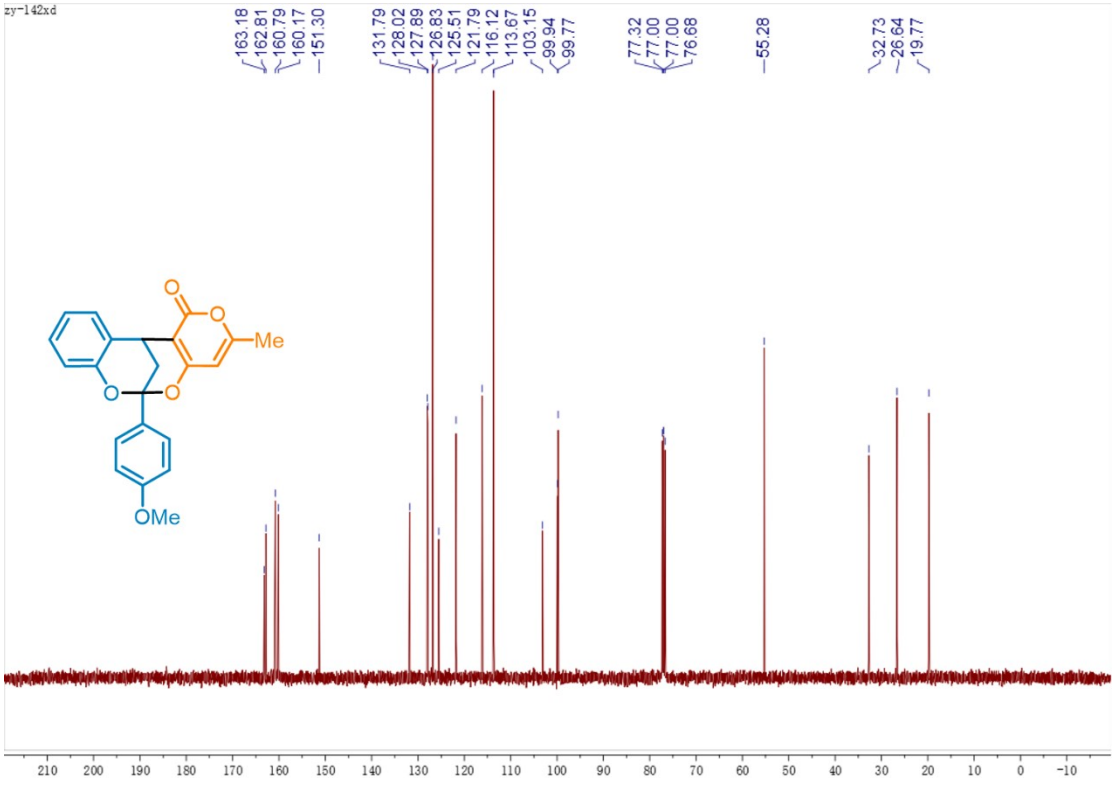
^{13}C NMR spectrum of **3q** (100 MHz, $CDCl_3$)



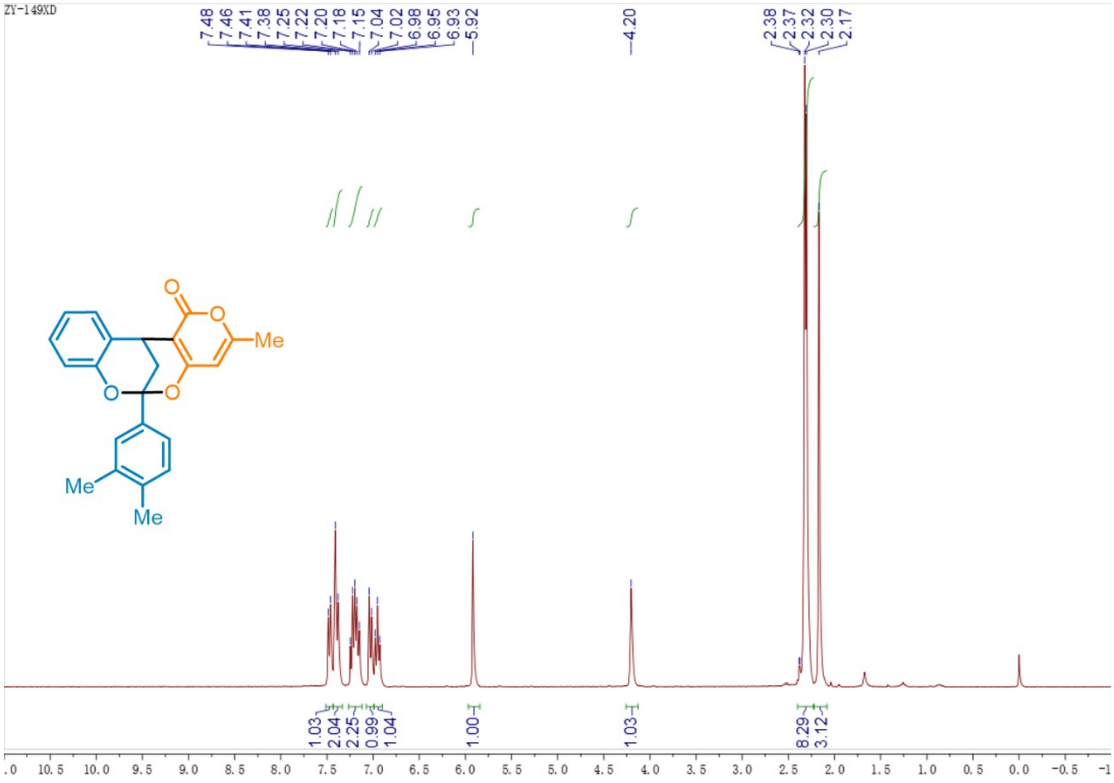
^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)



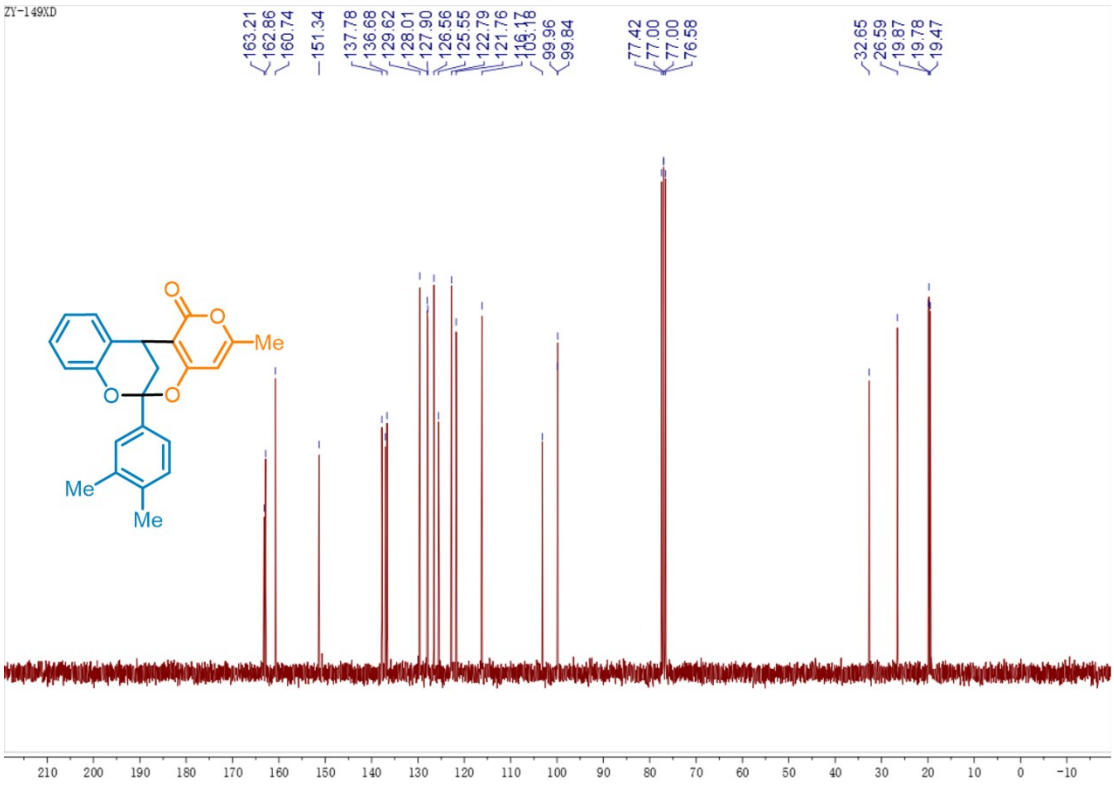
^{13}C NMR spectrum of **3r** (100 MHz, $CDCl_3$)



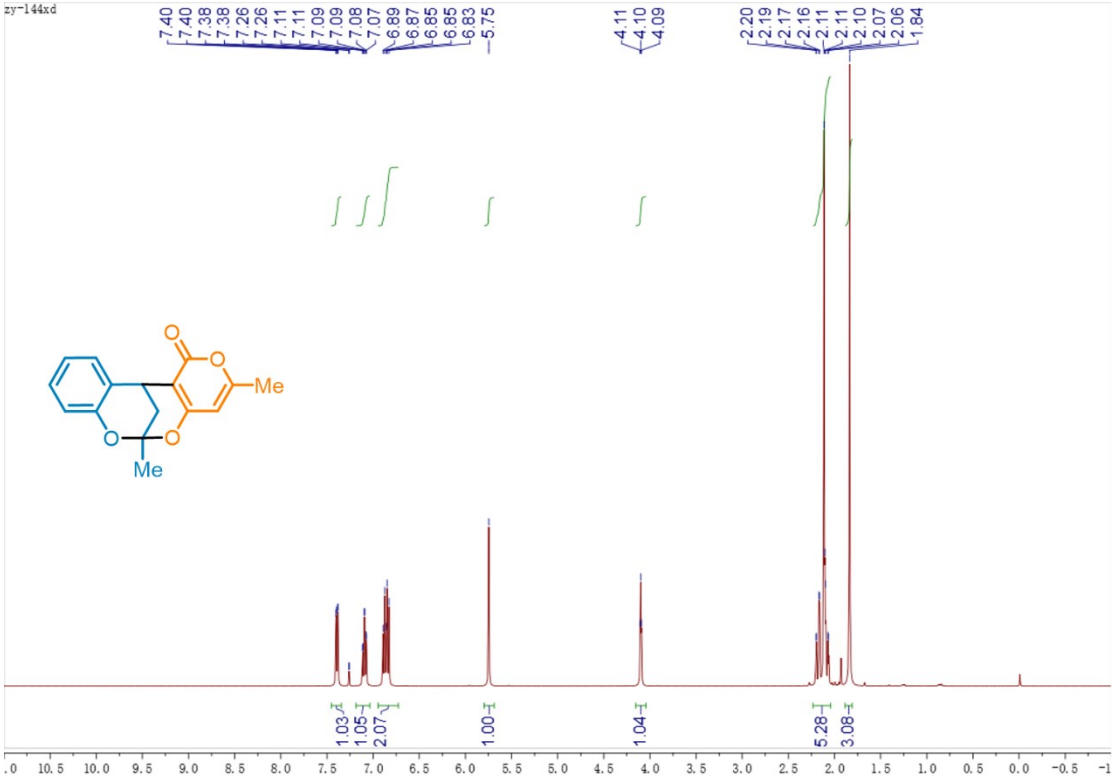
^{1}H NMR spectrum of **3s** (400 MHz, $CDCl_3$)



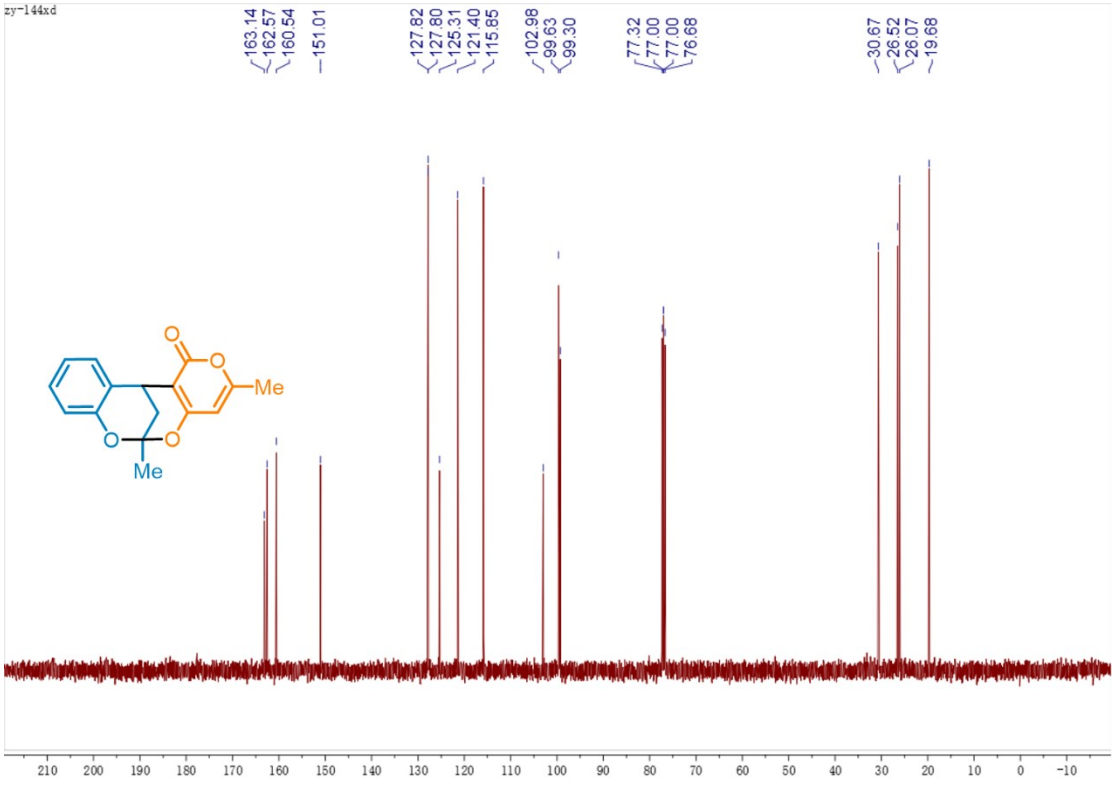
^{13}C NMR spectrum of **3s** (100 MHz, $CDCl_3$)



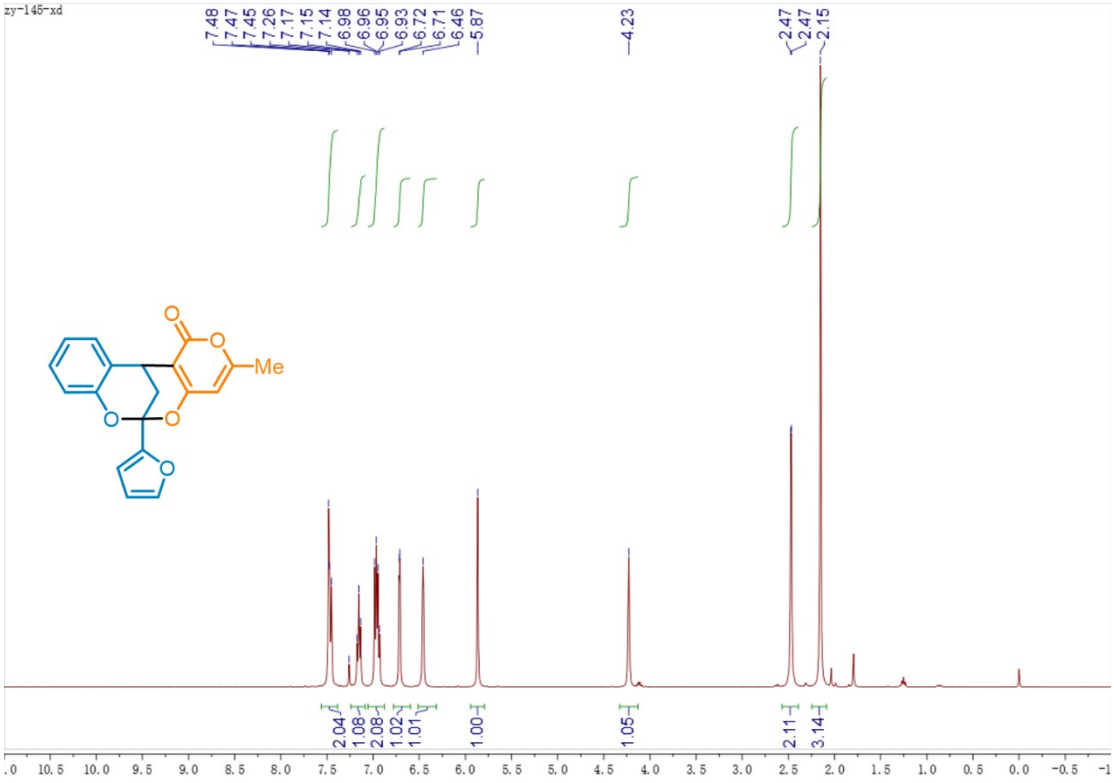
^{1}H NMR spectrum of **3t** (400 MHz, $CDCl_3$)



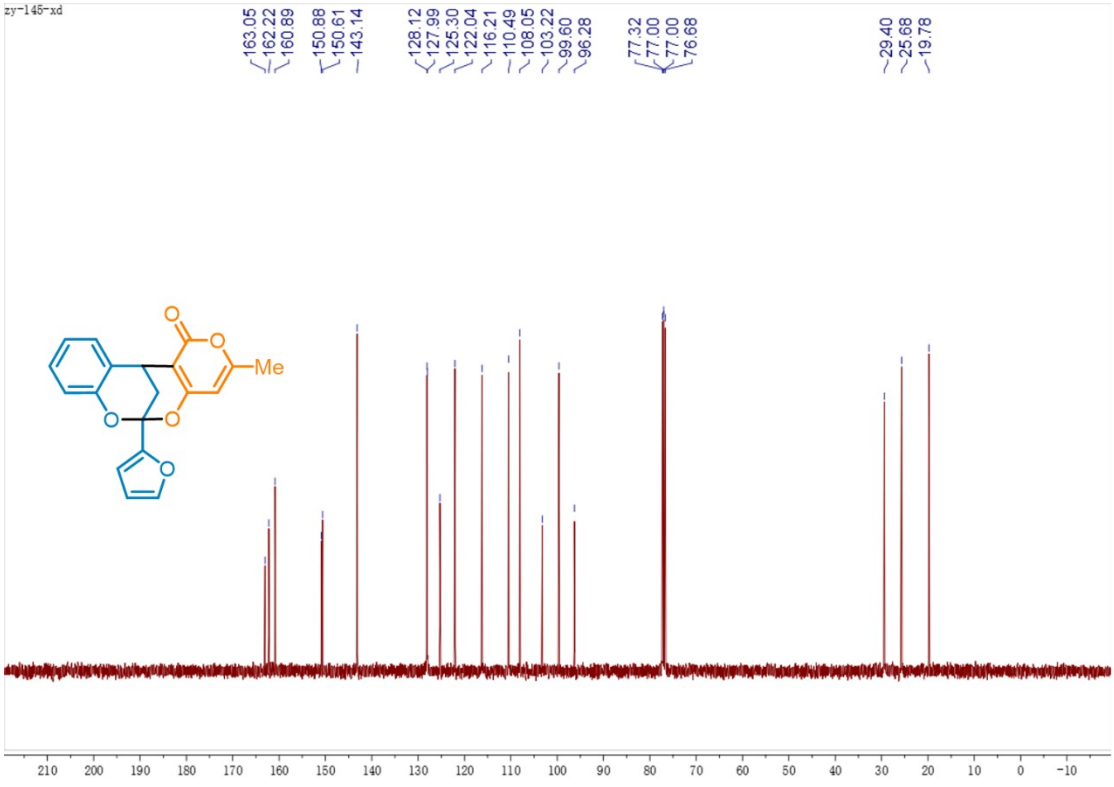
^{13}C NMR spectrum of **3t** (100 MHz, $CDCl_3$)



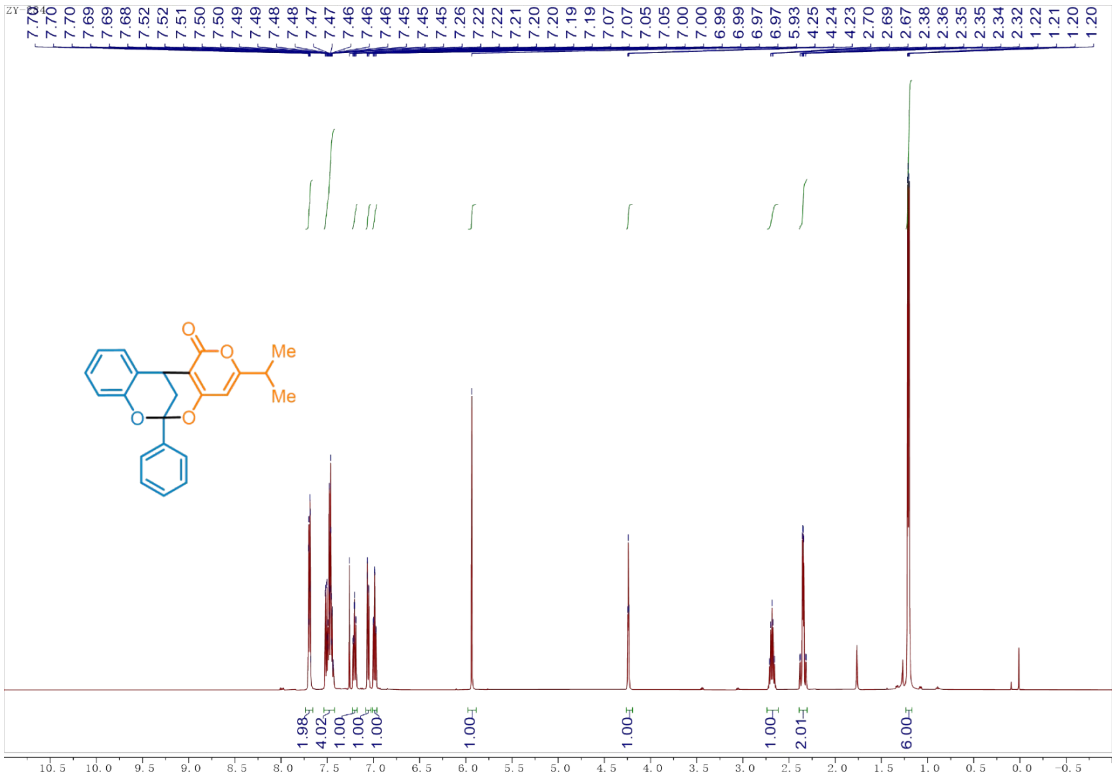
^{1}H NMR spectrum of **3u** (400 MHz, $CDCl_3$)



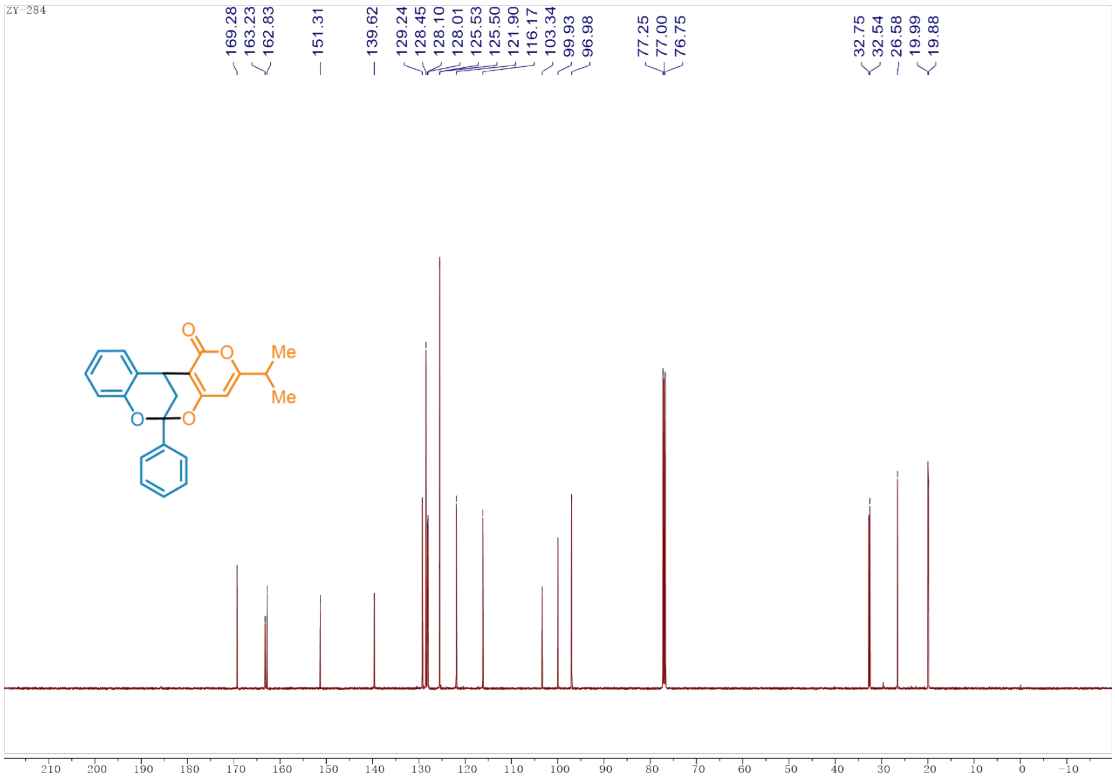
^{13}C NMR spectrum of **3u** (100 MHz, $CDCl_3$)



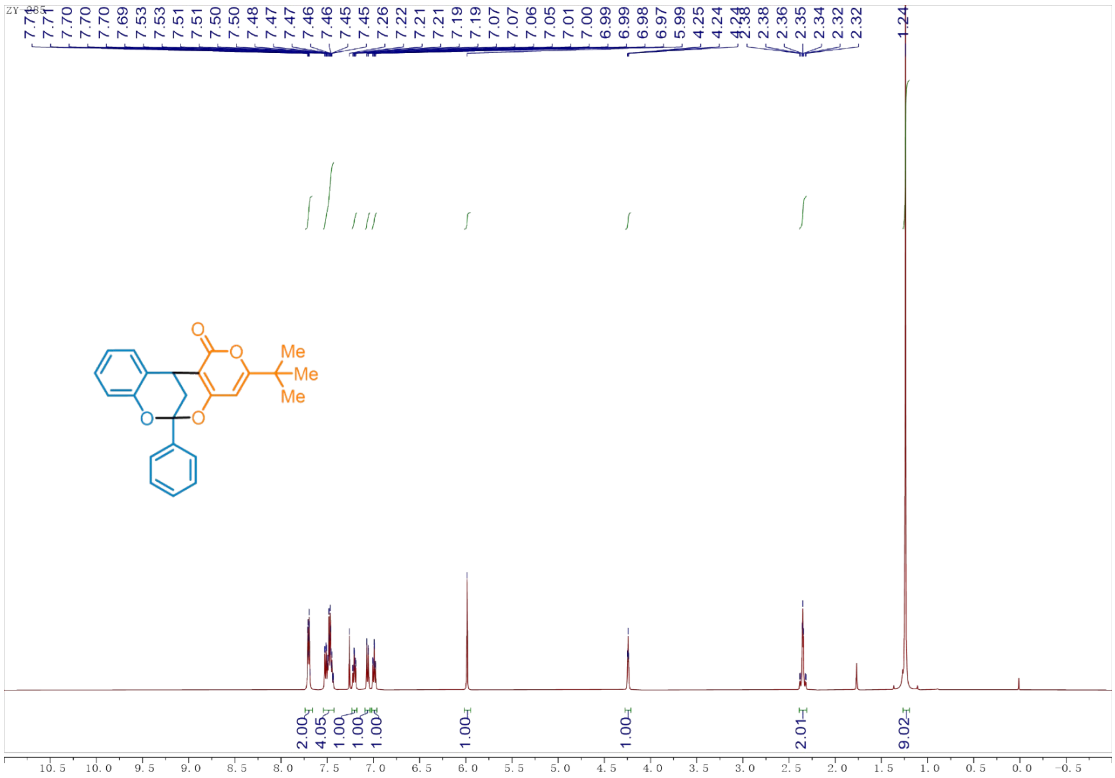
^{1}H NMR spectrum of **3v** (500 MHz, $CDCl_3$)



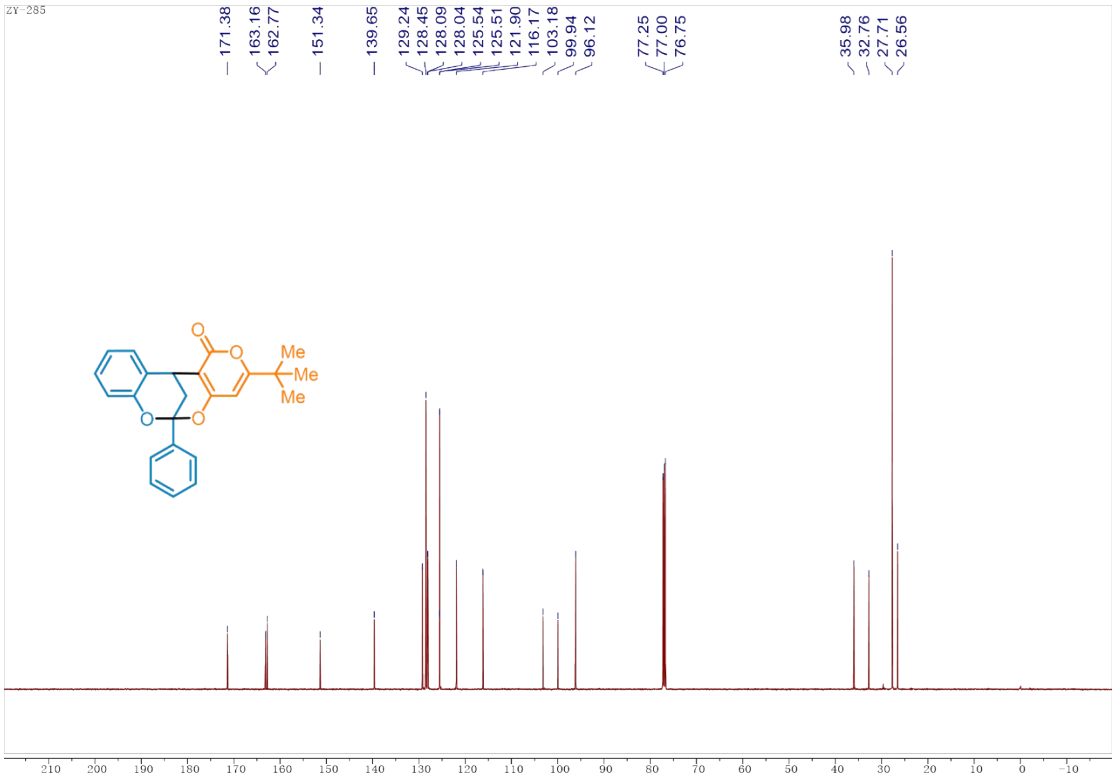
^{13}C NMR spectrum of **3v** (125 MHz, $CDCl_3$)



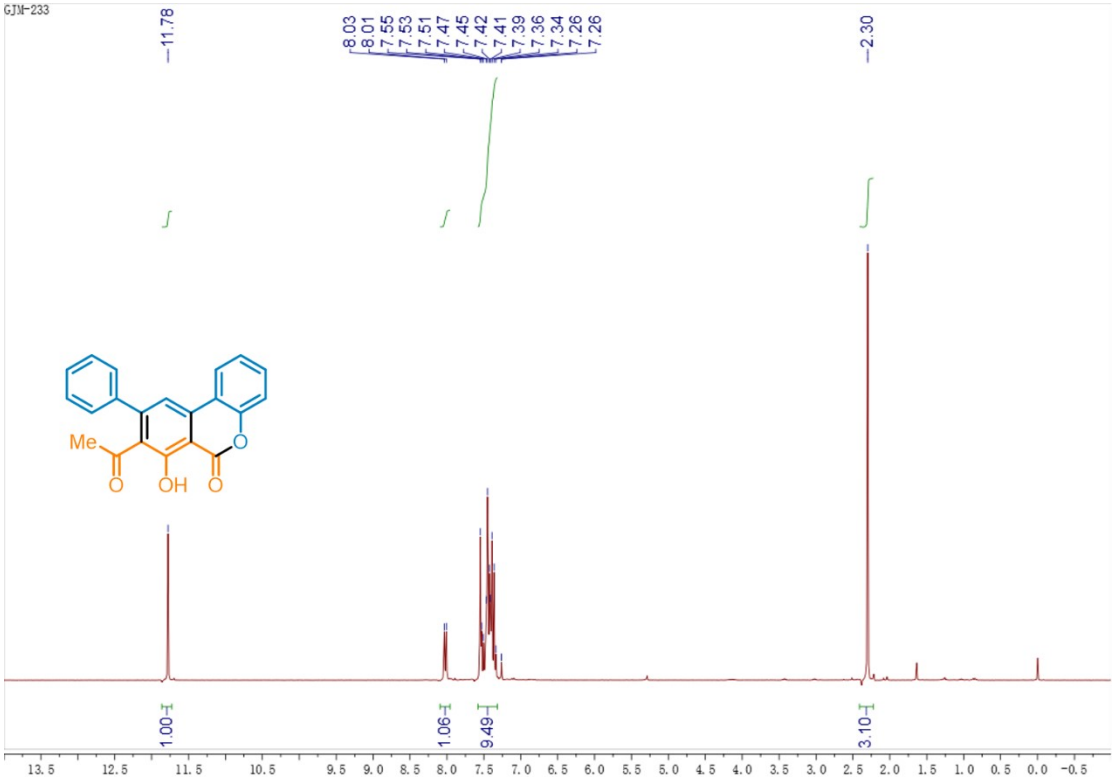
^{1}H NMR spectrum of **3w** (500 MHz, $CDCl_3$)



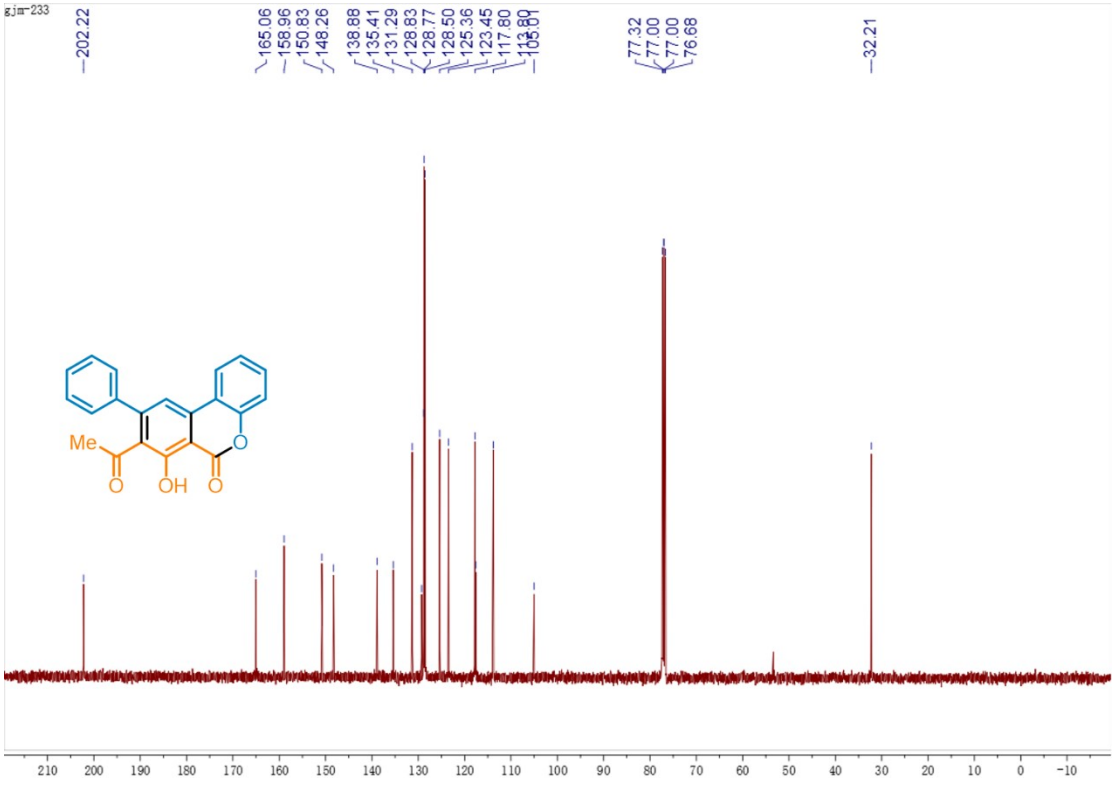
^{13}C NMR spectrum of **3w** (125 MHz, $CDCl_3$)



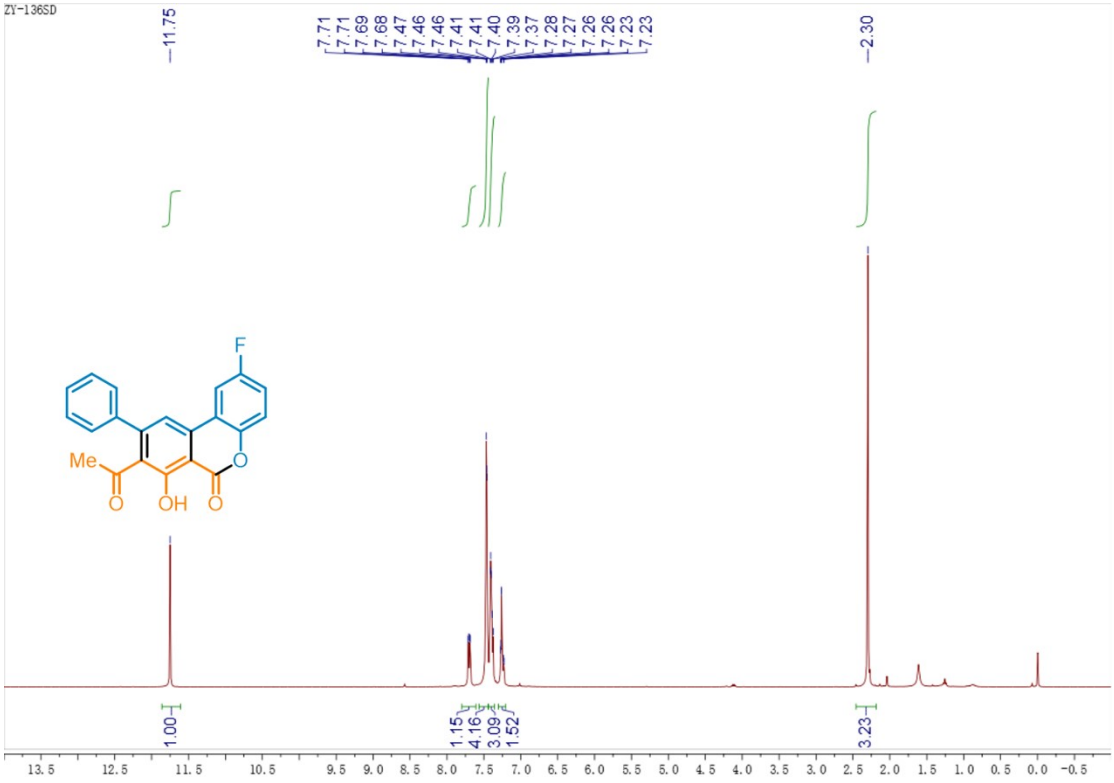
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



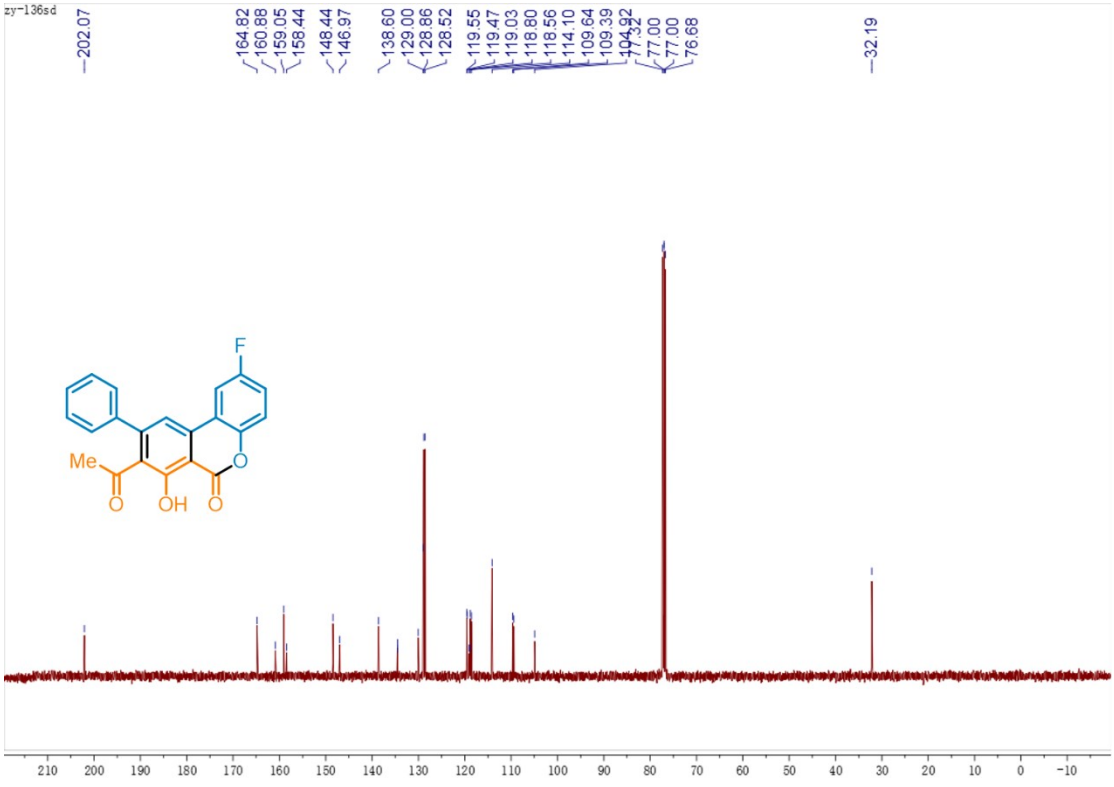
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



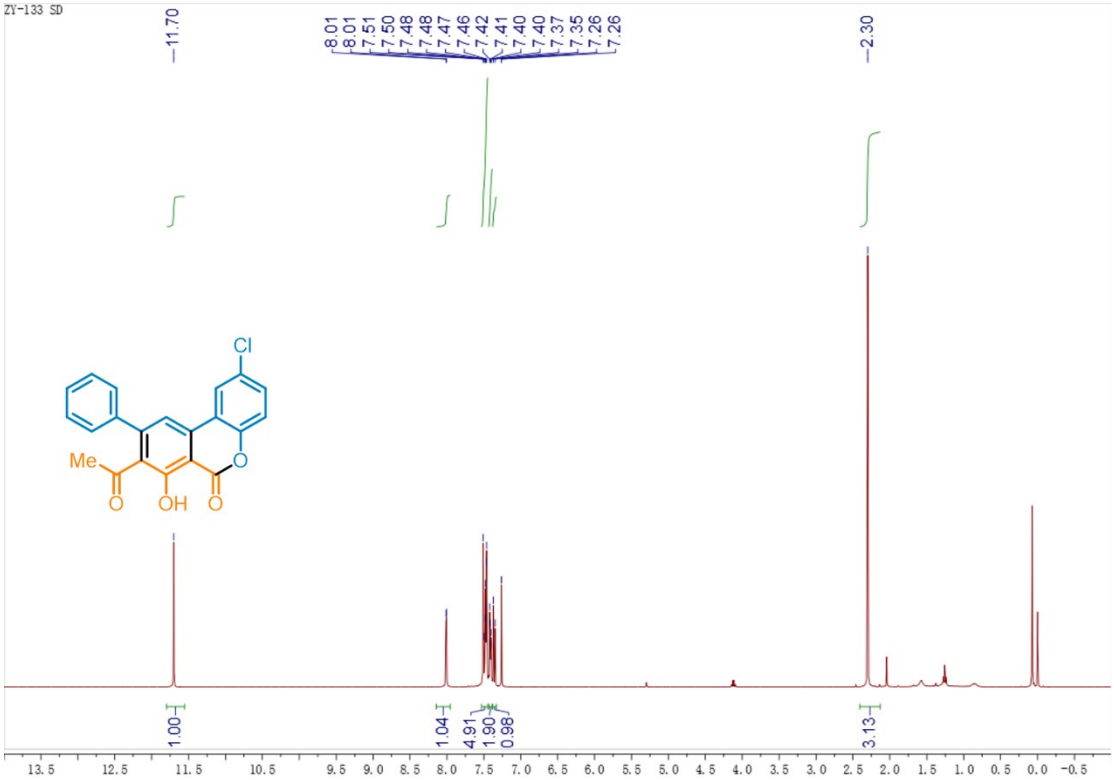
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$)



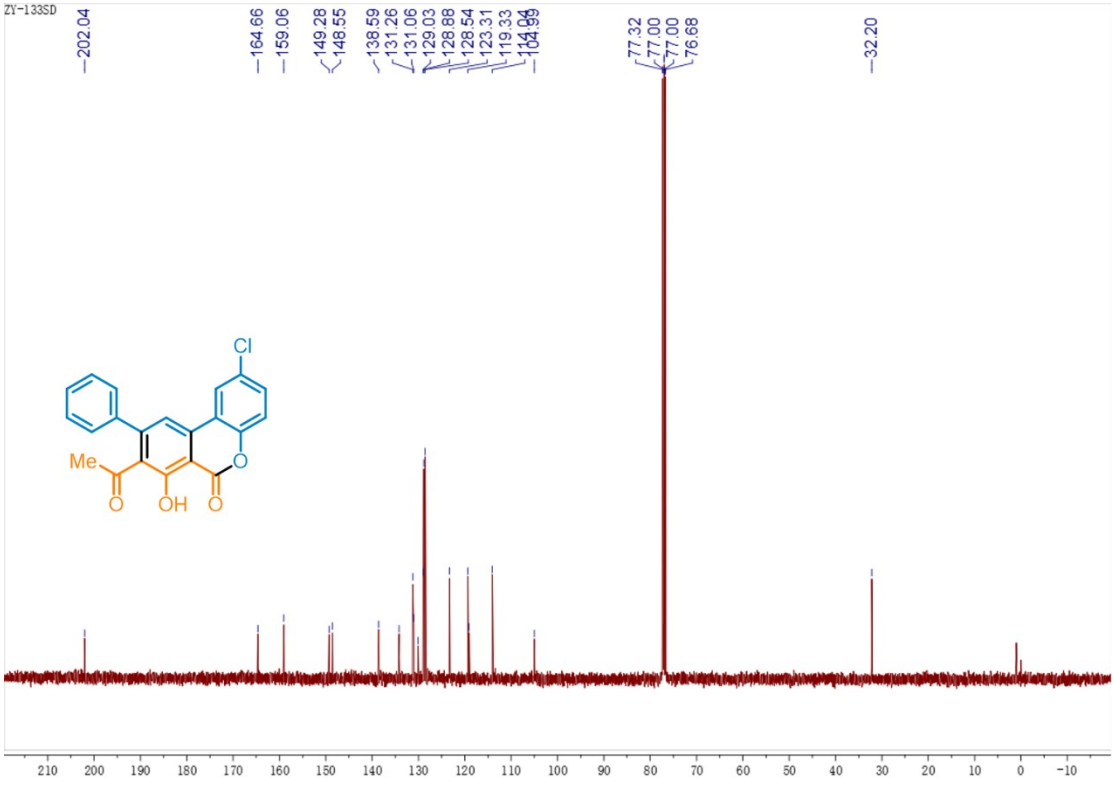
^{13}C NMR spectrum of **4b** (100 MHz, $CDCl_3$)



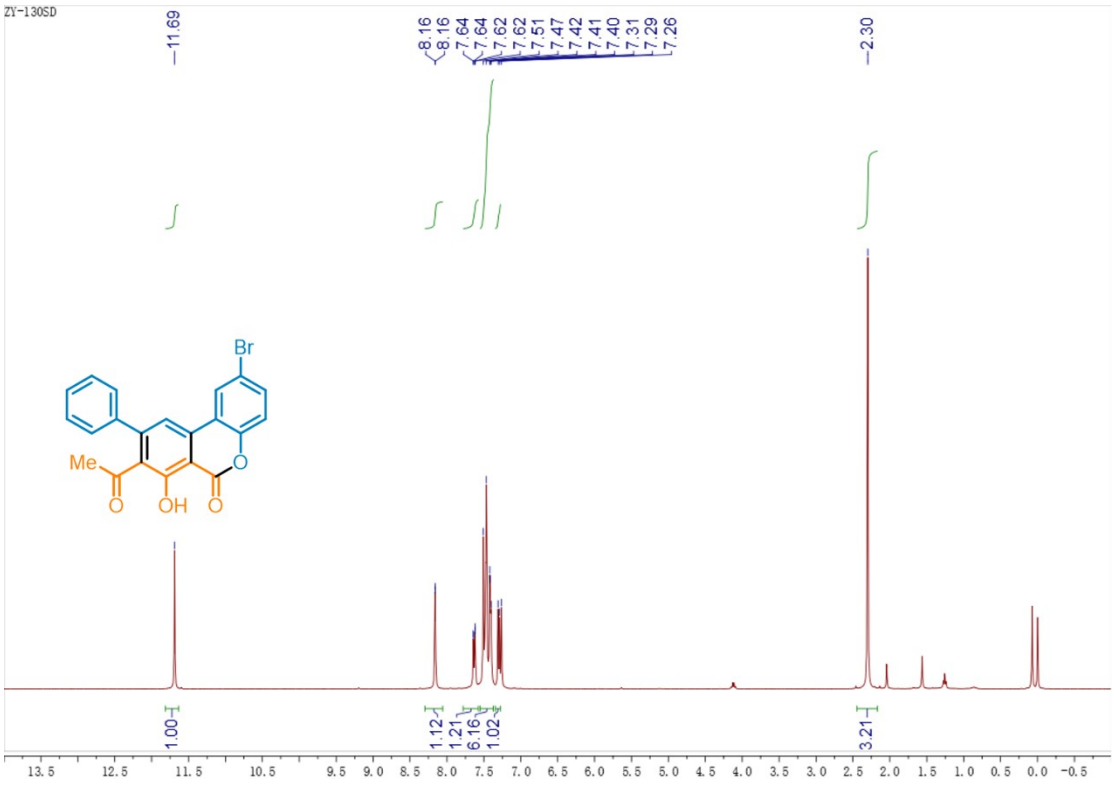
^{1}H NMR spectrum of **4c** (400 MHz, $CDCl_3$)



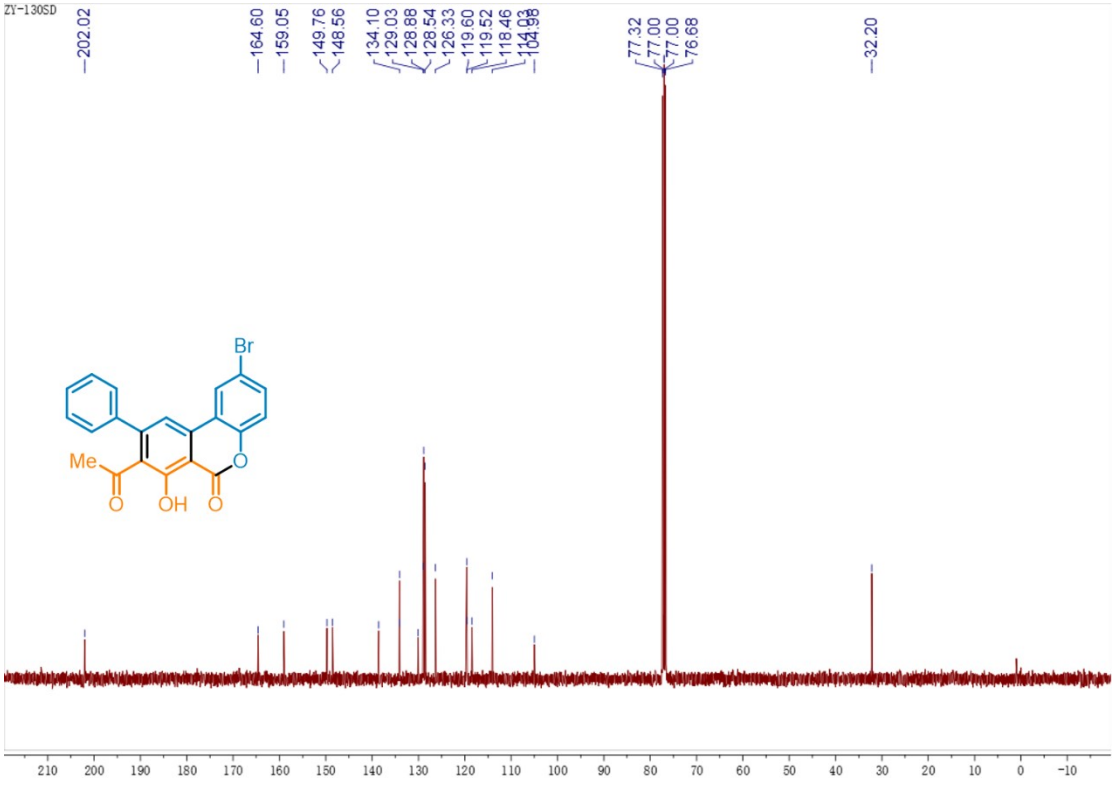
^{13}C NMR spectrum of **4c** (100 MHz, $CDCl_3$)



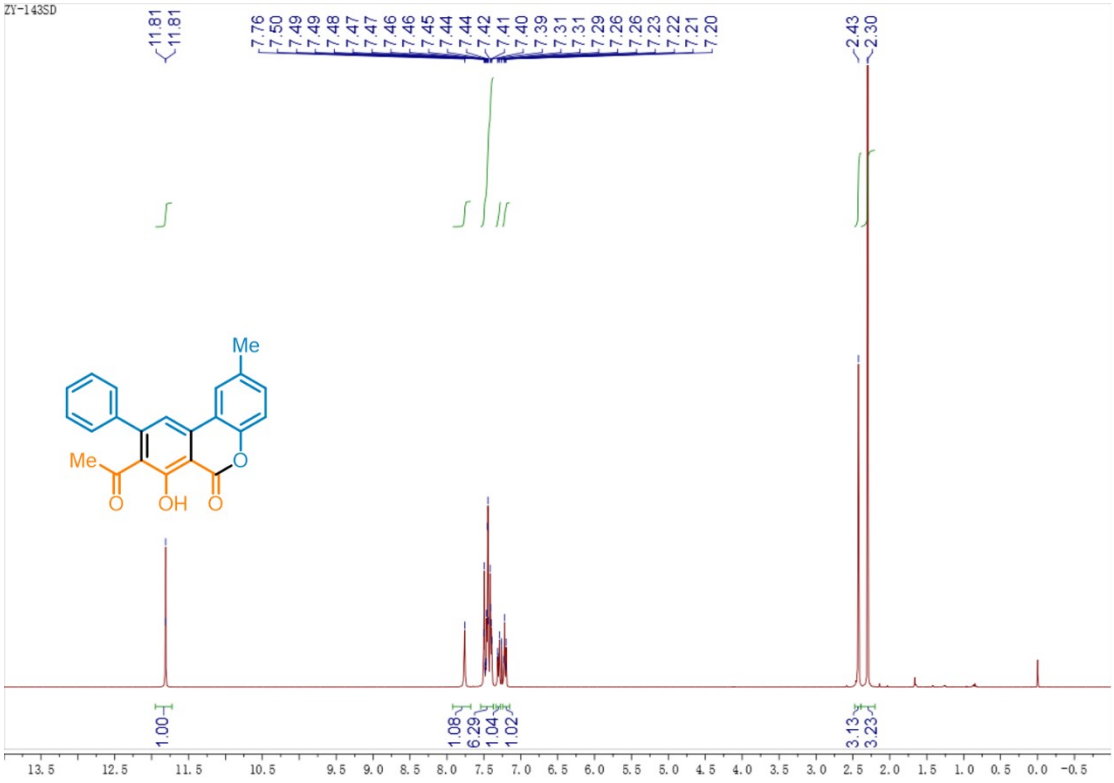
^{1}H NMR spectrum of **4d** (400 MHz, $CDCl_3$)



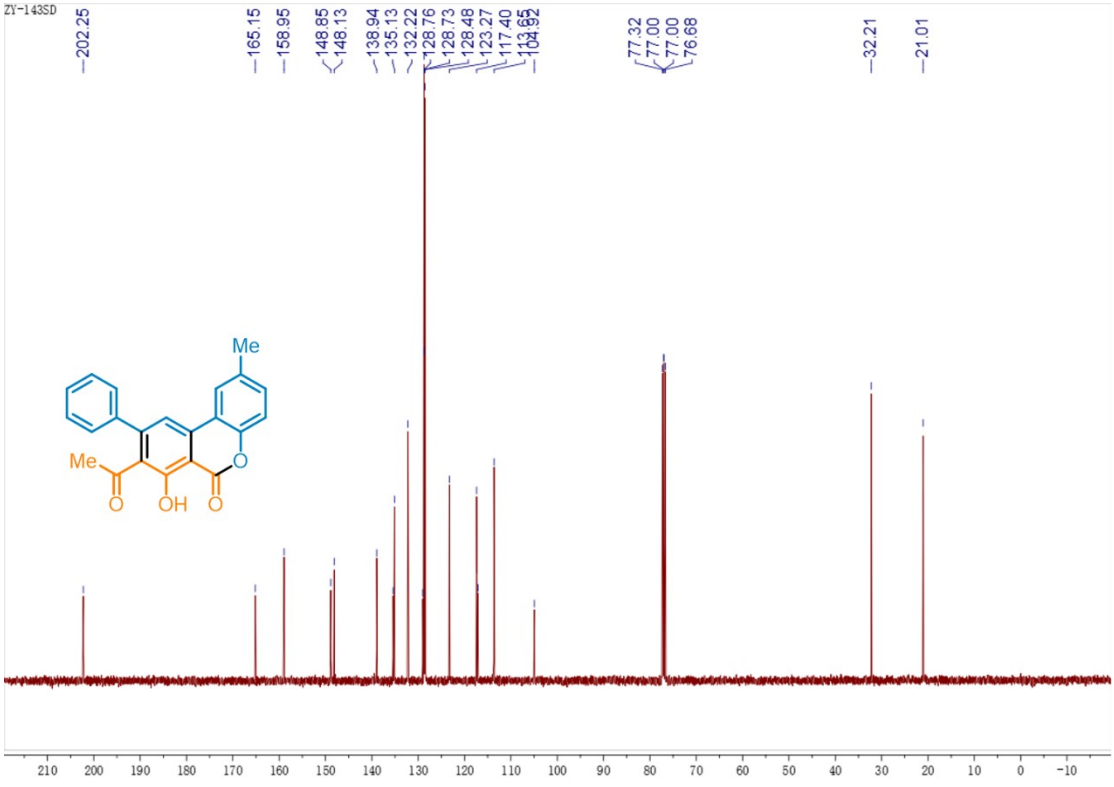
^{13}C NMR spectrum of **4d** (100 MHz, $CDCl_3$)



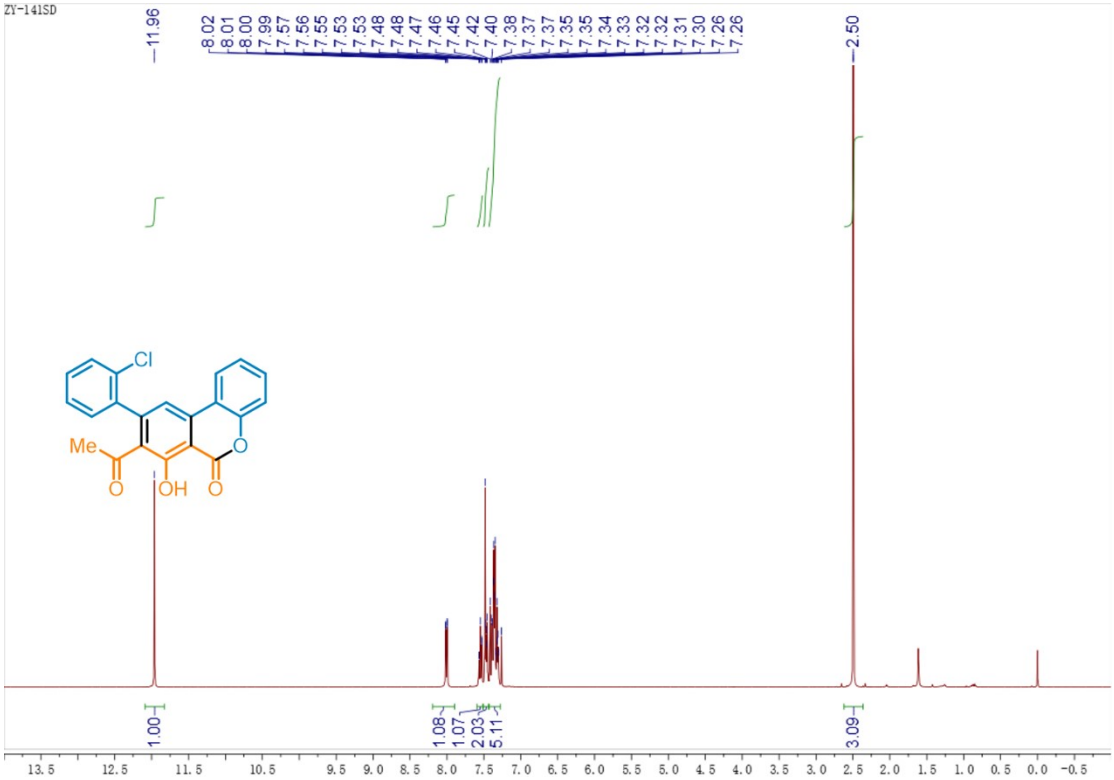
^{1}H NMR spectrum of **4e** (400 MHz, $CDCl_3$)



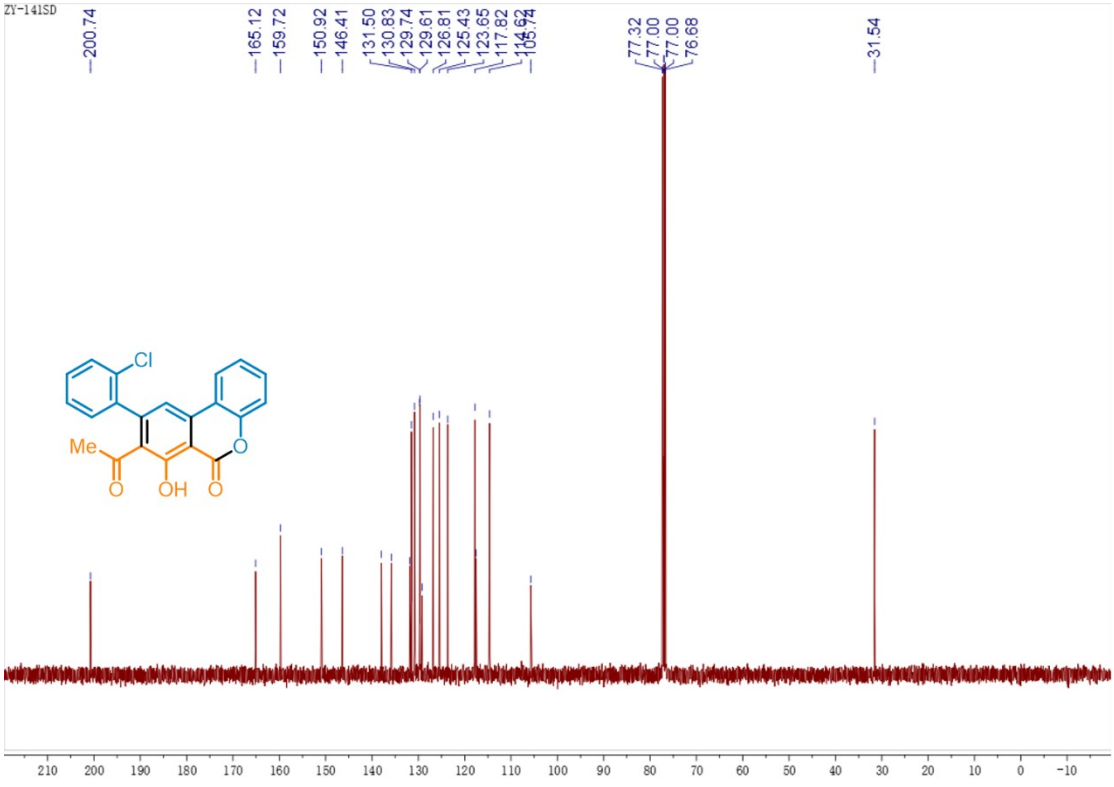
^{13}C NMR spectrum of **4e** (100 MHz, $CDCl_3$)



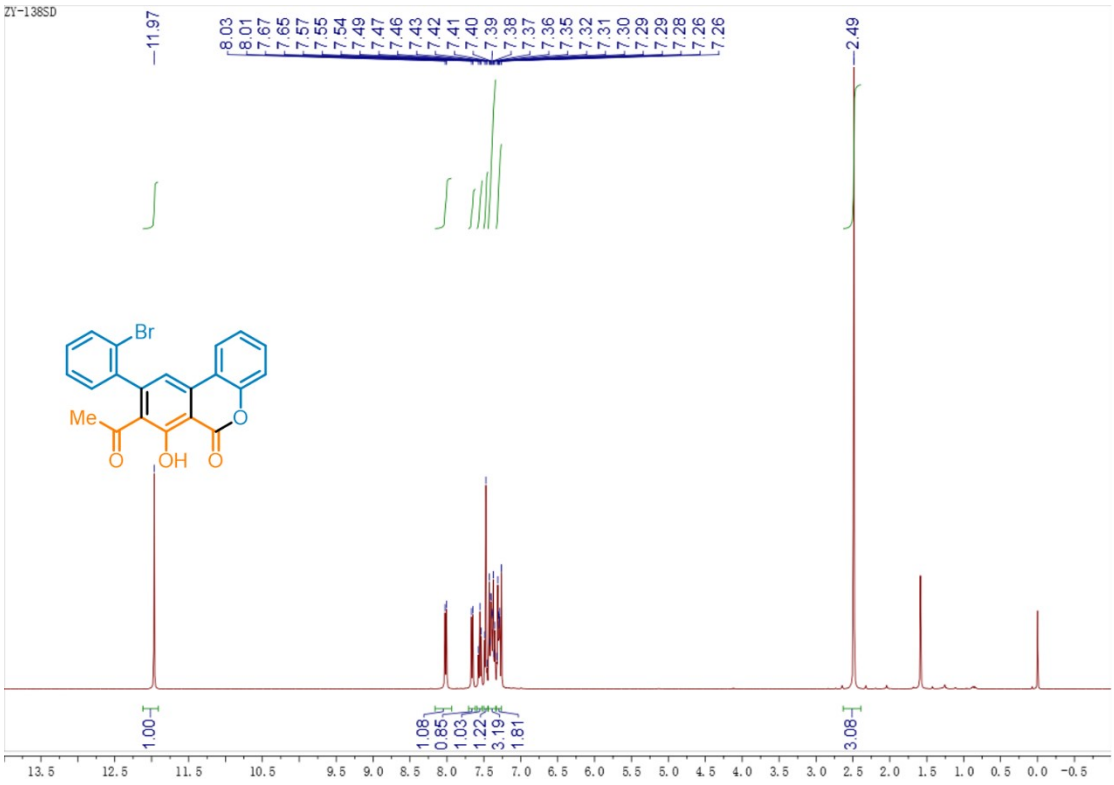
^{1}H NMR spectrum of **4f** (400 MHz, $CDCl_3$)



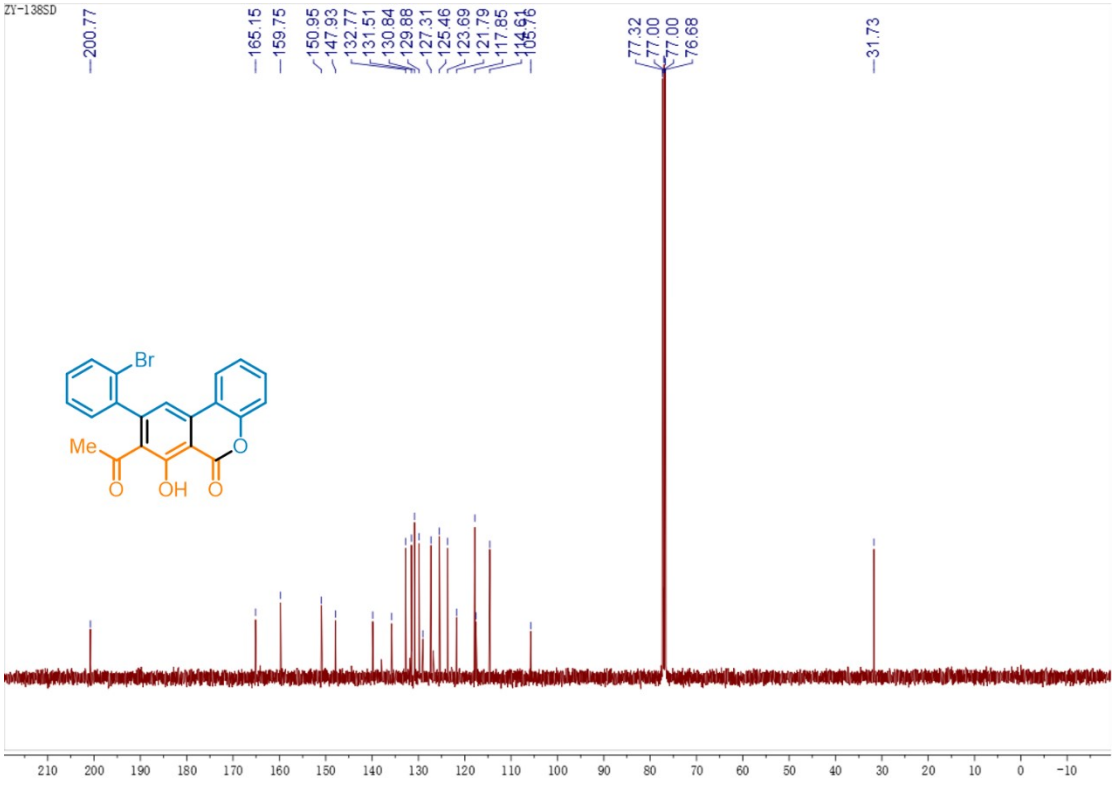
^{13}C NMR spectrum of **4f** (100 MHz, $CDCl_3$)



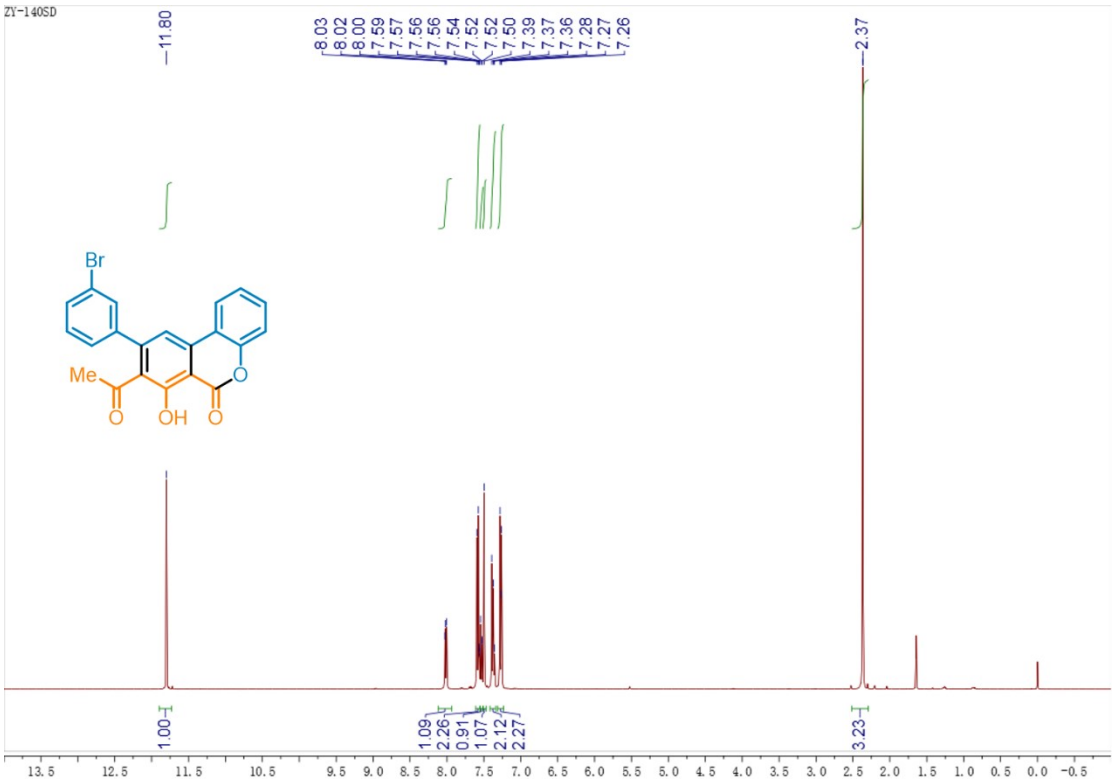
^{1}H NMR spectrum of **4g** (400 MHz, $CDCl_3$)



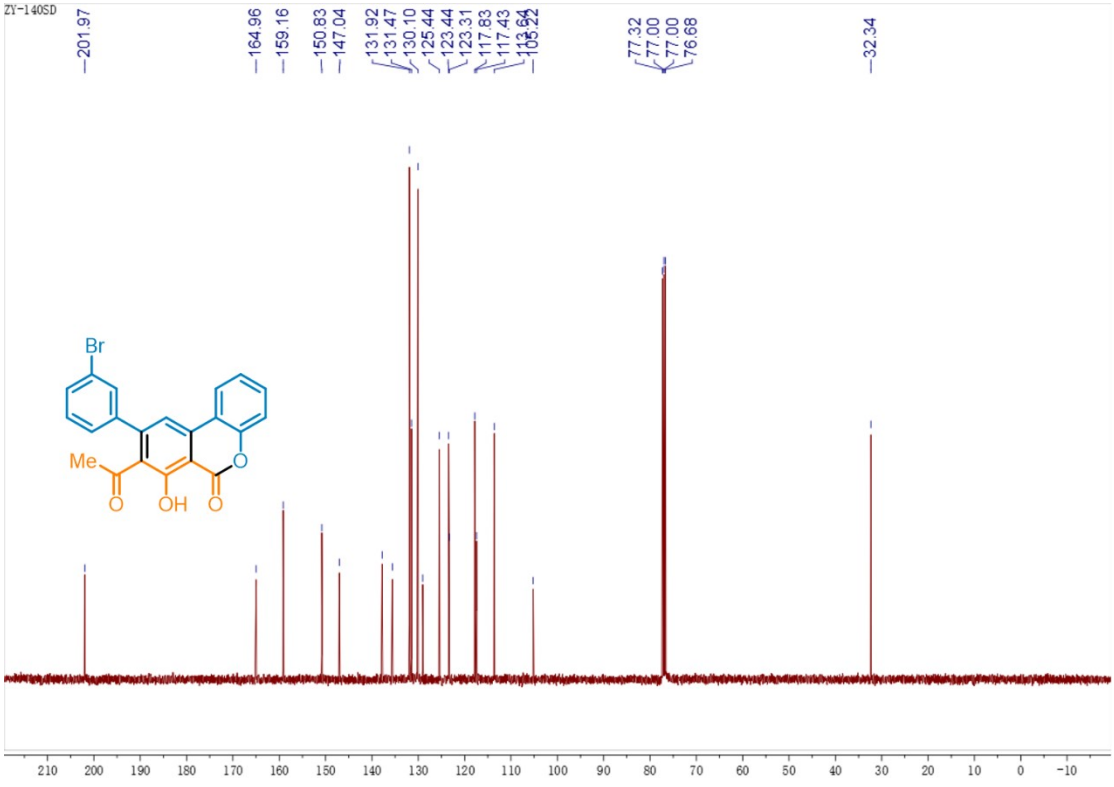
^{13}C NMR spectrum of **4g** (100 MHz, $CDCl_3$)



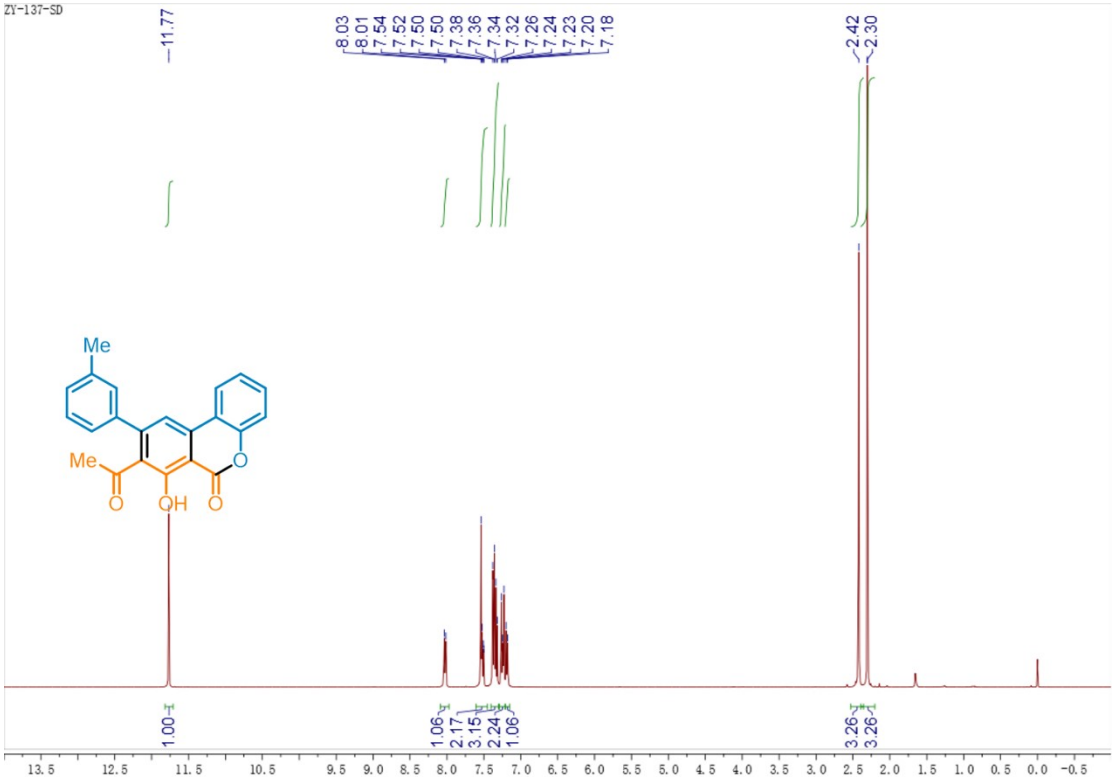
^{1}H NMR spectrum of **4h** (400 MHz, $CDCl_3$)



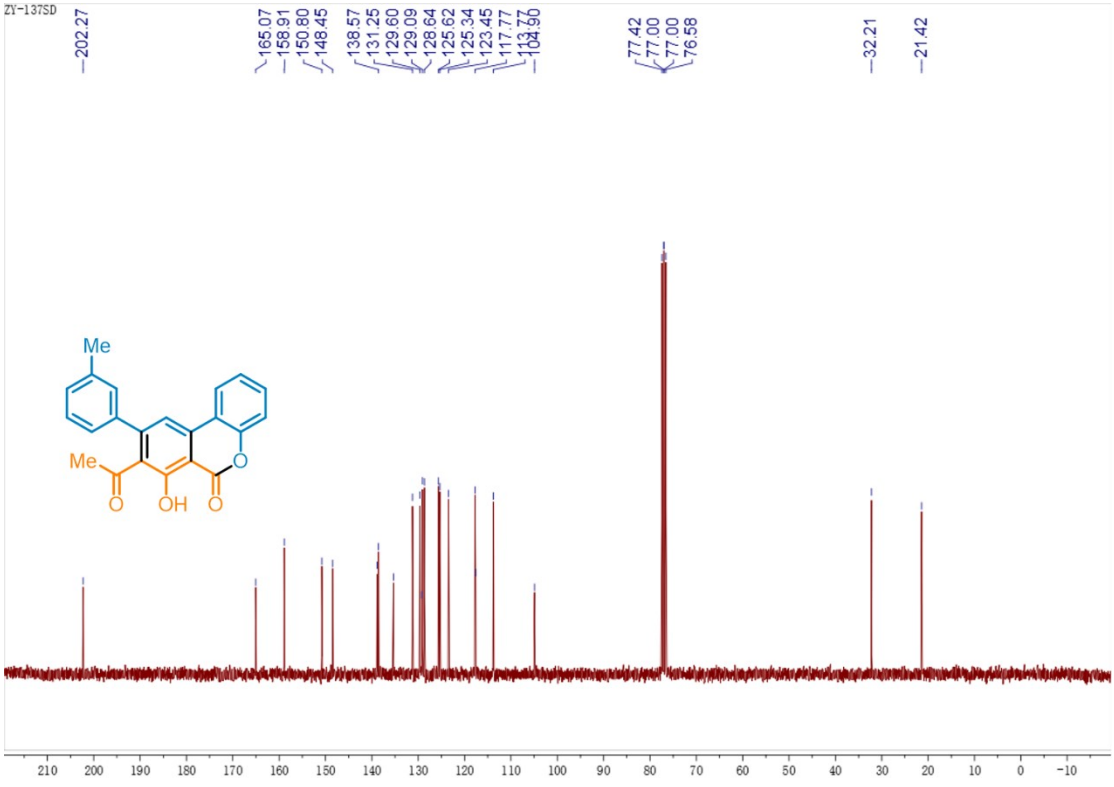
^{13}C NMR spectrum of **4h** (100 MHz, $CDCl_3$)



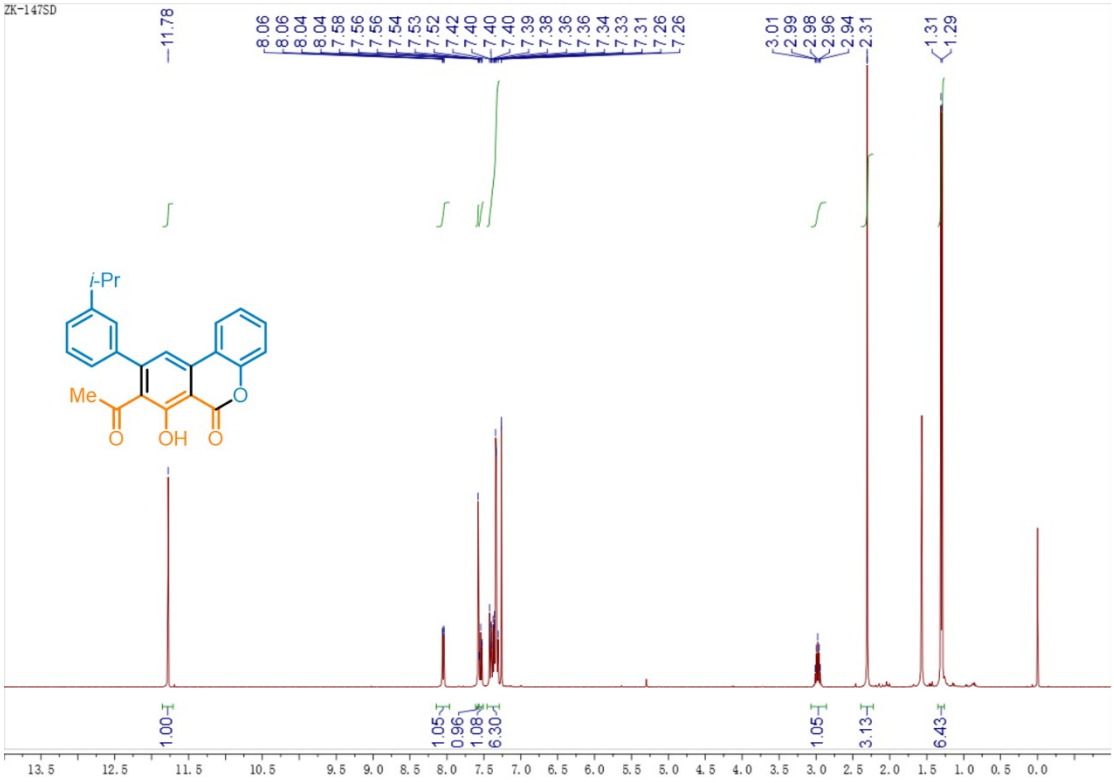
^{1}H NMR spectrum of **4i** (400 MHz, $CDCl_3$)



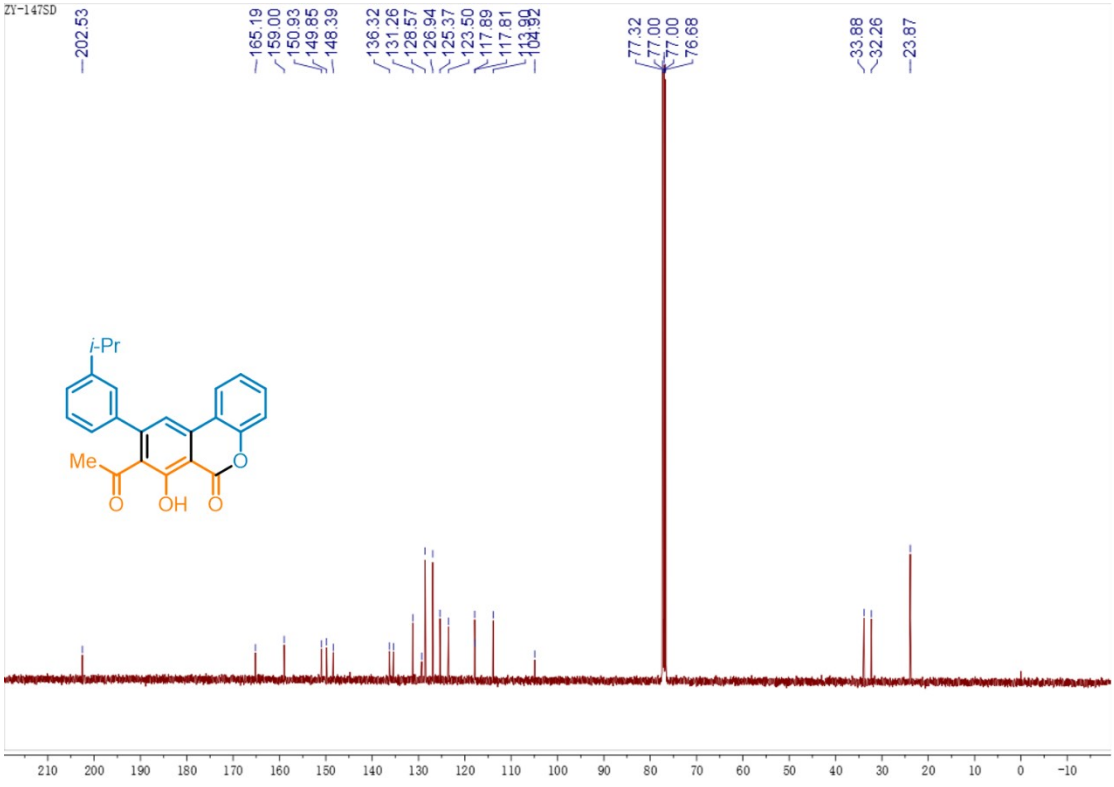
^{13}C NMR spectrum of **4i** (100 MHz, $CDCl_3$)



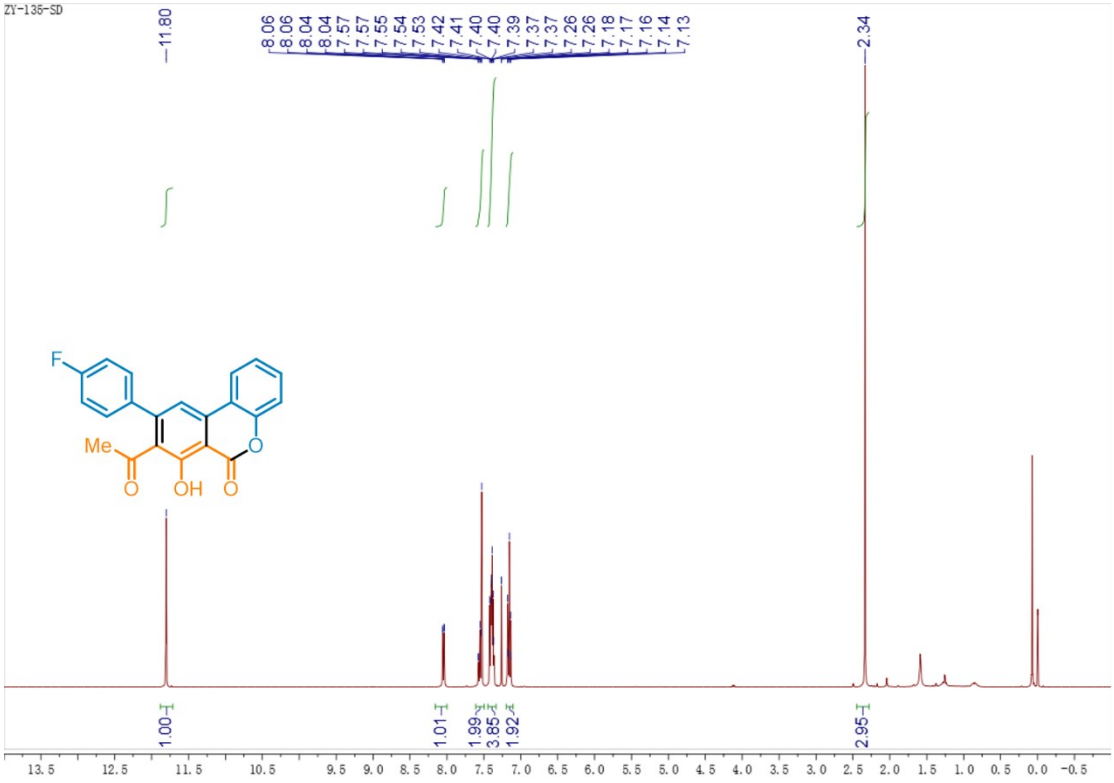
^{1}H NMR spectrum of **4j** (400 MHz, $CDCl_3$)



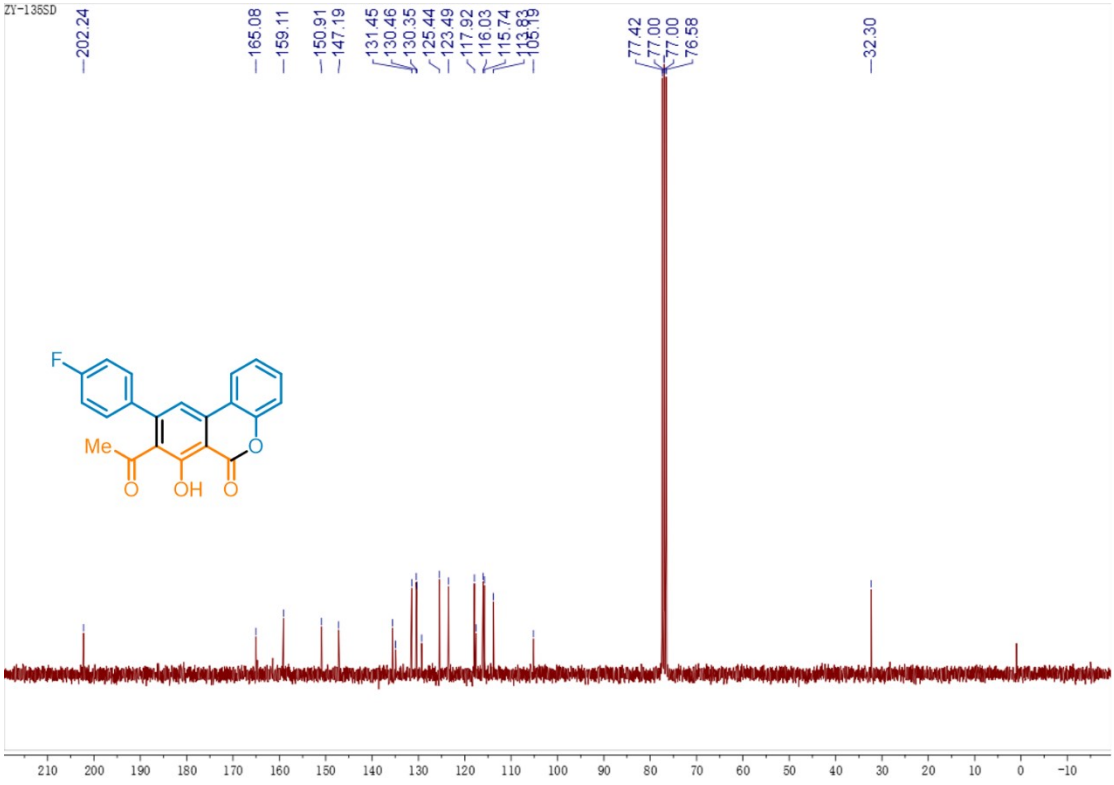
^{13}C NMR spectrum of **4j** (100 MHz, $CDCl_3$)



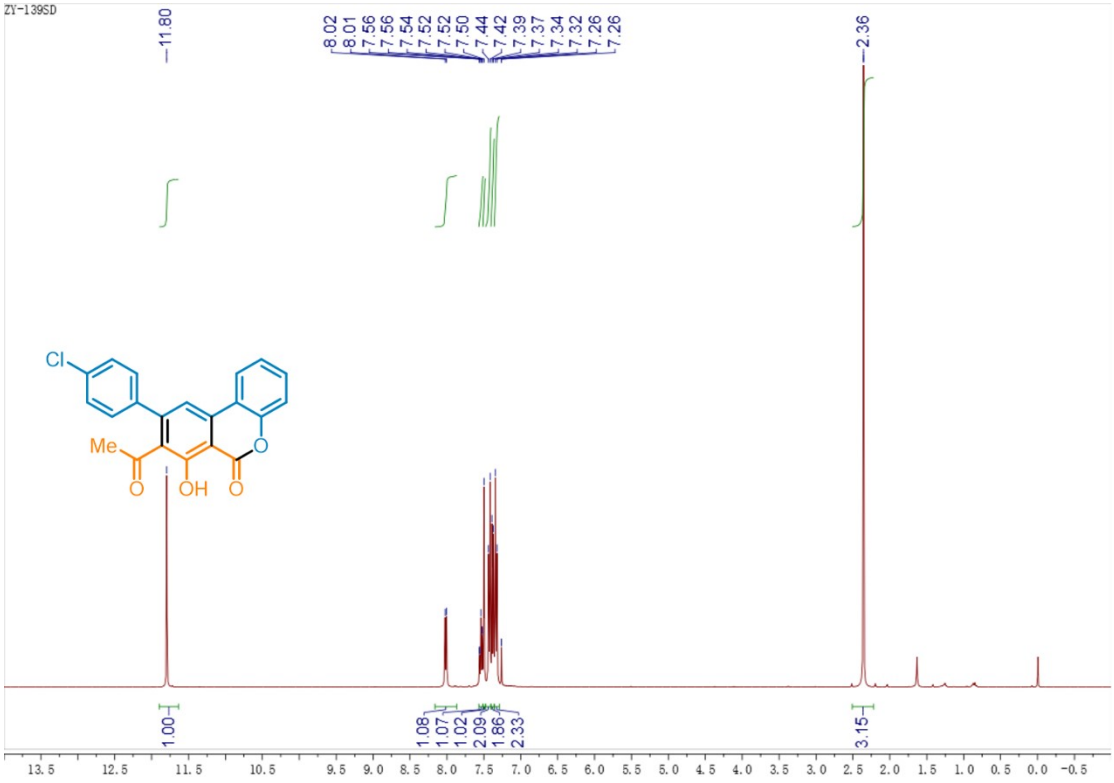
^{1}H NMR spectrum of **4k** (400 MHz, $CDCl_3$)



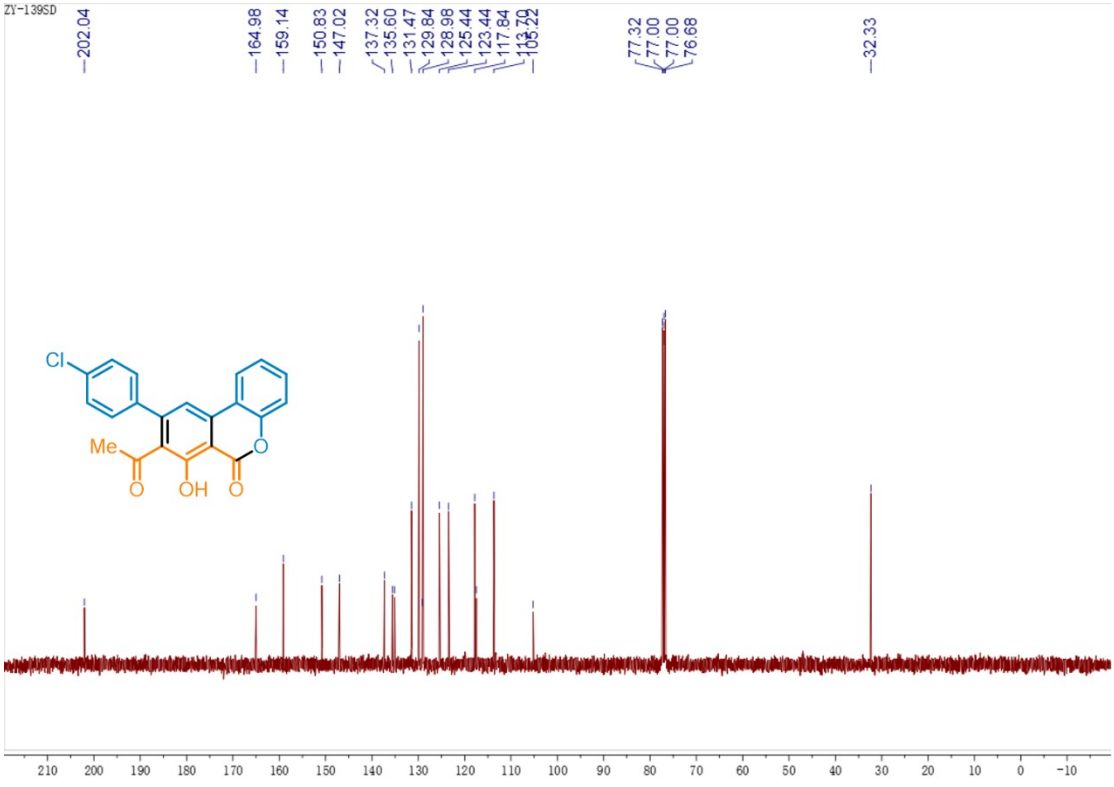
^{13}C NMR spectrum of **4k** (100 MHz, $CDCl_3$)



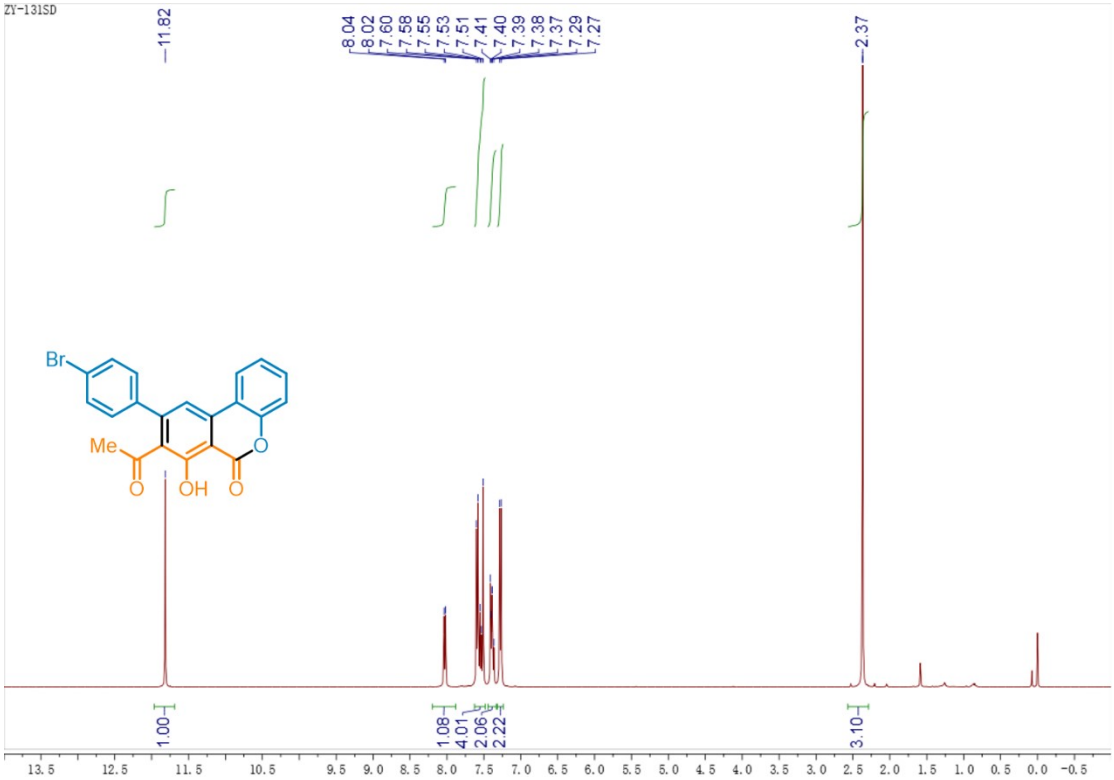
^{1}H NMR spectrum of **4l** (400 MHz, $CDCl_3$)



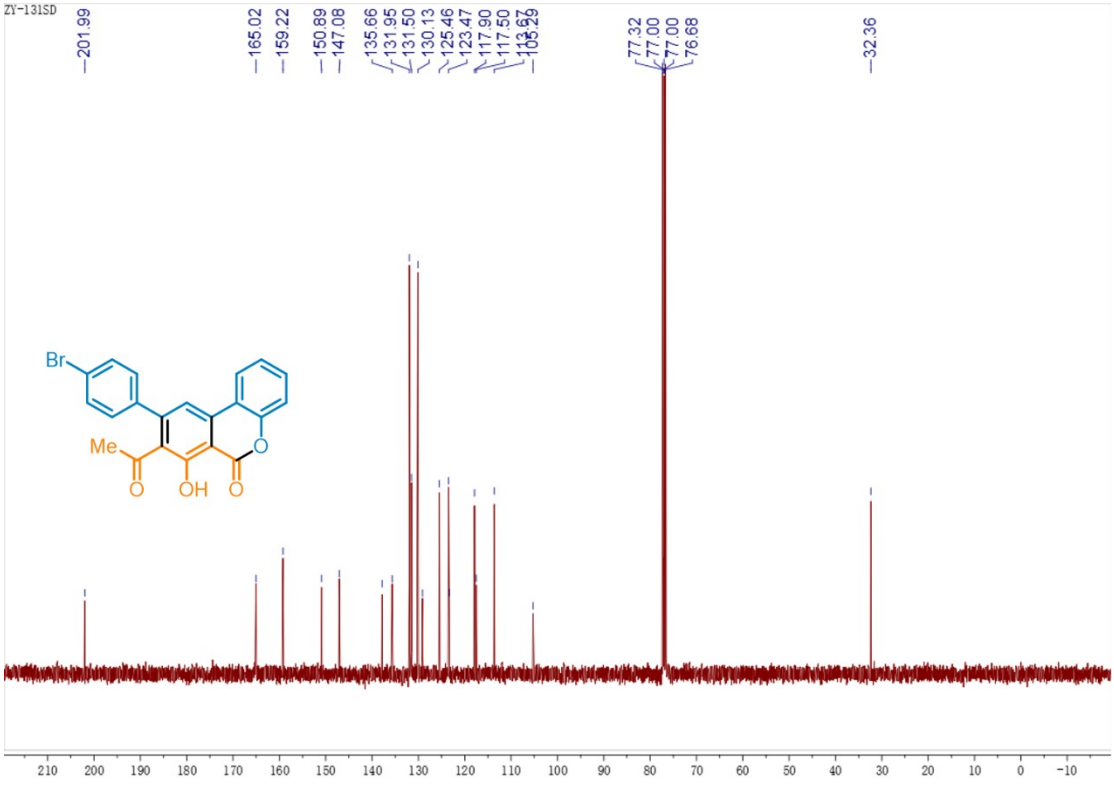
^{13}C NMR spectrum of **4l** (100 MHz, $CDCl_3$)



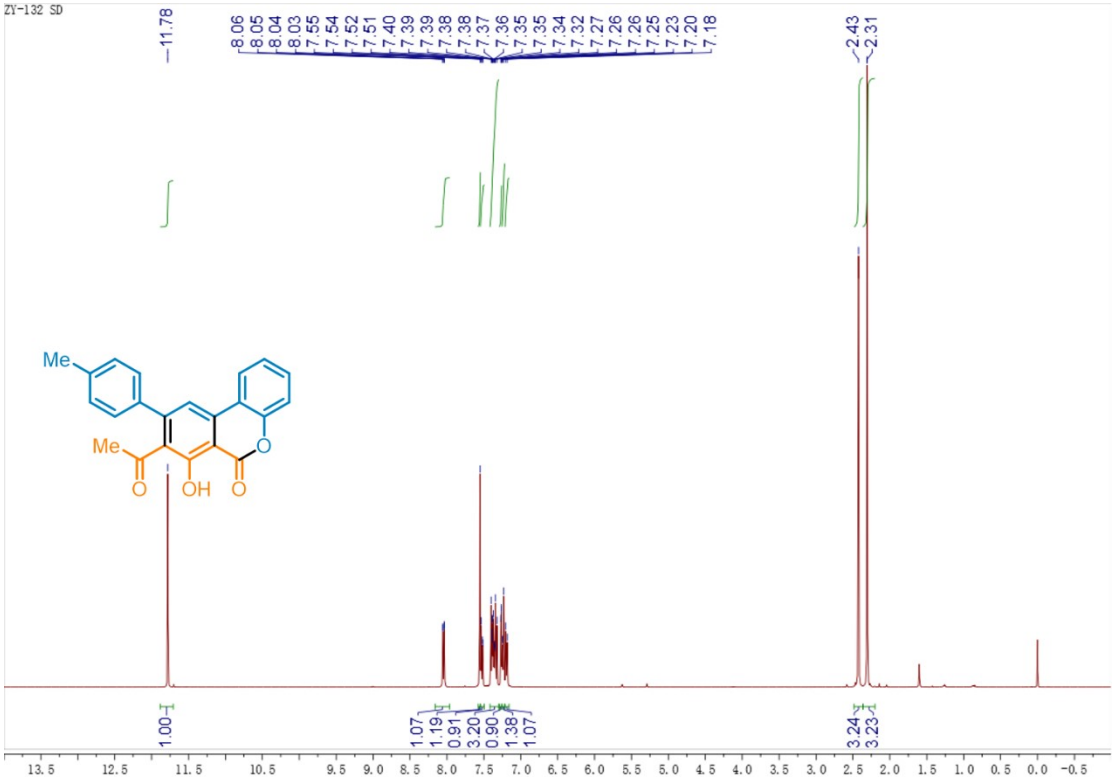
^{1}H NMR spectrum of **4m** (400 MHz, $CDCl_3$)



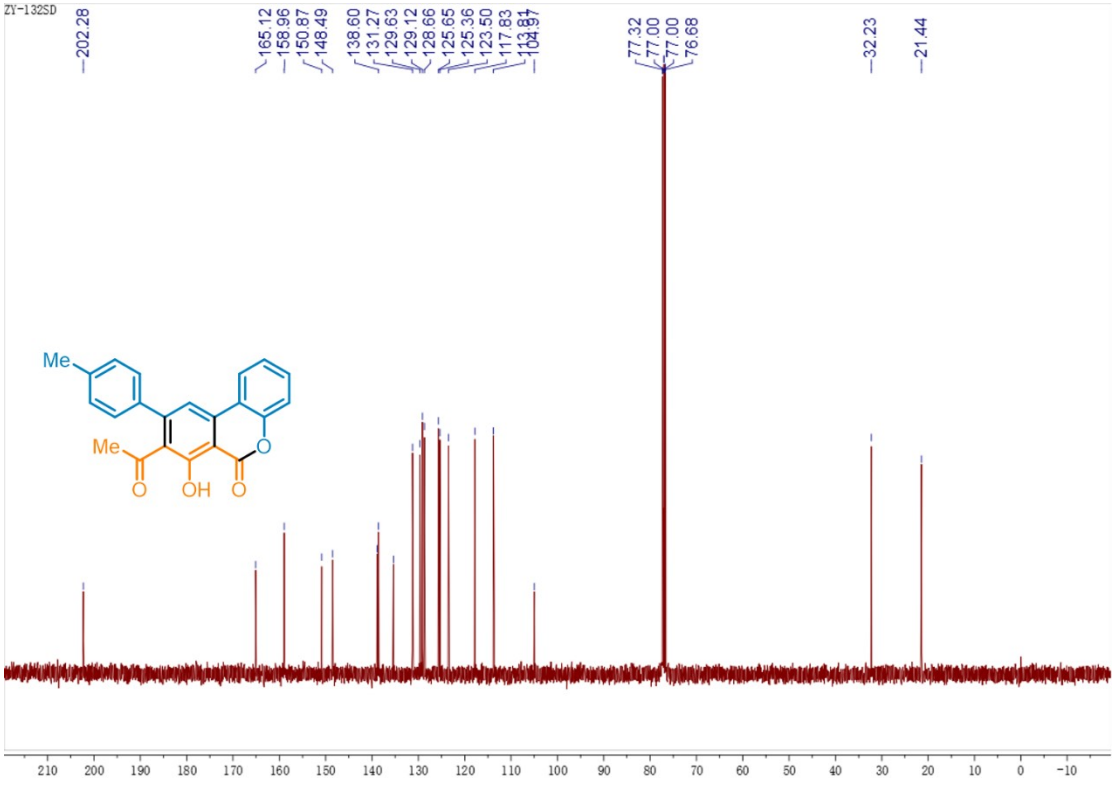
^{13}C NMR spectrum of **4m** (100 MHz, $CDCl_3$)



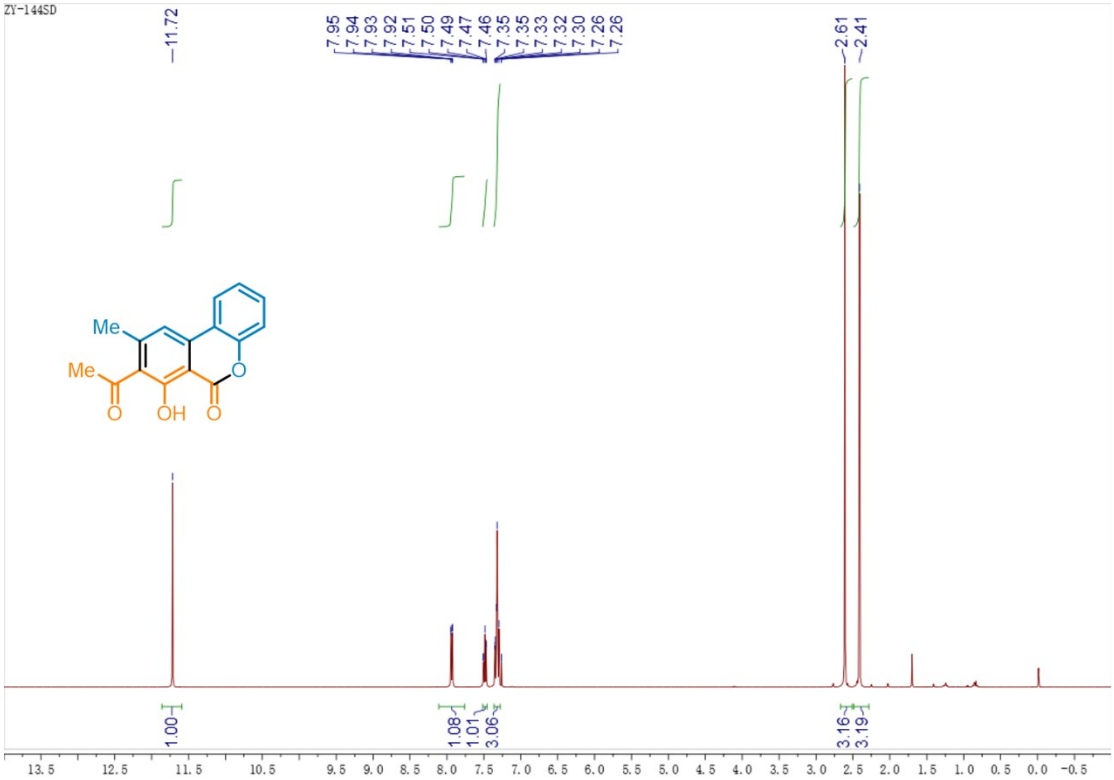
^{1}H NMR spectrum of **4n** (400 MHz, $CDCl_3$)



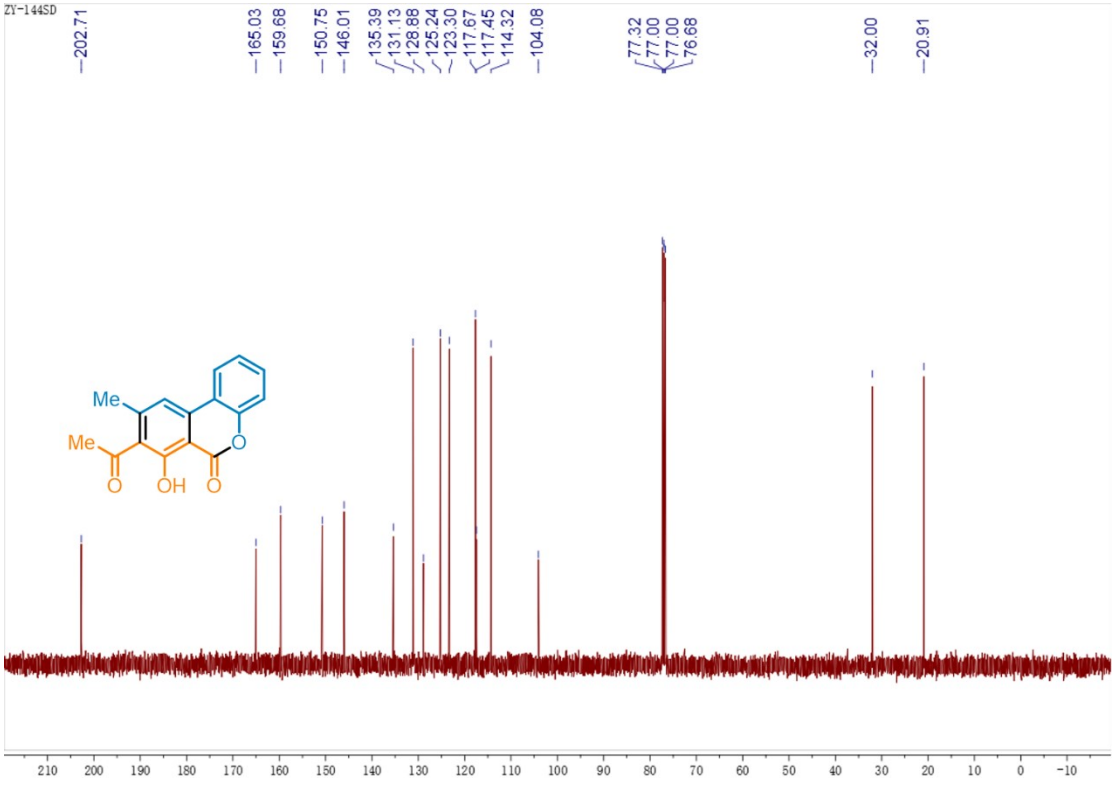
^{13}C NMR spectrum of **4n** (100 MHz, $CDCl_3$)



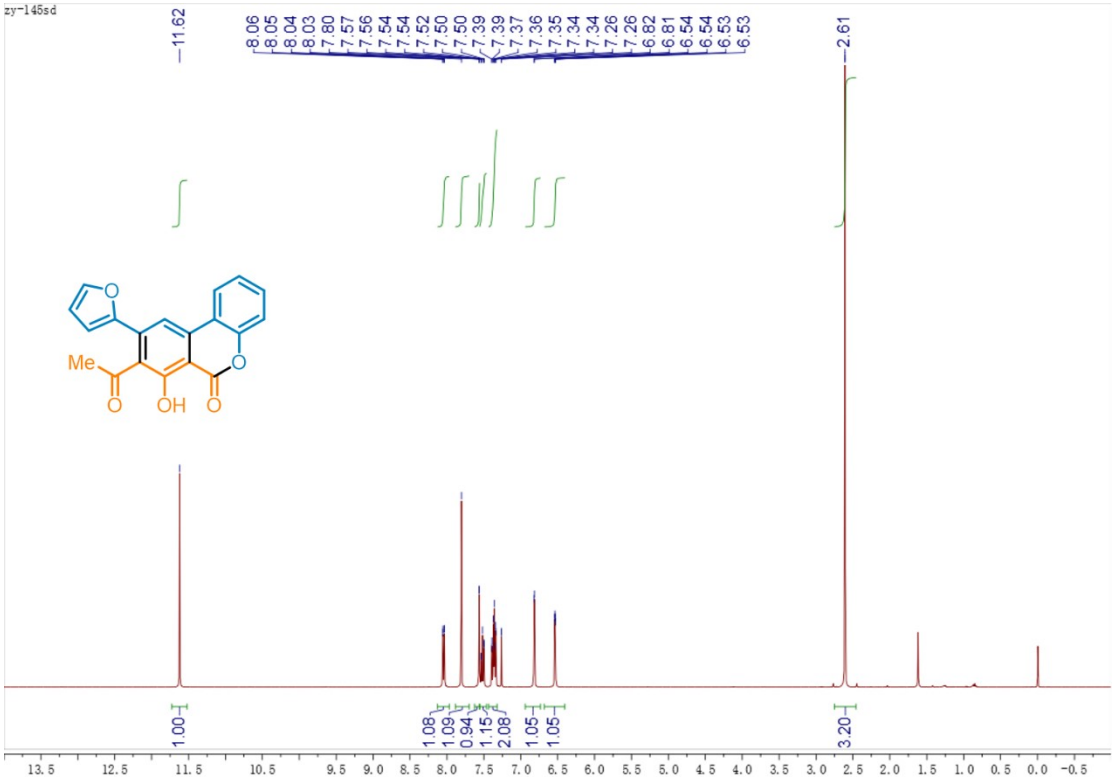
^{1}H NMR spectrum of **4o** (400 MHz, $CDCl_3$)



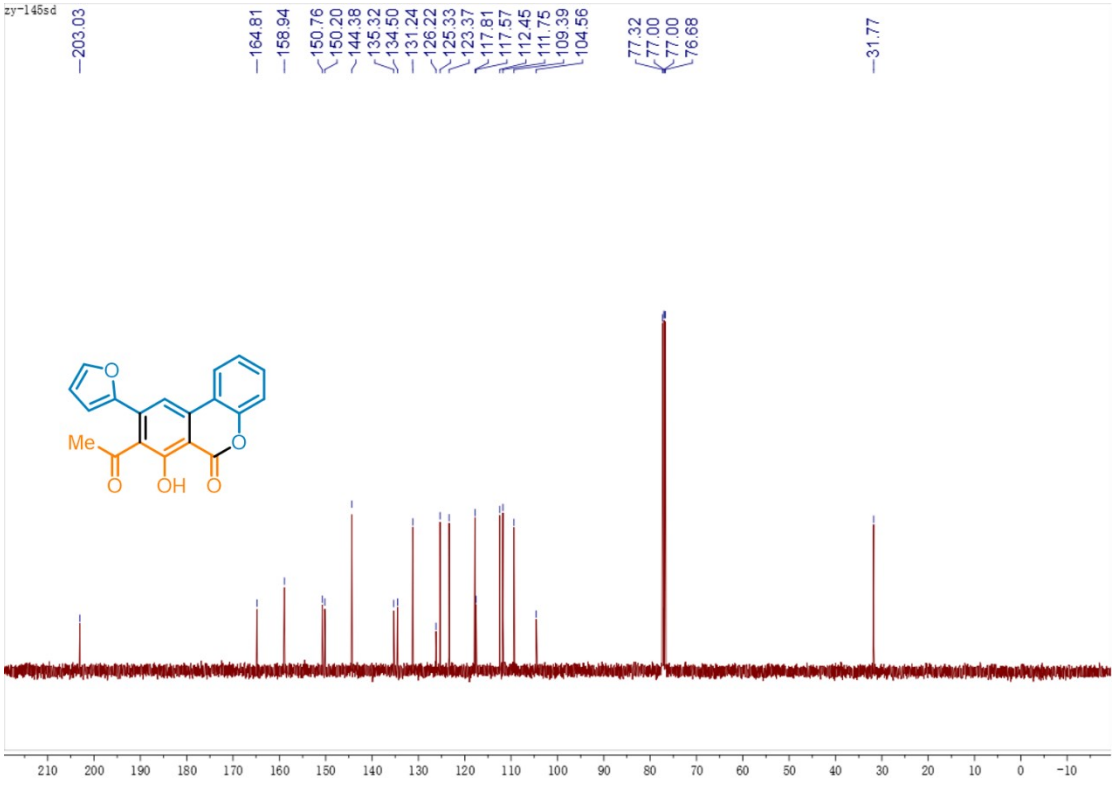
^{13}C NMR spectrum of **4o** (100 MHz, $CDCl_3$)



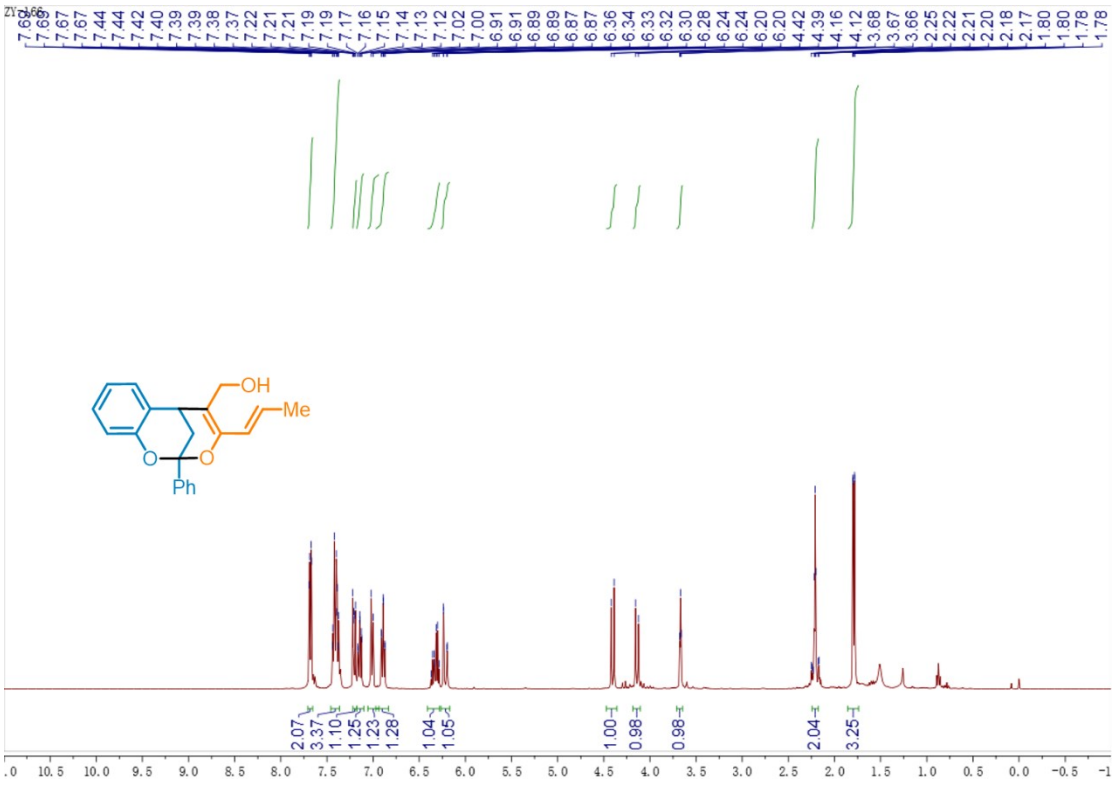
^{1}H NMR spectrum of **4p** (400 MHz, $CDCl_3$)



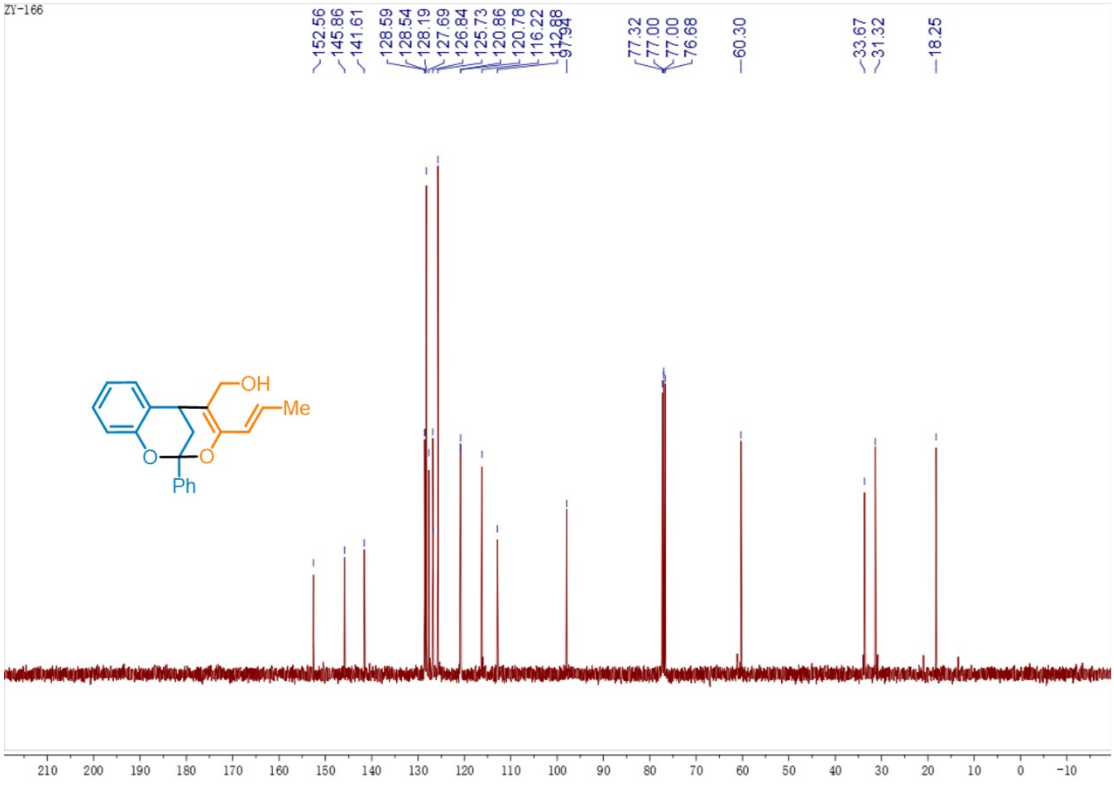
^{13}C NMR spectrum of **4p** (100 MHz, $CDCl_3$)



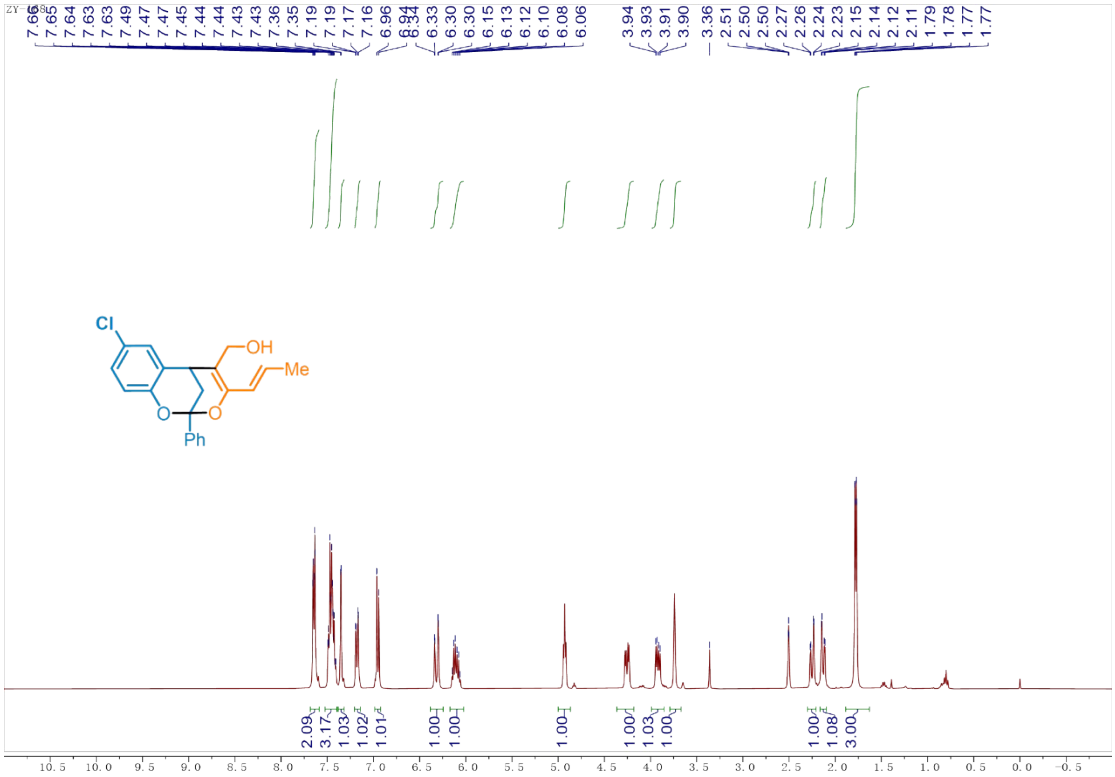
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)



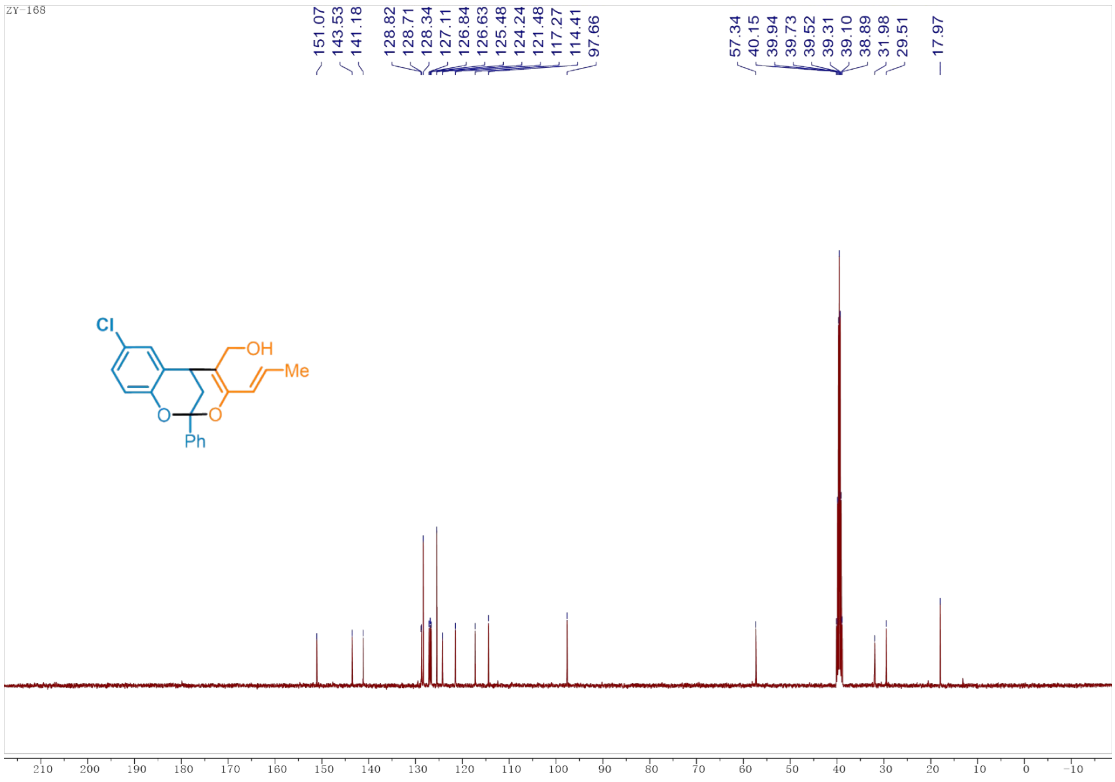
^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **6** (400 MHz, DMSO-d_6)



^{13}C NMR spectrum of **6** (100 MHz, DMSO-d_6)


ZY-168
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141.18
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128.71
128.34
127.11
126.84
126.63
125.48
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117.27
114.41
97.66
57.34
40.15
39.94
39.73
39.52
39.31
39.10
38.89
31.98
29.51
17.97
Cl
OH
Me
O
O
Ph
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200
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180
170
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150
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30
20
10
0
-10