SUPPORTING INFORMATION

Acid-promoted Formal [3+2] Cyclization/*N*, *O*-ketalization of *in situ* generated *ortho*-Alkynyl Quinone Methides: Access to Bridged 2,3-Cyclopentanoindoline Skeletons

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Content

General

All moisture or oxygen-sensitive reactions were carried out under an argon atmosphere in oven flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), CH_2Cl_2 (CaH_2), toluene (Na), $ClCH_2CH_2Cl$ (CaH_2). The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Anhui Liangchen Silicon Material Company in China. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian 500 MHz instrument. Chemical shifts were denoted in ppm (δ =), and calibrated by using residual undeuterated solvent ($CDCl_3$ (7.27 ppm), DMSO-d_6 (2.50 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for ^1H NMR and the deuterated solvent ($CDCl_3$ (77.00 ppm), DMSO-d_6 (39.51 ppm) or tetramethylsilane (0.00 ppm)) as internal standard for ^{13}C NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet. The MS data were obtained with ESI technique, and the relative intensity (%) is given in brackets. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. The IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer. The X-ray single- crystal determination was performed on a Bruker Smart 1000 CCD X-ray single crystal diffractometer. Compound **1a** was prepared according to the reported literature.[1,2]

1. Optimization of the Reaction Conditions.

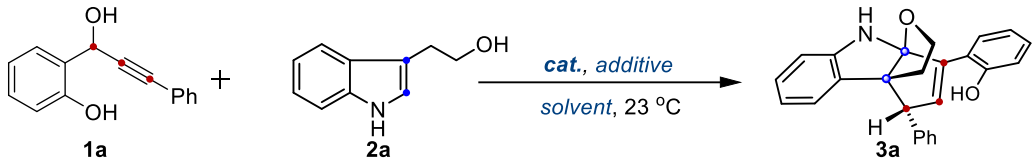


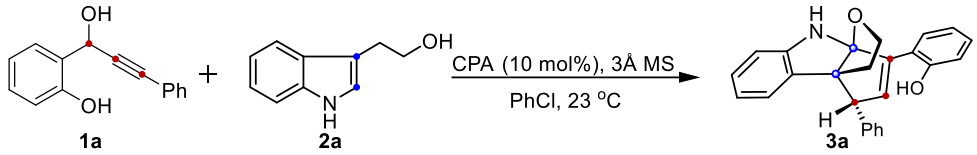
Table 1. Optimization of the Reaction Conditions

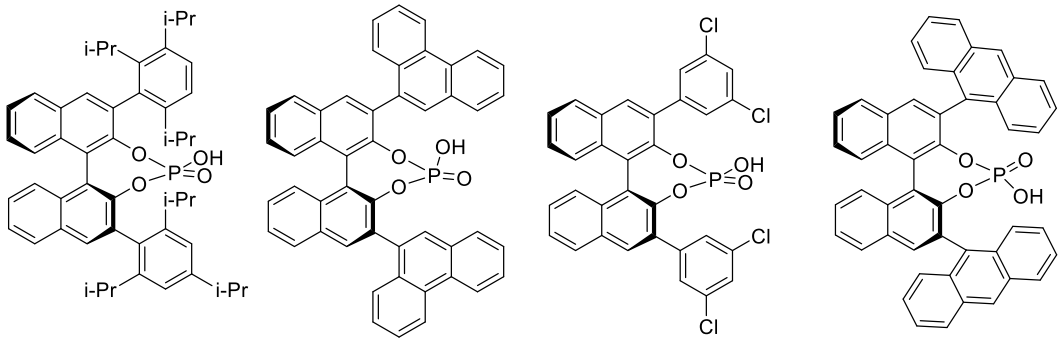
entry	catalyst	time/h	solvent	additive	yield (%)[a]	d.r.[b]
1	$AlCl_3$	12	CH_3CN	---	31	6:1
2	$Bi(OTf)_3$	12	CH_3CN	---	37	5:1
3	$BF_3{\cdot}OEt_2$	12	CH_3CN	---	42	6:1
4	$Al(OTf)_3$	12	CH_3CN	---	28	4:1
5	$Cu(OTf)_2$	12	CH_3CN	---	0	---
6	AgOTf	12	CH_3CN	---	0	---
7	(–)-CSA	12	CH_3CN	---	10	4:1
8	TFA	12	CH_3CN	---	trace	---
9	$AlCl_3$	12	DCE	---	18	10:1
10	$AlCl_3$	12	Toluene	---	16	8:1
11	CPA	12	Toluene	---	46	11:1
12	PA	24	CH_3CN	---	0	---
13	PA	24	$CHCl_3$	3Å MS	49	6:1
14	PA	24	DCE	3Å MS	37	11:1
15	PA	24	CH_2Cl_2	3Å MS	34	8:1
18	PA	12	Toluene	3Å MS	51	8:1
19	PA	12	PhF	3Å MS	21	8:1
20	CPA	12	PhCl	4 Å MS	46	8:1
21[c]	CPA(CuI)	12	PhCl	3Å MS	57	8:1
22	CPA(Ag2O)	12	PhCl	3Å MS	23	8:1
23	CPA	12	PhF	3Å MS	58	8:1
24	CPA	12	HFIP	3Å MS	0	---
25	PA	24	PhCl	3Å MS	57	20:1
26[d]	PA	72	PhCl	3Å MS	78	>20:1

Unless otherwise noted, all reactions were conducted with 0.20 mmol of **1** (1.0 equiv.), 0.30 mmol of **2** (1.5 equiv.), 10 mol% of catalyst and 3Å MS (50 mg, if applicable) in the solvent (2.0 mL) at 23 °C for the indicated time. [a]Yield of isolated **3a**. Only unidentified by-products were obtained. [b]Determined by ^1H NMR analysis. [c]The ratio of CPA and CuI is 2:1. [d]Another portion of 10 mol%

phosphonic acid was added after stirred for 24 hours. TFA = trifluoroacetic acid, CSA = camphorsulfonic acid, PA = 1,1′-binaphthyl-2,2′-diylhydrogenphosphate, CPA = R-(-)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate.

- Preliminary exploration on enantioselective version：





CPA 1
4% *e.e.*,
54 % *yield*,
14:1 *d.r.*

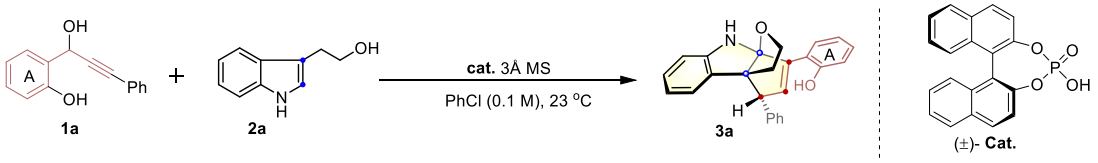
CPA 2
13% *e.e.*,
58% *yield*,
14:1 *d.r.*

CPA 3
8% *e.e.*,
43% *yield*,
14:1 *d.r.*

CPA 4
23% *e.e.*,
50% *yield*,
24:1 *d.r.*

A mixture of **1a** (44.8 mg, 0.20 mmol) and **2a** (48.2 mg, 0.30 mmol) was dissolved in chlorobenzene (1.0 mL), to the solution of the mixture was added **CPA** (0.02 mmol) and 3Å MS (50 mg) at 23 °C and stirred for 24 h. The reaction mixture without aqueous workup was directly purified by flash column chromatography on silica gel [gradient eluent: 15:1~10:1 petroleum ether/EtOAc] to give the chiral product **3a** as a solid. **Chiral HPLC:** (Chiralpak IB3, 5% ^{i}-PrOH, 95% hexane, 1.00 mL min^{-1}, λ = 254 nm) τ_R (minor) = 9.42 min, τ_R (major) = 13.95 min.

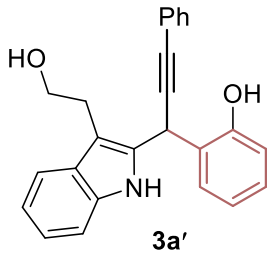
2. General Procedure for the Synthesis of Bridged 2, 3-Cyclopentanoindoline Skeletons and the Spectroscopic Data for the Compounds



For 0.2 mmol Scale:

A mixture of **1a** (44.8 mg, 0.20 mmol) and **2a** (48.2 mg, 0.30 mmol) was dissolved in

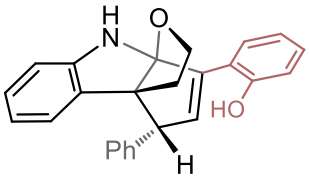
chlorobenzene (1.0 mL), to the solution of the mixture was added **Cat.** phosphonic acid (6.9 mg, 0.02 mmol) and 3Å MS (50 mg) at 23 °C and stirred for 24 h, then another portion of phosphonic acid (6.9 mg, 0.02 mmol) was added and stirred at 23 °C for another 48 h. The reaction mixture without aqueous workup was directly purified by flash column chromatography on silica gel [gradient eluent: 15:1~10:1 petroleum ether/EtOAc] to give the product **3a** as a solid (57.2 mg, 0.15 mmol) in 78% yield. (Note: Each 0.2 mmol scale reaction requires about 20 grams of silica gel.)



3a′

Compound 3a′: (92% yield, [15:1 petroleum ether/EtOAc], yellow crystal, mp. = 162.5 °C):

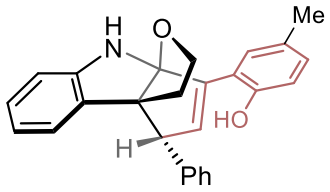
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 7.89 (s, 1H), 7.79 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.43 (dd, *J* = 6.8, 3.0 Hz, 2H), 7.28 (dt, *J* = 4.9, 2.5 Hz, 3H), 7.22 (s, 1H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.87 (s, 1H), 4.00 (dt, *J* = 9.8, 4.7 Hz, 1H), 3.92 (dt, *J* = 9.7, 4.8 Hz, 1H), 3.27 – 3.09 ppm (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 153.4, 135.6, 133.8, 131.7, 129.2 , 128.9, 128.4, 128.3, 128.1, 125.1, 122.8, 122.1, 121.1, 119.5, 119.8, 118.5, 117.1, 111.0, 108.4, 87.2, 85.0, 62.7 , 30.5, 27.0 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3407, 2921, 1455, 1037, 740, 691cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{22}NO_2$: 368.1651; found: 368.1661 $[M + H]^+$.



3a

Compound 3a: (78% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], white crystal, mp. = 102.5 °C):

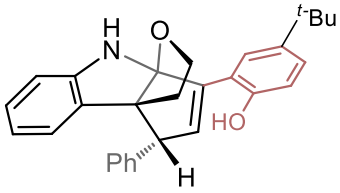
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.29 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.34 (dd, *J* = 12.0, 7.1 Hz, 4H), 7.28 (s, 2 H), 7.25 (m, *J* = 1.6 Hz, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.08 (d, *J* = 2.3 Hz, 2H), 4.80 (s, 1H), 4.39 (d, *J* = 2.2 Hz, 1H), 4.03 (ddd, *J* = 8.6, 6.7, 4.5 Hz, 1H), 3.88 (td, *J* = 8.5, 5.8 Hz, 1H), 2.03 – 1.93 (m, 1H), 1.81 ppm (ddd, *J* = 12.6, 5.7, 4.6 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.8, 148.5, 141.3, 140.4, 135.3 , 134.9, 131.5, 130.4, 128.7, 128.6, 128.6, 127.3, 123.7, 120.2, 119.9, 119.8, 117.8, 116.3, 110.2, 69.3, 67.7, 59.0, 37.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3391, 3272, 1482, 1234, 998, 733cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{22}NO_2$: 368.1651; found: 368.1661 $[M + H]^+$.



3b

Compound 3b: (78% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], pink oil):

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.07 (s, 1H), 7.40 (t, *J* = 7.4 Hz, 3H), 7.33 (dd, *J* = 13.0, 7.1 Hz,4H), 7.19 – 7.00 (m, 2H), 6.88 (t, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.06 (d, *J* = 2.1 Hz, 1H), 4.79 (s, 1H), 4.43 – 4.33 (m, 1H), 4.01 (ddd, *J* = 8.7, 6.8, 4.5 Hz, 1H), 3.86 (dd, *J* = 8.5, 5.9 Hz, 1H), 2.26 (s, 3H), 1.86 – 1.71 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ =152.6, 148.6, 141.4, 140.5, 135.0, 134.9, 131.7, 131.1, 128.9, 128.7, 128.6, 128.6, 127.2, 123.7, 120.2, 119.5, 117.7, 116.4, 110.2, 69.3, 67.6, 59.0, 37.4, 30.9, 20.3 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3226, 1607, 1464, 1034, 902, 726 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_2$: 382.1807; found: 382.1812 $[M + H]^+$.

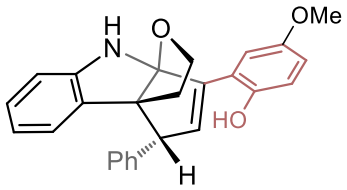


3c

Compound 3c: (50% yield, d.r. >20:1, [15:1 petroleum ether/EtOAc], brown oil):

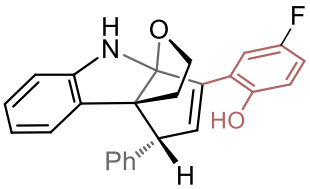
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.24 (s, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.15 (td, *J* = 8.6, 7.8, 1.0 Hz,1H), 6.97 (d, *J* =

8.6 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.12 (d, *J* = 2.3 Hz, 1H), 4.87 (s, 1H), 4.43 (d, *J* = 2.2 Hz, 1H), 4.04 (ddd, *J* = 8.6, 6.7, 4.7 Hz, 1H), 3.90 (td, *J* = 8.4, 5.9 Hz, 1H), 2.01 (ddd, *J* = 12.7, 8.2, 6.8 Hz, 1H), 1.89 – 1.73 (m, 1H), 1.32 ppm (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 152.5, 148.6, 142.5, 141.7, 140.5, 135.0, 128.7, 128.7, 128.6, 127.9, 127.7, 127.3, 123.7, 120.1, 118.8, 117.5, 116.3, 110.1, 69.1, 67.8, 59.1, 37.5, 34.0, 31.5 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3258, 2959, 1607,1483, 1033, 729 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{29}H_{30}NO_2$: 424.2277; found: 424.2285 $[M + H]^+$.



3d

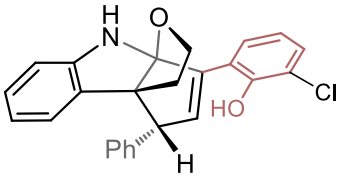
Compound 3d: (40% yield, d.r. >20:1, [10:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 8.89 (s, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.16 – 7.09 (m, 1H), 6.97 – 6.83 (m, 3H), 6.79 (d, *J* = 3.0 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.08 (d, *J* = 2.3 Hz, 1H), 4.82 (s, 1H), 4.38 (d, *J* = 2.1 Hz, 1H), 4.02 (ddd, *J* = 8.5, 6.7, 4.3 Hz, 1H), 3.86 (td, *J* = 8.6, 5.8 Hz, 1H), 3.75 (s, 3H), 1.97 (ddd, *J* = 12.7, 8.5, 6.8 Hz, 1H), 1.84 – 1.76 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 152.9, 148.8, 148.5, 141.2, 140.4, 135.3, 134.8, 128.7, 128.6, 128.6, 127.3, 123.7, 120.2, 120.1, 118.6, 116.4, 116.3, 115.7, 110.1, 69.3, 67.7, 58.9, 55.8, 37.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3262, 1607, 1488, 1207, 1033, 748 cm^{-1}； **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_3$: 398.1756; found: 398.1762 $[M + H]^+$.



3e

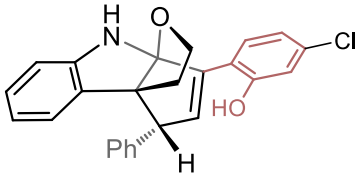
Compound 3e: (33% yield, d.r. >20:1, [10:1 petroleum ether/EtOAc], brown oil):

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.13 (s, 1H), 7.47 – 7.37 (m, 2H), 7.36 – 7.28 (m, 4H), 7.12 (td, *J* = 7.8, 1.1 Hz, 1H), 6.96 (ddd, *J* = 9.2, 7.2, 2.6 Hz, 2H), 6.94 – 6.84 (m, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.08 (d, *J* = 2.3 Hz, 1H), 4.79 (s, 1H), 4.37 (d, *J* = 2.2 Hz, 1H), 4.02 (ddd, *J* = 8.6, 6.8, 4.2 Hz, 1H), 3.85 (td, *J* = 8.7, 5.7 Hz, 1H), 1.97 (ddd, *J* = 12.7, 8.6, 6.8 Hz, 1H), 1.80 ppm (ddd, *J* = 12.6, 5.6, 4.3 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 157.3, 155.4, 150.9, 148.5, 140.4, 140.1, 136.1, 134.6, 128.8, 128.7, 128.6, 127.4, 123.7, 120.3, 118.8, 117.0, 116.8, 116.2, 110.2, 69.4, 67.8, 58.8, 37.4 ppm; **^{19}C NMR** (470 MHz, $CDCl_3$) δ = − 125.6 ppm; **ATR-FTIR** (cm^{-1}):$\bar{\upsilon}$ = 3236, 2874, 1607, 1484, 1033, 728 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}FNO_2$: 386.1556; found: 386.1564 $[M + H]^+$.



3f

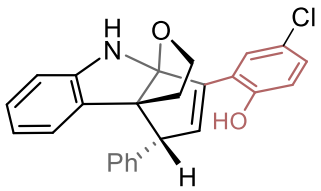
Compound 3f: (51% yield, d.r. = 12:1, [15:1 petroleum ether/EtOAc], white crystal), mp. = 61.2 °C)：**^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 7.45 – 7.40 (m, 2H), 7.39 – 7.30 (m, 5H), 7.22 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.14 (td, *J* = 7.7, 1.1 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.14 (d, *J* = 2.3 Hz, 1H), 4.80 (s, 1H), 4.40 (d, *J* = 2.2 Hz, 1H), 4.04 (ddd, *J* = 8.7, 6.8, 4.2 Hz, 1H), 3.92 – 3.79 (m, 1H), 1.99 (ddd, *J* = 12.7, 8.7, 6.8 Hz, 1H), 1.81 ppm (ddd, *J* = 12.7, 5.6, 4.2 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.6, 147.5, 139.5, 139.1, 135.6, 133.5, 129.5, 128.7, 127.7, 127.6, 127.5, 126.3, 122.7, 121.4, 120.7, 119.3, 119.2, 115.4, 109.2, 68.5, 66.8, 57.83, 36.3 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3389, 2950, 1604, 1451, 907, 731 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}ClNO_2$: 402.1261; found: 402.1270 $[M + H]^+$.



3g

Compound 3g: (61% yield, d.r. >20:1, [10:1 petroleum ether/EtOAc], brown crystal, mp. = 160.9 ºC):

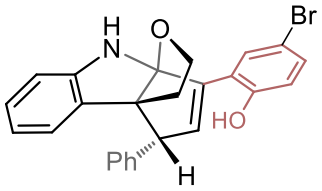
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.55 (s, 1H), 7.46 – 7.38 (m, 2H), 7.33 (q, *J* = 6.7, 5.8 Hz, 4H), 7.19 – 7.09 (m, 2H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.85 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.06 (d, *J* = 2.3 Hz, 1H), 4.75 (s, 1H), 4.37 (d, *J* = 2.2 Hz, 1H), 4.03 (ddd, *J* = 8.6, 6.8, 4.3 Hz, 1H), 3.86 (td, *J* = 8.6, 5.8 Hz, 1H), 1.98 (ddd, *J* = 12.7, 8.5, 6.8 Hz, 1H), 1.88 –1.74 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.6, 148.4, 140.4, 140.1, 135.7, 135.6, 134.6, 132.2, 128.8, 128.7, 128.6, 127.4, 123.7, 120.4, 120.2, 118.5, 118.0, 116.1, 110.2, 69.4, 67.7, 58.9, 37.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3262, 1592, 1247, 1028, 929, 749 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}ClNO_2$: 402.1261; found: 402.1267 $[M + H]^+$.



3h

Compound 3h: (62% yield, d.r. = 10:1, [15:1 petroleum ether/EtOAc], white crystal, mp. = 69.8 ºC):

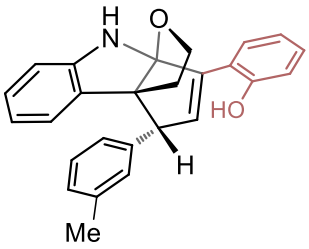
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.36 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32 (q, *J* = 6.1 Hz, 4H), 7.24 – 7.17 (m, 2H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.95 – 6.85 (m, 3H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.08 (d, *J* = 2.0 Hz, 1H), 4.40 – 4.35 (m, 1H), 4.07 – 3.97 (m, 1H), 3.85 (td, *J* = 8.6, 5.9 Hz, 1H), 2.01 – 1.90(m, 1H), 1.80 ppm (dt, *J* = 12.6, 5.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 153.6, 148.4, 140.3, 140.0, 136.3, 134.6, 130.6, 130.1, 128.8, 128.3, 128.5, 127.4, 124.5, 123.7, 121.4, 120.3, 119.2, 116.2, 110.2, 69.5, 67.8, 58.9, 37.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3138, 2912, 1479, 1255, 985, 711cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}ClNO_2$: 402.1261; found: 402.1269 $[M + H]^+$.



3i

Compound 3i: (40% yield, d.r. = 12:1, [15:1 petroleum ether/EtOAc], white crystal, mp. = 160.2 °C):

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.39 (s, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.18 – 7.01 (m, 2H), 6.98 – 6.78 (m, 3H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.09 (d, *J* = 2.2 Hz, 1H), 4.75 (s, 1H), 4.38 (s, *J* = 2.1 Hz, 1H), 4.03 (ddd, *J* = 8.6, 6.8, 4.3 Hz, 1H), 3.86 (td, *J* = 8.6, 5.8 Hz, 1H), 1.98 (ddd, *J* = 12.7, 8.5, 6.9 Hz, 1H), 1.86 – 1.68 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.1, 148.4, 140.2, 140.0, 136.3, 134.6, 133.5, 133.0, 128.8, 128.7, 128.6, 127.4, 123.7, 122.0, 120.4, 119.7, 116.2, 111.6, 110.3, 69.5, 67.8, 58.9, 37.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3268, 2879, 1607, 1478, 1031, 726 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}BrNO_2$: 446.0756; found: 446.0760 $[M + H]^+$.

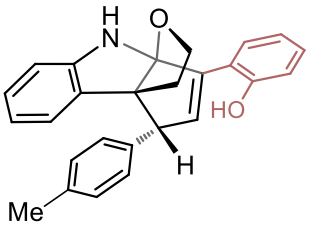


3j

Compound 3j: (70% yield, d.r. = 10:1, [10:1 petroleum ether/EtOAc], brown oil):

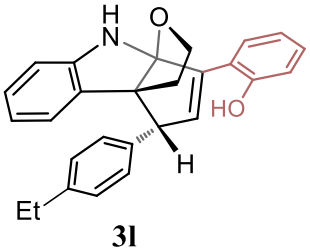
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.34 (s, 1H), 7.34 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.32 – 7.25 (m, 3H), 7.20 – 7.10 (m, 4H), 7.01 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.94 – 6.85 (m, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.08 (d, *J* = 2.4 Hz, 1H), 4.80 (s, 1H), 4.36 (d, *J* = 2.4 Hz, 1H), 4.08 – 3.99 (m, 1H), 3.88 (td, *J* = 8.5, 5.7 Hz, 1H), 2.42 (s, 3H), 2.01 (ddd, *J* = 12.6, 8.4, 6.7 Hz, 1H), 1.83 ppm (ddd, *J* = 12.7, 5.8, 4.4 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.9, 148.6, 141.1, 140.4, 138.5, 135.6, 135.0, 131.5, 130.5, 129.3, 128.6, 128.6, 128.1, 125.8, 123.8, 120.3, 120.0, 119.9, 117.9, 116.4, 110.2, 69.3, 67.7, 59.0, 37.5, 21.6 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3234, 2879, 1606, 1482,

1255, 730 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_2$: 382.1807; found: 382.1810 $[M + H]^+$.



3k

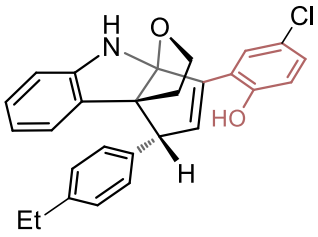
Compound 3k: (49% yield, d.r. >20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.31 (s, 1H), 7.29 (dd, *J* = 16.1, 7.2 Hz, 4H), 7.22 (d, *J* = 7.6 Hz, 3H), 7.18 – 7.09 (m, 1H), 6.99 (d, *J* = 8.1 Hz, 1H), 6.95 – 6.81 (m, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.05 (d, *J* = 2.2 Hz, 1H), 4.78 (s, 1H), 4.35 (s, 1H), 4.08 – 3.97 (m, 1H), 3.92 – 3.81 (m, 1H), 2.38 (s, 3H), 2.08 – 1.91 (m, 1H), 1.86 – 1.74 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.9, 148.5, 141.1, 137.3, 136.9, 135.6, 135.0, 131.5, 130.4, 129.4, 128.5, 128.5, 123.7, 120.2, 119.9, 119.9, 117.8, 116.3, 110.2, 69.2, 67.6, 58.7, 37.4, 30.8, 21.1 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3239, 1732, 1403, 1251, 1032, 735 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_2$: 382.1807; found: 382.1816 $[M + H]^+$.



3l

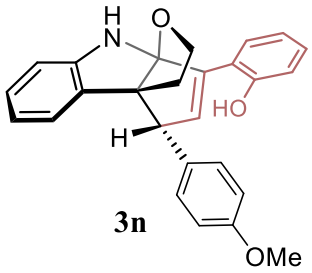
Compound 3l: (55% yield, d.r. >20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.31 (s, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.25 (s, 4H), 7.14 – 7.07 (m, 1H), 7.02 – 6.95 (m, 1H), 6.87 (q, *J* = 7.1 Hz, 2H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.06 (d, *J* = 2.2 Hz, 1H), 4.78 (s, 1H), 4.36 (d, *J* = 2.0 Hz, 1H), 4.02 (ddd, *J* = 8.5, 6.7, 4.7 Hz, 1H), 3.93 – 3.78 (m, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.07 – 1.95 (m, 1H), 1.87 – 1.76 (m, 1H), 1.27 ppm (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.9, 148.5, 143.3, 141.0, 137.6, 135.6, 135.0, 131.5, 130.4, 128.6, 128.5, 128.2, 123.7, 120.2, 119.9, 119.9, 117.8, 116.3, 110.2,

69.2, 67.7, 58.7, 37.4, 30.8, 28.5, 15.5 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3232, 1732, 1609, 1254, 1032, 738 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{26}NO_2$: 396.1964; found: 396.1969 $[M + H]^+$.



3m

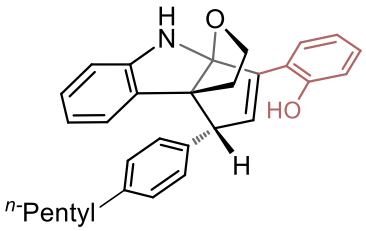
Compound 3m: (57% yield, d.r. >20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.41 (s, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.27 (s, 6H), 7.24 (d, *J* = 2.2 Hz, 2H), 7.22 (d, *J* = 2.6 Hz, 1H), 7.19 – 7.11 (m, 1H), 6.99 – 6.83 (m, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.10 (d, *J* = 2.3 Hz, 1H), 4.74 (d, *J* = 18.0 Hz, 1H), 4.37 (d, *J* = 2.3 Hz, 1H), 4.04 (ddd, *J* = 8.6, 6.7, 4.4 Hz, 1H), 3.88 (td, *J* = 8.6, 5.8 Hz, 1H), 2.71 (q, *J* = 7.6 Hz, 2H), 2.02 (ddd, *J* = 12.7, 8.4, 6.8 Hz, 1H), 1.90 – 1.77 (m, 1H), 1.29 ppm (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 153.6, 148.4, 143.4, 140.0, 137.2, 136.7, 134.7, 130.7, 130.0, 128.6, 128.5, 128.2, 124.5, 123.7, 121.4, 120.4, 119.2, 116.2, 110.3, 69.5, 67.8, 58.6, 37.4, 28.5, 15.5 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3133, 2927, 1608, 1465, 1030, 742 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{27}H_{25}ClNO_2$: 430.1574; found: 430.1580 $[M + H]^+$.



3n

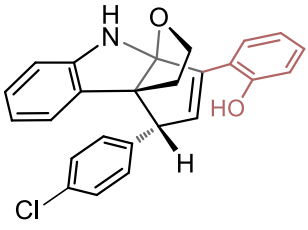
Compound 3n: (30% yield, d.r. >20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.33 (s, 1H), 7.36 – 7.25 (m, 3H), 7.24 (d, *J* = 4.1 Hz, 2H), 7.17 – 7.05 (m, 1H), 7.05 – 6.93 (m, 1H), 6.97(m,2H),6.89 (ddd, *J* = 7.4, 6.1, 1.2 Hz, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.05 (d, *J* = 2.4 Hz, 1H), 4.79 (s, 1H), 4.34 (d, *J* = 2.4 Hz, 1H), 4.02 (ddd, *J* = 8.5, 6.6, 4.5 Hz, 1H), 3.88 (td, *J* = 8.5, 5.8 Hz, 1H), 3.84 (s, 3H), 2.00 (ddd, *J* = 12.6, 8.3, 6.7 Hz, 1H), 1.81 ppm (ddd, *J* = 12.6, 5.8, 4.6

Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 148.5, 140.9, 135.7, 135.0, 132.4, 131.5, 130.4, 129.6, 128.5, 123.7, 120.2, 119.9, 119.9, 117.8, 116.3, 114.1, 110.2, 69.3, 67.7, 58.4, 55.3, 37.4, 30.9 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3262, 1607, 1488, 1207, 1033, 748 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_3$: 398.1756; found: 398.1762 [*M* + H]$^+$.



3o

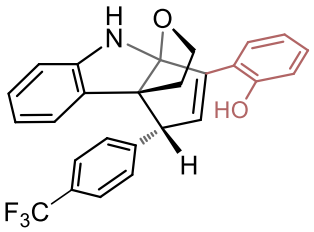
Compound 3o: (53% yield, d.r. = 8:1, [10:1 petroleum ether/EtOAc], pink oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.31 (s, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.29 – 7.26 (m, 4H), 7.22 (d, *J* = 6.2 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.87 (q, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.06 (d, *J* = 2.3 Hz, 1H), 4.78 (s, 1H), 4.35 (d, *J* = 2.1 Hz, 1H), 4.07 – 3.94 (m, 1H), 3.87 (td, *J* = 8.4, 5.9 Hz, 1H), 2.71 – 2.54 (m, 2H), 2.16 (s, 3H), 2.05 – 1.94 (m, 1H), 1.86 – 1.75 (m, 1H), 1.70 – 1.60 (m, 2H), 1.40 – 1.31 (m, 2H), 0.90 ppm (q, *J* = 5.9, 5.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.9, 148.5, 142.0, 141.0, 137.5, 135.6, 135.0, 131.5, 130.4, 128.7, 128.5, 128.3, 123.7, 120.2, 119.9, 119.9, 117.8, 116.3, 110.2, 69.2, 67.7, 58.7, 37.4, 35.6, 31.5, 31.1, 30.9, 22.5, 14.0; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3246, 1608, 1482, 1032, 909, 733 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{30}H_{32}NO_2$: 438.2433; found: 438.2441 [*M* + H]$^+$.



3p

Compound 3p: (65% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], white crystal, mp. = 98.6^{o}C):

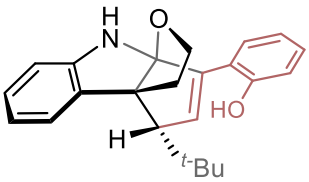
^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.21 (s, 1H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 7H), 7.23 – 7.21 (m, 1H), 7.15 – 7.08 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.94 – 6.76 (m, 3H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.01 (d, *J* = 2.2 Hz, 1H), 4.78 (s, 1H), 4.34 (d, *J* = 2.1 Hz, 1H), 4.03 (ddd, *J* = 8.7, 6.8, 4.1 Hz, 2H), 3.86 (td, *J* = 8.7, 5.8 Hz, 1H), 1.94 (ddd, *J* = 12.7, 8.7, 6.9 Hz, 2H), 1.85 – 1.72 ppm (m, 2H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ = 154.9, 148.6, 141.4, 137.9, 135.2, 134.8, 133.4, 132.6, 131.5, 130.5, 128.6, 127.8, 127.0, 126.4, 126.0, 123.8, 120.3, 120.0, 117.9, 116.4, 110.2, 69.3, 67.7, 59.1, 37.5 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ =3233, 2922, 1608, 1482, 1032, 729 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}ClNO_2$: 402.1261; found: 402.1267 $[M + H]^+$.



3q

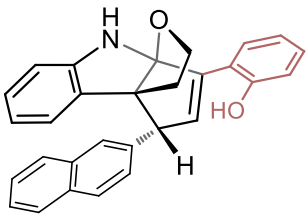
Compound 3q: (60% yield, d.r. = 10:1, [15:1 petroleum ether/EtOAc], white crystal, mp. = 67.6 ºC)

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.18 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.25 (m, 2H), 7.13 (td, *J* = 7.7, 1.3 Hz, 1H), 6.99 (dd, *J* = 8.3, 1.2 Hz, 1H), 6.88 (qd, *J* = 7.2, 1.1 Hz, 2H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 4.81 (s, 1H), 4.42 (d, *J* = 2.3 Hz, 1H), 4.05 (ddd, *J* = 8.7, 6.7, 3.8 Hz, 1H), 3.86 (td, *J* = 8.9, 5.7 Hz, 1H), 1.91 (ddd, *J* = 12.6, 9.0, 6.8 Hz, 1H), 1.82 ppm (ddd, *J* = 12.6, 5.7, 3.8 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.9, 148.7, 144.6, 142.2, 134.1, 131.5, 130.7, 129.0, 128.9, 125.8, 125.7, 125.7, 125.7, 123.6, 120.3, 120.1, 119.6, 118.0, 116.3, 110.2, 69.4, 67.7, 58.6, 37.5 ppm; **^{13}C NMR** (470 MHz, $CDCl_3$) δ = - 62.4 ppm; **ATR-FTIR** (cm^{-1})**:** $\bar{\upsilon}$ = 3154, 2877, 1610, 1451, 1324, 728cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{21}F_3NO_2$: 436.1524; found: 436.1528 $[M + H]^+$.



3r

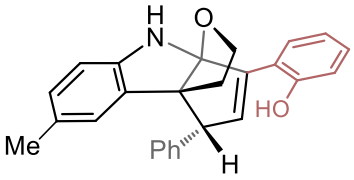
Compound 3r: (30% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.22 (s, 1H), 7.25 – 7.19 (m, 1H), 7.14 (ddd, *J* = 16.0, 7.6, 1.6 Hz, 2H), 7.09 – 7.03 (m, 1H), 6.94 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.81 (q, *J* = 7.8 Hz, 2H), 6.55 (d, *J* = 7.8 Hz, 1H), 5.92 (d, *J* = 2.3 Hz, 1H), 4.68 (s, 1H), 4.14 (ddd, *J* = 8.7, 6.5, 4.0 Hz, 1H), 3.94 (td, *J* = 8.7, 5.5 Hz, 1H), 2.91 (td, *J* = 7.7, 2.3 Hz, 1H), 2.53 (ddd, *J* = 12.4, 8.8, 6.6 Hz, 1H), 2.17 (ddd, *J* = 12.4, 5.4, 4.0 Hz, 1H), 1.82 – 1.66 (m, 1H), 1.63 – 1.48 (m, 3H), 1.43 (q, *J* = 7.3 Hz, 2H), 0.97 ppm (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.8, 148.7, 138.6, 137.7, 135.1, 131.4, 130.1, 128.3, 123.6, 120.2, 120.0, 119.7, 117.6, 116.7, 110.0, 69.0, 66.2, 53.5, 35.8, 31.5, 31.0, 22.9, 14.0 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3142, 2789, 1452, 897, 725，654cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{23}H_{26}NO_2$: 348.1964; found: 348.1921 $[M + H]^+$.



3s

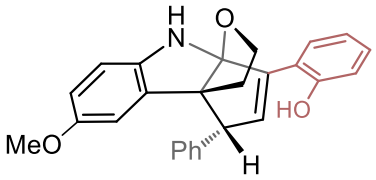
Compound 3s: (40% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.35 (s, 1H), 7.99 – 7.80 (m, 3H), 7.74 (s, 1H), 7.52 (t, *J* = 6.3 Hz, 3H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.92 (dd, *J* = 13.7, 7.2 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 2.2 Hz, 1H), 4.83 (s, 1H), 4.55 (d, *J* = 2.0 Hz, 1H), 4.18 – 3.95 (m, 1H), 3.95 – 3.79 (m, 1H), 2.08 – 1.93 (m, 2H), 1.81 ppm (dt, *J* = 12.6, 5.1 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.8, 148.6, 141.7, 138.9, 134.6, 134.4, 133.2, 131.4, 130.6, 129.9, 128.9, 128.7, 123.6, 120.2, 120.0, 119.7, 117.9, 116.2, 110.2,

69.3, 67.6, 58.3, 37.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3137, 2879, 1609, 1452, 897, 725 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{29}H_{24}NO_2$: 418.1807; found: 418.1823 $[M + H]^+$.



3t

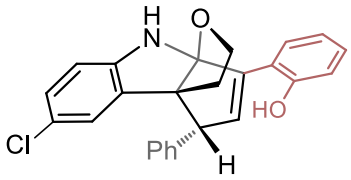
Compound 3t: (49% yield, d.r. = 5:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (dd, *J* = 7.7, 6.1 Hz, 3H), 7.30 – 7.21 (m, 3H), 7.13 (s, 1H), 7.03 – 6.96 (m, 1H), 6.93 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.86 (td, *J* = 7.4, 1.2 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 1H), 6.05 (d, *J* = 2.4 Hz, 1H), 4.38 (d, *J* = 2.3 Hz, 1H), 4.07 – 3.94 (m, 1H), 3.87 (td, *J* = 8.4, 5.9 Hz, 1H), 2.35 (s, 3H), 2.00 – 1.91 (m, 1H), 1.79 ppm (ddd, *J* = 12.6, 5.9, 4.7 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.9, 146.2, 141.3, 140.6, 135.4, 135.3, 131.5, 130.5, 129.9, 129.1, 128.8, 128.7, 128.0, 127.3, 124.3, 119.9, 117.9, 116.8, 110.5, 69.2, 67.7, 59.0, 37.4 21.0 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3232, 2871, 1484, 1252, 1031 ,702cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_2$: 382.1807; found: 382.1816 $[M + H]^+$.



3u

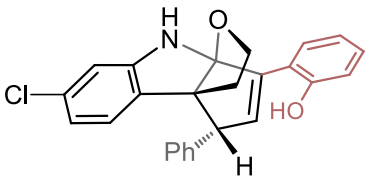
Compound 3u: (36% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 7.41 (dd, *J* = 8.3, 6.8 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 3H), 7.30 – 7.23 (m, 2H), 6.99 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.92 (d, *J* = 2.6 Hz, 1H), 6.87 (d, *J* = 1.3 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 1H), 6.06 (d, *J* = 2.3 Hz, 1H), 4.38 (d, *J* = 2.4 Hz, 1H), 4.00 (ddd, *J* = 8.7, 6.7, 4.9 Hz, 1H), 3.88 (td, *J* = 8.3, 5.9 Hz, 1H), 3.82 (s, 3H), 1.95 (ddd, *J* = 12.7, 8.0, 6.6 Hz, 1H), 1.84 – 1.75 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.9, 154.8, 142.3, 141.4, 140.4, 136.7, 135.2, 131.5, 130.5, 128.8, 128.6, 127.4, 119.9, 119.9, 117.9, 117.2,

113.2, 111.4, 110.7, 69.2, 68.0, 58.9, 56.1, 37.3 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3238, 2932, 1485, 1162, 1031, 729cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_3$: 398.1756; found: 398.1761 $[M + H]^+$.



3v

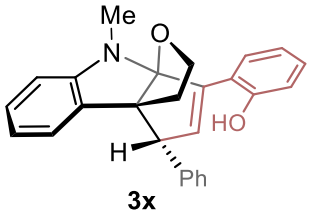
Compound 3v: (47% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.14 (s, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.30 (m, 3H), 7.30 – 7.23 (m, 3H), 7.07 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.2 Hz, 1H), 6.87 (td, *J* = 7.5, 1.3 Hz, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.07 (d, *J* = 2.3 Hz, 1H), 4.81 (s, 1H), 4.35 (d, *J* = 2.4 Hz, 1H), 4.02 (ddd, *J* = 8.7, 6.7, 4.4 Hz, 1H), 3.86 (td, *J* = 8.6, 5.8 Hz, 1H), 1.96 (ddd, *J* = 12.7, 8.5, 6.7 Hz, 1H), 1.77 ppm (ddd, *J* = 12.8, 5.8, 4.4 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.8, 147.1, 141.1, 140.0, 136.5, 135.3, 131.5, 130.6, 128.9, 128.6, 128.5, 127.5, 124.6, 124.0, 120.1, 119.6, 118.0, 116.7, 111.0, 69.4, 67.7, 58.8, 37.4 ppm ; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3263, 2920, 1603, 1480, 1250, 698cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}ClNO_2$: 402.1261; found: 402.1266 $[M + H]^+$.



3w

Compound 3w: (55% yield, d.r. > 20:1, [15:1 petroleum ether/EtOAc], brown oil): **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.13 (s, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.30 – 7.26 (m, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.84 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.56 (d, *J* = 1.6 Hz, 1H), 6.08 (d, *J* = 2.2 Hz, 1H), 4.90 (s, 1H), 4.35 (d, *J* = 2.1 Hz, 1H), 4.06 (ddd, *J* = 8.7, 6.8, 4.0 Hz, 1H), 3.87 (td, *J* = 8.8, 5.7 Hz, 1H), 1.98 (ddd, *J* = 12.7, 8.8, 7.0 Hz, 2H), 1.85 – 1.70 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.76, 149.73, 141.19, 140.10, 135.43, 134.28, 133.22, 131.49, 130.60, 128.84, 128.61, 127.45, 124.47, 120.10,

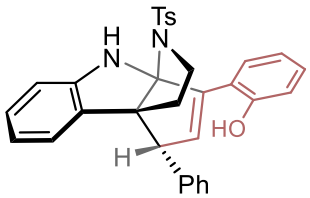
119.86, 119.70, 117.94, 116.66, 109.98, 69.54, 67.13, 58.95, 37.41 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3146, 1607, 1438, 1032, 906, 708 cm^{-1} ; **HRMS** (ESI): m/z calcd for $C_{25}H_{21}ClNO_2$: 402.1261; found: 402.1266 $[M + H]^+$.



3x

Compound 3x: (36% yield, d.r. = 2:1, [15:1 petroleum ether/EtOAc], white crystal, mp. = 92.1 °C):

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 9.44 (s, 1H), 7.44 – 7.36 (m, 2H), 7.36 – 7.30 (m, 3H), 7.29 – 7.25 (m, 1H), 7.21 – 7.14 (m, 2H), 7.01 – 6.94 (m, 2H), 6.89 – 6.82 (m, 1H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 5.98 (d, *J* = 2.0 Hz, 1H), 4.33 (d, *J* = 1.9 Hz, 1H), 4.17 – 4.04 (m, 1H), 3.66 (ddd, *J* = 10.7, 8.7, 5.0 Hz, 1H), 2.70 (s, 3H), 2.06 (ddd, *J* = 12.4, 10.8, 7.1 Hz, 1H), 1.75 ppm (ddd, *J* = 12.5, 4.9, 2.0 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 154.5, 151.3, 142.1, 140.1, 137.1, 133.0, 131.2, 130.1, 128.8, 128.6, 128.5, 127.2, 123.1, 122.3, 119.9, 118.4, 118.1, 117.2, 105.8, 70.1, 67.3, 57.6, 37.5, 29.1 ppm; **ATR-FTIR (cm^{-1})**: $\bar{\upsilon}$ = 3138, 2912, 1479, 1255, 985, 711cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{26}H_{24}NO_2$: 382.1807; found: 382.1816$[M + H]^+$.



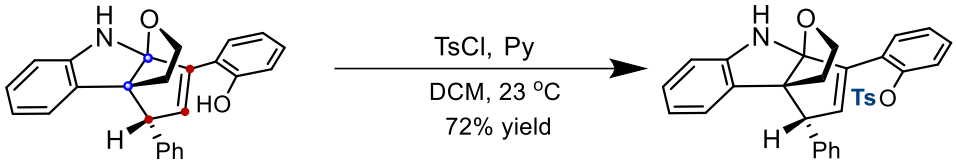
3y

Compound 3y: (35% yield, d.r. = 2:1, [15:1 petroleum ether/EtOAc], brown oil):

^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.04 (d, *J* = 44.8 Hz, 1H), 7.55 – 7.47 (m, 5H), 7.42 – 7.29 (m, 6H), 7.14 (ddq, *J* = 24.8, 16.7, 8.4, 7.9 Hz, 7H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.88 – 6.79 (m, 2H), 5.97 (d, *J* = 2.6 Hz, 1H), 4.33 (t, *J* = 6.1 Hz, 1H), 4.05 (s, 1H), 3.19 (q, *J* = 6.8 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 1H), 2.36 ppm (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.4, 154.3, 153.6, 143.2, 143.1, 140.0, 137.2, 136.8, 136.3, 135.5, 131.5, 130.2, 129.6, 129.5, 128.8, 128.7, 128.7, 128.6, 128.4, 127.9, 127.8,

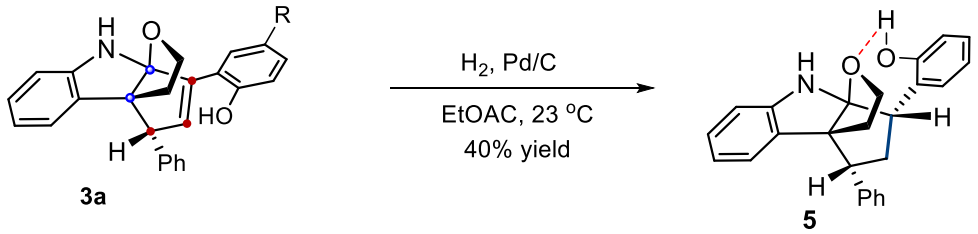
127.6, 127.0, 126.9, 126.9, 126.8, 126.2, 125.4, 124.5, 123.3, 122.7, 122.6, 121.8, 121.5, 120.0, 119.6, 118.8, 116.8, 111.4, 111.2, 111.0, 110.7, 109.0, 43.3, 43.1, 33.3, 25.4, 25.2, 21.5 ppm; **ATR-FTIR**(cm^{-1}) : $\bar{\upsilon}$ = 3138, 2912, 1479, 1255, 985, 711 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{32}H_{29}N_2SO_3$: 521.1899; found: 521.1826 $[M + H]^+$.

3. General Procedure for the Synthesis derivatives.

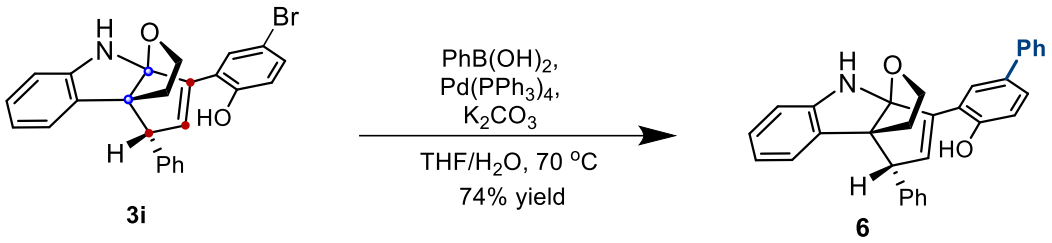


3a **4**

To a mixture of **3a** (36.7 mg, 0.10 mmol) and pyridine (1.0 mL), *p*-toluenesulfonyl chloride (27.4 mg, 0.12 mmol) in dry dichloromethane (10 mL) was added slowly and stirred at room temperature for 1 h. The reaction mixture was then washed with aqueous 1N HCl (10.0 mL) and extracted with diethyl ether (2 × 10 mL). The combined organic phases were washed with water (10.0 mL), brine solution (10 mL) and dried over anhydrous sodium sulfate. The filtered solution was concentrated and was purified by column chromatography [5% ethyl acetate in petroleum ether] to yield **4** (37.5 mg, 72%) as white crystals, mp. = 150-152 °C: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 8.00 – 7.88 (m, 1H), 7.50 – 7.36 (m, 2H), 7.36 – 7.20 (m, 7H), 7.18 – 7.12 (m, 2H), 7.07 (td, *J* = 7.6, 1.3 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 2H), 6.83 (td, *J* = 7.4, 1.0 Hz, 1H), 6.64 – 6.50 (m, 1H), 6.05 (d, J = 2.4 Hz, 1H), 4.80 (s, 1H), 3.85 (d, *J* = 2.5 Hz, 1H), 3.81 (ddd, *J* = 8.6, 6.8, 3.7 Hz, 1H), 3.67 (td, *J* = 8.9, 5.5 Hz, 1H), 2.21 (s, 3H), 1.74 (ddd, *J* = 12.4, 9.1, 6.8 Hz, 1H), 1.61 ppm (ddd, *J* = 12.4, 5.5, 3.6 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 149.6, 148.0, 145.1, 140.6, 137.5, 137.1, 135.4, 133.4, 130.3, 129.5, 129.0, 128.6, 128.6, 128.4, 128.2, 127.6, 127.3, 127.1, 123.7, 123.3, 119.9, 117.5, 110.4, 68.7, 67.5, 59.0, 37.3, 21.6 ppm, **HRMS** (ESI): m/z calcd for $C_{32}H_{28}NO_4S$: 522.1739; found: 522.1746 $[M + H]^+$.

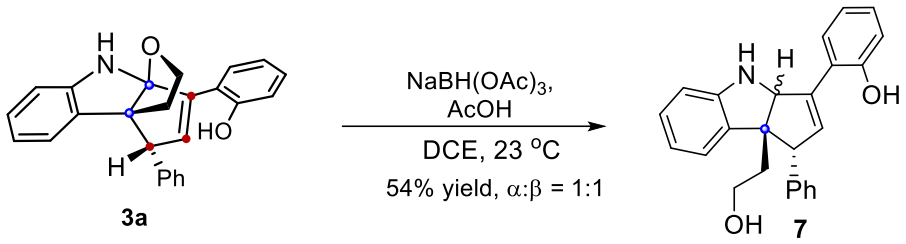


A solution of Pd/C (7.3 mg, 20%) in EtOAc (2.0 mL) was added **3a** (36.7 mg, 0.10 mmol) to a 15 mL Schlenk tube under H_2. After stirring for 12 hours at room temperature in a round bottom flask, the system was concentrated in vacuo and the chromatogram of the Flash residue (hexane/ether = 3:1 to 2:1) yield **5** (14.4 mg, 40%) as white crystals, mp. = 163.9 °C: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 8.22 (s, 1H), 7.33 – 7.26 (m, 4H), 7.16 – 7.07 (m, 3H), 7.05 (d, J = 8.1 Hz, 1H), 6.94 (t, J = 7.6 Hz, 2H), 6.44 (d, J = 7.8 Hz, 1H), 6.37 (t, J = 7.5 Hz, 1H), 5.75 (d, J = 7.5 Hz, 1H), 4.47 – 4.33 (m, 1H), 4.22 (s, 1H), 4.14 – 4.01 (m, 1H), 3.77 (dd, J = 12.9, 4.8 Hz, 1H), 3.69 (dd, J = 13.0, 4.7 Hz, 1H), 2.69 – 2.52 (m, 2H), 2.33 – 2.15 ppm (m, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.9, 149.9, 138.9, 129.4, 128.8, 128.4, 128.1, 128.1, 128.0, 127.1, 126.4, 123.2, 120.2, 118.5, 117.4, 112.7, 108.2, 70.2, 67.8, 54.8, 48.5, 42.0, 35.1 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3303, 1919, 1606, 1463, 1233, 745 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{24}NO_2$: 370.1807; found: 370.1816$[M + H]^+$.



Under nitrogen atmosphere, compound **3i** (22.0 mg, 0.05 mmol), phenylboronic acid (12.0 mg, 2.0 equiv.), K_2CO_3 (20.3 mg, 3.0 equiv.), $Pd(PPh_3)_4$ (5.6 mg, 0.1 equiv.), were successively added to a 25 mL Schlenk tube, followed by the addition of 2.0 mL of THF and 0.2 mL H_2O, the mixture was degassed and purged with N_2 and then heated to 70 °C for 24 h. After cooling to rt, the solvent was removed and purified by chromatography to yield a yellow foam **6** (16.2 mg, 0.04 mmol). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 9.40 (s, 1H), 7.53 (td, J = 8.7, 2.0 Hz, 2H), 7.48 (d, J = 2.4 Hz, 1H), 7.41 (dt, J = 7.5, 5.9 Hz, 3H), 7.38 – 7.17 (m, 6H), 7.13 (tt, J = 7.7, 1.8 Hz, 1H), 7.07

(d, *J* = 8.4 Hz, 1H), 6.89 (q, *J* = 8.7, 8.0 Hz, 2H), 6.62 (d, *J* = 7.8 Hz, 1H), 6.12 (dd, *J* = 28.5, 2.3 Hz, 1H), 4.83 (s, 1H), 4.39 (dd, *J* = 16.3, 2.4 Hz, 1H), 4.04 (tdd, *J* = 9.2, 6.7, 4.3 Hz, 1H), 3.88 (ddd, *J* = 12.9, 8.5, 5.9 Hz, 1H), 2.12 – 1.91 (m, 1H), 1.89 – 1.76 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 153.4, 147.5, 140.3, 139.5, 139.2, 135.4, 134.6, 133.8, 133.5, 132.5, 132.0, 129.0, 128.1, 127.7, 127.6, 127.5, 126.3, 125.6, 122.7, 119.2, 118.6, 117.3, 109.2, 68.3, 66.7, 58.0, 36.4 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3303, 1919, 1606, 1463, 1233, 745 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{31}H_{26}NO_2$: 444.1964; found: 444.1926$[M + H]^+$.



Under room temperature, compound **3a** (36.7 mg, 0.10 mmol) was dissolved in 2.0 mL DCE, $NaBH(OAc)_3$ (79.4 mg, 0.37 mmol), AcOH(14.3 μL, 0.25 mmol) were successively added to a 15 mL Schlenk tube. The solution was stirred for 3 hours until the **3a** was disappeared. The reaction was quenched with $NaHCO_3$ and extracted with CH_2Cl_2, the combined organic layers were washed with a saturated salt solution, dried with magnesium sulfate, and evaporated. The residue was purified by chromatography to give **7** (24.8 mg. 65%) as a gray solid, mp. = 101.7 °C: **^{1}H NMR** (500 MHz, Chloroform-*d*) δ = 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 8.1 Hz, 5H), 7.24 – 7.21 (m, 2H), 7.21 – 7.14 (m, 3H), 7.02 (dt, *J* = 20.1, 7.5 Hz, 3H), 6.85 (dt, *J* = 12.6, 6.5 Hz, 5H), 6.50 (t, *J* = 7.5 Hz, 1H), 6.04 (d, *J* = 2.4 Hz, 1H), 5.96 (s, 1H), 5.51 (d, *J* = 7.6 Hz, 1H), 5.16 (d, *J* = 16.9 Hz, 2H), 4.28 (d, *J* = 14.9 Hz, 1H), 3.61 (dt, *J* = 9.2, 4.5 Hz, 1H), 3.42 (dt, *J* = 11.3, 4.2 Hz, 1H), 3.14 (td, *J* = 10.6, 4.1 Hz, 1H), 3.02 (td, *J* = 11.0, 3.4 Hz, 1H), 2.33 (dd, *J* = 9.6, 5.0 Hz, 1H), 2.29 – 2.20 (m, 1H), 1.53 (ddd, *J* = 15.1, 10.6, 4.8 Hz, 2H), 1.47 – 1.39 ppm (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ = 155.1, 155.0, 147.6, 147.0, 143.2, 142.8, 140.6, 140.4, 138.6, 133.8, 133.7, 133.1, 130.6, 130.3, 129.6, 129.6, 129.4, 129.2, 128.5, 127.9, 127.9, 127.1, 127.1, 126.8, 123.4, 123.2, 122.7, 122.5, 121.5, 119.8, 119.6, 116.9, 116.8, 114.2, 114.0, 74.8, 74.4, 62.1,

62.1, 61.0, 60.5, 60.5, 59.4, 43.0, 40.0 ppm; **ATR-FTIR** (cm^{-1}): $\bar{\upsilon}$ = 3283, 2922, 1601, 1451, 1259, 729 cm^{-1}; **HRMS** (ESI): m/z calcd for $C_{25}H_{24}NO_2$: 370.1807; found: 370.1813$[M + H]^+$

4. Relative Configuration Assignment of 4 and 5 by X-Ray Crystallographic Analysis

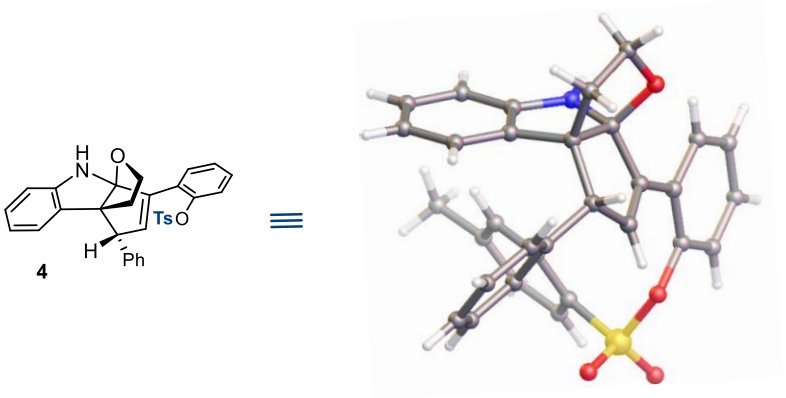
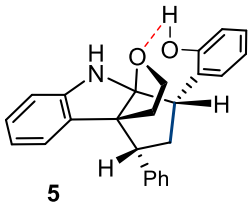


Table 2 Crystal data and structure refinement for 4.

Identification code	**4**
CCDC	2123850
Empirical formula	$C_{32}H_{27}NO_4S$
Formula weight	521.60
Temperature/K	298(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.0968(11)
b/Å	13.8829(15)
c/Å	16.8118(16)
α/°	90
β/°	101.868(3)
γ/°	90
Volume/$Å^3$	2534.6(4)
Z	4
$\rho_{calc}g/cm^3$	1.367
μ/mm^{-1}	0.168
F(000)	1096.0
Crystal size/mm^3	0.3 × 0.23 × 0.16
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	3.838 to 50.038
Index ranges	$-11 \leq h \leq 13$, $-16 \leq k \leq 16$, $-17 \leq l \leq 20$
Reflections collected	12496
Independent reflections	4458 [R_{int} = 0.1050, R_{sigma} = 0.0693]
Data/restraints/parameters	4458/0/344
Goodness-of-fit on F^2	0.961
Final R indexes [I>=2σ (I)]	R_1 = 0.0673, wR_2 = 0.1670
Final R indexes [all data]	R_1 = 0.0963, wR_2 = 0.1865
Largest diff. peak/hole / e $Å^{-3}$	0.28/-0.54



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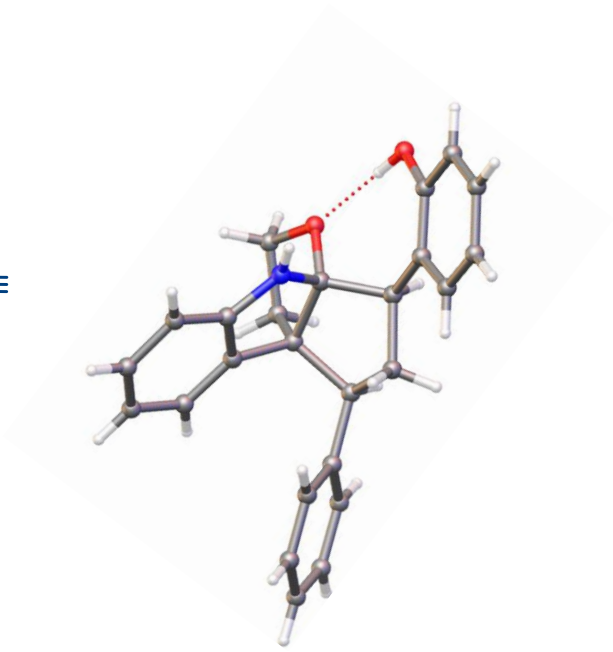


Table 3 Crystal data and structure refinement for 5.

Identification code	**5**
CCDC	2123851
Empirical formula	$C_{25}H_{23}NO_2$
Formula weight	369.44
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	19.8233(16)
b/Å	10.5498(9)
c/Å	18.1025(9)
α/°	90
β/°	90
γ/°	90

Volume/$Å^3$	3785.8(5)
Z	8
$\rho_{calc}g/cm^3$	1.296
μ/mm^{-1}	0.643
F(000)	1568.0
Crystal size/mm^3	0.15 × 0.13 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.922 to 132.092
Index ranges	$-23 \leq h \leq 11$, $-11 \leq k \leq 12$, $-21 \leq l \leq 17$
Reflections collected	8128
Independent reflections	3313 [R_{int} = 0.0475, R_{sigma} = 0.0623]
Data/restraints/parameters	3313/0/255
Goodness-of-fit on F^2	0.992
Final R indexes [I>=2σ (I)]	R_1 = 0.0558, wR_2 = 0.1414
Final R indexes [all data]	R_1 = 0.1010, wR_2 = 0.1669
Largest diff. peak/hole / e $Å^{-3}$	0.47/-0.30

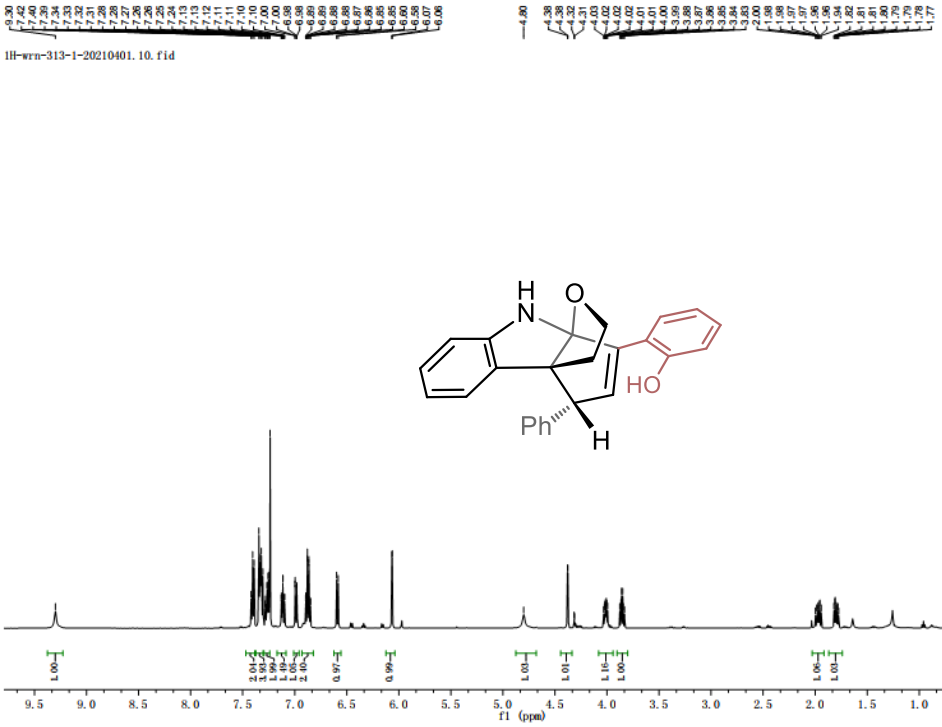
5. References

1. Du, J.-Y.; Ma, Y.-H.; Meng, F.-X.; Chen, B.-L.; Zhang, S.-L.; Li, Q.-L.; Gong, S.-W.; Wang, D.-Q.; Ma, C.-L. *Org. Lett.* **2018,** *20*, 4371-4374.

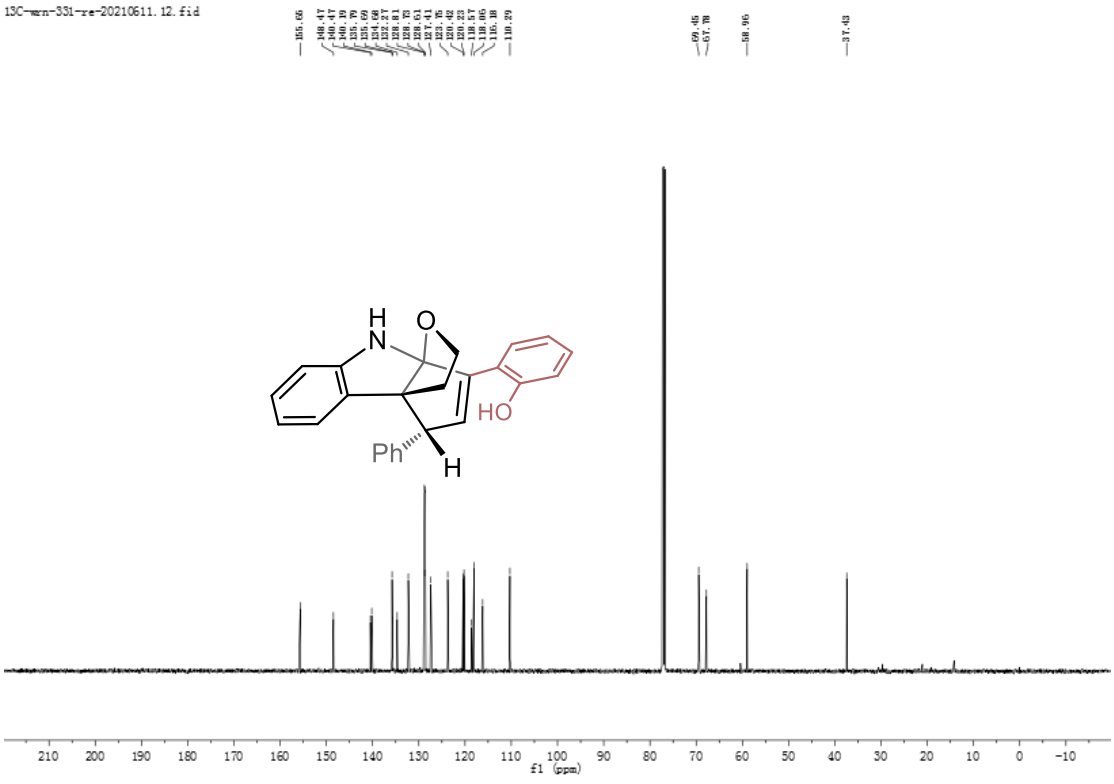
2. Du, J.-Y.; Ma, Y.-H.; Meng, F.-X.; Zhang, R.-R.; Wang, R.-N.; Shi, H.-L.; Wang, Q.; Fan, Y.-X.; Huang, H.-L.; Cui, J.-C.; Ma, C.-L. *Org. Lett.* **2019,** *21*, 465-468.

6. Copies of NMR and HPLC Spectra

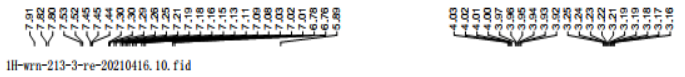
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a**

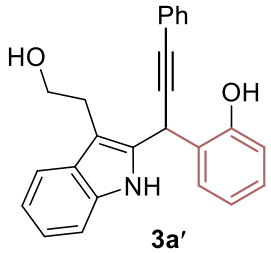


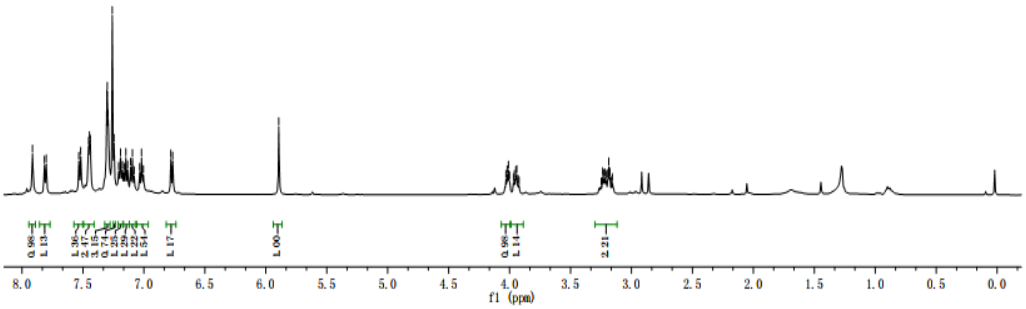
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3a**



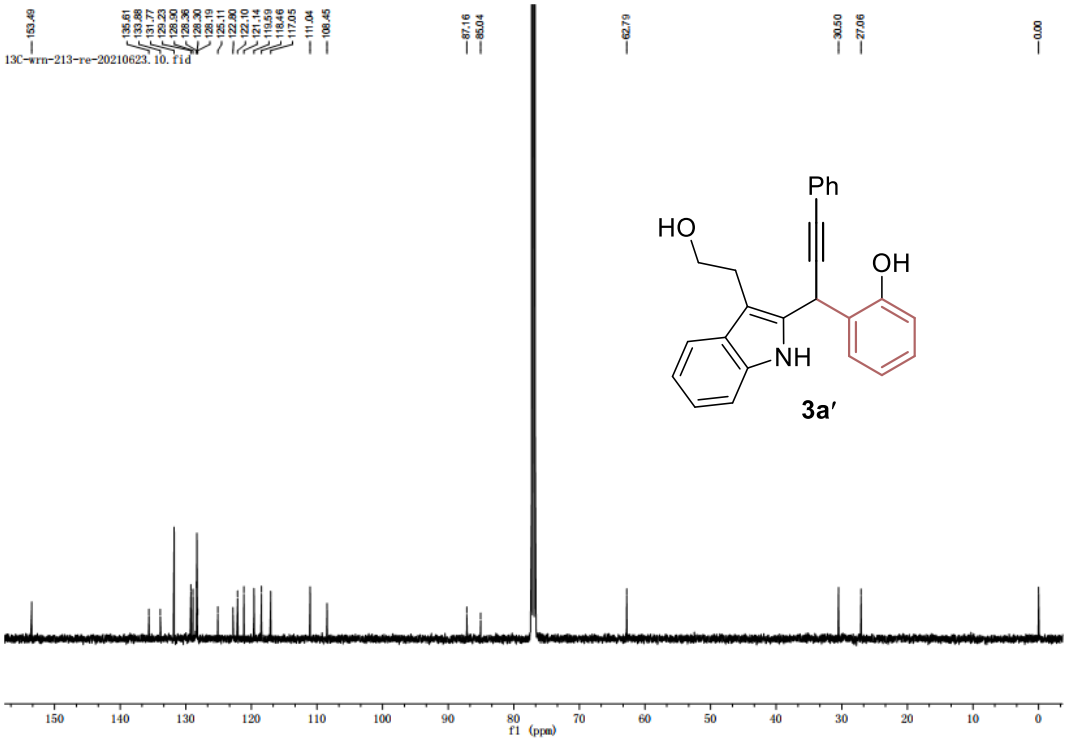
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3a'**



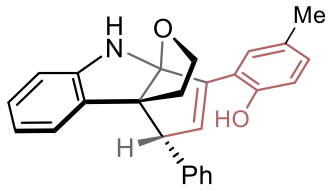


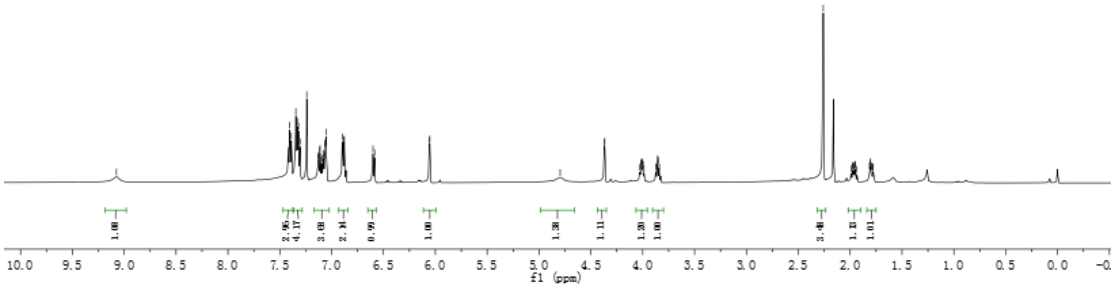


^{13}C NMR (500 MHz, $CDCl_3$) of compound **3a′**

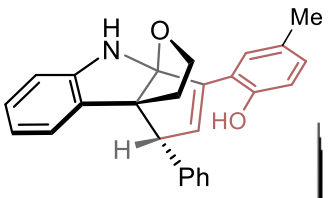


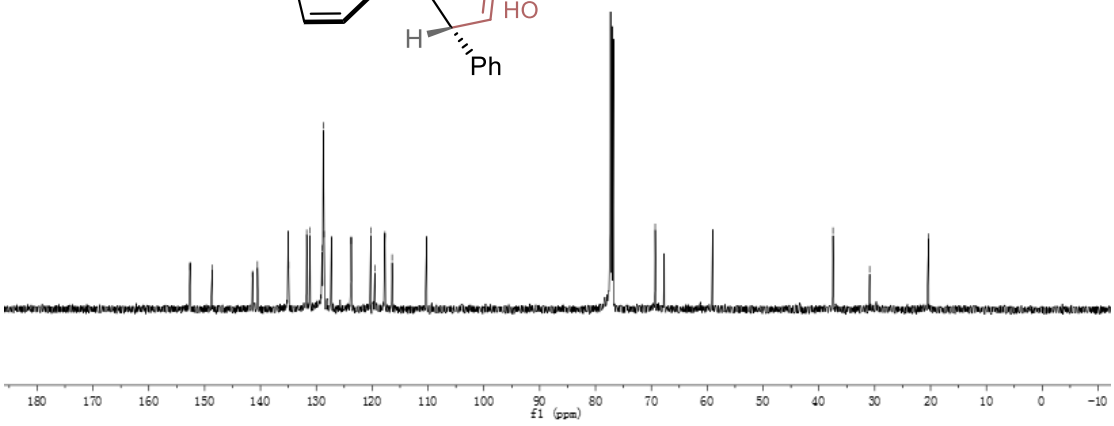
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3b**



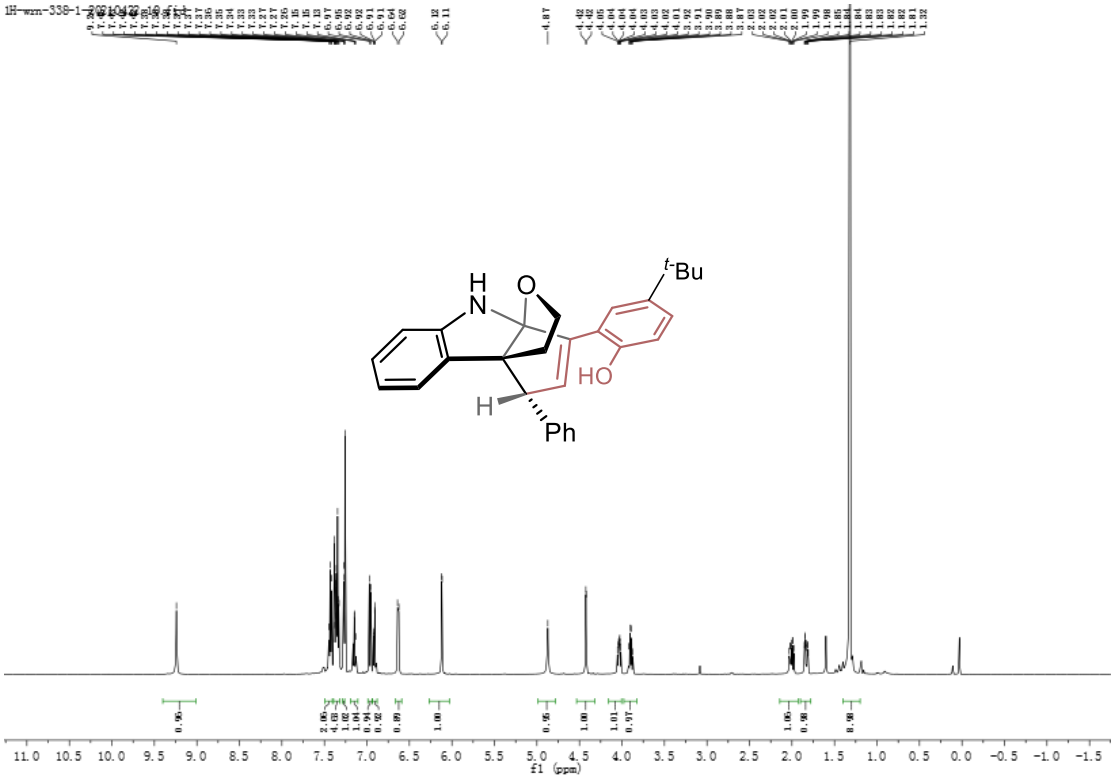


^{13}C NMR (500 MHz, $CDCl_3$) of compound **3b**

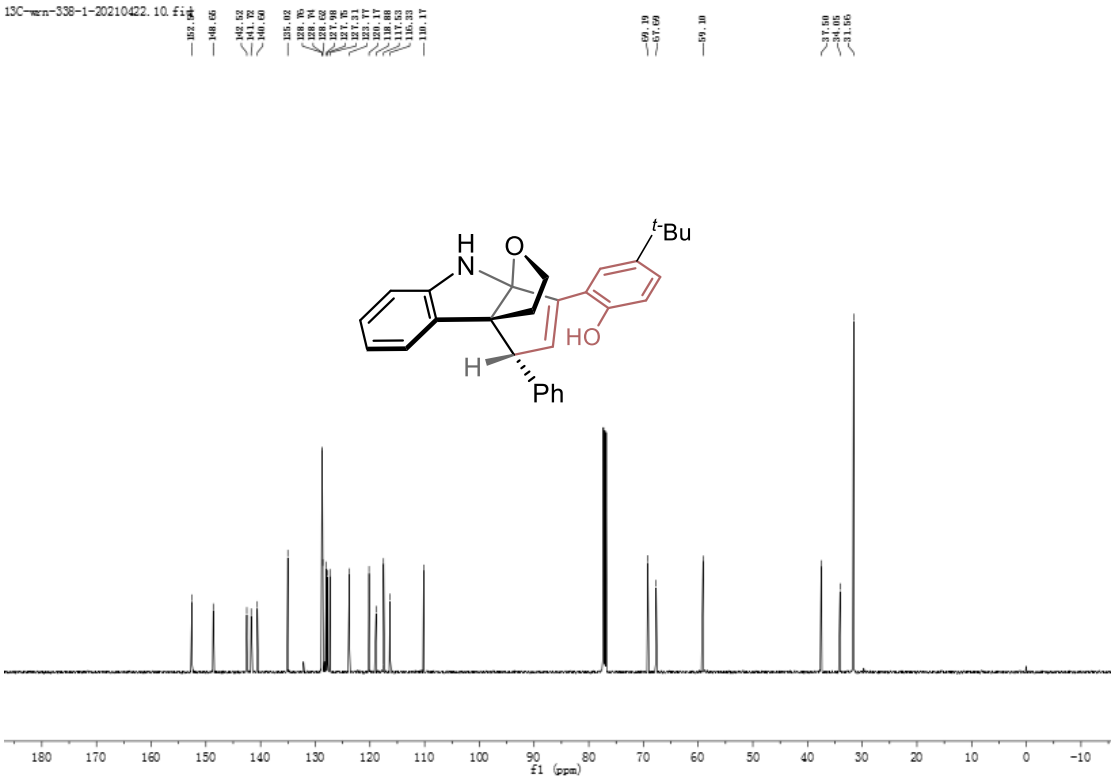




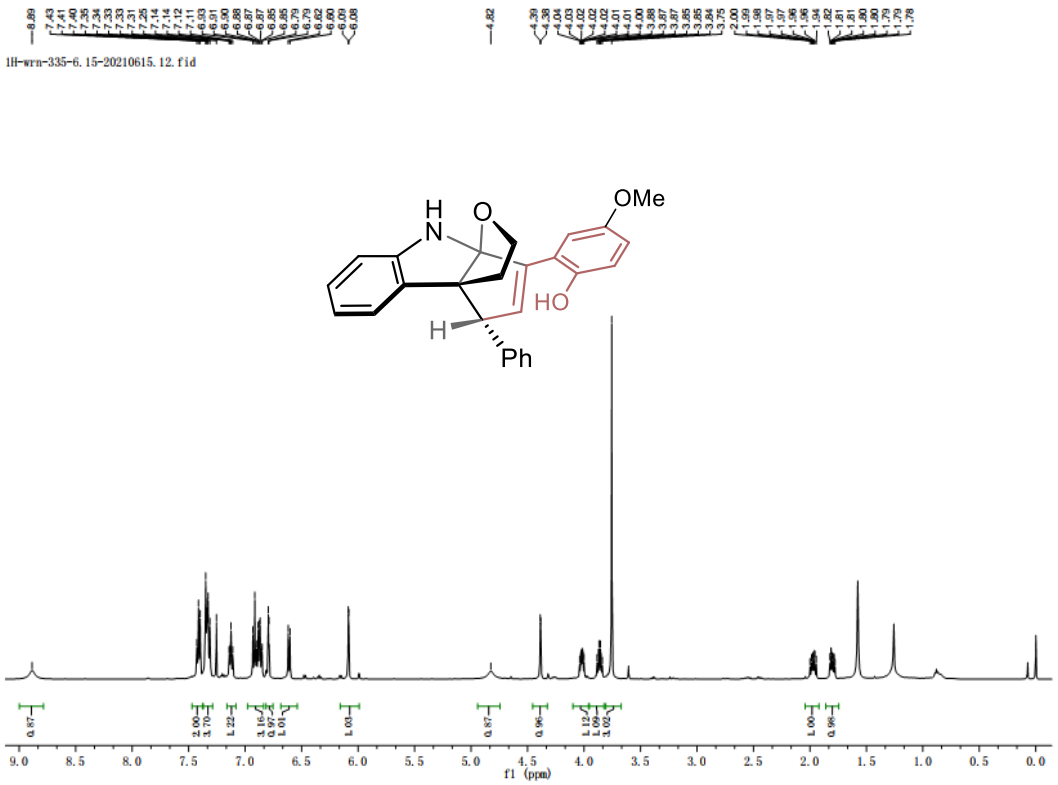
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**



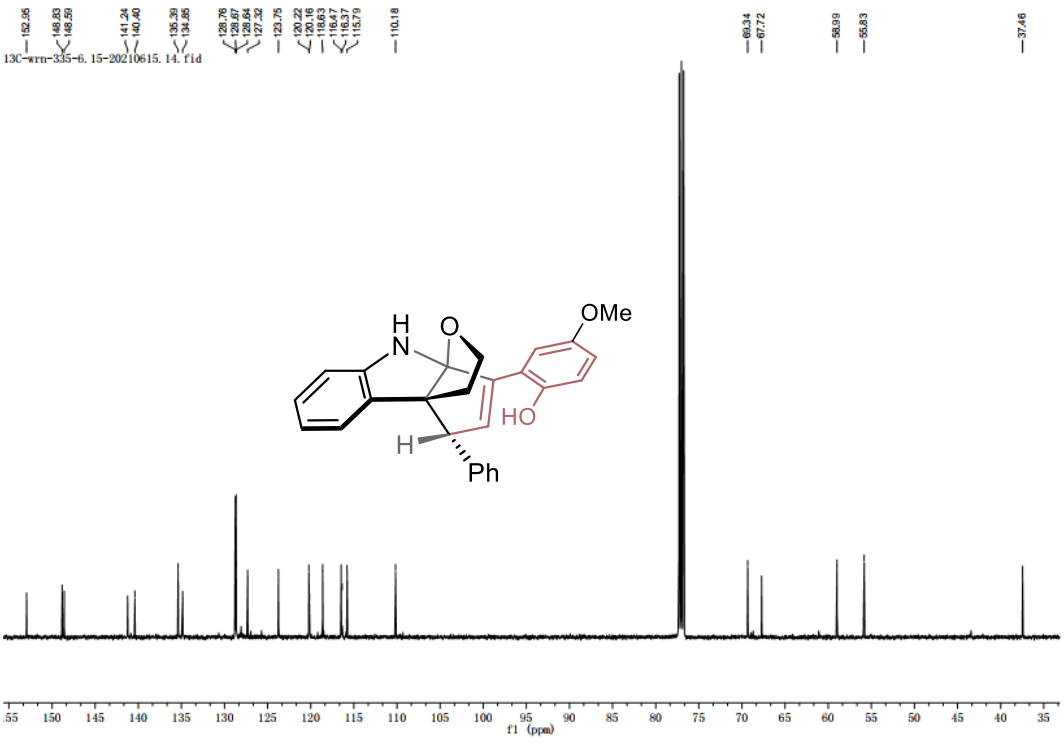
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3c**



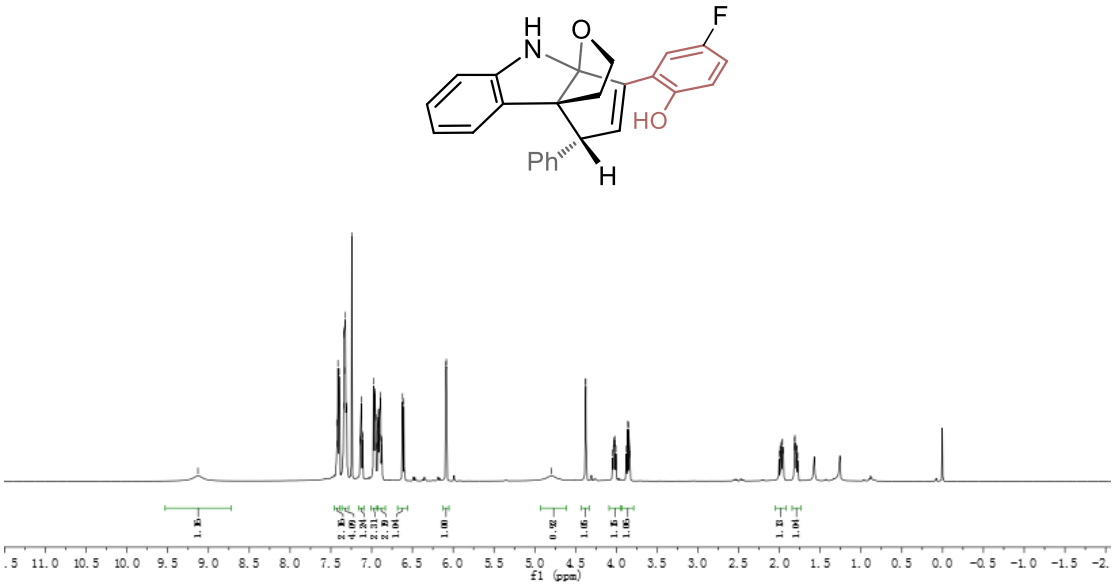
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**



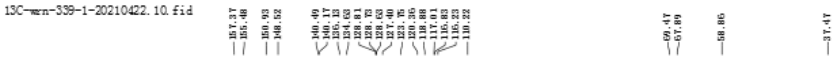
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3d**

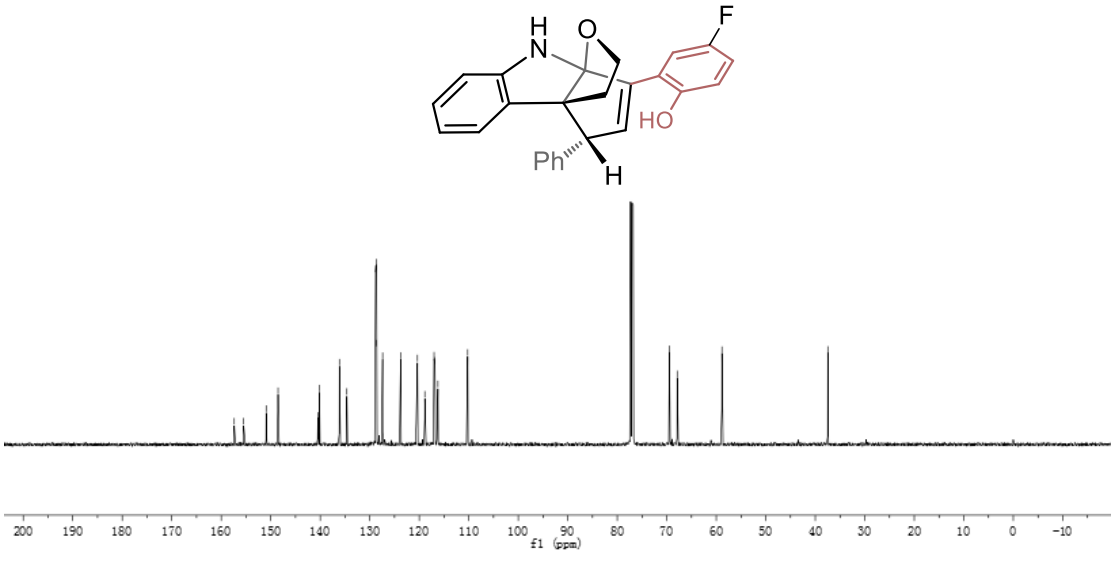


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e**

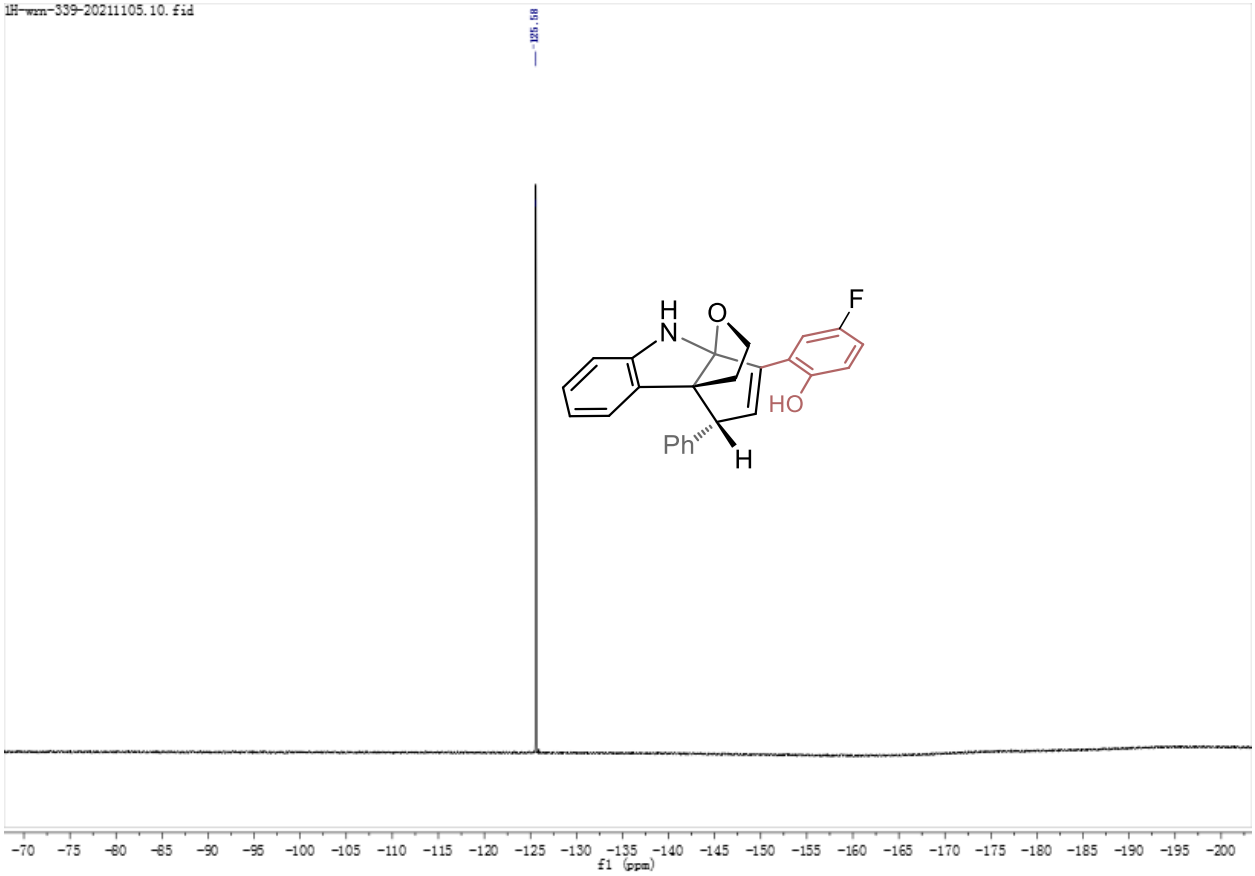


^{13}C NMR (500 MHz, $CDCl_3$) of compound **3e**

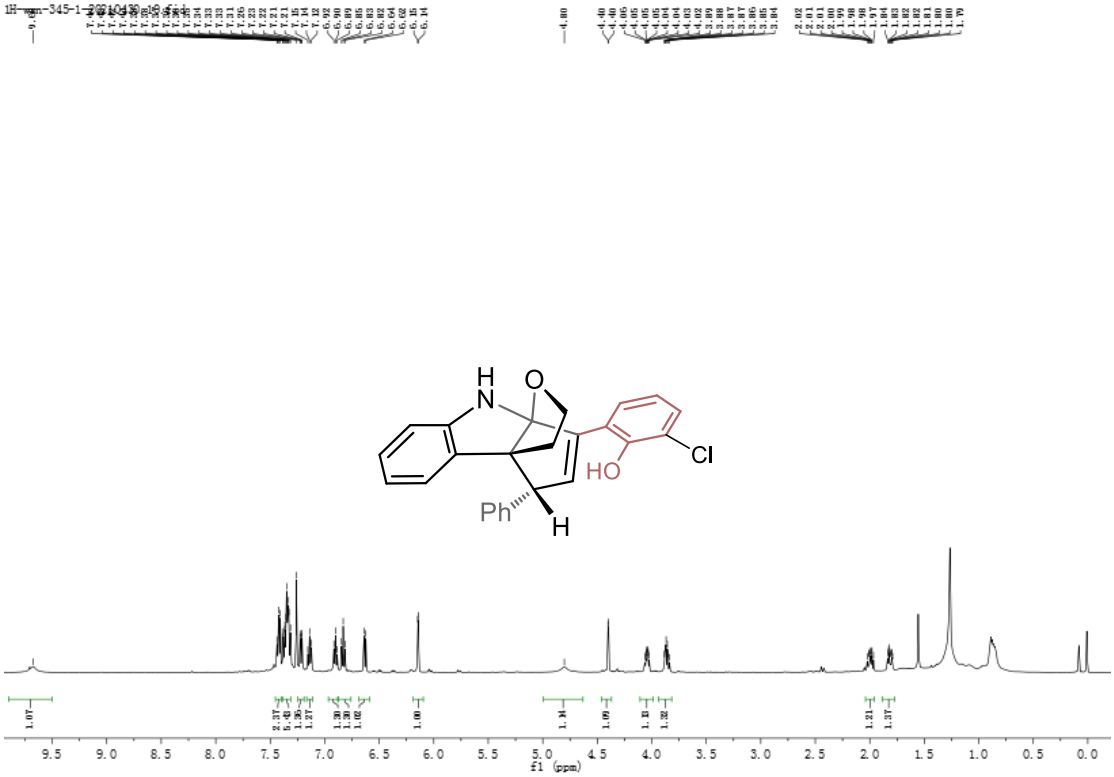




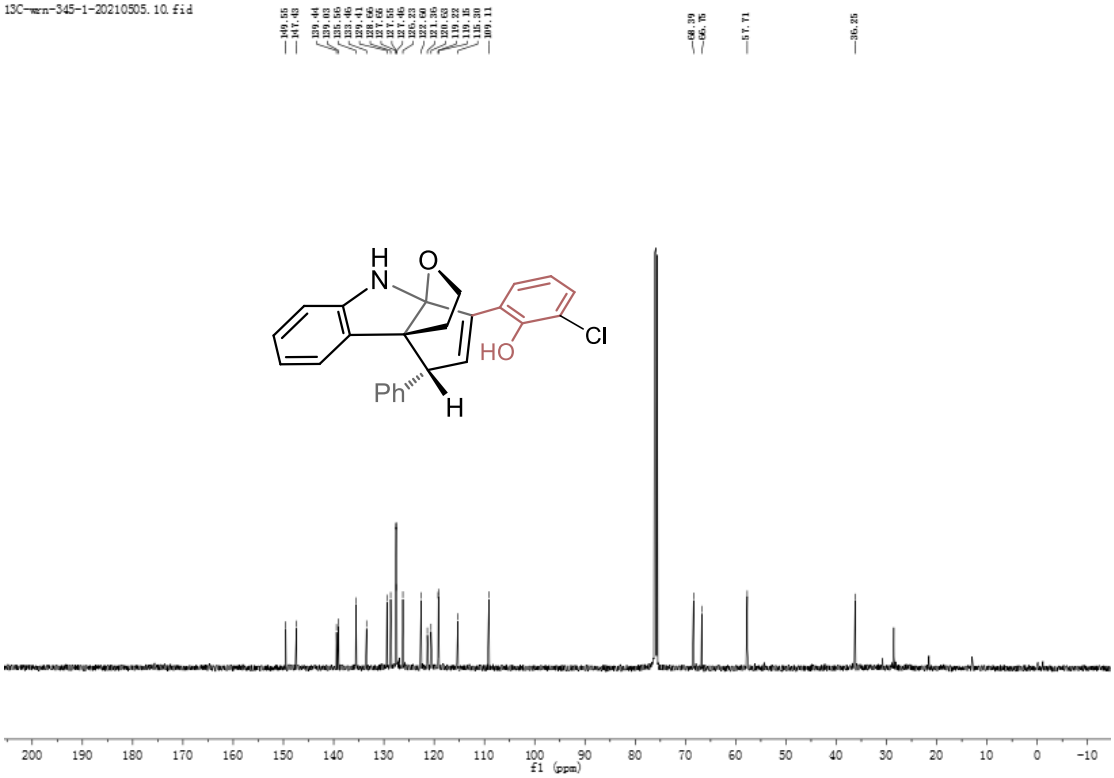
^{19}F NMR (500 MHz, $CDCl_3$) of compound **3e**



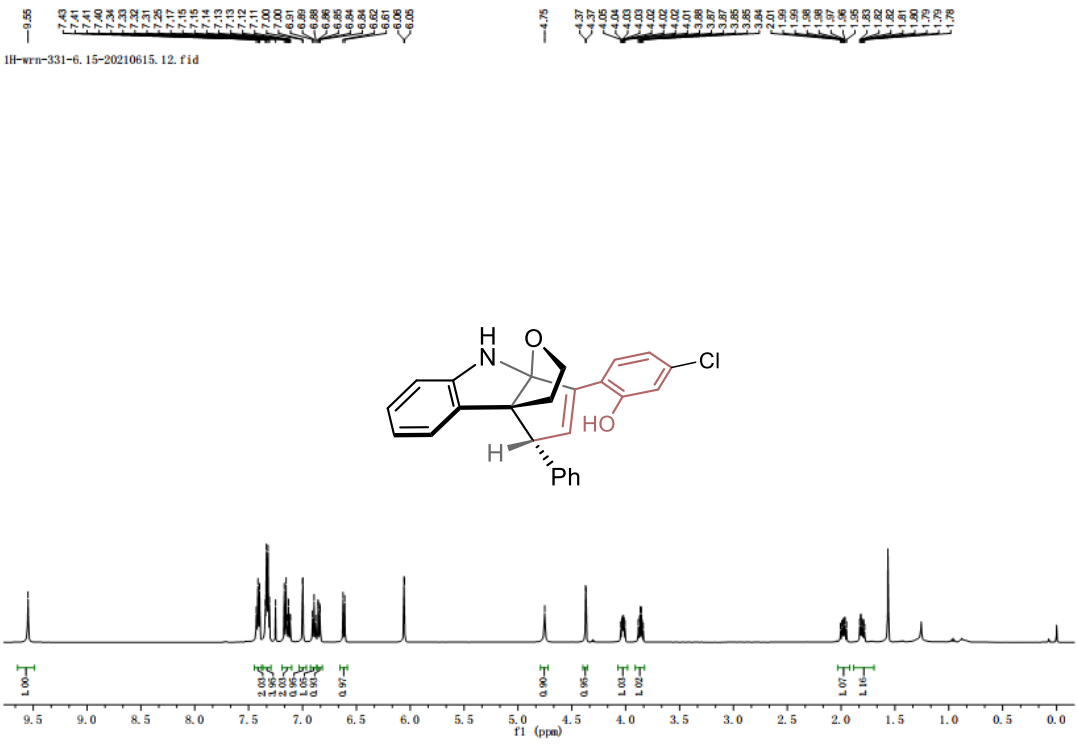
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f** (d.r. = 12:1)



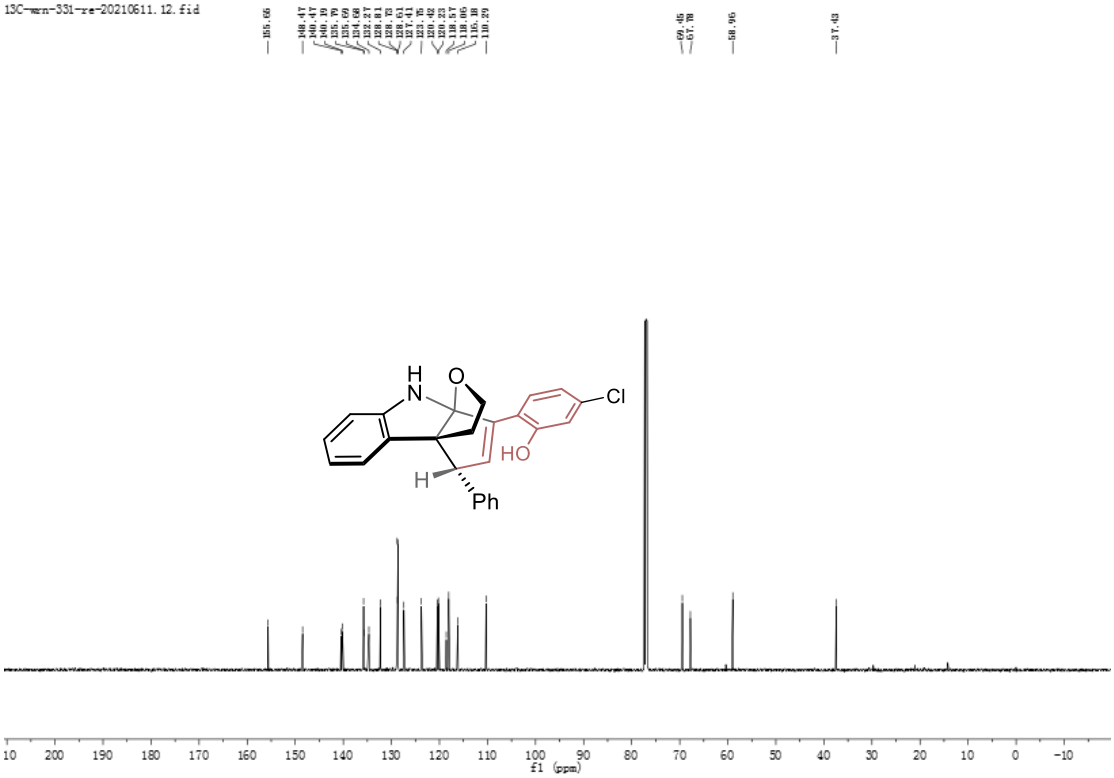
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3f** (d.r = 12:1)



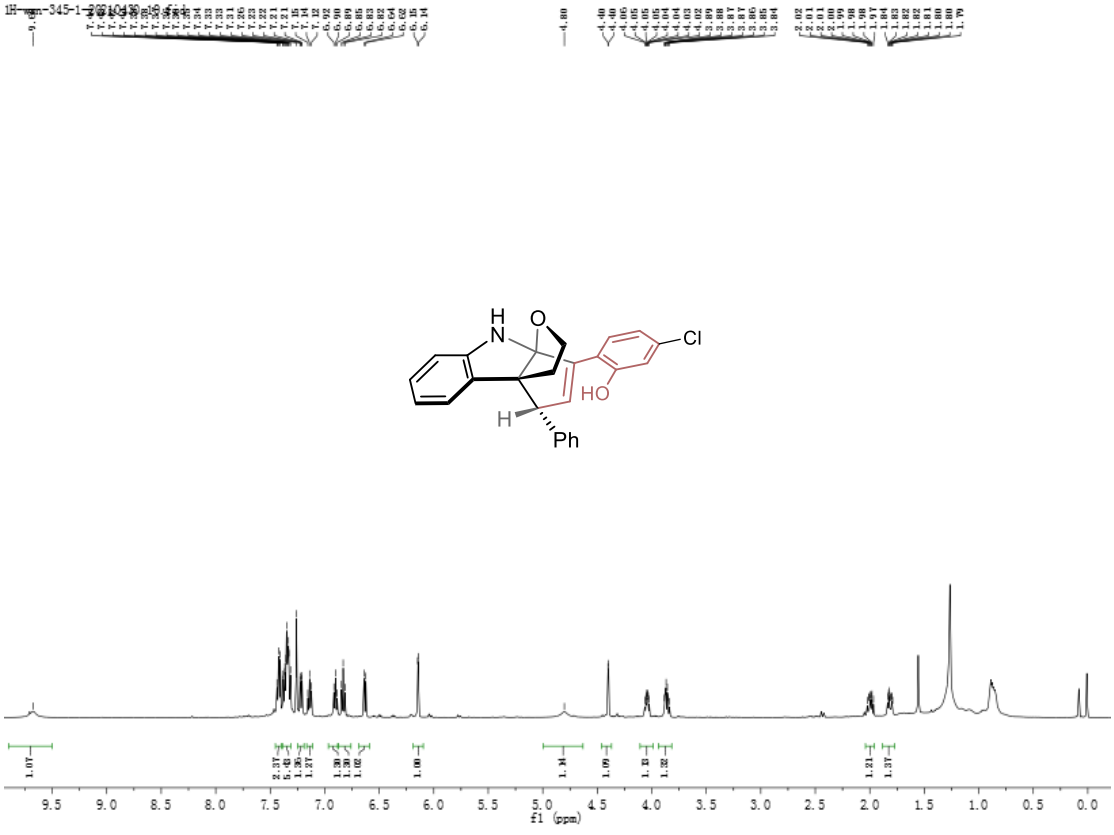
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3g**



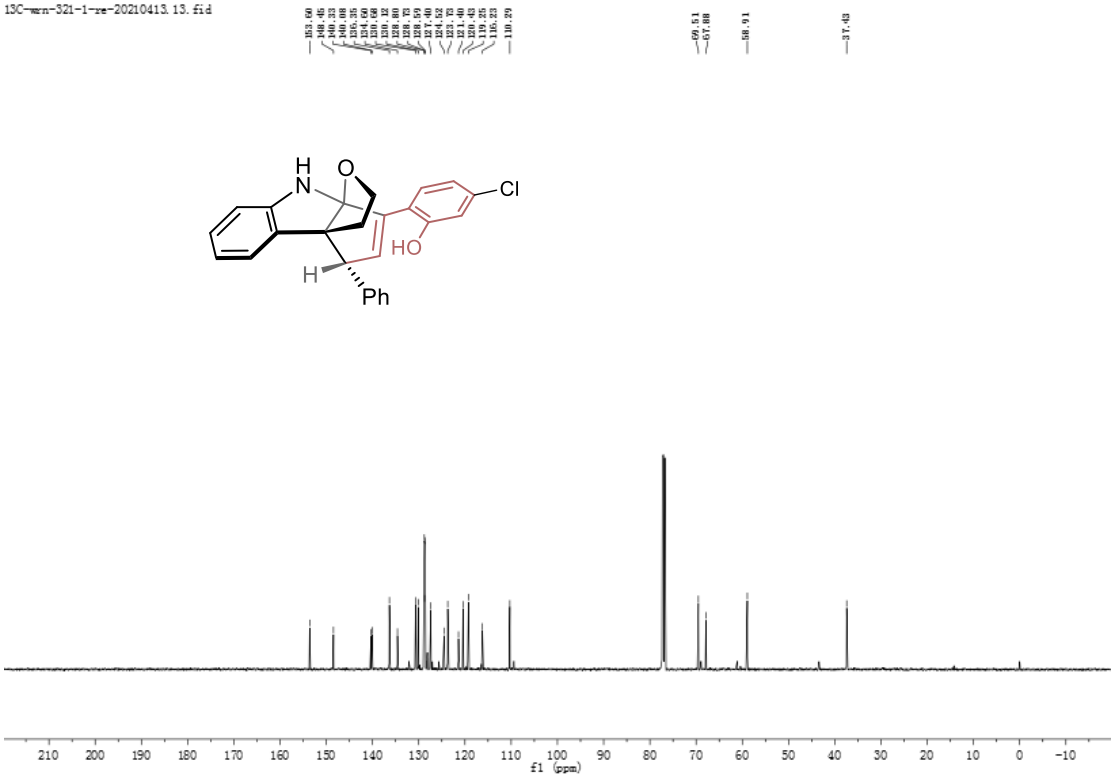
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3g**



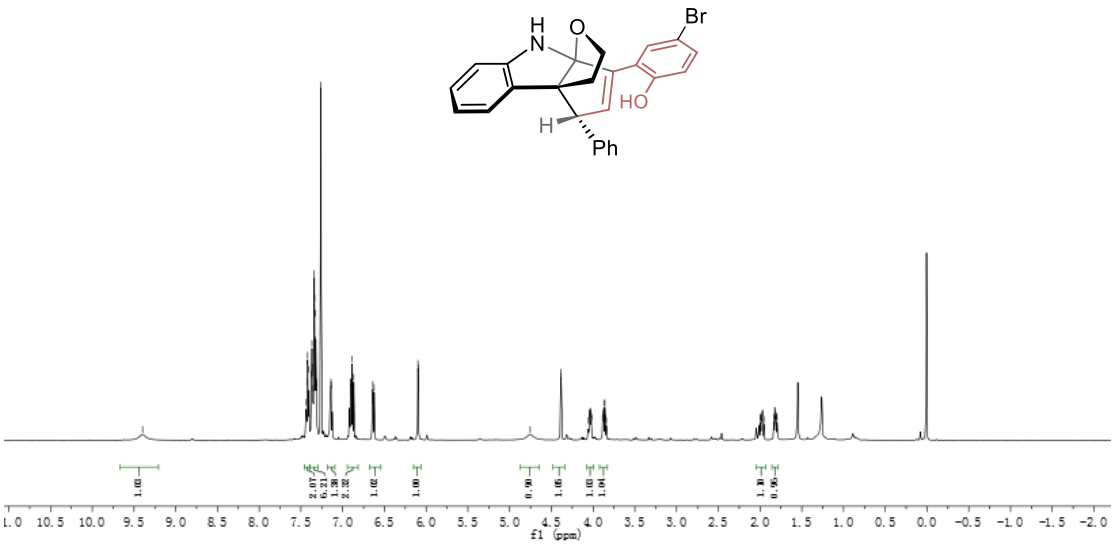
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3h** (d.r. = 10:1)



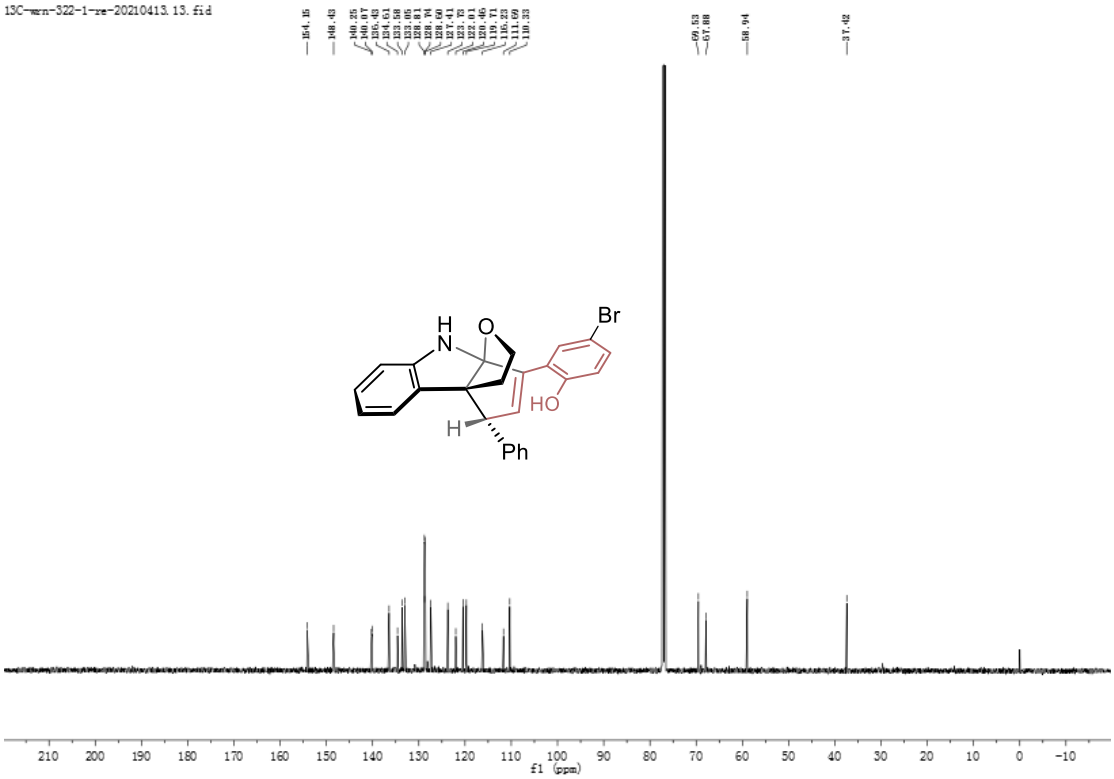
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3h** (d.r. = 10:1)



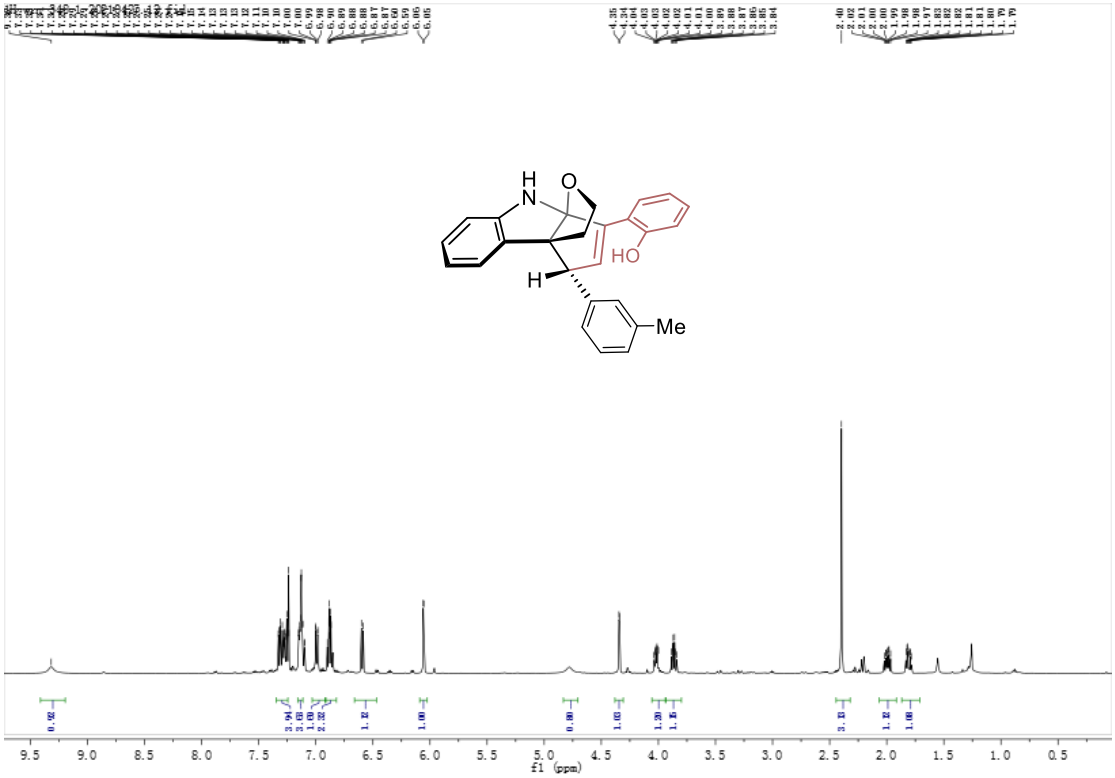
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3i** (d.r. = 12:1)



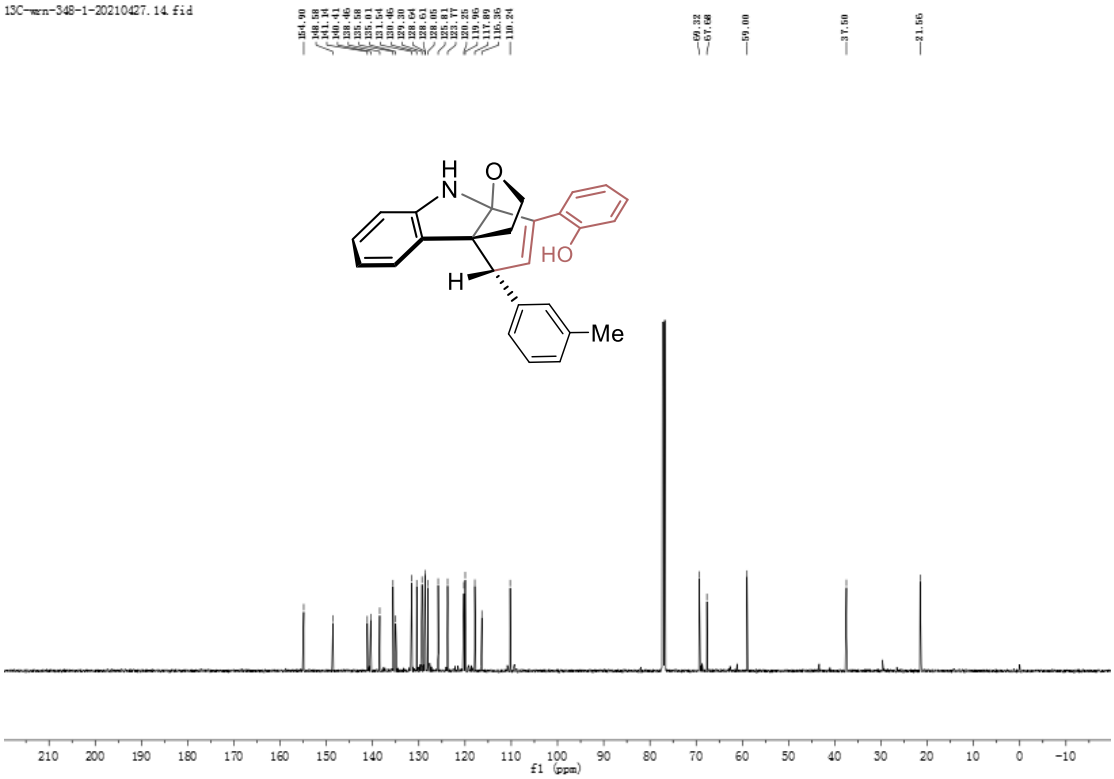
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3i**



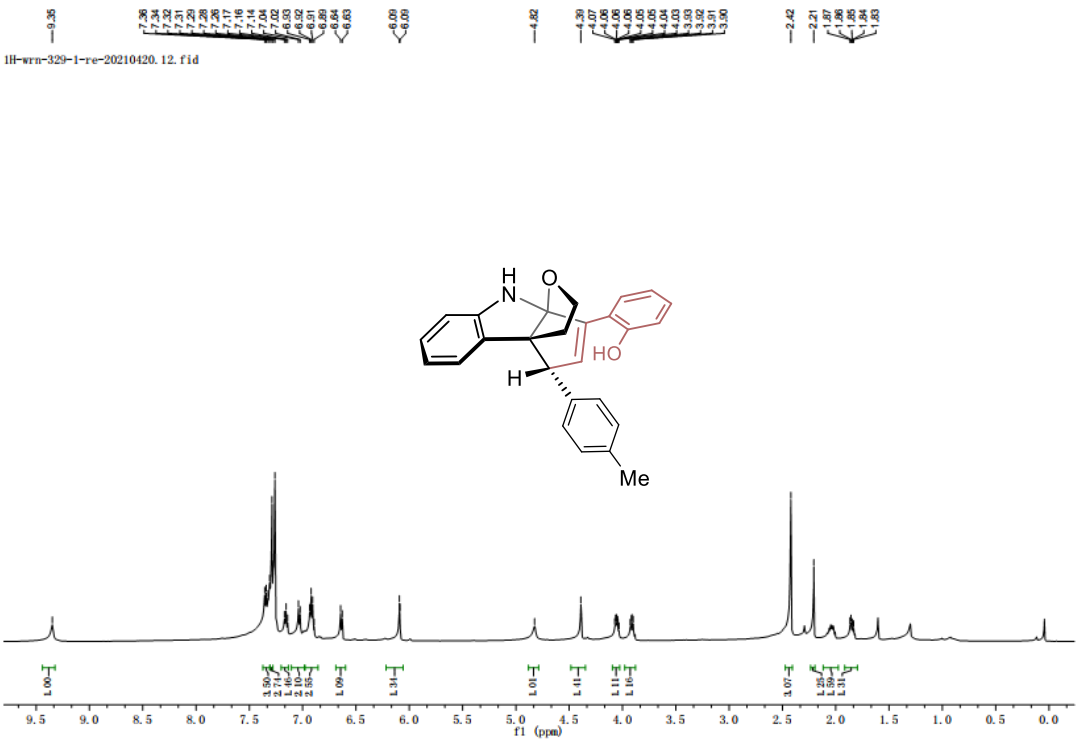
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3j** (d.r. = 10:1)



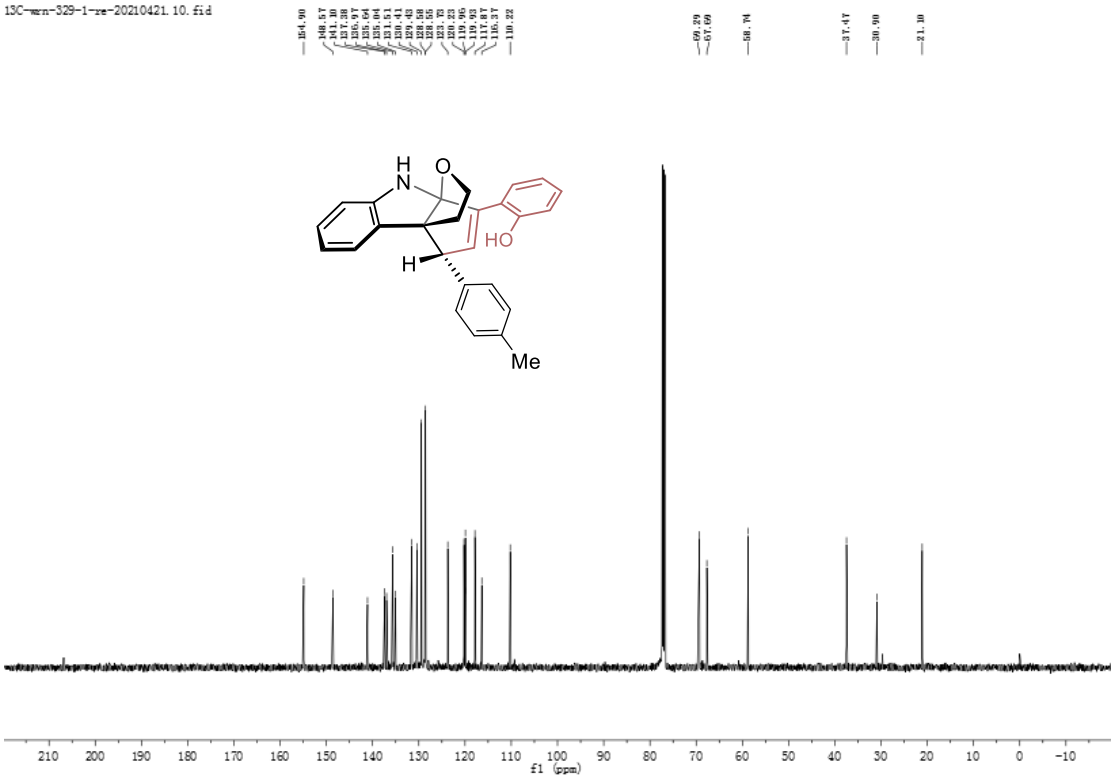
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3j** (d.r. = 12:1)



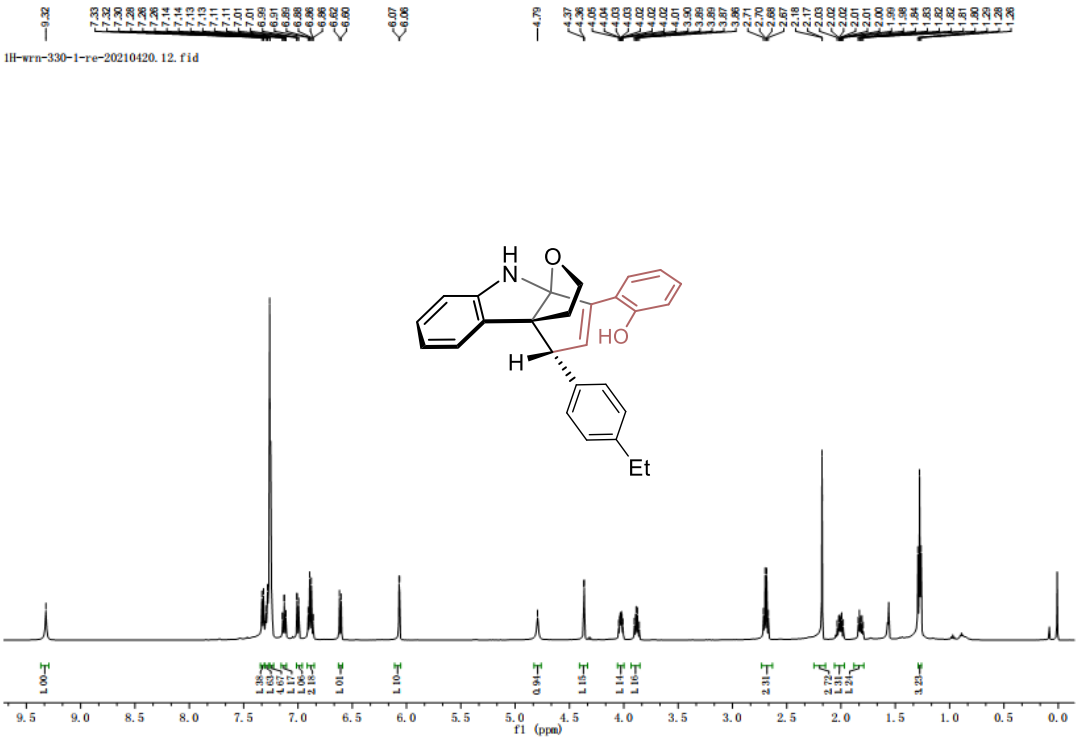
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3k**



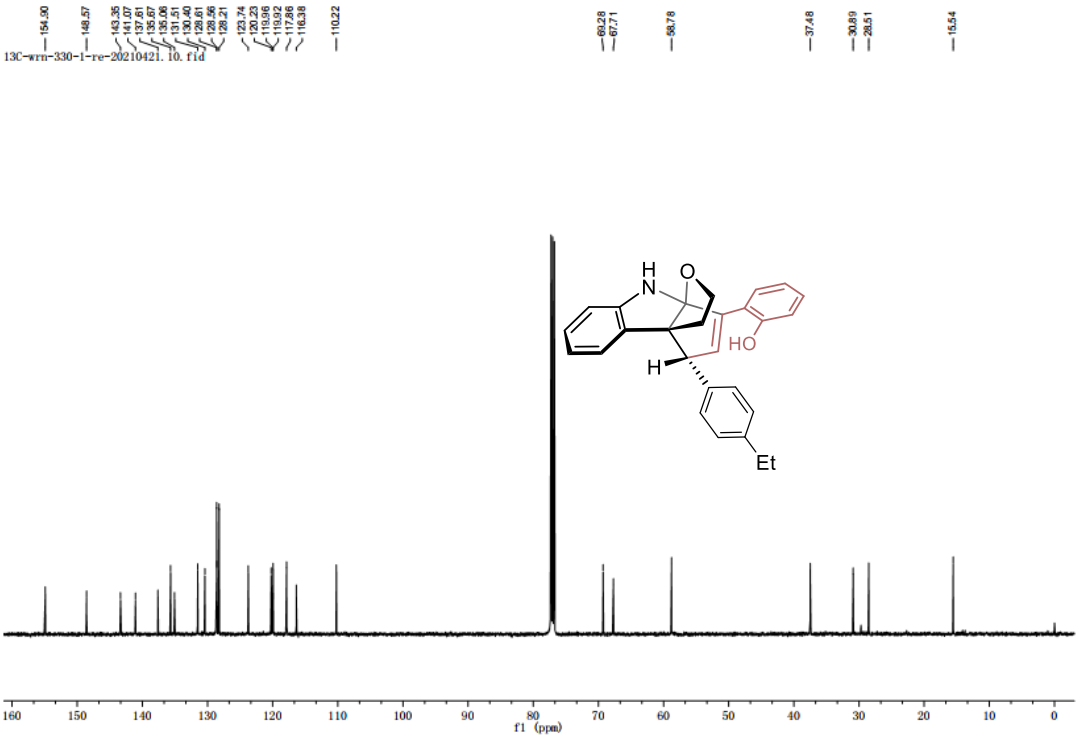
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3k**



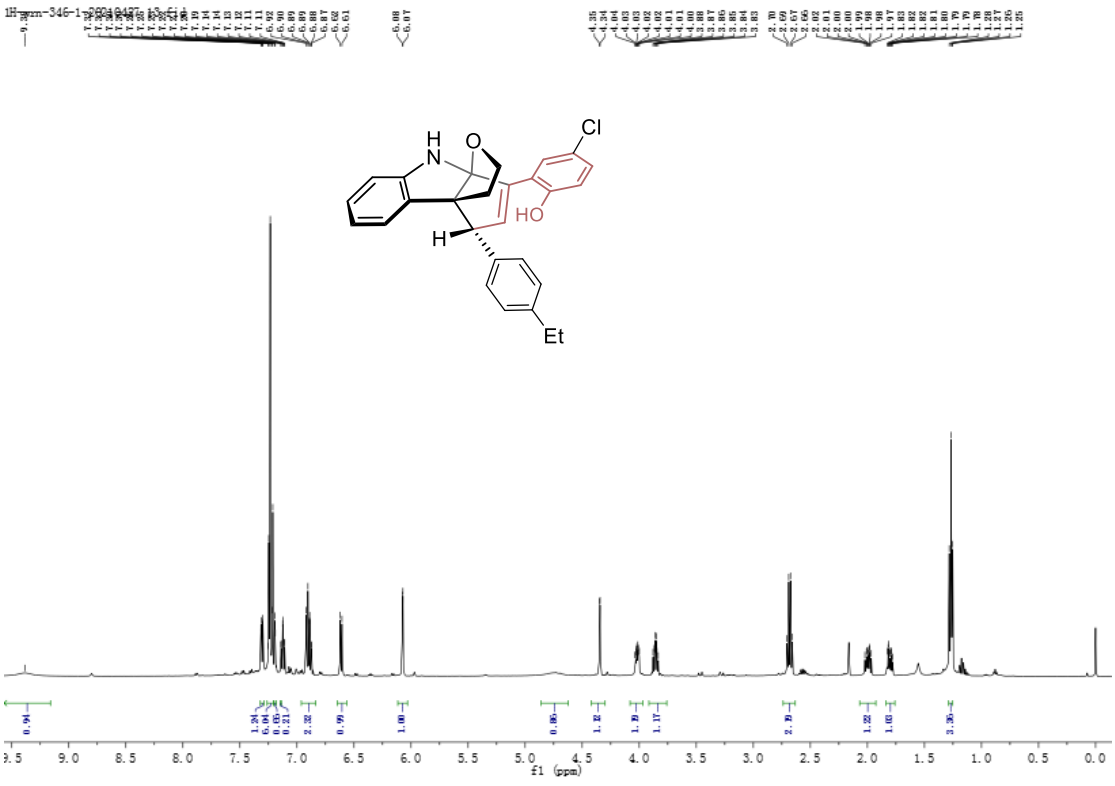
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3l**



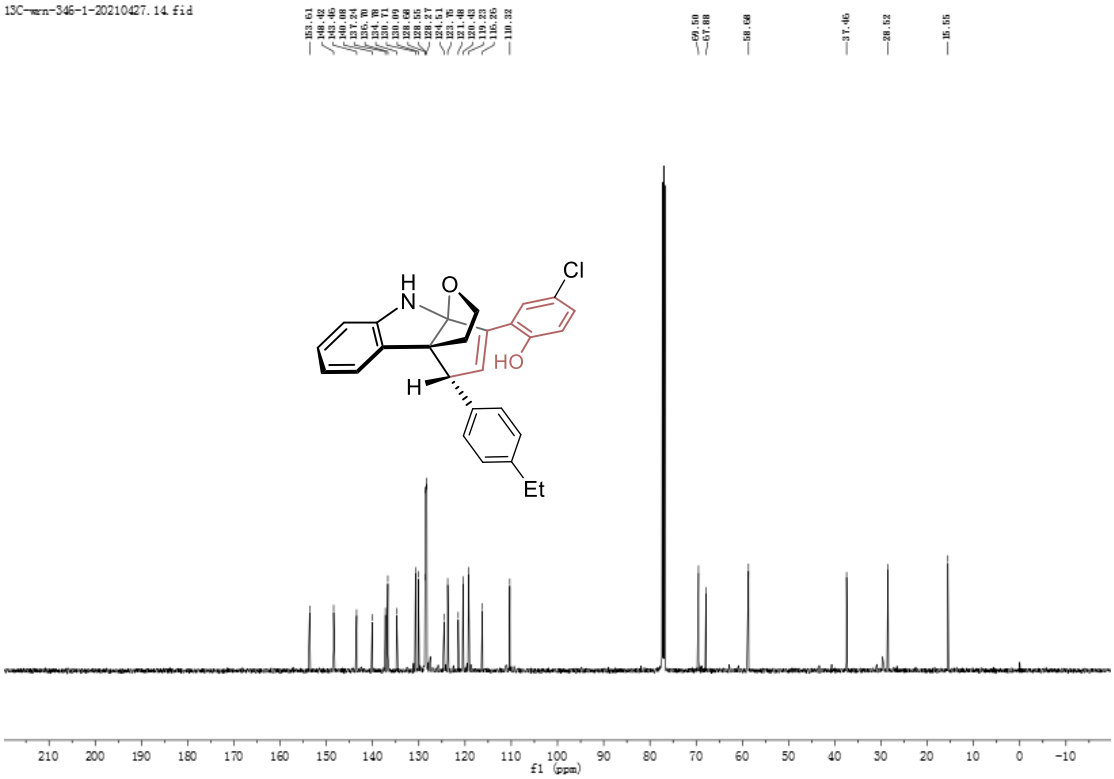
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3l**



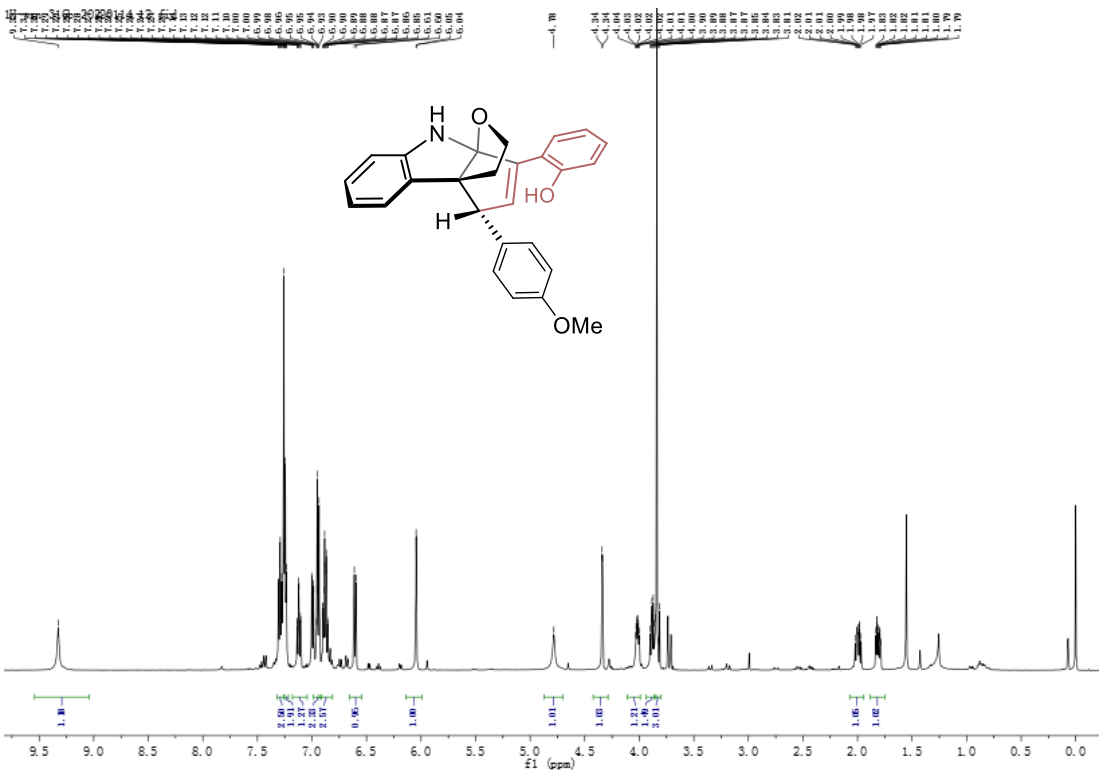
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3m**



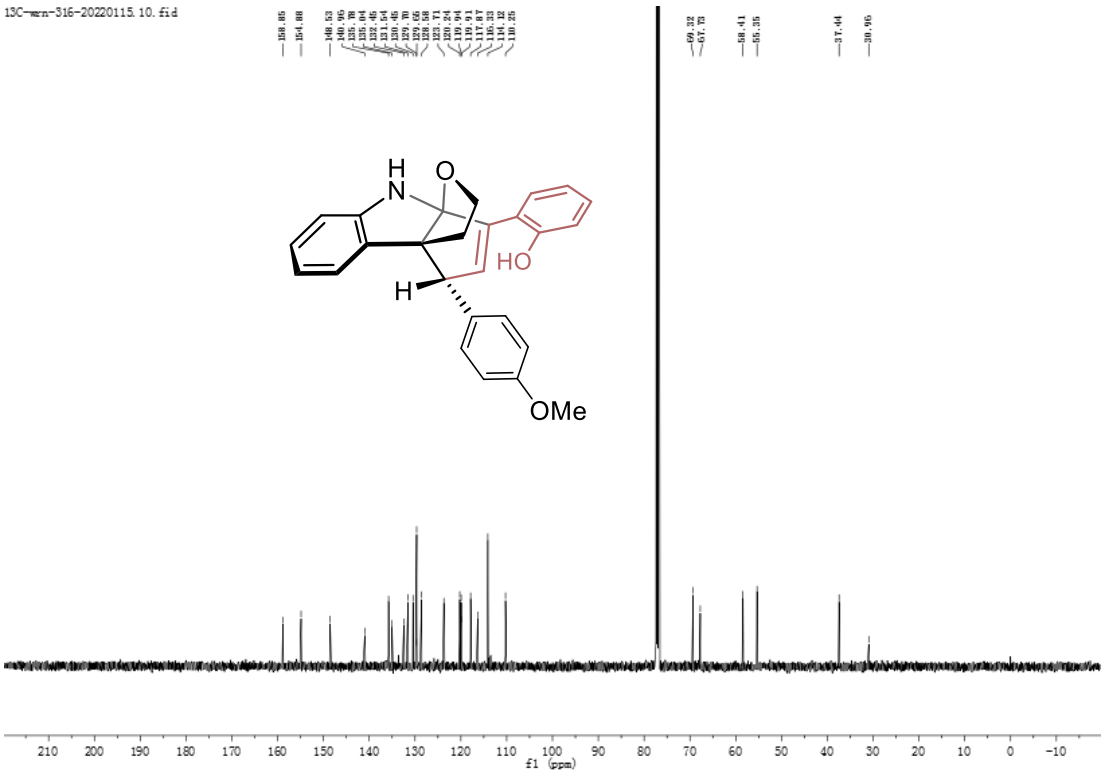
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3m**



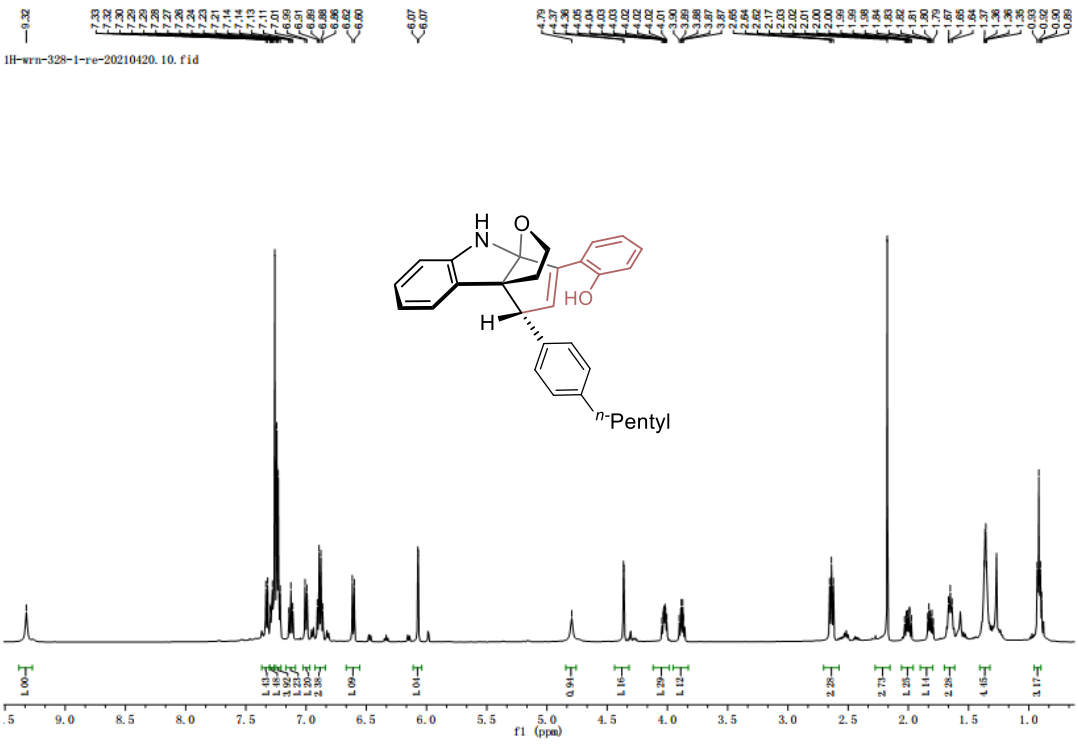
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3n**



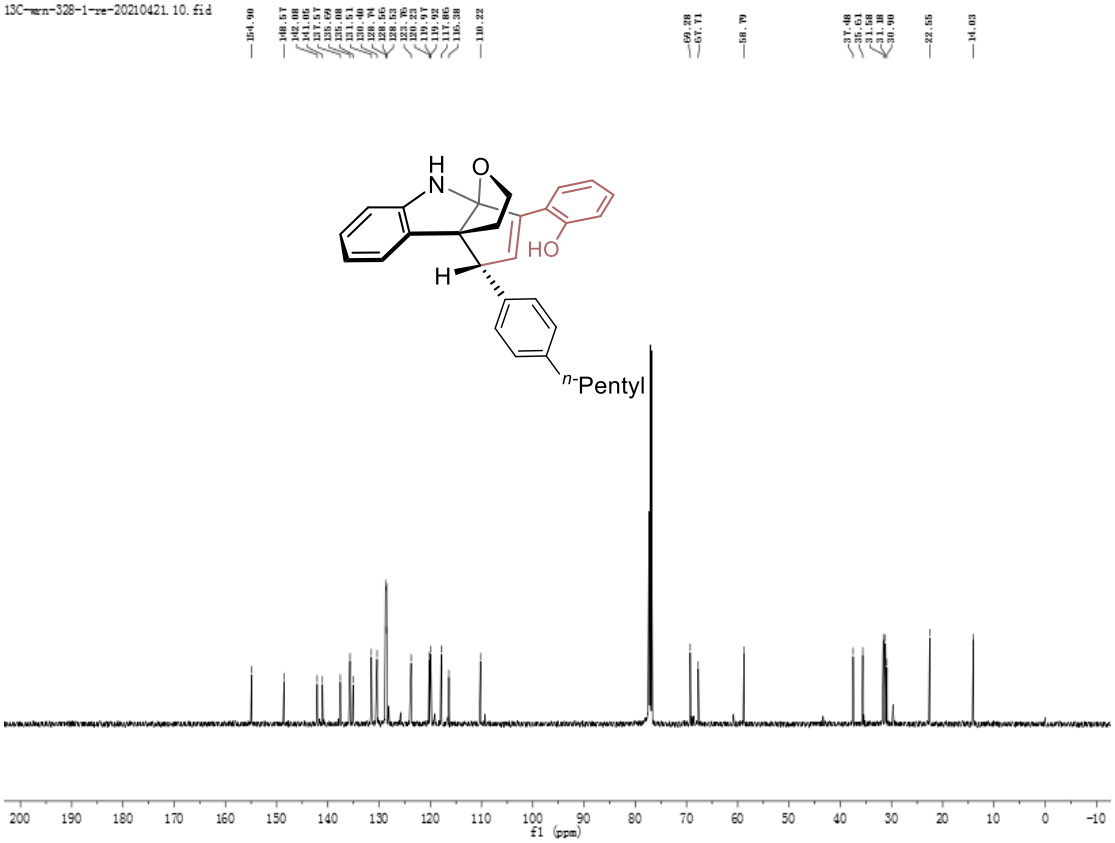
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3n**



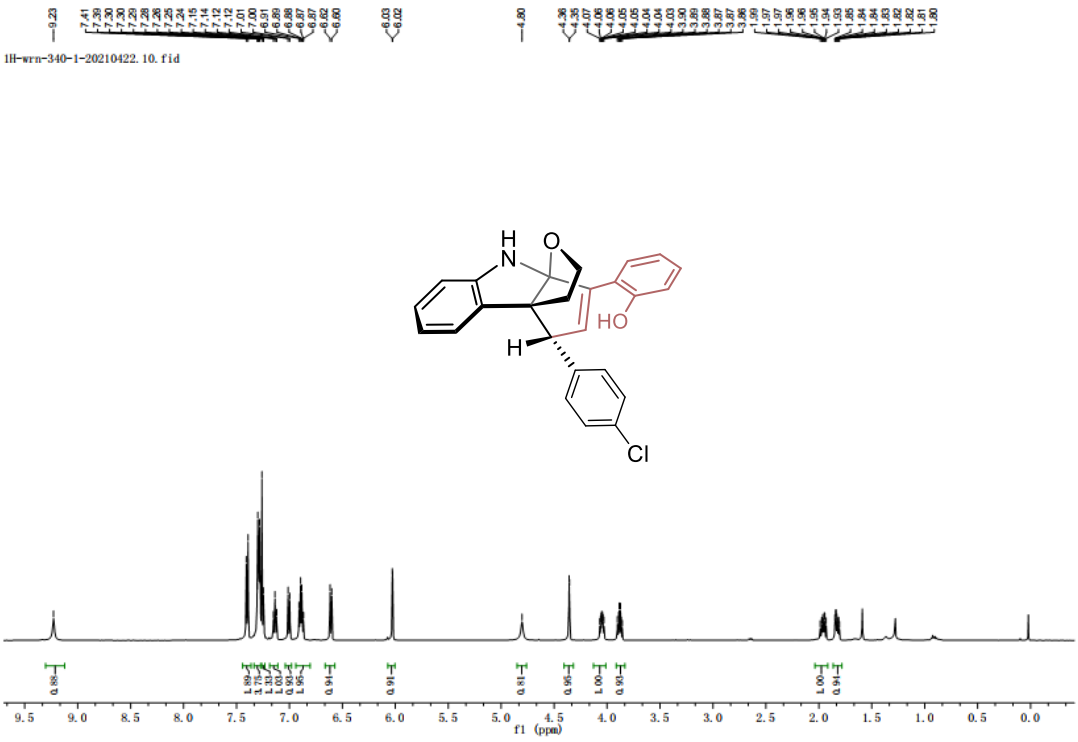
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3o** (d.r. = 8:1)



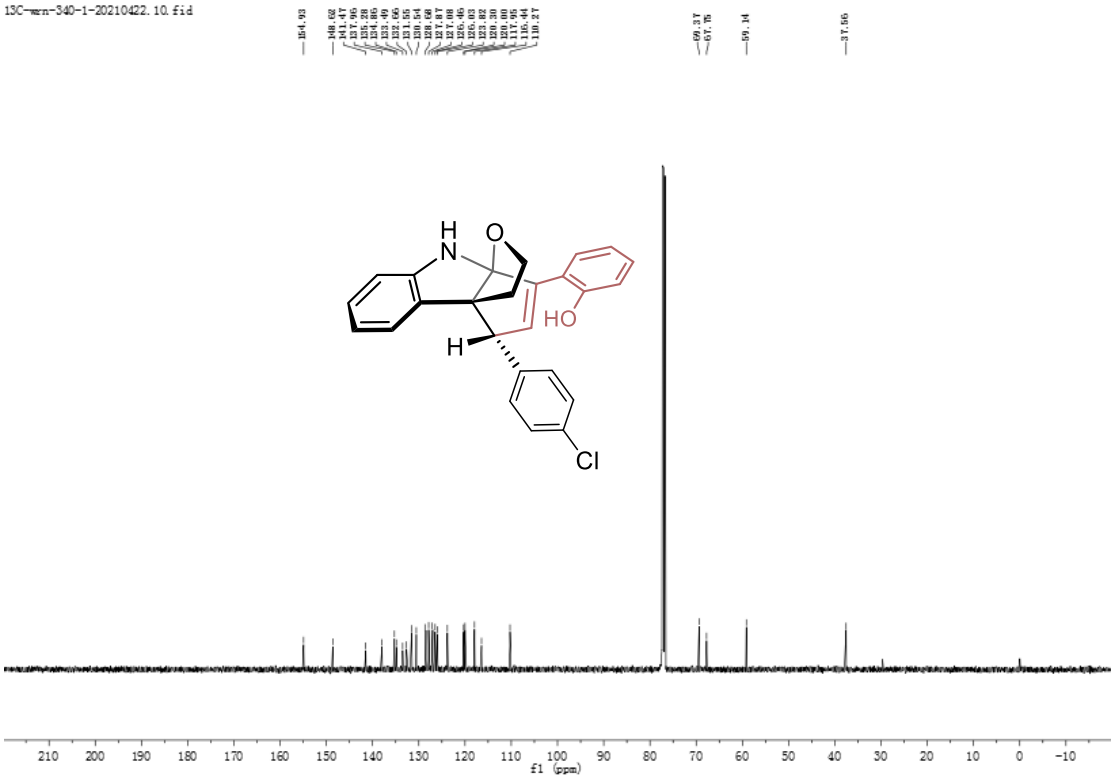
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3o** (d.r. = 8:1)



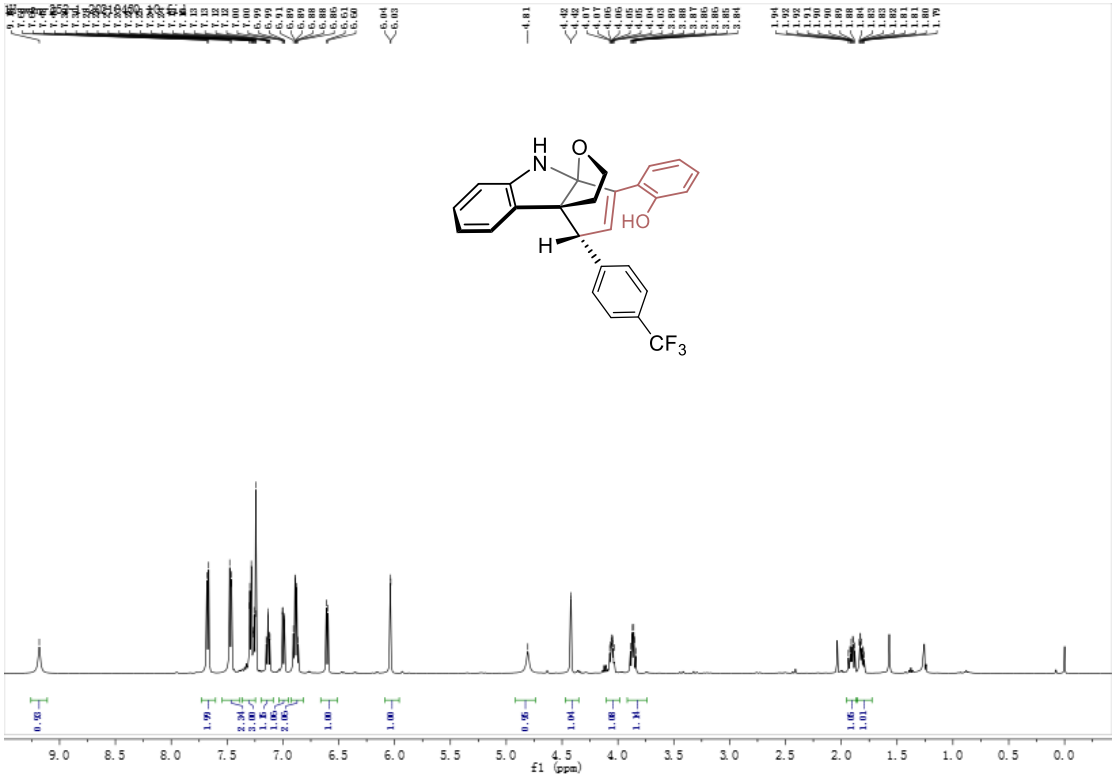
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3p**



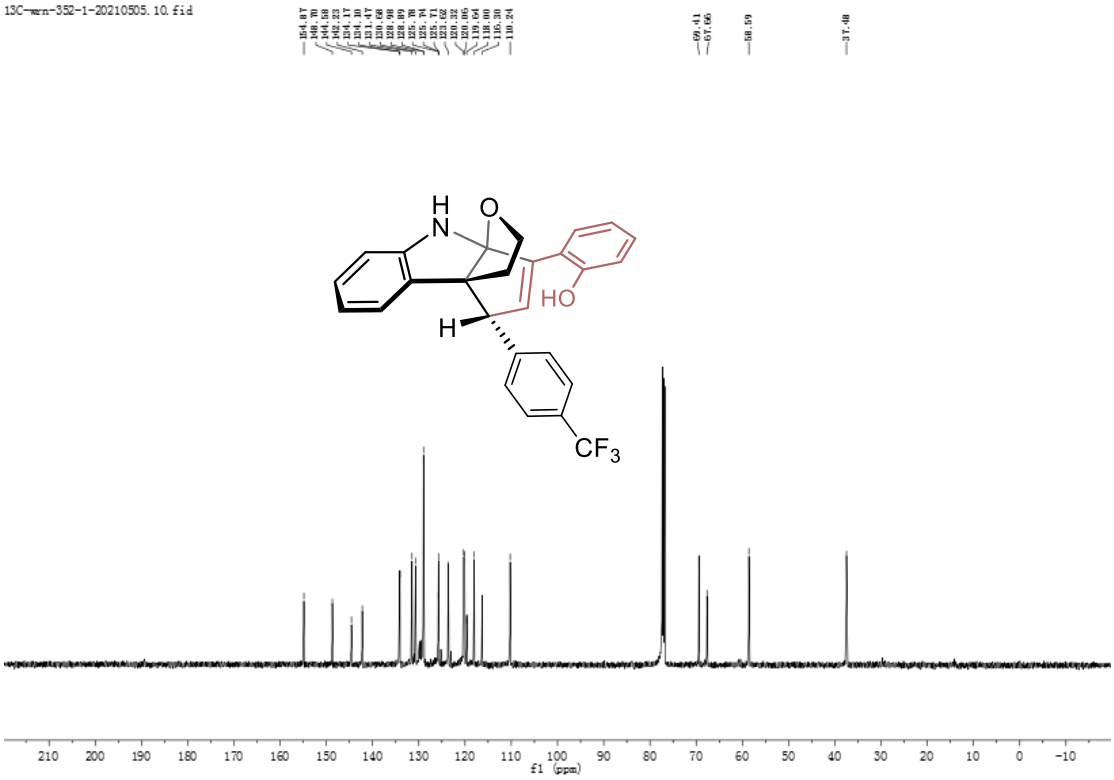
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3p**



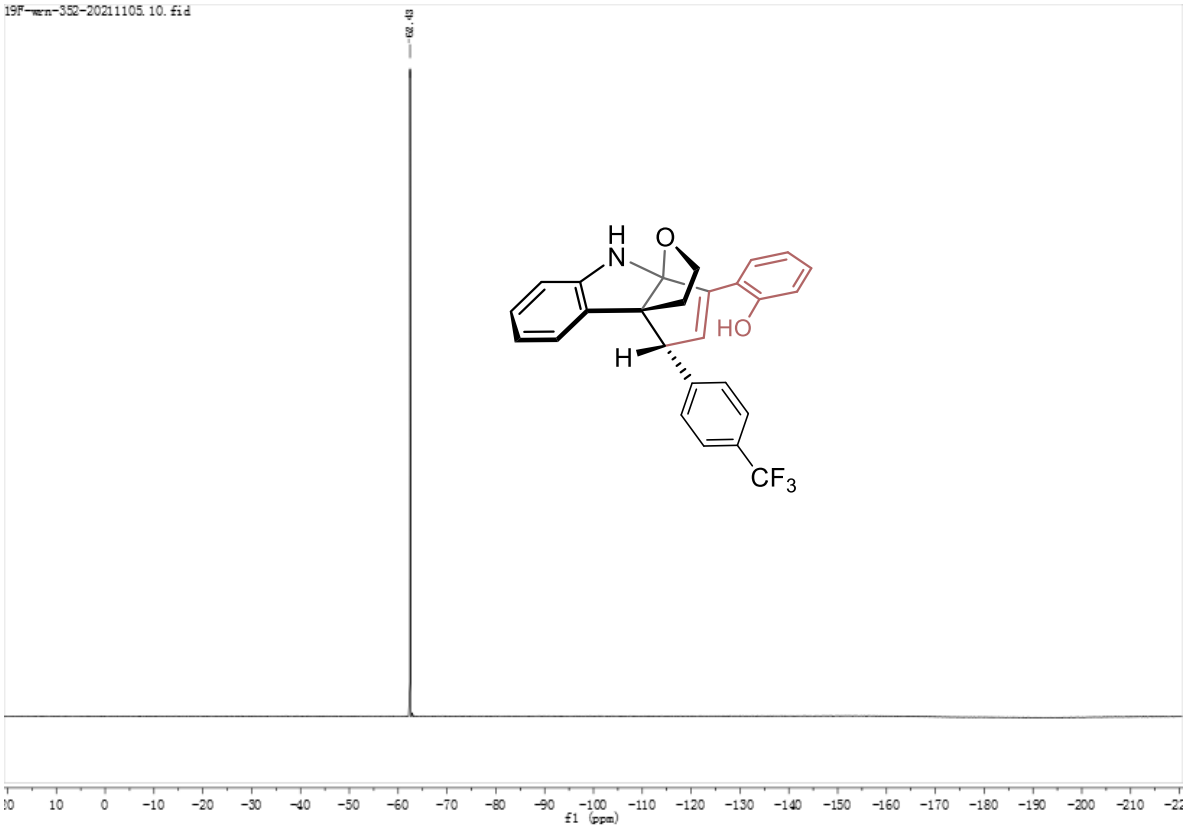
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3q** (d.r. = 10:1)



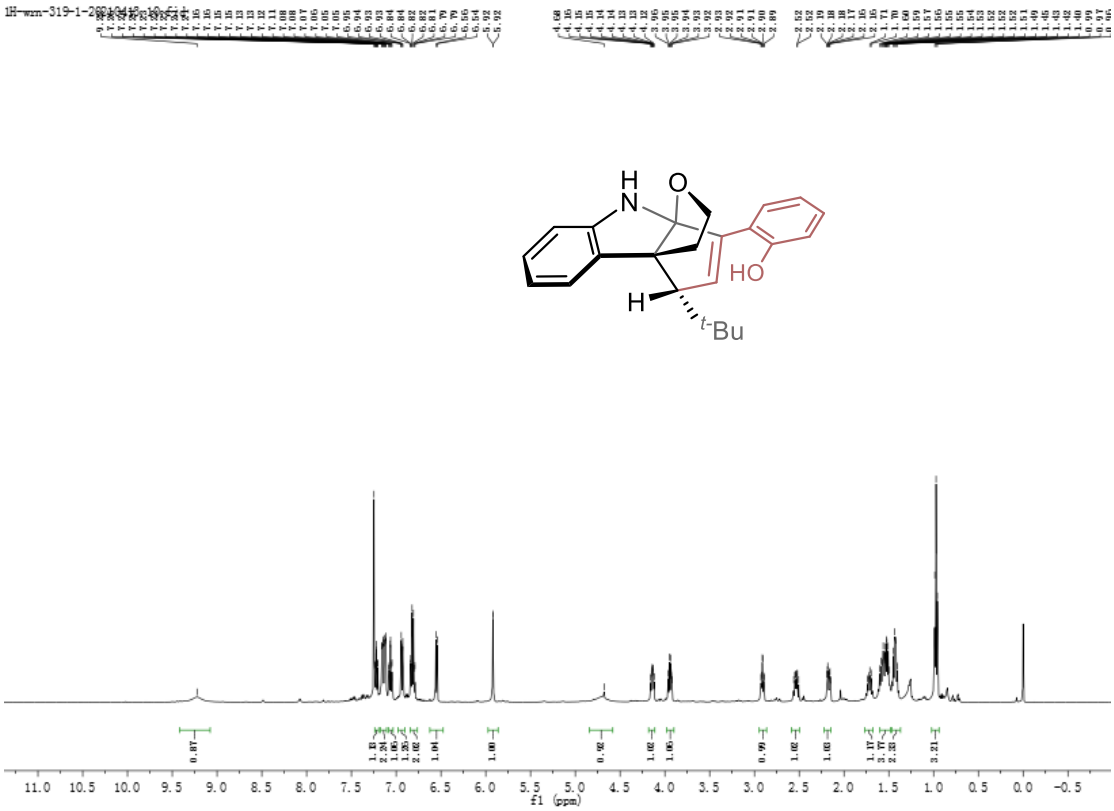
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3q** (d.r. = 12:1)



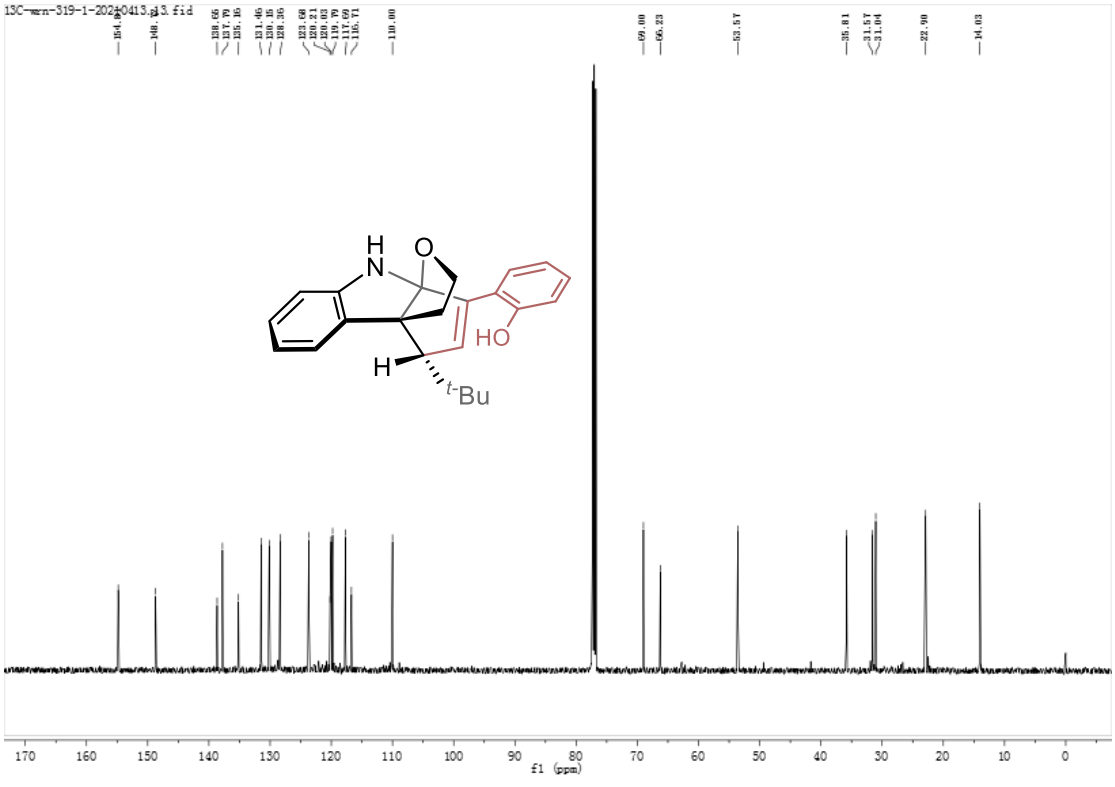
^{19}FNMR (500 MHz, $CDCl_3$) of compound **3q**



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



^{13}C NMR (500 MHz, $CDCl_3$) of compound **3r**



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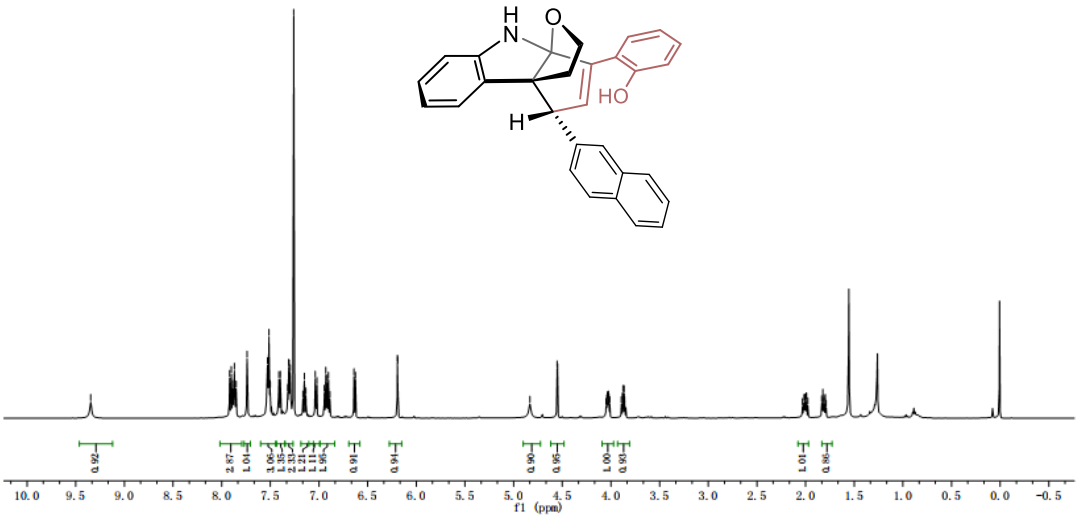
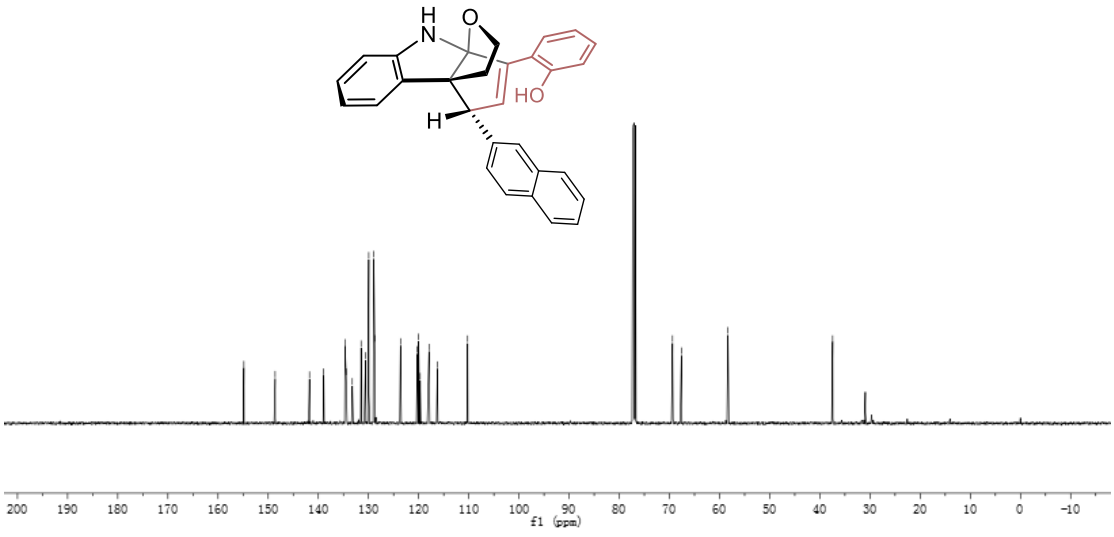
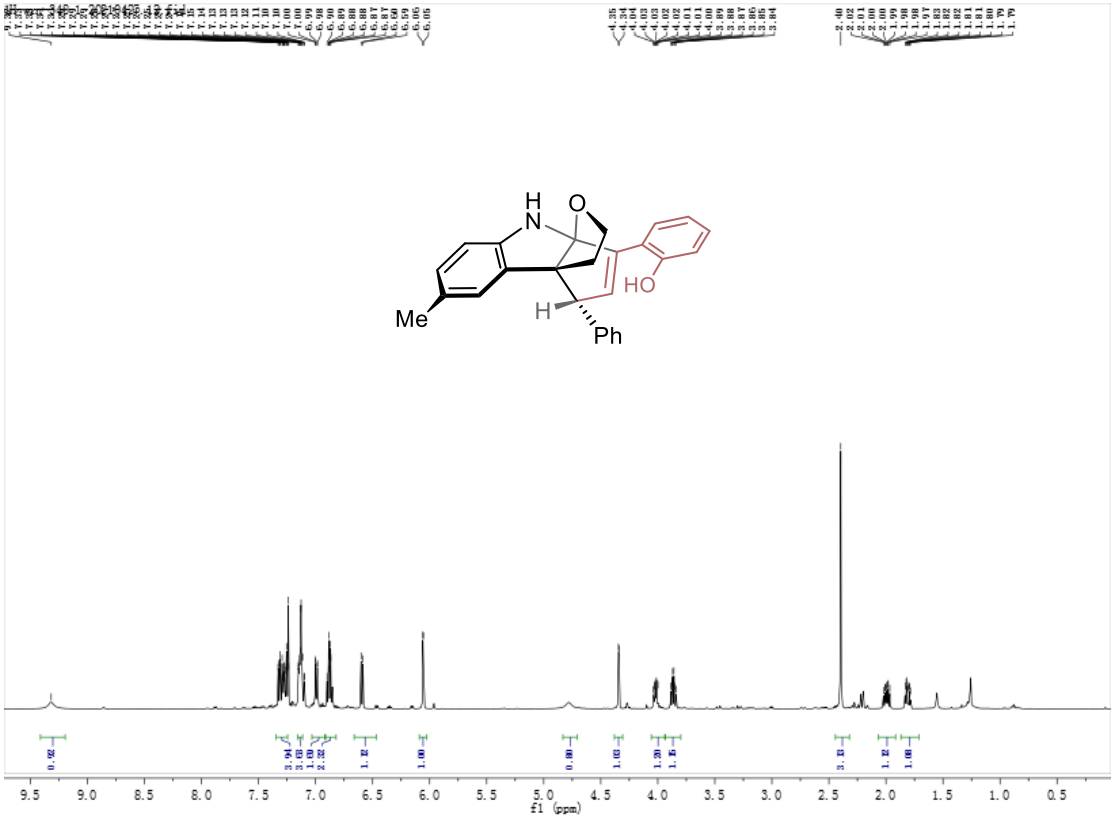


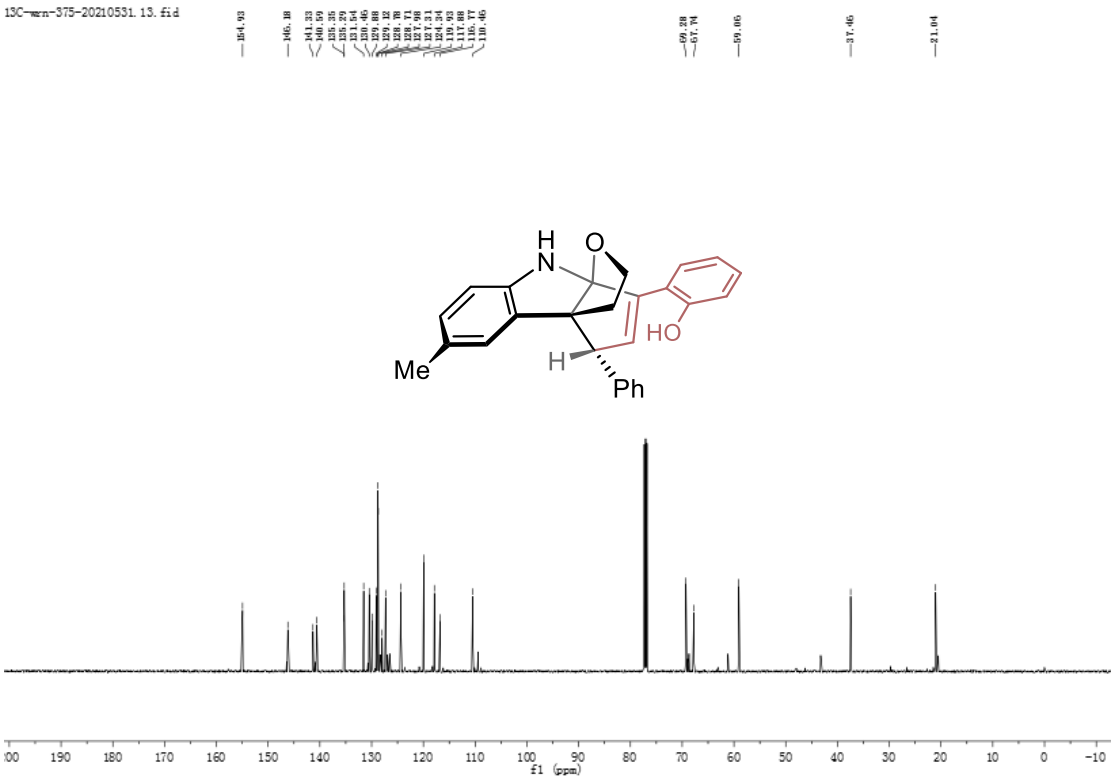
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3s**



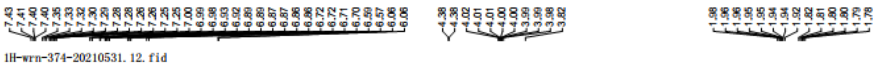
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3t** (d.r. = 5:1)

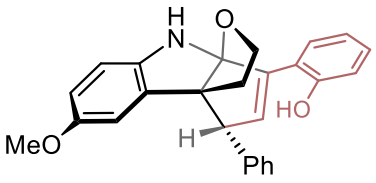


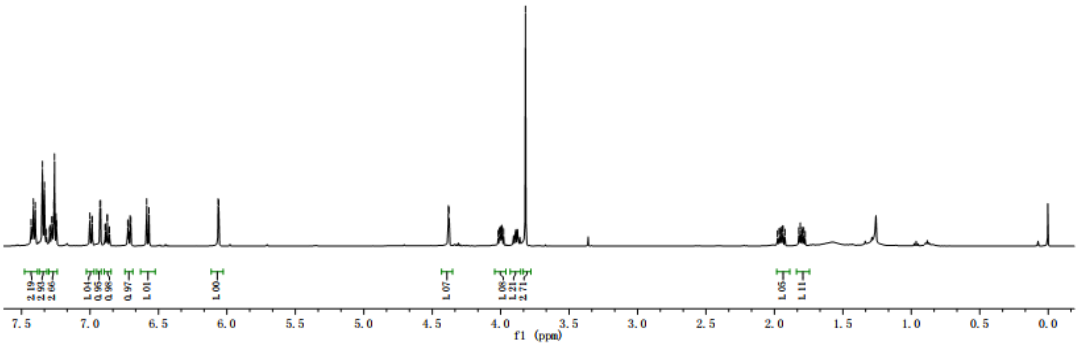
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3t** (d.r. = 5:1)



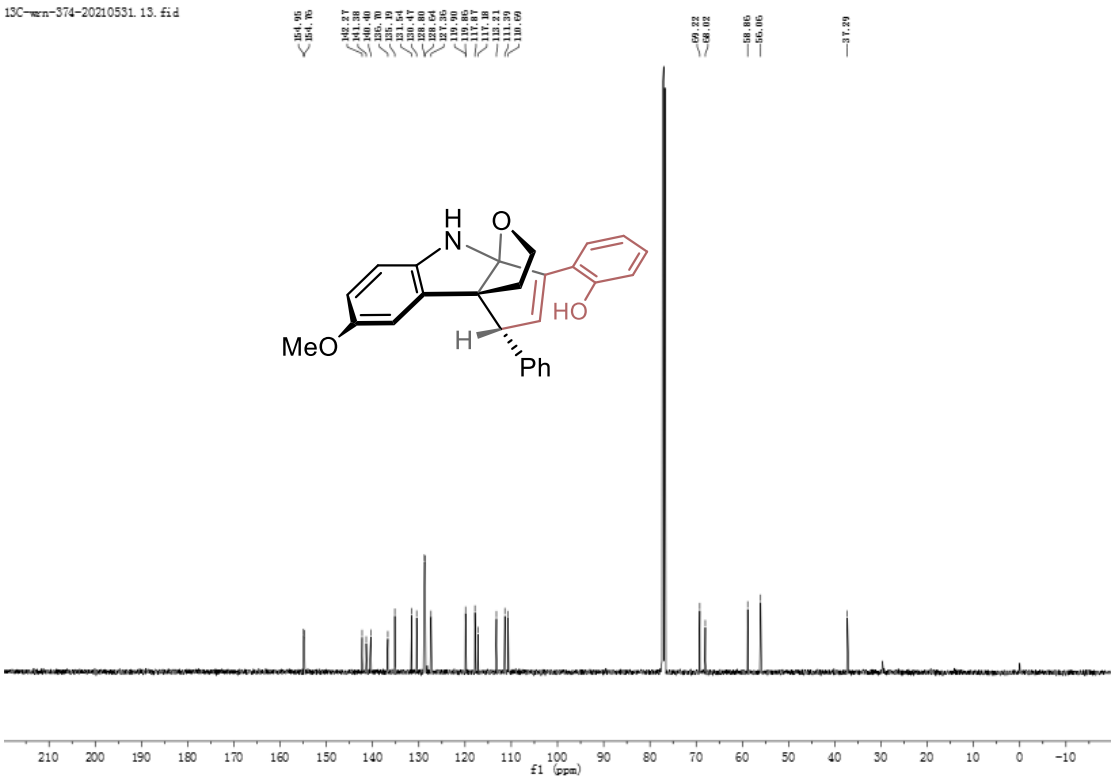
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3u**



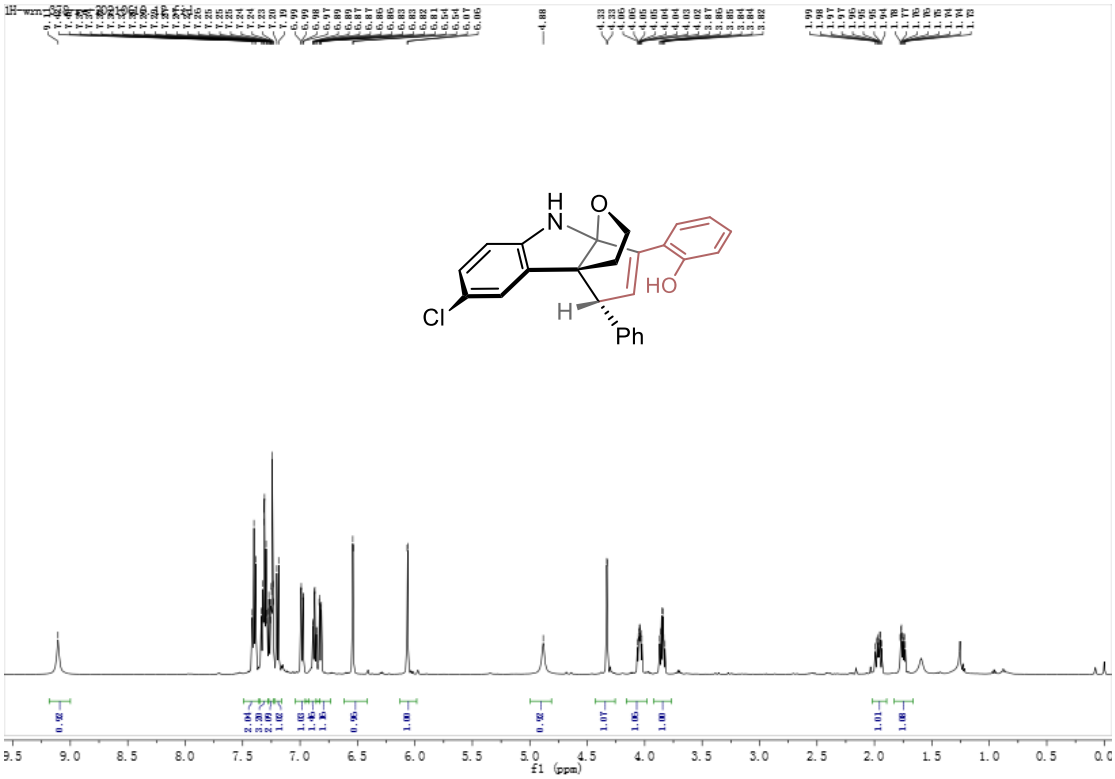




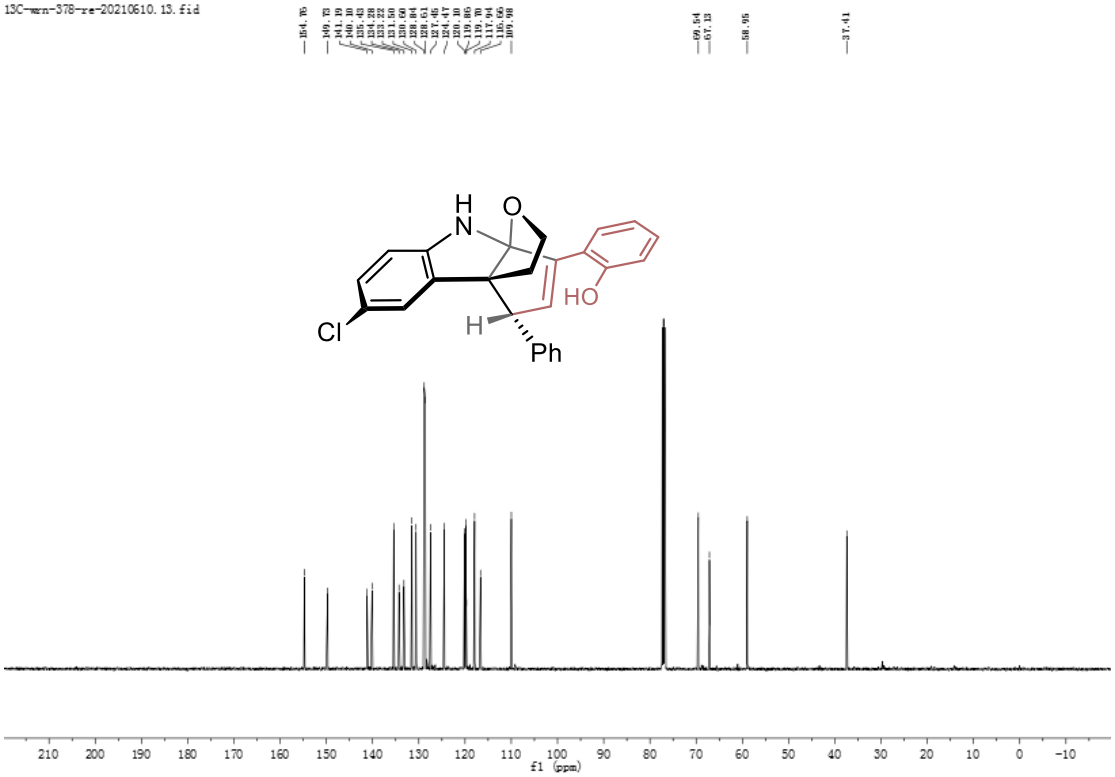
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3u**



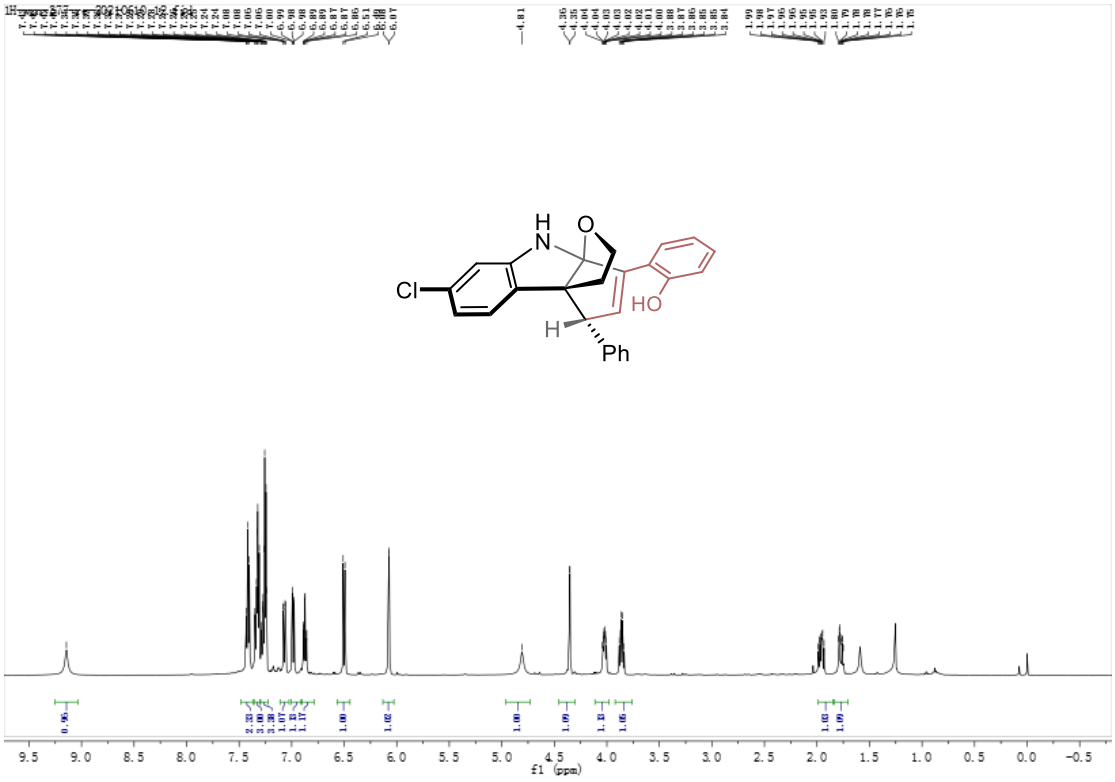
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3v**



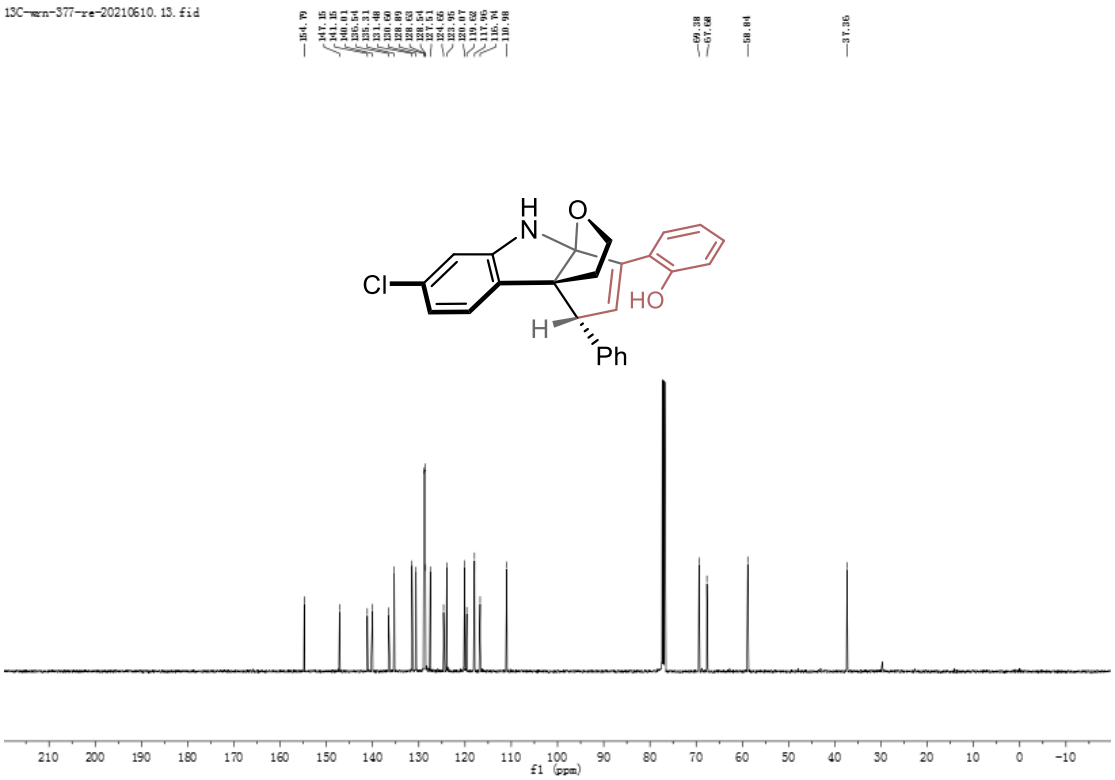
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3v**



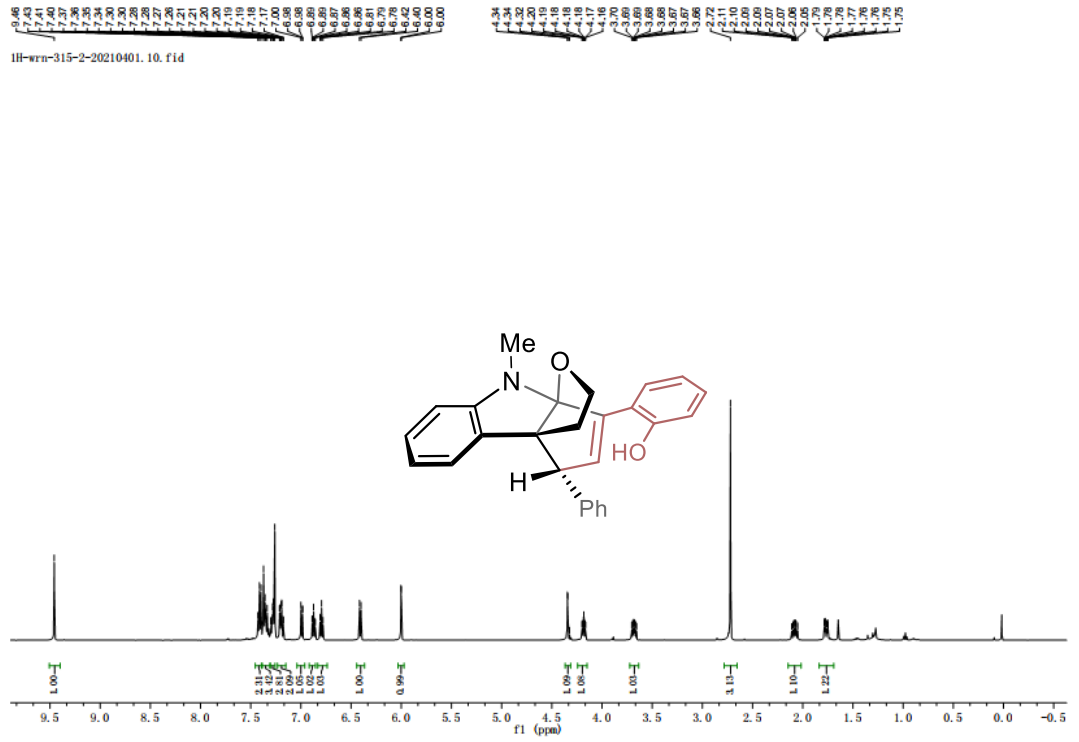
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3w**



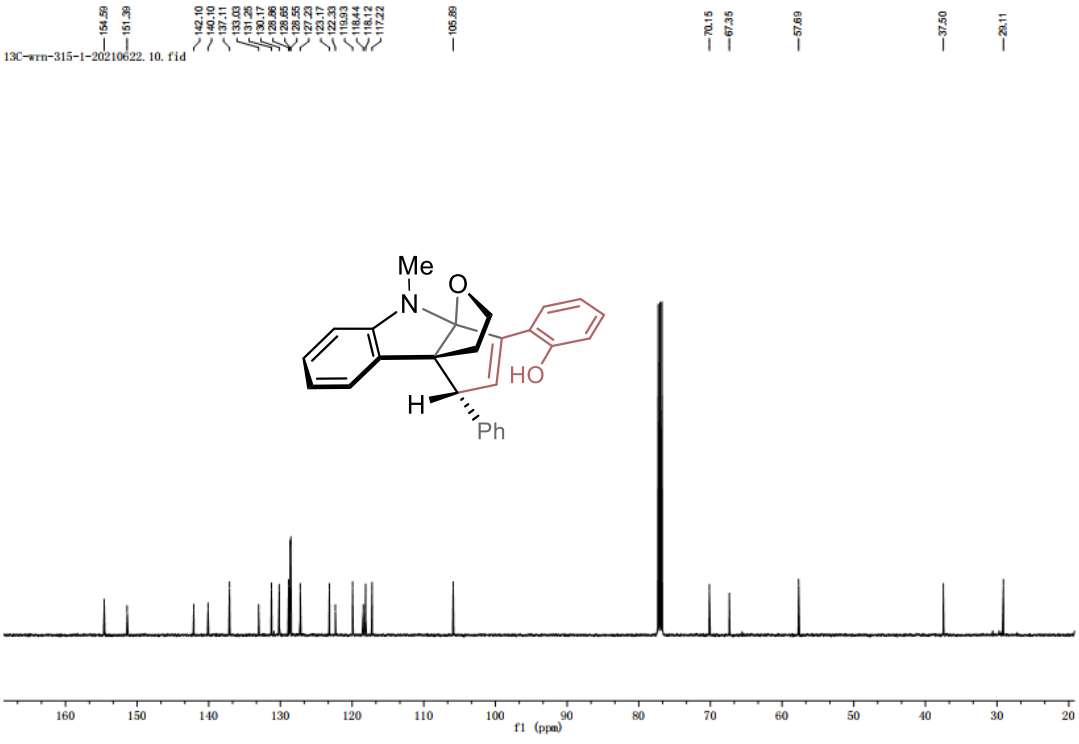
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3w**



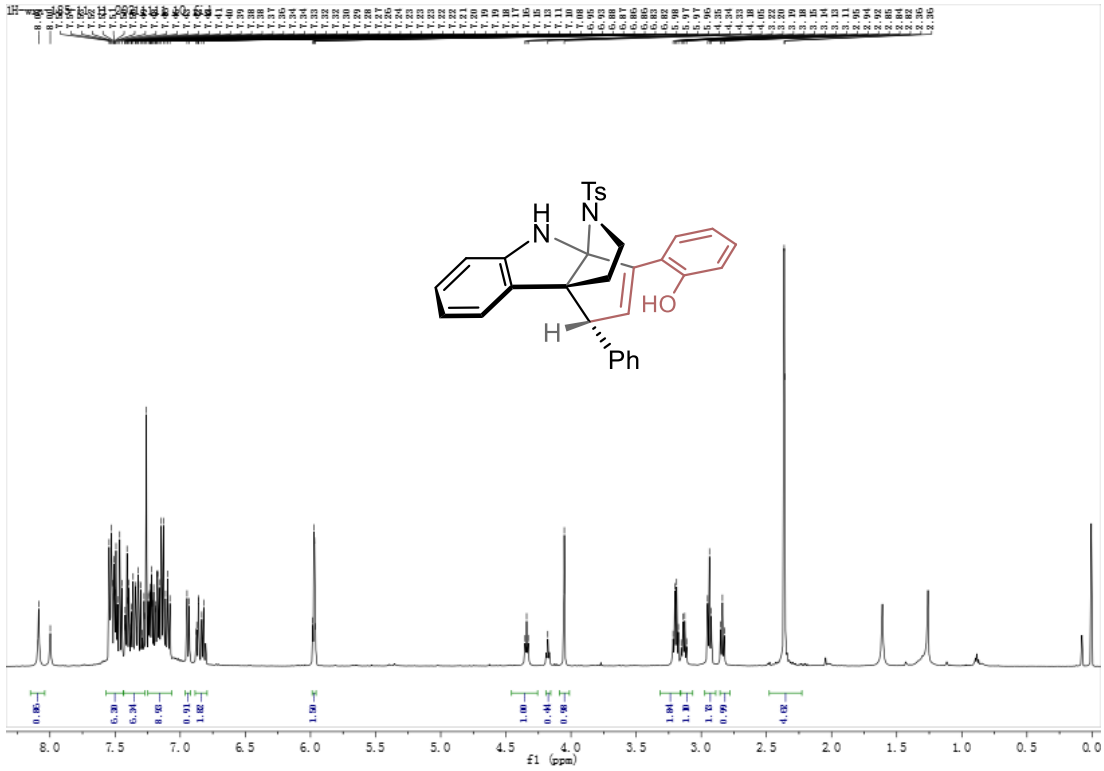
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3x** (d.r. = 2:1)



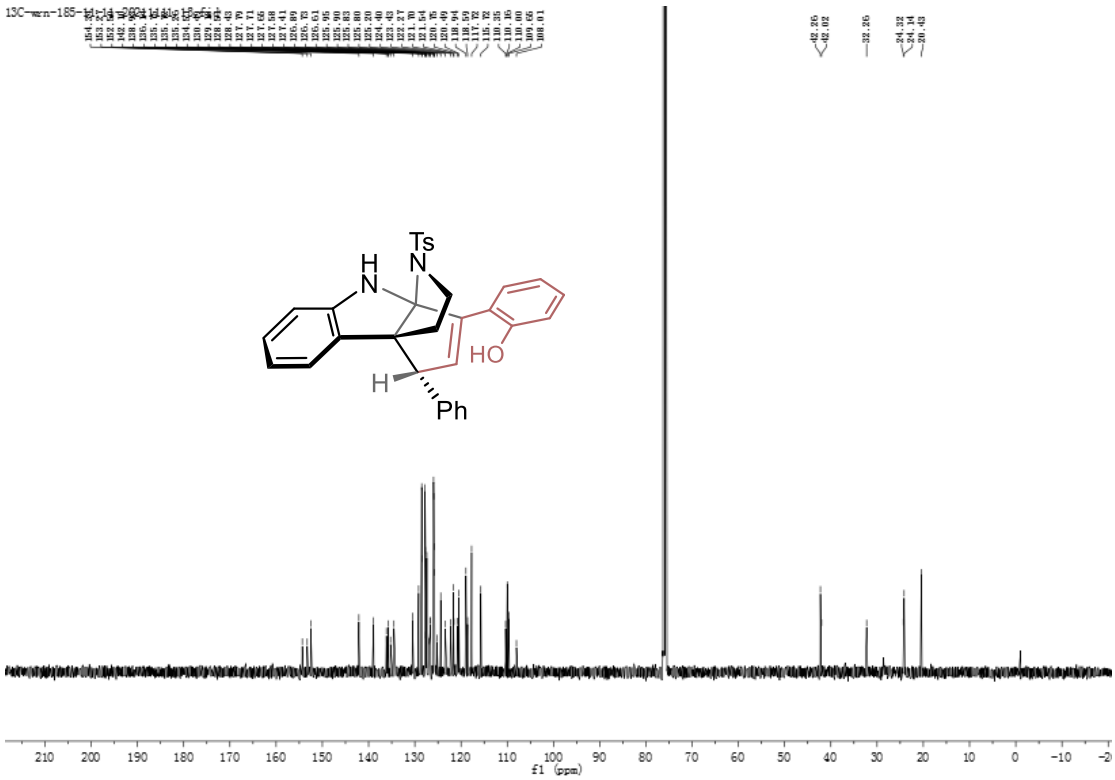
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3x** (d.r. = 2:1)



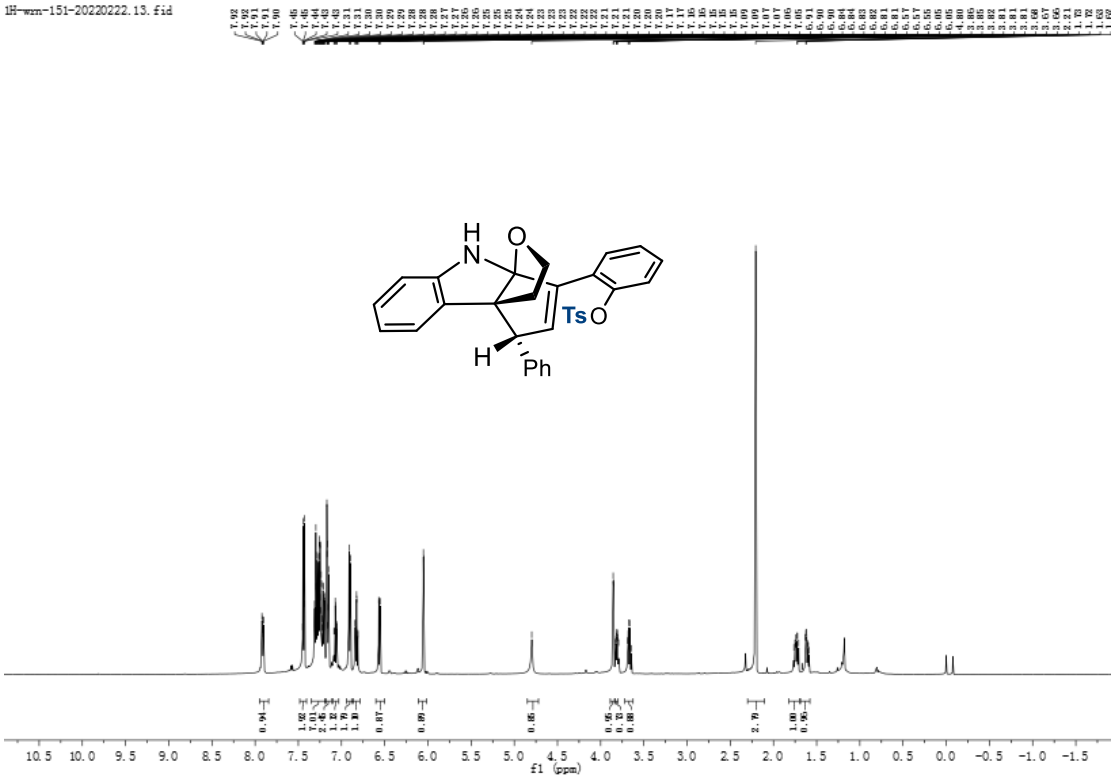
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3y** (d.r. = 2:1)



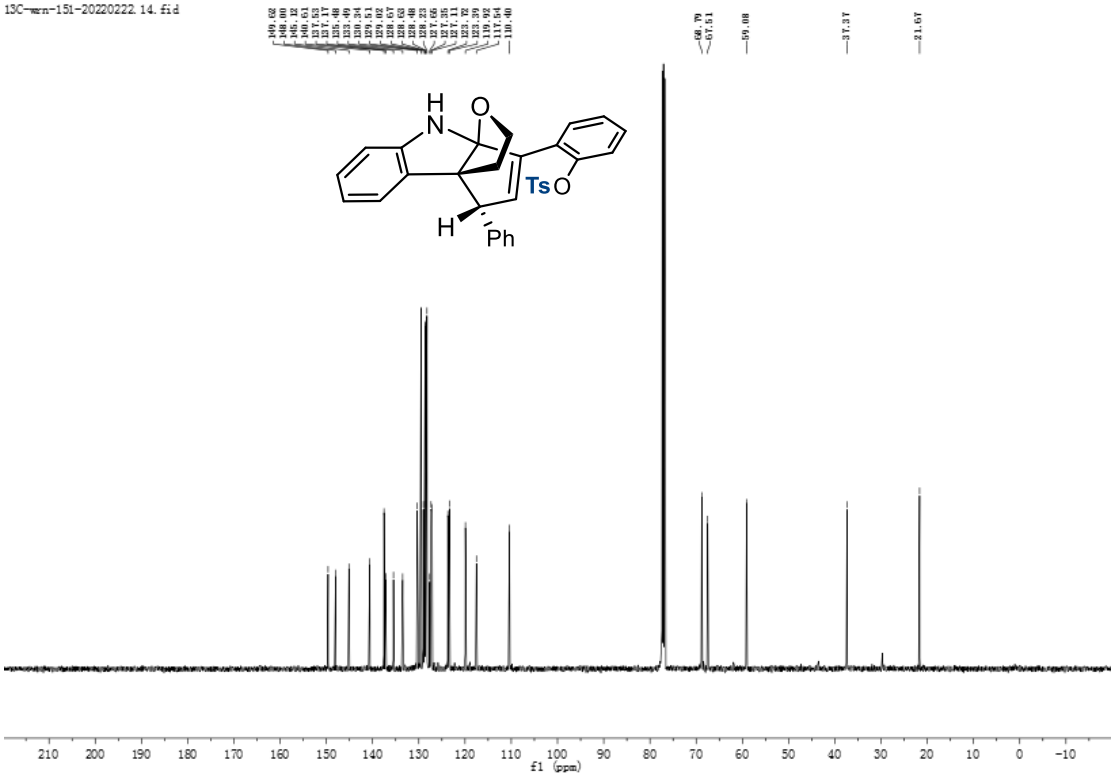
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3y** (d.r. = 2:1)



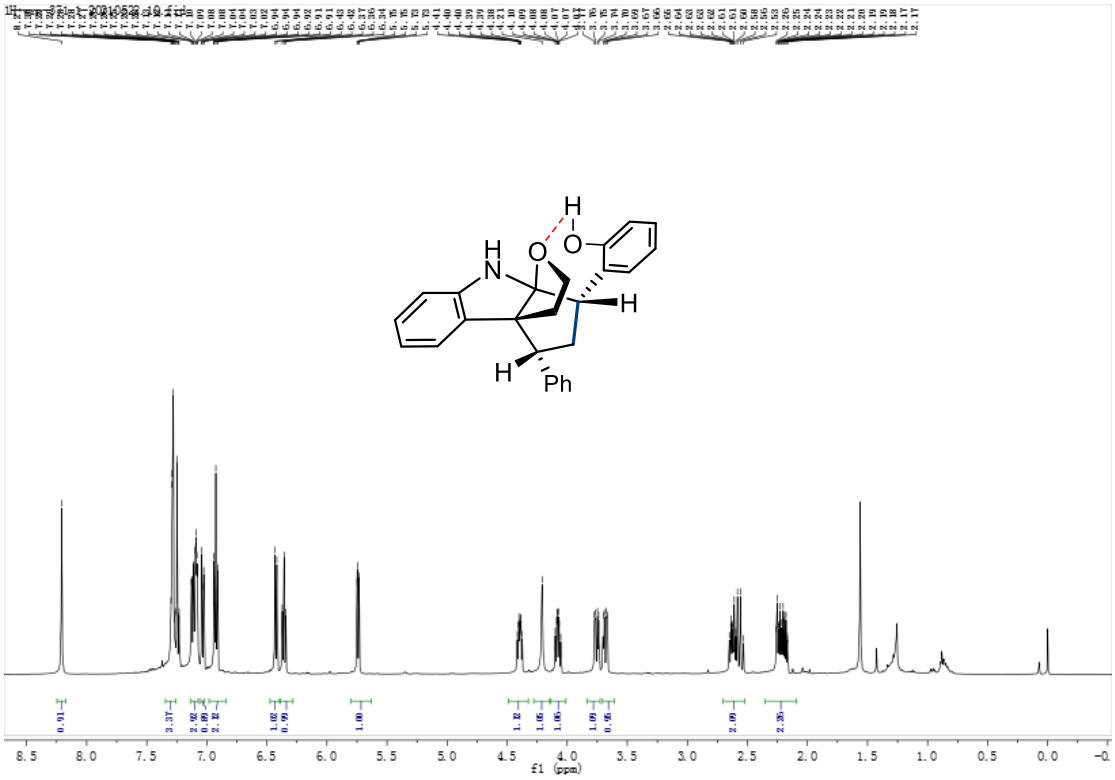
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4**



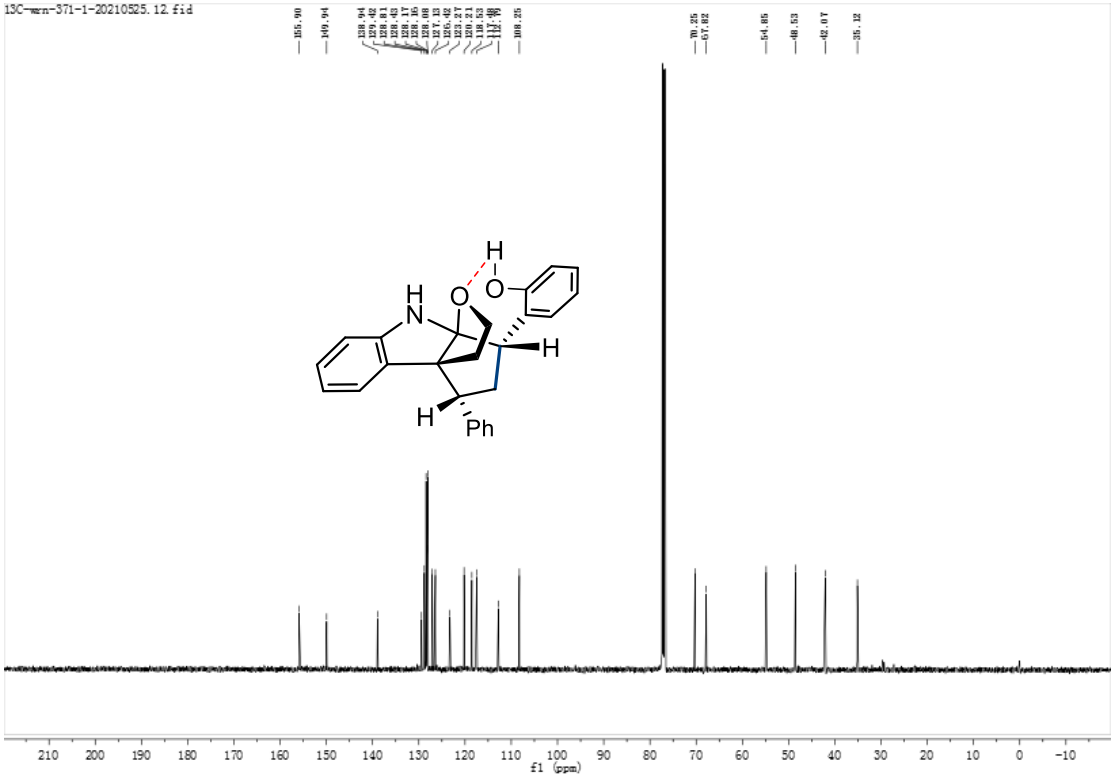
^{13}C NMR (500 MHz, $CDCl_3$) of compound **4**



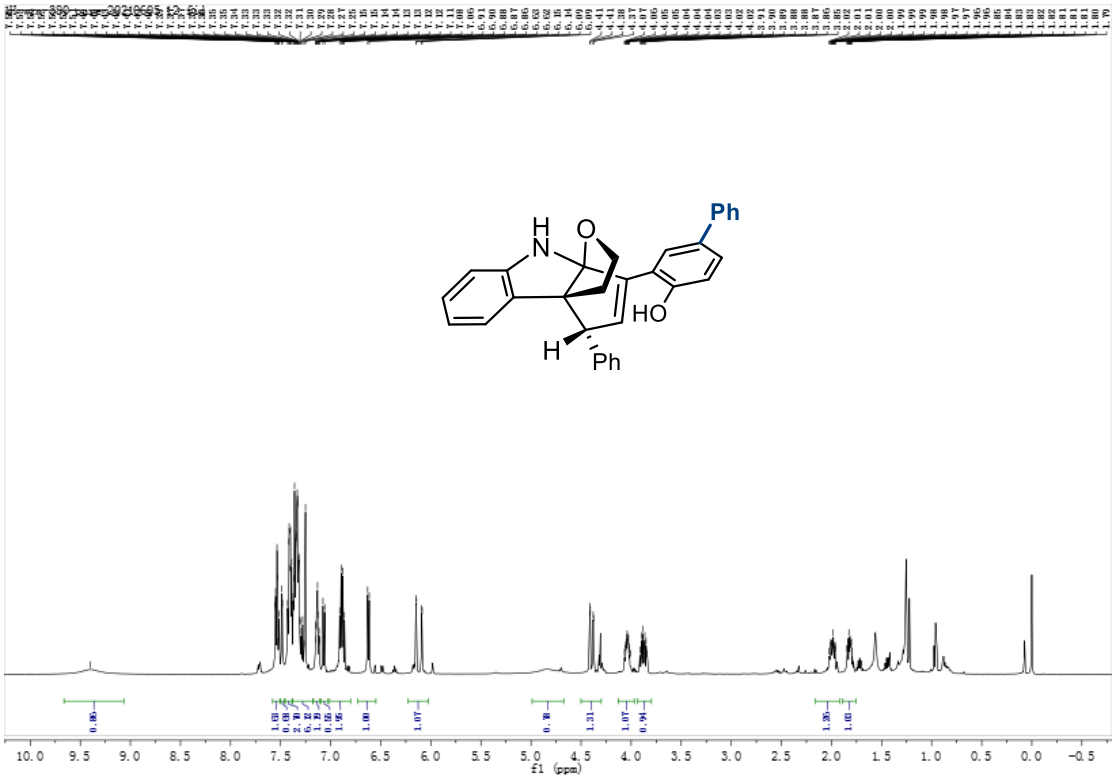
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**



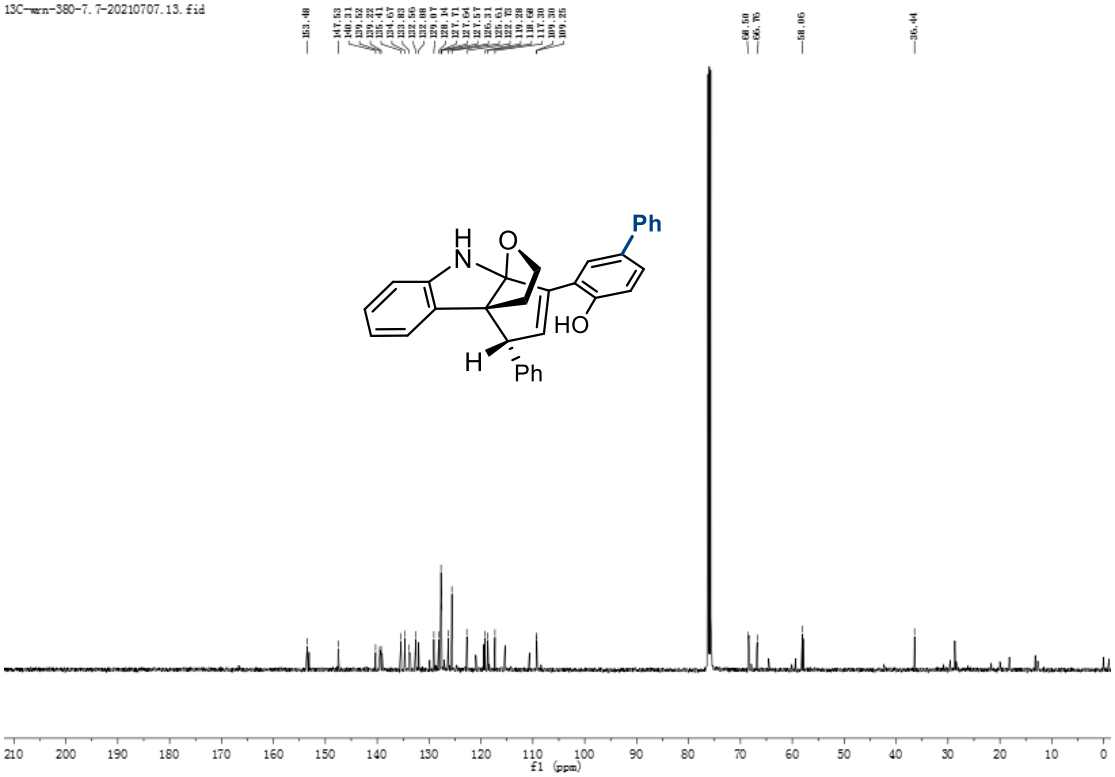
^{13}C NMR (500 MHz, $CDCl_3$) of compound **5**



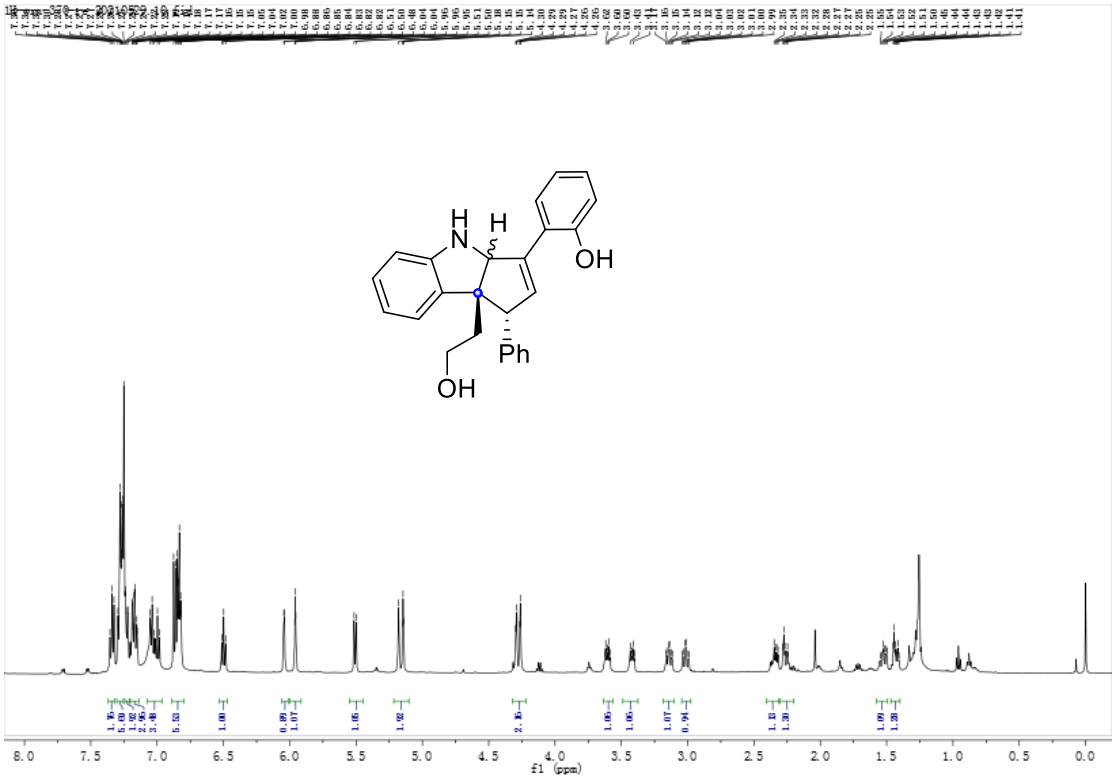
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**



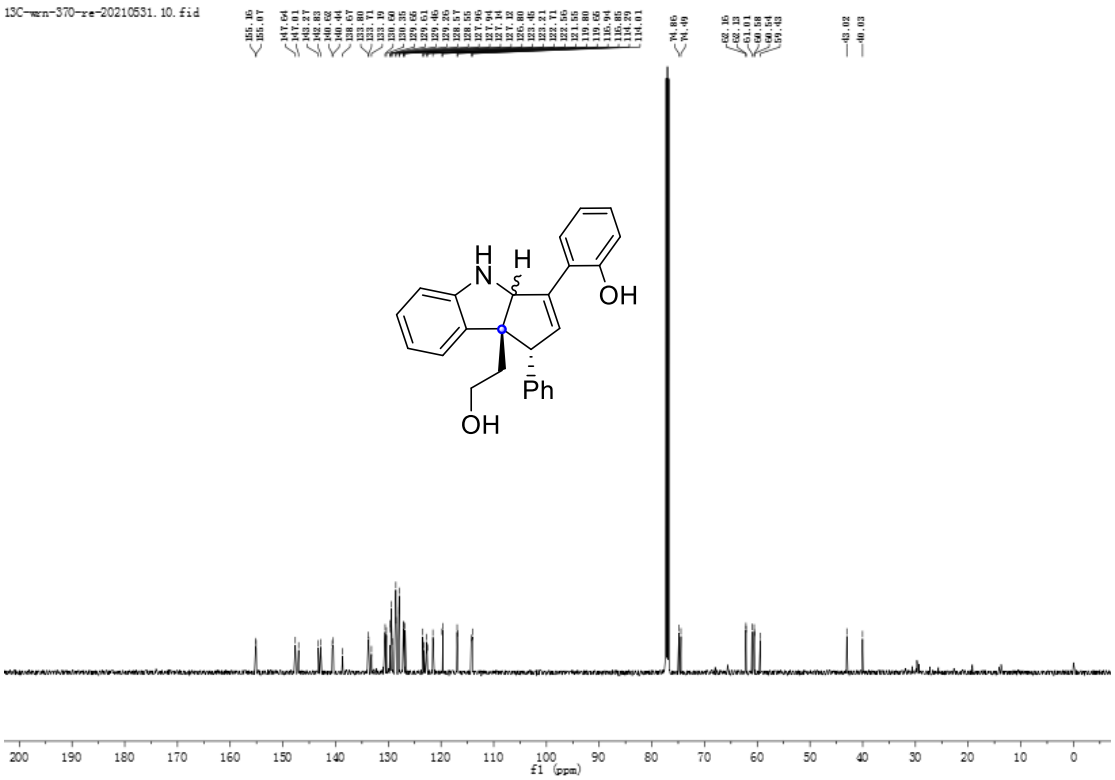
^{13}C NMR (500 MHz, $CDCl_3$) of compound **6**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **7** (d.r. = 1:1)



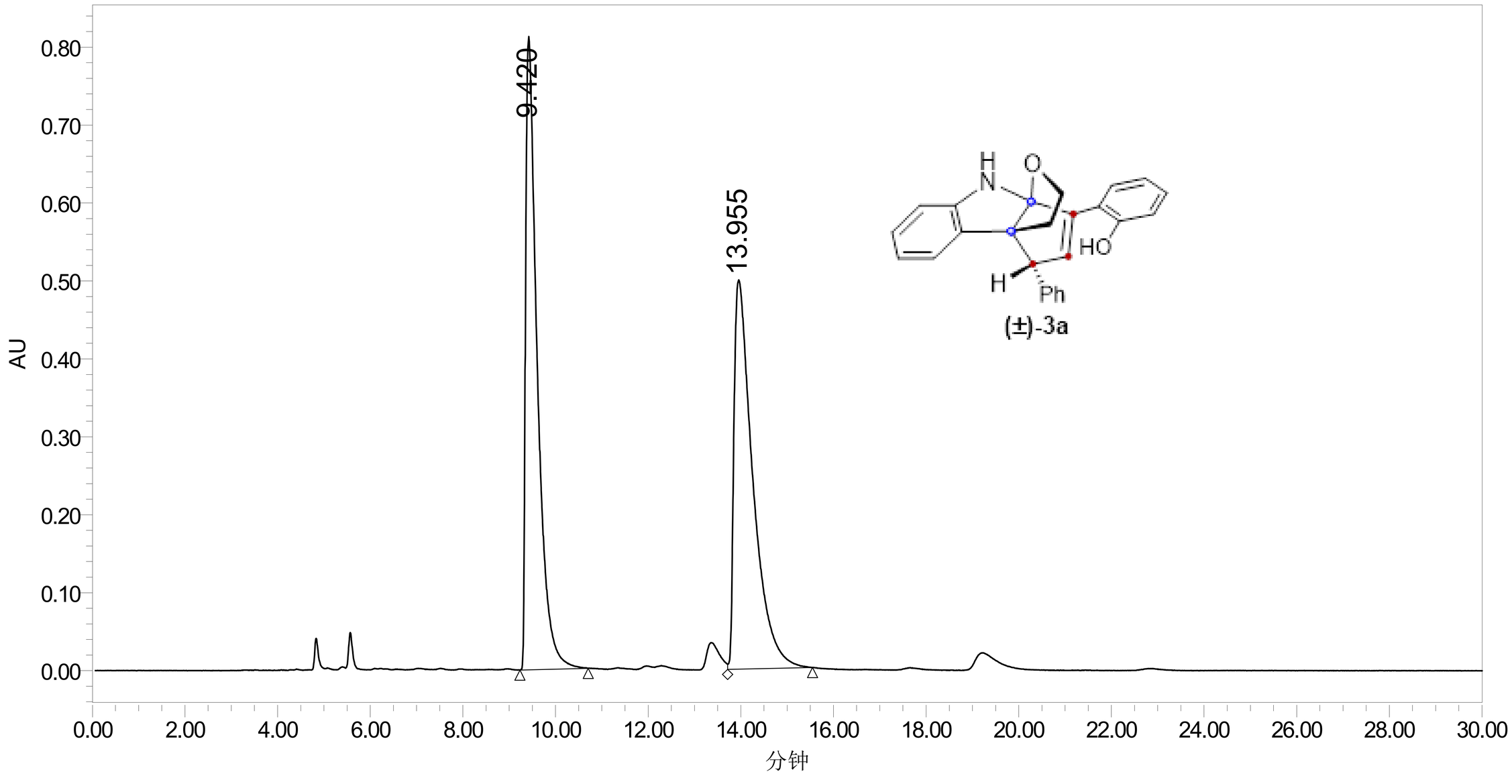
^{13}C NMR (500 MHz, $CDCl_3$) of compound **7** (d.r. = 1:1)



项目名称: Ge Xiao-Min
用户名称: Breeze 用户 (Breeze)

样品信息

样品名称:	rac-0119	采集者:	Breeze
样品类型:	标准样	样品组名称:	An
瓶号:	1:A,1	采集方法组:	1 mL IB3 Hexvsipr 95vs5
进样次数:	1	处理方法:	hex vs iPr 95vs5
进样体积:	3.00 ul	通道名称:	254.0 纳米
运行时间:	30.0 Minutes	处理通道注释:	PDA 254.0 纳米
采集时间:	2021/1/19 22:16:00 CST	色谱柱类型:	PDA 254.0 纳米
处理时间:	2021/1/19 23:01:12 CST		

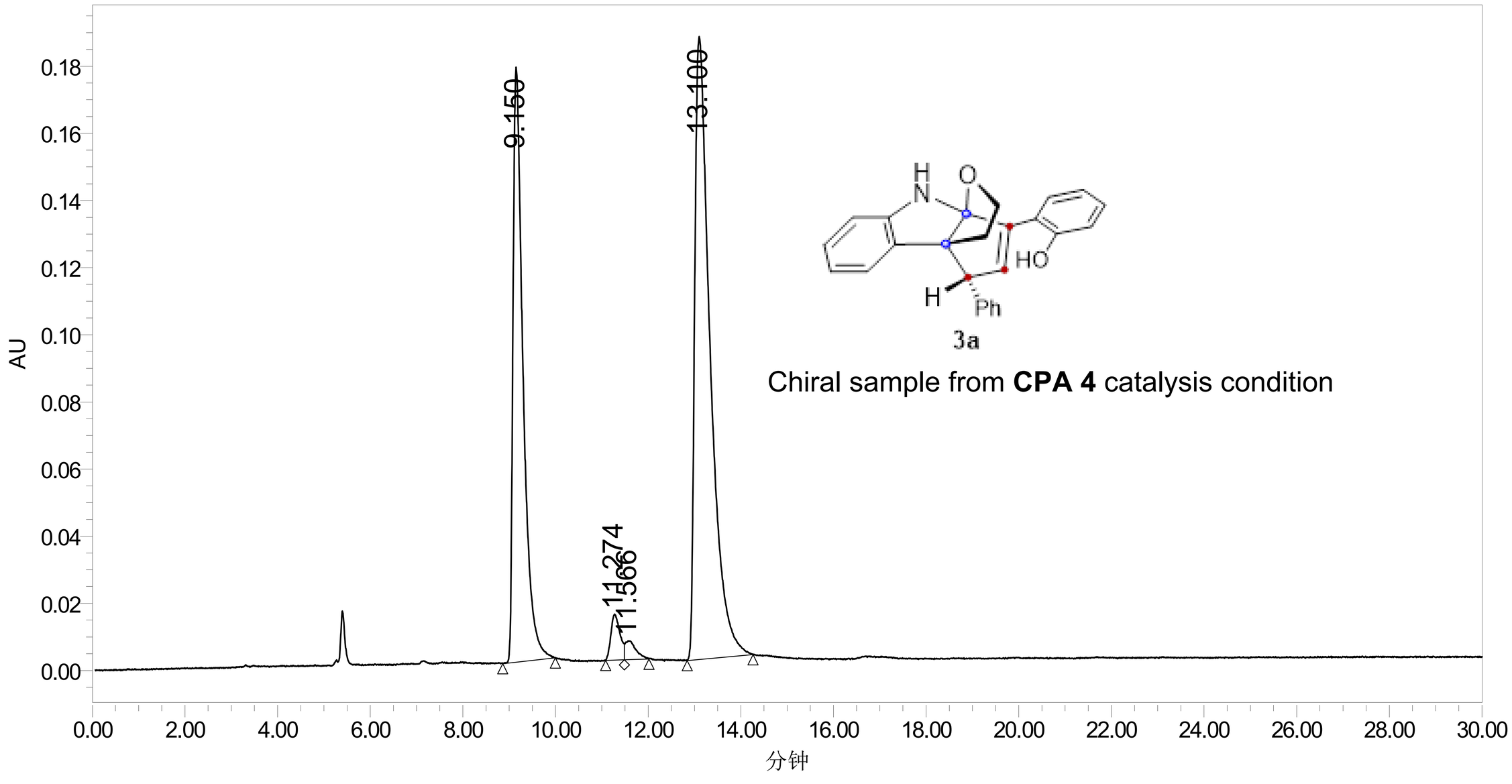


	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高度
1	9.420	14174560	50.05	812555	61.93
2	13.955	14145261	49.95	499597	38.07

项目名称: Ge Xiao-Min
用户名称: Breeze 用户 (Breeze)

样品信息

样品名称:	2	采集者:	Breeze
样品类型:	标准样	样品组名称:	An
瓶号:	1:A,3	采集方法组:	1 mL IB3 Hexvsipr 95vs5
进样次数:	1	处理方法:	hex vs iPr 95vs5
进样体积:	5.00 ul	通道名称:	254.0 纳米
运行时间:	30.0 Minutes	处理通道注释:	PDA 254.0 纳米
采集时间:	2021/1/20 13:26:55 CST	色谱柱类型:	PDA 254.0 纳米
处理时间:	2021/1/20 14:08:20 CST		



	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	% 高度
1	9.150	2670154	36.83	177237	46.39
2	11.274	186482	2.57	13643	3.57
3	11.566	91631	1.26	5634	1.47
4	13.100	4302637	59.34	185537	48.56