Supplementary Information

Rh(III)-catalyzed and synergistic dual directing groups-enabled redox-neutral [3+3] annulation of *N*-phenoxyacetamides with α-allenols

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I. General

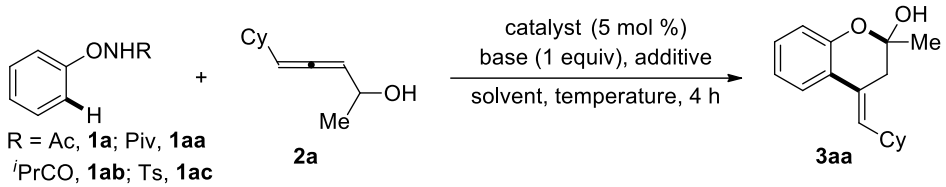
NMR spectra were recorded on JEOL 400 NMR (^{1}H 400 MHz; ^{13}C 100 MHz) in $CDCl_3$, CD_3OD or DMSO-d_6. Abbreviations for data quoted are s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_3OD-d_4: δ_H = 3.31 ppm, δ_C =49 ppm; d_6-DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm). Mass spectra and high-resolution mass spectra were measured on an agilent TOF-G6230B mass spectrometer and Thermo-DFS mass spectrometer. Thin-layer chromatographies were done on pre-coated silica gel 60 F254 plates (Merck). Silica gel 60H (200-300 mesh) and preparative TLC (200x200 mm, 0.2-0.25 mm in thickness) manufactured by Qingdao Haiyang Chemical Group Co. (China) were used for general chromatography. $[Cp^*IrCl_2]_2$, $[Cp^*RhCl_2]_2$, $[Ru(p\text{-cymene})Cl_2]_2$, $Cp^*Co(CO)I_2$ and NaOAc were purchased from Aldrich and used without further purification. Other chemicals were purchased from commercial suppliers and were dried and purified when necessary. *N*-phenoxy amides[S1] and α-allenol substrates[S2] were prepared according to published procedures. Alternatively, these chiral rhodium catalysts can be also purchased from Daicel Chiral Technologies (China) Co., LTD. No attempts were made to optimize yields for substrate synthesis.

II. Experimental Information and Characterization Data

Optimization studies:

The mixture of *N*-phenoxyacetamide **1a** (0.1 mmol, 1.0 equiv), 5-cyclohexylpenta-3,4-dien-2-ol **2a** (0.12 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %), base (1.0 equiv) and additive (1 equiv) in the solvent (0.5 mL) was stirred at the corresponding temperature without exclusion of air or moisture. Afterwards, it was diluted with EtOAc and filtered through a short silica gel column to remove the metal residues. Then, the reaction mixture was concentrated and purified by preparative TLC (eluent: DCM/PE = 5/1) to give the desired chroman-2-ol derivative **3aa**.

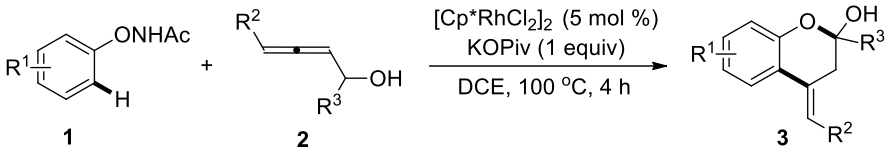
Table S1. Conditions screening for the synthesis of **3aa**.[a]



Entry	catalyst	base	solvent	*T* (°C)	yield (%)[b]
1	$[Cp^*RhCl_2]_2$	CsOAc	DCE	60	25
2	$[Cp^*RhCl_2]_2$	CsOAc	DCE	100	46
3	$[Cp^*RhCl_2]_2$	NaOAc	DCE	100	25
4	$[Cp^*RhCl_2]_2$	KOAc	DCE	100	43
5	$[Cp^*RhCl_2]_2$	AgOAc	DCE	100	42
6	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	DCE	100	n.r.
7	$[Cp^*RhCl_2]_2$	$Zn(OAc)_2$	DCE	100	<5
8	$[Cp^*RhCl_2]_2$	KOPiv	DCE	100	73
9	$[Cp^*RhCl_2]_2$	K_2CO_3	DCE	100	<5
10	$[Cp^*RhCl_2]_2$	Cs_2CO_3	DCE	100	<5
11	$[Cp^*RhCl_2]_2$	KOPiv	MeOH	100	37
12	$[Cp^*RhCl_2]_2$	KOPiv	MeCN	100	62
13	$[Cp^*RhCl_2]_2$	KOPiv	TFE	100	n.r.
14	$[Cp^*RhCl_2]_2$	KOPiv	THF	100	69
15	$[Cp^*RhCl_2]_2$	KOPiv	dioxane	100	61
16	$[Cp^*RhCl_2]_2$	KOPiv	toluene	100	55
17	$[Cp^ERhCl_2]_2$	KOPiv	DCE	100	n.r.
18	$[Cp^{Bn}RhCl_2]_2$	KOPiv	DCE	100	63
19	$[Cp^*IrCl_2]_2$	KOPiv	DCE	100	n.r.
20	$[Ru(p\text{-cymene})Cl_2]_2$	KOPiv	DCE	100	<5
21[c]	$Cp^*Co(CO)I_2$	KOPiv	DCE	100	n.r.
22[d]	$[Cp^*RhCl_2]_2$	KOPiv	DCE	100	22
23[e]	$[Cp^*RhCl_2]_2$	KOPiv	DCE	100	44
24[f]	$[Cp^*RhCl_2]_2$	KOPiv	DCE	100	n.r.
25[g]	$[Cp^*RhCl_2]_2$	KOPiv	DCE	100	61
26[h]	$[Cp^*RhCl_2]_2$	KOPiv	DCE	100	10
27[i]	$[Cp^*RhCl_2]_2$	KOPiv	DCE	25	34

[a]Reaction Conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (5 mol %) and base (1 equiv) in solvent (0.2 M) at the corresponding temperature in an oil bath for 4 h without exclusion of air or moisture. [b]Isolated yield. [c]10 mol % of catalyst was used. [d]**1aa** was used as the substrate. [e]**1ab** was used as the substrate. [f]**1ac** was used as the substrate. [g]HOPiv (1 equiv) was used as an additive. [h]KOH (1 equiv) was used as an additive. [i]The reaction was conducted for 24 h.

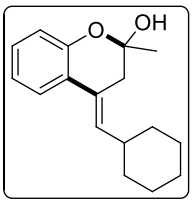
General procedure for the C-H [3+3] annulation:



The mixture of *N*-phenoxyacetamide **1** (0.2 mmol, 1.0 equiv), α-allenol **2** (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and KOPiv (1.0 equiv) in DCE (1 mL) was stirred at 100 °C for 4 h without exclusion of air or moisture. Afterwards, it was diluted with EtOAc and filtered through a short silica gel column to remove the metal residues. Then, the reaction mixture was concentrated and purified by preparative TLC to give the desired product **3**.

Characterization of products 3:

(*E*)-4-(cyclohexylmethylene)-2-methylchroman-2-ol (3aa)



This compound was obtained in 73% yield (37.3 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.4.

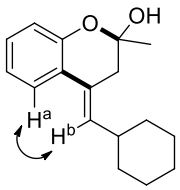
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.52 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.11-7.07 (m, 1H), 6.85-6.81 (m, 1H), 6.72 (dd, *J* = 8.1, 0.7 Hz, 1H), 6.44 (s, 1H), 5.94 (d, *J* = 9.0 Hz, 1H), 2.72 (d, *J* = 14.6 Hz, 1H), 2.41 (d, *J* = 14.7 Hz, 1H), 2.34-2.28 (m, 1H), 1.72-1.58 (m, 5H), 1.47 (s, 3H), 1.34-1.26 (m, 2H), 1.20 -1.12 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.4, 131.5, 129.3, 126.9, 124.2, 123.5, 121.6, 118.5, 98.1, 37.9, 37.2, 34.41, 34.39, 27.6, 27.14, 27.05, 27.0.

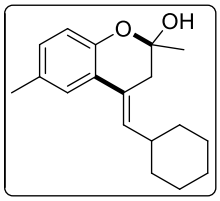
HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{17}H_{21}O_2$: 257.1547; found: 257.1542.

Scale-up synthesis of compound 3aa: The mixture of *N*-phenoxyacetamides **1a** (10 mmol, 1.0 equiv), α-allenol **2a** (12 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and KOPiv (1.0 equiv) in DCE (20 mL) was stirred at 100 °C for 4 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified with silica gel column chromatography to afford the corresponding chroman-2-ol derivative **3aa** in 68% (1.755 g) isolated yield.

^{1}H-^{1}H NOESY:



(*E*)-4-(cyclohexylmethylene)-2,6-dimethylchroman-2-ol (3ba)



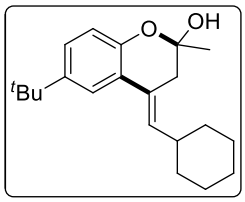
This compound was obtained in 63% yield (34.2 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.35.

^{1}H NMR (400 MHz, CD_3OD): δ 7.31 (s, 1H), 6.91-6.88 (m, 1H), 6.64 (d, *J* = 8.2 Hz, 1H), 5.96 (d, *J* = 9.1 Hz, 1H), 2.76 (d, *J* = 14.5 Hz, 1H), 2.48 (dd, *J* = 14.4, 1.7 Hz, 1H), 2.41-2.32 (m, 1H), 2.25 (s, 3H), 1.79-1.73 (m, 3H), 1.70-1.65 (m, 2H), 1.51 (s, 3H), 1.40-1.33 (m, 2H), 1.27-1.19 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 151.3, 131.2, 130.6, 130.0, 127.0, 124.4, 123.0, 118.3, 98.0, 37.9, 37.2, 34.43, 34.41, 27.6, 27.14, 27.8, 27.0, 20.8.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{18}H_{23}O_2$: 271.1703; found: 271.1694.

(*E*)-6-(*tert*-butyl)-4-(cyclohexylmethylene)-2-methylchroman-2-ol (3ca)



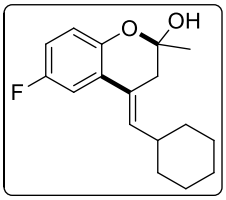
This compound was obtained in 79% yield (49.5 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.35.

^{1}H NMR (400 MHz, CD_3OD): δ 7.50 (s, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.95 (d, *J* = 9.1 Hz, 1H), 2.77 (d, *J* = 14.4 Hz, 1H), 2.51 (d, *J* = 14.4 Hz, 1H), 2.42-2.33 (m, 1H), 1.79-1.74 (m, 3H), 1.71-1.66 (m, 2H), 1.52 (s, 3H), 1.41-1.32 (m, 2H), 1.29 (s, 9H), 1.25-1.17 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 151.2, 144.0, 131.0, 127.4, 126.6, 122.3, 120.5, 118.0, 98.1, 38.0, 37.3, 35.0, 34.5, 32.0, 27.6, 27.13, 27.09.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{21}H_{29}O_2$: 313.2173; found: 313.2167.

(*E*)-4-(cyclohexylmethylene)-6-fluoro-2-methylchroman-2-ol (3da)



This compound was obtained in 68% yield (37.5 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.4.

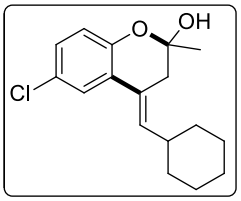
^{1}H NMR (400 MHz, CD_3OD): δ 7.23 (dd, *J* = 10.2, 2.9 Hz, 1H), 6.83 (td, *J* = 8.5, 2.9 Hz, 1H), 6.73 (dd, *J* = 8.9, 5.0 Hz, 1H), 5.97 (d, *J* = 9.1 Hz, 1H), 2.80 (d, *J* = 14.7 Hz, 1H), 2.47 (dd, *J* = 14.7, 2.0 Hz, 1H), 2.42-2.31 (m, 1H), 1.78-1.65 (m, 5H), 1.54 (s, 3H), 1.41-1.32 (m, 2H), 1.30-1.19 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 158.7 (d, *J* = 237.4 Hz), 149.5 (d, *J* = 1.8 Hz), 132.8, 126.3 (d, *J* = 2.3 Hz), 124.7 (d, *J* = 7.3 Hz), 119.7 (d, *J* = 8.2 Hz), 115.8 (d, *J* = 23.9 Hz), 109.8 (d, *J* = 24.1 Hz), 98.1, 37.9, 36.8, 34.2, 34.1, 27.7, 27.1, 27.02, 26.96.

^{19}F NMR (376 MHz, CD_3OD): δ -125.75 - -125.84 (m).

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{20}FO_2$: 275.1453; found: 275.1446.

(*E*)-6-chloro-4-(cyclohexylmethylene)-2-methylchroman-2-ol (3ea)



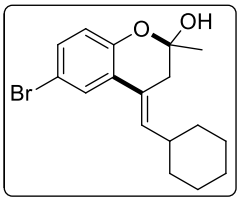
This compound was obtained in 54% yield (31.4 mg) as yellow solid. Eluent: DCM/PE = 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.48 (d, *J* = 2.5 Hz, 1H), 7.05 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 5.98 (d, *J* = 9.1 Hz, 1H), 2.80 (d, *J* = 14.1 Hz, 1H), 2.47 (dd, *J* = 14.6, 2.0 Hz, 1H), 2.42-2.32 (m, 1H), 1.80-1.64 (m, 5H), 1.54 (s, 3H), 1.42-1.32 (m, 2H), 1.30-1.20 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 152.1, 132.9, 128.9, 126.6, 126.0, 125.2, 123.8, 120.1, 98.3, 37.9, 36.8, 34.22, 34.15, 27.7, 27.1, 27.01, 26.96.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{20}ClO_2$: 291.1157; found: 291.1150.

(*E*)-6-bromo-4-(cyclohexylmethylene)-2-methylchroman-2-ol (3fa)



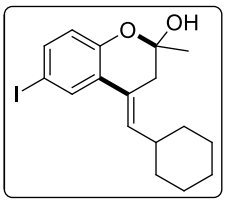
This compound was obtained in 67% yield (45.0 mg) as yellow solid. Eluent: DCM/PE = 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.62 (s, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 1H), 5.96 (d, *J* = 9.1 Hz, 1H), 2.80 (d, *J* = 14.6 Hz, 1H), 2.49-2.43 (m, 1H), 2.41-2.33 (m, 1H), 1.77-1.44 (m, 5H), 1.54 (s, 3H), 1.42-1.32 (m, 2H), 1.28-1.19 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 152.6, 133.0, 131.9, 126.9, 125.9, 125.8, 120.6, 113.9, 98.3, 37.9, 36.8, 34.22, 34.15, 27.6, 27.1, 27.01, 26.96.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{20}BrO_2$: 335.0652; found: 335.0642.

(*E*)-4-(cyclohexylmethylene)-6-iodo-2-methylchroman-2-ol (3ga)



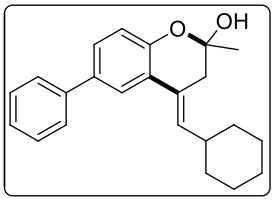
This compound was obtained in 55% yield (42.2 mg) as yellow solid. Eluent: DCM/PE = 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.79 (s, 1H), 7.36 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.58-6.54 (m, 1H), 5.94 (d, *J* = 9.1 Hz, 1H), 2.79 (d, *J* = 14.5 Hz, 1H), 2.46 (dd, *J* = 14.5, 1.6 Hz, 1H), 2.41-2.31 (m, 1H), 1.75-1.64 (m, 5H), 1.54 (s, 3H), 1.40-1.32 (m, 2H), 1.27-1.19 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.3, 137.9, 133.0, 132.8, 126.3, 125.8, 121.0, 98.3, 83.6, 37.9, 36.7, 34.24, 34.17, 27.6, 27.1, 27.02, 26.98.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{20}IO_2$: 383.0513; found: 383.0504.

(*E*)-4-(cyclohexylmethylene)-2-methyl-6-phenylchroman-2-ol (3ha)



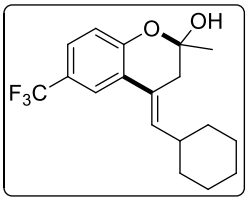
This compound was obtained in 62% yield (41.4mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.35.

^{1}H NMR (400 MHz, CD_3OD): δ 7.72 (s, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.40-7.33 (m, 3H), 7.26 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.06 (d, *J* = 9.2 Hz, 1H), 2.82 (d, *J* = 14.5 Hz, 1H), 2.53 (d, *J* = 14.5 Hz, 1H), 2.39 (q, *J* = 11.0 Hz, 1H), 1.78-1.75 (m, 3H), 1.71-1.67 (m, 2H), 1.56 (s, 3H), 1.40-1.32 (m, 2H), 1.27-1.20 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.1, 142.5, 134.9, 131.9, 129.7, 128.1, 127.6, 126.9, 123.6, 122.7, 119.0, 98.4, 38.0, 37.2, 34.4, 34.3, 27.6, 27.11, 27.08, 27.0.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{23}H_{25}O_2$: 333.1860; found: 333.1853.

(*E*)-4-(cyclohexylmethylene)-2-methyl-6-(trifluoromethyl)chroman-2-ol (3ia)



This compound was obtained in 47% yield (30.6 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.4.

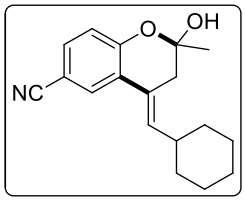
^{1}H NMR (400 MHz, CD_3OD): δ 7.76 (s, 1H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 6.04 (d, *J* = 9.2 Hz, 1H), 2.86 (d, *J* = 14.6 Hz, 1H), 2.51 (d, *J* = 14.6 Hz, 1H), 2.44-2.36 (m, 1H), 1.79-1.75 (m, 3H), 1.72-1.66 (m, 2H), 1.58 (s, 3H), 1.41 -1.33 (m, 2H), 1.30-1.23 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 156.2, 133.4, 133.3, 126.1 (q, *J* = 271.7 Hz), 125.9 (q, *J* = 3.03 Hz), 124.2, 123.7 (q, *J* = 32.3 Hz), 121.6 (q, *J* = 4.04 Hz), 119.2, 98.8, 38.0, 34.2, 34.1, 27.62, 27.56, 27.1, 27.00, 26.96.

^{19}F NMR (376 MHz, CD_3OD): δ -62.9.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{18}H_{20}F_3O_2$: 325.1421; found: 325.1410.

(*E*)-4-(cyclohexylmethylene)-2-hydroxy-2-methylchroman-6-carbonitrile (3ja)



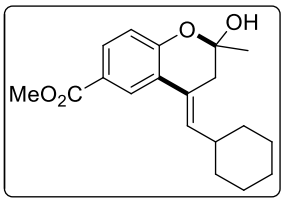
This compound was obtained in 33% yield (18.7 mg) as yellow solid. Eluent: DCM/PE = 5/1, R_f = 0.25.

^{1}H NMR (400 MHz, CD_3OD): δ 7.89 (s, 1H), 7.43-7.41 (m, 1H), 6.88 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.08 (d, *J* = 9.1 Hz, 1H), 2.85 (dd, *J* = 14.7, 2.5 Hz, 1H), 2.50 (dd, *J* = 14.5, 2.3 Hz, 1H), 2.42-2.37 (m, 1H), 1.78-1.74 (m, 3H), 1.69-1.65 (m, 2H), 1.58 (s, 3H), 1.40-1.33 (m, 2H), 1.29-1.23 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 157.2, 134.2, 132.7, 129.2, 125.3, 125.2, 120.3, 119.9, 104.7, 99.3, 38.0, 36.7, 34.2, 34.0, 27.6, 27.1, 26.96, 26.92.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{18}H_{20}NO_2$: 282.1499; found: 282.1491.

(*E*)-methyl 4-(cyclohexylmethylene)-2-hydroxy-2-methylchroman-6-carboxylate (3ka)



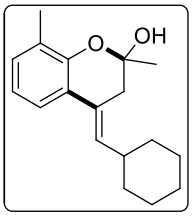
This compound was obtained in 38% yield (24.0 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.2.

^{1}H NMR (400 MHz, CD_3OD): δ 8.21 (s, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 1H), 6.06 (d, *J* = 9.5 Hz, 1H), 3.88 (s, 3H), 2.84 (d, *J* = 14.5 Hz, 1H), 2.52 (d, *J* = 14.6 Hz, 1H), 2.45-2.36 (m, 1H), 1.80-1.76 (m, 3H), 1.72-1.66 (m, 2H), 1.57 (s, 3H), 1.42-1.34 (m, 2H), 1.29-1.23 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 168.6, 157.6, 132.9, 130.6, 126.5, 126.1, 123.7, 123.4, 118.8, 99.0, 52.4, 37.9, 36.9, 34.3, 34.2, 27.6, 27.1, 27.02, 26.98.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{19}H_{23}O_4$: 315.1602; found: 315.1591.

(*E*)-4-(cyclohexylmethylene)-2,8-dimethylchroman-2-ol (3la)



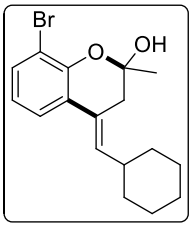
This compound was obtained in 68% yield (36.9 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.34 (d, *J* = 7.9 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 5.95 (d, *J* = 9.1 Hz, 1H), 2.76 (d, *J* = 14.4 Hz, 1H), 2.52 (d, *J* = 14.4 Hz, 1H), 2.43-2.31 (m, 1H), 2.16 (s, 3H), 1.78-1.67 (m, 5H), 1.54 (s, 3H), 1.44-1.33 (m, 2H), 1.30-1.17 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 151.5, 131.3, 130.4, 127.31, 127.29, 122.8, 122.0, 121.0, 98.0, 37.9, 37.1, 34.4, 27.5, 27.2, 27.1, 27.0, 16.5.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{18}H_{23}O_2$: 271.1703; found: 271.1693.

(*E*)-8-bromo-4-(cyclohexylmethylene)-2-methylchroman-2-ol (3ma)



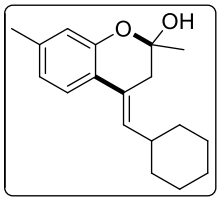
This compound was obtained in 46% yield (30.9 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 6.75 (t, *J* = 7.8 Hz, 1H), 6.02 (d, *J* = 9.2 Hz, 1H), 2.82 (d, *J* = 14.6 Hz, 1H), 2.50 (d, *J* = 14.5 Hz, 1H), 2.44-2.36 (m, 1H), 1.79-1.74 (m, 3H), 1.70-1.65 (m, 2H), 1.59 (s, 3H), 1.41-1.33 (m, 2H), 1.27-1.20 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 150.1, 133.0, 132.7, 126.4, 125.5, 123.7, 122.1, 112.7, 99.0, 38.0, 34.3, 34.2, 27.5, 27.1, 27.01, 26.97.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{20}BrO_2$: 335.0652; found: 335.0647.

(*E*)-4-(cyclohexylmethylene)-2,7-dimethylchroman-2-ol (3na)



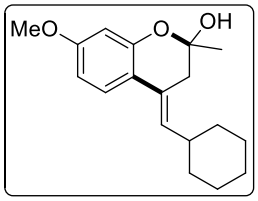
This compound was obtained in 69% yield (37.6 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.38 (d, *J* = 8.1 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.58 (s, 1H), 5.91 (d, *J* = 9.1 Hz, 1H), 2.75 (d, *J* = 14.6 Hz, 1H), 2.49 (dd, *J* = 14.5, 1.4 Hz, 1H), 2.40-2.31 (m, 1H), 2.24 (s, 3H), 1.77-1.73 (m, 3H), 1.70-1.63 (m, 2H), 1.51 (s, 3H), 1.40-1.32 (m, 2H), 1.26-1.17 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.3, 139.4, 130.5, 126.8, 124.1, 122.6, 120.6, 118.8, 98.1, 37.8, 37.2, 34.5, 27.5, 27.2, 27.09, 27.05, 21.2.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{18}H_{23}O_2$: 271.1703; found: 271.1697.

(*E*)-4-(cyclohexylmethylene)-7-methoxy-2-methylchroman-2-ol (3oa)



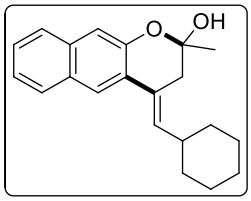
This compound was obtained in 57% yield (32.8 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.3.

^{1}H NMR (400 MHz, CD_3OD): δ 7.41 (d, *J* = 8.8 Hz, 1H), 6.46 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.31 (d, *J* = 3.0 Hz, 1H), 5.82 (d, *J* = 9.1 Hz, 1H), 3.73 (s, 3H), 2.75 (d, *J* = 14.5 Hz, 1H), 2.49 (d, *J* = 14.7 Hz, 1H), 2.39-2.29 (m, 1H), 1.79-1.73 (m, 3H), 1.69-1.63 (m, 2H), 1.52 (s, 3H), 1.42-1.32 (m, 2H), 1.26-1.18 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 161.5, 154.4, 129.4, 126.5, 125.2, 116.3, 108.7, 102.8, 98.4, 55.6, 37.8, 37.2, 34.6, 27.5, 27.2, 27.12, 27.08.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{18}H_{23}O_3$: 287.1652; found: 287.1644.

(*E*)-4-(cyclohexylmethylene)-2-methyl-3,4-dihydro-2*H*-benzo[*g*]chromen-2-ol (3pa)



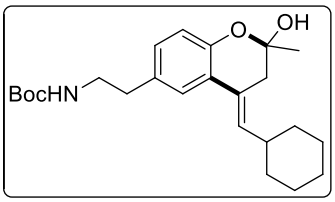
This compound was obtained in 54% yield (33.2 mg) as yellow liquid. Eluent: DCM/PE = 5/1, R_f = 0.35.

^{1}H NMR (400 MHz, CD_3OD): δ 8.02 (s, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.33-7.28 (m, 1H), 7.26-7.22 (m, 1H), 7.14 (s, 1H), 6.24 (d, *J* = 9.2 Hz, 1H), 2.89 (d, *J* = 14.3 Hz, 1H), 2.60 (dd, *J* = 14.5, 2.0 Hz, 1H), 2.48-2.39 (m, 1H), 1.82-1.77 (m, 3H), 1.74-1.70 (m, 2H), 1.60 (s, 3H), 1.42-1.36 (m, 2H), 1.30-1.26 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 152.3, 135.5, 133.1, 130.4, 128.9, 127.0, 126.8, 125.6, 124.6, 123.0, 112.9, 98.40, 98.35, 38.1, 34.32, 34.27, 27.9, 27.8, 27.2, 27.1, 27.0.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{21}H_{23}O_2$: 307.1703; found: 307.1695.

(*E*)-*tert*-butyl (2-(4-(cyclohexylmethylene)-2-hydroxy-2-methylchroman-6-yl) ethyl)carbamate (3qa)



This compound was obtained in 53% yield (42.1 mg) as yellow solid. Eluent: PE/EA= 3/1, R_f = 0.35.

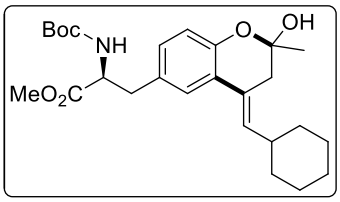
^{1}H NMR (400 MHz, CD_3OD): δ 7.36 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 6.00 (d, *J* = 9.0 Hz, 1H), 3.20 (t, *J* = 7.2 Hz, 2H), 2.77 (d, *J* = 14.5 Hz, 1H), 2.67 (t, *J* = 7.2 Hz, 2H), 2.50 (d, *J* = 14.6 Hz, 1H), 2.42-2.33 (m, 1H), 1.78-1.75 (m, 3H), 1.71-1.65 (m, 2H), 1.52 (s, 3H), 1.42 (s, 9H), 1.37-1.33 (m, 2H), 1.27-1.21 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 158.4, 152.0, 132.4, 131.4, 129.8, 127.0, 124.5, 123.2, 118.5, 98.1, 79.9, 43.3, 37.9, 37.2, 36.6, 34.5, 28.8, 27.5, 27.2, 27.1, 27.0.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{24}H_{34}NO_4$: 400.2493; found: 400.2483.

(*S*)-methyl 2-((*tert*-butoxycarbonyl)amino)-3-((*E*)-4-(cyclohexylmethylene)-2-

hydroxy-2-methylchroman-6-yl)propanoate (3ra)



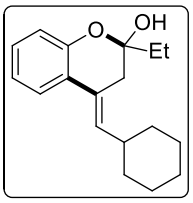
This compound was obtained in 47% yield (42.7 mg) as yellow solid. Eluent: DCM/PE= 5/1, R_f = 0.3.

^{1}H NMR (400 MHz, CD_3OD): δ 7.36 (s, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.00 (d, *J* = 9.1 Hz, 1H), 4.35-4.27 (m, 1H), 3.69 (s, 3H), 3.02 (dd, *J* = 13.8, 5.1 Hz, 1H), 2.86-2.74 (m, 2H), 2.49 (d, *J* = 14.5 Hz, 1H), 2.42-2.34 (m, 1H), 1.79-1.74 (m, 3H), 1.72-1.66 (m, 2H), 1.51 (s, 3H), 1.39 (s, 9H), 1.35-1.31 (m, 2H), 1.27-1.20 (m, 3H)

^{13}C NMR (100 MHz, CD_3OD): δ 174.3, 157.7, 152.4, 131.6, 130.1, 126.9, 125.1, 123.2, 118.5, 98.2, 80.6, 56.7, 52.6, 38.1, 38.1, 38.0, 37.1, 34.5, 28.7, 27.5, 27.2, 27.04, 27.00.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{26}H_{36}NO_6$: 458.2548; found: 458.2539.

(*E*)-4-(cyclohexylmethylene)-2-ethylchroman-2-ol (3ab)



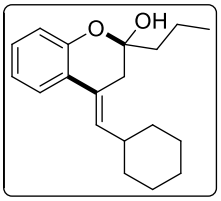
This compound was obtained in 51% yield (27.8 mg) as yellow liquid. Eluent: DCM/PE= 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.84 (t, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 5.98 (d, *J* = 9.1 Hz, 1H), 2.72 (d, *J* = 14.4 Hz, 1H), 2.51 (d, *J* = 14.4 Hz, 1H), 2.42-2.34 (m, 1H), 1.84-1.75 (m, 5H), 1.71-1.67 (m, 2H), 1.40-1.33 (m, 2H), 1.29-1.20 (m, 3H), 1.03 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.5, 131.5, 129.3, 126.7, 124.2, 123.7, 121.5, 118.5, 99.9, 37.9, 34.5, 34.4, 34.3, 33.8, 27.14, 27.06, 27.0, 8.3.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{18}H_{23}O_2$: 271.1703; found: 271.1696.

(*E*)-4-(cyclohexylmethylene)-2-propylchroman-2-ol (3ac)



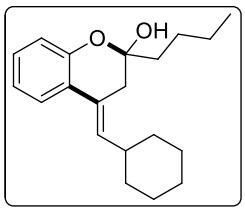
This compound was obtained in 43% yield (24.5 mg) as yellow liquid. Eluent: DCM/PE= 1/1, R_f = 0.35.

^{1}H NMR (400 MHz, CD_3OD): δ 7.50 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.98 (d, *J* = 9.0 Hz, 1H), 2.73 (d, *J* = 14.6 Hz, 1H), 2.52 (d, *J* = 14.5 Hz, 1H), 2.42-2.34 (m, 1H), 1.79-1.67 (m, 7H), 1.57-1.50 (m, 2H), 1.41-1.33 (m, 2H), 1.31-1.23 (m, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.5, 131.5, 129.3, 126.8, 124.2, 123.7, 121.5, 118.5, 99.7, 43.3, 37.9, 35.0, 34.43, 34.35, 27.2, 27.06, 27.05, 18.0, 14.7.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{19}H_{25}O_2$: 285.1860; found: 285.1850.

(*E*)-2-butyl-4-(cyclohexylmethylene)chroman-2-ol (3ad)



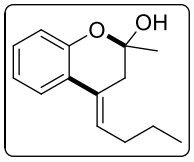
This compound was obtained in 39% yield (23.3 mg) as yellow liquid. Eluent: DCM/PE = 1/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.50 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.98 (d, *J* = 9.2 Hz, 1H), 2.71 (d, *J* = 14.5 Hz, 1H), 2.54 (d, *J* = 14.6 Hz, 1H), 2.42-2.33 (m, 1H), 1.80-1.74 (m, 5H), 1.70-1.65 (m, 2H), 1.52-1.45 (m, 2H), 1.41-1.33 (m, 4H), 1.28-1.20 (m, 3H), 0.94 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.5, 131.5, 129.3, 126.8, 124.2, 123.7, 121.5, 118.5, 99.8, 40.7, 38.0, 35.0, 34.43, 34.37, 27.2, 27.1, 27.0, 26.9, 24.1, 14.5.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{20}H_{27}O_2$: 299.2016; found: 299.2006.

(*E*)-4-butylidene-2-methylchroman-2-ol (3ae)



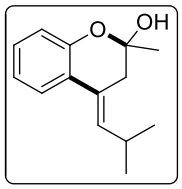
This compound was obtained in 37% yield (16.1 mg) as yellow liquid. Eluent: DCM/PE= 5/1, R_f = 0.3.

^{1}H NMR (400 MHz, CD_3OD): δ 7.54 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 6.18 (t, *J* = 7.4 Hz, 1H), 2.79 (d, *J* = 14.6 Hz, 1H), 2.50 (d, *J* = 14.6 Hz, 1H), 2.24-2.17 (m, 2H), 1.54 (s, 3H), 1.53-1.48 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.5, 133.0, 129.3, 126.6, 124.3, 123.4, 121.6, 118.5, 98.2, 28.0, 27.54, 27.49, 23.6, 23.5.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{14}H_{17}O_2$: 217.1234; found: 217.1223.

(*E*)-2-methyl-4-(2-methylpropylidene)chroman-2-ol (3af)



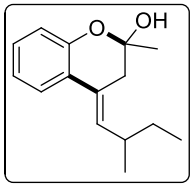
This compound was obtained in 65% yield (28.3 mg) as yellow liquid. Eluent: DCM/PE= 5/1, R_f = 0.3.

^{1}H NMR (400 MHz, CD_3OD): δ 7.52 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.97 (d, *J* = 9.2 Hz, 1H), 2.79 (d, *J* = 14.4 Hz, 1H), 2.75-2.67 (m, 1H), 2.51 (d, *J* = 14.6 Hz, 1H), 1.53 (s, 3H), 1.10-1.05 (m, 6H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.4, 132.9, 129.3, 126.6, 124.3, 123.4, 121.6, 118.5, 98.1, 37.0, 27.9, 27.6, 23.6, 23.5.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{14}H_{17}O_2$: 217.1234; found: 217.1222.

(*E*)-2-methyl-4-(2-methylbutylidene)chroman-2-ol (3ag)



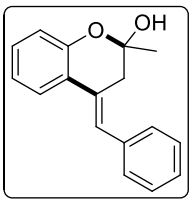
This compound was obtained in 83% yield (38.5 mg) as yellow liquid. Eluent: DCM/PE= 5/1, R_f = 0.35. An inseparable mixture of two diastereoisomers was obtained, and the ratio was determined to be 1/1 by ^{1}H-NMR analysis.

^{1}H NMR (400 MHz, CD_3OD): δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.08 (t, *J* = 7.7 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.92 (d, *J* = 9.4 Hz, 1H), 2.82-2.72 (m, 1H), 2.58-2.44 (m, 2H), 1.54 (s, 1.5H), 1.51 (s, 1.5H), 1.48-1.37 (m, 2H), 1.08-1.03 (m, 3H), 0.95-0.87 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.5, 153.4, 131.9, 129.3, 127.6, 127.5, 124.3, 123.4, 121.6, 98.3, 98.2, 37.41, 37.37, 35.0, 34.9, 31.6, 31.5, 27.6, 27.3, 21.4, 21.2, 12.6, 12.4.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{15}H_{19}O_2$: 231.1390; found: 231.1380.

(*E*)-4-benzylidene-2-methylchroman-2-ol (3ah)



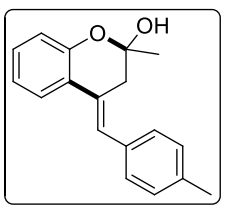
This compound was obtained in 43% yield (21.7 mg) as yellow solid. Eluent: DCM/PE= 5/1, R_f = 0.4.

^{1}H NMR (400 MHz, CD_3OD): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.38-7.34 (m, 4H), 7.26-7.22 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 3.07 (d, *J* = 14.6 Hz, 1H), 2.74 (d, *J* = 14.5 Hz, 1H), 1.52 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 154.0, 138.6, 130.9, 130.5, 130.1, 129.2, 127.8, 124.9, 124.8, 123.4, 121.8, 118.7, 98.0, 37.8, 27.8.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{15}O_2$: 251.1077; found: 251.1072.

(*E*)-2-methyl-4-(4-methylbenzylidene)chroman-2-ol (3ai)



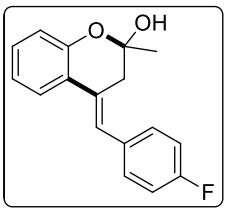
This compound was obtained in 42% yield (22.3 mg) as white solid. Eluent: DCM/PE= 5/1, R_f = 0.35.

^{1}H NMR (400 MHz, CD_3OD): δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.22-7.12 (m, 6H), 6.94-6.89 (m, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 3.05 (d, *J* = 14.6 Hz, 1H), 2.74 (d, *J* = 14.7 Hz, 1H), 2.34 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 153.9, 137.7, 135.7, 130.5, 130.0, 129.8, 124.9, 123.5, 121.8, 118.7, 98.0, 97.9, 37.9, 27.8, 21.3.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{18}H_{17}O_2$: 265.1234; found: 265.1229.

(*E*)-4-(4-fluorobenzylidene)-2-methylchroman-2-ol (3aj)



This compound was obtained in 39% yield (21.0 mg) as white solid. Eluent: DCM/PE= 5/1, R_f = 0.35.

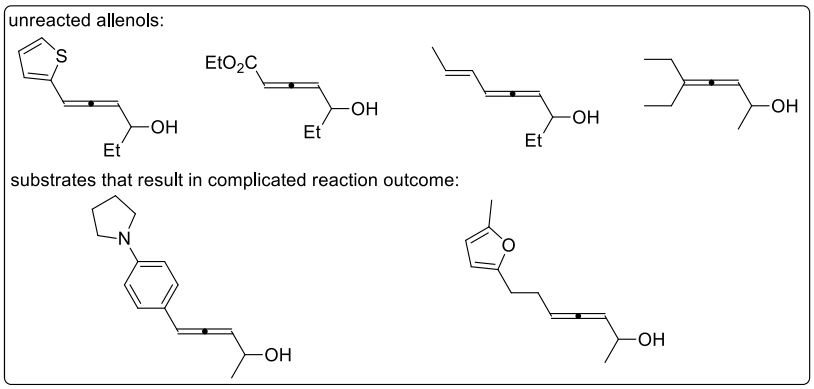
^{1}H NMR (400 MHz, CD_3OD): δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.38-7.33 (m, 2H), 7.23-7.15 (m, 2H), 7.13-7.07 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 3.02 (d, *J* = 14.6 Hz, 1H), 2.72 (d, *J* = 14.7 Hz, 1H), 1.53 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 163.0 (d, *J* = 246.1 Hz), 153.9, 134.8 (d, *J* = 2.8 Hz), 132.3 (d, *J* = 7.8 Hz), 130.9, 130.2, 124.9, 123.7 (d, *J* = 3.8 Hz), 123.2, 121.8, 118.7, 115.9 (d, *J* = 21.6 Hz), 97.9 (d, *J* = 5.5 Hz), 37.7, 27.8.

^{19}F NMR (376 MHz, CD_3OD): -177.47.

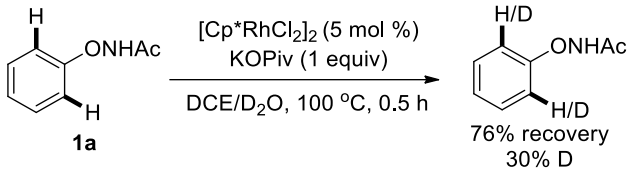
HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{14}FO_2$: 269.0983; found: 269.0977.

The tested unsuccessful allenols:

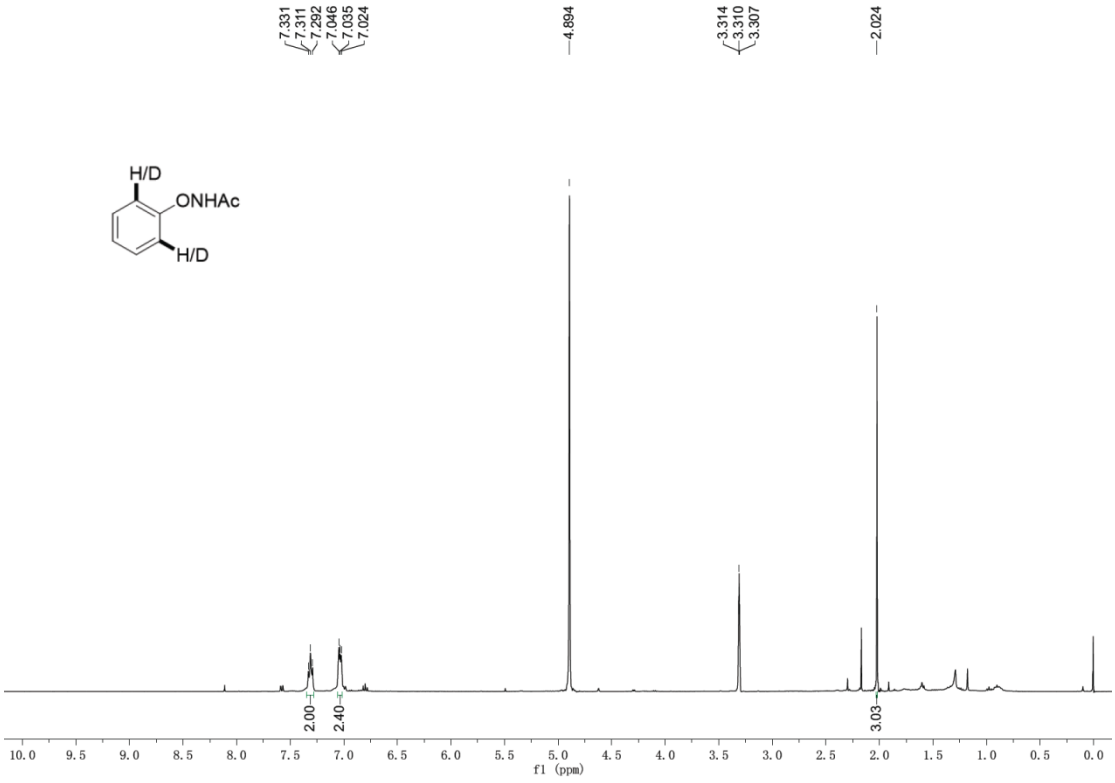


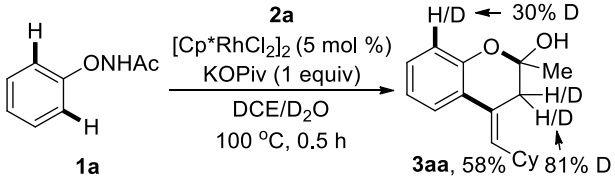
III. Experimental Mechanistic Studies

Deuterium-labeling experiments:



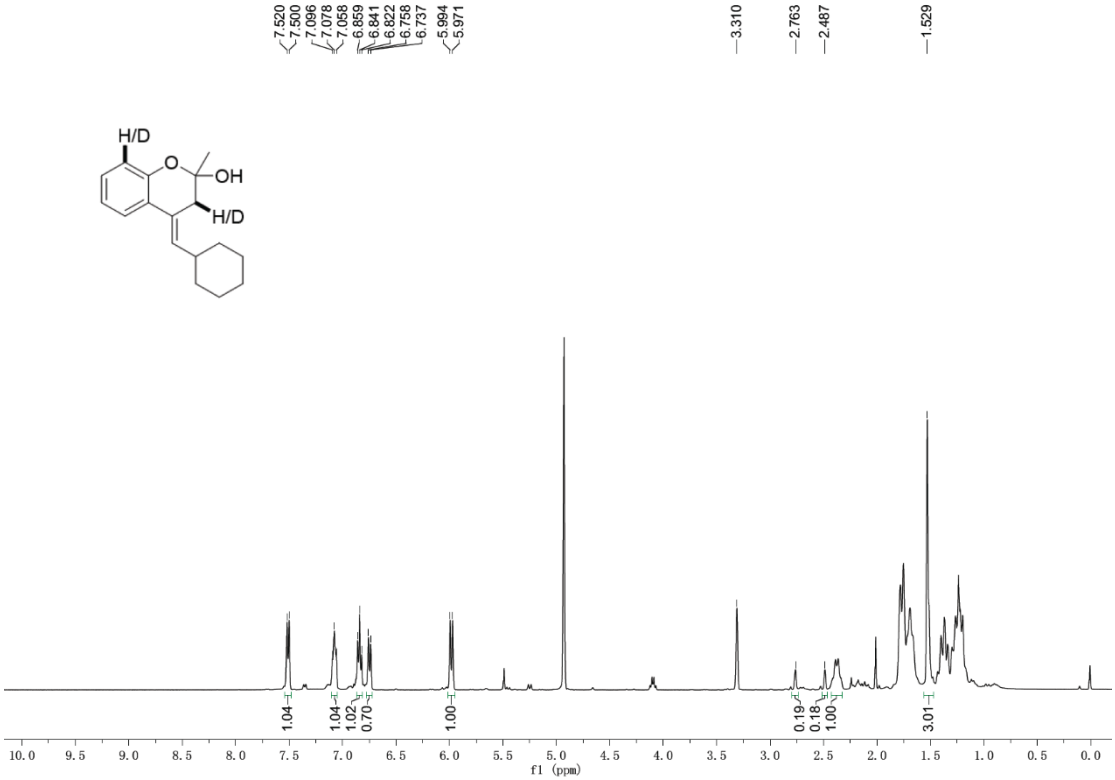
N-phenoxyacetamide **1a** (0.10 mmol) was dissolved in DCE (0.5 mL) in the presence of $[Cp^*RhCl_2]_2$ (5 mol %) and KOPiv (0.1 mmol). D_2O (20 equiv) was used as the deuterium source. The reaction was conducted under the standard condition for 0.5 h, afterwards, **1a** was recovered by flash column chromatography on silica gel (Eluent: PE/EA = 2/1) and was analyzed by ^{1}H-NMR spectroscopy. 30% deuteration was detected by ^{1}H-NMR analysis.

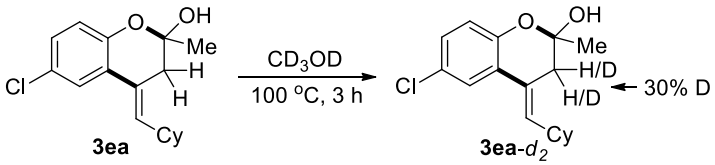




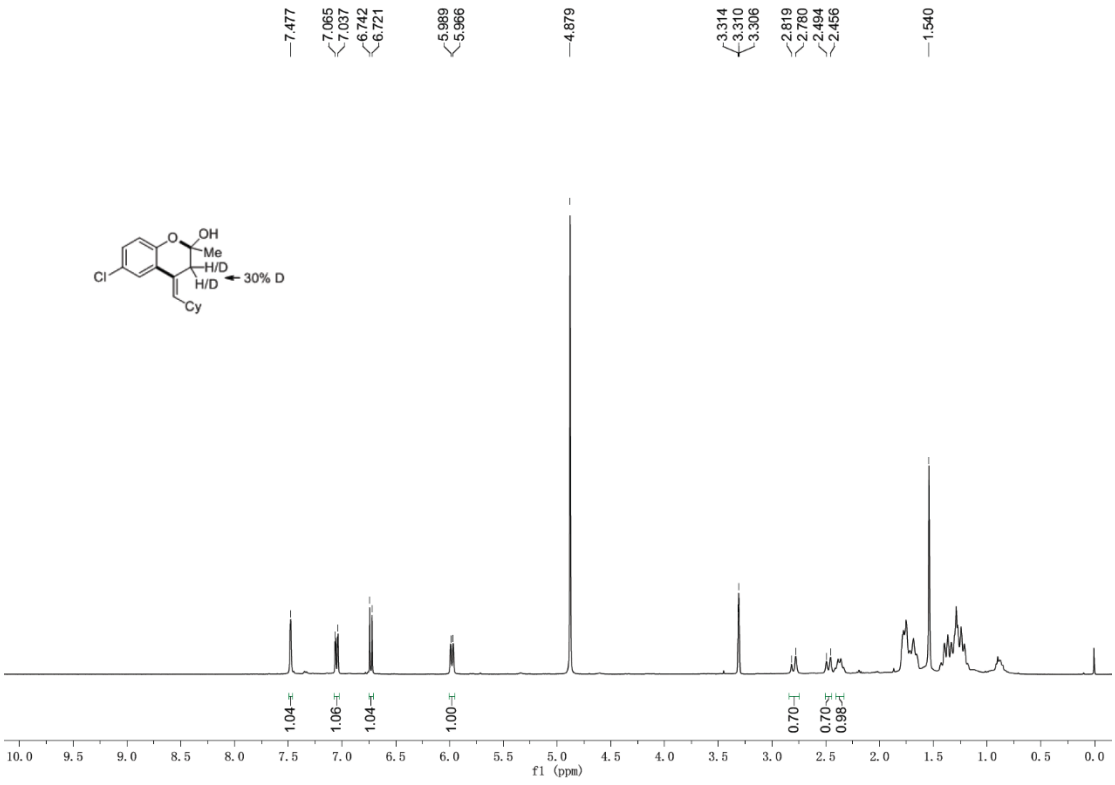
The mixture of *N*-phenoxyacetamide **1a** (0.10 mmol, 1.0 equiv), α-allenol **2a** (0.12 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and KOPiv (0.1 mmol, 1.0 equiv) in DCE

(0.5 mL) was stirred under the standard conditions for 0.5 h. D_2O (20 equiv) was used as the deuterium source. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC (eluent: DCE/PE = 5/1) to afford the desired product **3aa** in 58% yield. The deuterium incorporation was analyzed by ^{1}H-NMR spectroscopy. The result showed that approximately 30% deuteration was observed at the *ortho* position of the directing group and 81% deuteration at the allylic position.

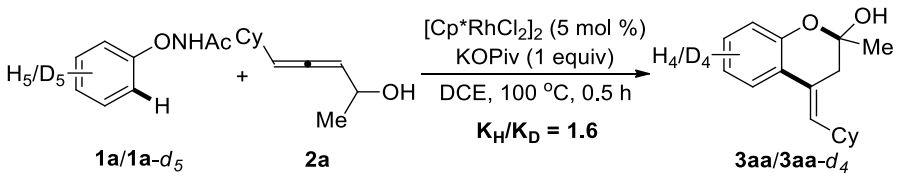




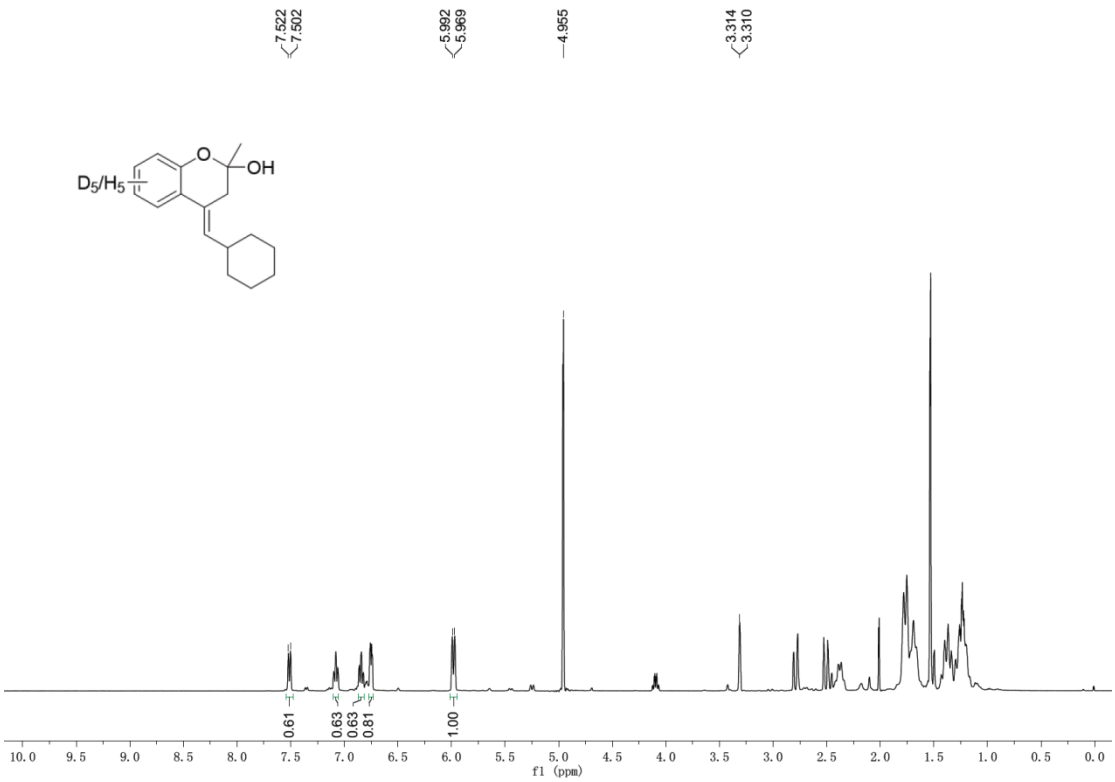
In a sealed tube, the mixture of **3ea** (0.10 mmol) in CD_3OD (0.5 mL) was stirred at 100 °C for 3 h. Afterwards, **3ea** was recovered by removal of the solvent and analyzed by ^{1}H-NMR spectroscopy. 30% deuteration was detected at the allylic position.



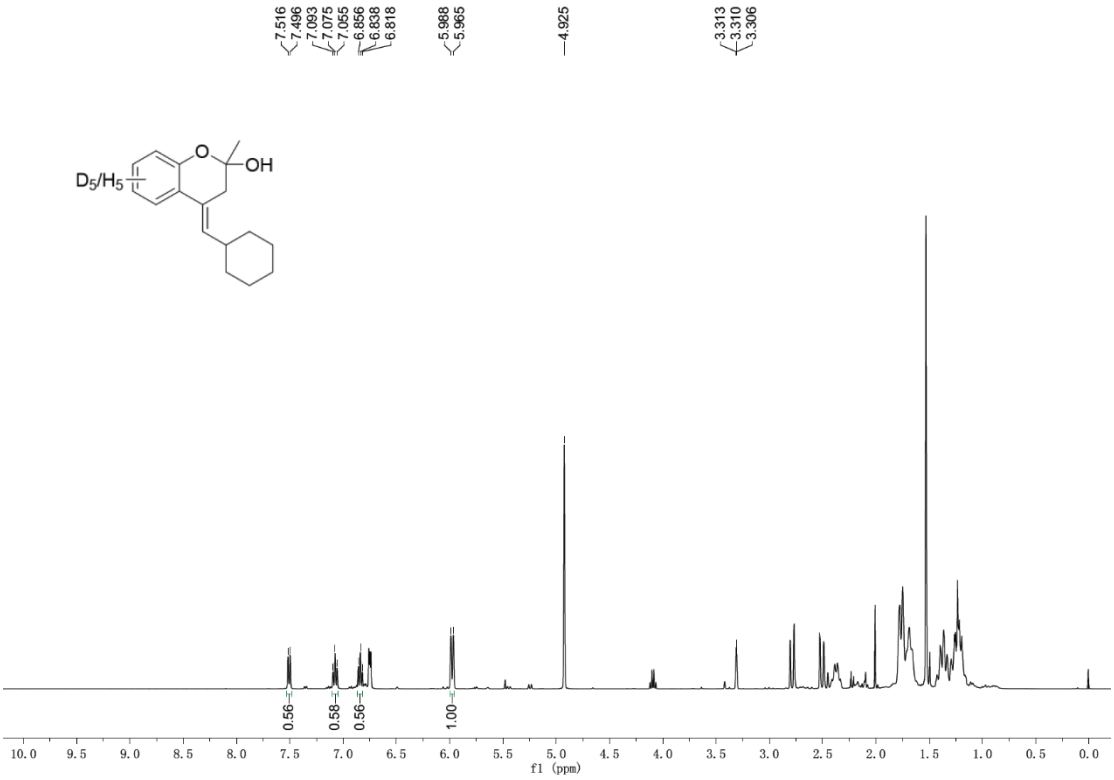
General procedure for estimation of the KIE:



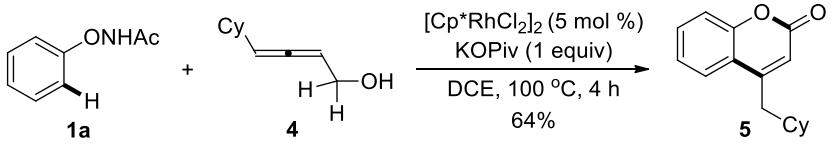
An equimolar mixture of **1a** (0.1 mmol, 1.0 equiv) and **1a-*d*$_5$** (0.1 mmol, 1.0 equiv) was allowed to react with **2a** (0.12 mmol, 1.2 equiv) in DCE (0.5 mL) in the presence of [Cp*RhCl$_2$]$_2$ (5 mol %) and KOPiv (0.1 mmol, 1.0 equiv). The reaction was stopped after 0.5 h, and the product was isolated in 31% (7.9 mg) isolated yield by preparative TLC and analyzed by ^{1}H-NMR spectroscopy. The doublet at δ: 7.51 (0.61H) were used for calculation and an average value of k_H/k_D = 1.6 was obtained.



Another two parallel KIE experiments were performed by treating 1 equiv of **1a** or 1 equiv of **1a**-d_5 with 1.2 equiv of **2a** separately under the standard conditions for 0.5 h. Afterwards, the two reactions were mixed and the solvent was removed under reduce pressure, the resulted mixture was purified by preparative TLC to afford the corresponding product **3aa** in 35% (9.1 mg) isolated yield. The doublet at δ: 7.51 (0.56H) were used for calculation and an average value of k_H/k_D = 1.3 was obtained.



Control experiment:

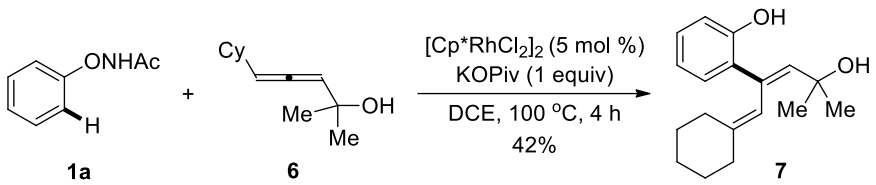


The mixture of *N*-phenoxyacetamide **1a** (0.2 mmol, 1.0 equiv), α-allenol **4** (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and KOPiv (0.2 mmol, 1.0 equiv) in DCE (1.0 mL) was stirred at 100 °C in an oil bath for 4 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC (Eluent: DCM/PE= 5/1, R_f = 0.4) to afford the desired product **5** in 64% (30.8 mg) isolated yield as yellow solid.

^{1}H NMR (400 MHz, CD_3OD): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.39-7.33 (m, 2H), 6.26 (s, 1H), 2.71 (d, *J* = 7.0 Hz, 2H), 1.79-1.71 (m, 4H), 1.70-1.63 (m, 2H), 1.27-1.19 (m, 3H), 1.12-1.03 (m, 2H).

^{13}C NMR (100 MHz, CD_3OD): δ 162.8, 157.6, 155.0, 133.1, 126.4, 125.7, 120.7, 118.1, 115.5, 40.6, 38.7, 34.4, 27.34, 27.25.

HRMS (ESI) *m*/*z*: [M+H]$^+$ Calcd for $C_{16}H_{19}O_2$: 243.1380; found: 243.1377.

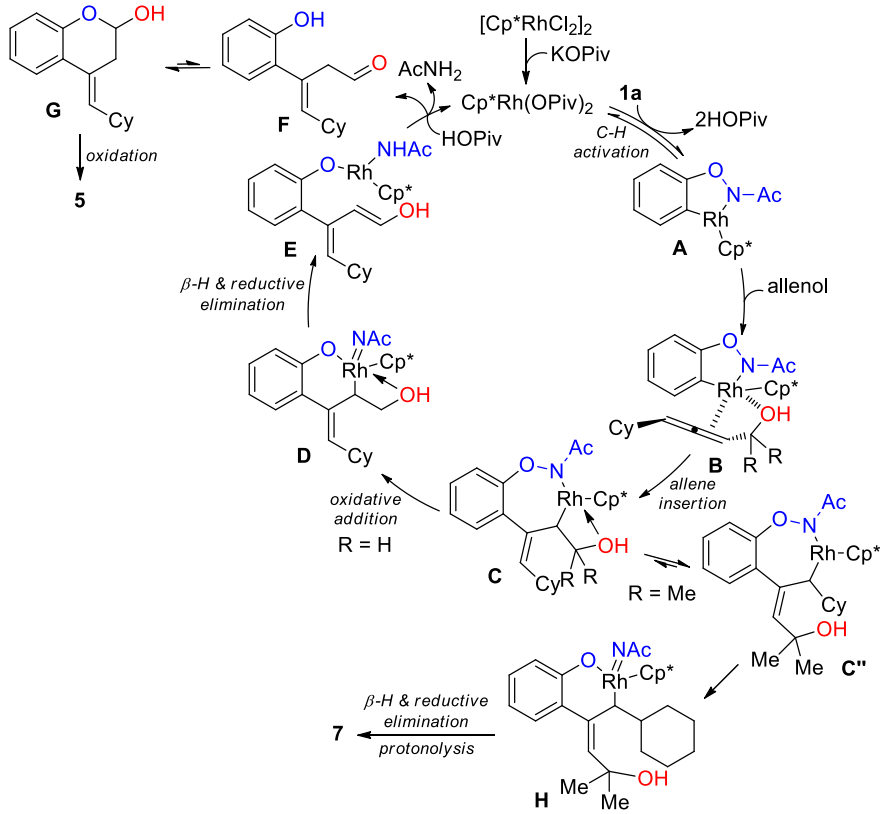


The mixture of *N*-phenoxyacetamide **1a** (0.2 mmol, 1.0 equiv), α-allenol **6** (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and KOPiv (0.2 mmol, 1.0 equiv) in DCE (1.0 mL) was stirred at 100 °C in an oil bath for 4 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC (Eluent: PE/EA= 5/1, R_f = 0.3) to afford the desired product **7** in 42% (23.0 mg) isolated yield as yellow liquid.

^{1}H NMR (400 MHz, CD_3OD): δ 7.10 (td, *J* = 7.6, 1.5 Hz, 1H), 6.94 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.82-6.76 (m, 2H), 5.74 (s, 1H), 5.72 (s, 1H), 2.11-2.02 (m, 4H), 1.57-1.51 (m, 4H), 1.42-1.37 (m, 2H), 1.12 (s, 6H).

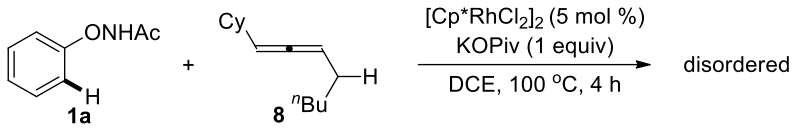
^{13}C NMR (100 MHz, CD_3OD): δ 154.9, 142.4, 140.0, 135.4, 131.5, 129.4, 129.1, 126.9, 120.5, 116.5, 72.0, 39.4, 30.1, 30.0, 29.1, 27.9.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{18}H_{23}O_2$: 271.1703; found: 271.1698.

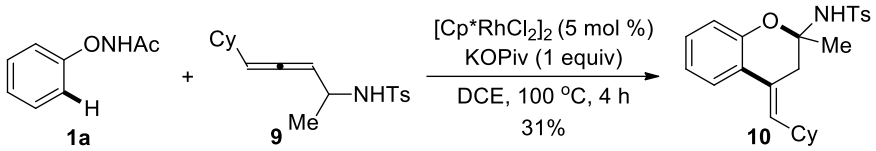


Scheme S1 Proposed catalytic cycle for the formation of compound **5** and **7**

Study on the coordination effect:



The mixture of *N*-phenoxyacetamide **1a** (0.2 mmol, 1.0 equiv), allene **8** (0.24 mmol, 1.2 equiv), [Cp*RhCl$_2$]$_2$ (5 mol %) and KOPiv (0.2 mmol, 1.0 equiv) in DCE (1.0 mL) was stirred at 100 °C in an oil bath for 4 h without exclusion of air or moisture. Afterwards, the reaction was monitored by TLC and resulted in inseparable complexes.



The mixture of *N*-phenoxyacetamide **1a** (0.2 mmol, 1.0 equiv), NHTs-tethered allene **9** (0.24 mmol, 1.2 equiv), [Cp*RhCl$_2$]$_2$ (5 mol %) and KOPiv (0.2 mmol, 1.0 equiv) in DCE (1.0 mL) was stirred at 100 °C in an oil bath for 4 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure, and the resulted mixture was purified by preparative TLC (Eluent: DCM/PE = 3/1, R_f = 0.3) to afford the desired product **10** in 31% (25.5 mg) isolated yield as yellow solid.

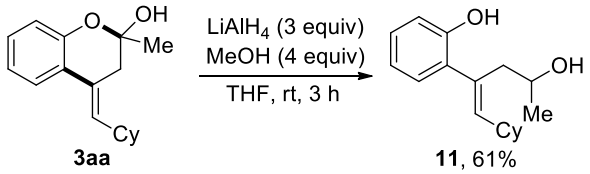
^{1}H NMR (400 MHz, CDCl$_3$): δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.88-6.78 (m, 2H), 6.11 (d, *J* = 9.1 Hz, 1H), 5.90 (d, *J* = 8.0 Hz, 1H), 5.35 (s, 1H), 2.93 (d, *J* = 14.4 Hz, 1H), 2.38 (s, 3H), 2.36-2.27 (m, 2H), 1.87 (s, 3H), 1.79-1.59 (m, 5H), 1.35-1.30 (m, 2H), 1.28-1.14 (m, 3H).

^{13}C NMR (100 MHz, CDCl$_3$): δ 150.1, 143.2, 138.5, 134.3, 129.3, 128.6, 127.3, 123.1, 122.9, 121.1, 120.9, 117.5, 85.1, 37.2, 36.8, 33.9, 33.2, 26.3, 25.9, 21.6.

HRMS (ESI) *m*/*z*: [M+H]$^+$ Calcd for $C_{24}H_{30}NO_3S$: 412.1941; found: 412.1941.

IV. Synthetic Applications

Derivatizations of product 3aa:



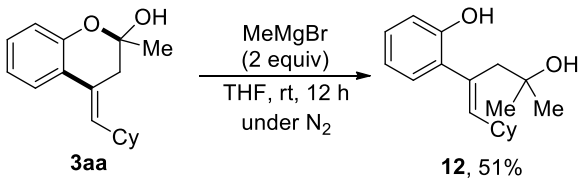
The mixture of chroman-2-ol **3aa** (0.2 mmol, 1.0 equiv) and $LiAlH_4$ (0.6 mmol, 3.0

equiv) in THF (1.0 mL) was added methanol (4.0 equiv), the resulted mixture was stirred at room temperature for 4 h without exclusion of air or moisture. Afterwards, the reaction was quenched by methanol, diluted with EtOAc and filtered through a short silica gel column to remove the metal residues. Then, the reaction mixture was concentrated and purified by preparative TLC (eluent: PE/EA = 5/1) to give the desired (*E*)-2-(1-cyclohexyl-4-hydroxypent-1-en-2-yl) phenol **11** in 61% isolated yield (31.7 mg) as light yellow solid.

^{1}H NMR (400 MHz, CD_3OD): δ 7.04 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.78-6.72 (m, 2H), 5.26 (d, *J* = 9.5 Hz, 1H), 3.65-3.59 (m, 1H), 2.83-2.76 (m, 1H), 2.56-2.50 (m, 1H), 2.46-2.38 (m, 1H), 1.78-1.66 (m, 5H), 1.40-1.29 (m, 3H), 1.16-1.11 (m, 2H), 1.08 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 155.4, 139.4, 135.5, 132.5, 131.5, 128.8, 120.5, 116.2, 67.6, 41.4, 38.5, 34.44, 34.36, 27.2, 27.1, 23.1.

HRMS (ESI) *m/z*: [M-H]$^+$ Calcd for $C_{17}H_{23}O_2$: 259.1703; found: 259.1706.

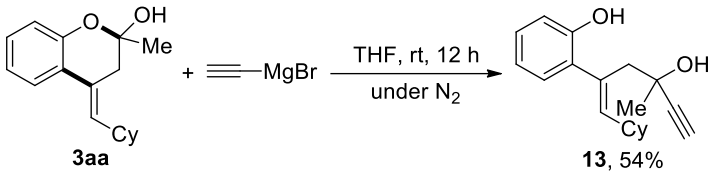


The mixture of **3aa** (0.2 mmol, 1.0 equiv) and methylmagnesium bromide (0.4 mmol, 2.0 equiv) in THF (1.0 mL) was stirred at room temperature for 12 h under an atmosphere of nitrogen. Afterwards, the reaction was quenched by saturated ammonium chloride solution and diluted with EtOAc. Then, the reaction mixture was concentrated and purified by preparative TLC (eluent: PE/EA = 5/1) to give the desired (*E*)-2-(1-cyclohexyl-4-hydroxy-4-methylpent-1-en-2-yl) phenol **12** in 51% isolated yield (28.0 mg) as light yellow solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.10 (s, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.94-6.91 (m, 1H), 6.73-6.67 (m, 2H), 5.15 (d, *J* = 9.7 Hz, 1H), 4.09 (s, 1H), 2.70 (s, 2H), 2.44-2.34 (m, 1H), 1.71-1.63 (m, 5H), 1.30-1.23 (m, 2H), 1.13-1.04 (m, 3H), 0.87 (s, 6H).

^{13}C NMR (100 MHz, CD_3OD): δ 155.2, 140.9, 135.2, 134.0, 131.5, 128.6, 120.6, 116.4, 72.5, 44.5, 38.8, 34.2, 29.6, 27.2, 27.1.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{18}H_{25}O_2$: 273.1860; found: 273.1867.



The mixture of chroman-2-ol **3a** (0.2 mmol, 1.0 equiv) and ethynylmagnesium bromide (0.4 mmol, 2.0 equiv) in THF (1.0 mL) was stirred at room temperature for 12 h under an atmosphere of nitrogen. Afterwards, the reaction was quenched by saturated ammonium chloride solution and diluted with EtOAc. Then, the reaction mixture was concentrated and purified by preparative TLC (eluent: PE/EA = 5/1) to give the desired (*E*)-2-(1-cyclohexyl-4-hydroxy-4-methylhex-1-en-5-yn-2-yl) phenol **13** in 54% isolated yield (30.8 mg) as light yellow solid.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.11 (s, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.95-6.92 (m, 1H), 6.72-6.66 (m, 2H), 5.21 (d, *J* = 9.7 Hz, 1H), 5.15 (s, 1H), 2.99 (s, 1H), 2.94 (d, *J* = 14.6 Hz, 1H), 2.86 (d, *J* = 14.5 Hz, 1H), 2.46-2.41 (m, 1H), 1.73-1.60 (m, 5H), 1.31-1.22 (m, 3H), 1.20-1.10 (m, 2H), 1.04 (s, 3H).

^{13}C NMR (100 MHz, CD$_3$OD): δ 155.2, 141.9, 134.0, 133.4, 131.9, 128.7, 120.4, 116.1, 89.0, 72.3, 68.8, 44.3, 38.6, 34.3, 34.2, 30.1, 27.2, 27.1, 27.0.

HRMS (ESI) *m*/*z*: [M-H]$^+$ Calcd for $C_{19}H_{23}O_2$: 283.1703; found: 283.1709.

V. X-Ray Crystallographic Data

Experimental: The sample was dissolved in appropriate amount of EtOAc followed by the addition of PE to furnish a saturated solution. Afterwards, the mixture was allowed to stand at -20 ºC to form the crystals. A suitable crystal was selected and measured on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 149.99(10) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The crystallographic data have already been deposited at the Cambridge Crystallographic Data Centre (CCDC numbers: 2084815), which can be acquired from

www.ccdc.cam.ac.uk/data_request/cif.

The ellipsoid contour percent probability level is 50% for the image of the structure.

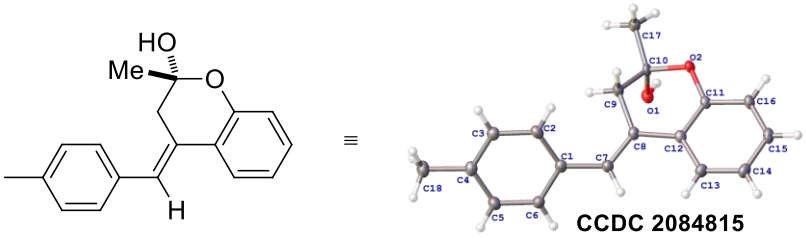


Table S2. Crystal data and structure refinement for **3ai**

Identification code	127-3
Empirical formula	$C_{18}H_{18}O_2$
Formula weight	266.32
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.3313(17)
b/Å	8.8068(15)
c/Å	10.2625(15)
α/°	77.537(14)
β/°	72.055(16)
γ/°	75.300(16)
Volume/Å^3	685.1(2)
Z	2
ρ_{calc}g/cm^3	1.291
μ/mm^{-1}	0.083
F(000)	284.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/ °	4.22 to 49.994
Index ranges	-7 ≤ h ≤ 9, -10 ≤ k ≤ 10, -9 ≤ l ≤ 12
Reflections collected	4266
Independent reflections	2399 [R_{int} = 0.0788, R_{sigma} = 0.1001]
Data/restraints/parameters	2399/0/184
Goodness-of-fit on F^2	0.998
Final R indexes [I>=2σ (I)]	R_1 = 0.0832, wR_2 = 0.2123
Final R indexes [all data]	R_1 = 0.1104, wR_2 = 0.2471
Largest diff. peak/hole / e Å^{-3}	0.41/-0.43

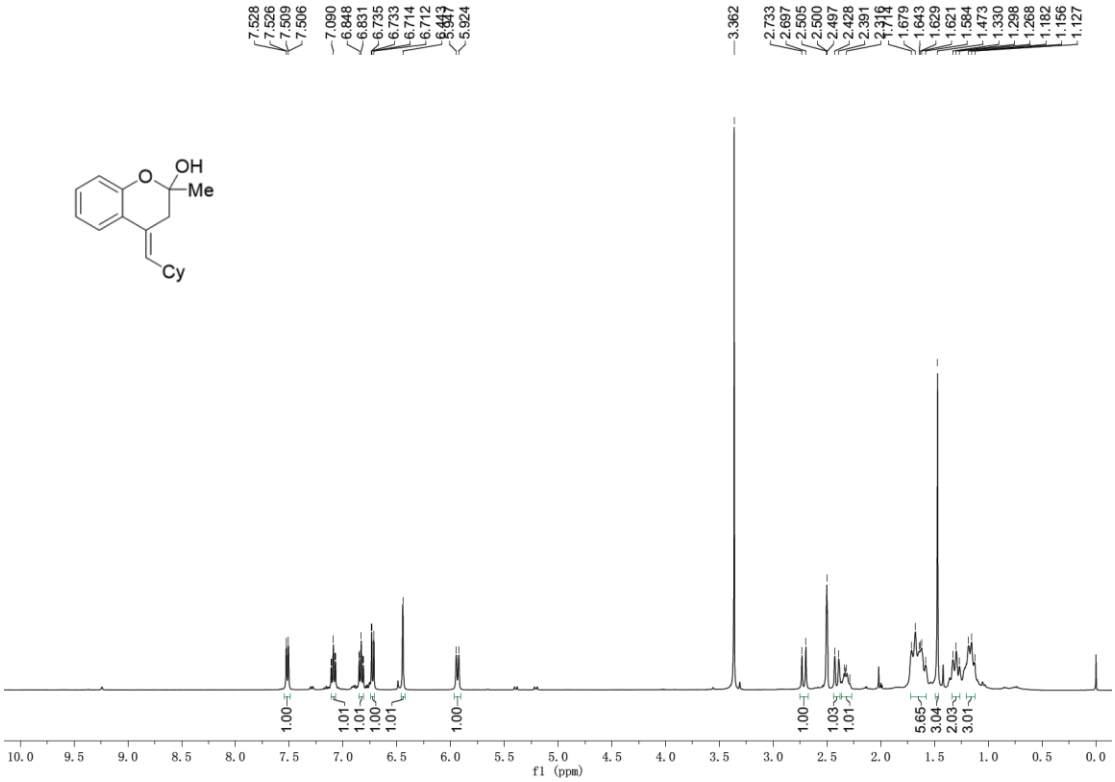
VI. References

[S1] (a) H. M. Petrassi, K. B. Sharpless and J. W. Kelly, *Org. Lett*., 2001, **3**, 139; (b) N. Takeda, O. Miyata and T. Naito, *Eur. J. Org. Chem*., 2007, 1491; (c) D. Tang, Y. Gai, A. Polemeropoulos, Z. Chen and Z. Wang, *Bioorg. Med. Chem. Lett*., 2008, **18**, 5078; (d) G. Liu, Y. Shen, Z. Zhou and X. Lu, *Angew. Chem., Int. Ed.,* 2013, **52**, 6033.

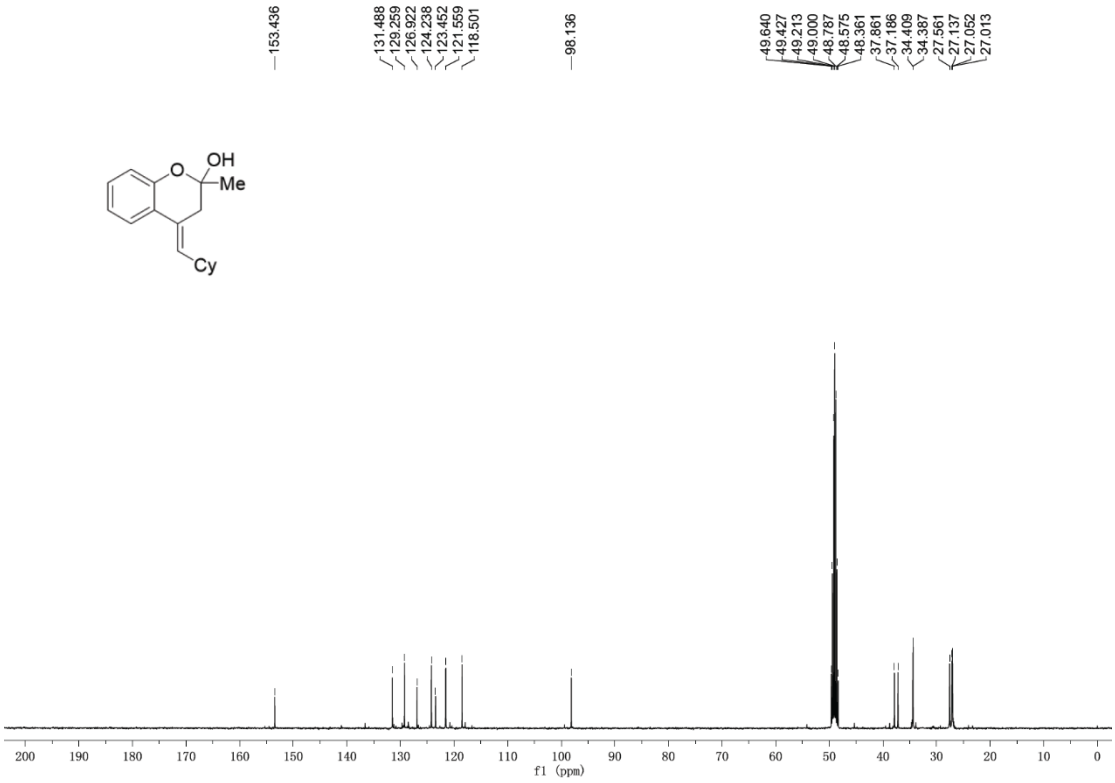
[S2] (a) J. Ye, S. Li, B. Chen, W. Fan, J. Kuang, J. Liu, Y. Liu, B. Miao, B. Wan, Y. Wang, X. Xie, Q. Yu, W. Yuan and S. Ma, *Org. Lett*., 2012, **14**, 1346; (b) J. Kuang, H. Luo and S. Ma, *Adv. Synth. Catal*., 2012, **354**, 933.

VII. Copies of ^{1}H and ^{13}C NMR Spectra

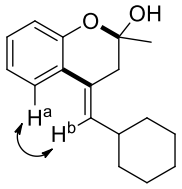
3aa-^{1}H NMR (400 MHz, DMSO-d_6)

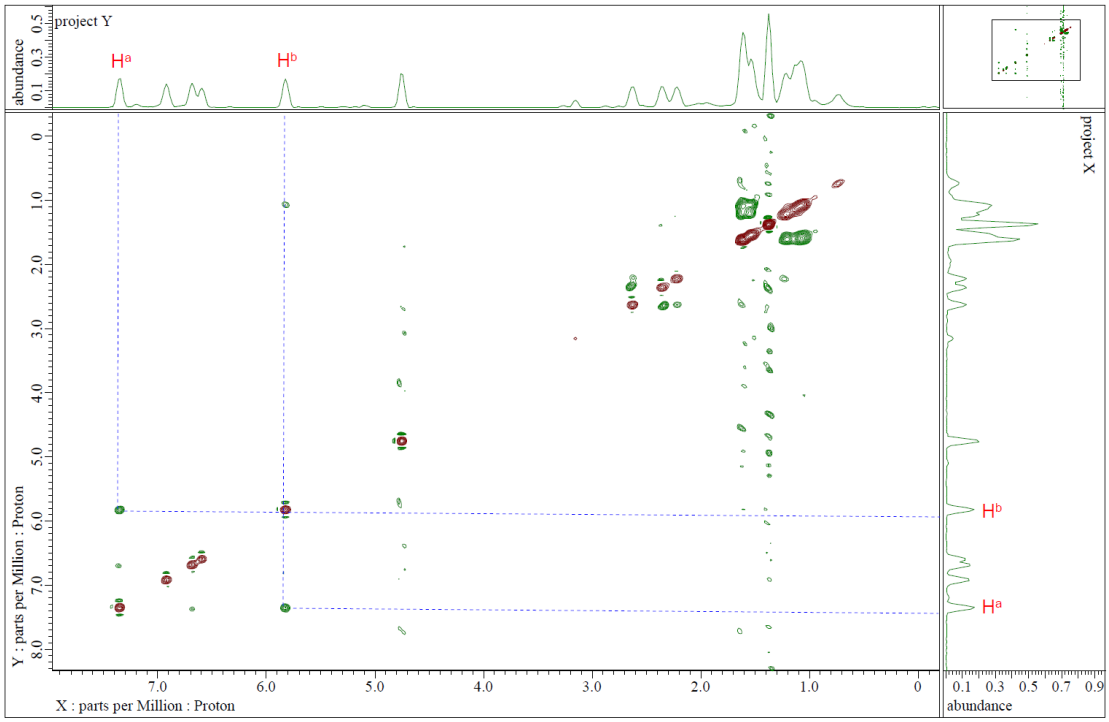


3aa-^{13}C NMR (100 MHz, CD_3OD)

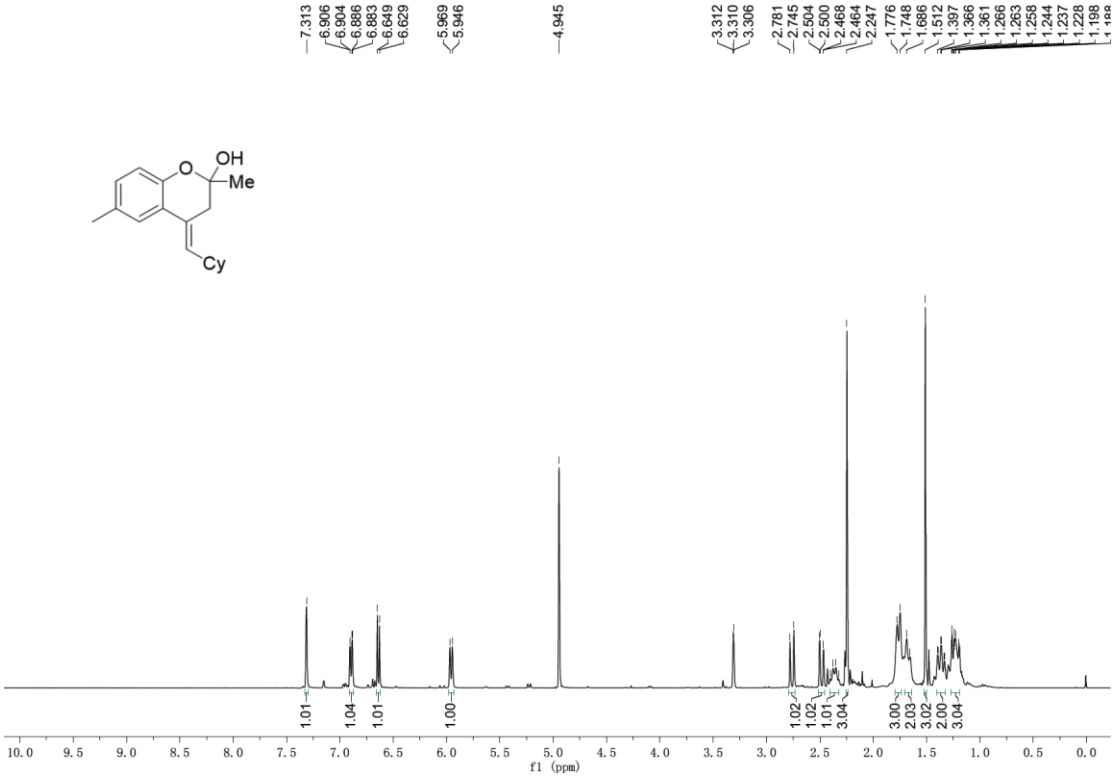


^{1}H-^{1}H NOESY spectrum of 3aa:

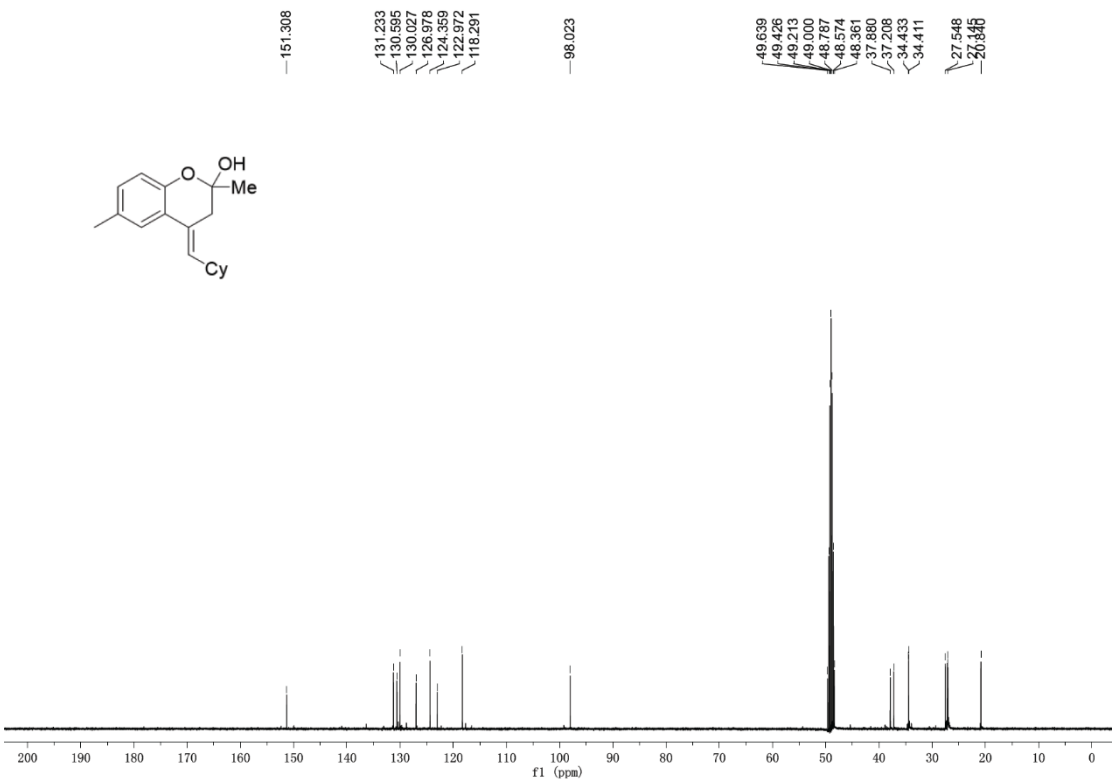




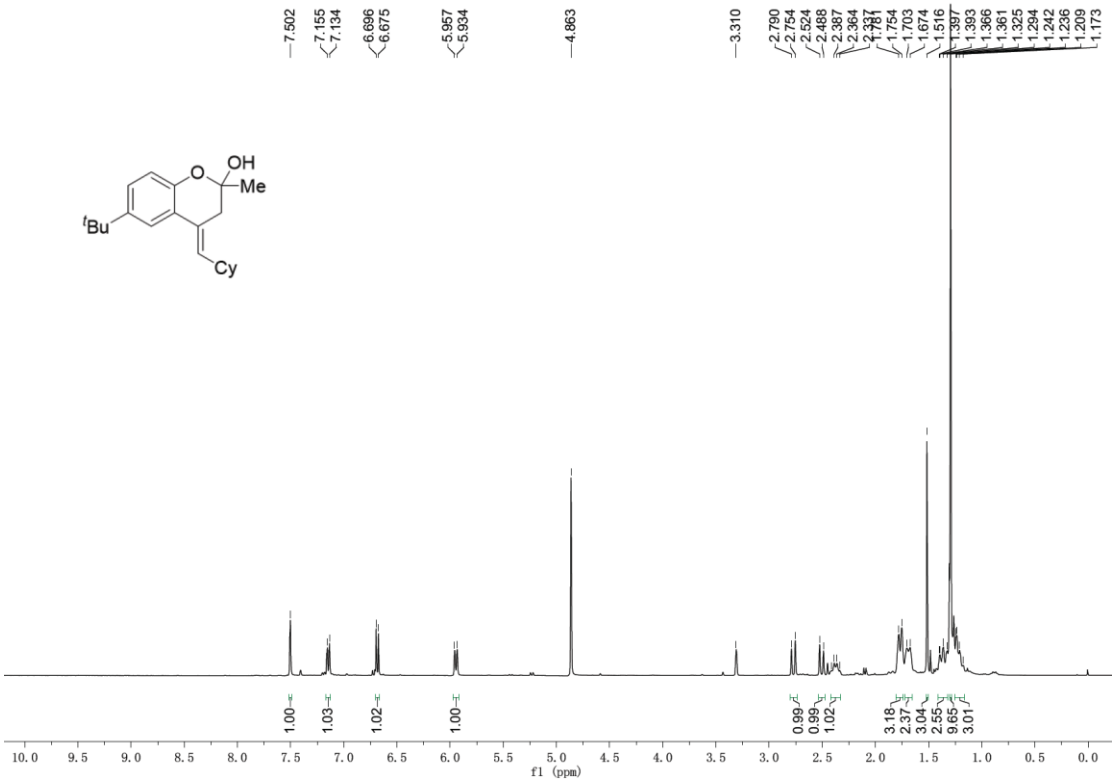
3ba-^{1}H NMR (400 MHz, CD_3OD)



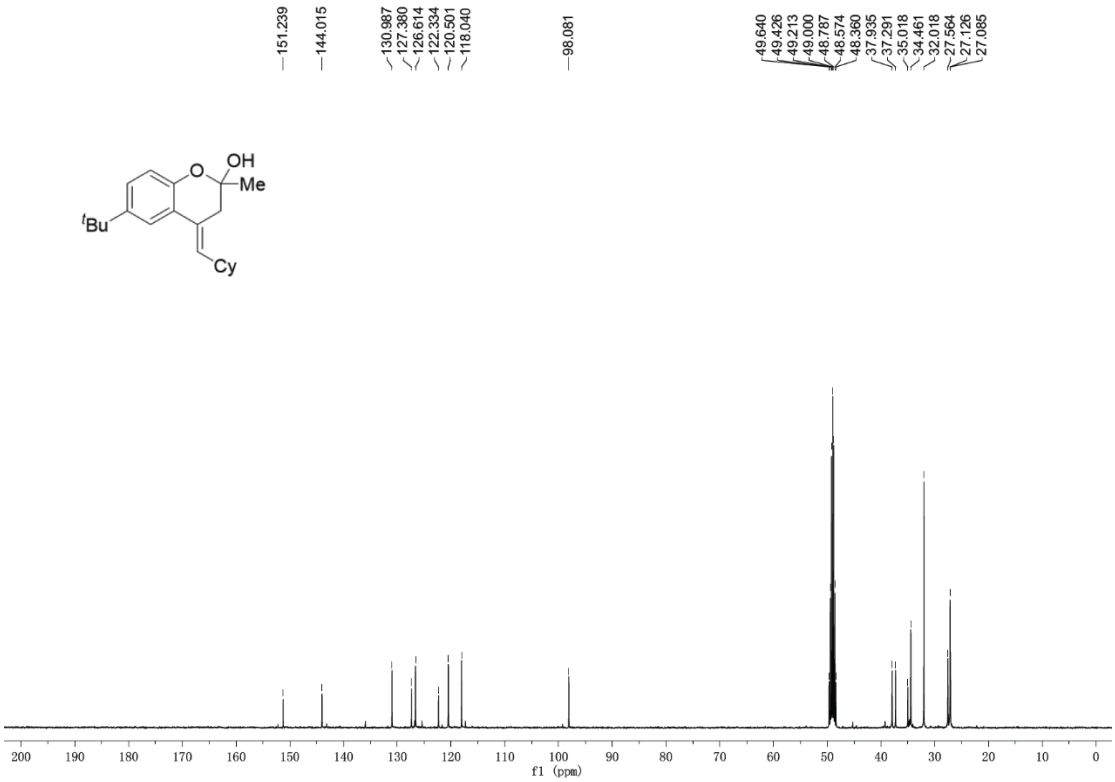
3ba-^{13}C NMR (100 MHz, CD_3OD)



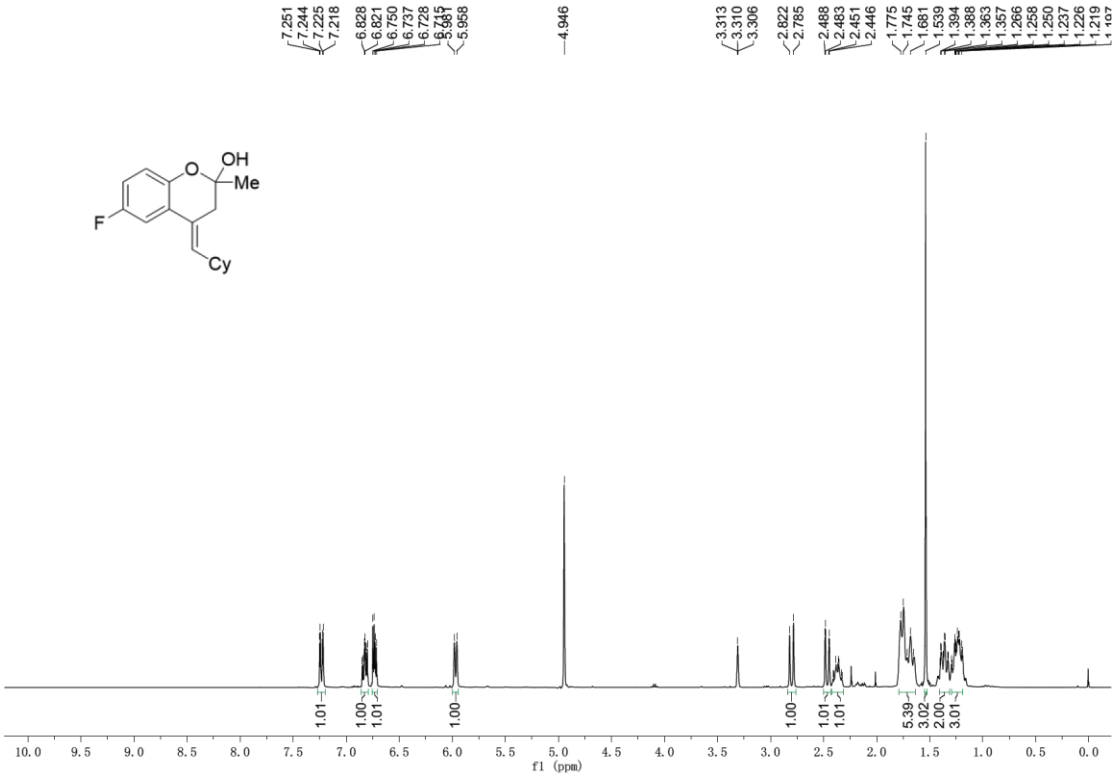
3ca-^{1}H NMR (400 MHz, CD_3OD)



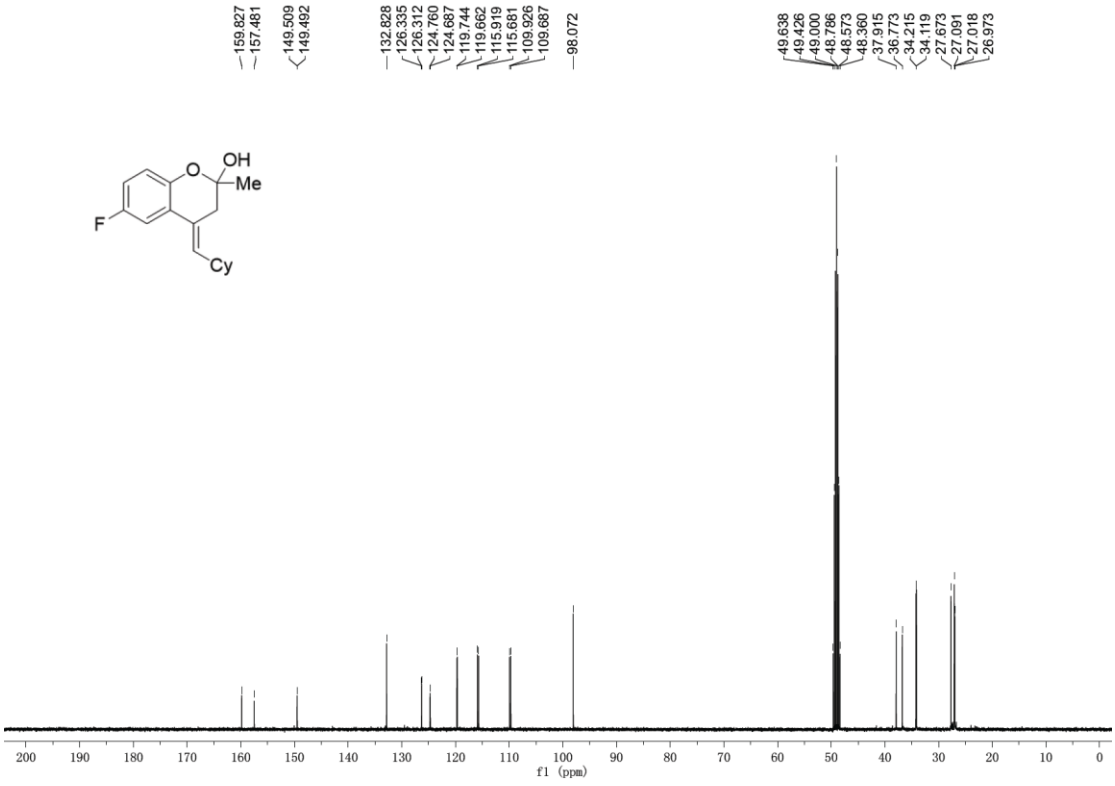
3ca-^{13}C NMR (100 MHz, CD_3OD)



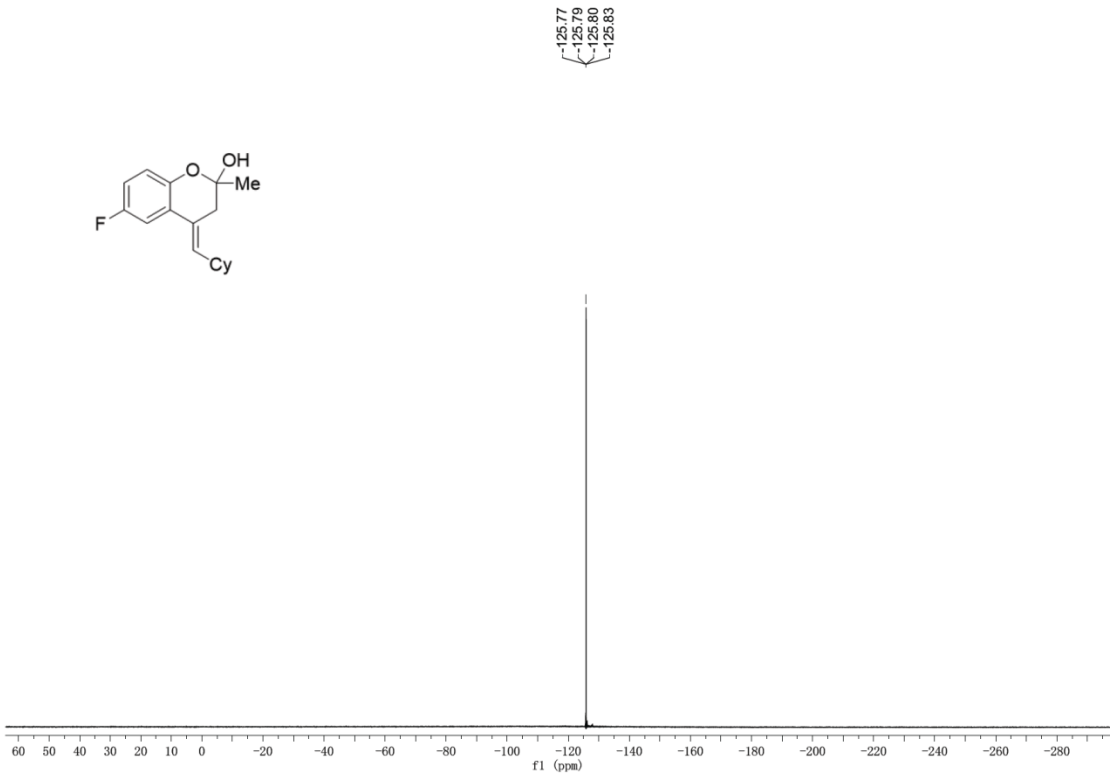
3da-^{1}H NMR (400 MHz, CD_3OD)



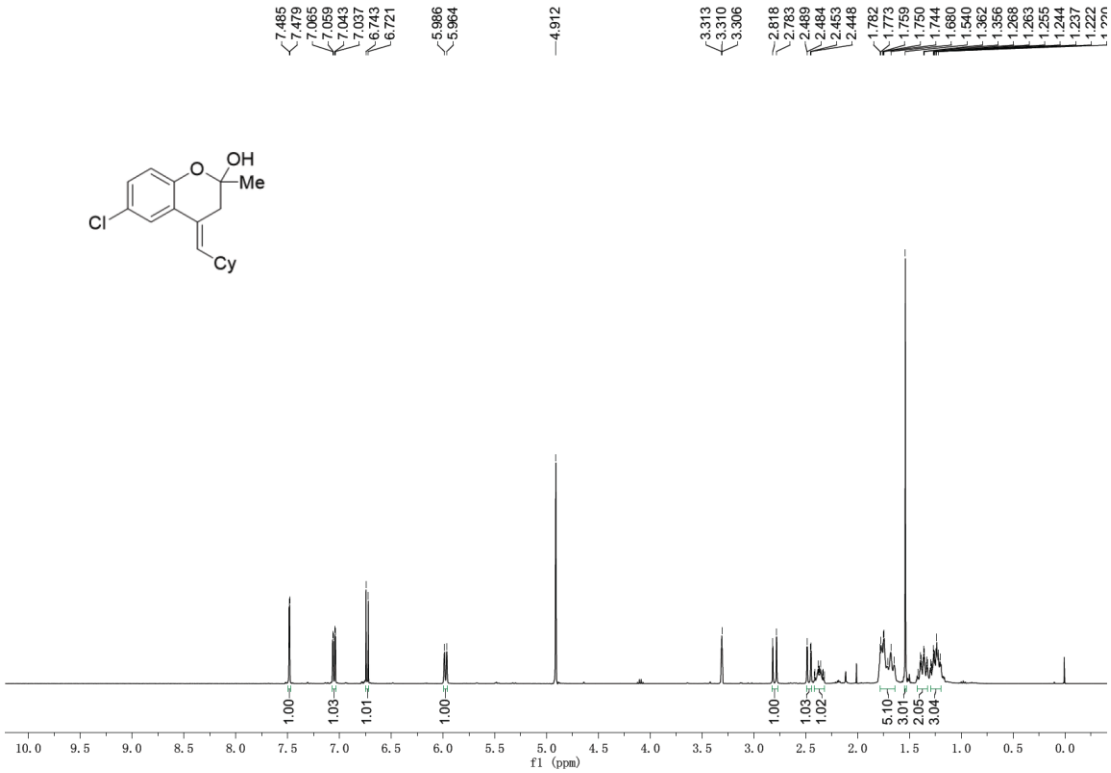
3da-^{13}C NMR (100 MHz, CD_3OD)



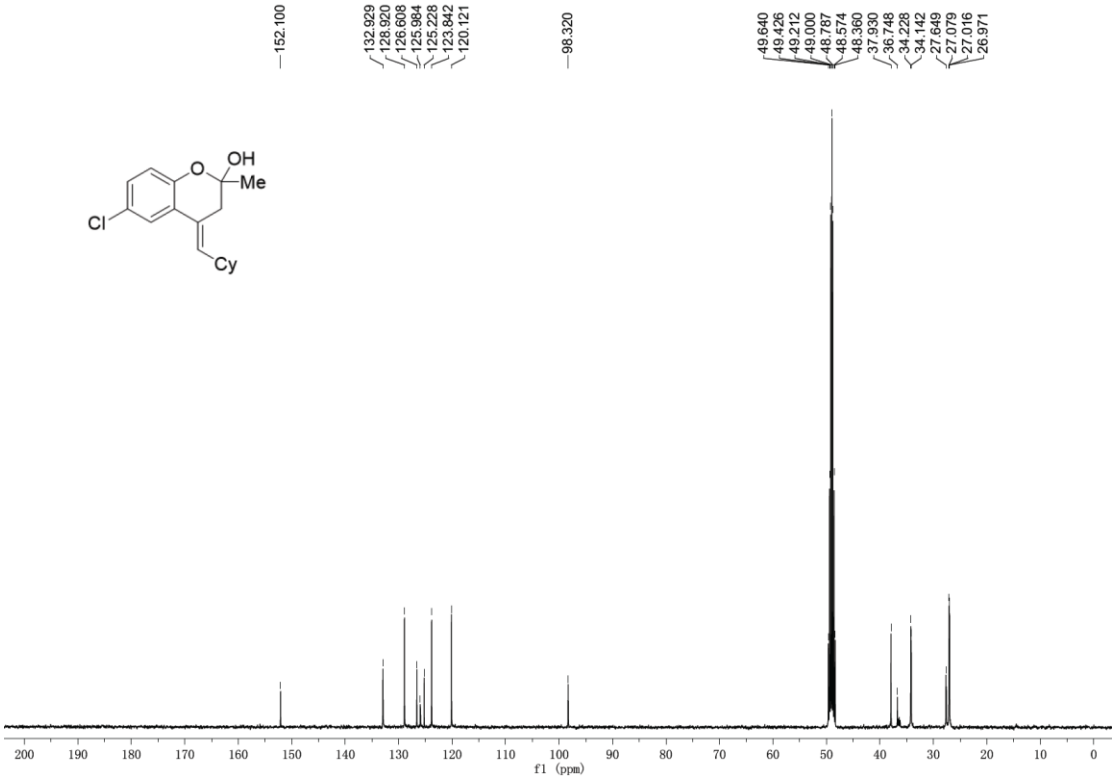
3da-^{19}F NMR (376 MHz, CD_3OD)



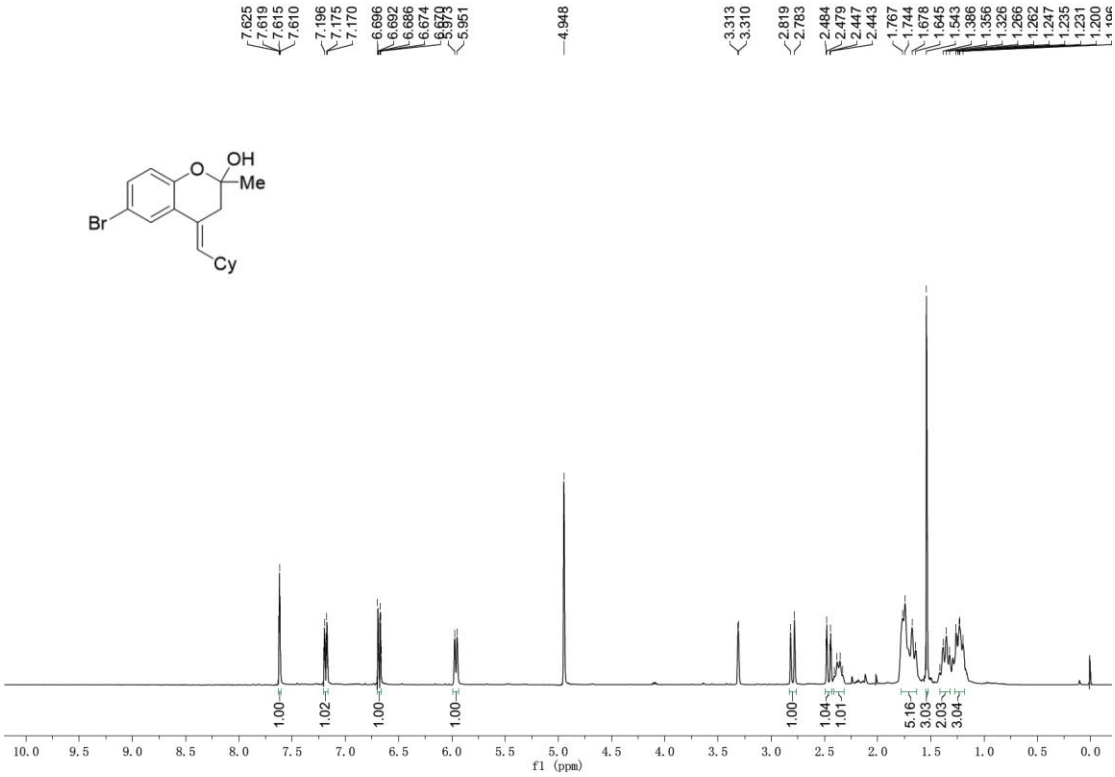
3ea-^{1}H NMR (400 MHz, CD_3OD)



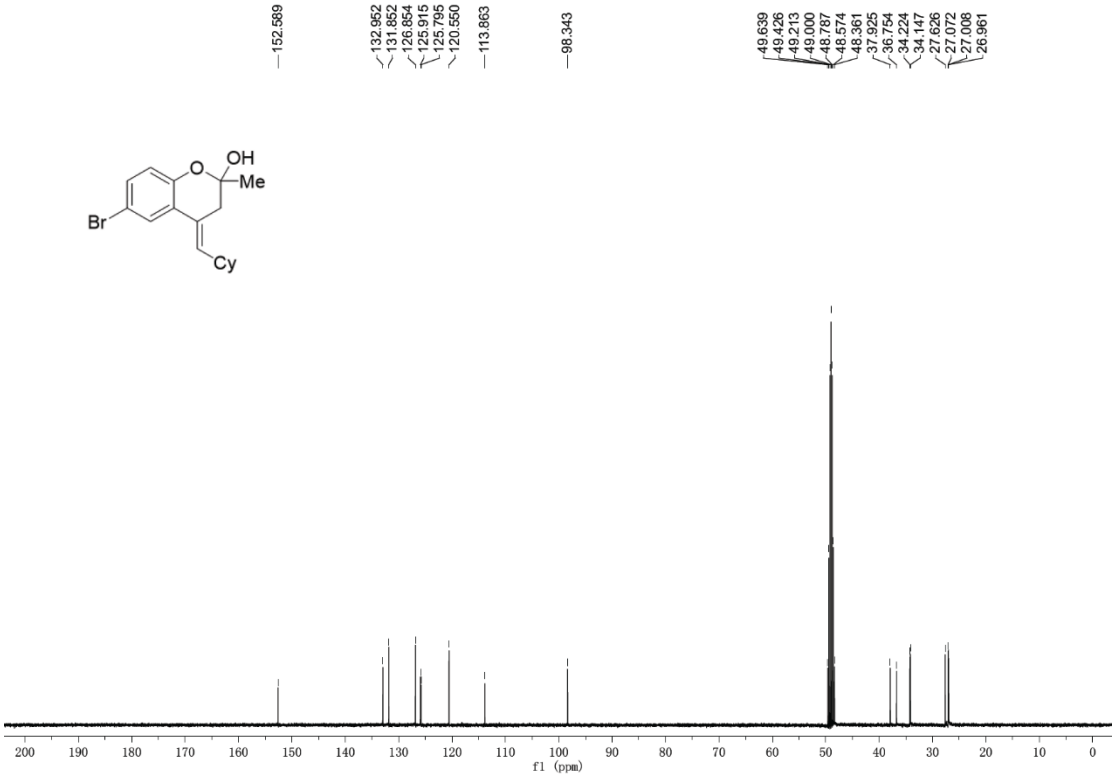
3ea-^{13}C NMR (100 MHz, CD_3OD)



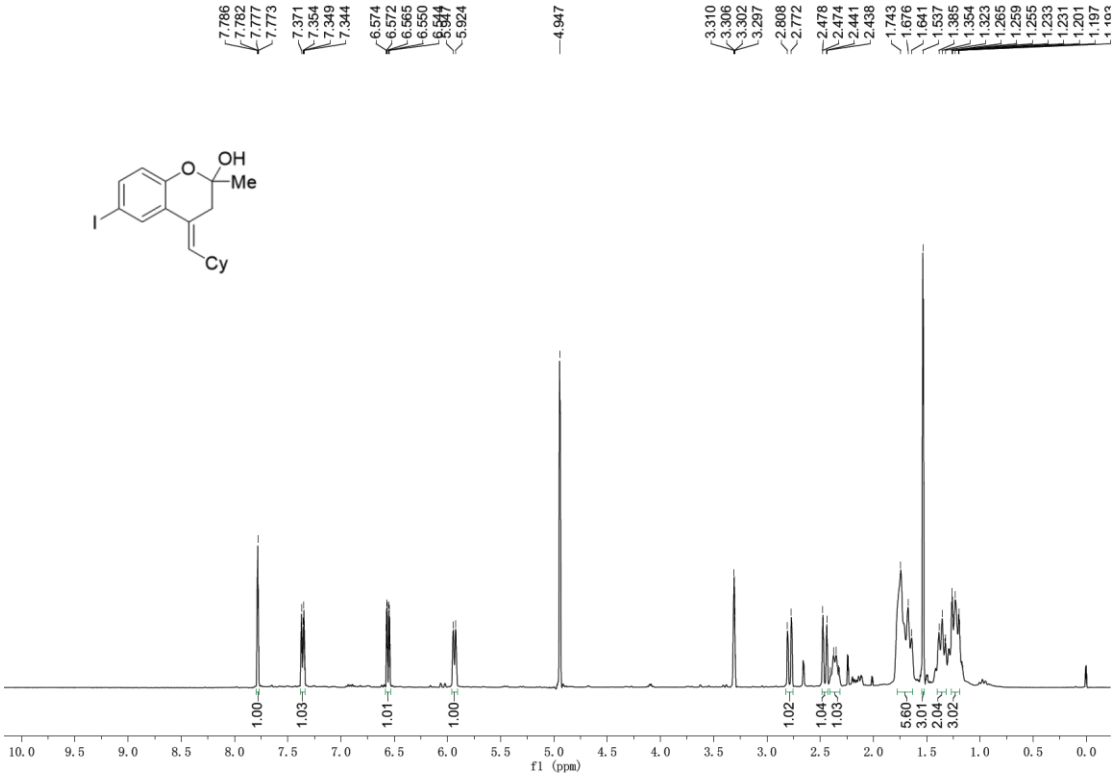
3fa-[1]H NMR (400 MHz, CD_3OD)



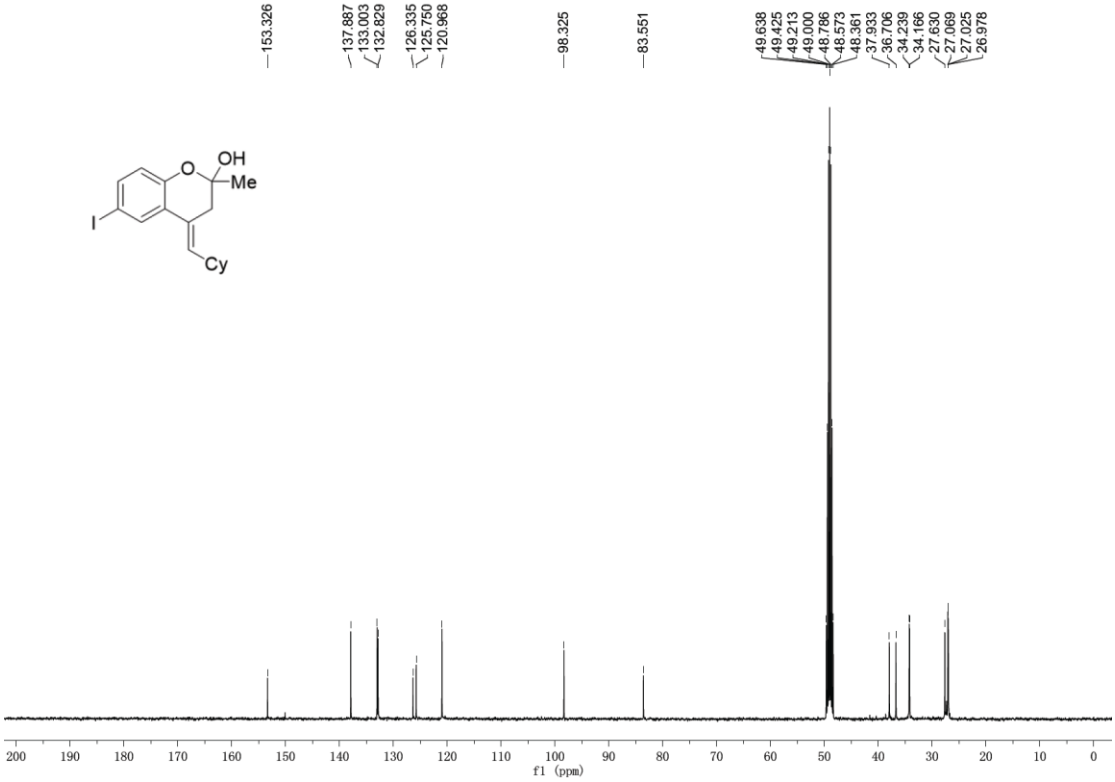
3fa-[13]C NMR (100 MHz, CD_3OD)



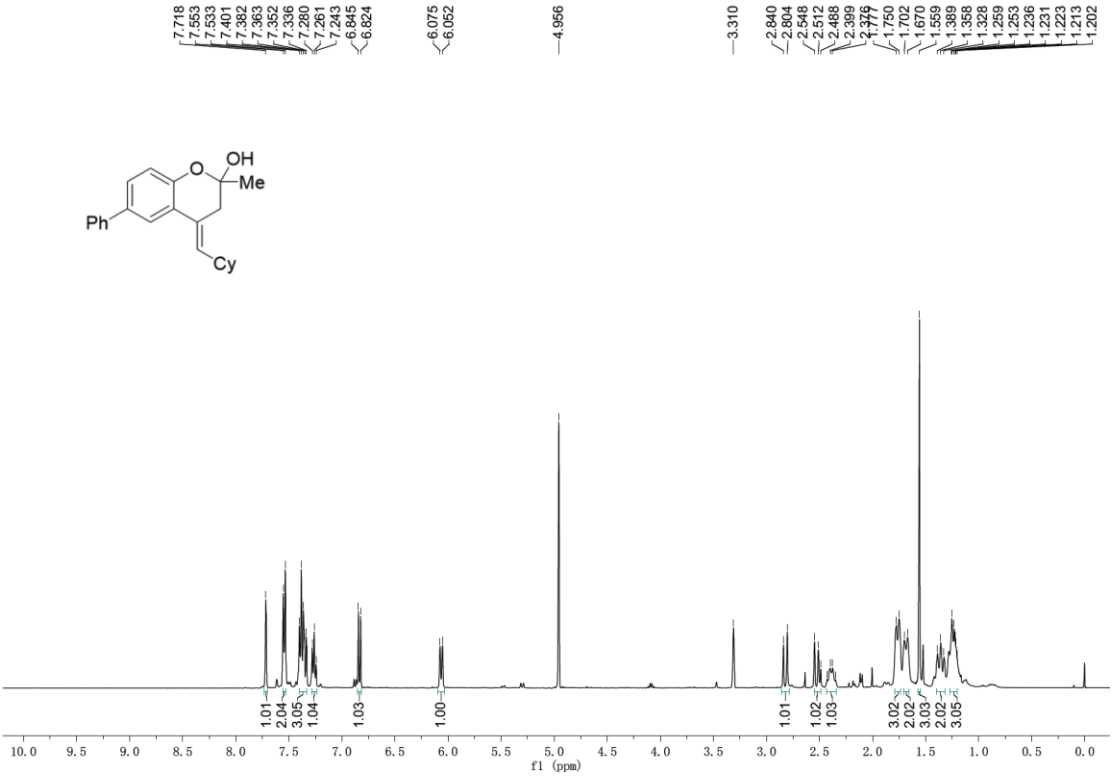
3ga-^{1}H NMR (400 MHz, CD_3OD)



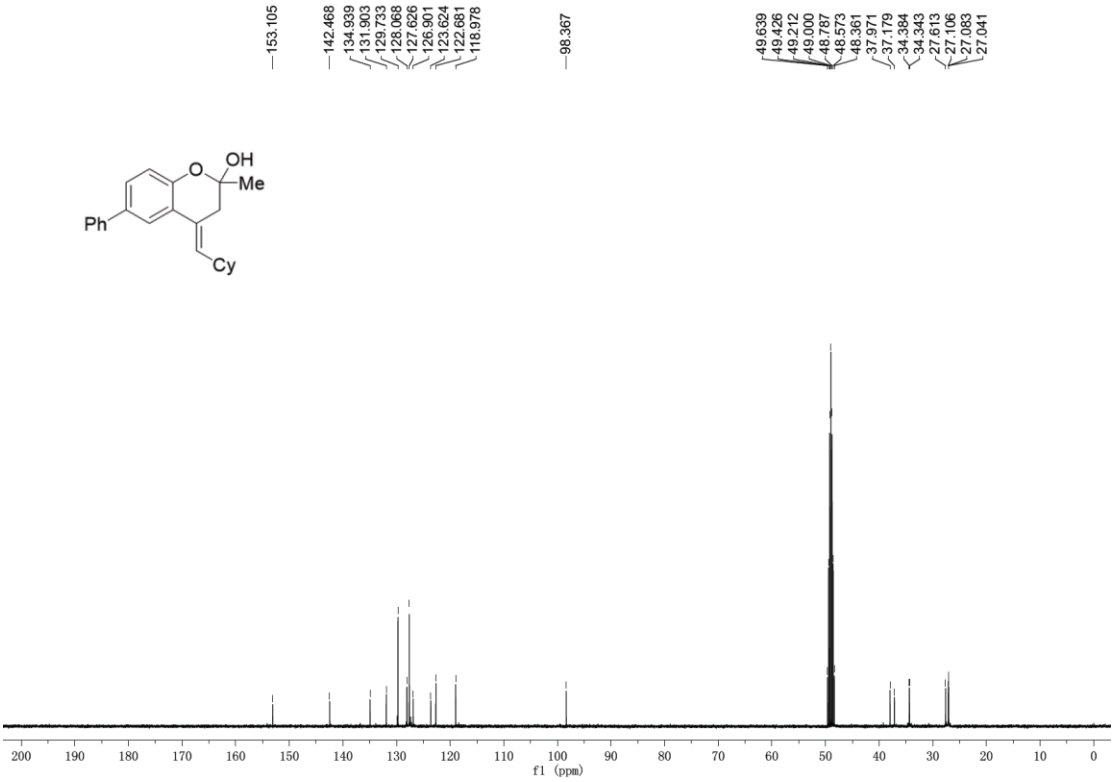
3ga-^{13}C NMR (100 MHz, CD_3OD)



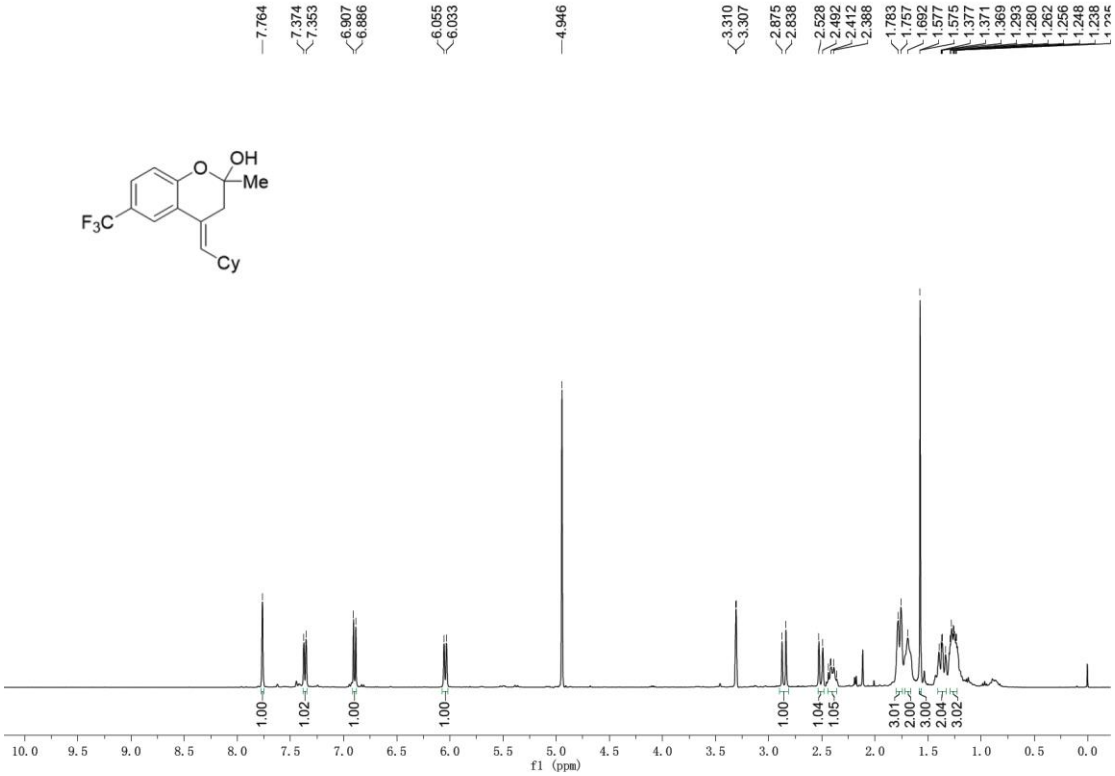
3ha-^{1}H NMR (400 MHz, CD_3OD)



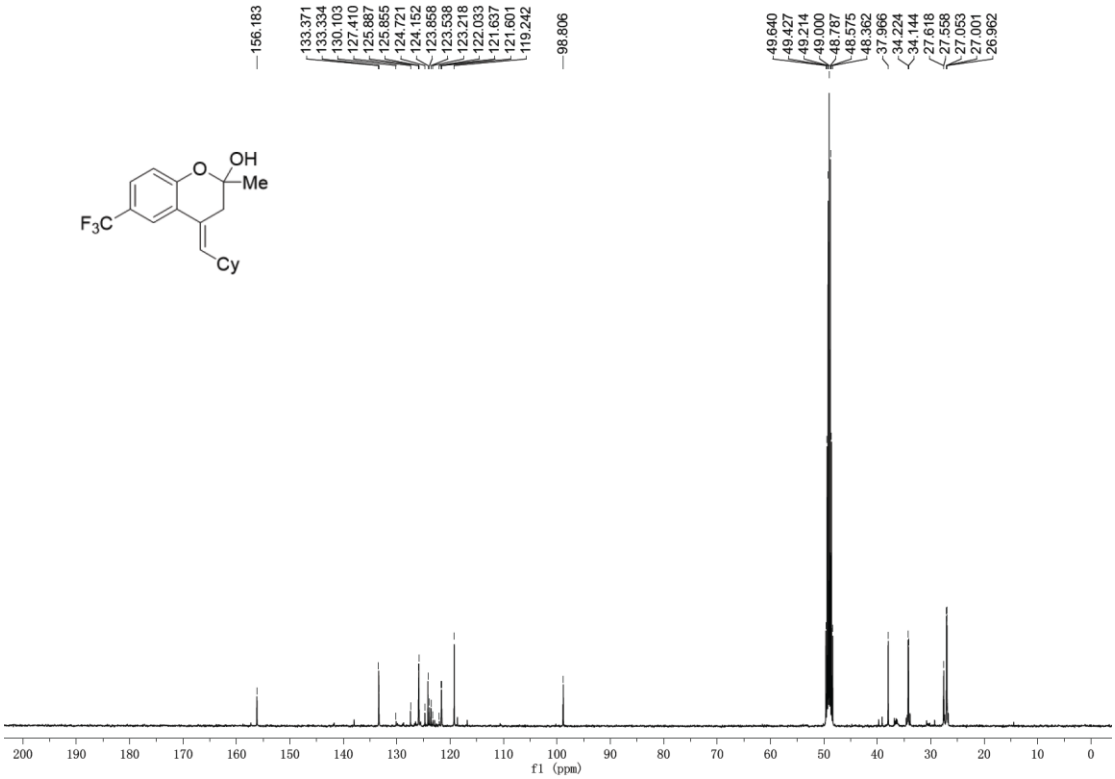
3ha-^{13}C NMR (100 MHz, CD_3OD)



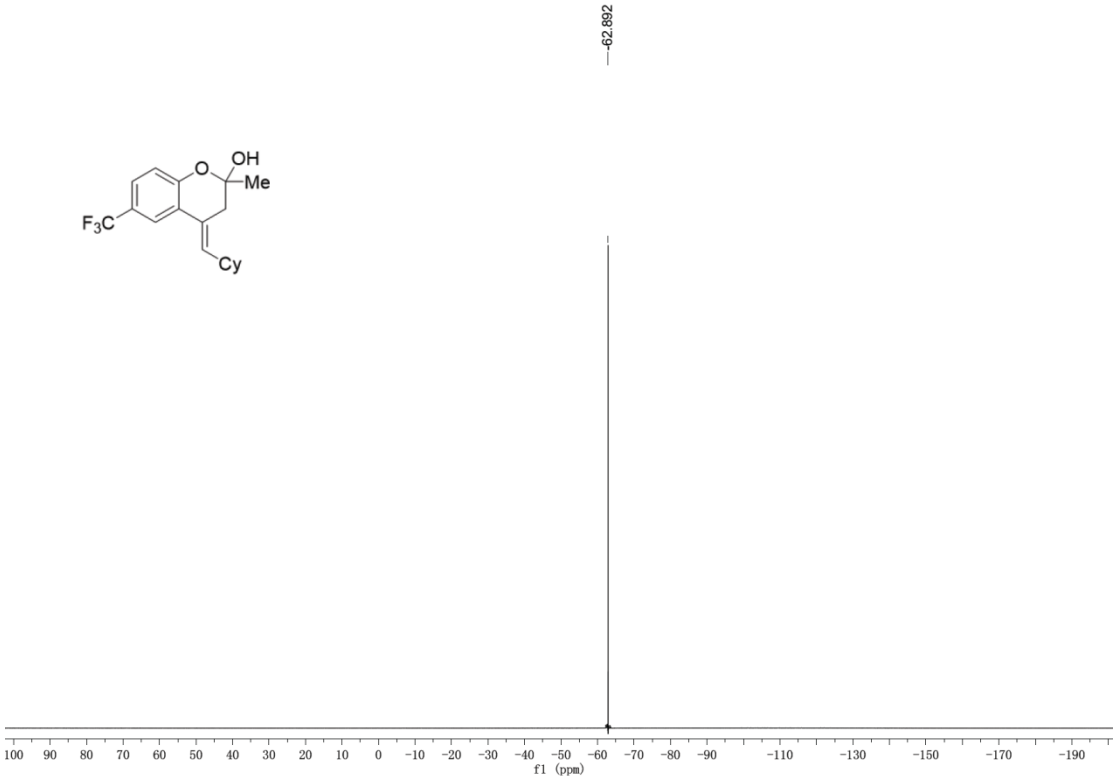
3ia-^{1}H NMR (400 MHz, CD_3OD)



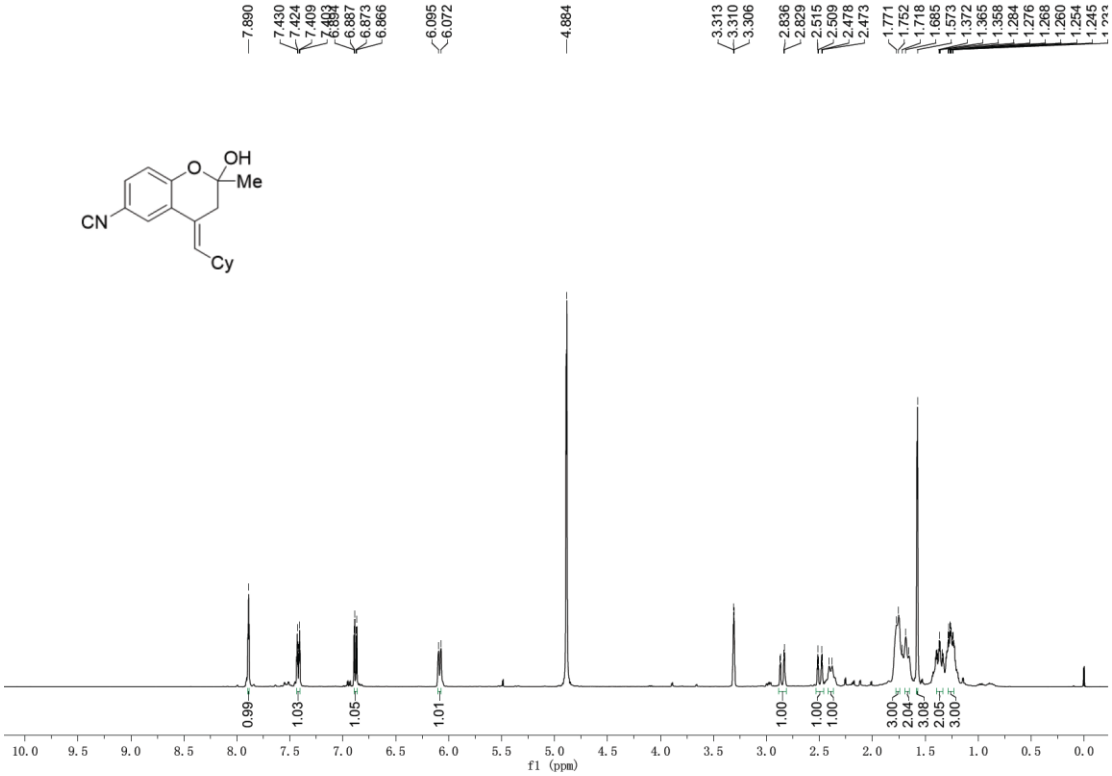
3ia-^{13}C NMR (100 MHz, CD_3OD)



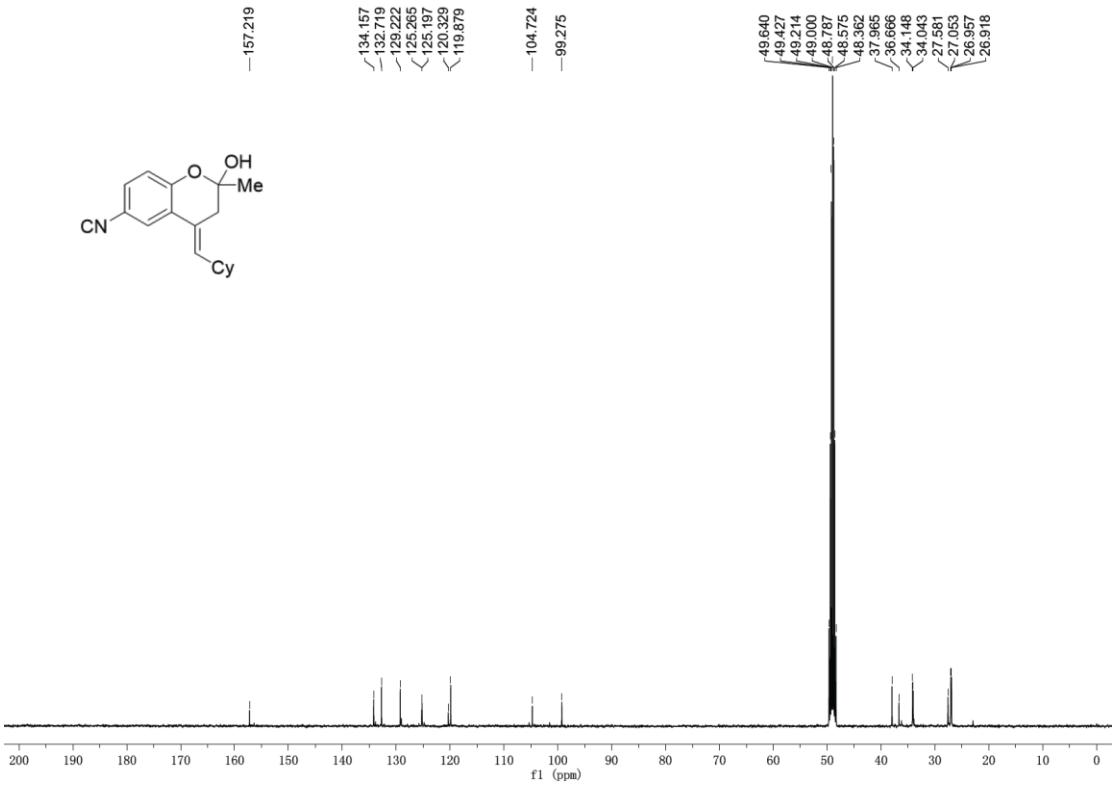
3ia-^{19}F NMR (376 MHz, CD_3OD)



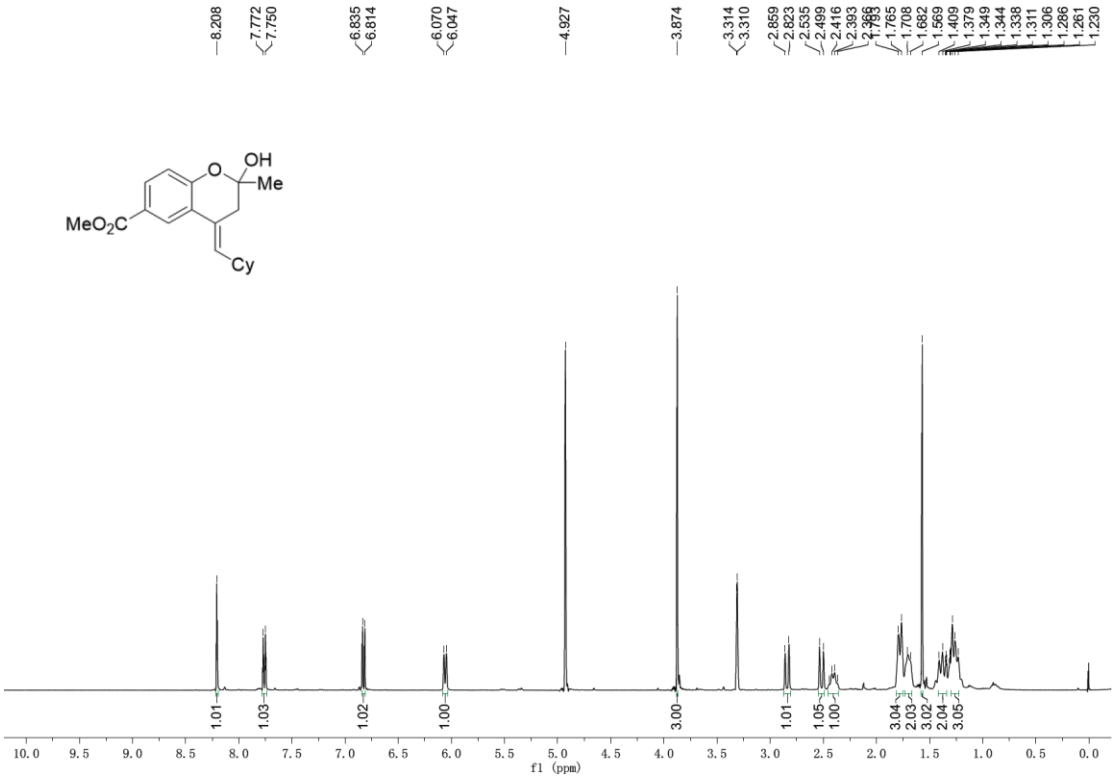
3ja-^{1}H NMR (400 MHz, CD_3OD)



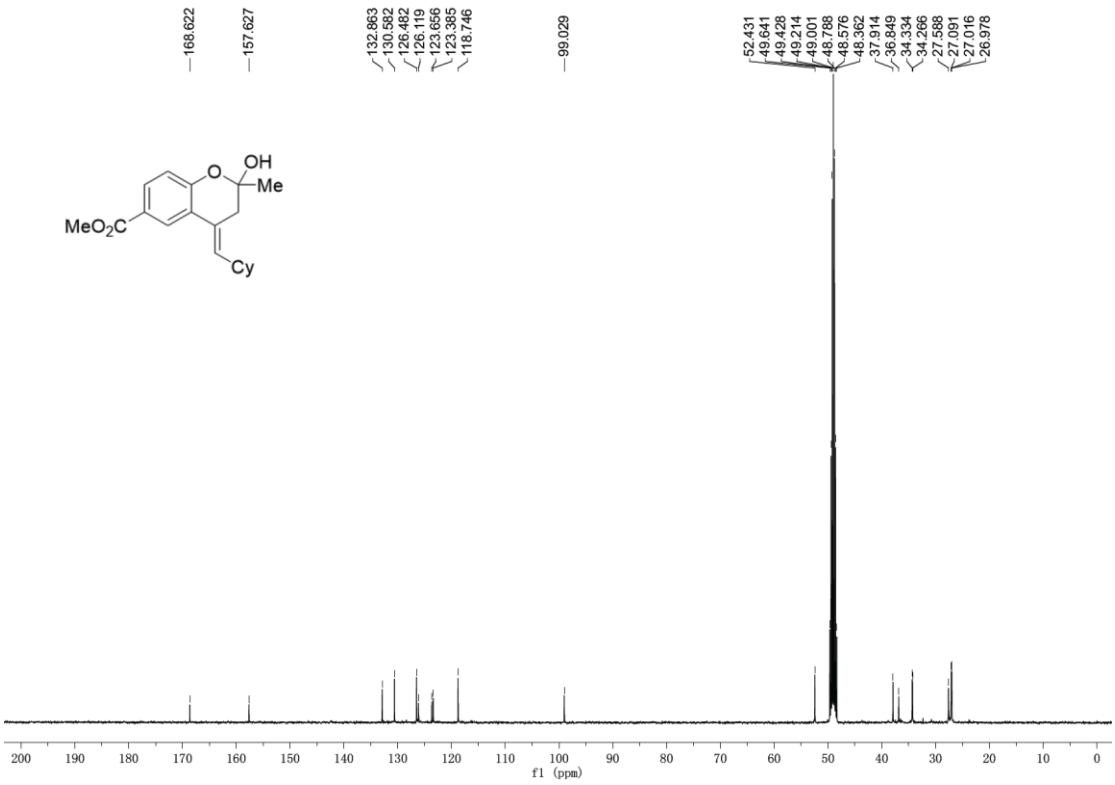
3ja-^{13}C NMR (100 MHz, CD_3OD)



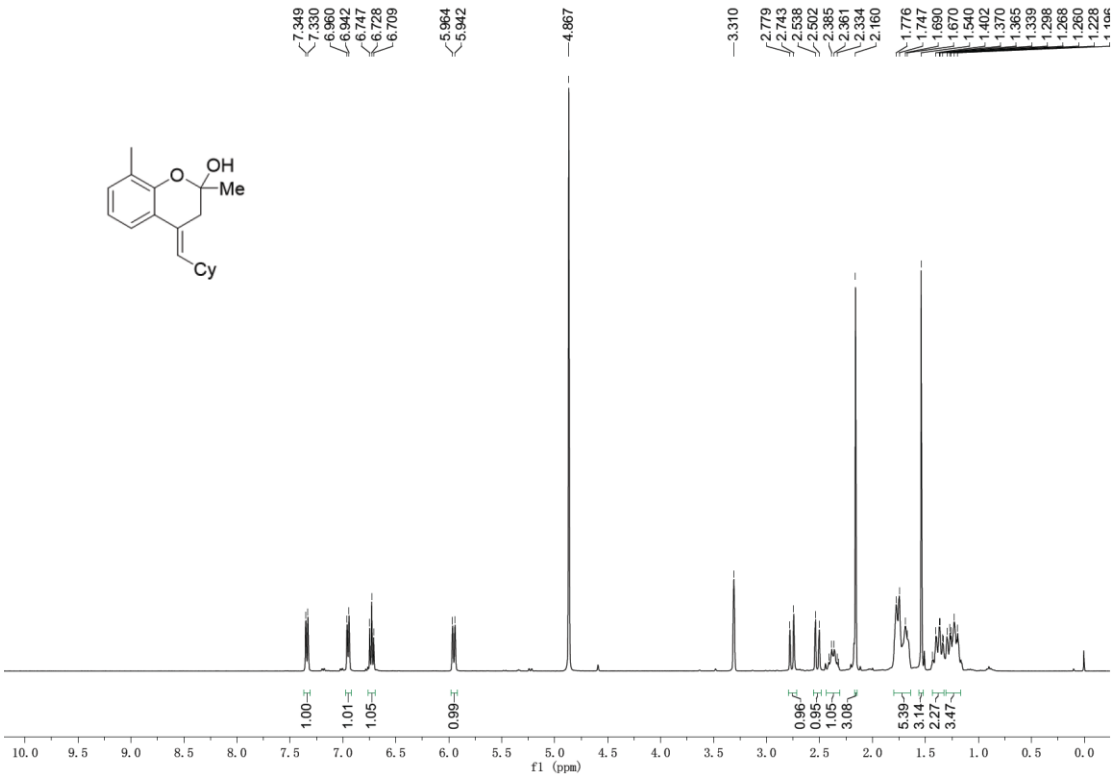
3ka-^{1}H NMR (400 MHz, CD_3OD)



3ka-^{13}C NMR (100 MHz, CD_3OD)



3la-^{1}H NMR (400 MHz, CD_3OD)



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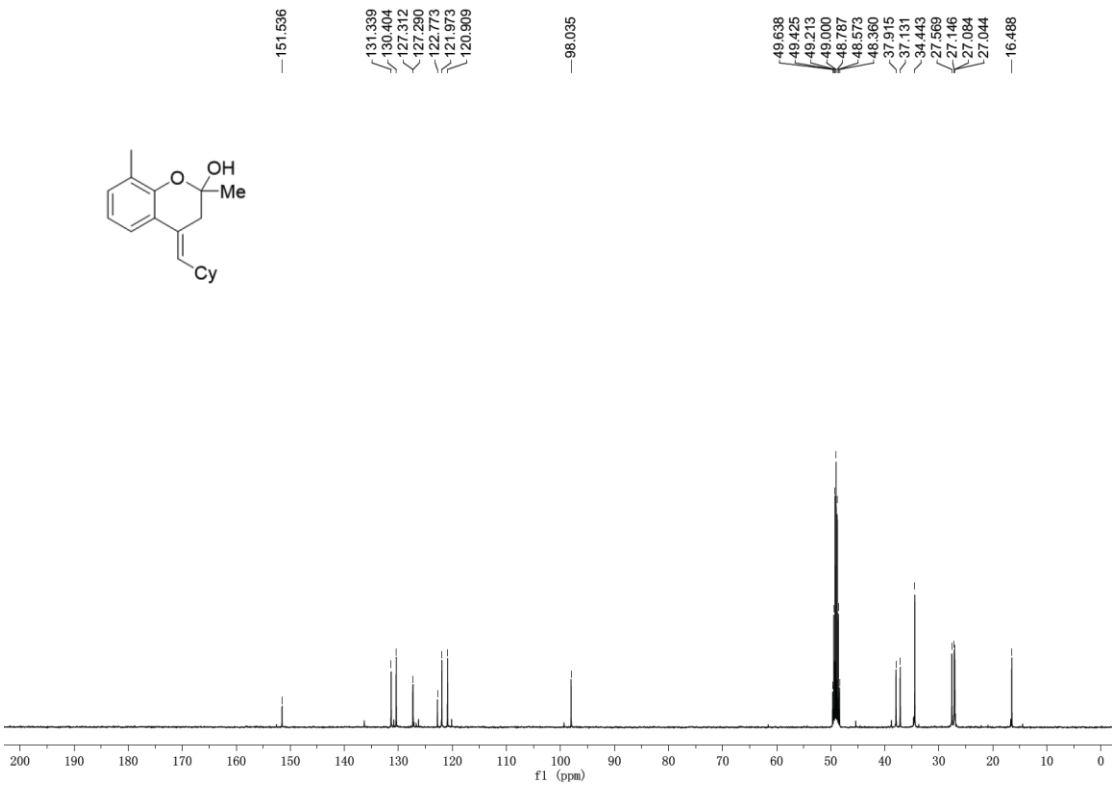
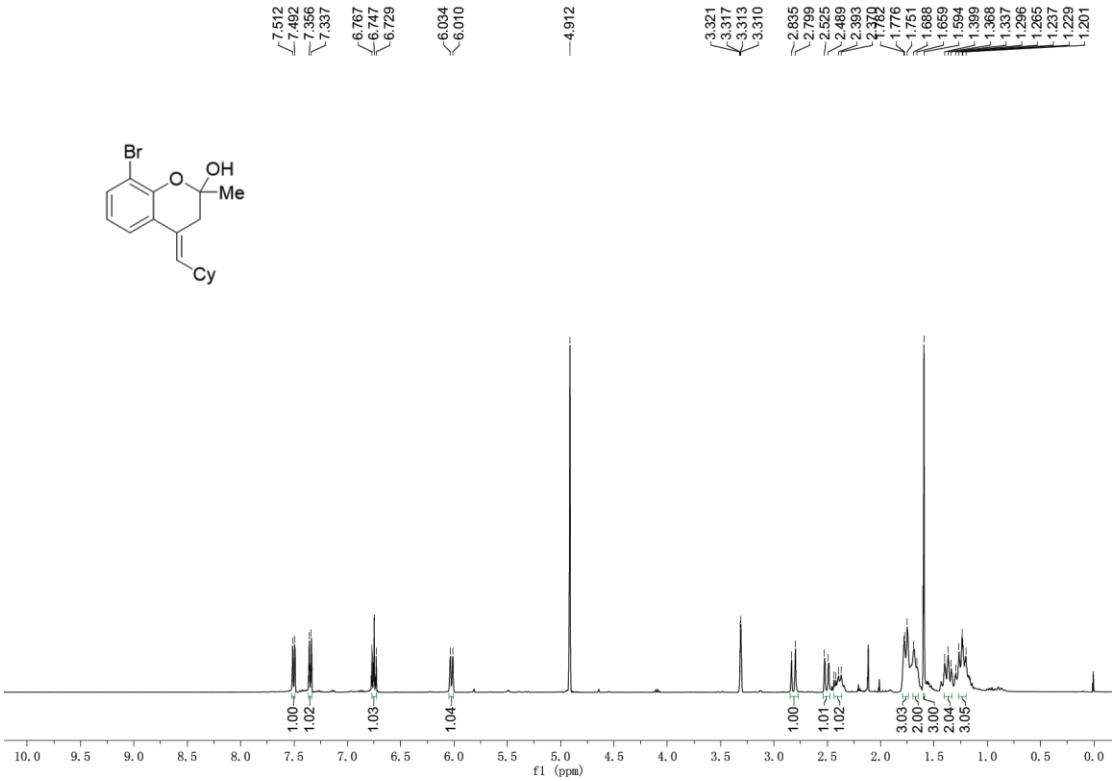
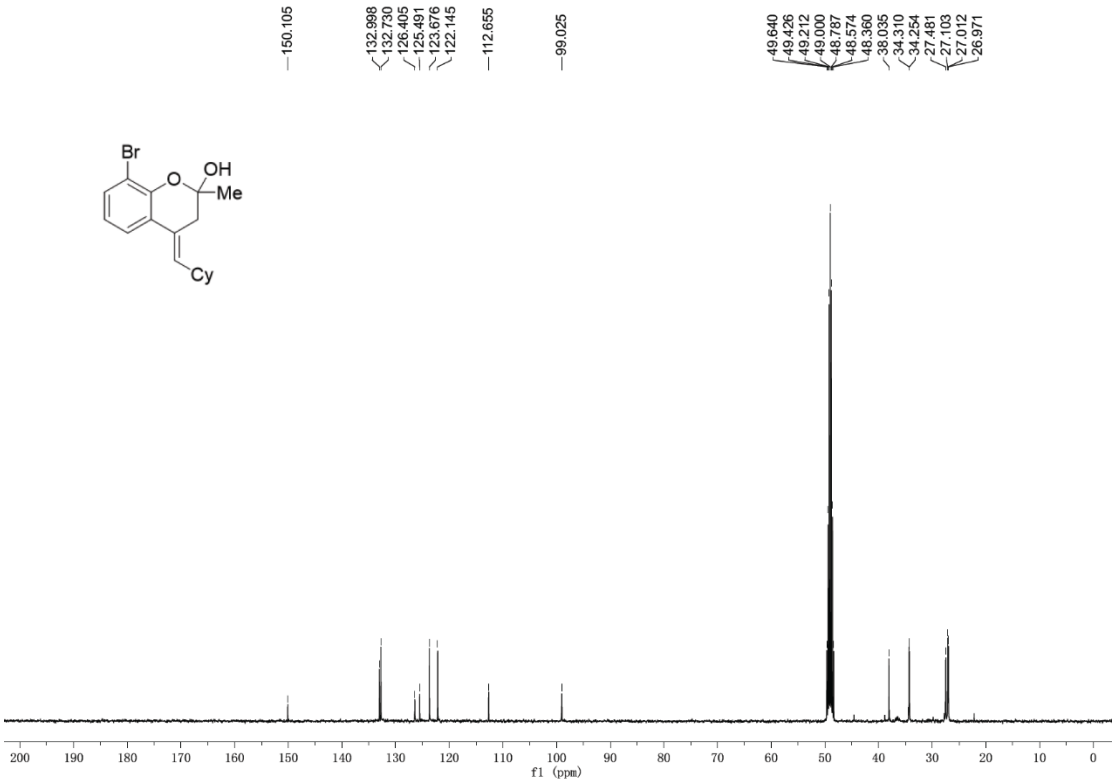


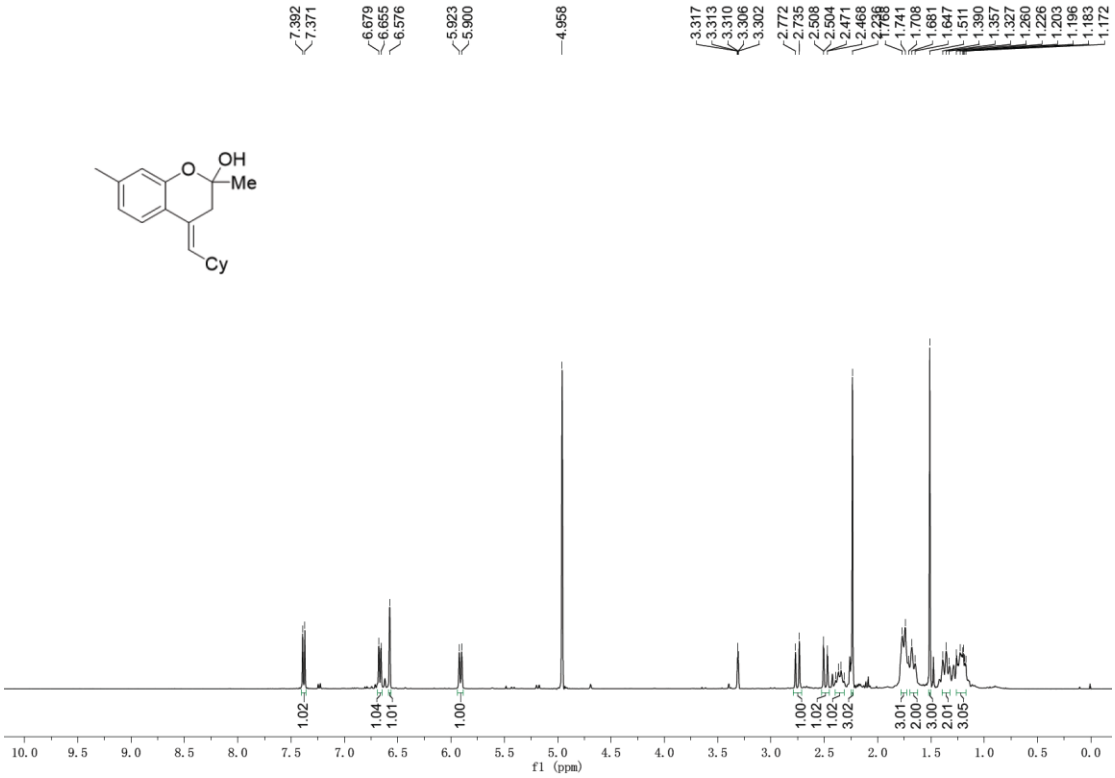
3ma-^{1}H NMR (400 MHz, CD_3OD)



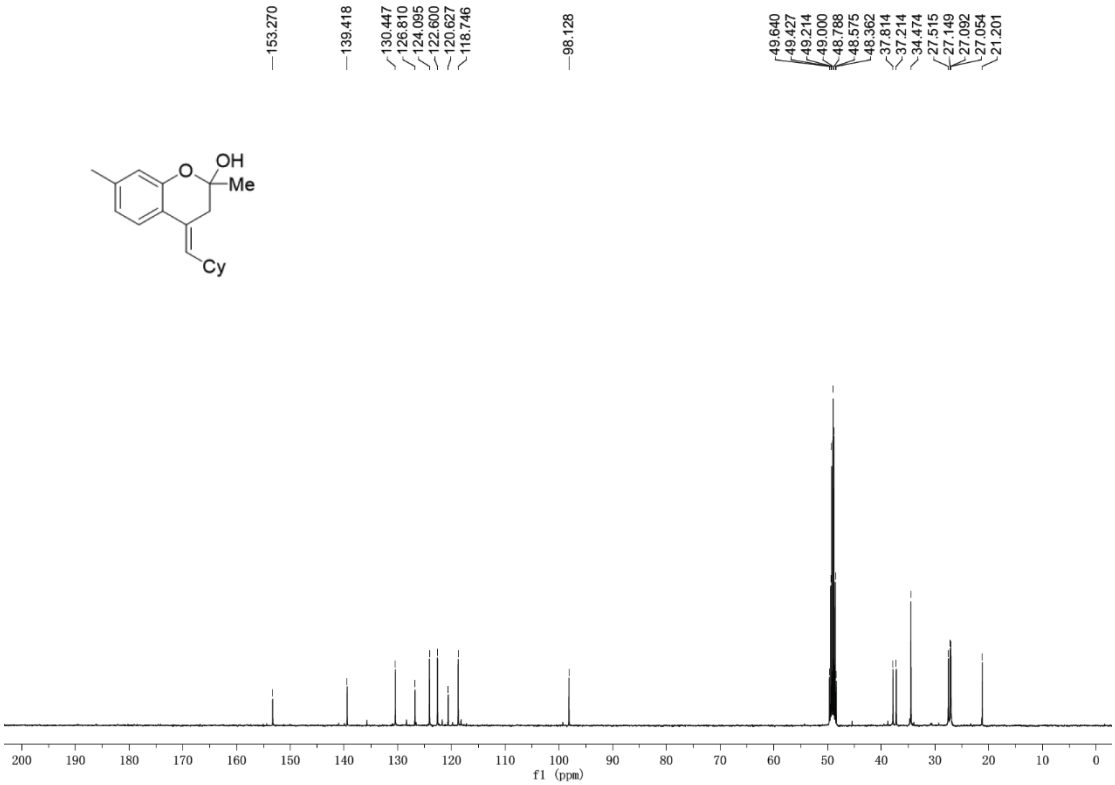
3ma-^{13}C NMR (100 MHz, CD_3OD)



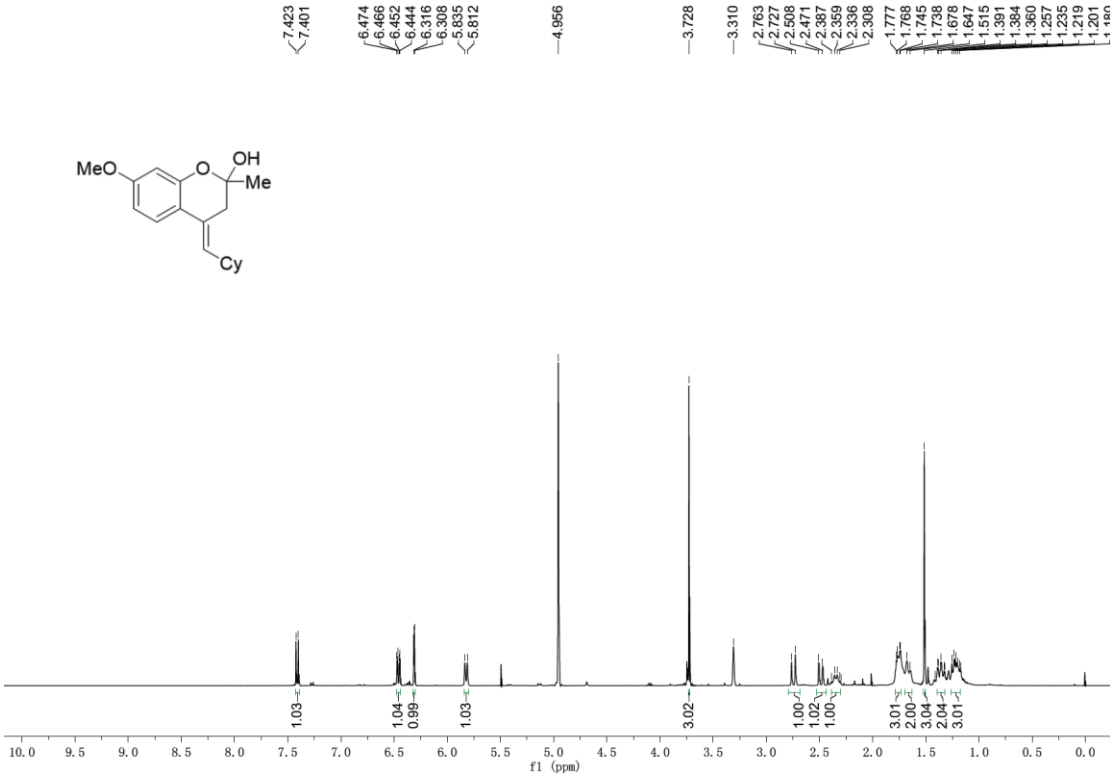
3na-^{1}H NMR (400 MHz, CD_3OD)



3na-^{13}C NMR (100 MHz, CD_3OD)



3oa-^{1}H NMR (400 MHz, CD_3OD)



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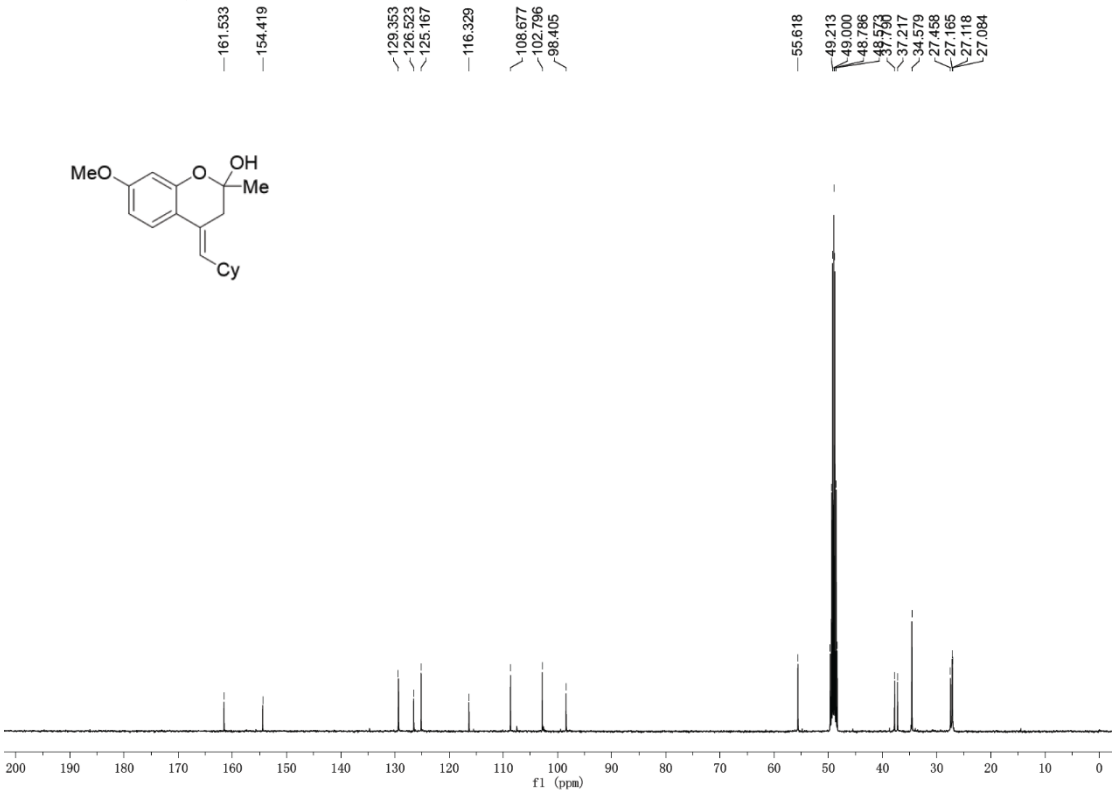
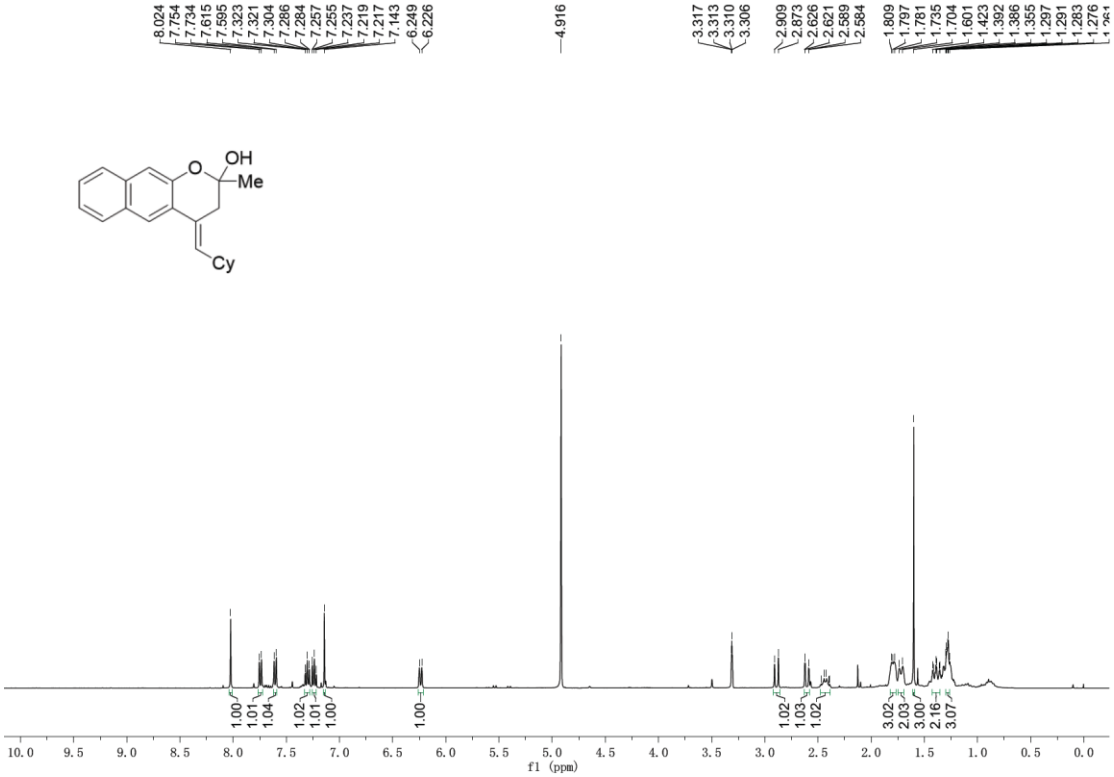
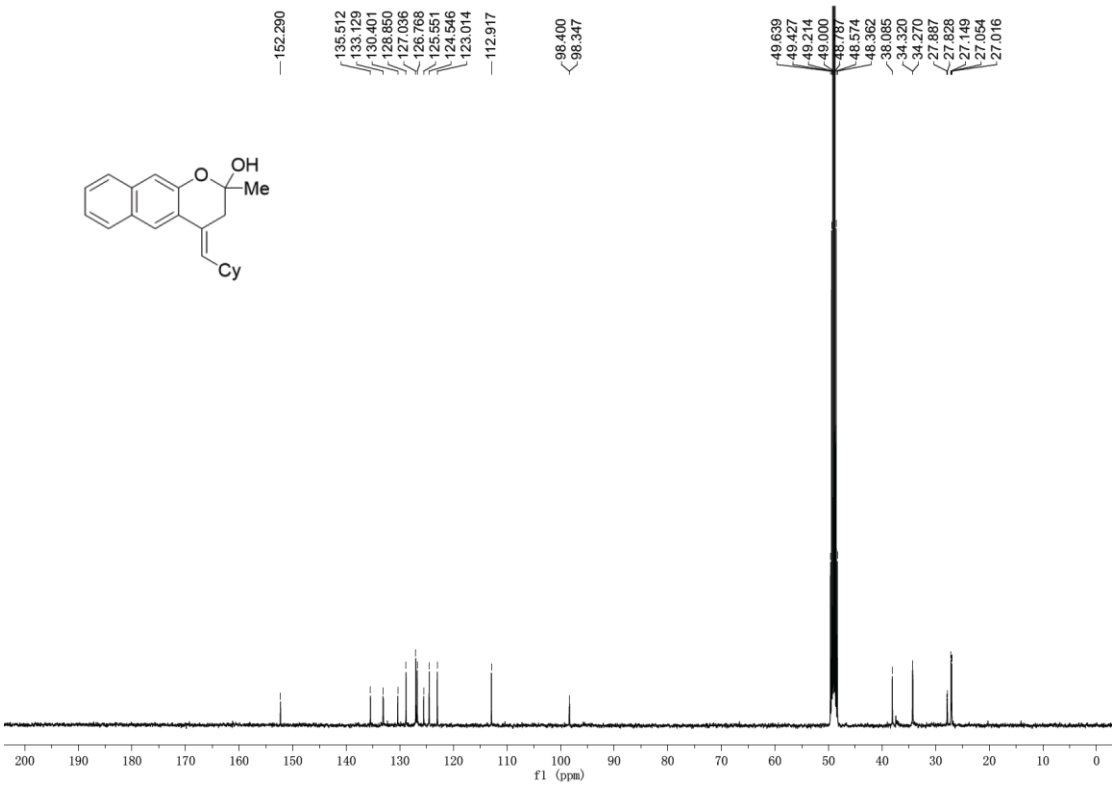


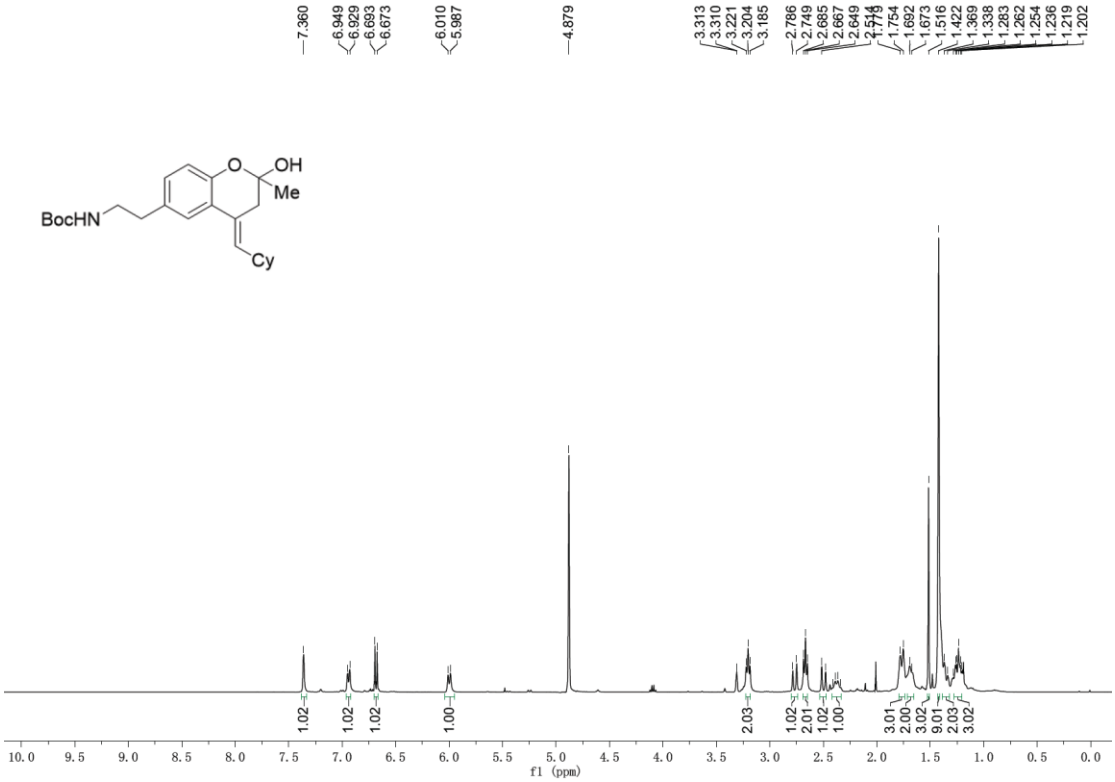
3pa-^{1}H NMR (400 MHz, CD_3OD)



3pa-^{13}C NMR (100 MHz, CD_3OD)



3qa-^{1}H NMR (400 MHz, CD_3OD)



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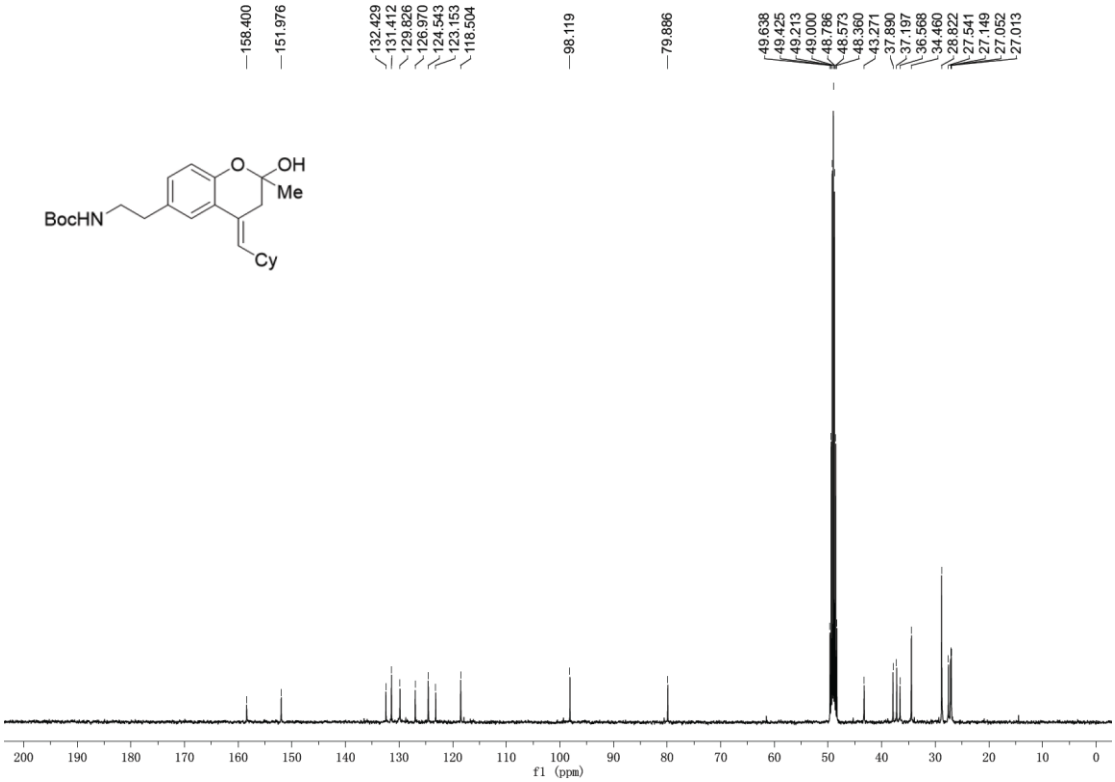

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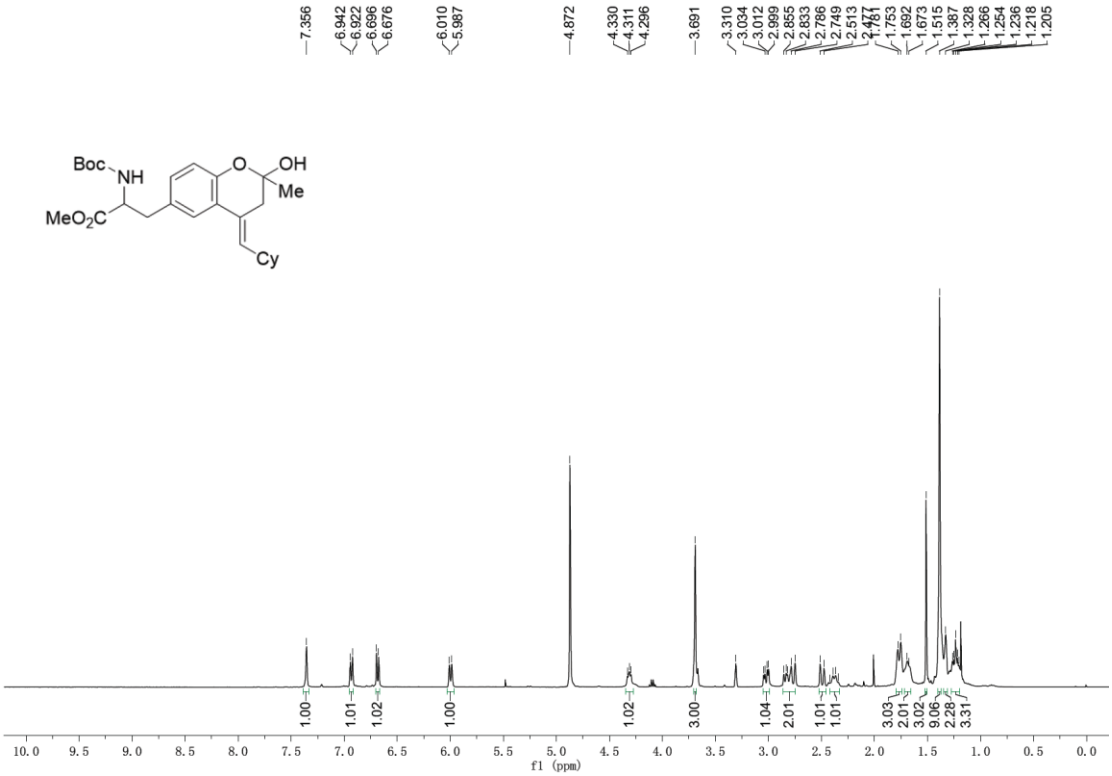
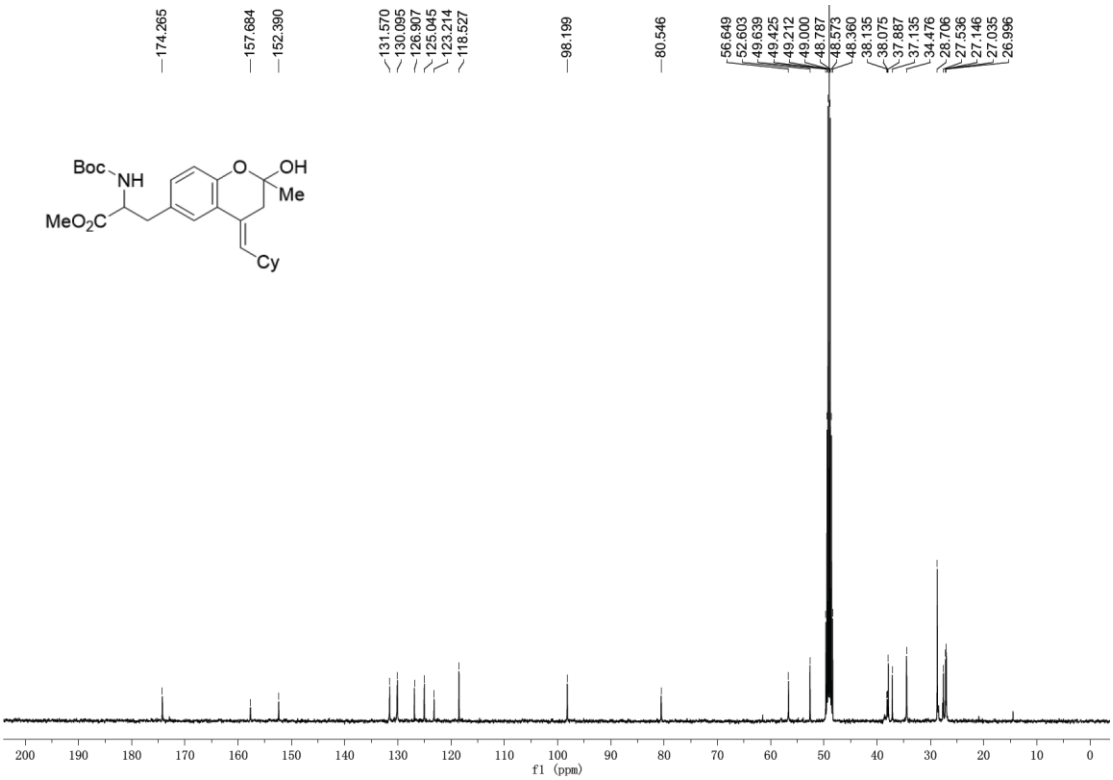
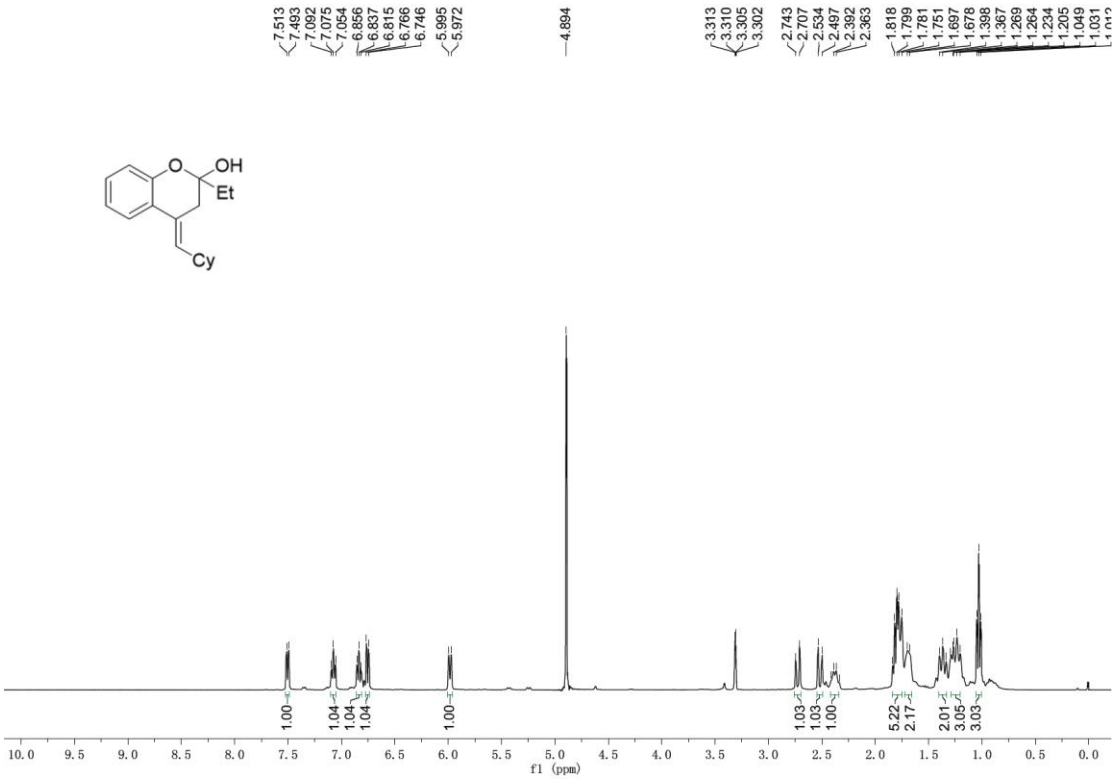


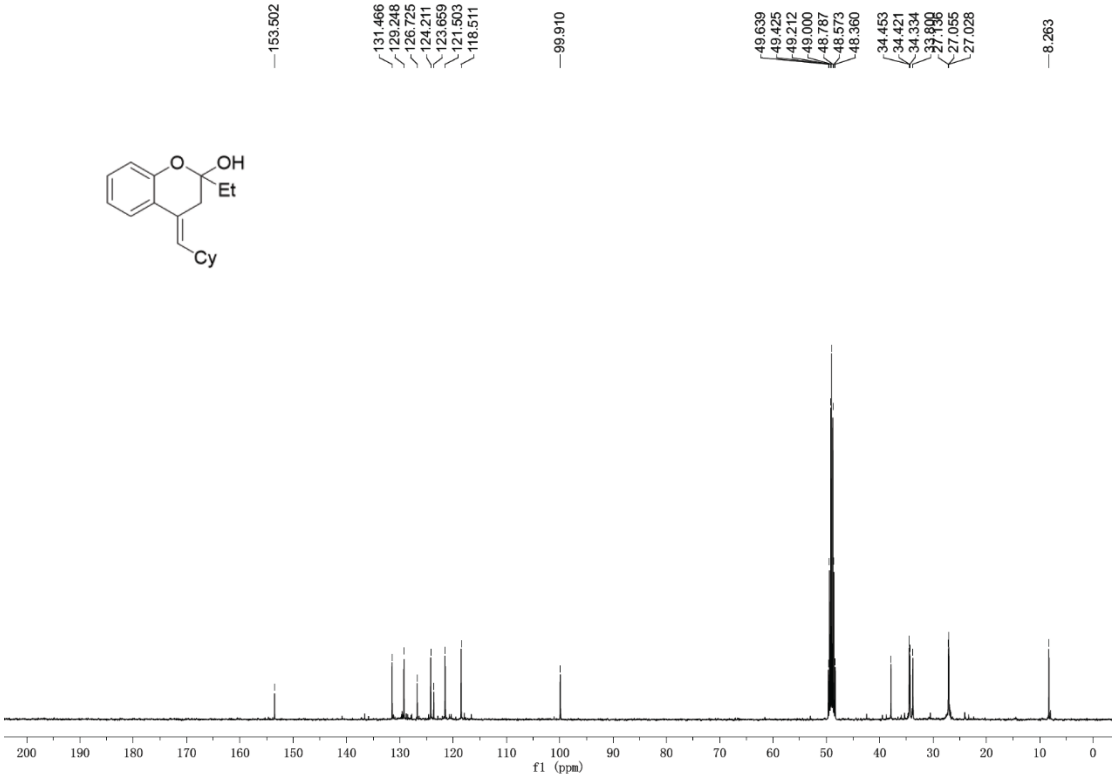
3ra-^{13}C NMR (100 MHz, CD_3OD)



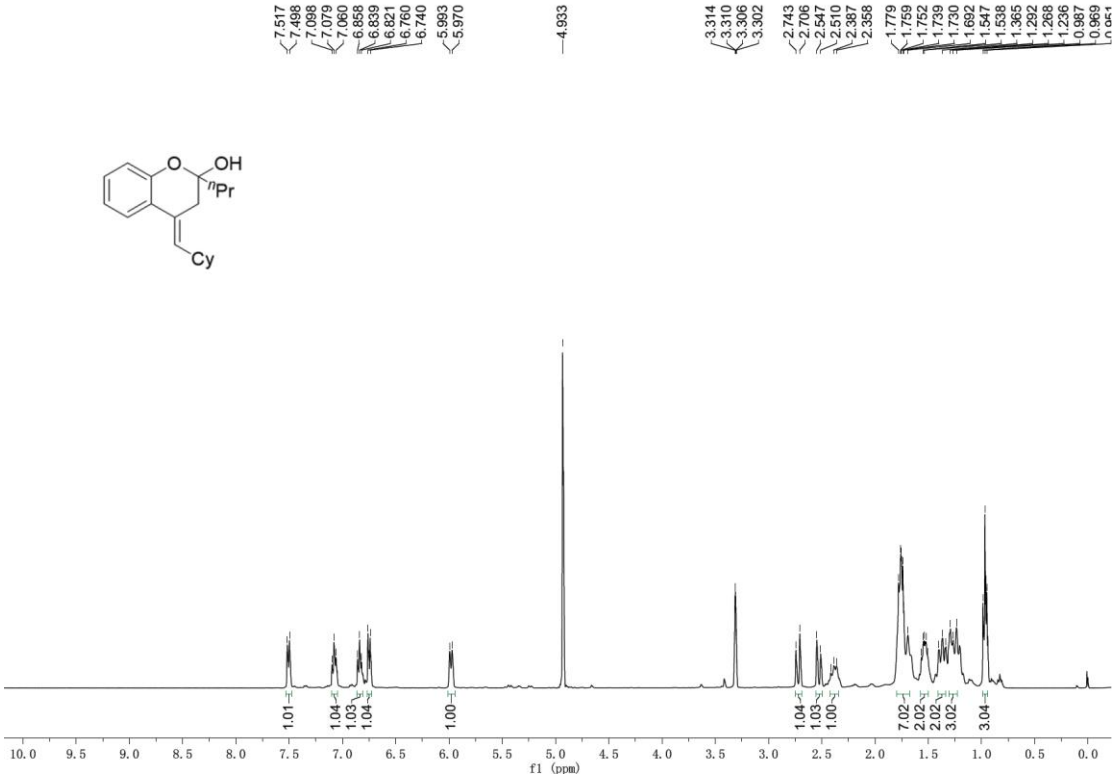
3ab-[1]H NMR (400 MHz, CD_3OD)



3ab-[13]C NMR (100 MHz, CD_3OD)



3ac-^{1}H NMR (400 MHz, CD_3OD)



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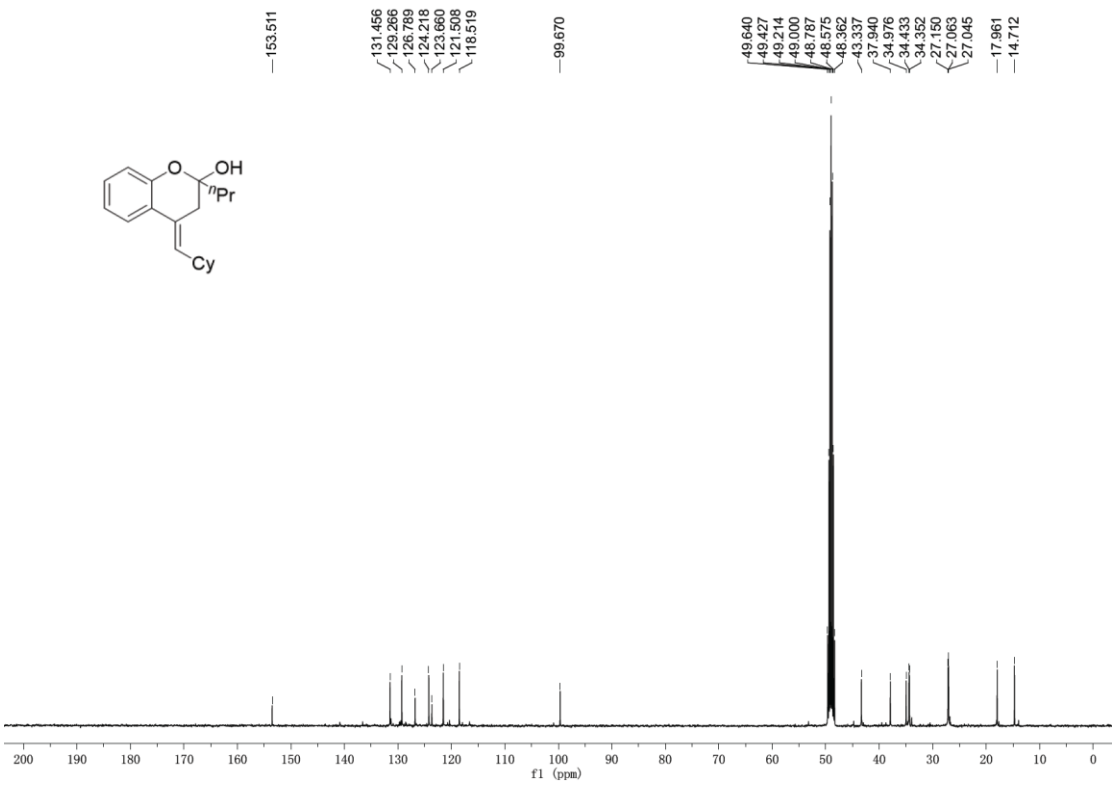
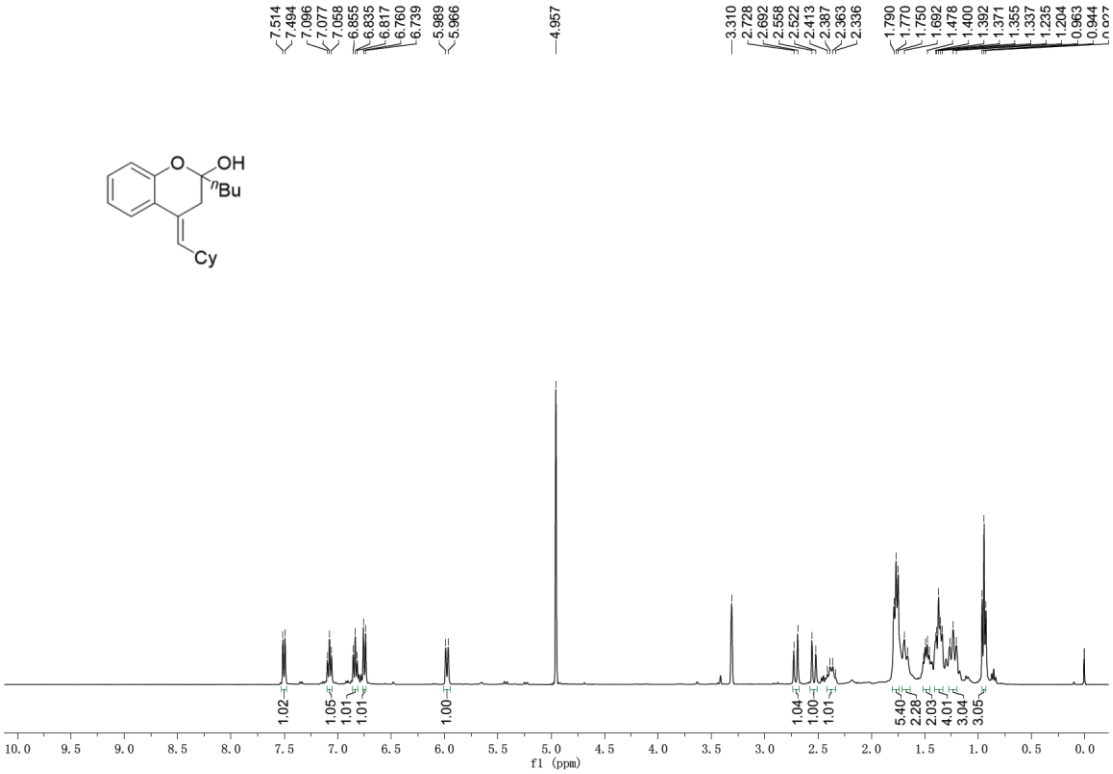
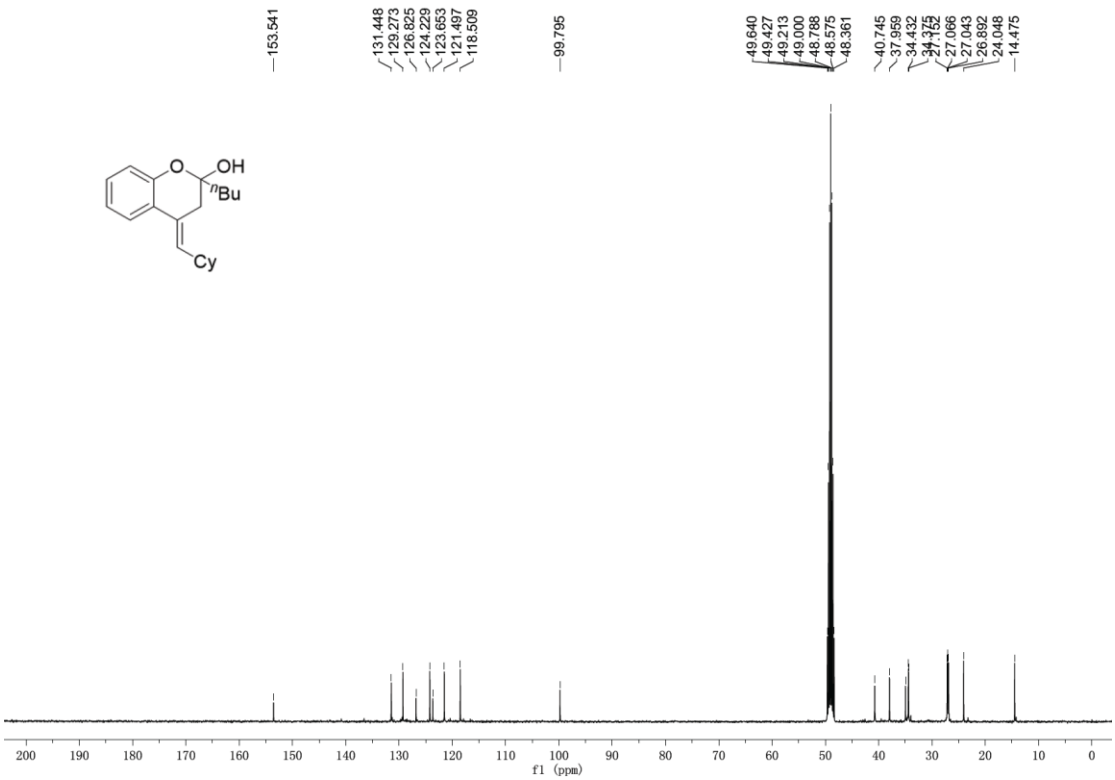


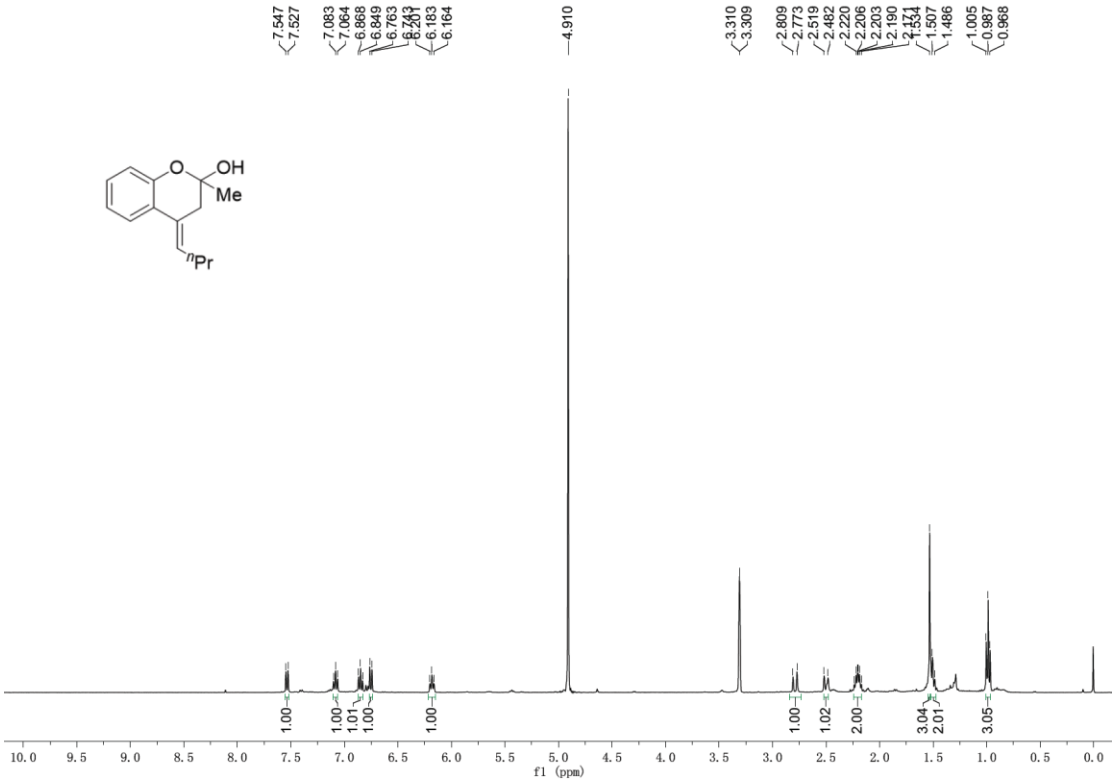
3ad-^{1}H NMR (400 MHz, CD_3OD)



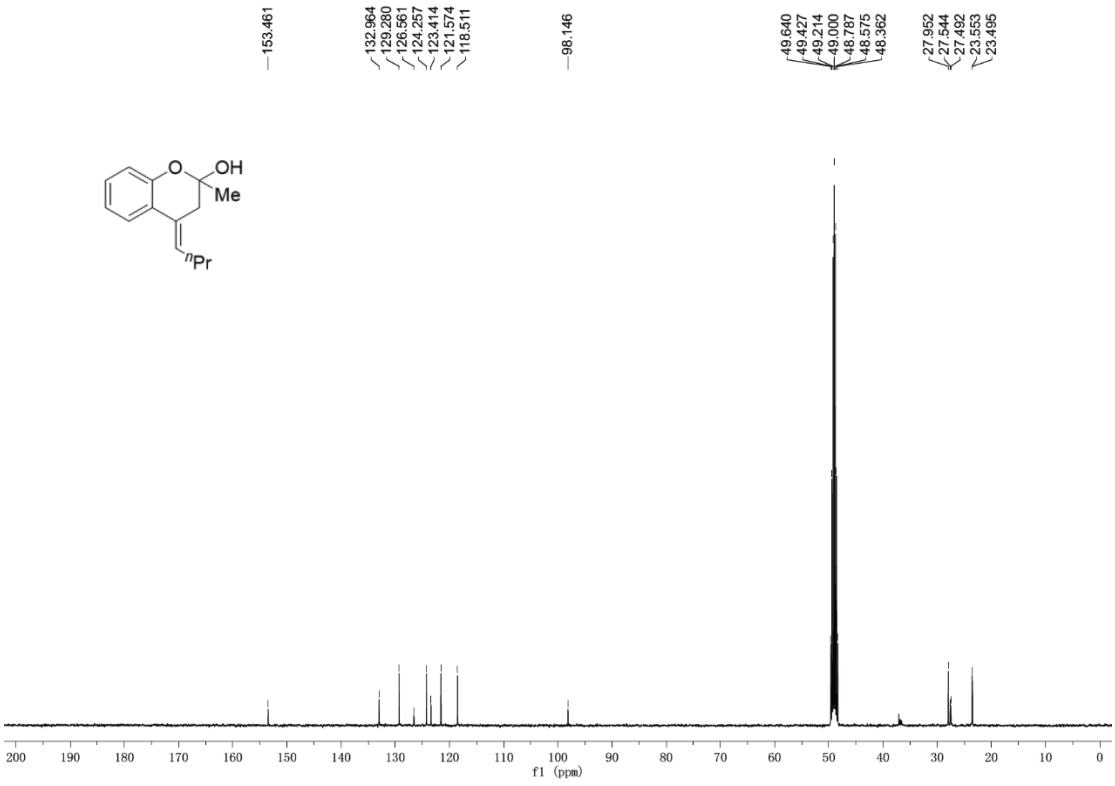
3ad-^{13}C NMR (100 MHz, CD_3OD)



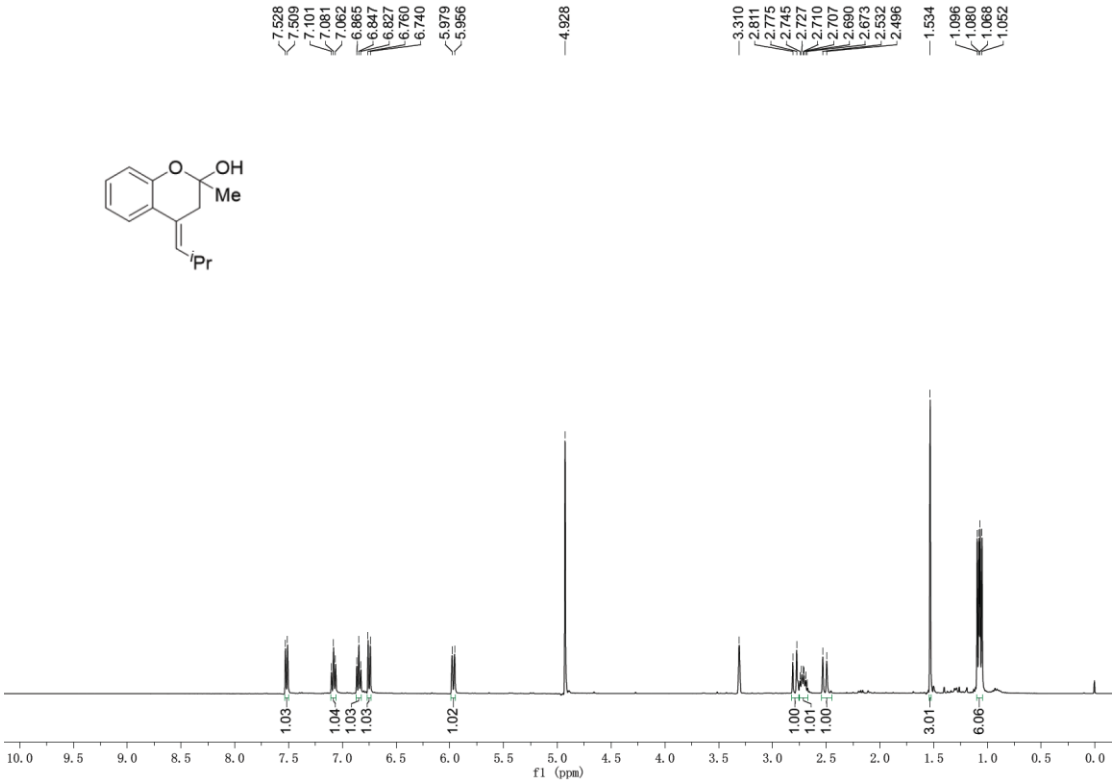
3ae-^{1}H NMR (400 MHz, CD_3OD)



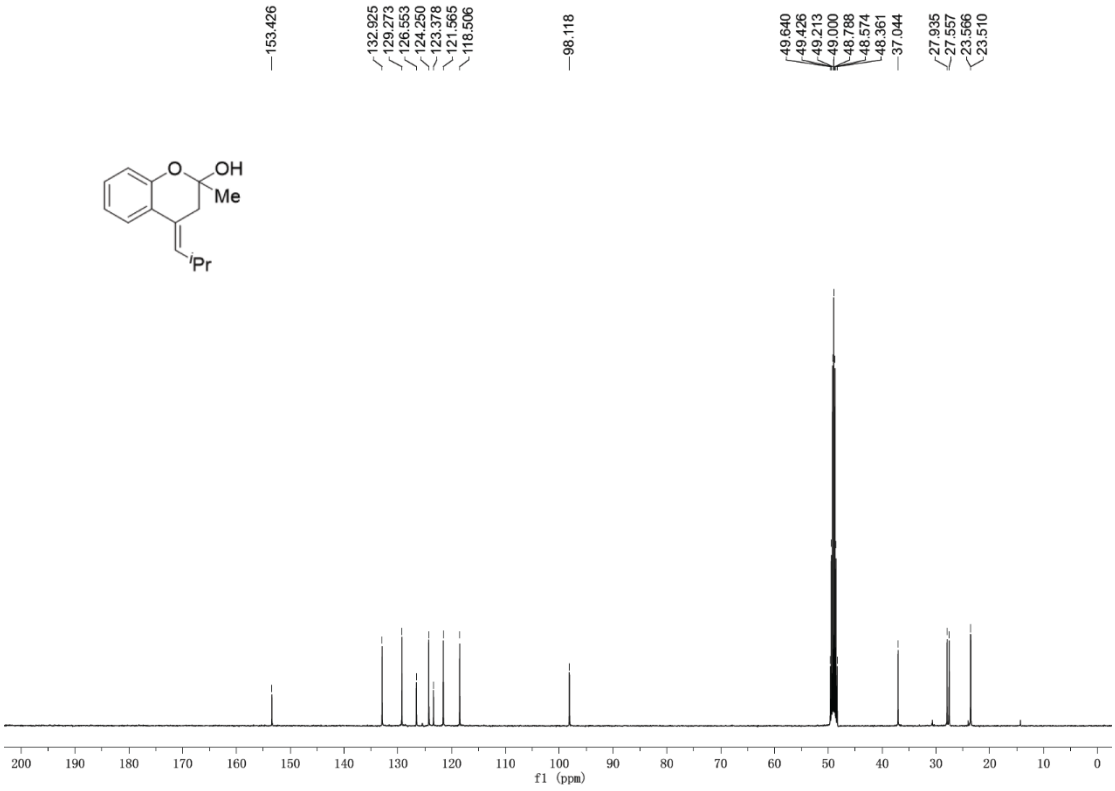
3ae-^{13}C NMR (100 MHz, CD_3OD)



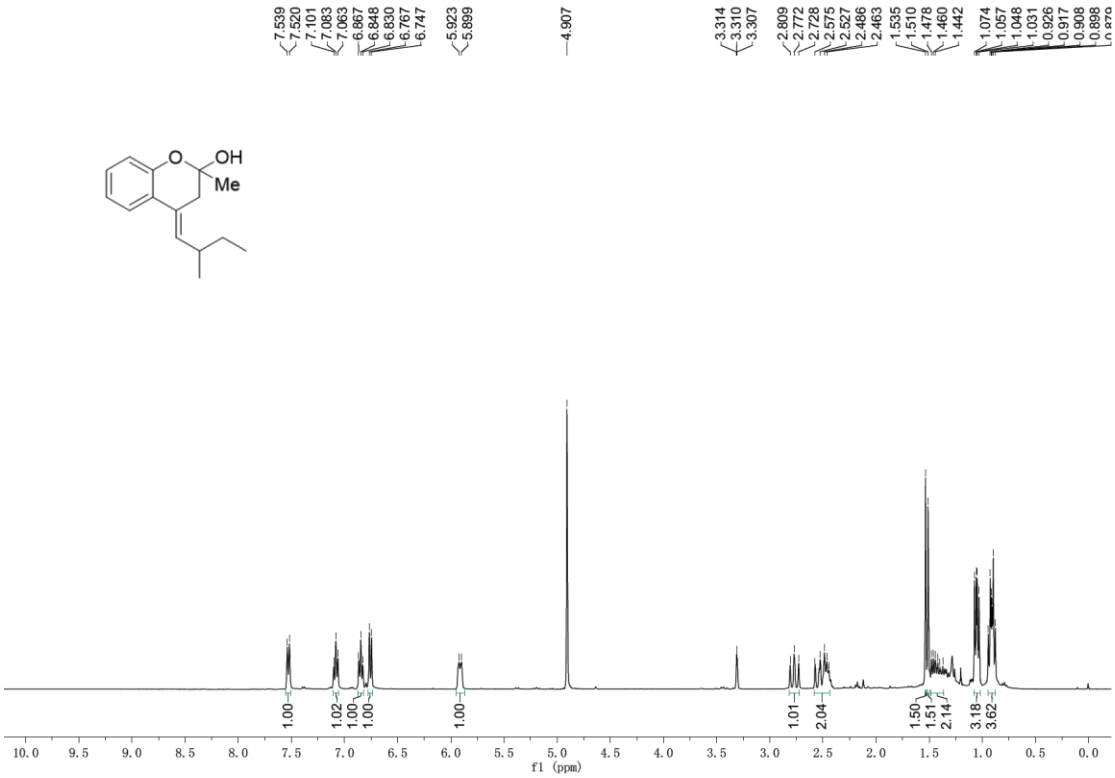
3af-^{1}H NMR (400 MHz, CD_3OD)



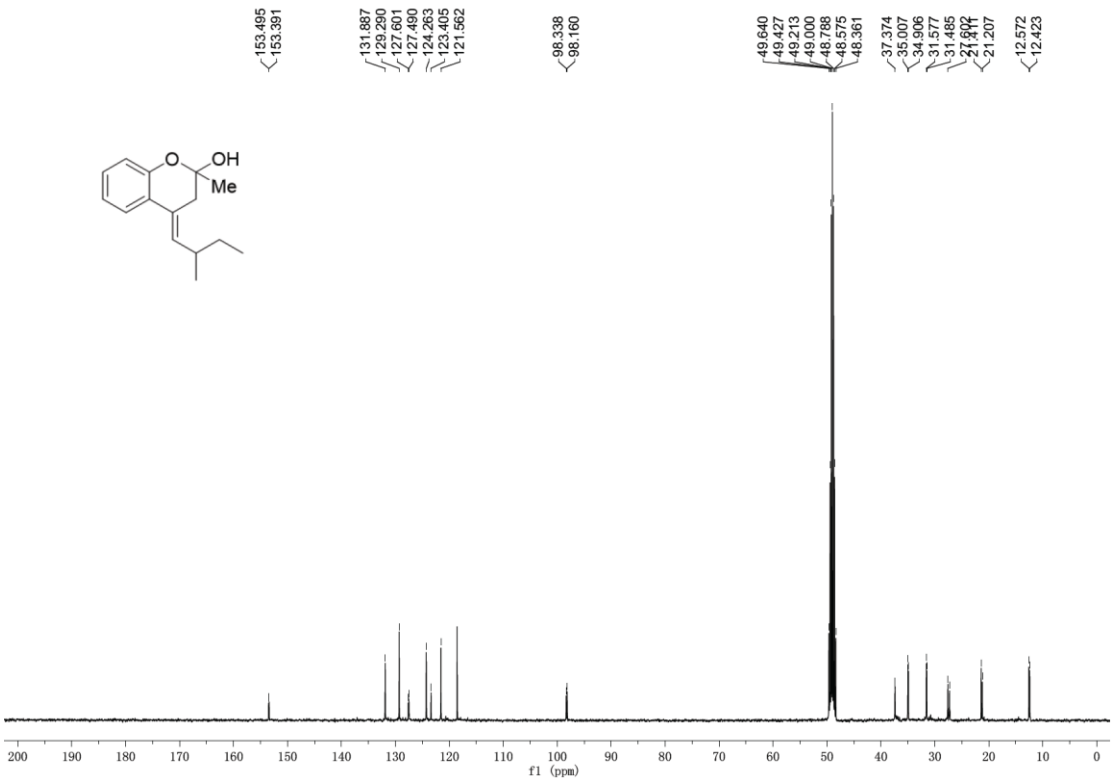
3af-^{13}C NMR (100 MHz, CD_3OD)



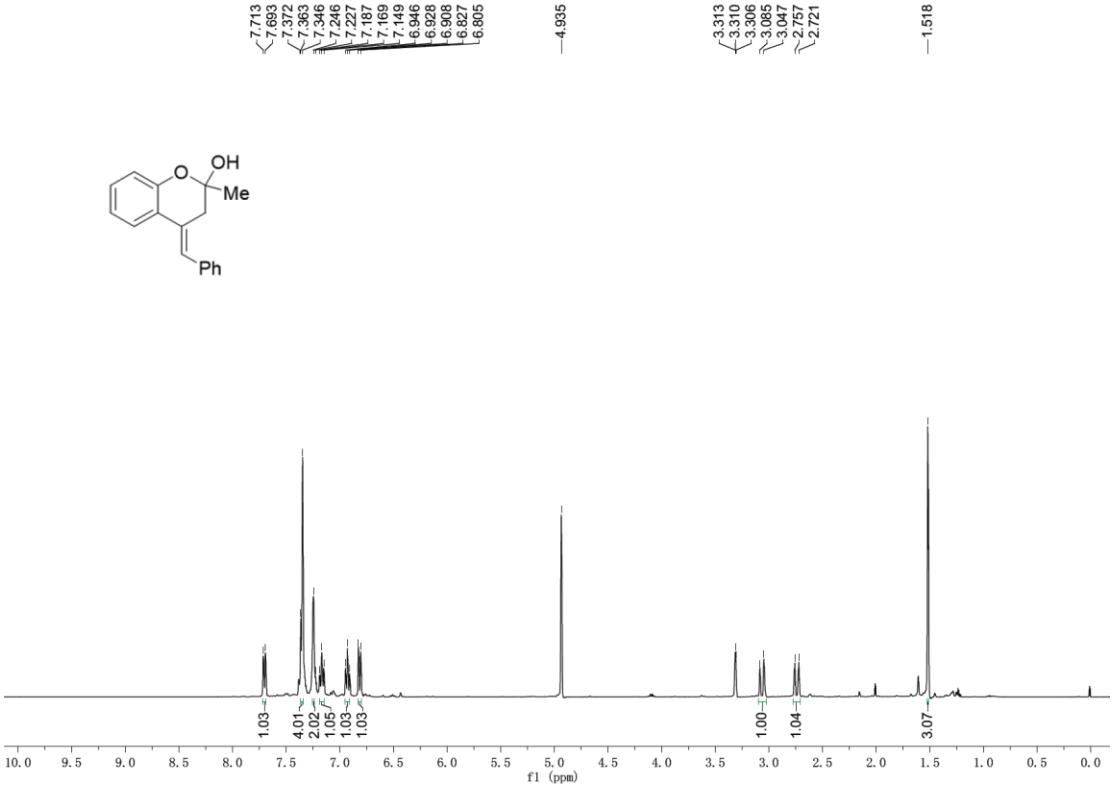
3ag-^{1}H NMR (400 MHz, CD_3OD)



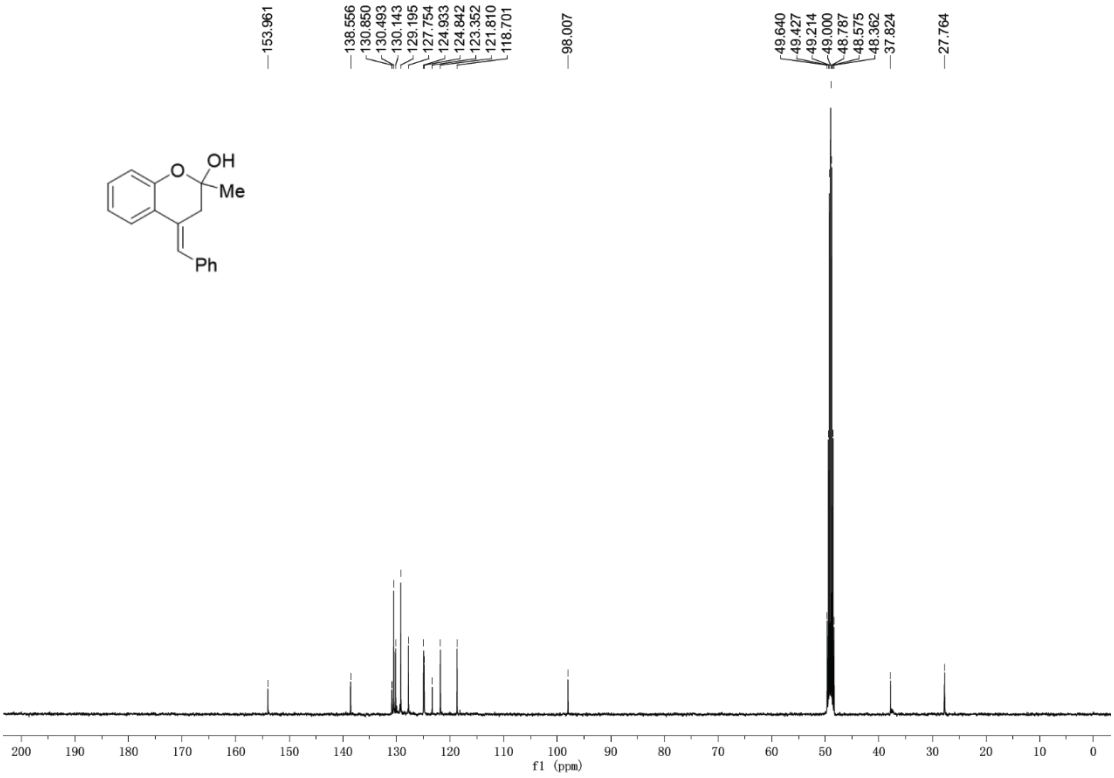
3ag-^{13}C NMR (100 MHz, CD_3OD)



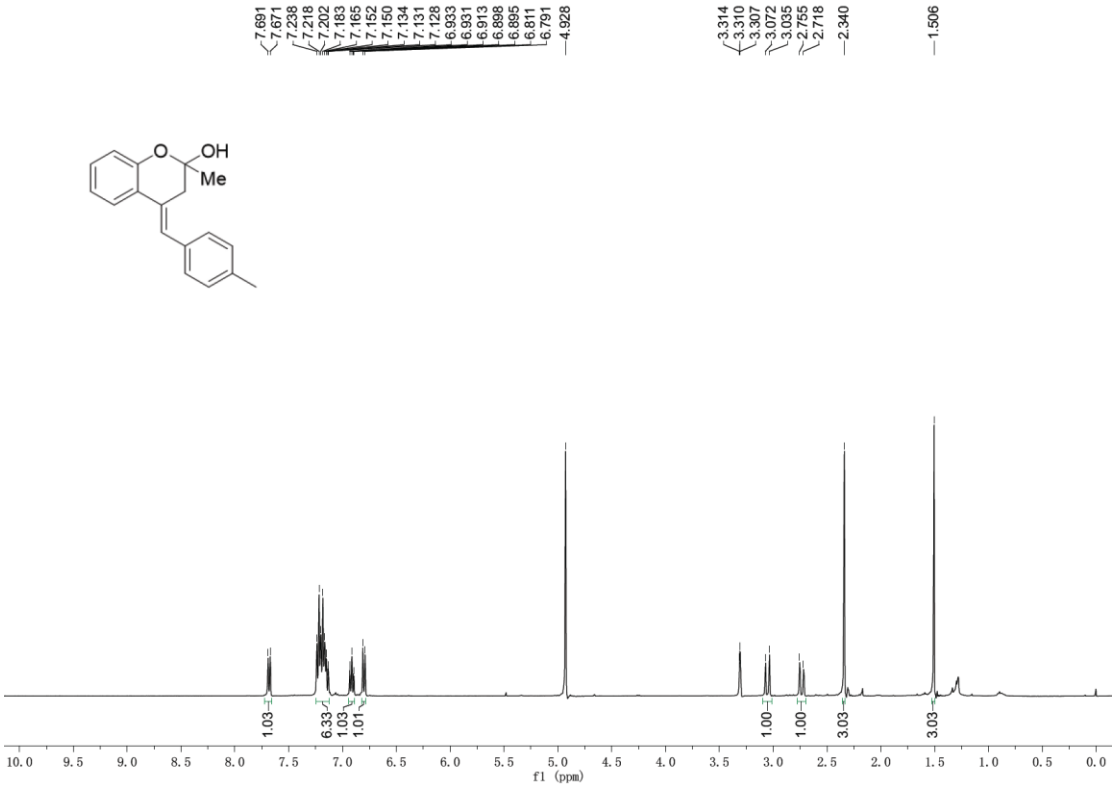
3ah-^{1}H NMR (400 MHz, CD_3OD)



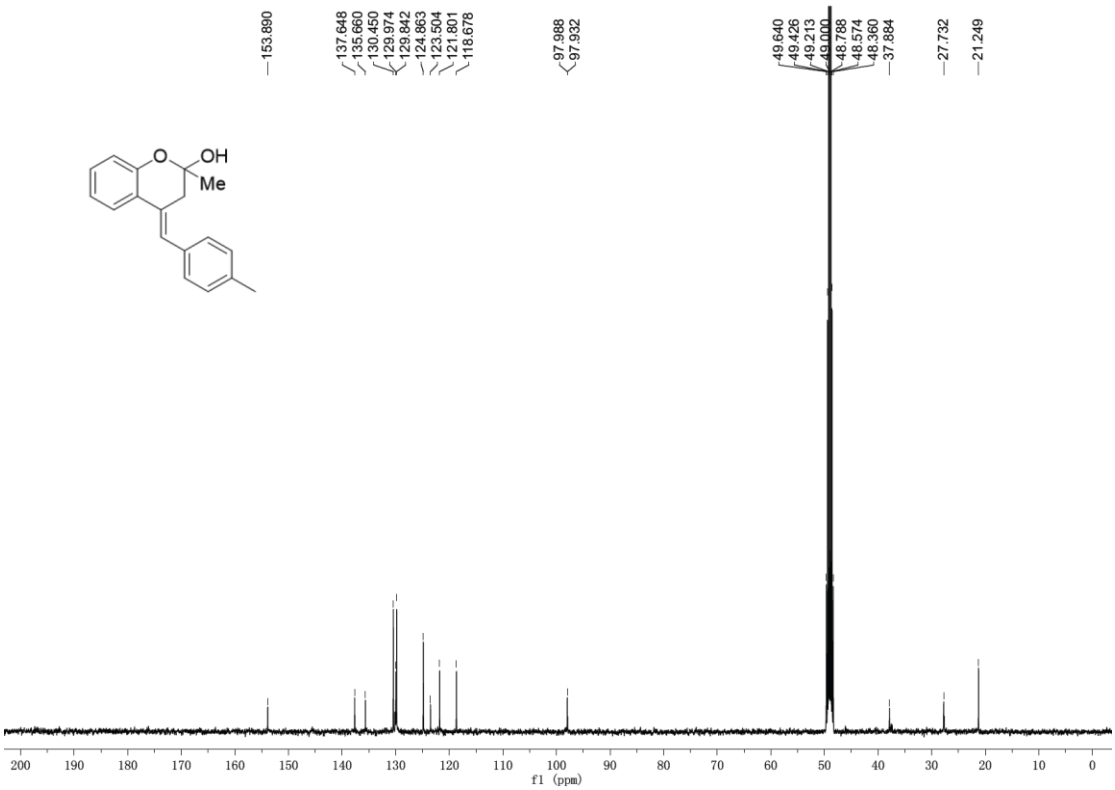
3ah-^{13}C NMR (100 MHz, CD_3OD)



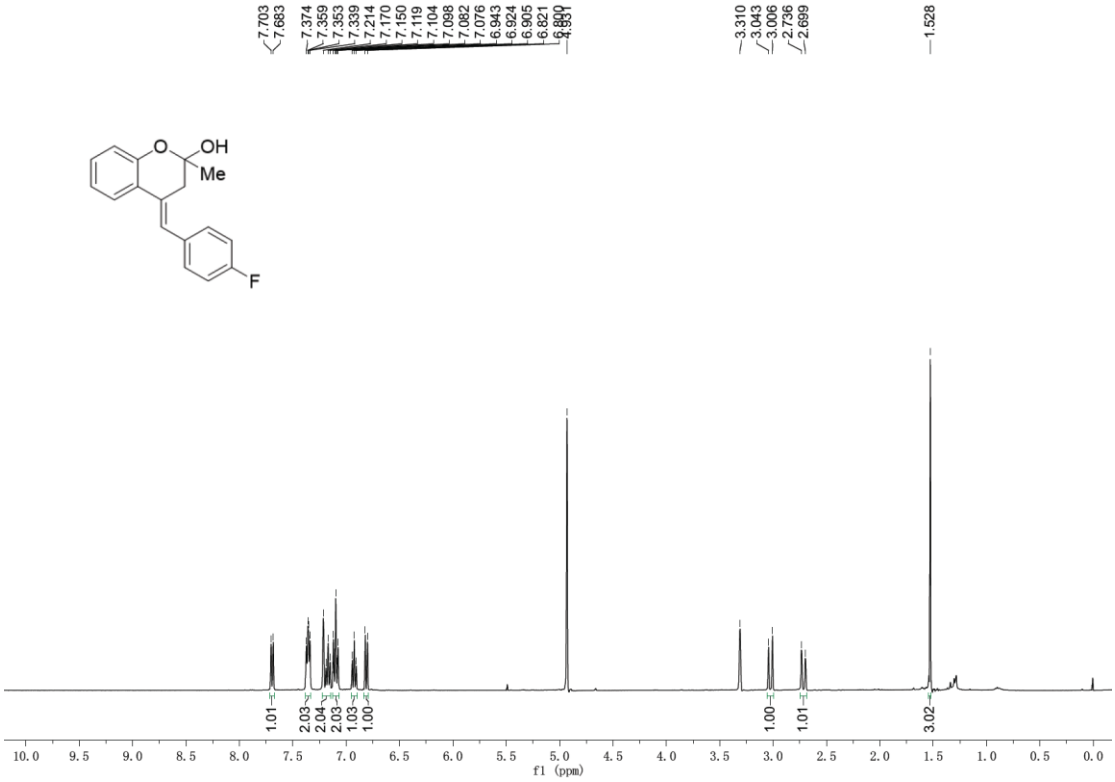
3ai-[1]H NMR (400 MHz, CD_3OD)



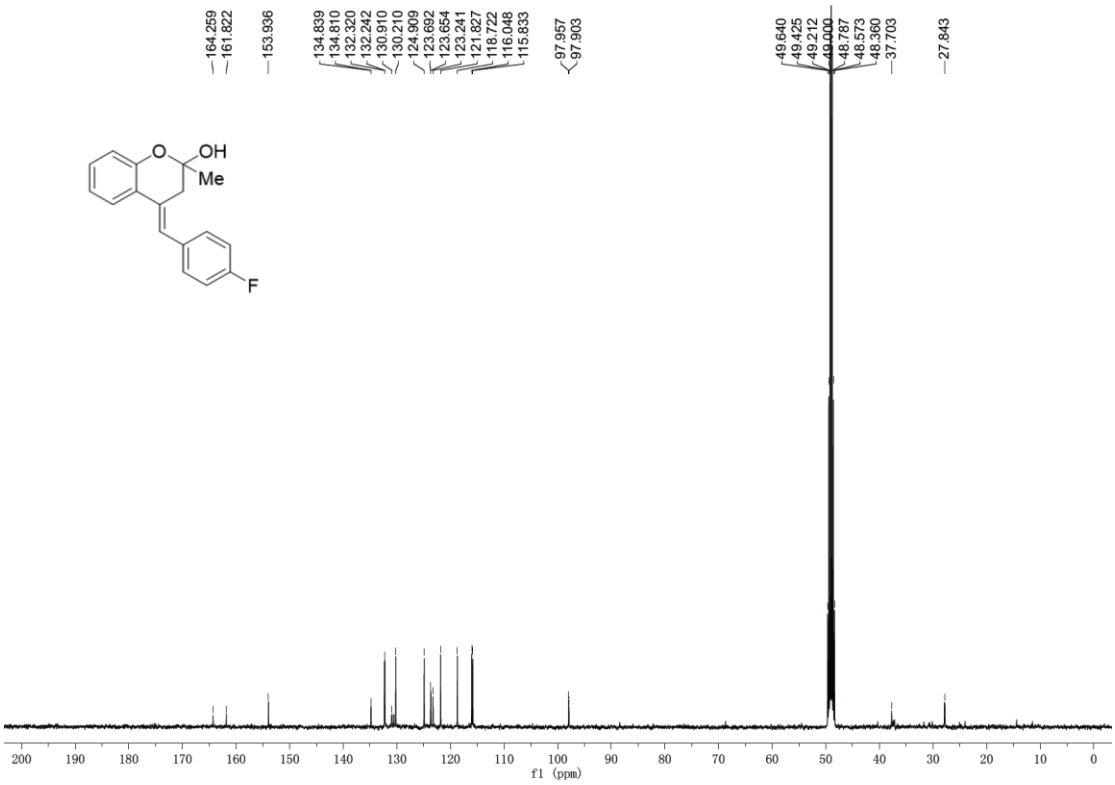
3ai-[13]C NMR (100 MHz, CD_3OD)



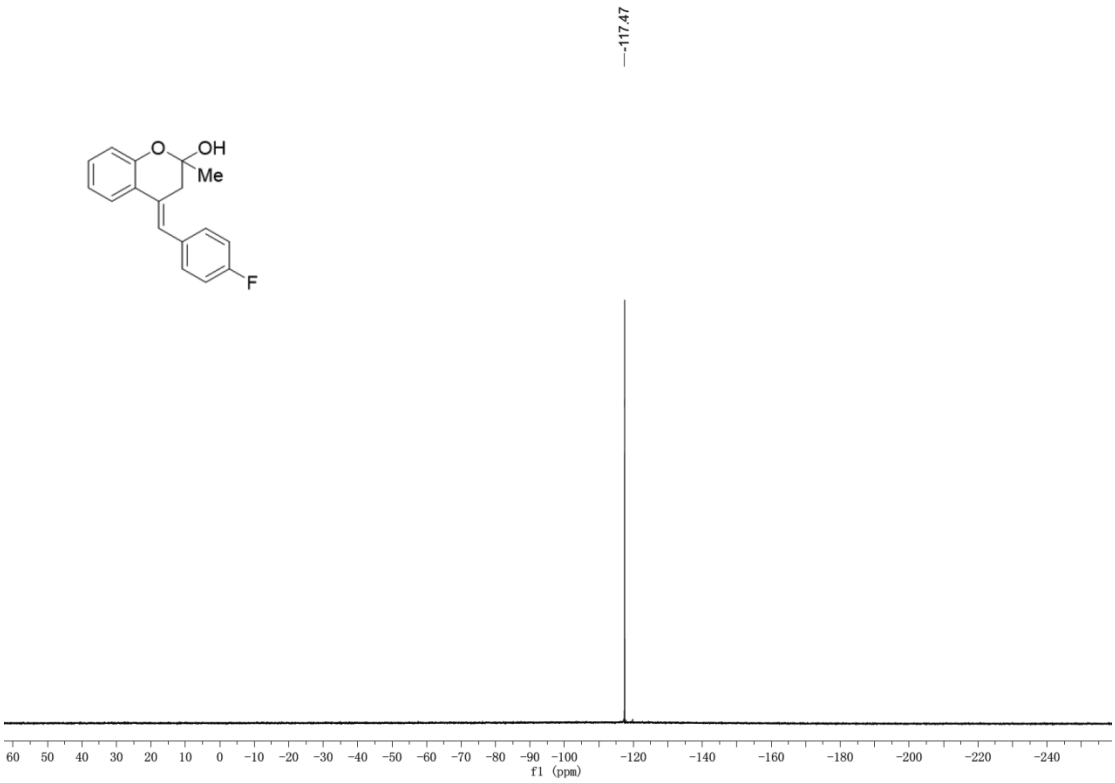
3aj-^{1}H NMR (400 MHz, CD_3OD)



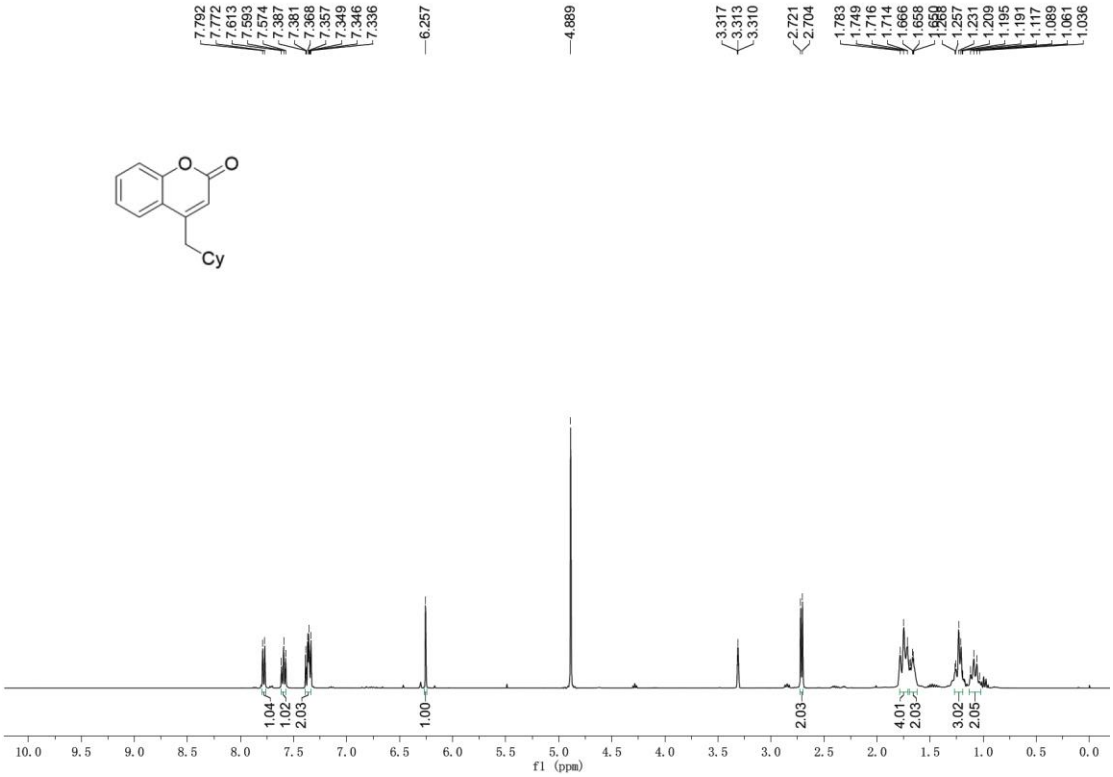
3aj-^{13}C NMR (100 MHz, CD_3OD)



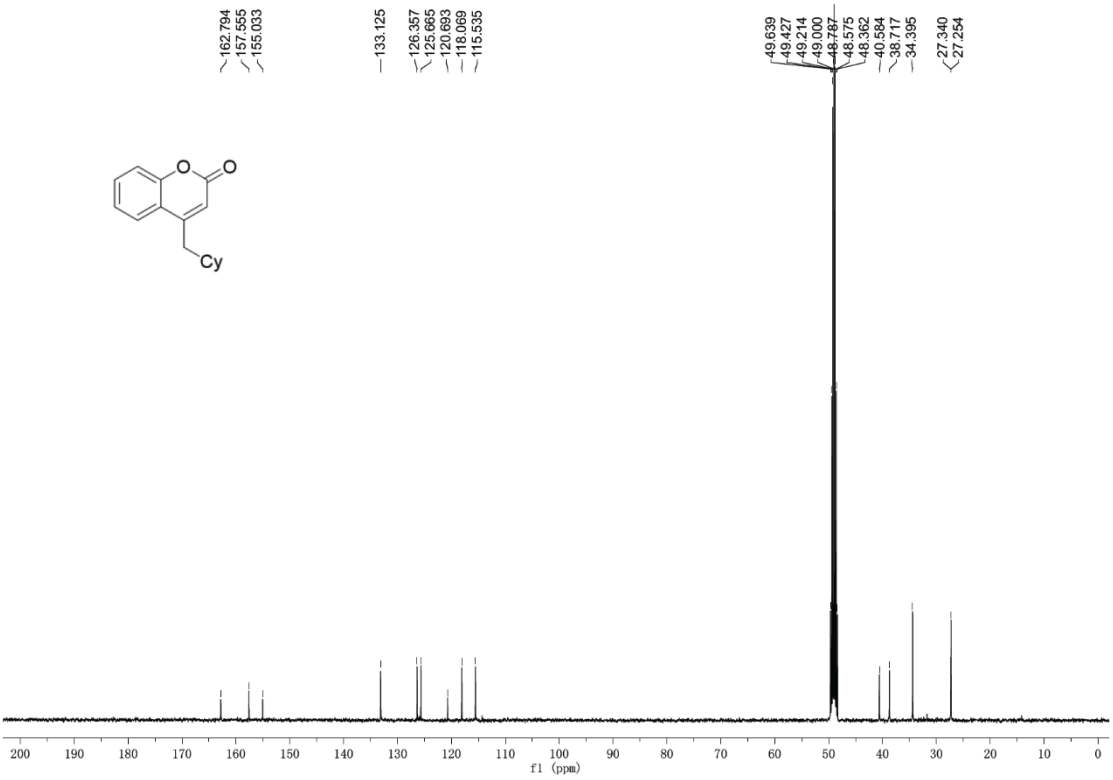
3aj-^{19}F NMR (376 MHz, CD_3OD)



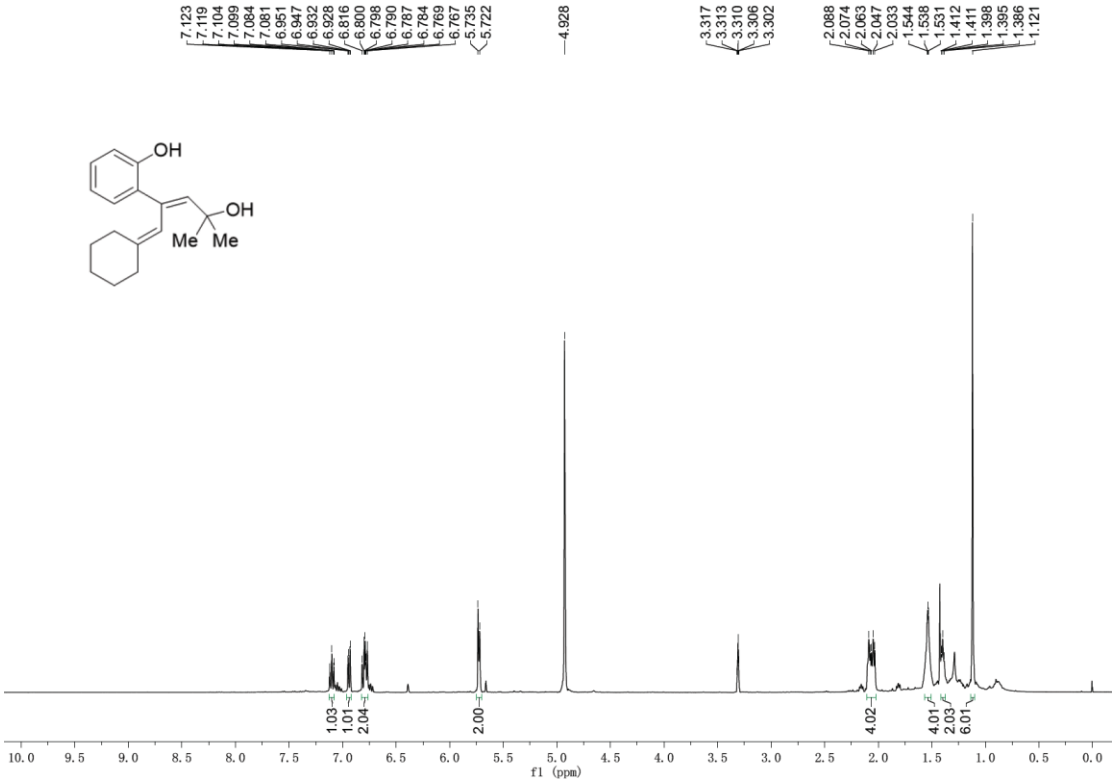
5-^{1}H NMR (400 MHz, CD_3OD)



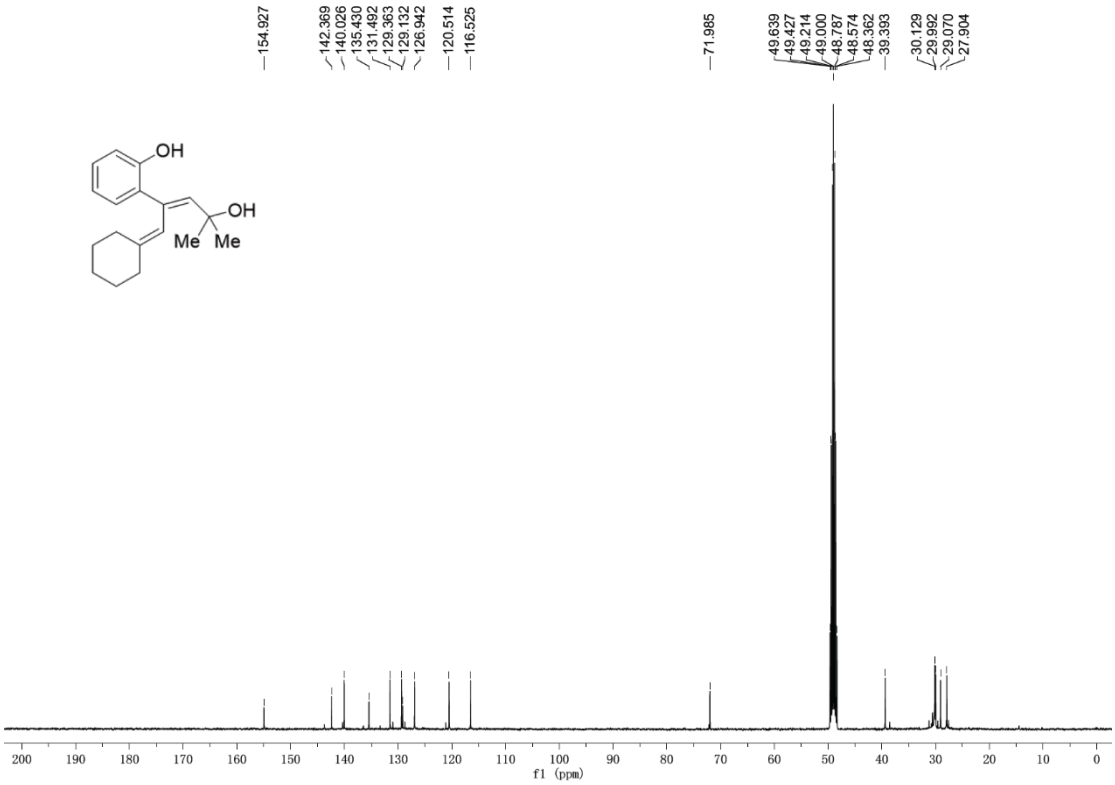
5-^{13}C NMR (100 MHz, CD_3OD)



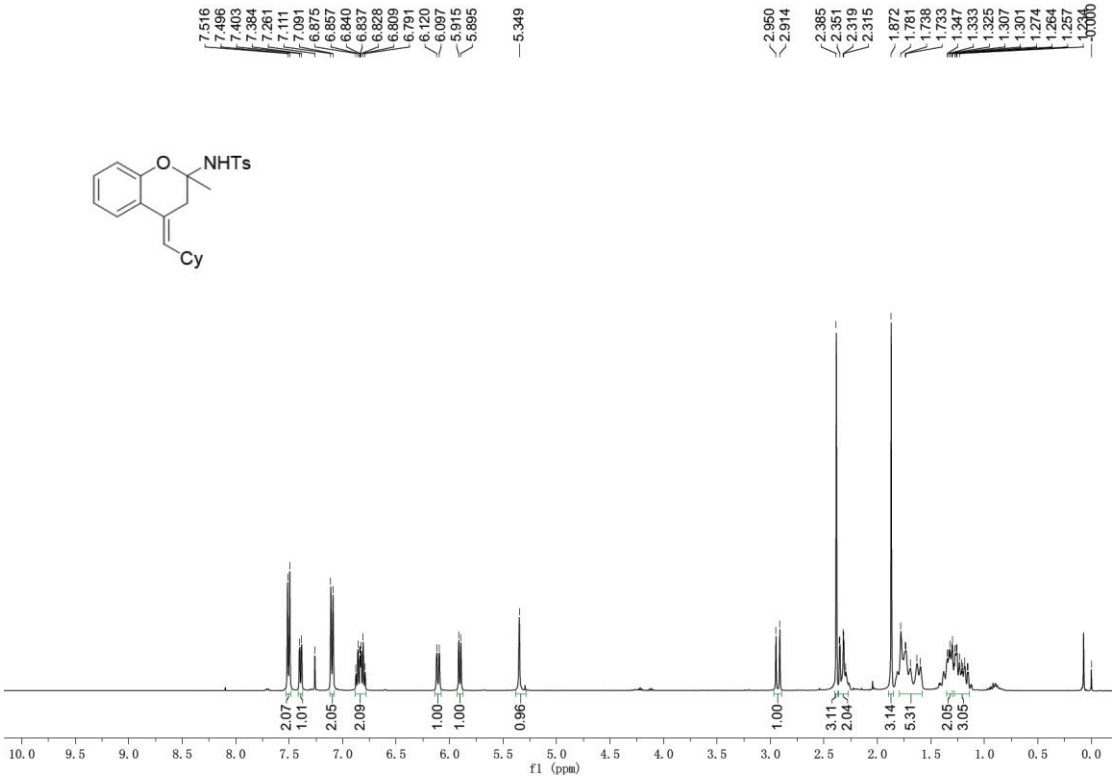
7-^{1}H NMR (400 MHz, CD_3OD)



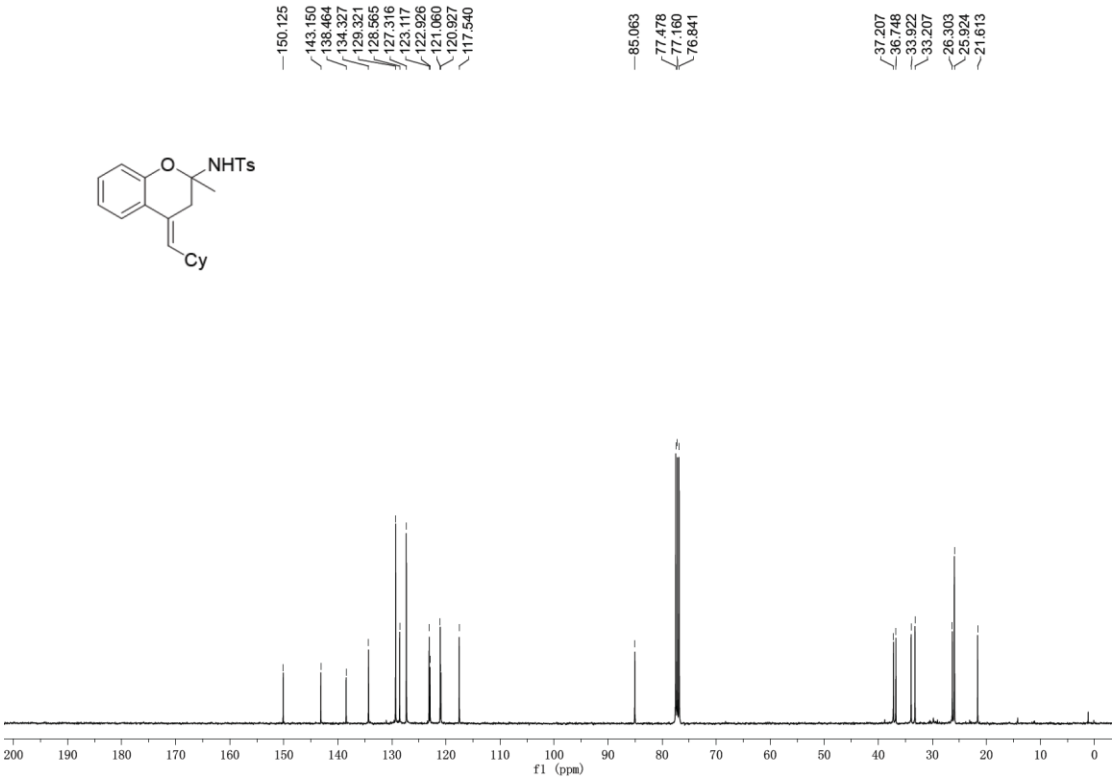
7-^{13}C NMR (100 MHz, CD_3OD)



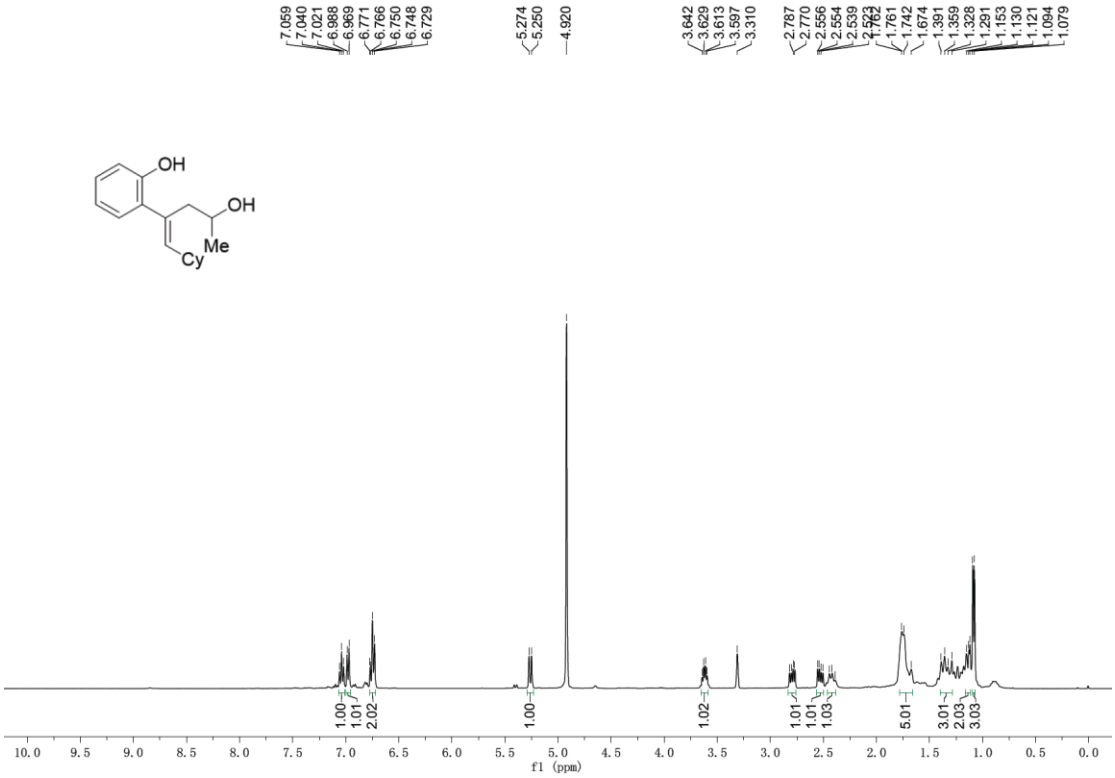
10-^{1}H NMR (400 MHz, $CDCl_3$)



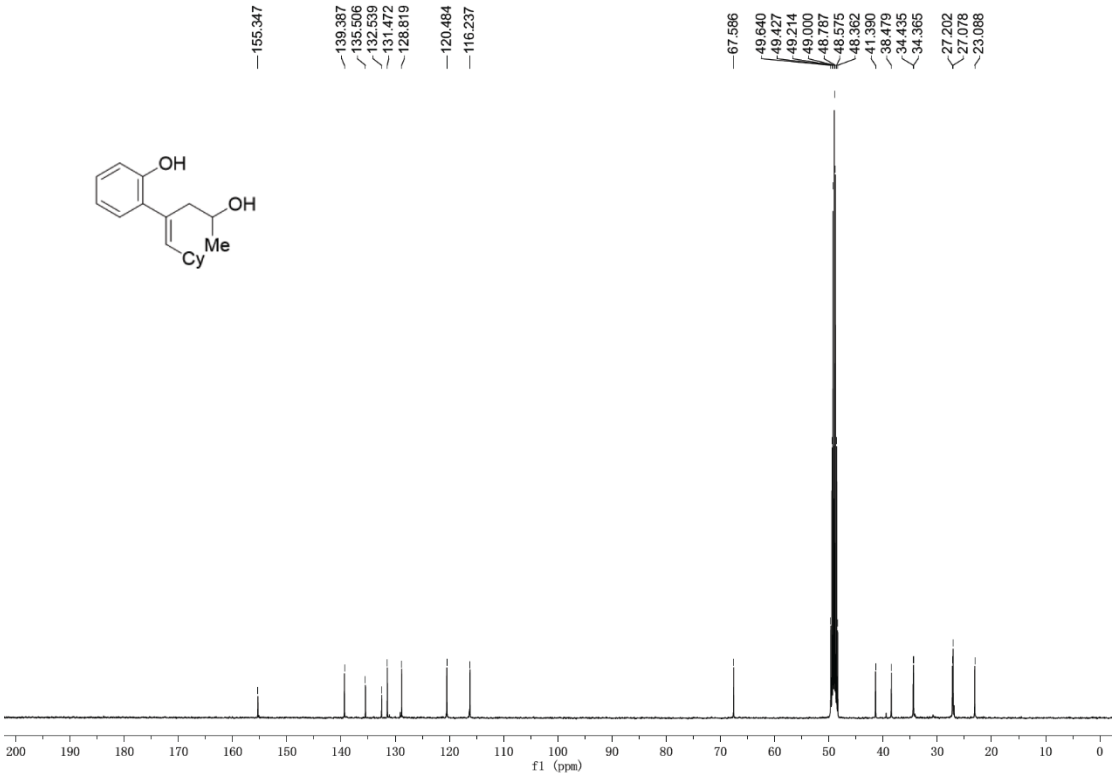
10-^{13}C NMR (100 MHz, $CDCl_3$)



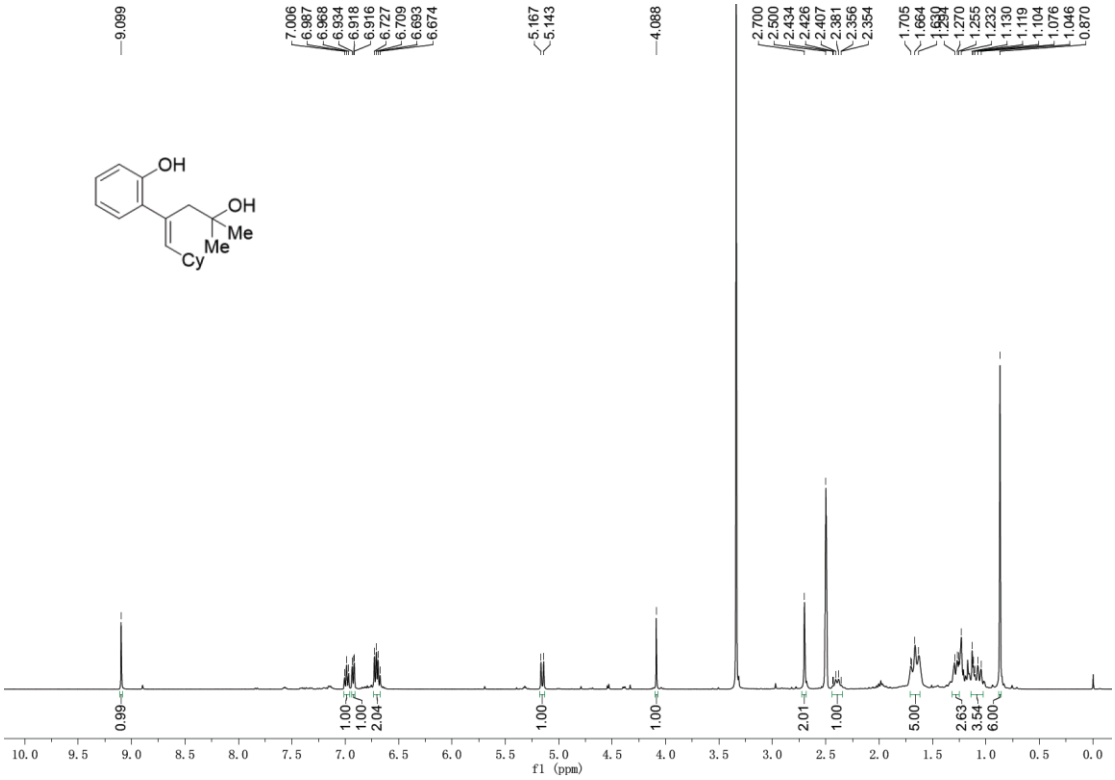
11-^{1}H NMR (400 MHz, CD_3OD)



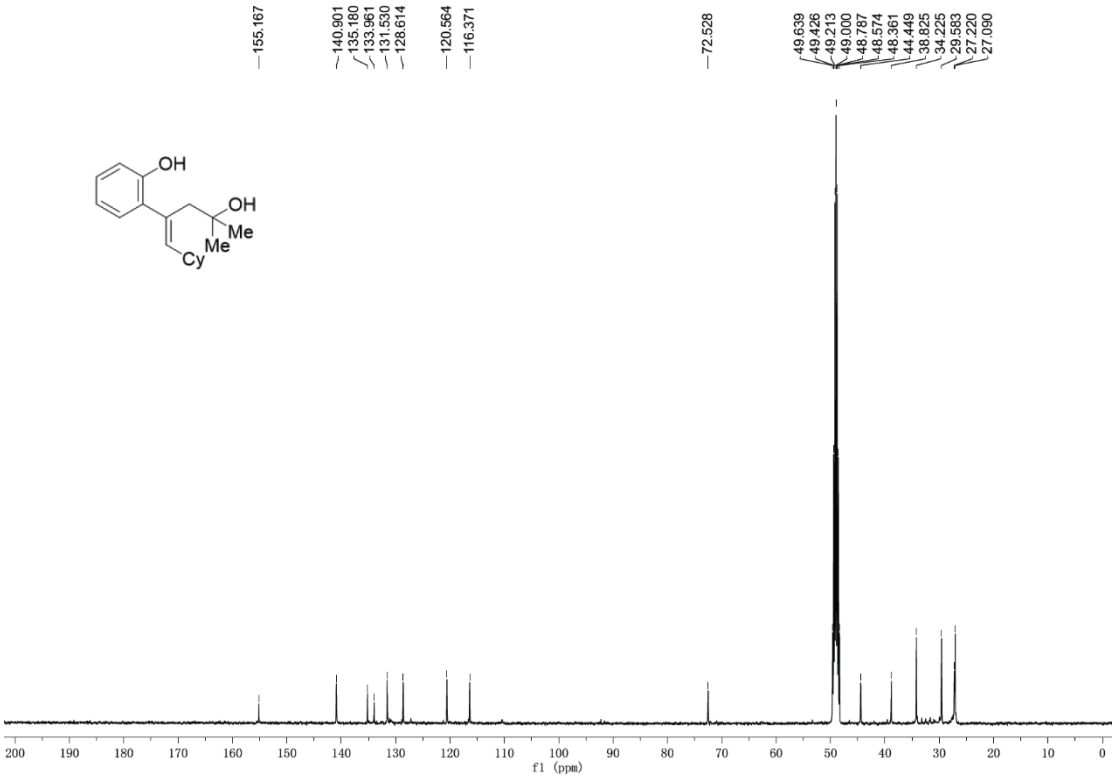
11-^{13}C NMR (100 MHz, CD_3OD)



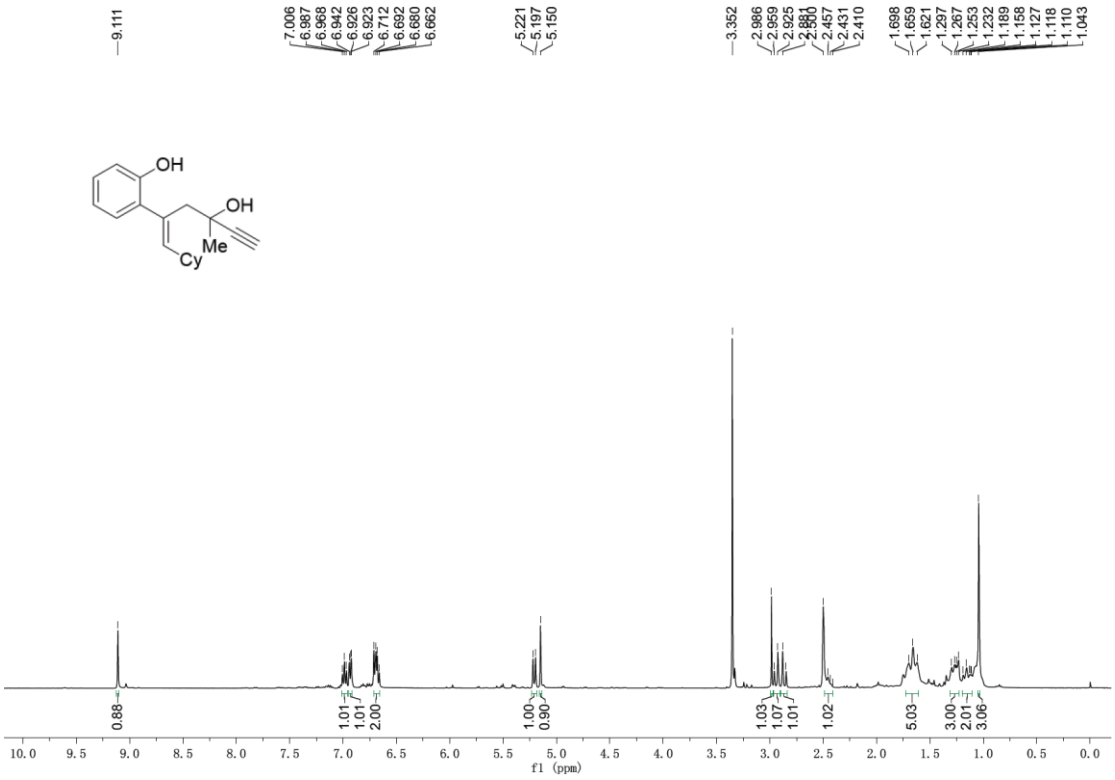
12-^{1}H NMR (400 MHz, DMSO-d_6)



12-^{13}C NMR (100 MHz, CD_3OD)



13-^{1}H NMR (400 MHz, DMSO-d_6)



13-^{13}C NMR (100 MHz, CD_3OD)