Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

of

Highly diastereoselective synthesis of 3-hydroxy-2,2,3-trisubstituted indolines *via* intramolecular trapping of ammonium ylides with ketones

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1. General Information:

All solvents were purified and dried using standard procedures. Diazo compounds **1**,[1] 2′-Aminochalcones **2**,[2] and 2-(*N*-alkylamino)phenyl ketones **7**[3] were prepared according to literature procedures. All NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts (δ value) were reported in ppm down field from internal tetramethylsilane (TMS). HRMS (ESI) Mass Spectra were recorded on IonSpec FT-ICR mass spectrometer.

2. Experimental Procedures

2.1 General procedure for $Rh_2(OAc)_4$-catalyzed reaction of diazo compounds and 2′-aminochalcones:

Diazo compound **1** (0.48 mmol) in 1.5 mL of CH_2Cl_2 was added to the mixture of **2** (0.30 mmol), $Rh_2(OAc)_4$ (1.0 mmol%) and 4 Å MS (300 mg) in 1.5 mL of CH_2Cl_2 *via* syringe pump over 1 h at 40 ºC. The reaction mixture was purified by flash chromatography on silica gel to give pure *cis*-**3**.

2.2 General procedure for $Rh_2(OAc)_4$-catalyzed reaction of diazo compounds and 2-(*N*-alkylamino)phenyl ketones:

Diazo compound **1** (0.36 mmol) in 1.5 mL of toluene was added to the mixture of **7** (0.30 mmol), $Rh_2(OAc)_4$ (1.0 mmol%), 4 Å MS (300 mg) in 1.5 mL of toluene *via* syringe pump over 1 h at 25 ºC. The reaction mixture was purified by flash chromatography on silica gel to give pure *cis*-**8**.

2.3 Procedure for the reaction between aryldiazoacetate 1a and 2′-aminoacetophenone 4a:

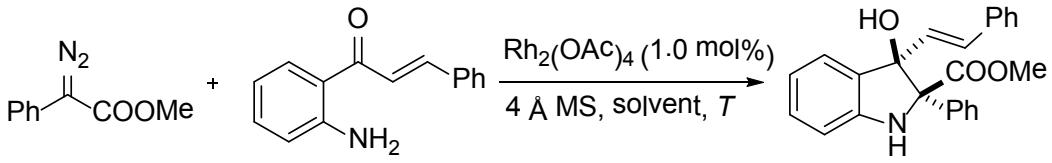
1a (0.24 mmol) in CH_2Cl_2 (1.0 mL) was added to a mixture of **4a** (0.20 mmol) and $Rh_2(OAc)_4$ (1 mol%) in CH_2Cl_2 (1.0 mL) over a period of 1 h *via* syringe pump at 25 ^oC. The reaction mixture was purified by flash chromatography to give pure **5a** (48.2mg, 85% yield).

2.4 Procedure for preparation of compound 9 from *cis*-8a:

A mixture of compound *cis*-**8a** (29.7 mg, 0.10 mmol), *p*-toluenesulfonic acid monohydrate (3.8 mg, 0.02 mmol) and cyclohexane (1.0 mL) was refluxed for 2 h under azeotropic distillation. TLC indicated the reaction was complete. The reaction mixture was cooled to room temperature. The solvent was removed under vacuum to give the crude product. The resulted crude product was purified by column chromatography on silica gel to give the product **9** (25.0 mg, 90% yield).

3. Table S1 and S2 for detailed condition optimizations.

Table S1 Condition optimization for $Rh_2(OAc)_4$-catalyzed reaction of **1a** and **2a**. [a]

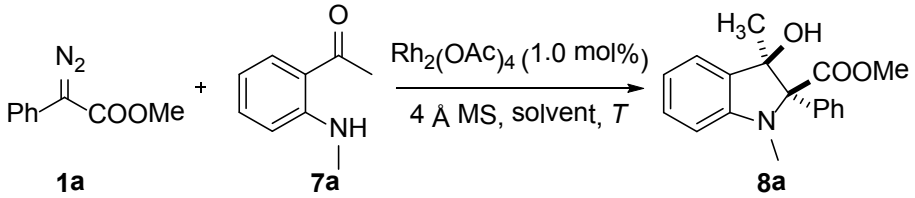


1a **2a** **3a**

Entry	Solvent	*T* (ºC)	Eq.(**1a**:**2a**)	Yield (%)[b]	Dr[c]
1[d]	CH_2Cl_2	40	1.4:1.0	72	>95:5
2	CH_2Cl_2	40	1.4:1.0	87	>95:5
3	DCE	40	1.4:1.0	81	>95:5
4	toluene	40	1.4:1.0	75	>95:5
5	CH_2Cl_2	25	1.4:1.0	79	>95:5
6	CH_2Cl_2	40	1.6:1.0	94	>95:5

[a] Unless otherwise noted, the reaction was carried out on a 0.10 mmol scale. Methyl phenyldiazoacetate **1a** in 0.5 mL of solvent was added to the mixture of **2a**, $Rh_2(OAc)_4$ (1.0 mmol%) and 4 Å MS (100 mg) within 1 h *via* syringe pump. [b] Isolated yield. [c] Determined by ^{1}H NMR spectroscopy of the crude reaction mixture. [d] Without the addition of 4 Å MS.

Table S2 Condition optimization for $Rh_2(OAc)_4$-catalyzed reaction of **1a** and **7a**. [a]



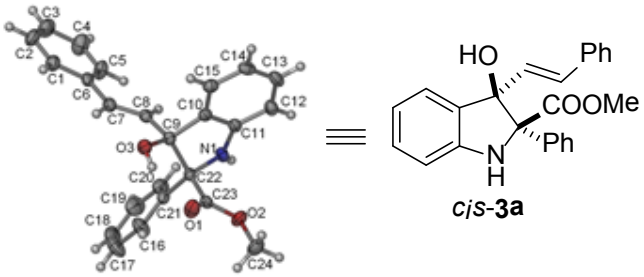
1a **7a** **8a**

Entry	Solvent	*T* (°C)	Yield (%)[b]	Dr[c]
1	CH_2Cl_2	25	89	>95:5
2	toluene	25	97	>95:5
3	DCE	25	90	>95:5
4	toluene	40	96	>95:5
5	toluene	0	93	>95:5

[a] Unless otherwise noted, the reaction was carried out on a 0.10 mmol scale, **1a**:**7a** = 1.2:1.0. Aryldiazoacetate **1a** (0.12 mmol) in 0.5 mL of solvent was added to the mixture of **7a** (0.10 mmol), $Rh_2(OAc)_4$ (1.0 mmol%), 4 Å MS (100 mg) in 0.5 mL of solvent *via* syringe pump over 1 h. [b] Isolated yield of **8a**. [c] Determined by ^{1}H NMR of the crude reaction mixture.

4. X-ray diffraction parameters and data

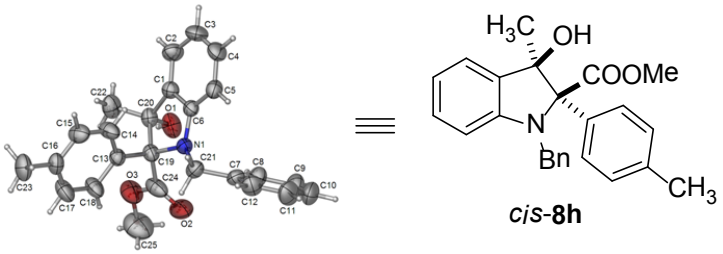
4.1. X-ray diffraction parameters and data for *cis*-3a (CCDC 957672)



Identification code	z
Empirical formula	C24 H21 N O3
Formula weight	371.42
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 10.7586(6) A alpha = 90 deg.
	b = 16.5601(10) A beta = 90 deg.
	c = 21.4710(13) A gamma = 90 deg.
Volume	3825.3(4) A^3
Z, Calculated density	8, 1.290 Mg/m^3
Absorption coefficient	0.085 mm^-1
F(000)	1568
Crystal size	0.55 x 0.45 x 0.24 mm
Theta range for data collection	1.90 to 25.01 deg.
Limiting indices	-12<=h<=12, -19<=k<=19, -25<=l<=25
Reflections collected / unique	41206 / 3370 [R(int) = 0.0502]
Completeness to theta = 25.01	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9799 and 0.9548
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3370 / 0 / 253

Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0460, wR2 = 0.1189
R indices (all data)	R1 = 0.0550, wR2 = 0.1283
Largest diff. peak and hole	0.563 and -0.621 e.A^-3

4.2. X-ray diffraction parameters and data for *cis*-8h (CCDC 957673)



Identification code	z
Empirical formula	C25 H25 N O3
Formula weight	387.46
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.0938(5) A alpha = 90 deg. b = 19.9876(10)A beta = 115.150(2) deg. c = 11.2239(6) A gamma = 90 deg.
Volume	2049.76(18) A^3
Z, Calculated density	4, 1.256 Mg/m^3
Absorption coefficient	0.082 mm^-1
F(000)	824
Crystal size	0.24 x 0.19 x 0.12 mm
Theta range for data collection	2.23 to 25.01 deg.
Limiting indices	-12<=h<=12, -23<=k<=23, -13<=l<=13
Reflections collected / unique	23363 / 3577 [R(int) = 0.0477]
Completeness to theta = 25.01	99.0 %

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9902 and 0.9806
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3577 / 0 / 262
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0639, wR2 = 0.1741
R indices (all data)	R1 = 0.0930, wR2 = 0.2001
Largest diff. peak and hole	1.183 and -0.272 e.A^-3

5. Notes and References

1. Doyle, M. P., Mckervey, M. A. and Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, (1998).

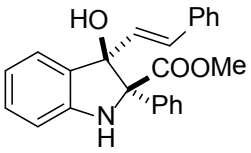
2. Y. Xia, Z-Y Yang, P Xia, K. F. Bastow, Y. Tachibana, S.-C. Kuo, E. Hamel, T. Hackl, and K.-H. Lee, *J. Med. Chem.*, 1998, **41**, 1155.

3. M. Martjuga, S. Belyakov, E. Liepinsh, E. Suna, *J. Org. Chem.*, 2011, **76**, 2635; A. F. Bella, A. M. Z. Slawin, and J. C. Walton, *J. Org. Chem.*, 2004, **69**, 5926.

6. Analytical Data for the Products

6.1 Analytical Data for 3

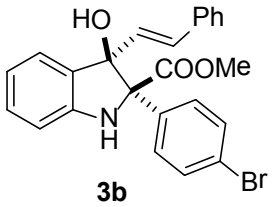
(2*S,3*R**)-methyl 3-hydroxy-2-phenyl-3-((*E*)-styryl)indoline-2-carboxylate (3a)**



3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.32-7.29 (m, 3H), 7.21-7.12 (m, 5H), 7.03-7.01 (m, 2H), 6.86-6.82 (m, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 5.73 (d, *J* = 15.9 Hz, 1H), 5.11 (s, 1H), 4.76 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.61, 147.49, 136.98, 136.69, 131.92, 129.93, 129.59, 128.97, 128.38, 128.28, 128.25, 127.24, 126.55, 126.21, 124.34, 120.61, 110.29 , 85.88, 79.56, 53.01; HRMS (ESI): Exact mass calcd for $C_{24}H_{21}NNaO_3$ $[M+Na]^+$: 394.1414, Found 394.1408.

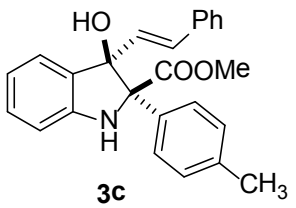
(2*S,3*R**)-methyl**
2-(4-bromophenyl)-3-hydroxy-3-((*E*)-styryl)indoline-2-carboxylate (3b)



3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.45-7.42 (m, 2H), 7.20-7.15 (m, 5H), 7.07-7.05 (m, 2H), 6.87-6.82 (m, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 5.71 (d, *J* = 15.9 Hz, 1H), 5.06 (s, 1H), 4.77 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.27, 147.13, 136.71, 135.81, 131.91, 131.49, 129.72, 129.37, 129.29, 128.40, 128.15, 127.48, 126.59, 124.27, 122.42, 120.93, 110.58, 85.89, 79.11, 53.24; HRMS (ESI): Exact mass calcd for $C_{24}H_{20}BrNNaO_3$ $[M+Na]^+$: 394.1414, Found 394.1406.

(2*S,3*R**)-methyl 3-hydroxy-3-((*E*)-styryl)-2-(p-tolyl)indoline-2-carboxylate (3c)**



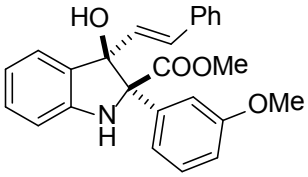
3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.20-7.11 (m, 7H), 7.07-7.05

(m, 2H), 6.86-6.81 (m, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 5.78 (d, *J* = 15.9 Hz, 1H), 5.12 (s, 1H), 4.76 (s, 1H), 3.69 (s, 3H) , 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.77, 147.53, 138.03, 137.03, 133.59, 131.97, 129.90, 129.59, 129.15, 128.85, 128.28, 127.24, 126.62, 126.12, 124.33, 120.55, 110.27, 85.74, 79.39, 53.05, 21.15; HRMS (ESI): Exact mass calcd for $C_{25}H_{23}NNaO_3$ $[M+Na]^+$: 408.1570, Found 408.1569.

(2*S,3*R**)-methyl**

3-hydroxy-2-(3-methoxyphenyl)-3-((*E*)-styryl)indoline-2-carboxylate (3d)

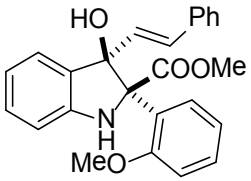


3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.11 (m, 8H), 7.07-7.05 (m, 2H), 6.88-6.81 (m, 3H), 6.43 (d, *J* = 15.9 Hz, 1H), 5.77 (dd, *J* = 15.9, 0.5 Hz, 1H), 5.22 (d, *J* = 0.6 Hz, 1H), 4.76 (s, 1H), 3.72 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.67, 159.61, 147.37, 138.18, 136.96, 131.89, 129.84, 129.61, 129.47, 128.89, 128.30, 127.29, 126.59, 124.33, 120.65, 118.55, 113.86, 111.96, 110.32, 85.81, 79.38, 55.26, 53.13; HRMS (ESI): Exact mass calcd for $C_{25}H_{23}NNaO_4$ $[M+Na]^+$: 424.1519, Found 424.1515.

(2*S,3*R**)-methyl**

3-hydroxy-2-(2-methoxyphenyl)-3-((*E*)-styryl)indoline-2-carboxylate (3e)

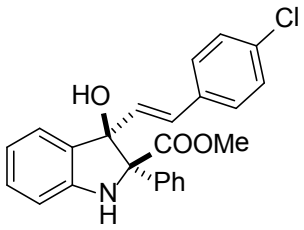


3e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.26-7.21 (m, 2H), 7.18-7.09 (m, 4H), 6.99-6.97 (m, 3H), 6.89-6.87 (m, 2H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 5.87 (s, 1H), 5.76 (d, *J* = 15.9 Hz, 1H), 4.32 (s, 1H), 3.78 (s, 3H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.80, 157.34, 146.73, 137.12, 132.33, 131.14, 129.40, 129.10, 128.22, 127.90, 127.80, 127.13, 126.87, 126.53, 124.33, 120.69,

120.54, 111.69, 109.80, 86.18, 56.08, 52.56; HRMS (ESI): Exact mass calcd for $C_{25}H_{23}NNaO_4$ $[M+Na]^+$: 424.1519, Found 424.1518.

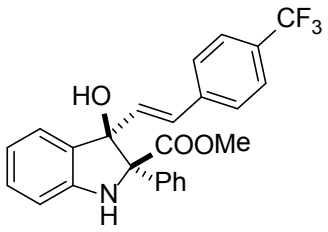
(2*S,3*R**)-methyl**
3-((*E*)-4-chlorostyryl)-3-hydroxy-2-phenylindoline-2-carboxylate (3f)



3f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.34-7.27 (m, 3H), 7.21-7.17 (m, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.88-6.82 (m, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.70 (d, *J* = 15.9 Hz, 1H), 5.26 (s, 1H), 4.76 (s, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.76, 147.35, 136.49, 135.45, 132.85, 131.80, 130.68, 129.63, 128.41, 128.36, 127.72, 127.63, 126.09, 124.23, 120.71, 110.39, 85.79, 79.39, 53.10; HRMS (ESI): Exact mass calcd for $C_{24}H_{20}ClNNaO_3$ $[M+Na]^+$: 428.1024, Found 428.1017.

(2*S,3*R**)-methyl**
3-hydroxy-2-phenyl-3-((*E*)-4-(trifluoromethyl)styryl)indoline-2-carboxylate (3g)



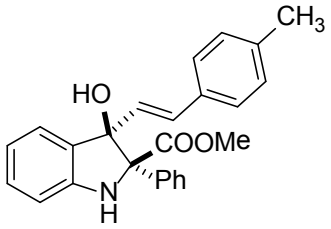
3g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.35-7.30 (m, 3H), 7.24-7.20 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.89-6.83 (m, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 5.83 (d, *J* = 15.9 Hz, 1H), 5.36 (d, *J* = 0.7 Hz, 1H), 4.78 (s, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.80, 147.28, 140.47, 140.46, 136.38, 132.68, 131.67, 129.70, 129.00 (q, *J* = 257.1 Hz), 128.47, 128.43, 127.36, 126.63, 126.04, 125.22 (q, *J* = 30.2 Hz), 124.16, 120.79, 110.46, 85.74, 79.32, 53.14; HRMS (ESI):

Exact mass calcd for $C_{25}H_{20}F_3NNaO_3$ $[M+Na]^+$: 462.1287, Found 462.1283.

(2*S,3*R**)-methyl**

3-hydroxy-3-((*E*)-4-methylstyryl)-2-phenylindoline-2-carboxylate (3h)

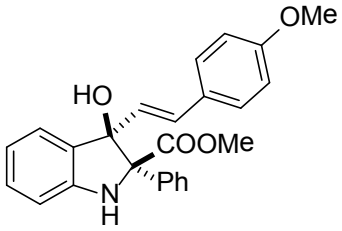


3h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.32-7.27 (m, 3H), 7.22-7.16 (m, 2H), 6.97-6.91 (m, 4H), 6.86-6.81 (m, 2H), 6.39 (d, *J* = 15.9 Hz, 1H), 5.68 (d, *J* = 15.9 Hz, 1H), 5.09 (s, 1H), 4.77 (s, 1H), 3.68 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.65, 147.55, 137.06, 136.75, 134.16, 131.99, 129.60, 129.00, 128.90, 128.89, 128.38, 128.27, 126.49, 126.26, 124.40, 120.58, 110.29, 85.94, 79.60, 53.04, 21.15; HRMS (ESI): Exact mass calcd for $C_{25}H_{23}NNaO_3$ $[M+Na]^+$: 408.1570, Found 408.1567.

(2*S,3*R**)-methyl**

3-hydroxy-3-((*E*)-4-methoxystyryl)-2-phenylindoline-2-carboxylate (3i)

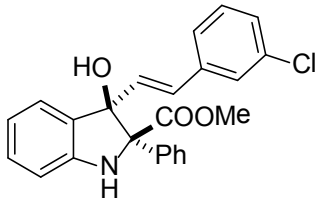


3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.34-7.28 (m, 3H), 7.21-7.17 (m, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.87-6.82 (m, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.34 (d, *J* = 15.9 Hz, 1H), 5.58 (d, *J* = 15.9 Hz, 1H), 5.08 (s, 1H), 4.76 (s, 1H), 3.72 (s, 3H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.64, 158.99, 147.53, 136.77, 132.01, 129.74, 129.56, 128.52, 128.35, 128.24, 127.79, 127.71, 126.24, 124.40, 120.56, 113.70, 110.26, 85.95, 79.59, 55.21, 53.02; HRMS (ESI): Exact mass calcd for $C_{25}H_{23}NNaO_4$ $[M+Na]^+$: 424.1519, Found 424.1516.

(2*S,3*R**)-methyl**

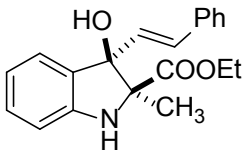
3-((*E*)-3-chlorostyryl)-3-hydroxy-2-phenylindoline-2-carboxylate (3j)



3j

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 2H), 7.34-7.28 (m, 3H), 7.20-7.17 (m, 2H), 7.06-7.05 (m, 2H), 6.98 (s, 1H), 6.88-6.82 (m, 3H), 6.37 (d, *J* = 15.9 Hz, 1H), 5.74 (d, *J* = 15.9 Hz, 1H), 5.30 (s, 1H), 4.78 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.79, 147.31, 138.90, 136.43, 134.17, 131.78, 131.55, 129.66, 129.48, 128.46, 128.41, 127.47, 127.17, 126.49, 126.09, 124.70, 124.18, 120.74, 110.43, 85.75, 79.37, 53.12; HRMS (ESI): Exact mass calcd for $C_{24}H_{20}ClNNaO_3$ $[M+Na]^+$: 428.1024, Found 428.1024.

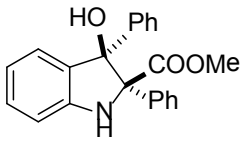
(2*S,3*R**)-ethyl 3-hydroxy-2-methyl-3-((*E*)-styryl)indoline-2-carboxylate (3k)**



3k

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23-7.18 (m, 2H), 6.88 (d, *J* = 16.1 Hz, 1H), 6.84-6.78 (m, 2H), 6.48 (d, *J* = 16.0 Hz, 1H), 4.41 (s, 1H), 4.34-4.21 (m, 2H), 2.65 (s, 1H), 1.45 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.14, 148.74, 136.78, 131.66, 130.81, 130.42, 128.62, 127.78, 127.57, 126.71, 125.04, 120.02, 111.57, 84.64, 75.20, 61.51, 23.25, 14.23; HRMS (ESI): Exact mass calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$: 346.1419, Found 346.1418.

(2*S,3*R**)-methyl 3-hydroxy-2,3-diphenylindoline-2-carboxylate (3l)**

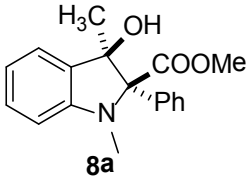


3l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 1H), 7.21-7.19 (m, 2H), 7.14-7.12 (m, 1H), 7.10-7.03 (m, 3H), 6.99-6.92 (m, 3H), 6.90-6.90 (m, 1H), 6.88-6.85 (m, 3H), 5.57 (s, 1H), 4.70 (s, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.16, 148.23, 140.13, 136.45, 133.93, 129.63, 127.73, 127.41, 126.89, 126.82, 126.03, 124.73, 120.90, 110.20, 88.18, 80.45, 53.02; HRMS (ESI): Exact mass calcd for $C_{22}H_{19}NNaO_3$ $[M+Na]^+$: 368.1257, Found 368.1261.

6.2 Analytical Data for 8 and 9

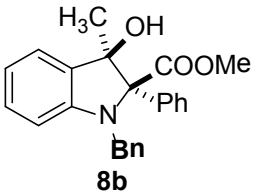
(2*S**,3*R**)-methyl 3-hydroxy-1,3-dimethyl-2-phenylindoline-2-carboxylate (8a)



8a

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 7.25-7.20 (m, 2H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 7.7 Hz, 1H), 3.83 (s, 1H), 3.74 (s, 3H), 2.77 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.88, 149.47, 135.83, 134.29, 129.43, 128.10, 127.99, 127.22, 121.90, 119.13, 107.25, 86.05, 83.44, 51.78, 32.45, 25.41; HRMS (ESI): Exact mass calcd for $C_{18}H_{19}NNaO_3$ $[M+Na]^+$: 320.1257, Found 320.1286.

(2*S**,3*R**)-methyl 1-benzyl-3-hydroxy-3-methyl-2-phenylindoline-2-carboxylate (8b)

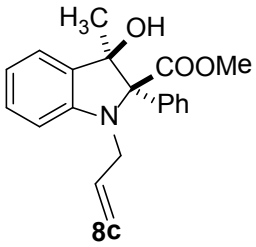


8b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.37-7.24 (m, 9H), 7.05-7.01 (m, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.19 (d, *J* = 7.8 Hz, 1H), 4.40 (d, *J* = 16.7 Hz, 1H), 4.16 (d, *J* = 16.7 Hz, 1H), 3.94 (s, 1H), 3.74 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 172.30, 148.84, 138.41, 136.04, 134.61, 129.25, 128.62, 128.37, 128.16, 126.80, 126.77, 126.45, 121.86, 119.49, 109.07, 86.51, 83.29, 52.01, 51.16, 24.65; HRMS (ESI): Exact mass calcd for $C_{24}H_{23}NNaO_3$ $[M+Na]^+$: 396.1570, Found 396.1563.

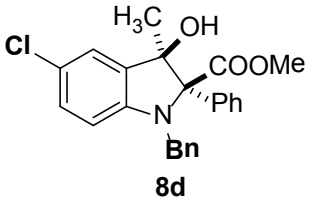
(2*S,3*R**)-methyl 1-allyl-3-hydroxy-3-methyl-2-phenylindoline-2-carboxylate (8c)**



8c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 5H), 7.24-7.22 (m, 1H), 7.17-7.13 (m, 1H), 6.84-6.80 (m, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.06-5.97 (m, 1H), 5.36-5.24 (m, 2H), 3.96 (s, 1H), 3.86-3.80 (m, 1H), 3.72 (s, 3H), 3.58-3.52 (m, 1H), 1.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.34, 148.74, 136.09, 134.77, 134.61, 129.14, 128.22, 128.09, 127.02, 121.78, 119.27, 116.19, 108.56, 86.30, 83.31, 51.97, 49.86, 25.09; HRMS (ESI): Exact mass calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$: 346.1414, Found 346.1410.

(2*S,3*R**)-methyl 1-benzyl-5-chloro-3-hydroxy-3-methyl-2-phenylindoline-2-carboxylate (8d)**



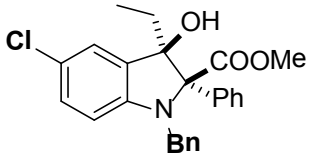
8d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.26 (m, 10H), 7.22 (d, *J* = 2.2 Hz, 1H), 6.96 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.08 (d, *J* = 8.4 Hz, 1H), 4.44 (d, *J* = 16.8 Hz, 1H), 4.12 (d, *J* = 16.8 Hz, 1H), 4.12 (s, 1H), 3.74 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.22, 147.19, 137.83, 136.71, 135.44, 128.90, 128.77, 128.49, 128.37, 126.99,

126.71, 126.33, 124.45, 122.35, 110.07, 86.52, 83.03, 52.17, 51.09, 24.90; HRMS (ESI): Exact mass calcd for $C_{24}H_{22}ClNNaO_3$ $[M+Na]^+$: 430.1180, Found 430.1180.

(2*S,3*R**)-methyl**

1-benzyl-5-chloro-3-ethyl-3-hydroxy-2-phenylindoline-2-carboxylate (8e)

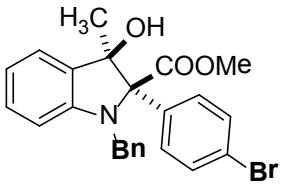


8e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 6H), 7.33-7.29 (m, 4H), 7.22 (d, *J* = 2.2 Hz, 1H), 6.94 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.07 (d, *J* = 8.3 Hz, 1H), 4.68 (d, *J* = 17.0 Hz, 1H), 4.65 (d, *J* = 2.2 Hz, 1H), 3.99 (d, *J* = 17.0 Hz, 1H), 3.71 (s, 3H), 1.53-1.47 (m, 1H), 1.05-0.96 (m, 1H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.05, 146.67, 137.72, 135.82, 134.80, 128.91, 128.39, 128.29, 128.27, 127.04, 126.90, 126.12, 124.58, 123.65, 110.59, 86.95, 85.02, 52.14, 51.07, 29.63, 7.11; HRMS (ESI): Exact mass calcd for $C_{25}H_{24}ClNNaO_3$ $[M+Na]^+$: 444.1337, Found 444.1329.

(2*S,3*R**)-methyl**

1-benzyl-2-(4-bromophenyl)-3-hydroxy-3-methylindoline-2-carboxylate (8f)

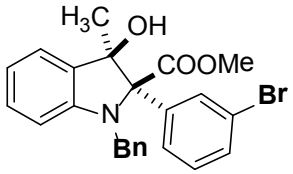


8f

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 6H), 7.29-7.23 (m, 4H), 7.06-7.02 (m, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.20 (d, *J* = 7.8 Hz, 1H), 4.35 (d, *J* = 16.7 Hz, 1H), 4.13 (d, *J* = 16.8 Hz, 1H), 3.83 (s, 1H), 3.73 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.76, 148.68, 138.08, 135.21, 134.38, 131.52, 129.38, 128.70, 128.63, 126.91, 126.38, 122.25, 121.89, 119.75, 109.19, 86.29, 83.29, 52.15, 51.15, 24.86; HRMS (ESI): Exact mass calcd for $C_{24}H_{22}BrNNaO_3$ $[M+Na]^+$: 474.0675, Found 474.0668.

(2*S,3*R**)-methyl**

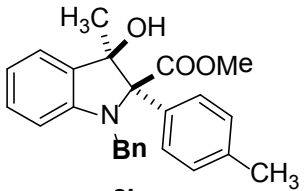
1-benzyl-2-(3-bromophenyl)-3-hydroxy-3-methylindoline-2-carboxylate (8g)



8g

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.5 Hz, 1H), 7.46-7.34 (m, 5H), 7.27-7.24 (m, 3H), 7.16 (t, *J* = 7.9 Hz, 1H), 7.06-7.02 (m, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.21 (d, *J* = 7.8 Hz, 1H), 4.37 (d, *J* = 16.7 Hz, 1H), 4.14 (d, *J* = 16.8 Hz, 1H), 3.82 (s, 1H), 3.74 (s, 3H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.59, 148.67, 138.52, 138.06, 134.29, 131.32, 130.11, 129.89, 129.41, 128.69, 126.93, 126.42, 125.47, 122.48, 121.92, 119.77, 109.18, 86.24, 83.44, 52.21, 51.21, 24.97; HRMS (ESI): Exact mass calcd for $C_{24}H_{22}BrNNaO_3$ $[M+Na]^+$: 474.0675, Found 474.0674.

(2*S,3*R**)-methyl 1-benzyl-3-hydroxy-3-methyl-2-(p-tolyl)indoline-2-carboxylate (8h)**

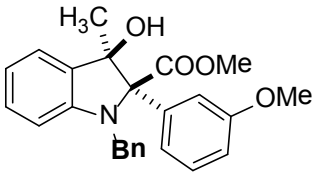


8h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05-7.01 (m, 1H), 6.82-6.78 (m, 1H), 6.18 (d, *J* = 7.8 Hz, 1H), 4.36 (d, *J* = 16.7 Hz, 1H), 4.16 (d, *J* = 16.7 Hz, 1H), 3.89 (s, 1H), 3.73 (s, 3H), 2.32 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.41, 149.00, 138.53, 137.95, 134.55, 133.02, 129.26, 129.09, 128.60, 126.73, 126.48, 121.88, 119.37, 108.95, 86.42, 83.23, 51.98, 51.15, 24.51, 21.08; HRMS (ESI): Exact mass calcd for $C_{25}H_{25}NNaO_3$ $[M+Na]^+$: 410.1727, Found 410.1713.

(2*S,3*R**)-methyl**

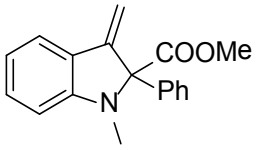
1-benzyl-3-hydroxy-2-(3-methoxyphenyl)-3-methylindoline-2-carboxylate (8i)



8i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28-7.20 (m, 3H), 7.04-7.02 (m, 1H), 6.93-6.91 (m, 2H), 6.86-6.80 (m, 2H), 6.22 (d, *J* = 7.8 Hz, 1H), 4.45 (d, *J* = 16.8 Hz, 1H), 4.18 (d, *J* = 16.9 Hz, 1H), 4.03 (s, 1H), 3.74 (s, 3H), 3.54 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.30, 159.46, 148.71, 138.49, 137.51, 134.71, 129.39, 129.21, 128.63, 126.77, 126.41, 121.82, 119.57, 119.30, 113.90, 112.31, 108.92, 86.46, 83.33, 54.97, 52.05, 51.09, 24.80; HRMS (ESI): Exact mass calcd for $C_{25}H_{25}NNaO_4$ $[M+Na]^+$: 426.1676, Found 426.1670.

Methyl 1-methyl-3-methylene-2-phenylindoline-2-carboxylate (9)



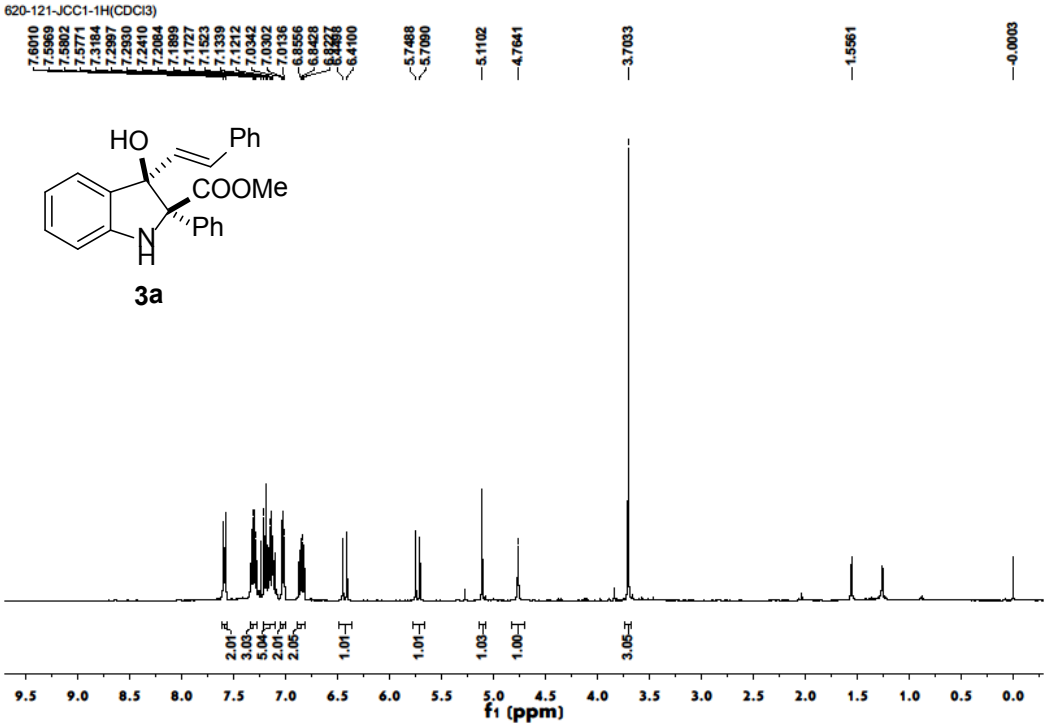
9

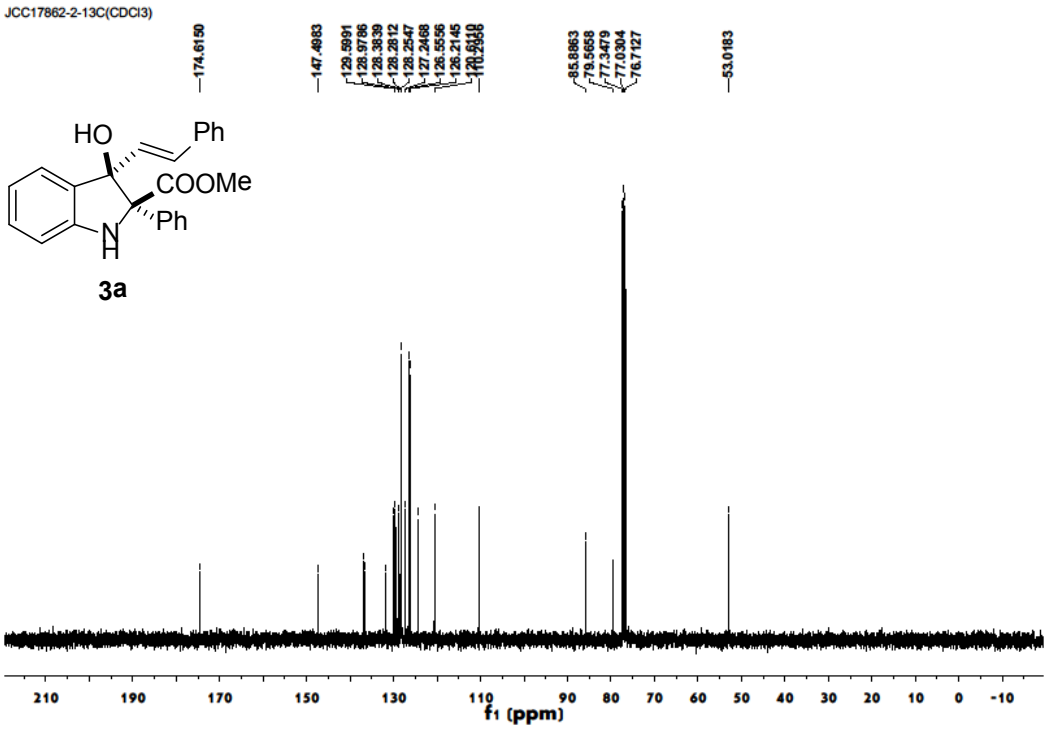
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.21 (m, 6H), 7.14-7.10 (m, 1H), 6.62-6.58 (m, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.56 (s, 1H), 5.03 (s, 1H), 3.72 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.87, 150.85, 147.74, 139.03, 129.72, 127.28, 126.88, 126.81, 123.23, 119.43, 116.00, 104.79, 104.67, 78.99, 51.65, 28.60; HRMS (ESI): Exact mass calcd for $C_{18}H_{17}NNaO_2$ $[M+Na]^+$: 302.1151, Found 302.1189.

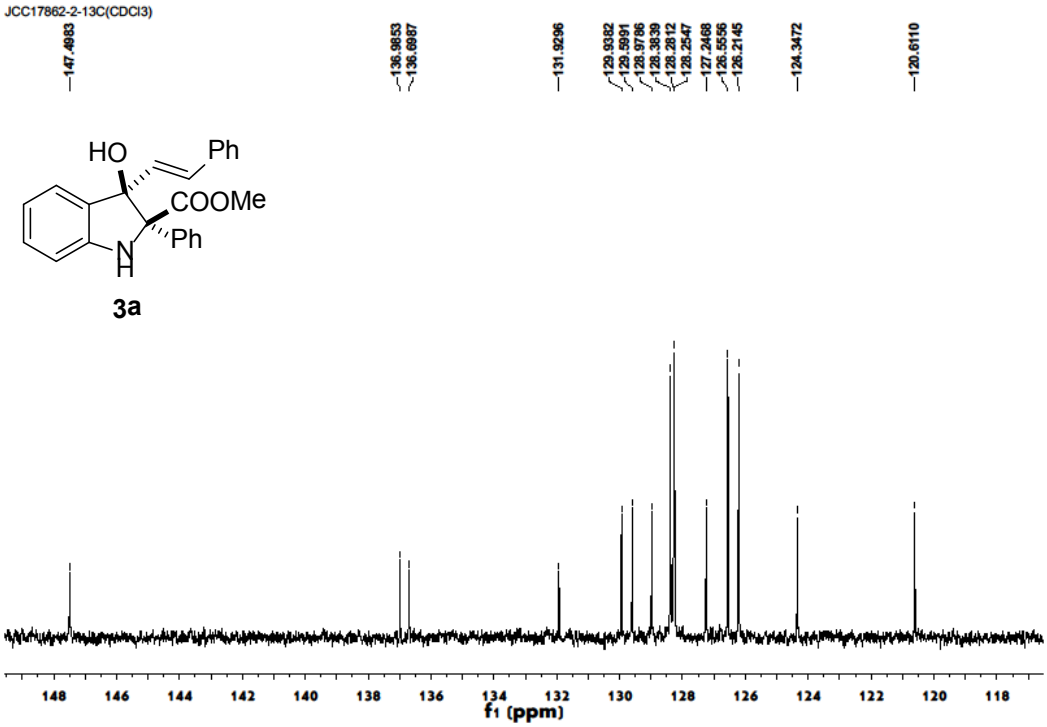
7. NMR spectra for the Products

7.1 NMR spectra for 3

(2*S,3*R**)-methyl 3-hydroxy-2-phenyl-3-((*E*)-styryl)indoline-2-carboxylate (3a)**

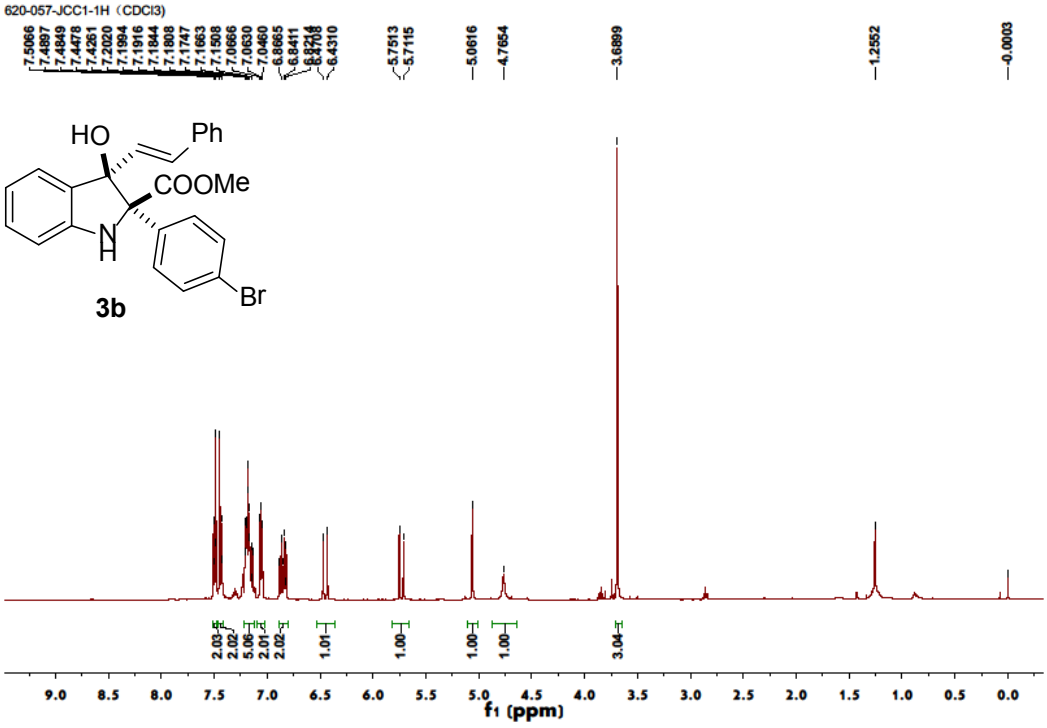


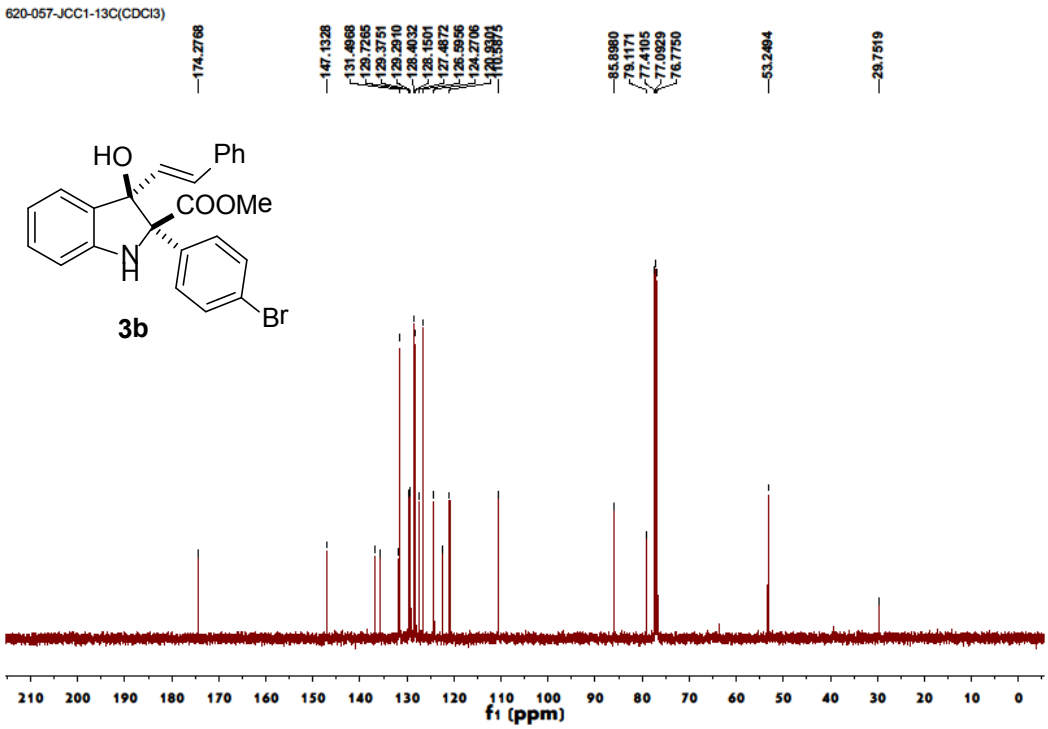


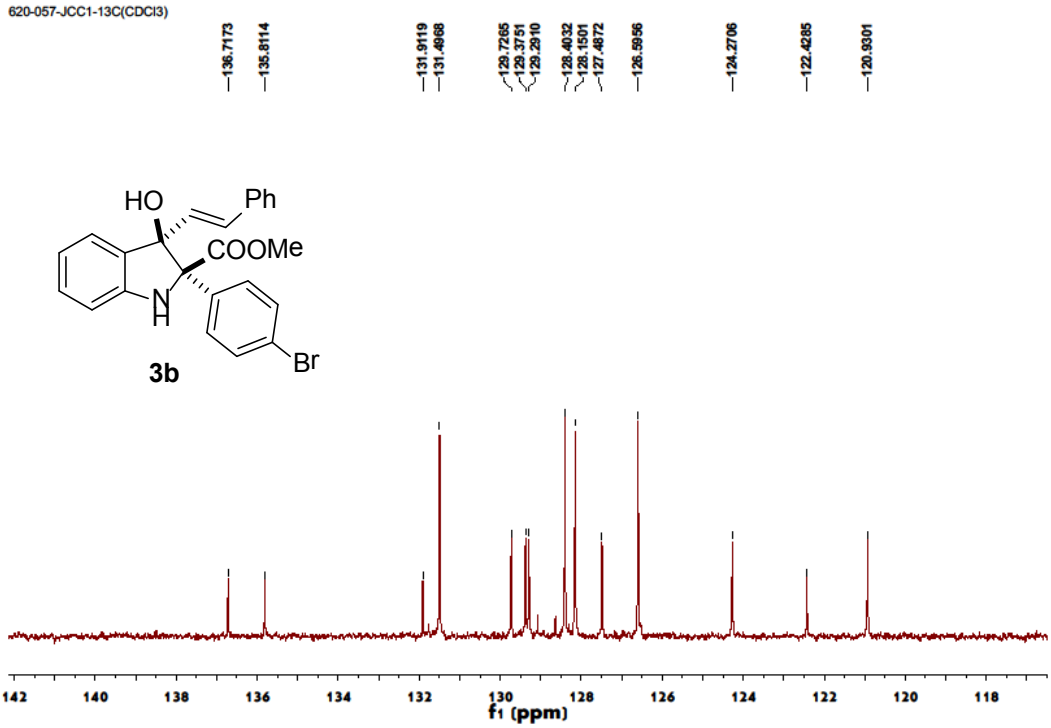


(2*S,3*R**)-methyl**

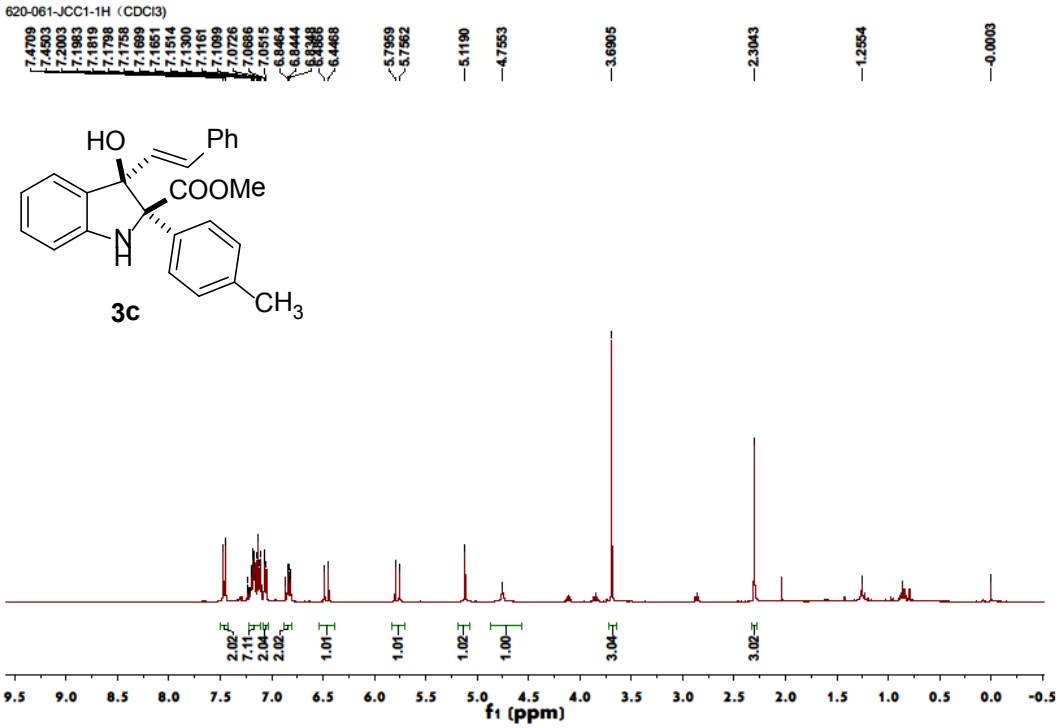
2-(4-bromophenyl)-3-hydroxy-3-((*E*)-styryl)indoline-2-carboxylate (3b)

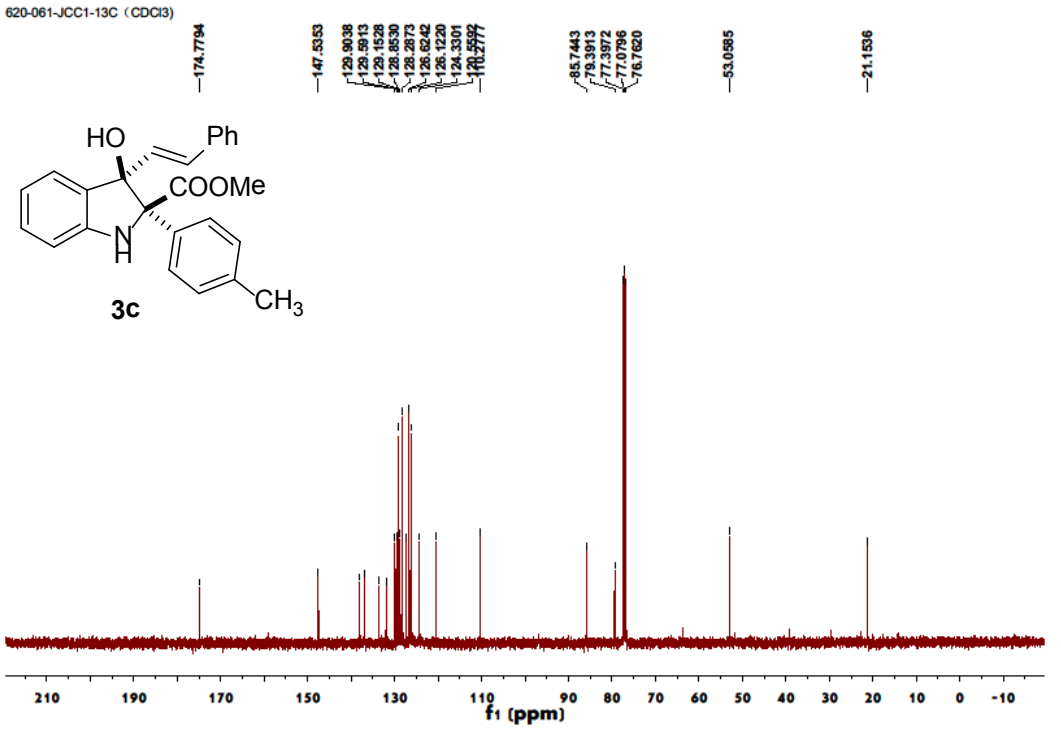


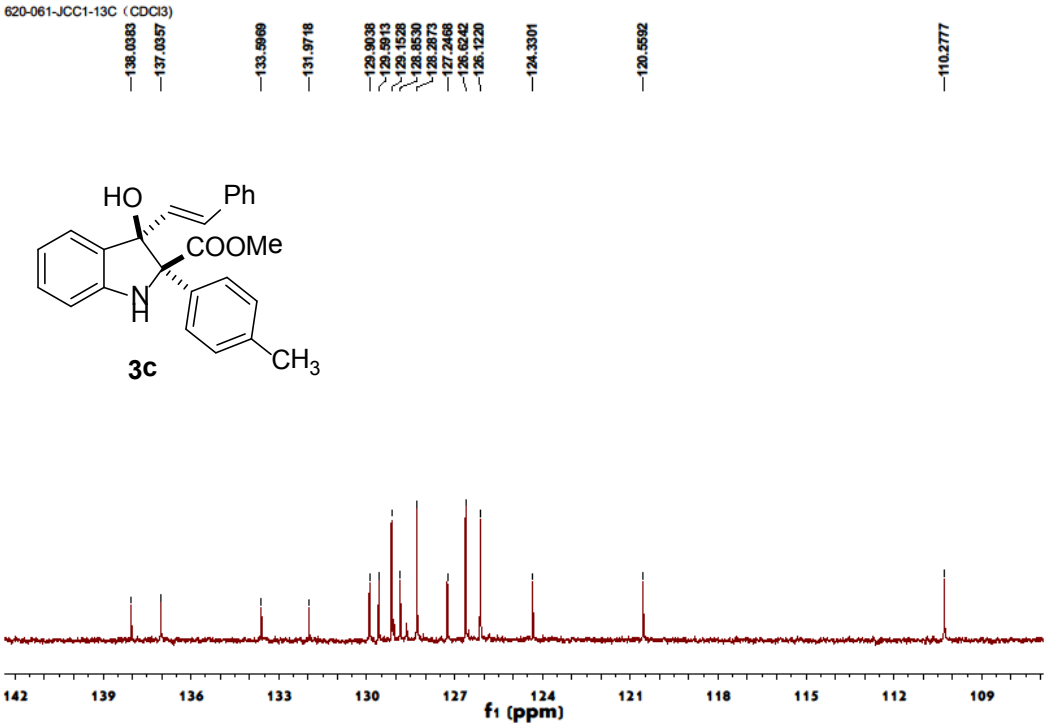

620-057-JCC1-13C(CDCl3)
174.2768
147.1328
131.4968
129.7265
129.3751
129.2910
128.4032
128.1501
127.4872
126.5956
124.2706
120.9301
110.5875
85.8980
79.1171
77.4105
77.0929
76.7750
53.2494
29.7519
HO
Ph
COOMe
N
H
Br
3b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


620-057-JCC1-13C(CDCl3)
136.7173
135.8114
131.9119
131.4968
129.7265
129.3751
129.2910
128.4032
128.1501
127.4872
126.5956
124.2706
122.4285
120.9301
HO
Ph
COOMe
N
H
Br
3b
142 140 138 136 134 132 130 128 126 124 122 120 118
f1 (ppm)

(2*S,3*R**)-methyl 3-hydroxy-3-((*E*)-styryl)-2-(p-tolyl)indoline-2-carboxylate (3c)**

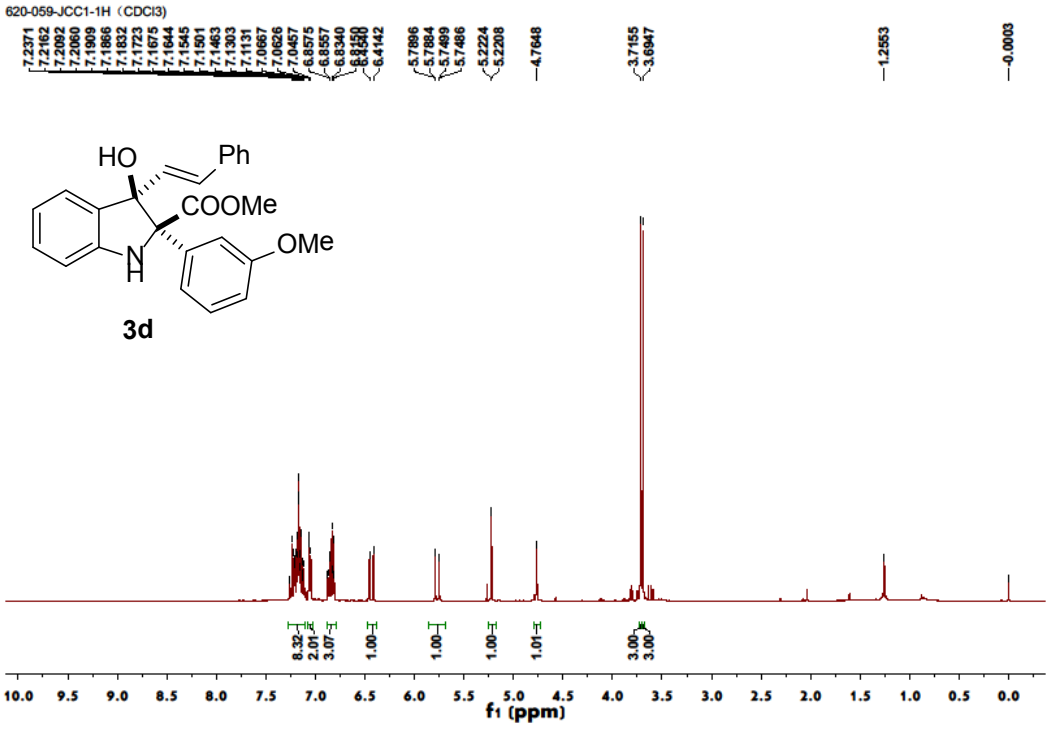


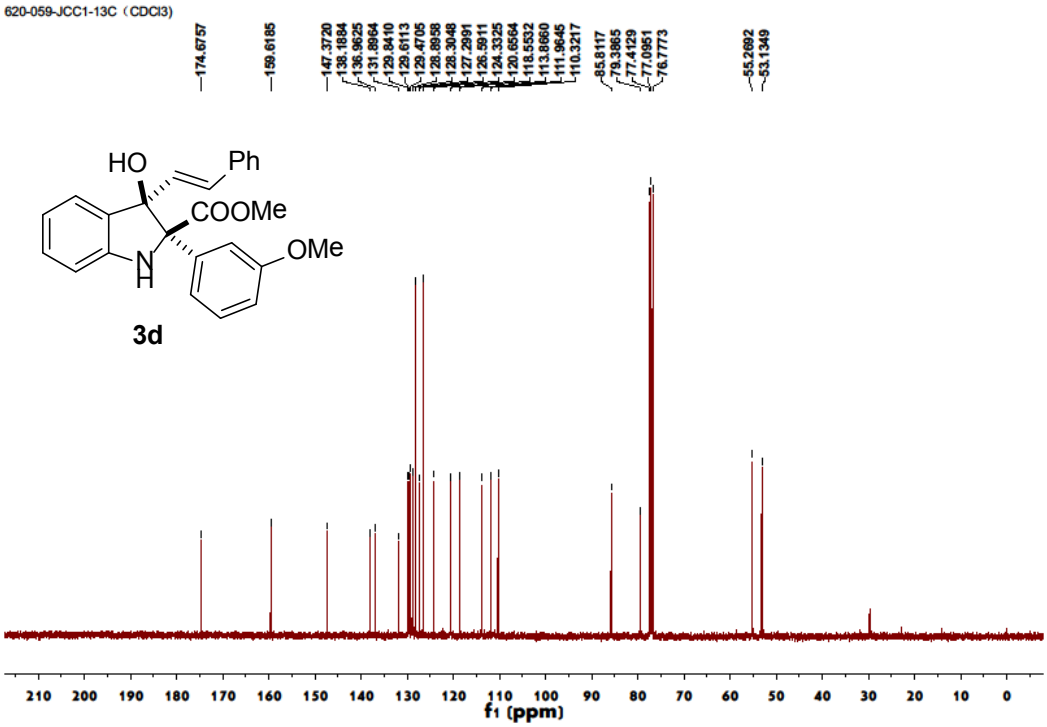




(2*S,3*R**)-methyl**

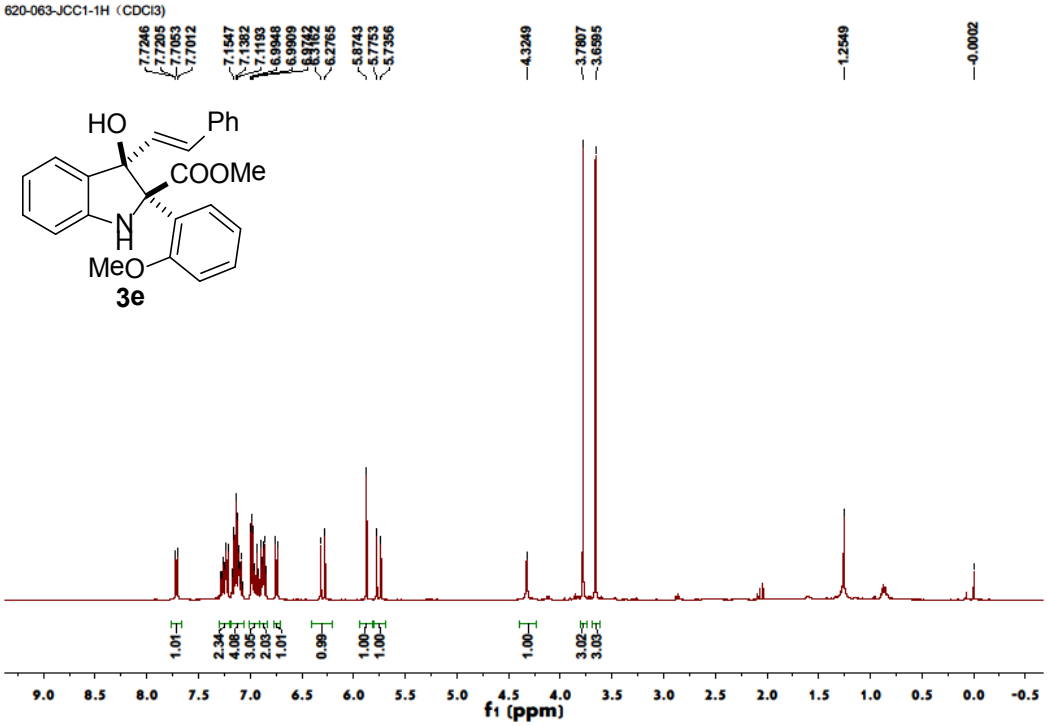
3-hydroxy-2-(3-methoxyphenyl)-3-((*E*)-styryl)indoline-2-carboxylate (3d)

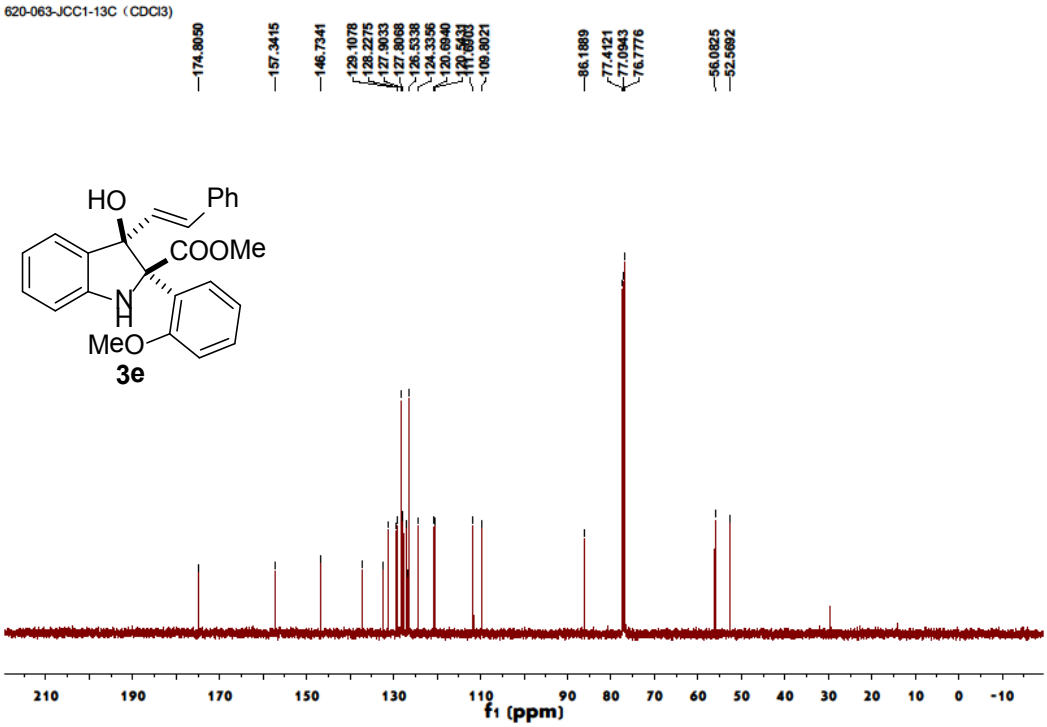


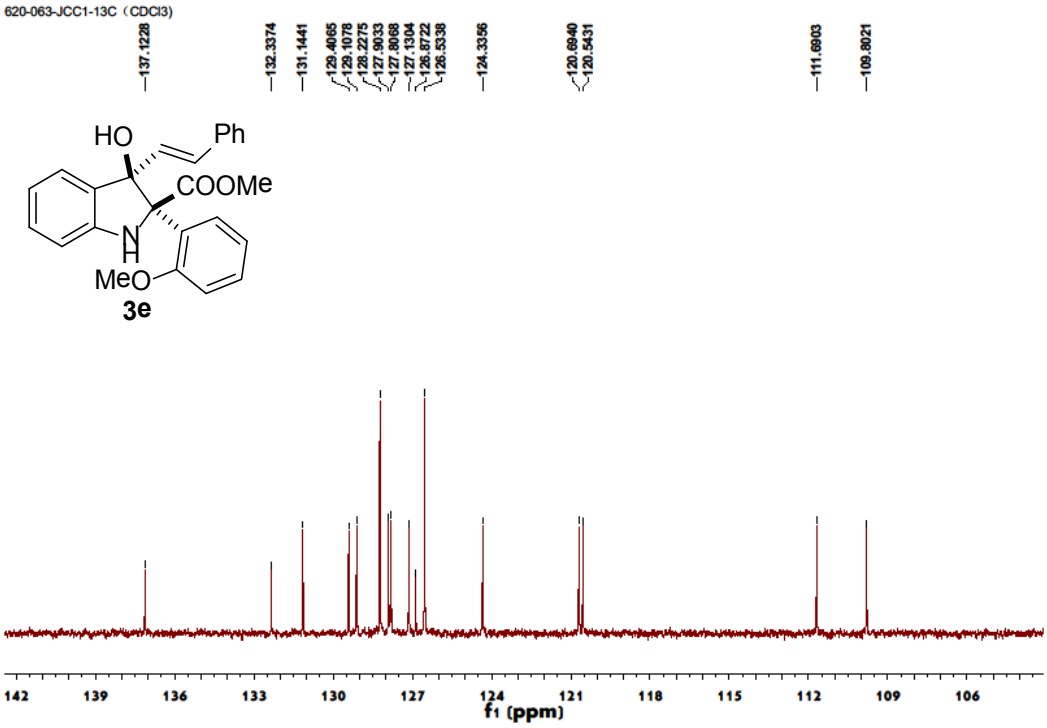


(2*S,3*R**)-methyl**

3-hydroxy-2-(2-methoxyphenyl)-3-((*E*)-styryl)indoline-2-carboxylate (3e)

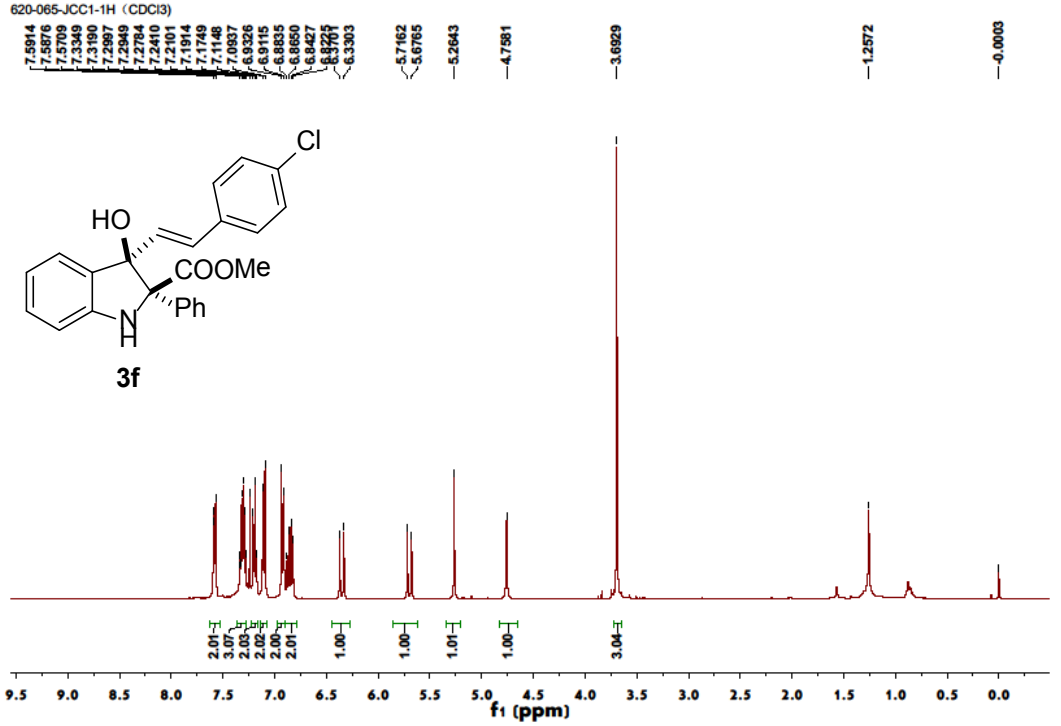


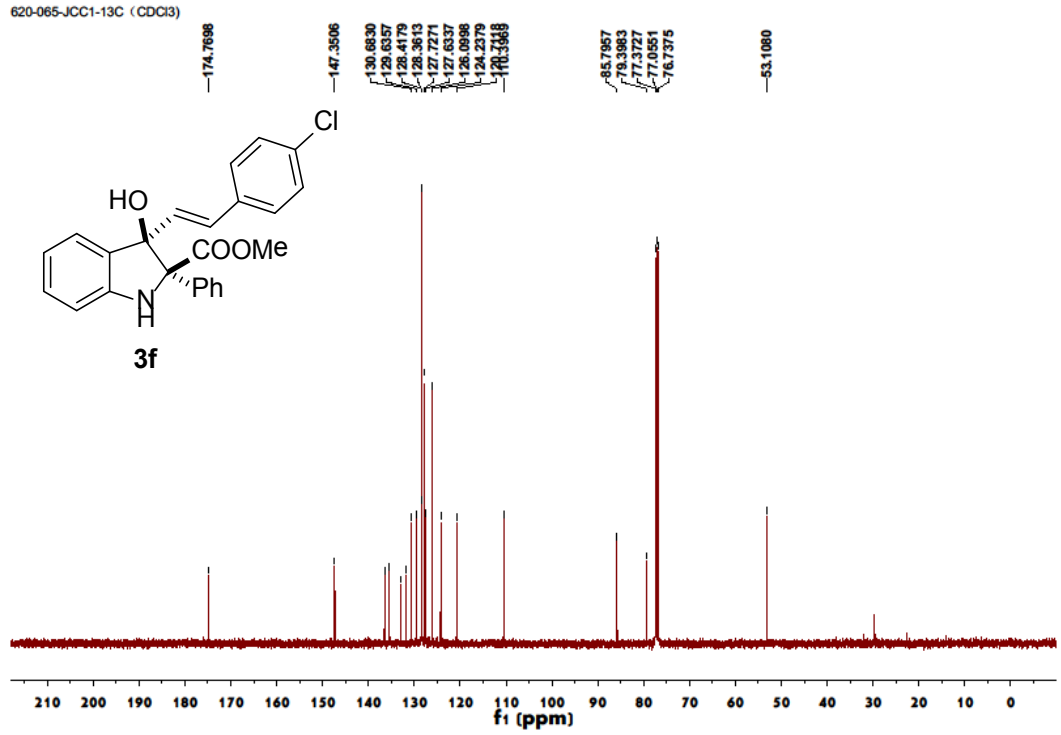

620-063-JCC1-13C（CDCl3）
174.8050
157.3415
146.7341
129.1078
128.2275
127.9033
127.8068
126.5338
124.3356
120.6940
120.5431
111.6903
109.8021
86.1889
77.4121
77.0943
76.7776
56.0825
52.5692
HO
Ph
COOMe
N
H
MeO
3e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

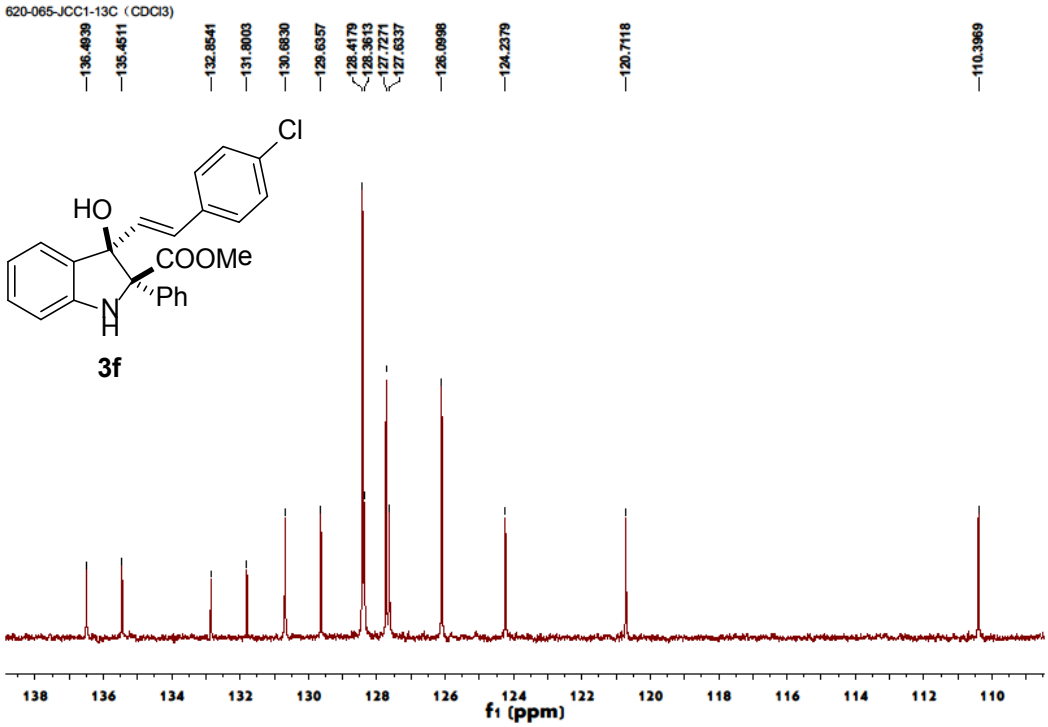

620-063-JCC1-13C（CDCl3）
137.1228
132.3374
131.1441
129.4065
129.1078
128.2275
127.9033
127.8068
127.1304
126.8722
126.5338
124.3356
120.6940
120.5431
111.6903
109.8021
HO
Ph
COOMe
N
H
MeO
3e
142
139
136
133
130
127
124
121
118
115
112
109
106
f1 (ppm)

(2*S,3*R**)-methyl**

3-((*E*)-4-chlorostyryl)-3-hydroxy-2-phenylindoline-2-carboxylate (3f)

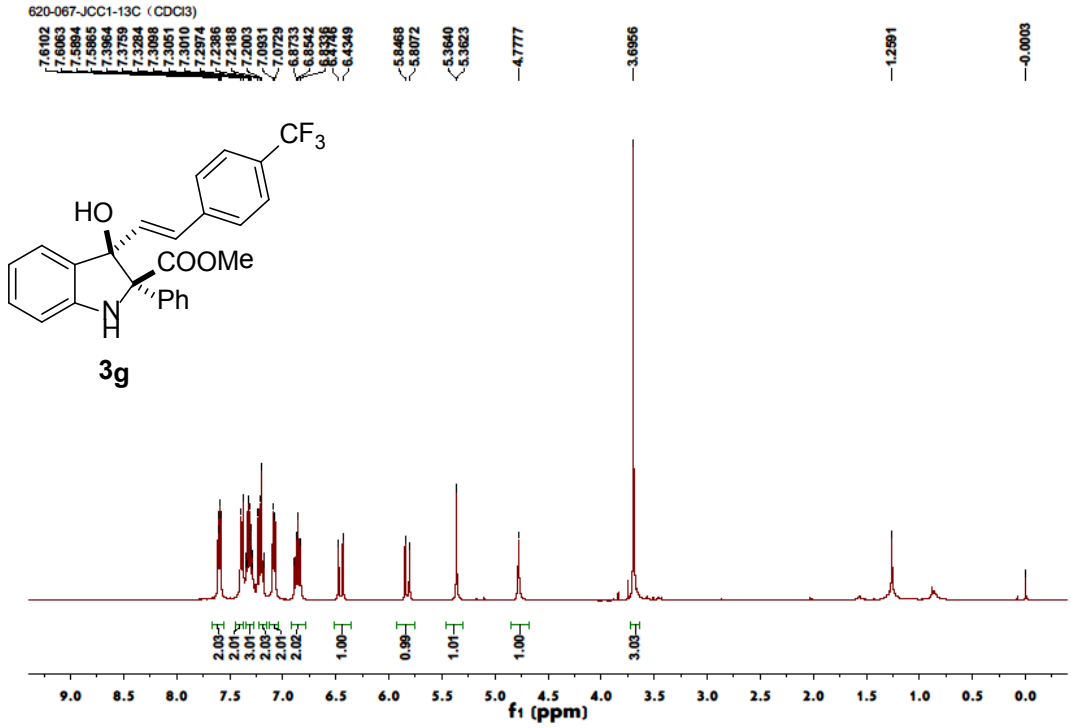


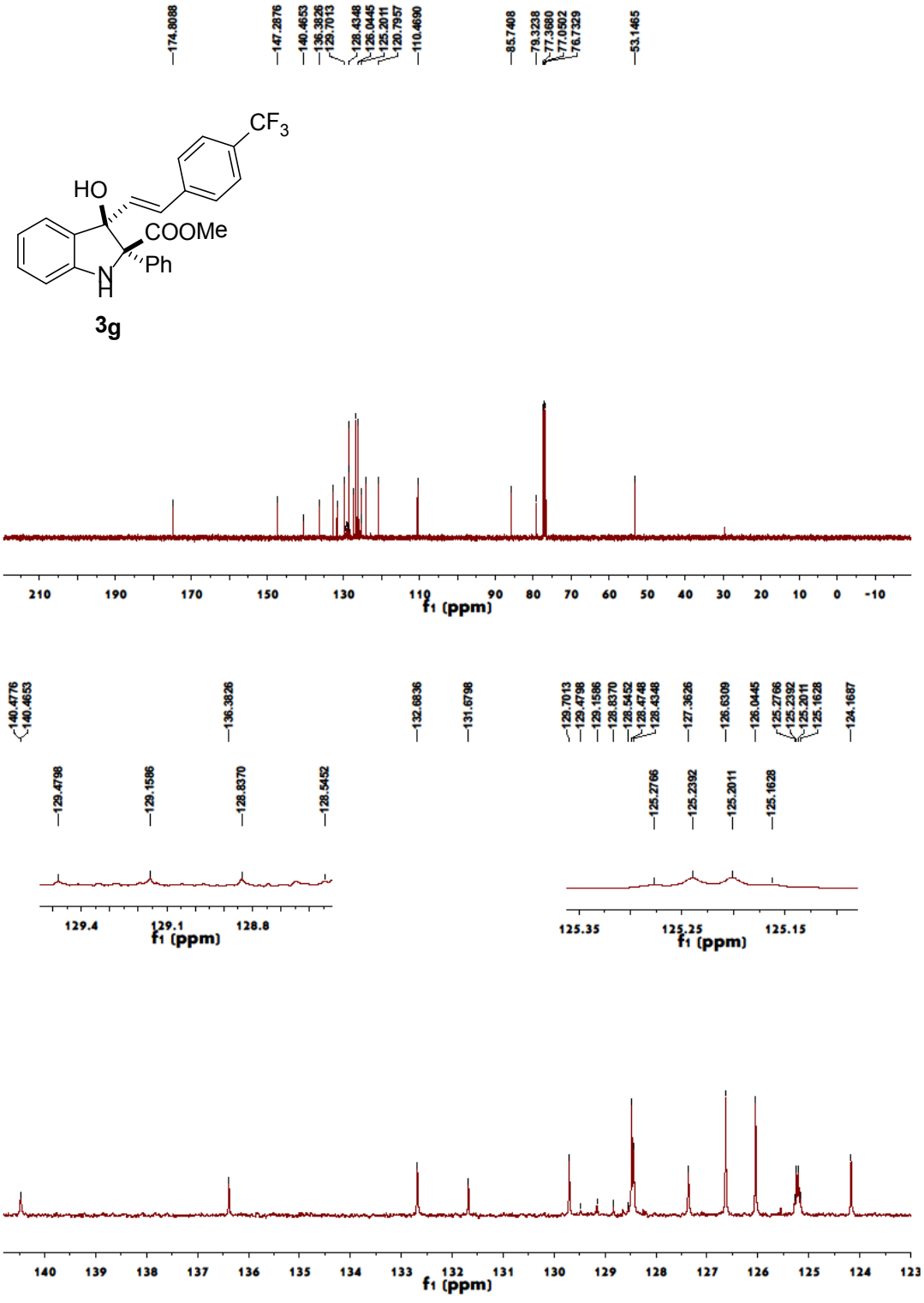




(2*S,3*R**)-methyl**

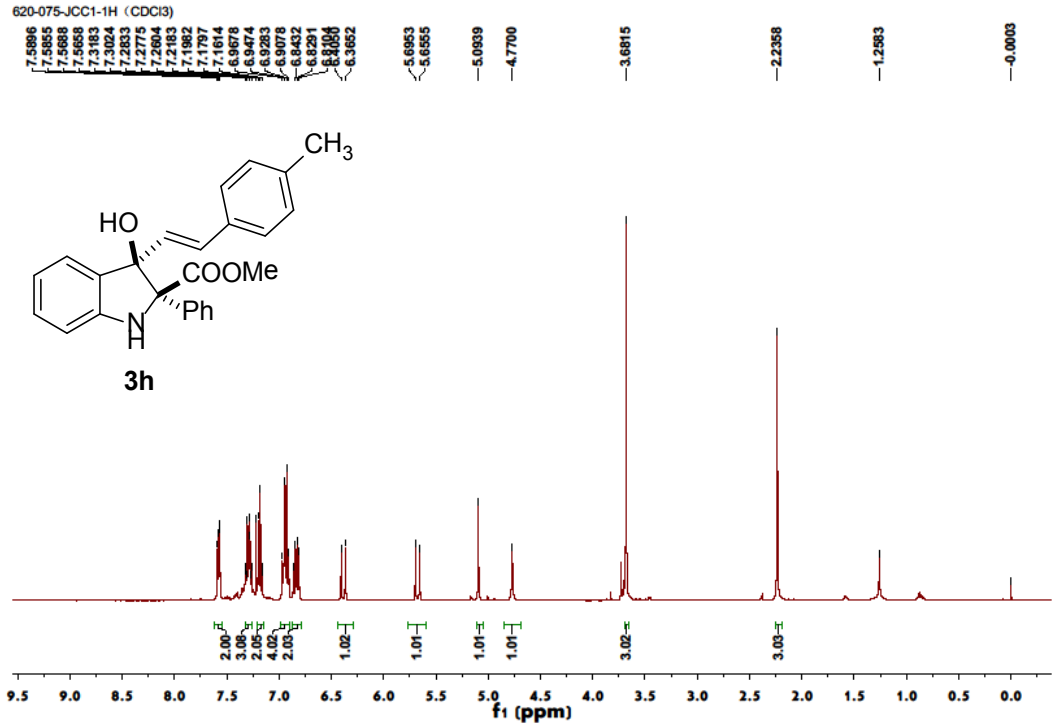
3-hydroxy-2-phenyl-3-((*E*)-4-(trifluoromethyl)styryl)indoline-2-carboxylate (3g)

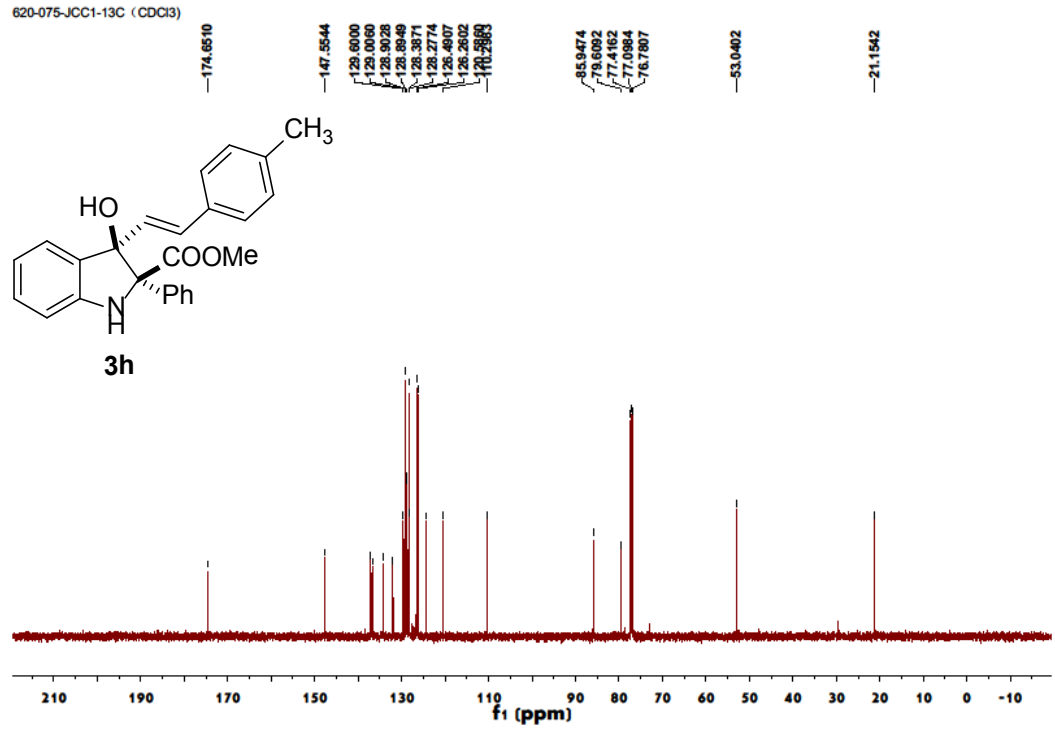


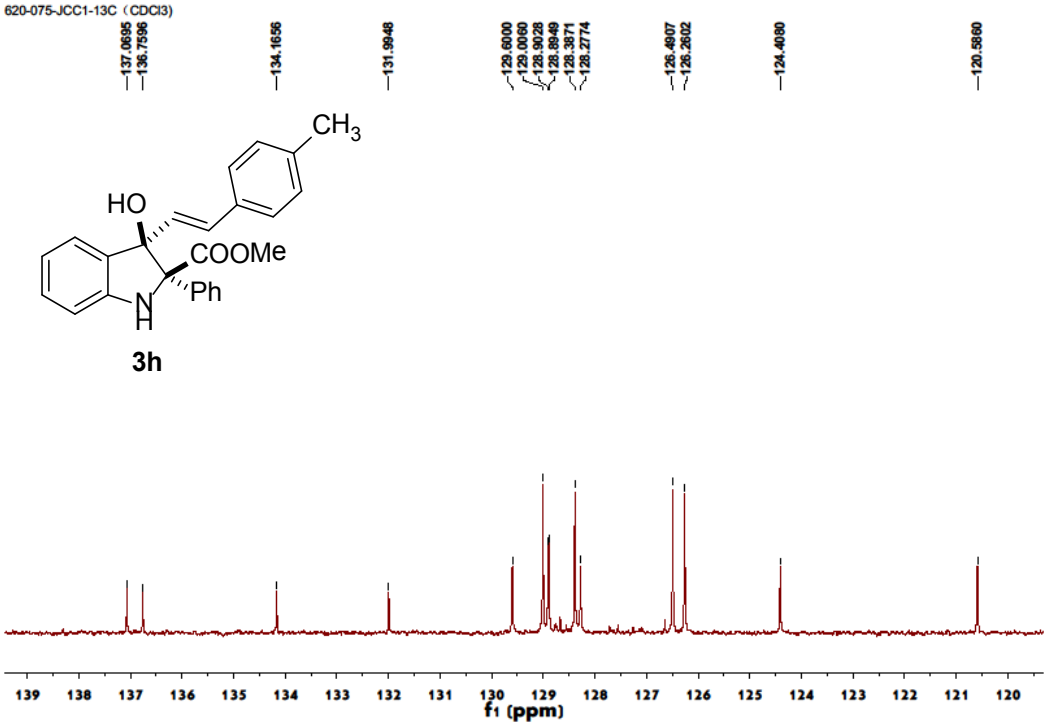

174.8088
147.2876
140.4653
136.3826
129.7013
128.4348
126.0445
125.2011
120.7957
110.4690
85.7408
79.3238
77.3680
77.0502
76.7329
53.1465
CF3
HO
COOMe
Ph
N
H
3g
f1 (ppm)
140.4776
140.4653
136.3826
132.6836
131.6798
129.7013
129.4798
129.1586
128.8370
128.5452
128.4748
128.4348
127.3626
126.6309
126.0445
125.2766
125.2392
125.2011
125.1628
124.1687
129.4798
129.1586
128.8370
128.5452
125.2766
125.2392
125.2011
125.1628
129.4
129.1
128.8
125.35
125.25
125.15
f1 (ppm)
f1 (ppm)

(2*S,3*R**)-methyl**

3-hydroxy-3-((*E*)-4-methylstyryl)-2-phenylindoline-2-carboxylate (3h)



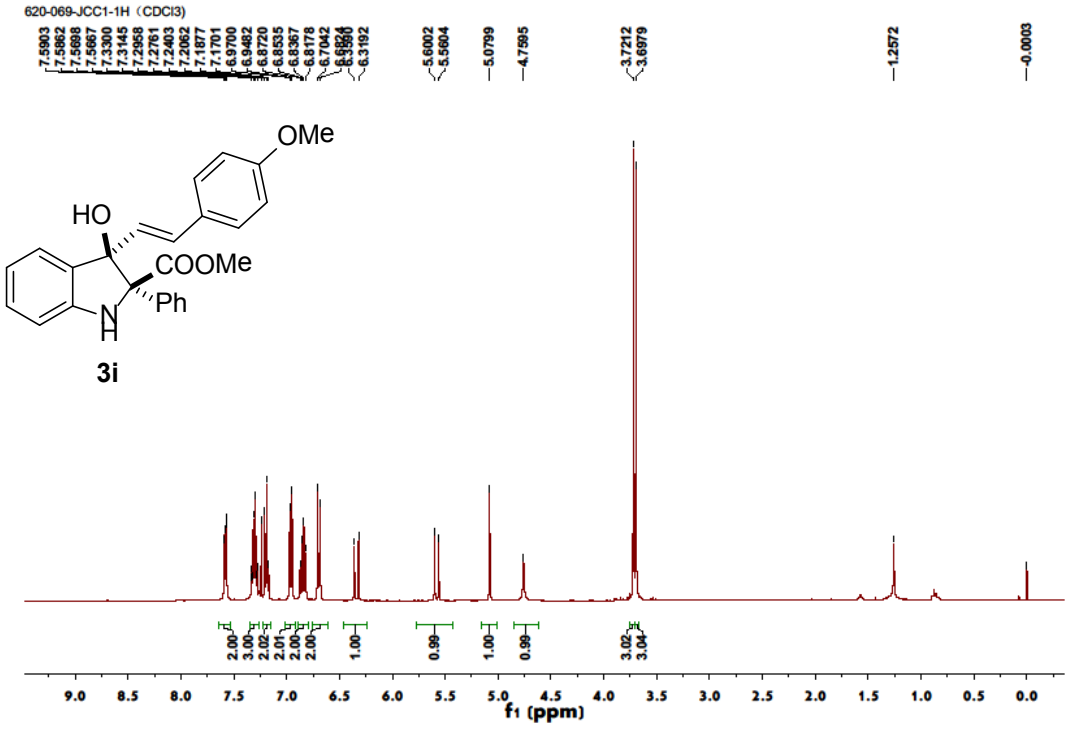




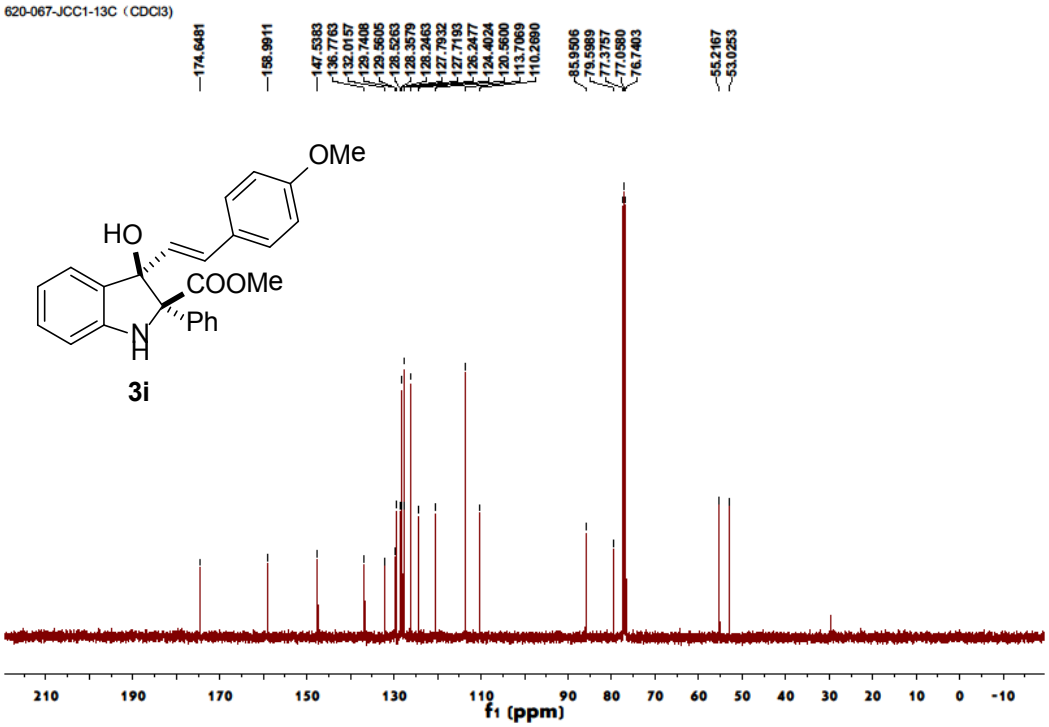
3h

(2*S,3*R**)-methyl**

3-hydroxy-3-((*E*)-4-methoxystyryl)-2-phenylindoline-2-carboxylate (3i)

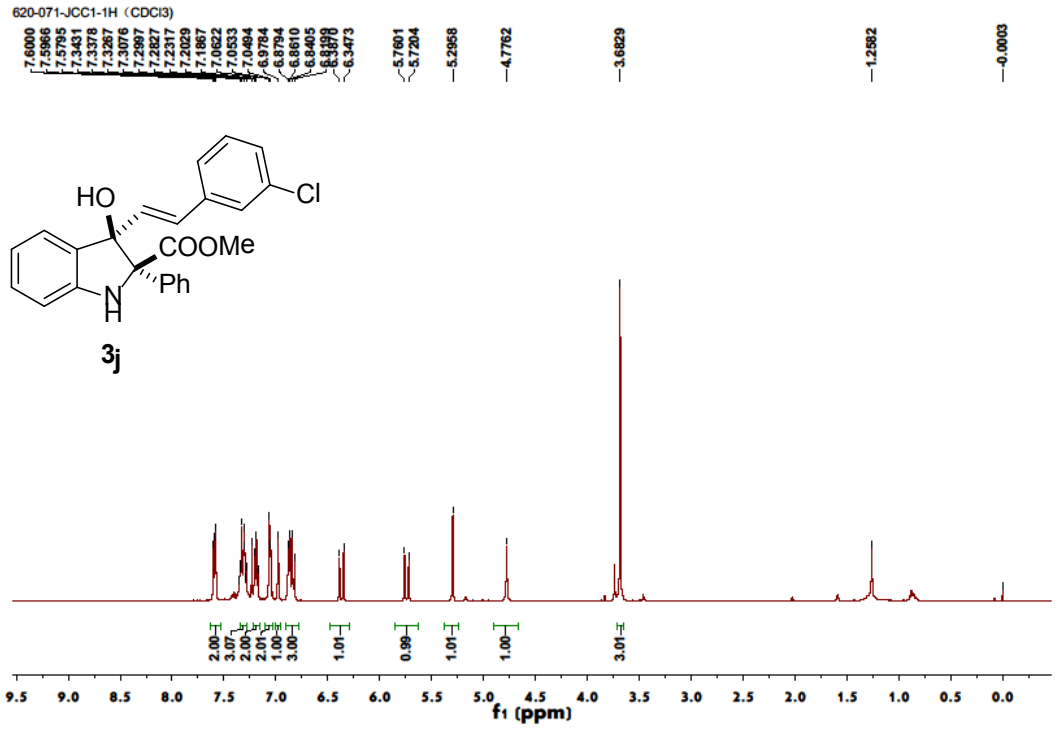


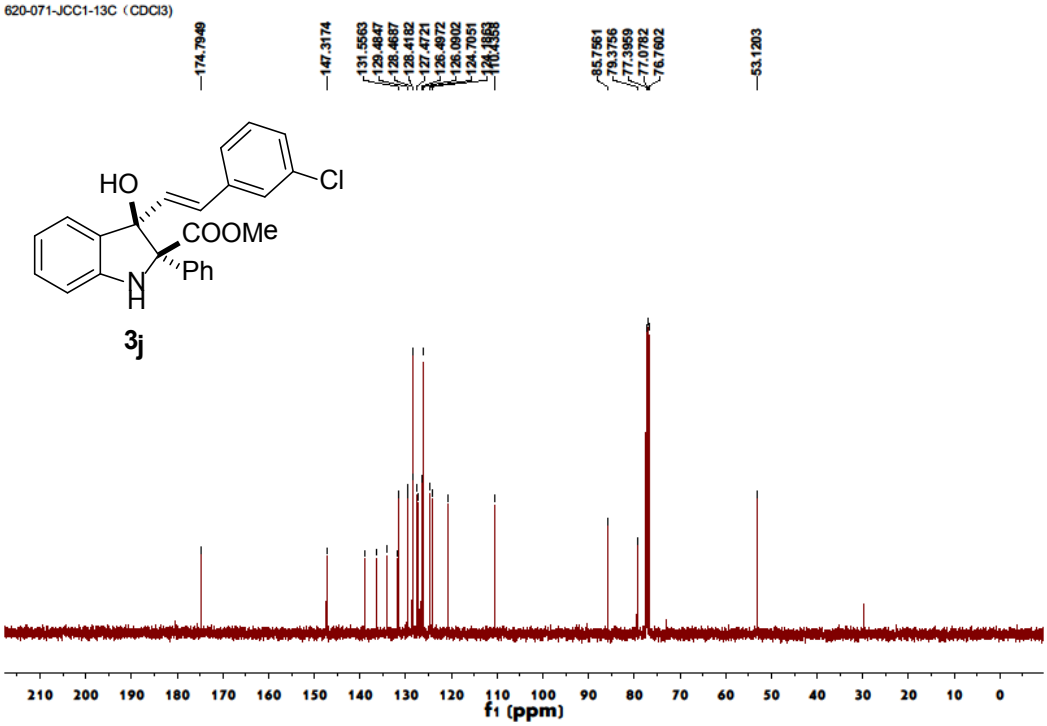
3i

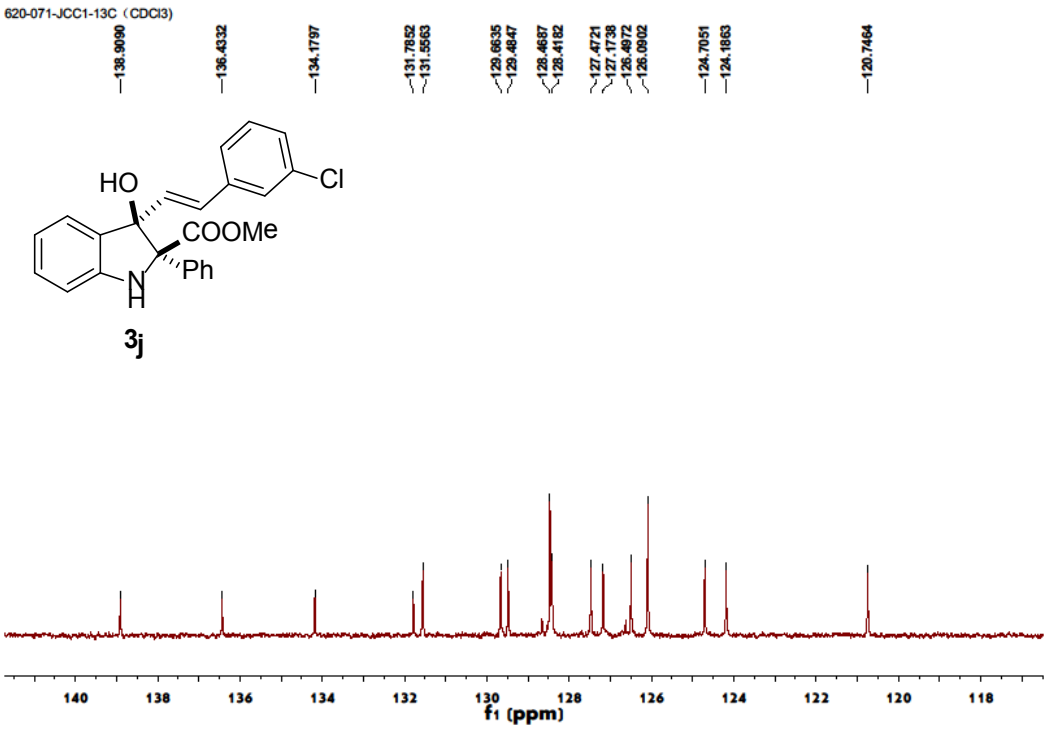


(2*S,3*R**)-methyl**

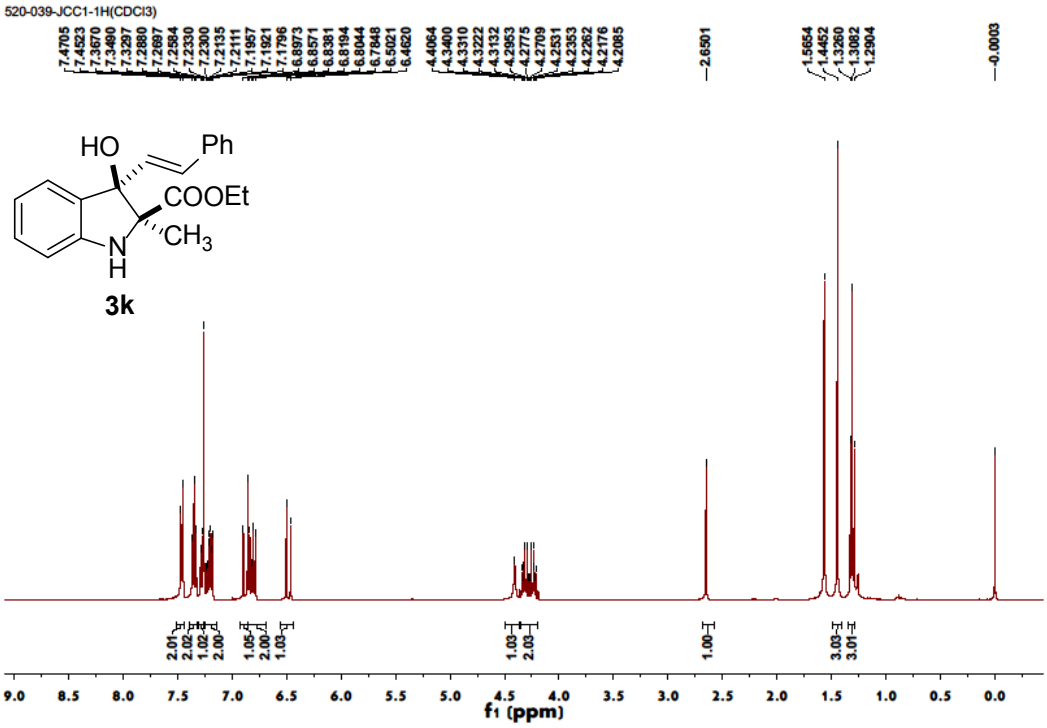
3-((*E*)-3-chlorostyryl)-3-hydroxy-2-phenylindoline-2-carboxylate (3j)

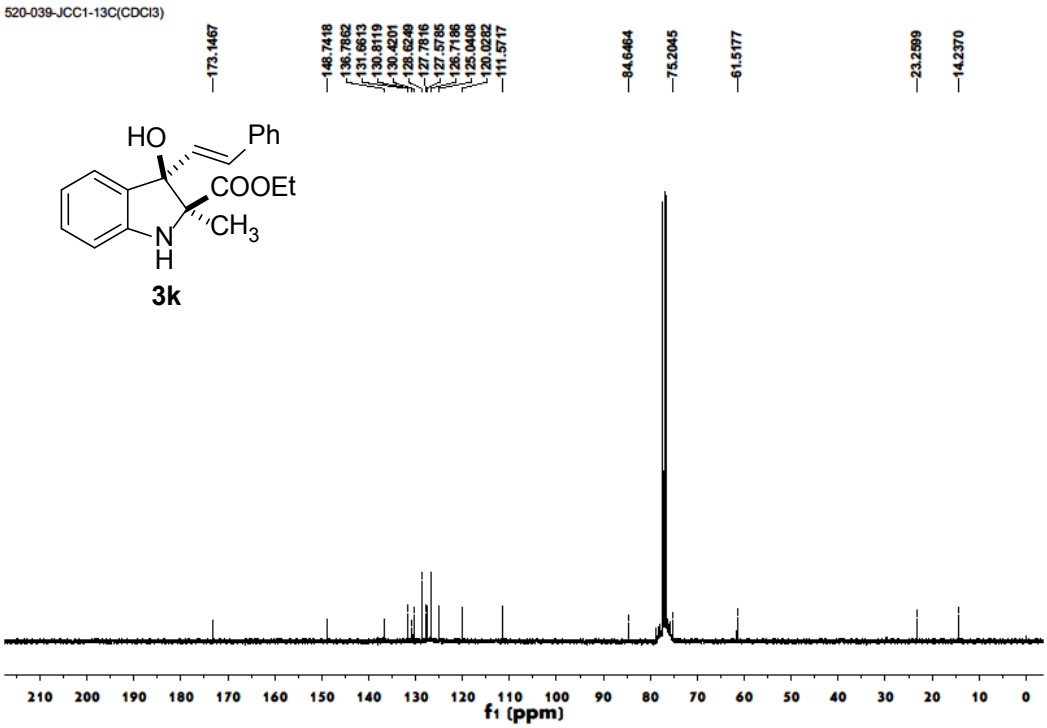



620-071-JCC1-13C（CDCl3）
174.7949
147.3174
131.5563
129.4847
128.4687
128.4182
127.4721
126.4972
126.0902
124.7051
124.1863
110.4358
85.7561
79.3756
77.3959
77.0782
76.7602
53.1203
HO
Cl
COOMe
Ph
N
H
3j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

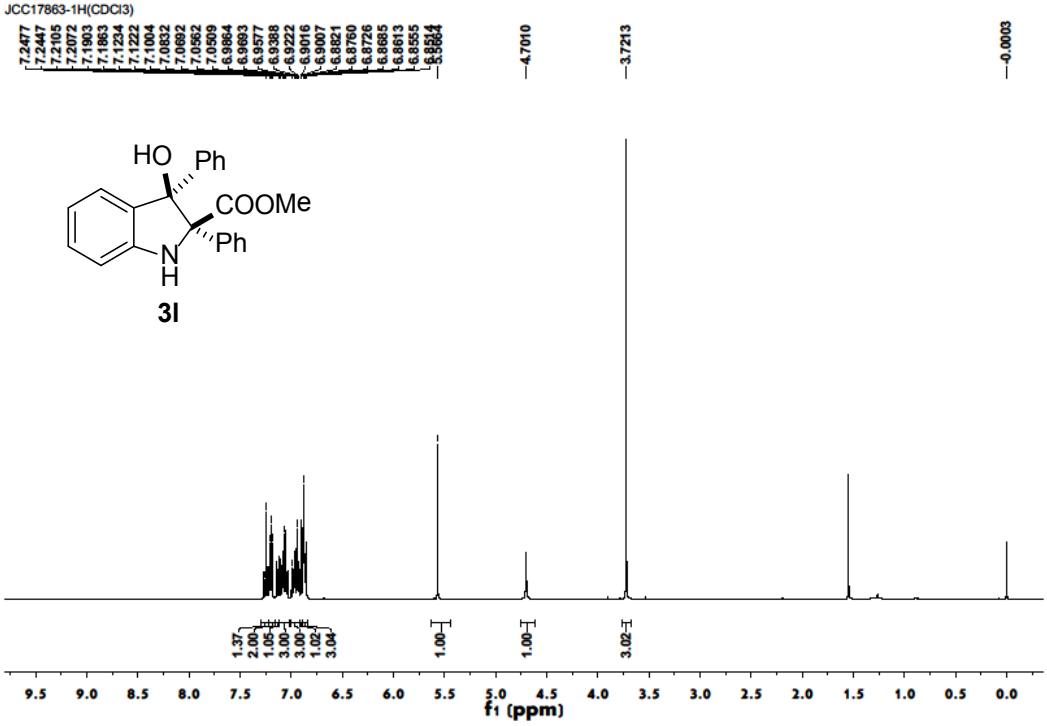

620-071-JCC1-13C（CDCl3）
138.9090
136.4332
134.1797
131.7852
131.5563
129.6635
129.4847
128.4687
128.4182
127.4721
127.1738
126.4972
126.0902
124.7051
124.1863
120.7464
HO
Cl
COOMe
Ph
N
H
3j
140 138 136 134 132 130 128 126 124 122 120 118
f1 (ppm)

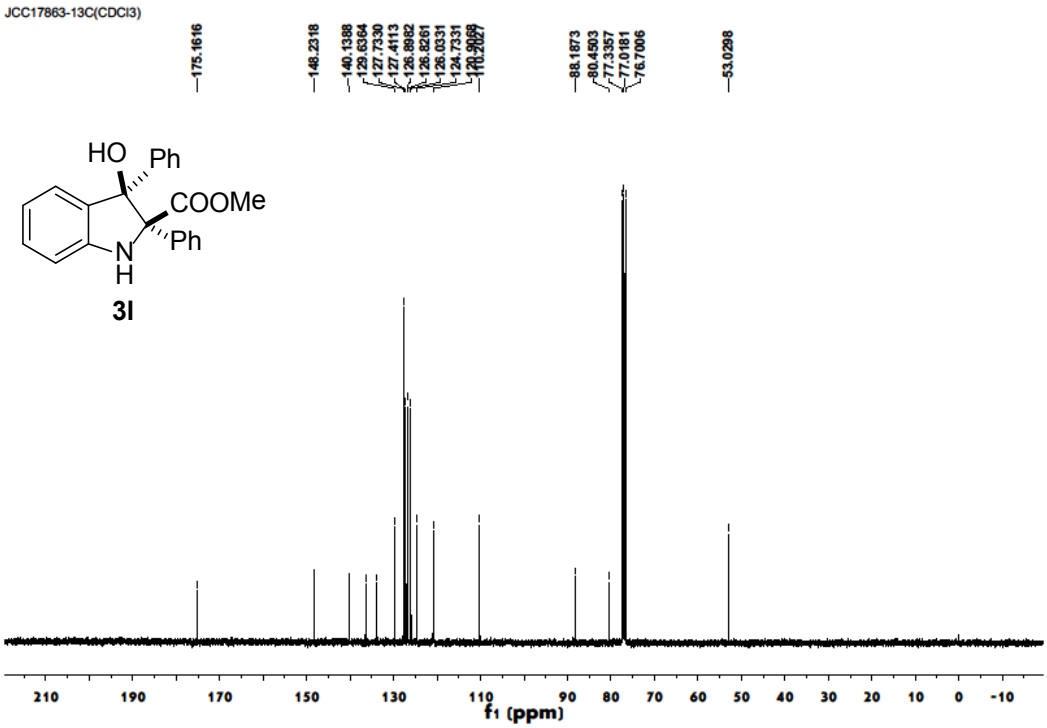
(2*S,3*R**)-ethyl 3-hydroxy-2-methyl-3-((*E*)-styryl)indoline-2-carboxylate (3k)**





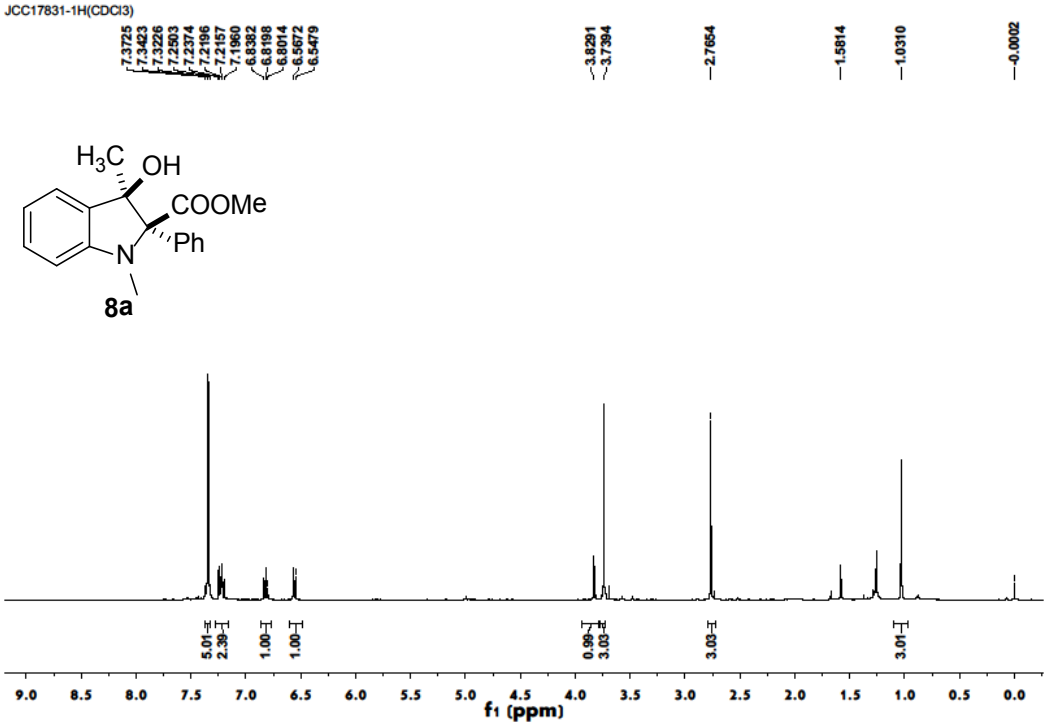
(2*S,3*R**)-methyl 3-hydroxy-2,3-diphenylindoline-2-carboxylate (3l)**

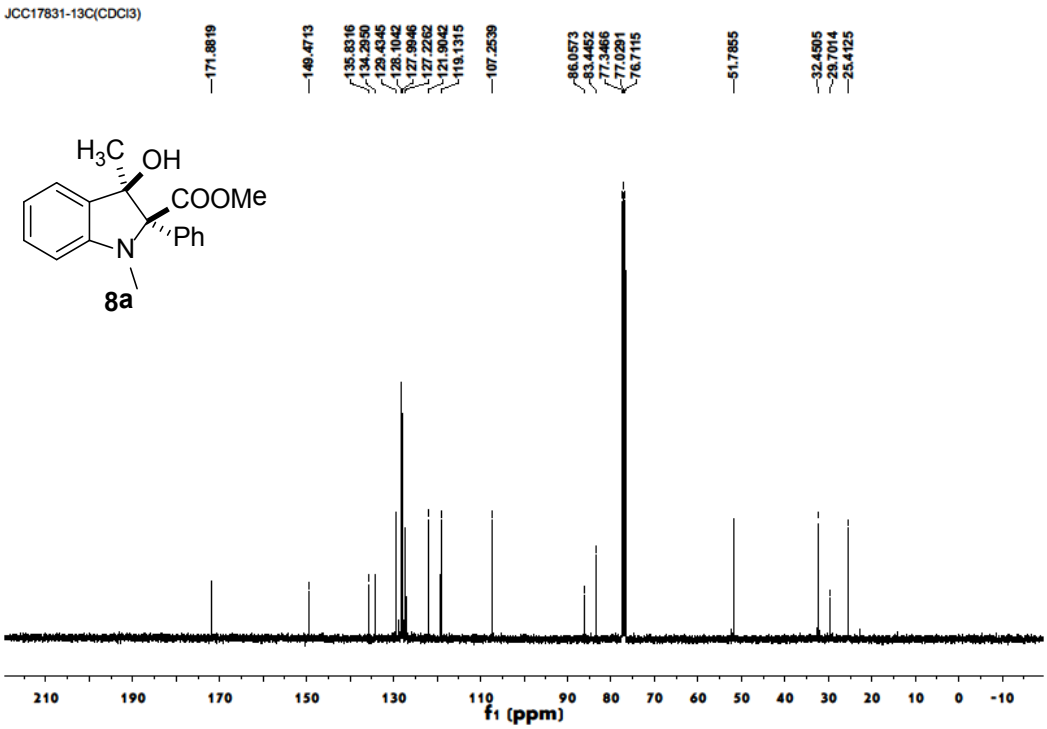




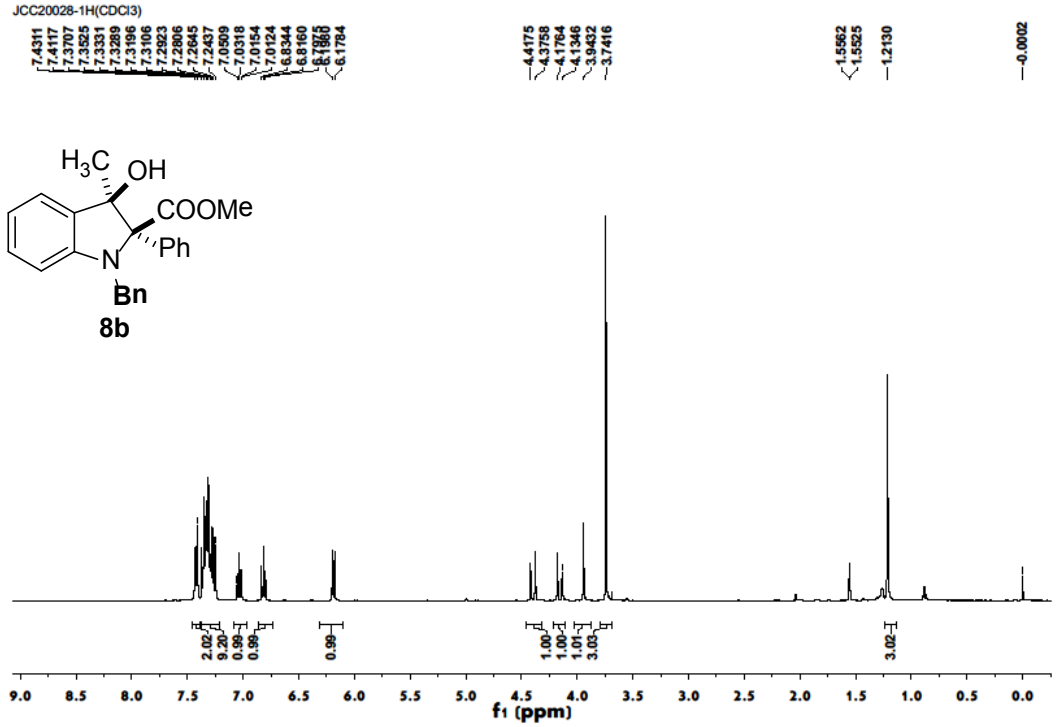
7.2 Analytical Data for 8 and 9

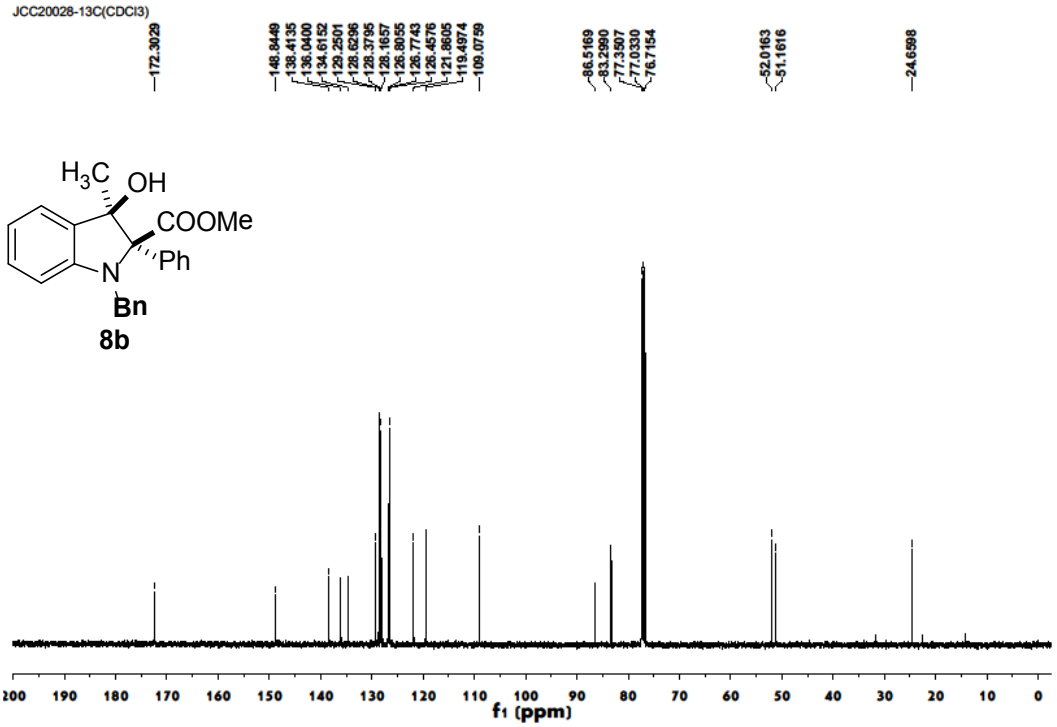
(2*S**,3*R**)-methyl 3-hydroxy-1,3-dimethyl-2-phenylindoline-2-carboxylate (8a)



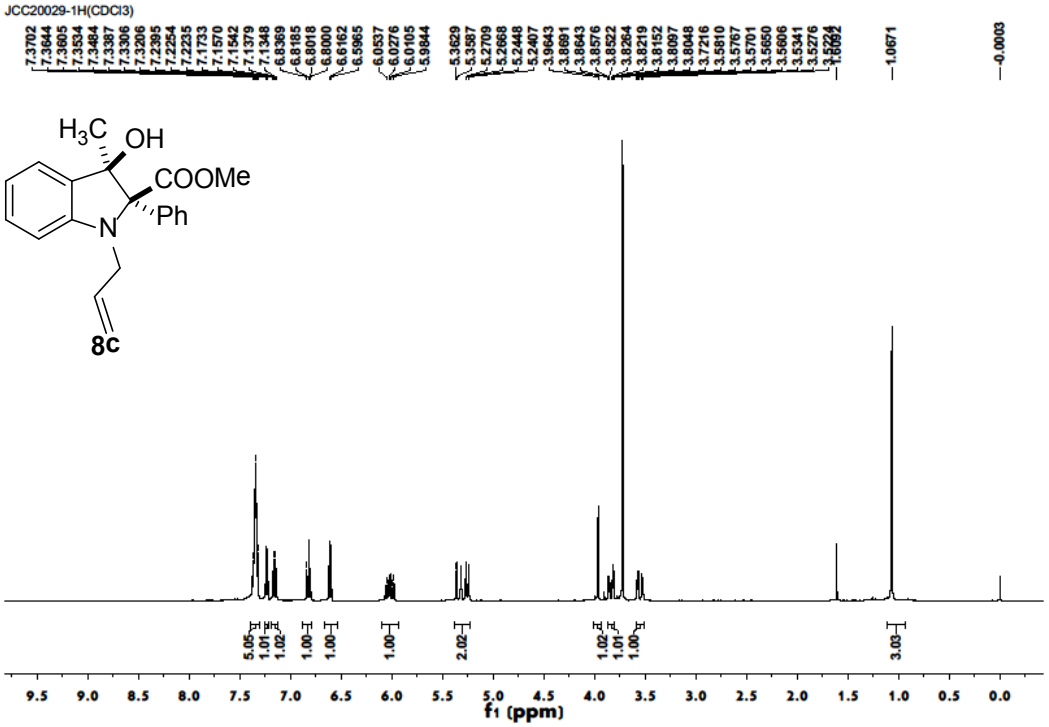


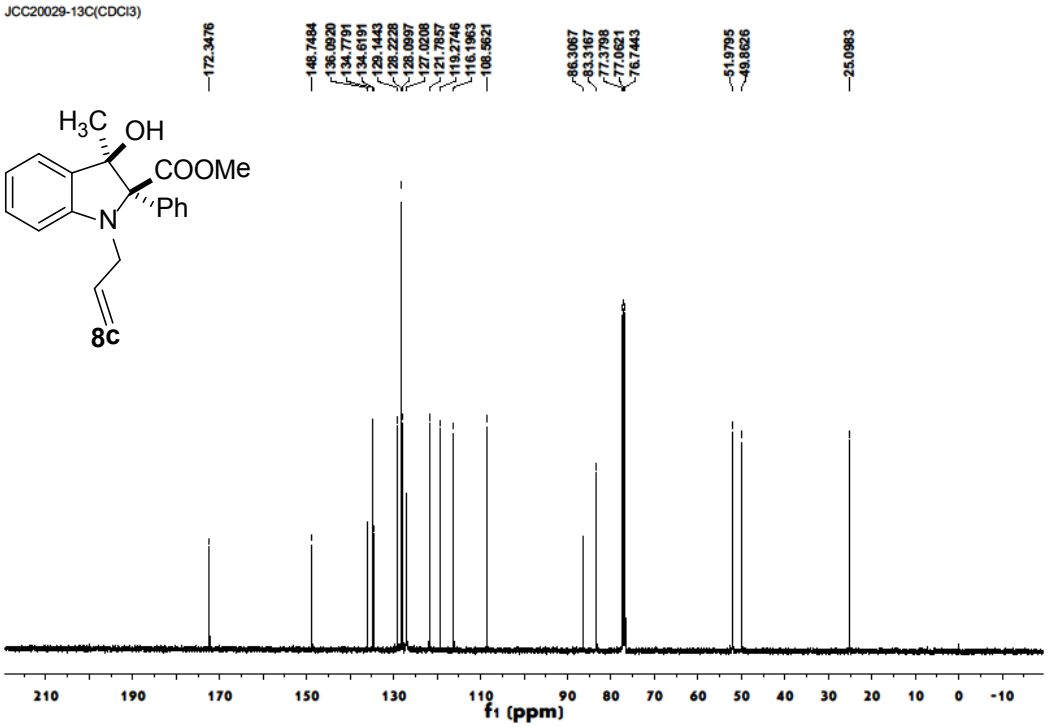
(2*S,3*R**)-methyl 1-benzyl-3-hydroxy-3-methyl-2-phenylindoline-2-carboxylate (8b)**





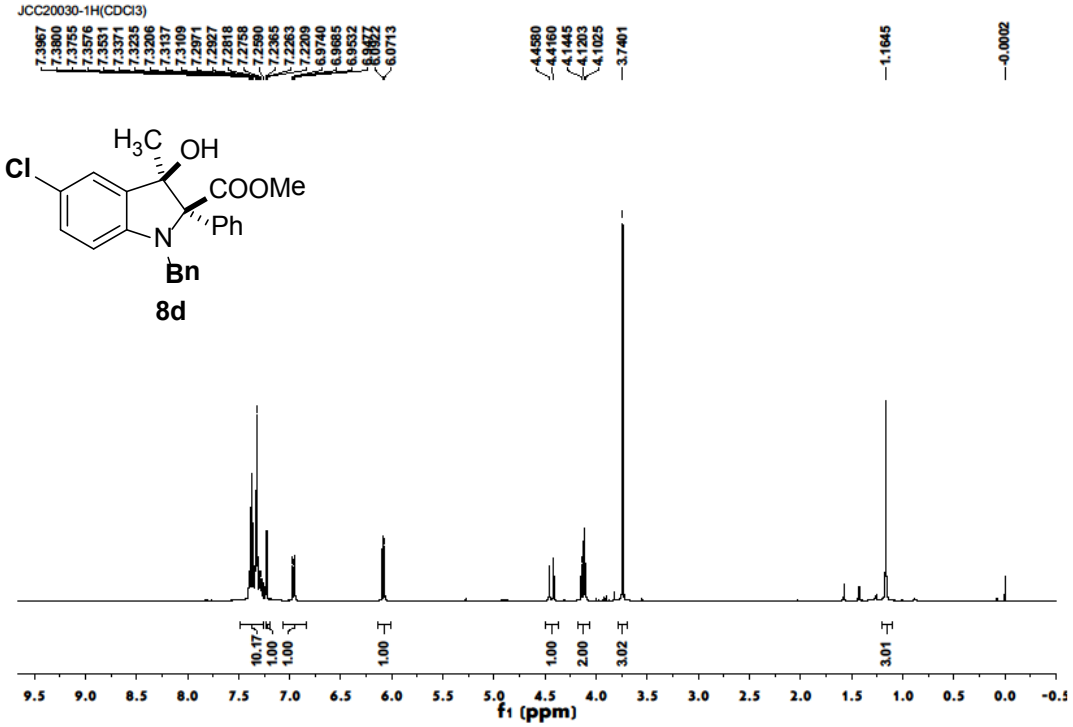
(2*S,3*R**)-methyl 1-allyl-3-hydroxy-3-methyl-2-phenylindoline-2-carboxylate (8c)**

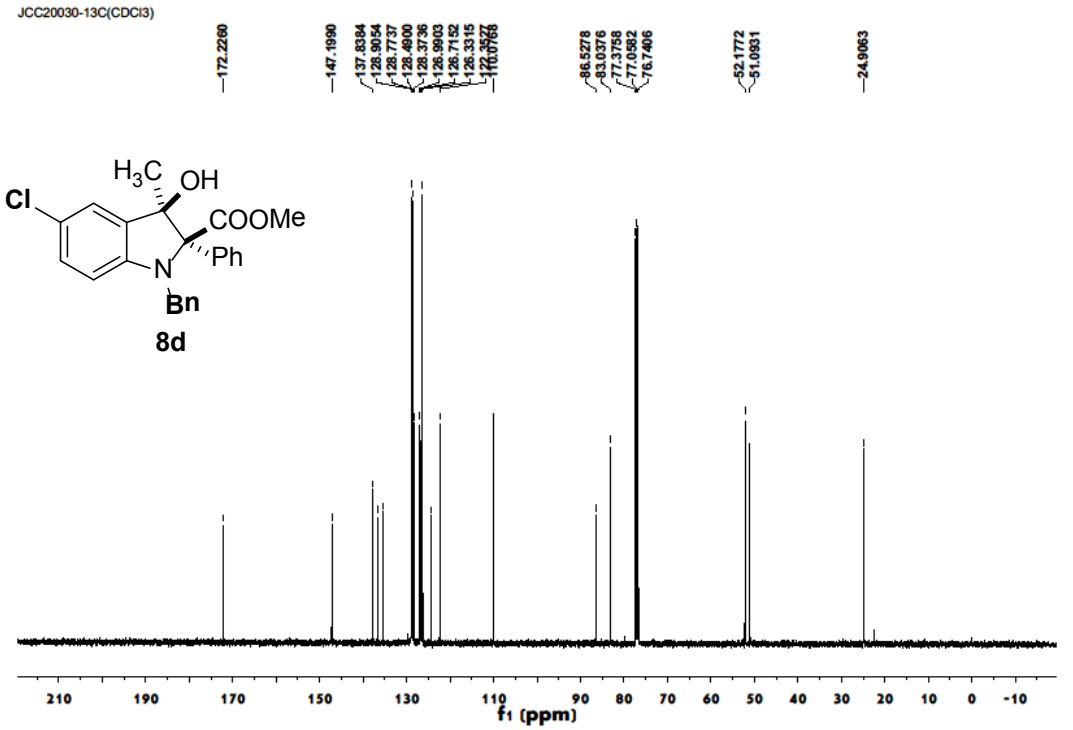


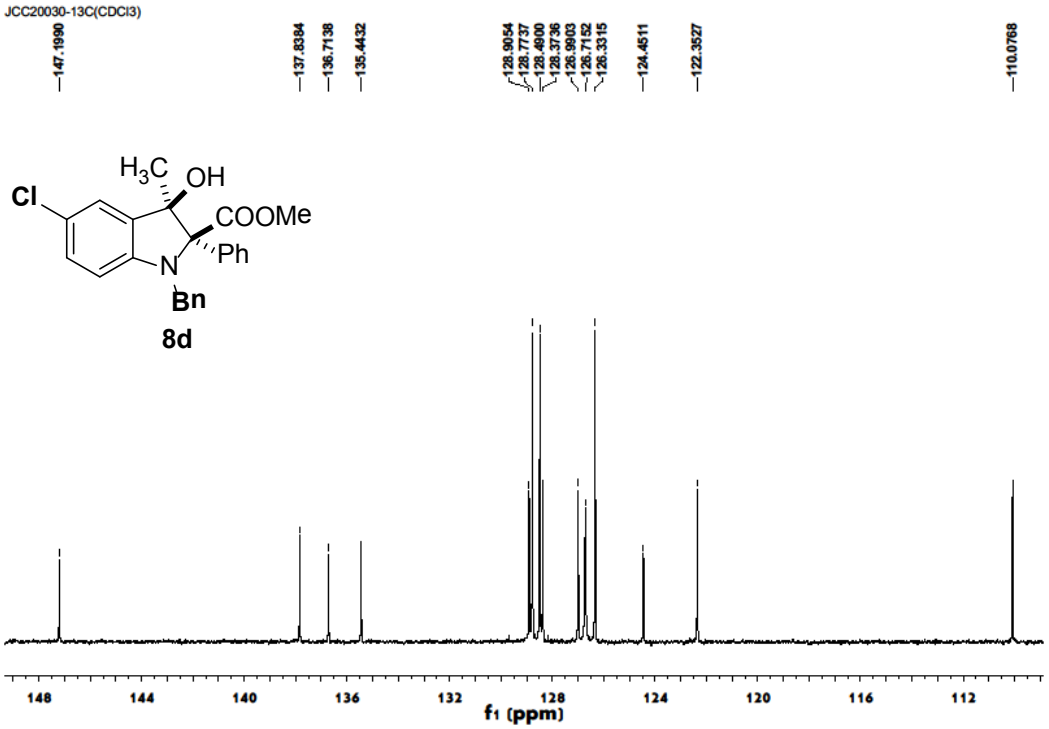


(2*S,3*R**)-methyl**

1-benzyl-5-chloro-3-hydroxy-3-methyl-2-phenylindoline-2-carboxylate (8d)

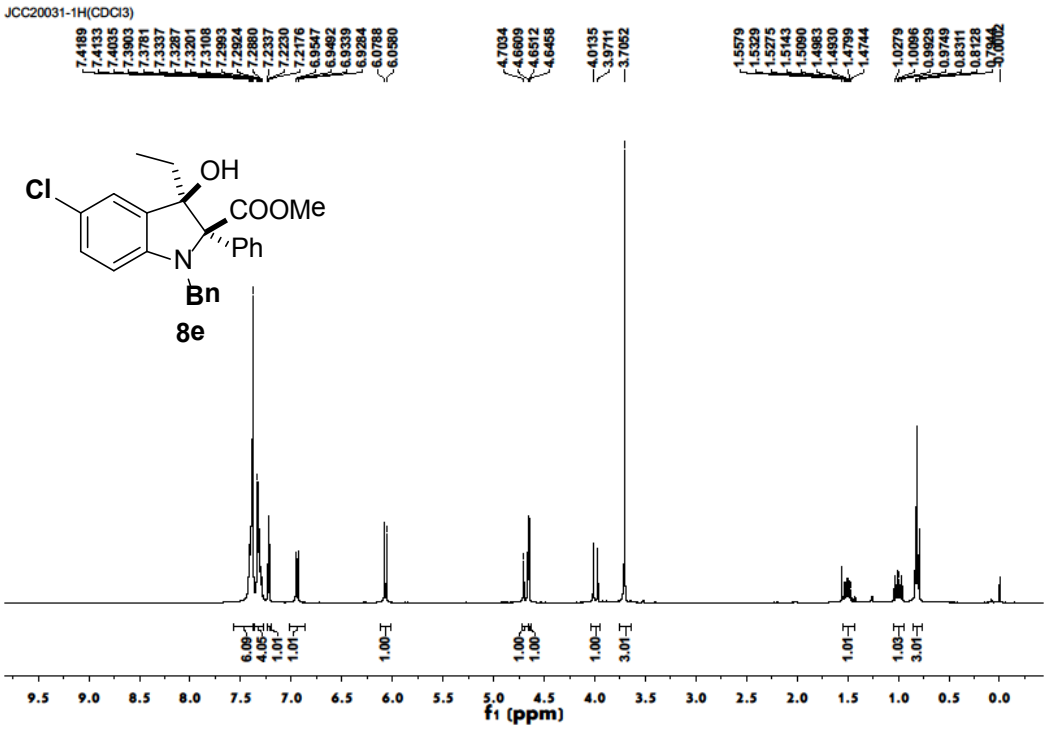


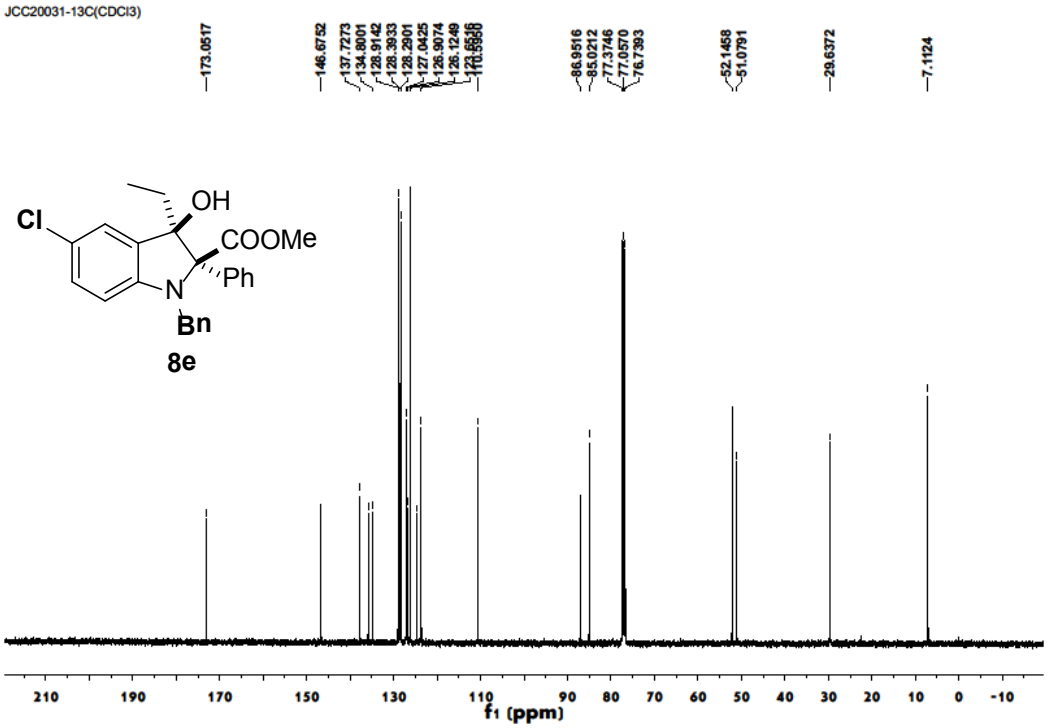


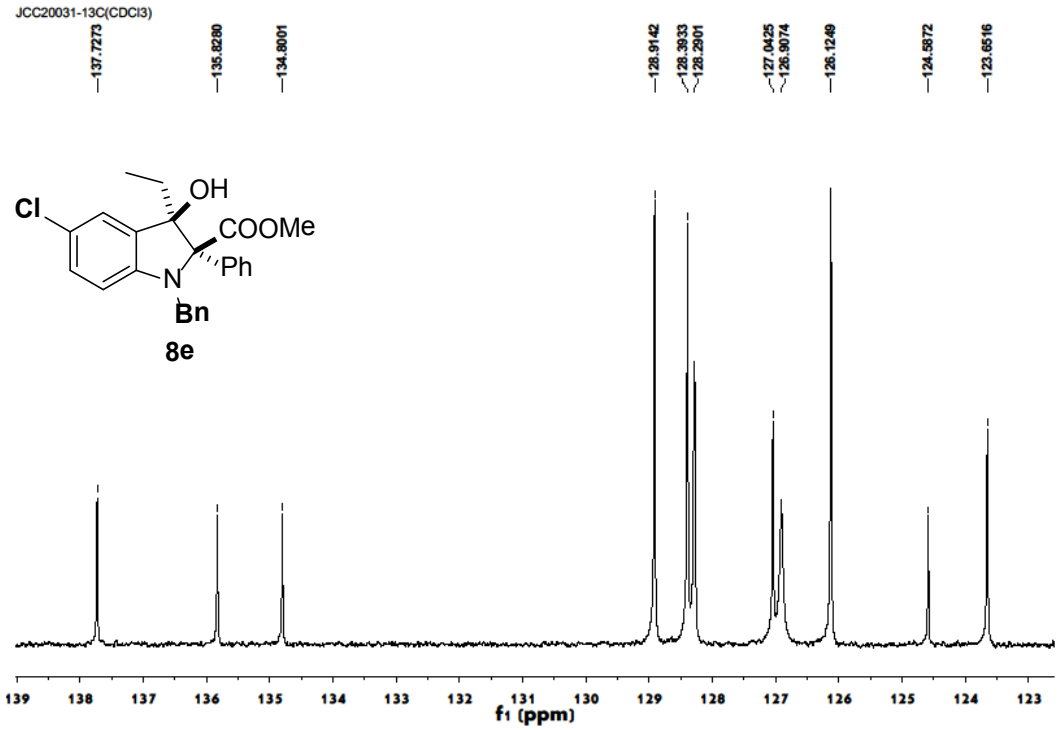


(2*S,3*R**)-methyl**

1-benzyl-5-chloro-3-ethyl-3-hydroxy-2-phenylindoline-2-carboxylate (8e)

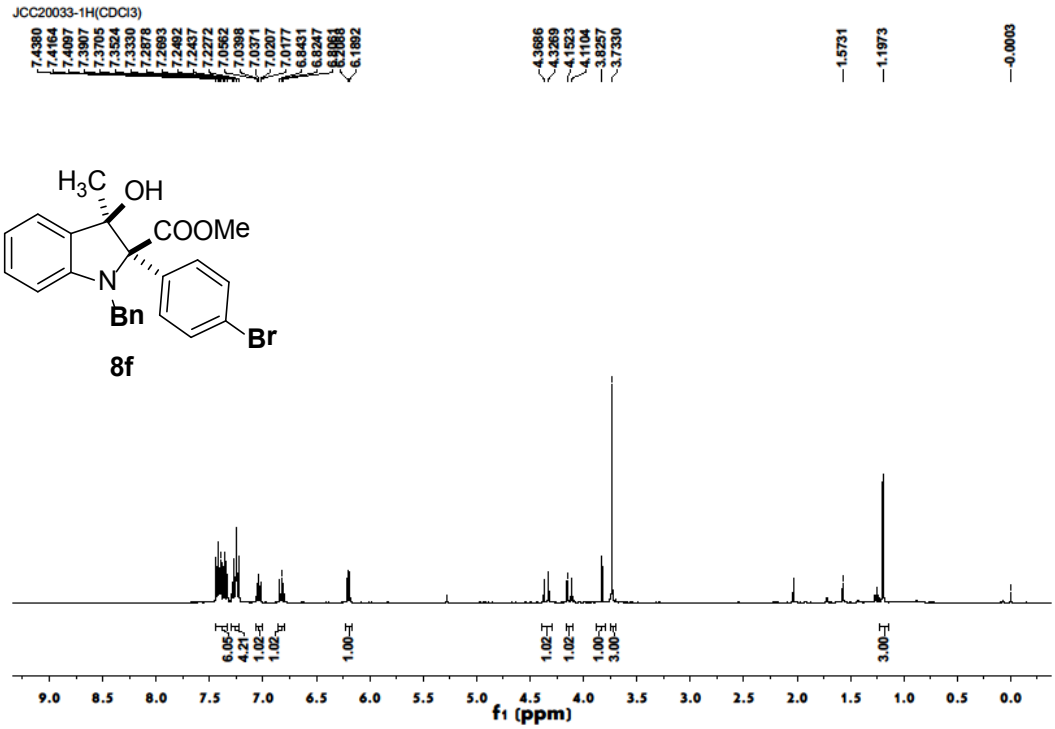


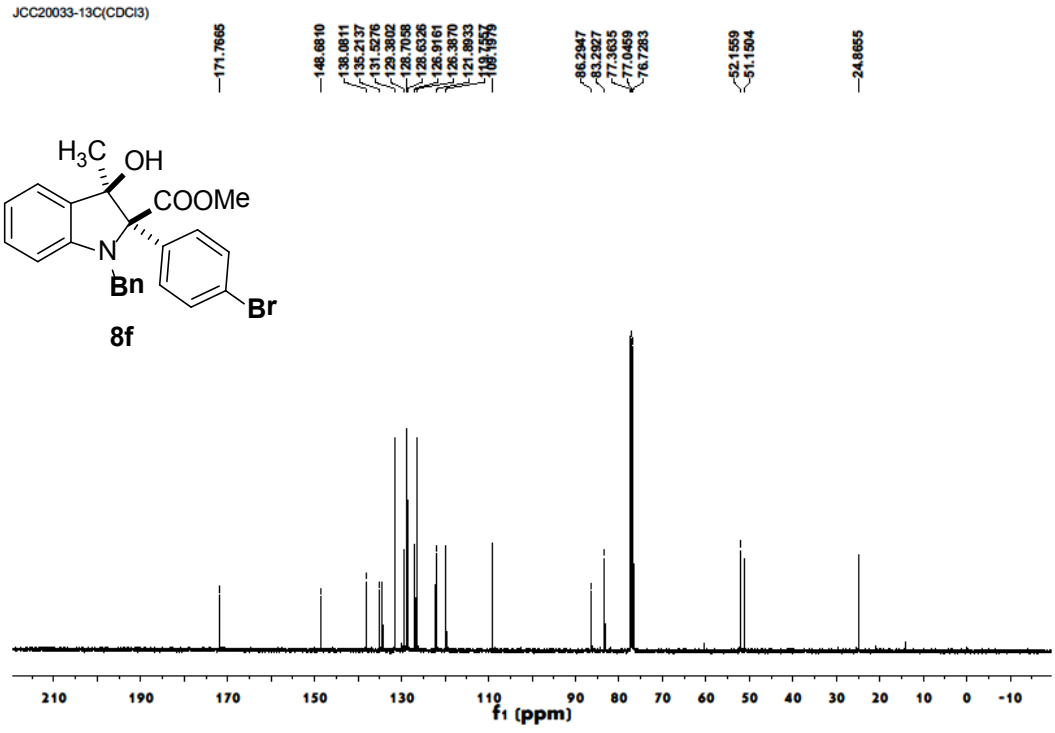

JCC20031-13C(CDCl3)
173.0517
146.6752
137.7273
134.8001
128.9142
128.3933
128.2901
127.0425
126.9074
126.1249
123.6556
110.5936
86.9516
85.0212
77.3746
77.0570
76.7393
52.1458
51.0791
29.6372
7.1124
Cl
OH
COOMe
Ph
N
Bn
8e
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

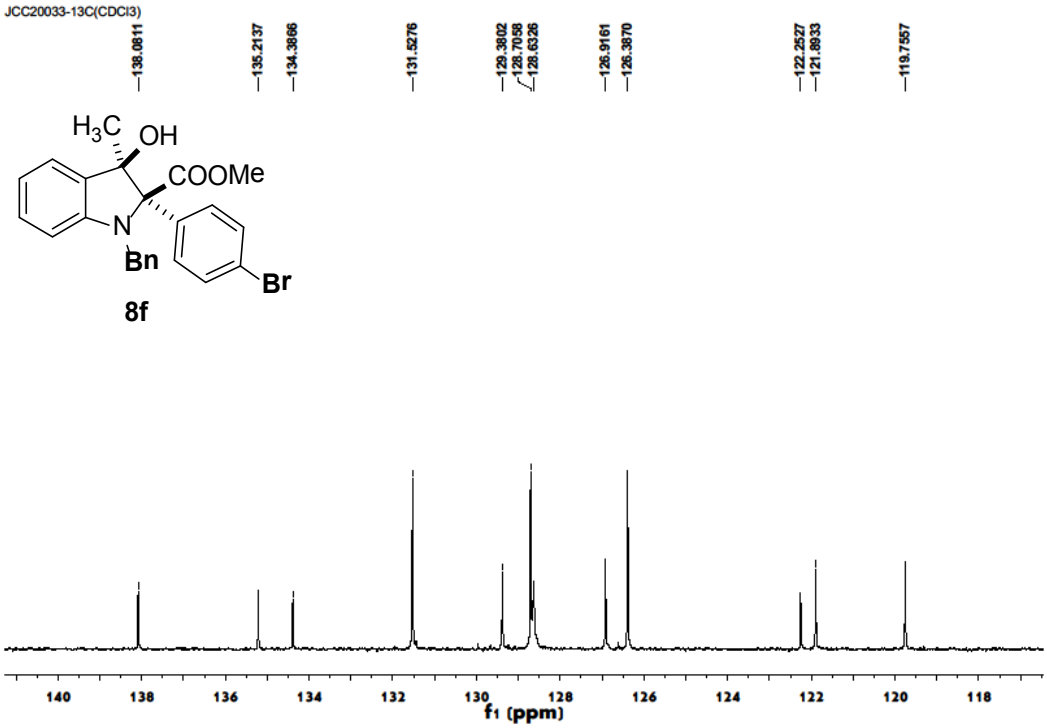

JCC20031-13C(CDCl3)
137.7273
135.8280
134.8001
128.9142
128.3933
128.2901
127.0425
126.9074
126.1249
124.5872
123.6516
Cl
OH
COOMe
Ph
N
Bn
8e
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
f1 (ppm)

(2*S,3*R**)-methyl**

1-benzyl-2-(4-bromophenyl)-3-hydroxy-3-methylindoline-2-carboxylate (8f)

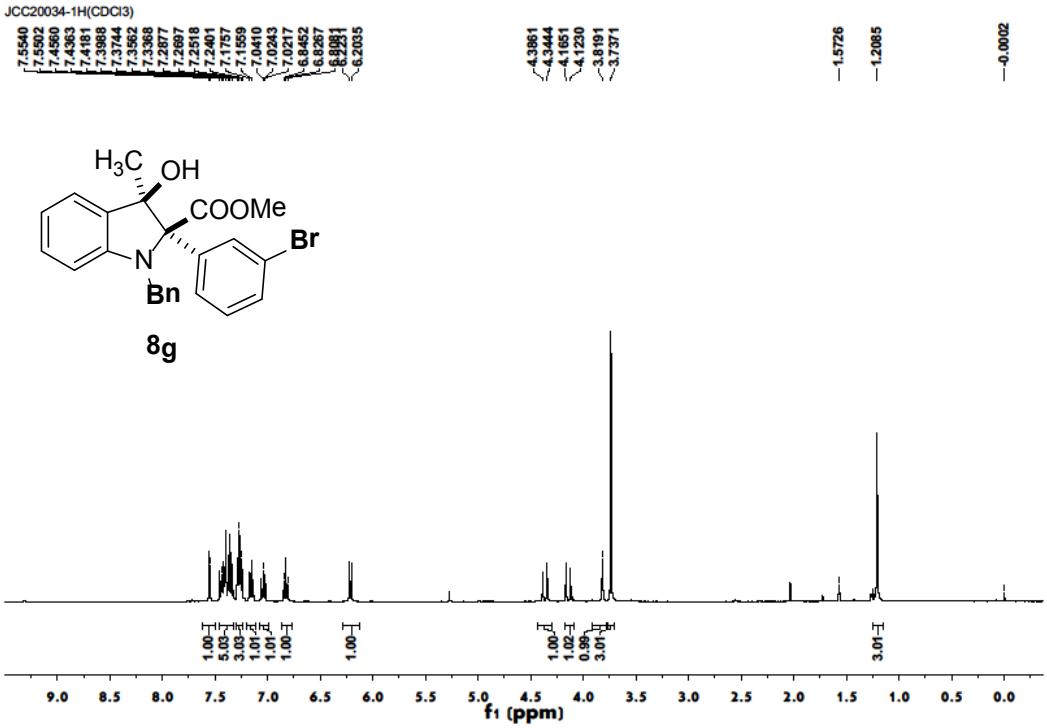


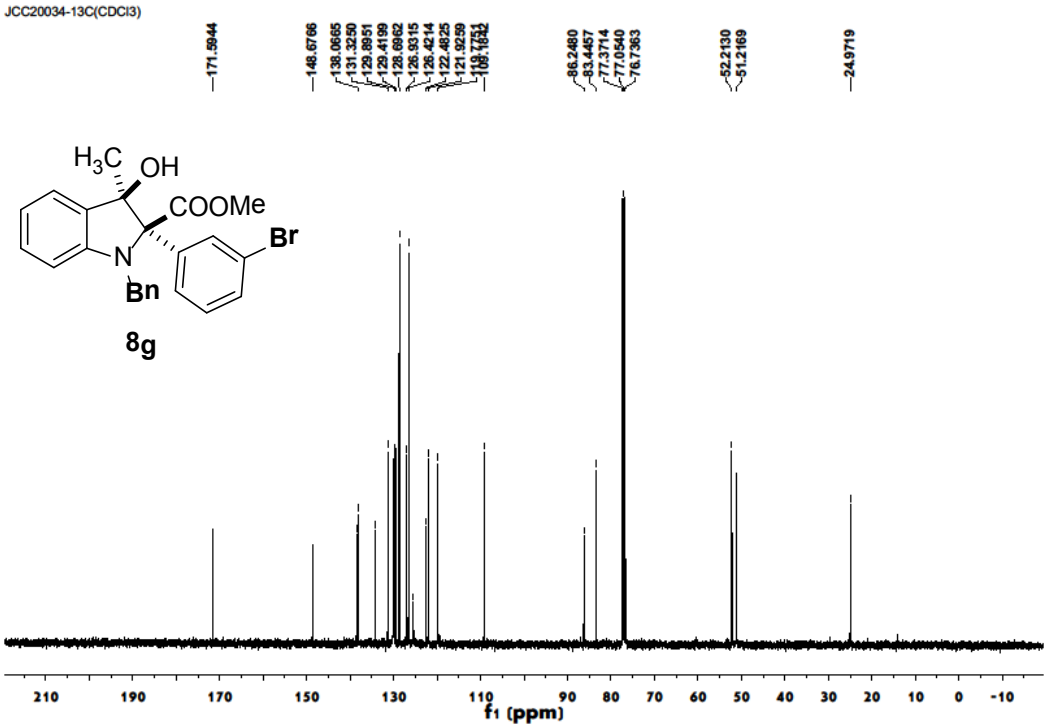


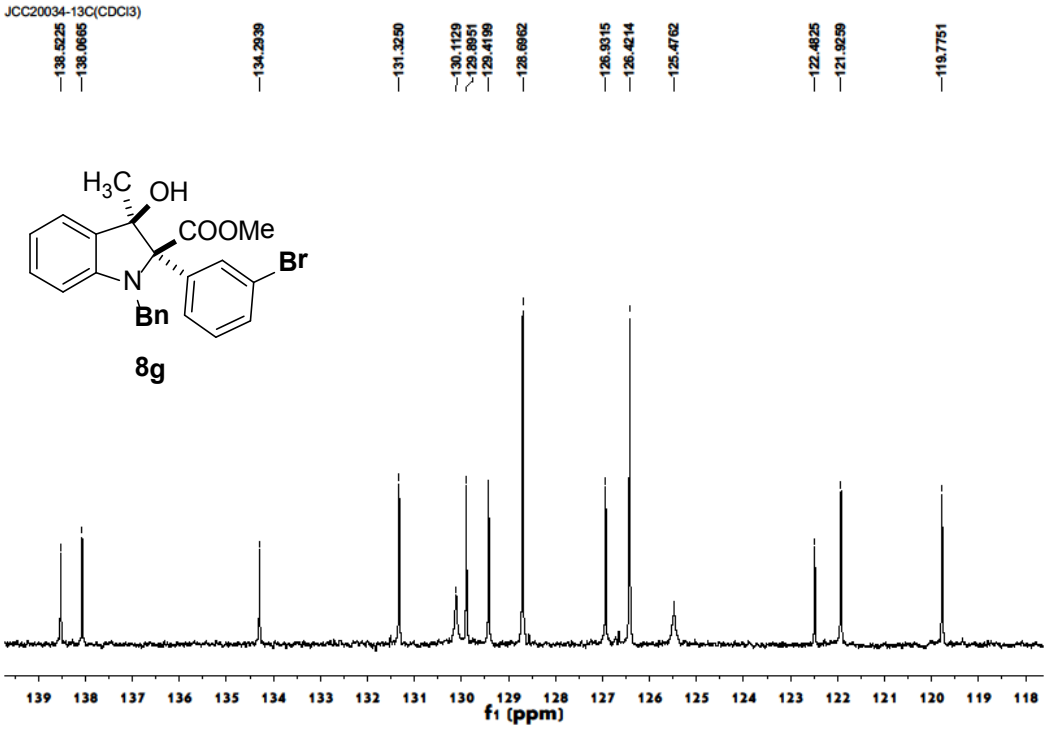


(2*S,3*R**)-methyl**

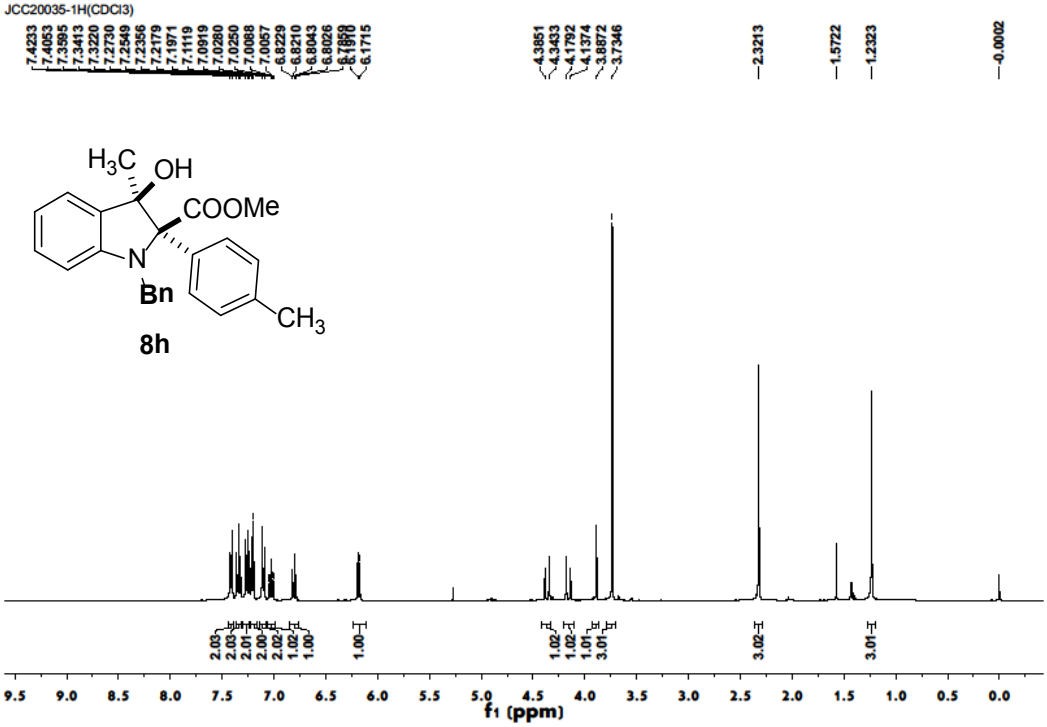
1-benzyl-2-(3-bromophenyl)-3-hydroxy-3-methylindoline-2-carboxylate (8g)

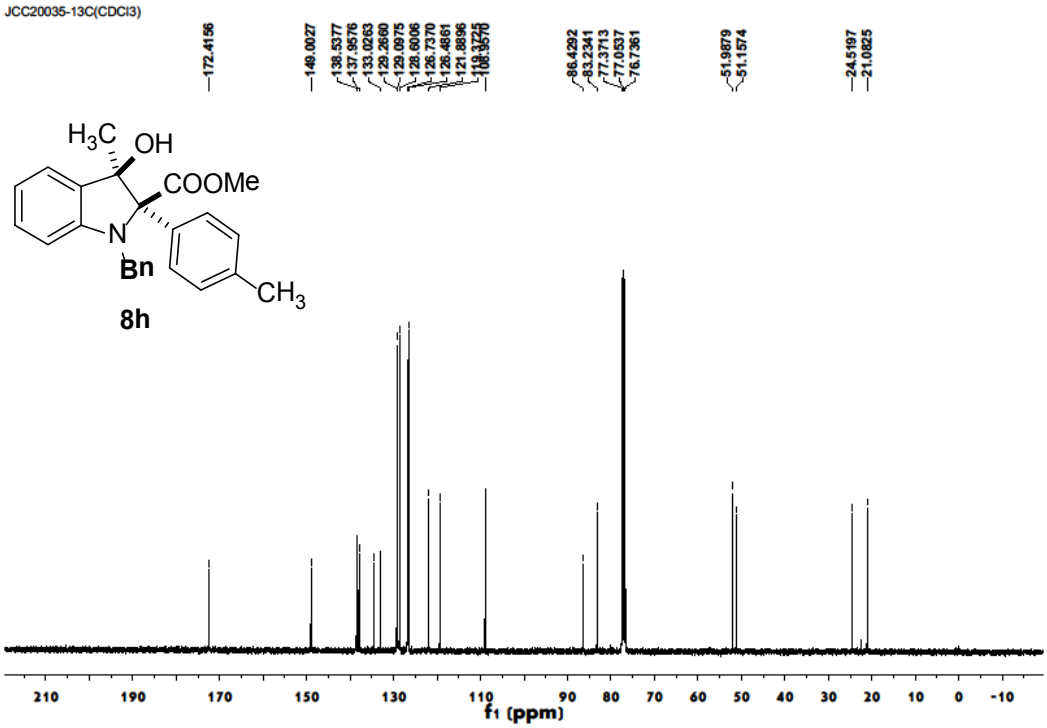


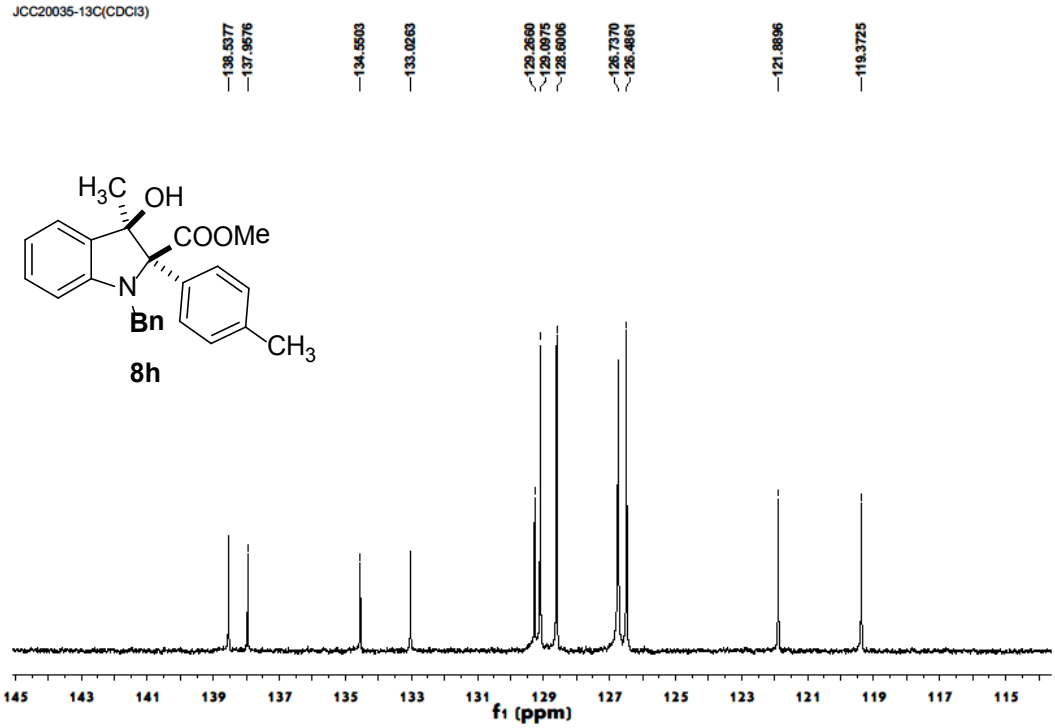

JCC20034-13C(CDCl3)
171.5944
148.6766
138.0665
131.3250
129.8951
129.4199
128.6962
126.9315
126.4214
122.4825
121.9259
119.7751
86.2480
83.4457
77.3714
77.0540
76.7363
52.2130
51.2169
24.9719
H3C
OH
COOMe
Br
N
Bn
8g
f1 (ppm)


JCC20034-13C(CDCl3)
138.5225
138.0665
134.2939
131.3250
130.1129
129.8951
129.4199
128.6962
126.9315
126.4214
125.4762
122.4825
121.9259
119.7751
H3C
OH
COOMe
Br
N
Bn
8g
f1 (ppm)

(2*S,3*R**)-methyl 1-benzyl-3-hydroxy-3-methyl-2-(p-tolyl)indoline-2-carboxylate (8h)**

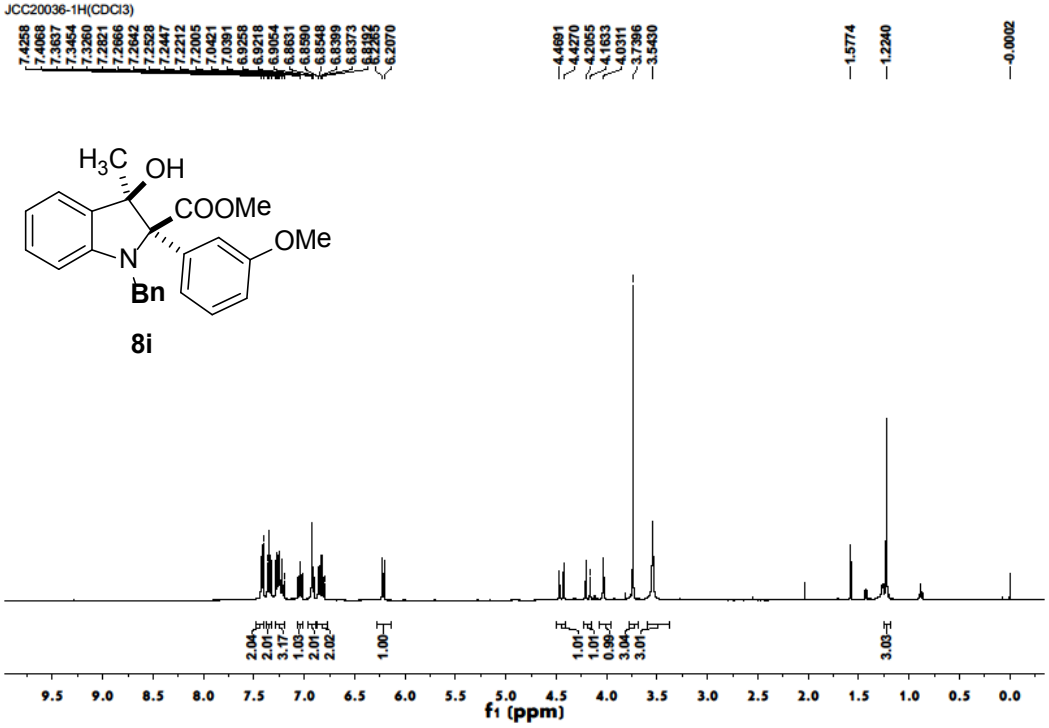


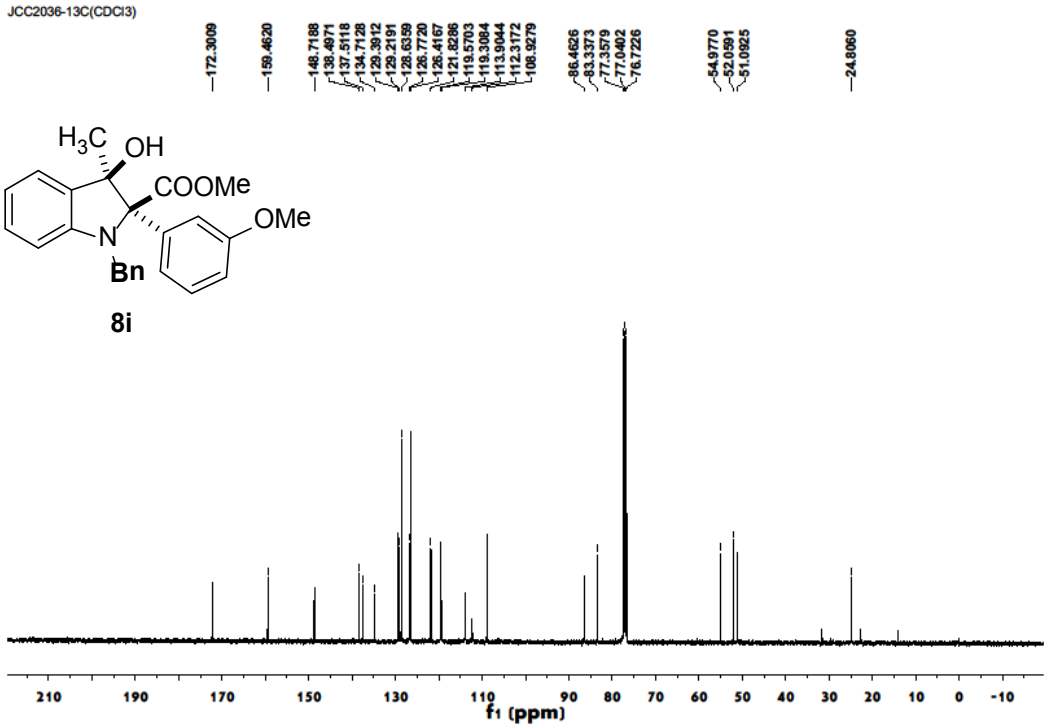




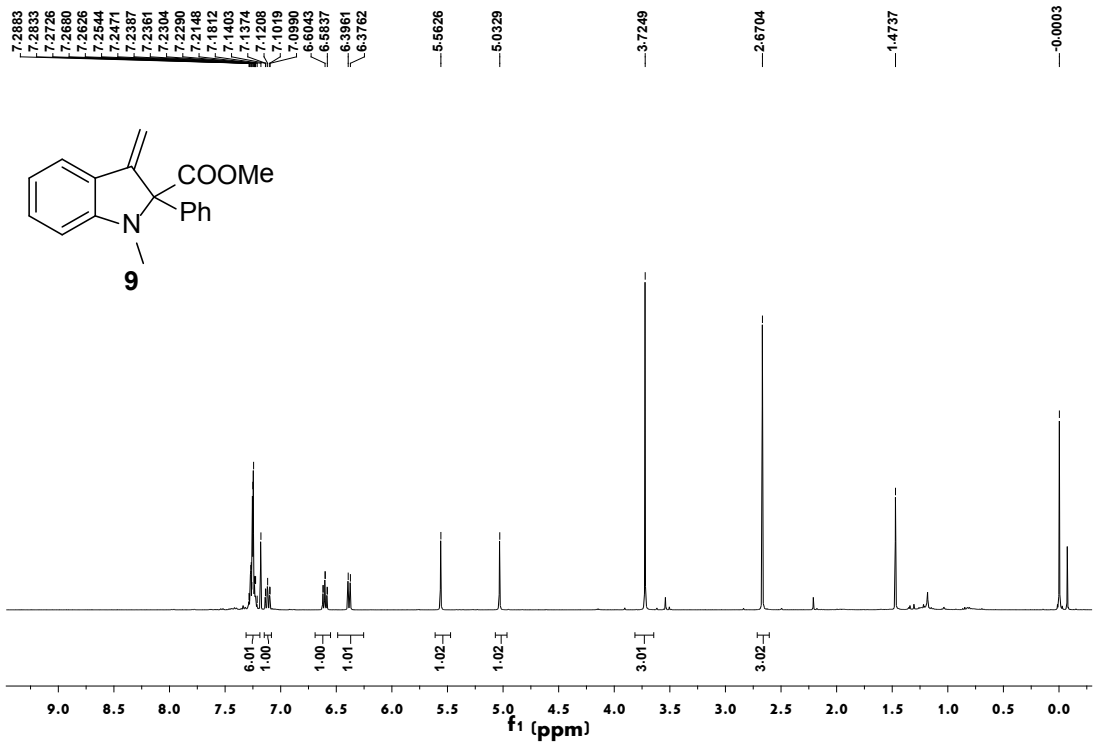
(2*S,3*R**)-methyl**

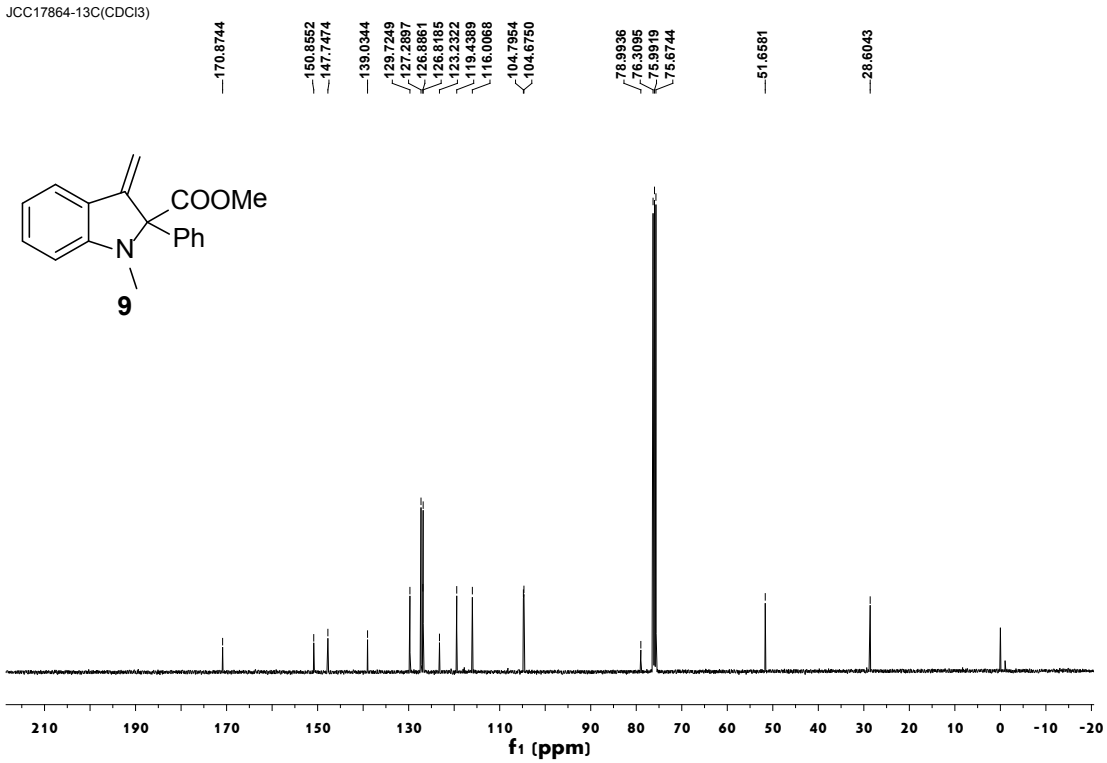
1-benzyl-3-hydroxy-2-(3-methoxyphenyl)-3-methylindoline-2-carboxylate (8i)





Methyl 1-methyl-3-methylene-2-phenylindoline-2-carboxylate (9)

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28.6043
COOMe
Ph
N
9
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150
130
110
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)