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Supplementary information

Enantio- and Diastereoselective NHC/Cu-Catalyzed Intermolecular Dearomative Cyclopropanation of Indoles with Diazo Esters

Jiawei Lu, Sheng Liu, Lin-Xin Ruan, Shu-Li You, Shi-Liang Shi

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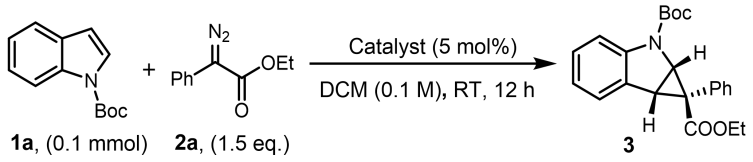
1. General Information

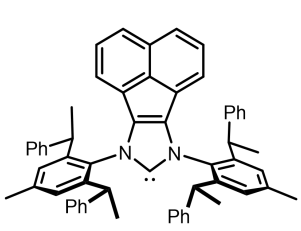
All the reactions were conducted under a N_2 atmosphere with standard dry box or vacuum-line techniques, and the glassware was dried in oven (140 °C) or flame-dried. Reaction solvents, including anhydrous tetrahydrofuran (THF), dichloromethane (DCM), toluene, *n*-hexane, etc. were purchased from Energy Chemical Co. Ltd. or J&K Chemical Co. Ltd. and used as received. Copper chloride was purchased from Strem Chemicals Inc. and used as received. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy, and melting point (if solids). NMR spectra were recorded on an Agilent 400 MHz or 600MHz, Varian 400 MHz or Bruker 400 MHz spectrometers and were calibrated using residual solvent as an internal reference ($CDCl_3$: 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). Melting points were measured on a SGW X-4 apparatus. All IR spectra were taken on a BRUKER TENSOR 27 FT-IR spectrometer. EI-HRMS spectra were obtained on a Waters Micromass G1540N/GCT Premier, and ESI-HRMS spectra were obtained on a Thermo Fisher Scientific LTQ FT Ultra or an Agilent Technologies 6224 TOF LC/MS. GC-MS analysis was performed on a Shimadzu QP2010 SE using a DB-5MS column (30 m, 0.25 mm I.D.). The enantiomeric excess (ee) values of the products were determined by high-performance liquid chromatography (HPLC) analysis performed on a Shimadzu LC-20AT chromatograph or BRUKER SFC 1260 chromatography using a chiral column (15 or 25 cm) as noted for each compound. Optical rotations were measured on a Rudolph Research Analytical Autopol VI Polarimeter and Autopol I Polarimeter with [α]D values reported in degrees; concentration (c) is in g/100 mL. Indoles[1] and diazo esters[2] were prepared according to literatures.

2. Reaction Optimization

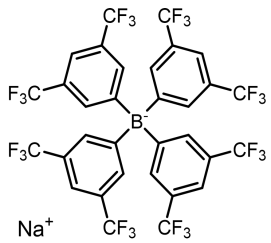
Table S1 Screening of the catalysts



1a, (0.1 mmol) **2a**, (1.5 eq.) **3**



L1

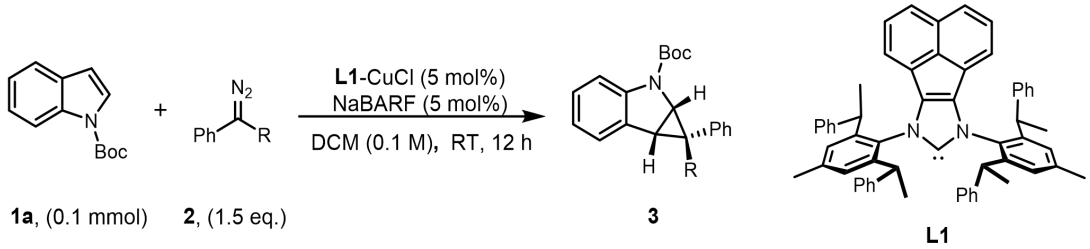


NaBARF

Entry	Cat.[a]	Yield (%)[b]	d.r.[b]	ee (%)[c]
1	$Rh_2(OAc)_4$, **L1**/HCl, KO^{t}Bu, NaBARF	N.D.	N.D.	N.D
2	**L1**-AgCl, NaBARF	N.D.	N.D.	N.D.
3	**L1**-Pd(cin)Cl, NaBARF	82	>20:1	0
4	**L1**-CuCl，NaBARF	90	>20:1	19

[a]Reaction conditions: N-protected indoles **1a** (0.1 mmol), diazo ester **2a** (0.15 mmol), catalyst (5.0 mol %), NaBArF (5.0 mol%), under N_2 atmosphere for 12 h. [b]The yield and d.r. were determined by ^{1}H NMR of crude sample with $C_2H_2Cl_4$ as an internal standard . [c]Determined by chiral HPLC.

Table S2 Screening of the diazo compounds



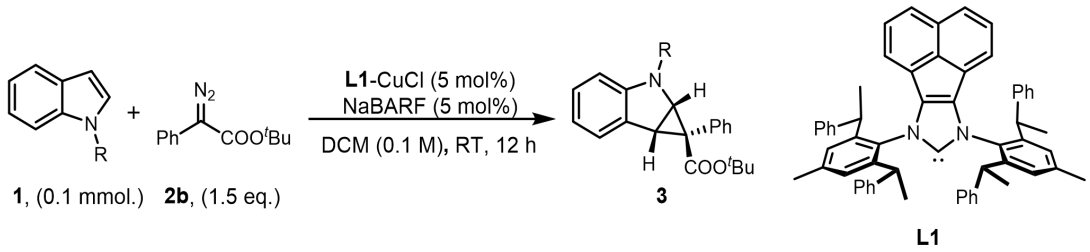
1a, (0.1 mmol) **2**, (1.5 eq.) **3** **L1**

Entry	R	Yield (%)[a]	d.r.[a]	ee (%)[b]
1	COOMe	99	>20:1	14
2	COOEt	90	>20:1	19
3	COOBn	99	>20:1	22
4	COO^{i}Pr	99	>20:1	33
5	COO^{t}Bu	95	>20:1	49
6	COO(2,6-$Me_2C_6H_3$)	N.D.	N.D.	N.D.
7	P(O)$(OMe)_2$	N.D.	N.D.	N.D.

[a]The yield and d.r. were determined by ^{1}H NMR of crude sample with $C_2H_2Cl_4$ as an internal standard .

[b]Determined by chiral HPLC.

Table S3 Screening of the protecting group of indole



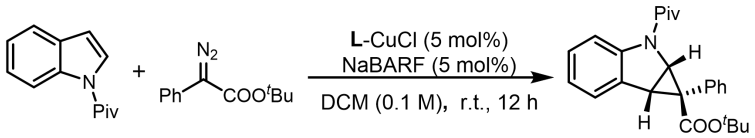
1, (0.1 mmol.) **2b**, (1.5 eq.) **3** **L1**

Entry	R	Yield (%)[a]	d.r.[a]	ee (%)[b]
1	Me	N.D.	>20:1	N.D.
2	TMS	N.D.	>20:1	N.D.
3	Boc	95	>20:1	49
4	Ts	32	>20:1	69
5	COO^{t}Bu	39	>20:1	14
6	Ac	39	>20:1	61
7	Bz	60	>20:1	56
8	COAd	60	>20:1	64
9	Piv	87	>20:1	72

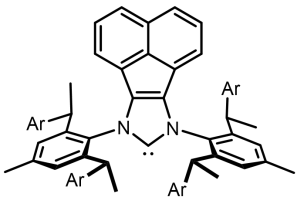
[a]The yield and d.r. were determined by ^{1}H NMR of crude sample with $C_2H_2Cl_4$ as an internal standard .

[b]Determined by chiral HPLC.

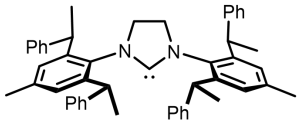
Table S4 Screening of the ligands



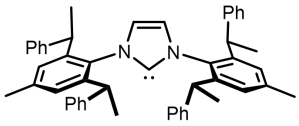
1b, (0.1 mmol) **2b**, (1.5 eq.) **3**



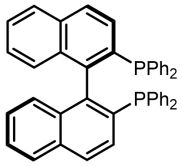
L1 (Ar = Ph), (*R*,*R*,*R*,*R*)-ANIPE
L4 (Ar = 3,5-xylyl), (*R*,*R*,*R*,*R*)-DM-ANIPE



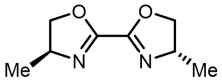
L2 (*R*,*R*,*R*,*R*)-SIPE



L3 (*R*,*R*,*R*,*R*)-IPE



L5 (*R*)-BINAP



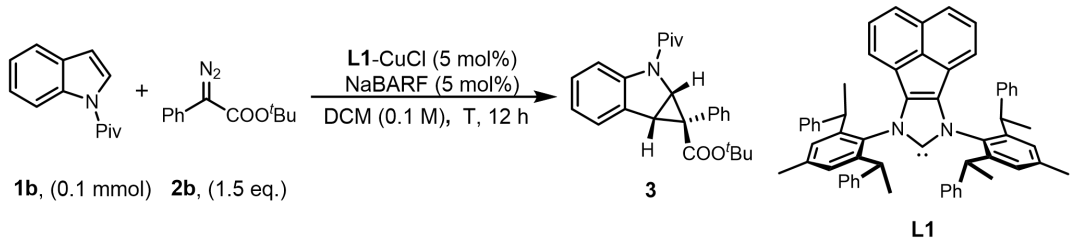
L6

Entry	Ligand	Yield (%)[a]	d.r.[a]	ee (%)[b]
1	**L1**	87	>20:1	72
2	**L2**	82	>20:1	56
3	**L3**	84	>20:1	41
4	**L4**	94	>20:1	37
5	**L5**	N.D.	N.D.	N.D.
6	**L6**	N.D.	N.D	N.D.

[a]The yield and d.r. were determined by ^{1}H NMR of crude sample with $C_2H_2Cl_4$ as an internal standard .

[b]Determined by chiral HPLC.

Table S5 Screening of the temperature



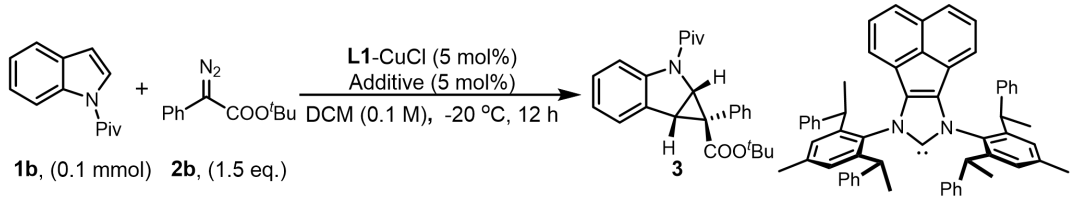
1b, (0.1 mmol) **2b**, (1.5 eq.) **3** **L1**

Entry	T (°C)	NMR Yield (%)[a]	d.r.[a]	ee (%)[b]
1	25	87	>20:1	72
2	-10	80	>20:1	81
3	-20	57	>20:1	85
4	-30	54	>20:1	81
5	-40	56	>20:1	80
6	-20[c]	86	>20:1	85

[a]The yield and d.r. were determined by ^{1}H NMR of crude sample with $C_2H_2Cl_4$ as an internal standard .

[b]Determined by chiral HPLC. [c]Using 2.0 eq. diazo ester.

Table S6 Screening of the additives



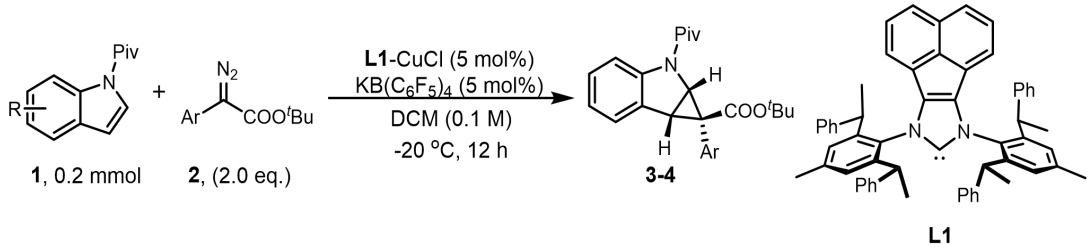
1b, (0.1 mmol) **2b**, (1.5 eq.) **3** **L1**

Entry	Additive	NMR Yield (%)[a]	d.r.[a]	ee (%)[b]
1	None	N.D.	>20:1	N.D.
2	$AgSbF_6$	78	>20:1	75
3	$AgBF_4$	83	>20:1	51
4	$AgPF_6$	75	>20:1	72
5	AgOTf	63	>20:1	13
6	$KAsF_6$	N.D.	N.D.	N.D.
7	NaBARF	86	>20:1	86
8	$KB(C_6F_5)_4$	89	>20:1	89

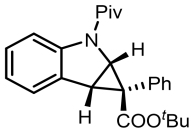
[a]The yield and d.r. were determined by ^{1}H NMR of crude sample with $C_2H_2Cl_4$ as an internal standard .

[b]Determined by chiral HPLC.

3. General procedure for the asymmetric intermolecular cyclopropanation of indoles with diazo esters



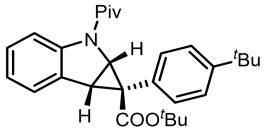
In a nitrogen-filled glovebox, an oven-dried screw-cap reaction tube equipped with a magnetic stir bar was charged with **L1**-CuCl (8.8 mg, 0.01 mmol, 5 mol%) and $KB(C_6F_5)_4$ (7.2 mg, 0.01 mmol, 5 mol%), the indole substrate (0.2 mmol, 1.0 eq.), and dichloromethane (1 mL). The reaction tube was sealed with a screw-cap septum and stirred at -20 ℃ for 1 hour. The diazo compound (0.4 mmol, 2.0 eq.) was dissolved in dichloromethane (1 mL) and frozen at -20 ℃ for 1 hour before being slowly added dropwise to the reaction mixture. The reaction mixture was stirred within the sealed tube at -20 ℃ for 12 h. After the reaction was complete, the mixture was concentrated under reduced pressure to give the crude product. The diastereomeric ratio (d.r.) value of the crude products was determined by ^{1}H NMR. The crude residue was purified via column chromatography to afford the desired product. The enantiomeric excess (ee) value was determined by chiral HPLC analysis of the isolated product.



***tert*-butyl (1*R*,1a*S*,6b*S*)-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa[*b*]indole-1-carboxylate (3a)**

Following the **General Procedure** using 1-(1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 85% yield (66.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 1H), 7.42 – 7.37 (m, 1H), 7.06 – 6.93 (m, 7H), 5.15 (d, *J* = 7.0 Hz, 1H), 3.81 (d, *J* = 7.0 Hz, 1H), 1.60 (s, 9H), 1.42 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.7, 144.1, 131.6, 130.7, 128.9, 127.7, 127.5, 126.9, 125.0, 123.5, 117.8, 81.8, 51.4, 40.8, 35.5, 33.4, 28.2, 28.0. **IR(neat cm^{-1})** 2923, 2853, 1730, 1513, 1257, 1015, 773. **HRMS(ESI)** calculated for $C_{25}H_{29}NO_3Na$ $[M+Na]^+$ *m/z* 414.2040, found 414.2041. $[\alpha]_D^{25}$= -56.7 (c =1.0, $CHCl_3$)。**HPLC analysis** (IA-H, 0.5% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 89% ee: t_R(minor) = 8.6 min, t_R(major) = 9.5 min. **Melting point**: 117-118 ℃.

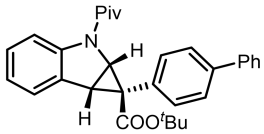


***tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-(*tert*-butyl)phenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3b)

Following the **General Procedure** using 1-(1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (109.7 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 85% yield (76.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.79 (m, 1H), 7.38 – 7.33 (m, 1H), 7.02 – 6.89 (m, 4H), 6.88 – 6.82 (m, 2H), 5.10 (d, J = 7.0 Hz, 1H), 3.75 (d, J = 7.0 Hz, 1H), 1.56 (s, 9H), 1.40 (s, 9H), 1.14 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.8, 149.5, 144.2, 131.2, 128.9, 127.6, 127.3, 124.9, 124.3, 123.4, 117.8, 81.6, 51.2, 40.8, 35.4, 34.3, 33.2, 31.1, 28.2, 28.0. **IR (neat, cm^{-1})** 2963, 2932, 2917, 2369, 1701, 1463, 1402. **HRMS(DART)** calculated for $C_{29}H_{38}NO_3$ $[M+H]^+$ *m/z* 448.2846, found 448.2844. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$ = -52.9 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1.0% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 86% ee: t_R(minor) = 16.8 min, t_R(major) = 14.2 min. **Melting point**: 117-118 ℃.

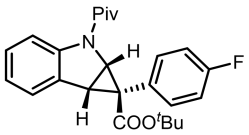


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-([1,1'-biphenyl]-4-yl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3c)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-([1,1'-biphenyl]-4-yl)-2-diazoacetate (117.7 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 86% yield (80.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 1H), 7.40 – 7.36 (m, 2H), 7.34 – 7.24 (m, 3H), 7.22 – 7.15 (m, 3H), 6.97 – 6.83 (m, 4H), 5.07 (d, *J* = 7.0 Hz, 1H), 3.73 (d, *J* = 7.0 Hz, 1H), 1.51 (s, 9H), 1.34 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.6, 144.2, 140.6, 139.3, 132.0, 129.8, 128.8, 128.6, 127.9, 127.1, 126.9, 126.1, 124.9, 123.6, 117.9, 81.9, 51.5, 40.8, 35.5, 33.2, 28.2, 28.0. **IR (neat, cm^{-1})** 2964, 2929, 1700, 1602, 1462, 1257, 957. **HRMS (ESI)** calculated for $C_{31}H_{34}NO_3$ $[M+H]^+$ *m/z* 468.2533, found 468.2536. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$ = -39.1 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 0.5% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 82% ee: t_R (minor) = 11.3 min, t_R (major) = 12.4 min. **Melting point**: 154-155 ℃.

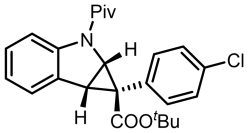


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-fluorophenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa-[*b*]indole-1-carboxylate (3d)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(4-fluorophenyl)acetate (94.4 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 88% yield (72.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 1H), 7.42 – 7.34 (m, 1H), 7.07 – 6.89 (m, 4H), 6.72 (t, *J* = 8.7 Hz, 2H), 5.13 (d, *J* = 7.0 Hz, 1H), 3.79 (d, *J* = 7.0 Hz, 1H), 1.58 (s, 9H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.5, 161.5 (d, *J* = 246.2 Hz), 144.1, 133.2 (d, *J* = 8.2 Hz), 128.6, 127.9, 126.6 (d, *J* = 3.3 Hz), 124.9, 123.6, 117.8, 114.6 (d, *J* = 21.6 Hz), 82.0, 51.4, 40.8, 35.5, 32.7, 28.1, 28.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -114.73. **IR (neat, cm^{-1})** 2975, 2931, 2361, 1702, 1462, 1260, 955. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3F$ $[M+H]^+$ *m/z* 410.2126, found 410.2129. $[\alpha]_D^{27}$ = -43.1 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 0.5% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 87% ee: t_R(minor) = 12.1 min, t_R(major) = 13.7 min. **Melting point**: 115-116 ℃.



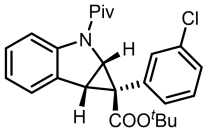
***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-chlorophenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa-[*b*]indole-1-carboxylate (3e)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-(4-chlorophenyl)-2-diazoacetate (100.8 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 82% yield (70.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.81 (m, 1H), 7.39 – 7.33 (m, 1H), 7.04 – 6.92 (m, 4H), 6.91 – 6.85 (m, 2H), 5.11 (d, *J* = 7.0 Hz, 1H), 3.77 (d, *J* = 7.0 Hz, 1H), 1.55 (s, 9H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.2, 144.0, 132.9, 132.9, 129.4, 128.5, 128.0, 127.8, 124.9, 123.7, 117.9, 82.1, 51.5, 40.8, 35.5, 32.8, 28.1, 28.0. **IR (neat, cm^{-1})** 2959, 2926, 2855, 1704, 1494, 1256, 956. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3Cl$ $[M+H]^+$ *m/z* 426.1830, found 426.1826. $[\alpha]_D^{27}$= -45.9 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 0.5% IPA in hexanes, 0.5 mL/min, 254 nm) indicated 86% ee: t_R (minor) = 27.3 min, t_R (major) = 24.1

min. **Melting point**: 120-121 ℃.

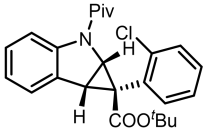


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(3-chlorophenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa-[*b*]indole-1-carboxylate (3f)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-(3-chlorophenyl)-2-diazoacetate (100.8 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 89% yield (75.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 1H), 7.34 – 7.27 (m, 1H), 6.96 – 6.81 (m, 5H), 6.80 – 6.73 (m, 1H), 5.03 (d, *J* = 7.0 Hz, 1H), 3.70 (d, *J* = 7.0 Hz, 1H), 1.48 (s, 9H), 1.32 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.8, 171.0, 143.9, 133.0, 132.8, 132.0, 129.7, 128.7, 128.4, 128.1, 127.2, 125.0, 123.7, 118.0, 82.2, 51.5, 40.8, 35.5, 32.9, 28.2, 28.0. **IR (neat, cm^{-1})** 2962, 2927, 2855, 1704, 1600, 1463, 1258. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3Cl$ $[M+H]^+$ *m/z* 426.1830, found 426.1825. $[\alpha]_D^{27}$ = -45.7 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1.0% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 87% ee: t_R (minor) = 16.4 min, t_R (major) = 15.0 min. **Melting point**: 105-106 ℃.

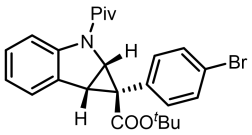


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(2-chlorophenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa-[*b*]indole-1-carboxylate (3g)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-(2-chlorophenyl)-2-diazoacetate (100.8 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a colorless liquid in 45% yield (38.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.03 – 6.93 (m, 2H), 6.91 – 6.84 (m, 3H), 6.81 – 6.73 (m, 1H), 5.01 (d, *J* = 6.9 Hz, 1H), 3.86 (d, *J* = 6.9 Hz, 1H), 1.51 (s, 9H), 1.30 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.8, 169.8, 143.0, 135.4, 129.4, 129.0, 128.1, 127.5, 126.8, 126.6, 124.7, 124.3, 122.2, 116.2, 80.9, 50.9, 39.8, 36.1, 30.3, 27.1, 26.8. **IR (neat, cm^{-1})** 3076, 2972, 2931, 2353, 1704, 1665, 1603. **HRMS (ESI)** calculated for $C_{25}H_{28}NO_3ClNa$ $[M+Na]^+$ *m/z* 448.1650, found 448.1652. $[\alpha]_D^{25}$ = -34.5 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1.0% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 76% ee: t_R (minor) = 8.1 min, t_R (major) = 10.0 min.

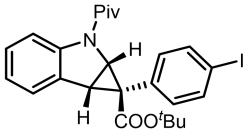


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-bromophenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa-[*b*]indole-1-carboxylate (3h)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-(4-bromophenyl)-2-diazoacetate (118.4 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 82% yield (76.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 1H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.03 – 6.90 (m, 2H), 6.86 – 6.79 (m, 2H), 5.11 (d, *J* = 7.0 Hz, 1H), 3.77 (d, *J* = 7.0 Hz, 1H), 1.55 (s, 9H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.1, 144.0, 133.2, 130.8, 129.9, 128.4, 128.1, 124.9, 123.7, 121.2, 117.9, 82.1, 51.5, 40.8, 35.4, 32.8, 28.2, 28.0. **IR (neat, cm^{-1})** 3624, 3584, 3521, 1703, 1521, 1366, 1254. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3Br$ $[M+H]^+$ *m/z* 470.1325, found 470.1325. $[\alpha]_D^{27}$= -59.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1.0% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 87% ee: t_R (minor) = 15.4 min, t_R (major) = 14.1 min. **Melting point**: 131-132 ℃.

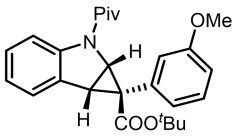


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-iodophenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa[*b*]i-ndole-1-carboxylate (3i)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *ter*t-butyl 2-diazo-2-(4-iodophenyl)acetate (137.6 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 92% yield (95.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 1H), 7.37 (t, *J* = 8.3 Hz, 3H), 7.07 – 6.95 (m, 2H), 6.74 – 6.69 (m, 2H), 5.12 (d, *J* = 7.0 Hz, 1H), 3.79 (d, *J* = 7.0 Hz, 1H), 1.57 (s, 9H), 1.41 (s, 9H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.1, 144.0, 136.7, 133.5, 130.6, 128.4, 128.1, 124.9, 123.7, 117.9, 93.0, 82.1, 51.4, 40.8, 35.4, 33.0, 28.1, 28.0. **IR (neat, cm^{-1})** 2962, 2926, 2854, 1702, 1463, 1258, 956. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3I$ $[M+H]^+$ *m/z* 518.1187, found 518.1186. $[\alpha]_D^{27}$= -59.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1.0% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_R (minor) = 6.3 min, t_R (major) = 7.8 min. **Melting point**: 154-155 ℃.

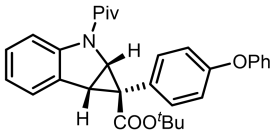


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-methoxyphenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa-[*b*]indole-1-carboxylate (3j)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(3-methoxyphenyl)acetate (99.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 72% yield (60.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 1H), 7.40 – 7.34 (m, 1H), 7.02 – 6.89 (m, 3H), 6.59 – 6.53 (m, 2H), 6.49 – 6.44 (m, 1H), 5.10 (d, *J* = 7.0 Hz, 1H), 3.76 (d, *J* = 6.9 Hz, 1H), 3.59 (s, 3H), 1.56 (s, 9H), 1.40 (s, 9H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.8, 170.5, 157.6, 143.2, 131.0, 127.8, 127.3, 126.8, 123.9, 123.3, 122.5, 116.9, 116.0, 112.1, 80.8, 54.1, 50.4, 39.8, 34.4, 32.4, 27.2, 27.0. **IR (neat, cm^{-1})** 2963, 2928, 2854, 2351, 1722, 1664, 1602. **HRMS (ESI)** calculated for $C_{26}H_{31}NO_4Na$ $[M+Na]^+$ *m/z* 444.2141, found 444.2145. $[\alpha]_D^{27}$ = -53.6 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 86% ee: t_R (minor) = 18.1 min, t_R (major) = 13.2 min. **Melting point**: 137-138 ℃.

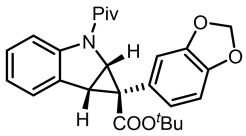


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-phenoxyphenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa-[*b*]indole-1-carboxylate (3k)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(4-phenoxyphenyl)acetate (124.0 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 72% yield (69.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 1H), 7.40 – 7.34 (m, 2H), 7.33 – 7.29 (m, 1H), 7.29 – 7.23 (m, 2H), 7.20 – 7.14 (m, 3H), 6.96 – 6.92 (m, 2H), 6.92 – 6.83 (m, 2H), 5.07 (d, *J* = 7.0 Hz, 1H), 3.72 (d, *J* = 7.0 Hz, 1H), 1.51 (s, 9H), 1.33 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.9, 170.5, 143.1, 139.5, 138.3, 130.9, 128.7, 127.7, 127.6, 126.8, 126.1, 125.8, 125.1, 123.9, 122.5, 116.9, 80.8, 50.4, 39.8, 34.4, 32.2, 27.2, 27.0. **IR (neat, cm^{-1})** 3533, 3068, 2959, 2899, 2839, 2343, 1694. **HRMS (ESI)** calculated for $C_{31}H_{34}NO_4$ $[M+H]^+$ *m/z* 484.2476, found 484.2482. $[\alpha]_D^{27}$ = -51.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 84% ee: t_R (minor) = 9.7 min, t_R (major) = 11.7 min. **Melting point**: 169-170 ℃.

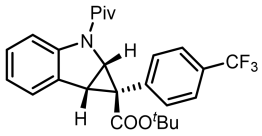


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(benzo[*d*][1,3]dioxol-5-yl)-2-pivaloyl-1,1a,2,6b-tetrahydrocycl-opropa[*b*]indole-1-carboxylate (3l)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-(benzo[*d*][1,3]dioxol-5-yl)-2-diazoacetate (104.8 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 77% yield (67.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 1H), 7.42 – 7.34 (m, 1H), 7.08 – 6.95 (m, 2H), 6.51 – 6.39 (m, 3H), 5.80 (s, 2H), 5.10 (d, *J* = 7.0 Hz, 1H), 3.75 (d, *J* = 7.0 Hz, 1H), 1.57 (s, 9H), 1.43 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.7, 146.7, 146.3, 144.2, 128.8, 127.8, 125.3, 124.9, 124.1, 123.6, 117.9, 111.9, 107.5, 100.7, 81.8, 51.5, 40.8, 35.5, 33.2, 28.2, 28.0. **IR (neat, cm^{-1})** 2956, 2928, 2430, 1761, 1467, 1257, 1205. **HRMS (ESI)** calculated for $C_{26}H_{29}NO_5Na$ $[M+Na]^+$ *m/z* 458.1933, found 458.1938. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$= -49.8 (c =1.0, $CHCl_3$). **HPLC analysis** (OD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 83% ee: t_R (minor) = 9.6 min, t_R (major) = 10.8 min. **Melting point**: 135-136 ℃.

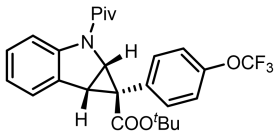


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-2-pivaloyl-1-(4-(trifluoromethyl)phenyl)-1,1a,2,6b-tetrahydro-cyclopropa[*b*]indole-1-carboxylate (3m)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (114.4 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 95% yield (87.2 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 1H), 7.44 – 7.37 (m, 1H), 7.34 – 7.26 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.06 – 6.94 (m, 2H), 5.18 (d, *J* = 7.0 Hz, 1H), 3.84 (d, *J* = 7.0 Hz, 1H), 1.59 (s, 9H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 170.9, 143.9, 135.0 (q, *J* = 1.5 Hz), 131.9, 129.0 (q, *J* = 32.3 Hz), 128.2, 128.2, 125.3, 124.4 (q, *J* = 3.8 Hz), 124.9, 123.8, 124.0 (q, *J* = 272.1 Hz)， 118.0, 82.3, 51.5, 40.8, 35.5, 33.0, 28.1, 28.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.94. **IR (neat, cm^{-1})** 2978, 2933, 2381, 1704, 1664, 1619, 1604. **HRMS (ESI)** calculated for $C_{26}H_{29}NO_3F_3$ $[M+H]^+$ *m/z* 460.2090, found 460.2094. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$= -108.1 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 75% ee: t_R (minor) = 6.5 min, t_R (major) = 10.9 min. **Melting point**: 130-131 ℃.

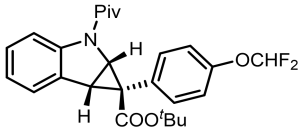


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-2-pivaloyl-1-(4-(trifluoromethoxy)phenyl)-1,1a,2,6b-tetrahydro-cyclopropa[*b*]indole-1-carboxylate (3n)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(4-(trifluoromethoxy)phenyl)acetate (120.8 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 84% yield (79.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 5.6 Hz, 1H), 7.02 – 6.89 (m, 4H), 6.89 – 6.82 (m, 2H), 5.14 (d, *J* = 7.0 Hz, 1H), 3.79 (d, *J* = 7.0 Hz, 1H), 1.56 (s, 9H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.8, 171.1, 148.0, 147.9, 143.9, 133.0, 129.6, 128.4, 128.0, 124.9, 123.7, 120.3 (q, *J* = 253.9 Hz), 119.8, 117.9, 82.1, 51.4, 40.8, 35.5, 32.7, 28.1, 27.9. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -58.94. **IR (neat, cm^{-1})** 2979, 1703, 1664, 1511, 1477, 1402, 1257. **HRMS (ESI)** calculated for $C_{26}H_{29}NO_4F_3$ $[M+H]^+$ *m/z* 476.2043, found 476.2035. $[\alpha]_D^{27}$ = -73.4 (c =1.0, $CHCl_3$). **HPLC analysis** (OD-H, 0.5% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 79% ee: t_R (minor) = 24.1 min, t_R (major) = 25.9 min. **Melting point**: 147-148 °C.



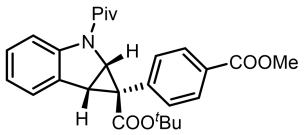
***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(4-((difluoromethylene)-λ^4-oxidaneyl)phenyl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa[*b*]indole-1-carboxylate (3o)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(4-(difluoromethoxy)phenyl)acetate (113.6 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 84% yield (76.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.78 (m, 1H), 7.39 (m, 1H), 7.06 – 6.92 (m, 4H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.35 (t, *J* = 74.2 Hz, 1H), 5.14 (d, *J* = 7.0 Hz, 1H), 3.80 (d, *J* = 7.0 Hz, 1H), 1.58 (s, 9H), 1.42 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.3, 150.2, 144.0, 133.1, 128.5, 128.0, 127.9, 124.9, 123.7, 118.2, 117.9, 115.9 (t, *J* = 257.2 Hz), 82.1, 51.4, 40.8, 35.5, 28.1, 28.0. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -80.53. **IR (neat, cm^{-1})** 2962, 2925, 2854, 1704, 1667, 1463, 1366. **HRMS (ESI)** calculated for $C_{26}H_{30}NO_4F_2$ $[M+H]^+$ *m/z* 458.2137, found 458.2144. $[\alpha]_D^{27}$ = -63.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 2% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 81% ee: t_R (minor) = 4.6 min, t_R (major) = 6.1 min.

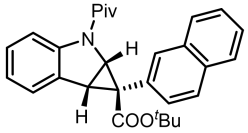
Melting point: 147-148 °C.



***Tert*-butyl**
(1*R*,1a*S*,6b*S*)-1-(4-(methoxycarbonyl)phenyl)-2-pivaloyl-1,1a,2,6b-tetrahydro-cycloprop a[*b*]indole-1-carboxylate (3p)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and methyl 4-(2-(*tert*-butoxy)-1-diazo-2-oxoethyl)benzoate (110.4 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 80% yield (71.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 1H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.32 – 7.26 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.91 – 6.81 (m, 2H), 5.06 (d, *J* = 7.0 Hz, 1H), 3.76 – 3.60 (m, 4H), 1.48 (s, 9H), 1.28 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.8, 170.9, 166.8, 143.9, 136.3, 131.6, 128.7, 128.6, 128.3, 128.0, 125.0, 123.7, 117.9, 82.2, 51.9, 51.5, 40.8, 35.5, 33.2, 28.2, 28.0. **IR (neat, cm^{-1})** 2964, 2930, 2855, 1723, 1705, 1463, 1402. **HRMS (DART)** calculated for $C_{27}H_{32}NO_5$ $[M+H]^+$ *m/z* 450.2272, found 450.2275. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$ = -42.9 (c =1.0, $CHCl_3$). **HPLC analysis** (IA-H, 2% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 80% ee: t_R (minor) = 3.3 min, t_R (major) = 3.6 min. **Melting point**: 168-169 °C.

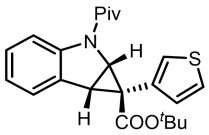


***Tert*-butyl**
(1*R*,1a*S*,6b*S*)-1-(naphthalen-2-yl)-2-pivaloyl-1,1a,2,6b-tetrahydrocycloprop-a[*b*]indole-1-carboxylate (3q)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(naphthalen-2-yl)acetate (107.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 76% yield (67.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 1H), 7.67 – 7.61 (m, 1H), 7.58 – 7.53 (m, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.37 – 7.30 (m, 2H), 7.12 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.95 – 6.85 (m, 2H), 5.21 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 7.0 Hz, 1H), 1.63 (s, 9H), 1.39 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.8, 170.6, 143.2, 131.7, 131.1, 129.8, 128.4, 127.6, 127.2, 126.8, 126.7, 126.3, 125.9, 124.7, 124.4, 123.9, 122.4, 116.8, 80.9, 50.6, 39.8, 34.6, 32.4, 27.3, 27.0. **IR (neat, cm^{-1})** 2962, 2926, 2854, 1703, 1666, 1463, 1260. **HRMS (ESI)** calculated for $C_{29}H_{32}NO_3$ $[M+H]^+$ *m/z* 442.2377, found 442.2376. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{25}}$= -52.0 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 84% ee:

t_R (minor) = 17.0 min, t_R (major) = 14.8 min. **Melting point**: 151-152 °C.

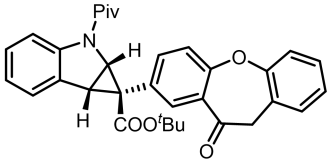


***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-2-pivaloyl-1-(thiophen-3-yl)-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3r)

Following the **General Procedure** using 1-(1*H* -indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-(thiophen-3-yl)acetate (89.6 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 90% yield (71.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.12 – 7.05 (m, 1H), 7.04 – 6.92 (m, 2H), 6.73 – 6.68 (m, 2H), 5.08 (d, *J* = 7.0 Hz, 1H), 3.78 (d, *J* = 7.0 Hz, 1H), 1.55 (s, 9H), 1.45 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.3, 144.7, 130.3, 130.1, 128.5, 128.0, 125.9, 124.7, 123.6, 123.5, 117.8, 81.9, 51.7, 40.7, 36.1, 29.3, 28.0, 28.0. **IR (neat, cm^{-1})** 2961, 2924, 2853, 1702, 1667, 1461, 1362. **HRMS (ESI)** calculated for $C_{23}H_{28}NO_3S$ $[M+H]^+$ *m/z* 398.1784, found 398.1786. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$ = -52.1 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 90% ee: t_R (minor) = 10.4 min, t_R (major) = 13.1 min. **Melting point**: 108-109 °C.



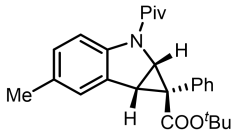
***Tert*-butyl**

(1*R*,1a*S*,6b*S*)-1-(11-oxo-10,11-dihydrodibenzo[*b*,*f*]oxepin-2-yl)-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa[*b*]indole-1-carboxylate (3s)

Following the **General Procedure** using 1-(1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (40.2 mg, 0.2 mmol, 1.0 eq.) and *ter*t-butyl 2-diazo-2-(11-oxo-10,11-dihydrodibenzo[*b*,*f*]oxepin-2-yl)acetate (89.6 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 58% yield (60.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.4 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.55 – 7.40 (m, 3H), 7.32 – 7.26 (m, 1H), 7.06 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.16 (d, *J* = 6.9 Hz, 1H), 5.09 – 4.98 (m, 2H), 3.81 (d, *J* = 6.9 Hz, 1H), 1.63 (s, 9H), 1.43 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 190.1, 177.0, 171.4, 160.1, 144.1, 140.3, 138.6, 135.7, 135.5, 132.7, 129.5, 129.2, 128.6, 128.0, 127.8, 125.0, 124.5, 124.4, 123.6, 119.9, 117.9, 82.1, 73.5, 51.6, 40.9, 35.6, 32.6, 28.2, 28.1. **IR (neat, cm^{-1})** 2977, 2933, 1703, 1662, 1608, 1492, 1401. **HRMS (ESI)** calculated for $C_{33}H_{33}NO_5Na$ $[M+Na]^+$ *m/z* 546.2251, found

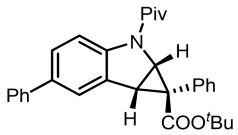
546.2247. $[\alpha]_D^{27}$ = -169.9 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 71% ee: t_R (minor) = 13.6 min, t_R (major) = 17.9 min. **Melting point**: 189-190 °C.



***Tert*-butyl (1*R*,1a*S*,6b*S*)-5-methyl-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3t)**

Following the **General Procedure** using 2,2-dimethyl-1-(5-methyl-1*H*-indol-1-yl)propan-1-one (43.0 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 80% yield (64.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.20 (s, 1H), 7.07 – 6.95 (m, 5H), 6.83 – 6.77 (m, 1H), 5.12 (d, *J* = 7.0 Hz, 1H), 3.74 (d, *J* = 7.0 Hz, 1H), 2.28 (s, 3H), 1.59 (s, 9H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.6, 170.7, 140.9, 132.1, 130.5, 129.7, 127.8, 127.3, 126.4, 125.8, 124.4, 116.4, 80.6, 50.4, 39.6, 34.4, 32.6, 27.2, 27.0, 19.9. **IR (neat, cm^{-1})** 2968, 2928, 1702, 1663, 1479, 1401, 1259. **HRMS (ESI)** calculated for $C_{26}H_{31}NO_5Na$ $[M+Na]^+$ *m/z* 428.2196, found 428.2189. $[\alpha]_D^{27}$ = -13.7 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 84% ee: t_R (minor) = 14.2 min, t_R (major) = 12.2 min. **Melting point**: 120-121 °C.

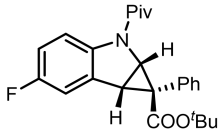


***Tert*-butyl (1*R*,1a*S*,6b*S*)-1,5-diphenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa[*b*]indo-le-1-carboxylate (3u)**

Following the **General Procedure** using 2,2-dimethyl-1-(5-phenyl-1*H*-indol-1-yl)propan-1-one (55.4 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 76% yield (71.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.22 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.00 (s, 5H), 5.15 (d, *J* = 7.0 Hz, 1H), 3.83 (d, *J* = 7.0 Hz, 1H), 1.58 (s, 9H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.9, 171.6, 143.5, 140.8, 136.7, 131.6, 130.6, 129.6, 128.8,

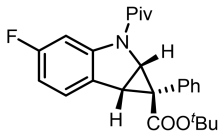
127.5, 127.0, 126.9, 126.7, 123.4, 117.9, 81.8, 51.6, 40.8, 35.4, 33.7, 28.2, 28.0. **IR (neat, cm^{-1})** 2975, 2934, 1704, 1664, 1619, 1476, 1402. **HRMS (ESI)** calculated for $C_{31}H_{34}NO_3$ $[M+H]^+$ *m/z* 468.2533, found 468.2530. $[\alpha]_D^{27}$ = -43.9 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 82% ee: t_R (minor) = 11.1 min, t_R (major) = 10.2 min. **Melting point**: 150-151 °C.



***Tert*-butyl (1*R*,1a*S*,6b*S*)-5-fluoro-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocycloprop-a[*b*]indole-1-carboxylate (3v)**

Following the **General Procedure** using 1-(5-fluoro-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (43.8 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 81% yield (66.3 mg).

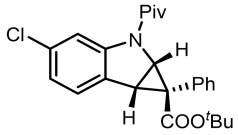
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 11.1, 2.5 Hz, 1H), 7.23 – 7.16 (m, 1H), 6.99 – 6.92 (m, 3H), 6.91 – 6.84 (m, 2H), 6.56 (td, *J* = 8.5, 2.5 Hz, 1H), 5.06 (d, *J* = 7.0 Hz, 1H), 3.65 (d, *J* = 7.0 Hz, 1H), 1.49 (s, 9H), 1.31 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.0, 171.4, 162.3 (d, *J* = 242.6 Hz), 145.2 (d, *J* = 13.0 Hz), 131.5, 130.4, 127.6, 127.0, 125.2 (d, *J* = 10.1 Hz), 124.5 (d, *J* = 2.4 Hz), 110.2 (d, *J* = 23.4 Hz), 105.9 (d, *J* = 29.7 Hz), 81.9, 52.1, 40.8, 34.7, 33.3, 28.1, 27.9. **IR (neat, cm^{-1})** 2961, 2926, 1260, 1191, 1156, 1090, 1018. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -119.29. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3F$ $[M+H]^+$ *m/z* 410.2126, found 410.2123. $[\alpha]_D^{27}$= -52.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 83% ee: t_R (minor) = 7.7 min, t_R (major) = 9.2 min. **Melting point**: 120-121 °C.



***Tert*-butyl (1*R*,1a*S*,6b*S*)-6-fluoro-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3w)**

Following the **General Procedure** using 1-(6-fluoro-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (43.8 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 76% yield (62.2 mg).

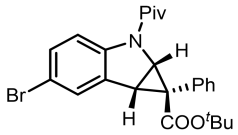
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 9.0, 4.9 Hz, 1H), 7.12 – 6.94 (m, 6H), 6.68 (td, *J* = 9.0, 2.7 Hz, 1H), 5.14 (d, *J* = 6.9 Hz, 1H), 3.76 (d, *J* = 7.0 Hz, 1H), 1.59 (s, 9H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.6, 171.4, 159.0 (d, *J* = 242.1 Hz), 140.3 (d, *J* = 2.1 Hz), 131.4, 130.5 (d, *J* = 9.0 Hz), 130.4, 127.6, 127.1, 118.7 (d, *J* = 8.3 Hz), 114.2 (d, *J* = 22.6 Hz), 111.9 (d, *J* = 24.3 Hz), 82.0, 51.7, 40.7, 35.1, 33.6, 28.2, 28.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ -119.53. **IR (neat, cm^{-1})** 2975, 2934, 1704, 1664, 1619, 1476, 1402. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3F$ $[M+H]^+$ *m/z* 410.2126, found 410.2124. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$ = -54.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 85% ee: t_R (minor) = 6.7 min, t_R (major) = 7.7 min. **Melting point**: 120-121 ℃.



***Tert*-butyl (1*R*,1a*S*,6b*S*)-4-chloro-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3x)**

Following the **General Procedure** using 1-(6-chloro-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (47.0 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 74% yield (62.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.0 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.00 – 6.94 (m, 3H), 6.90 – 6.81 (m, 3H), 5.04 (d, *J* = 7.0 Hz, 1H), 3.65 (d, *J* =7.0 Hz, 1H), 1.49 (s, 9H), 1.31 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.6, 171.4, 159.0 (d, *J* = 242.1 Hz), 140.3 (d, *J* = 2.1 Hz), 131.4, 130.5 (d, *J* = 9.0 Hz), 130.4, 127.6, 127.1, 118.7 (d, *J* = 8.3 Hz), 114.2 (d, *J* = 22.6 Hz), 111.9 (d, *J* = 24.3 Hz), 82.0, 51.7, 40.7, 35.1, 33.6, 28.2, 28.0. **IR (neat, cm^{-1})** 2966, 1705, 1666, 1477, 1403, 1259, 1159. **HRMS (ESI)** calculated for $C_{25}H_{28}NO_3ClNa$ $[M+Na]^+$ *m/z* 448.1650, found 448.1654. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$= -55.9 (c =1.0, $CHCl_3$). **HPLC analysis** (OJ-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 86% ee: t_R (minor) = 6.6 min, t_R (major) = 7.0 min. **Melting point**: 122-123 ℃.

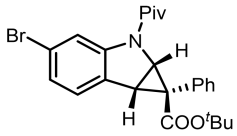


***Tert*-butyl (1*R*,1a*S*,6b*S*)-5-bromo-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3y)**

Following the **General Procedure** using 1-(5-bromo-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (55.8 mg, 0.2 mmol, 1.0 eq.) and

tert-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 67% yield (62.7 mg).

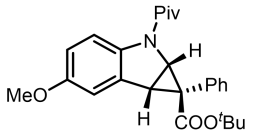
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 2.1 Hz, 1H), 7.10 – 7.02 (m, 4H), 6.97 – 6.92 (m, 2H), 5.10 (d, *J* = 7.0 Hz, 1H), 3.73 (d, *J* = 6.9 Hz, 1H), 1.55 (s, 9H), 1.38 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.6, 171.4, 159.0 (d, *J* = 242.1 Hz), 140.3 (d, *J* = 2.1 Hz), 131.4, 130.5 (d, *J* = 9.0 Hz), 175.8, 170.3, 142.2, 130.4, 130.1, 129.6, 129.2, 126.7, 126.7, 126.1, 118.0, 114.8, 81.0, 50.4, 39.8, 33.8, 32.3, 27.1, 26.9. **IR (neat, cm^{-1})** 2961, 2924, 2853, 1259, 1157, 1089, 1018. **HRMS (ESI)** calculated for $C_{25}H_{29}NO_3Br$ $[M+H]^+$ *m/z* 470.1325, found 470.1324. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{27}}$ = -58.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 2% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 86% ee: t_R (minor) = 7.1 min, t_R (major) = 5.7 min. **Melting point**: 130-131 °C.



***Tert*-butyl (1*R*,1a*S*,6b*S*)-4-bromo-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (3z)**

Following the **General Procedure** using 1-(6-bromo-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (55.8 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (5% EtOAc in hexanes) to provide the title compound as a white solid in 75% yield (70.8 mg).

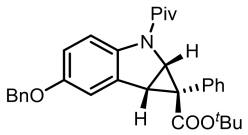
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.8 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.11 – 7.04 (m, 4H), 6.99 – 6.93 (m, 2H), 5.12 (d, *J* = 7.0 Hz, 1H), 3.74 (d, *J* = 7.0 Hz, 1H), 1.58 (s, 9H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.0, 171.3, 145.2, 131.5, 130.3, 128.0, 127.7, 127.2, 126.5, 125.8, 121.3, 120.9, 82.0, 51.7, 40.8, 35.0, 33.3, 28.1, 28.0. **IR (neat, cm^{-1})** 2961, 2925, 2853, 1702, 1460, 1261, 954 **HRMS (ESI)** calculated for $C_{25}H_{28}NO_3BrNa$ $[M+Na]^+$ *m/z* 492.1145, found 492.1143. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{26}}$ = -58.8 (c =1.0, $CHCl_3$). **HPLC analysis** (OD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 83% ee: t_R (minor) = 9.5 min, t_R (major) = 8.6 min. **Melting point**: 130-131 °C.



***Tert*-butyl (1*R*,1a*S*,6b*S*)-5-methoxy-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (4a)**

Following the **General Procedure** using 1-(5-methoxy-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (46.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 74% yield (62.2 mg).

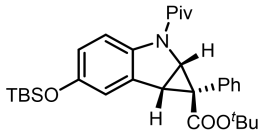
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.0 Hz, 1H), 6.97 – 6.83 (m, 6H), 6.43 (dd, *J* = 9.0, 2.7 Hz, 1H), 5.02 (d, *J* = 6.9 Hz, 1H), 3.72 – 3.56 (m, 4H), 1.48 (s, 9H), 1.31 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.3, 170.5, 155.1, 137.0, 130.4, 129.6, 129.1, 126.5, 125.9, 117.4, 111.4, 110.0, 80.7, 54.6, 50.6, 39.5, 34.3, 32.9, 27.2, 27.0. **IR (neat, cm^{-1})** 2964, 2930, 1719, 1701, 1462, 1259, 974. **HRMS (ESI)** calculated for $C_{26}H_{32}NO_4$ $[M+H]^+$ *m/z* 422.2326, found 422.2325. $[\alpha]_D^{27}$ = -16.8 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 0.5 mL/min, 254 nm) indicated 88% ee: t_R (minor) = 22.1 min, t_R (major) = 23.5 min. **Melting point**: 135-136 ℃.



***Tert*-butyl (1*R*,1a*S*,6b*S*)-5-methoxy-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopro-pa[*b*]indole-1-carboxylate (4b)**

Following the **General Procedure** using 1-(5-(benzyloxy)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (61.4 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 69% yield (68.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 9.0 Hz, 1H), 7.45 – 7.31 (m, 5H), 7.07 – 6.92 (m, 6H), 6.62 (dd, *J* = 9.0, 2.7 Hz, 1H), 5.11 (d, *J* = 6.9 Hz, 1H), 5.03 (d, *J* = 1.5 Hz, 2H), 3.73 (d, *J* = 6.9 Hz, 1H), 1.58 (s, 9H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.4, 171.6, 155.1, 138.2, 137.1, 131.4, 130.6, 130.1, 128.6, 127.9, 127.5, 127.4, 126.9, 118.5, 114.0, 112.0, 81.8, 70.4, 51.6, 40.6, 35.3, 33.9, 28.2, 28.0. **IR (neat, cm^{-1})** 2976, 2933, 1700, 1656, 1614, 1491, 1401. **HRMS (ESI)** calculated for $C_{32}H_{36}NO_4$ $[M+H]^+$ *m/z* 498.2639, found 498.2632. $[\alpha]_D^{25}$ = -59.6 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 85% ee: t_R (minor) = 17.8 min, t_R (major) = 18.8 min. **Melting point**: 158-159 ℃.

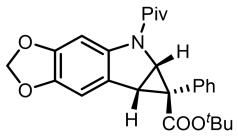


***Tert*-butyl (1*R*,1a*S*,6b*S*)-5((*tert*-butyldimethylsilyl)oxy)-1-phenyl-2-pivaloyl-1,1a,2,6b-tetrahydrocyclopropa[*b*]indole-1-carboxylate (4c)**

Following the **General Procedure** using 1-(5-((*tert*-butyldimethylsilyl)oxy)-1*H*-indol-1-yl)-2,2-dimethylpropan-1-one (66.2 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 65% yield (67.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.9 Hz, 1H), 7.05 – 6.94 (m, 5H), 6.85 (d, *J* = 2.6 Hz, 1H), 6.44 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.08 (d, *J* = 7.0 Hz, 1H), 3.69 (d, *J* = 7.0 Hz, 1H), 1.55 (s, 9H), 1.38 (s, 9H), 0.96 (s, 9H), 0.14 (s, 3H), 0.12 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 175.3, 170.5, 150.8, 137.4, 130.4, 129.7, 128.9, 126.5, 125.8, 118.4, 117.4, 115.7, 80.7, 76.3, 76.0, 75.7, 50.5, 39.6, 34.3, 32.8, 27.2, 27.0, 24.7, 17.2, -5.47, -5.53. **IR (neat,**

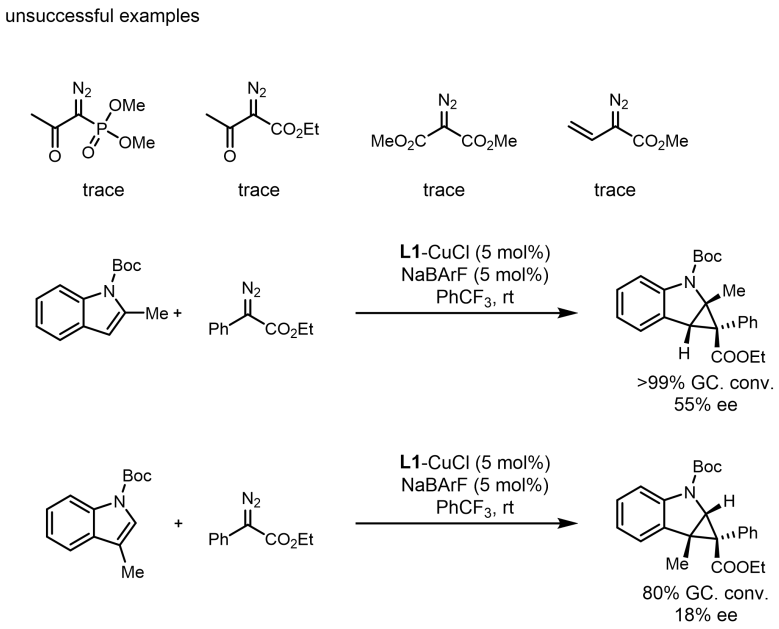
cm^{-1}) 2978, 2929, 1705, 1666, 1463, 1403, 1259. **HRMS (ESI)** calculated for $C_{31}H_{44}NO_4Si$ $[M+H]^+$ *m/z* 522.3034, found 522.3038. $[\alpha]_D^{26}$ = -59.7 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 2% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 87% ee: t_R (minor) = 6.4 min, t_R (major) = 7.8 min. **Melting point**: 147-148 °C.



***Tert*-butyl (5a*S*,6*R*,6a*S*)-6-phenyl-5-pivaloyl-5,5a,6,6a-tetrahydrocyclopropa[*b*][1,3]dio-xolo[4,5-*f*]indole-6-carboxylate (4d)**

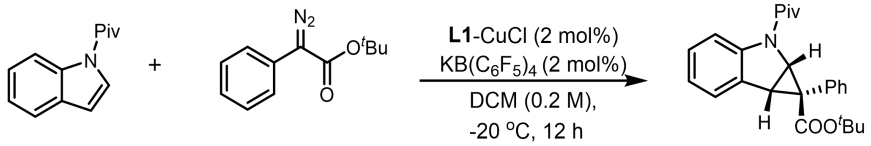
Following the **General Procedure** using 1-(*5H*-[1,3]dioxolo[4,5-*f*]indol-5-yl)-2,2-dimethylpropan-1-one (49.0 mg, 0.2 mmol, 1.0 eq.) and *tert*-butyl 2-diazo-2-phenylacetate (87.2 mg, 0.4 mmol, 2.0 eq.), the crude product was purified by column chromatography (10% EtOAc in hexanes) to provide the title compound as a white solid in 86% yield (74.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.08 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.01 – 6.96 (m, 2H), 6.83 (s, 1H), 5.84 (dd, *J* = 14.2, 1.4 Hz, 2H), 5.11 (d, *J* = 7.1 Hz, 1H), 3.68 (d, *J* = 7.1 Hz, 1H), 1.57 (s, 9H), 1.40 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 176.5, 171.6, 146.9, 143.7, 138.7, 131.5, 130.7, 127.6, 127.0, 121.5, 104.9, 101.2, 100.5, 81.7, 52.0, 40.7, 35.5, 33.5, 28.2, 28.0. **IR (neat, cm^{-1})** 3728, 3698, 3676, 3657, 3641, 3622, 2964. **HRMS (DART)** calculated for $C_{26}H_{30}NO_5$ $[M+H]^+$ *m/z* 436.2118, found 436.2116. $[\alpha]_D^{26}$= -59.0 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1.5% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 84% ee: t_R (minor) = 16.9 min, t_R (major) = 17.9 min. **Melting point**: 154-155 °C.



4. Synthetic Applications

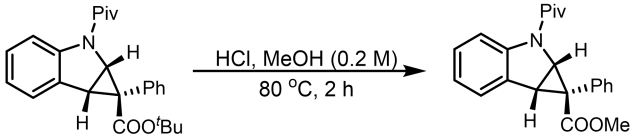
Gram-scale reaction



1b, 5 mmol **2b**, 2.0 eq **3a**, 1.58 g
81% yield
86% ee

In a nitrogen-filled glovebox, an oven-dried 50 mL round-bottom flask equipped with a magnetic stir bar was charged with ANIPE-CuCl (88.8 mg, 0.1 mmol, 2 mol%), $KB(C_6F_5)_4$ (71.8 mg, 0.1 mmol, 2.0 mol%), *N*-Piv indole (1.05 g, 5 mmol, 1.0 eq.) and DCM (5 mL). The reaction mixture was stirred at -20 ℃. The *tert*-butyl 2-diazo-2-phenylacetate (2.18 g, 10.0 mmol, 2.0 eq.), dissolved in dichloromethane (5 mL), was then slowly dropwise added to the system. The reaction mixture was stirred within the sealed flask at -20 ℃ for 12 h. After the reaction was complete, the reaction mixture was directly filtered through a short pad of silica gel (CH_2Cl_2 as eluent) to give the crude product. After concentration, the crude residue was purified via column chromatography to afford the desired product **3a** in 81% yield (1.58 g) and 86% ee.

Transformation of product **3a**

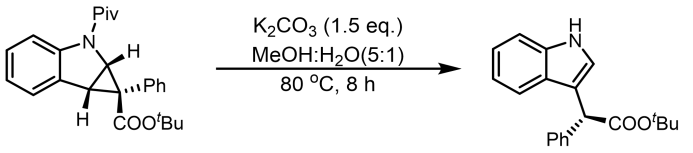


3a, 0.2 mmol
86% ee, >20:1 dr

4e, 88% yield
86% ee, >20:1 dr

An oven-dried screw-cap reaction tube equipped with a magnetic stir bar was charged with substrate **3a** (78.2 mg, 0.2 mmol, 1.0 eq.), methanol (1 mL) and 3 drops of 1M HCl. The reaction tube was sealed with a screw-cap septum and heated at 80 ℃ for 2 hours. After the reaction was completed, the reaction mixture was concentrated and purified via column chromatography to afford the desired product **4e** as a white solid in 88% yield (61.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 1H), 7.42 – 7.37 (m, 1H), 7.08 – 6.94 (m, 7H), 5.23 (d, *J* = 7.0 Hz, 1H), 3.86 (d, *J* = 7.0 Hz, 1H), 3.71 (s, 3H), 1.59 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 177.0, 173.4, 144.1, 131.8, 129.9, 128.4, 128.0, 127.7, 127.3, 125.0, 123.6, 117.8, 53.0, 51.9, 40.8, 36.7, 32.3, 28.2. **IR (neat, cm^{-1})** 2959, 1710, 1664, 1464, 1434, 1402, 1361. **HRMS (ESI)** calculated for $C_{22}H_{24}NO_3$ $[M+H]^+$ *m/z* 350.1751, found 350.1747. $[\alpha]_D^{27}$ = -59.3 (c =1.0, $CHCl_3$). **HPLC analysis** (AD-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 86% ee: t_R (minor) = 9.5 min, t_R (major) = 9.8 min.



3a, 0.2 mmol
89% ee, >20:1 dr

4f, 83% yield, 89% ee

An oven-dried screw-cap reaction tube equipped with a magnetic stir bar was charged with substrate **3a** (78.2 mg, 0.2 mmol, 1.0 eq.), K2CO3 (41.4 mg, 0.3 mmol, 1.5 eq..), methanol (1 mL), and water (200 μL). The reaction tube was sealed with a screw-cap septum and heated at 80 ℃ for 2 hours. After the reaction was completed, the reaction mixture was concentrated and purified via column chromatography to afford the desired product **4f** as colorless liquid in 83% yield (83% yield)**.**

^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.47 – 7.42 (m, 1H), 7.41 – 7.37 (m, 2H), 7.30 – 7.17 (m, 4H), 7.15 – 7.09 (m, 1H), 7.06 – 7.00 (m, 2H), 5.14 (s, 1H), 1.43 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 139.2, 136.3, 128.5, 128.5, 127.1, 126.8, 123.3, 122.2, 119.6, 119.1, 114.1, 111.3, 81.3, 50.1, 28.1. **IR (neat, cm^{-1})** 3414, 2977, 2928, 1713, 1494, 1455, 1367. **HRMS (ESI)** calculated for $C_{20}H_{21}NO_2Na$ $[M+Na]^+$ *m/z* 330.1465, found 330.1466. $\boldsymbol{\alpha_D^{27}}$= -84.4 (c =1.0, $CHCl_3$). **HPLC analysis** (OJ-H, 1% IPA in hexanes, 1.0 mL/min, 254 nm) indicated 89% ee: t_R (minor) = 13.5 min, t_R (major) = 12.3 min.

5. Mechanistic studies

5.1 Parallel kinetic isotope effect experiments

We performed parallel kinetic isotope effect (KIE) experiments using indole and deuterated indole under standard reaction conditions. The results are shown in Table S7.

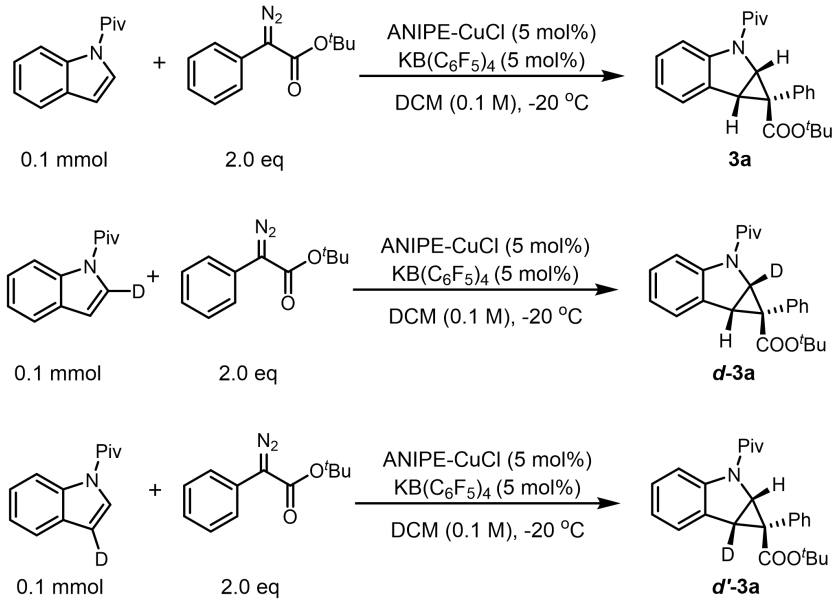
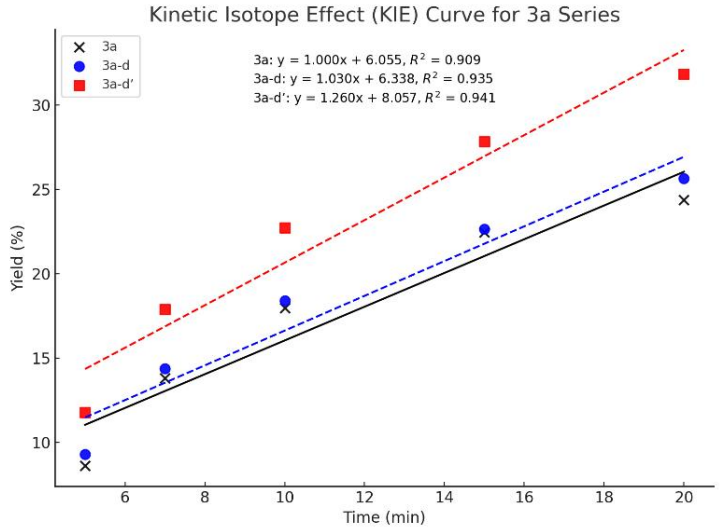


Table S7 Kinetic isotope effect experiment of the cyclopropanation reaction of indole

Time	Yield of **3a**	Yield of *d*-**3a**	Yield of *d*'-**3a**
5 min	8.64%	9.3%	11.79%
7 min	13.82%	14.38%	17.90%
10 min	17.97%	18.40%	22.74%
15 min	22.45%	22.64%	27.85%
20 min	24.37%	25.66%	31.84%



C2: KIE = 1.000/1.030 =0.97; C3: KIE = 1.000/1.260 = 0.79

5.2 Hammett correlation study

We also carried out a Hammett correlation study on the reaction of indole with *N*-Piv indole and various para-substituted diazo esters. The obtained $\log(k_X/k_H)$ values for each substrate were plotted against the σ values taken from the literature[3].

Para-substituent	σ	$\log(k_X/k_H)$
p-tBu	-0.15	-0.024
p-OMe	-0.12	-0.007
p-Ph	0.05	0.014
p-F	0.15	0.014
p-CF_3	0.53	0.177

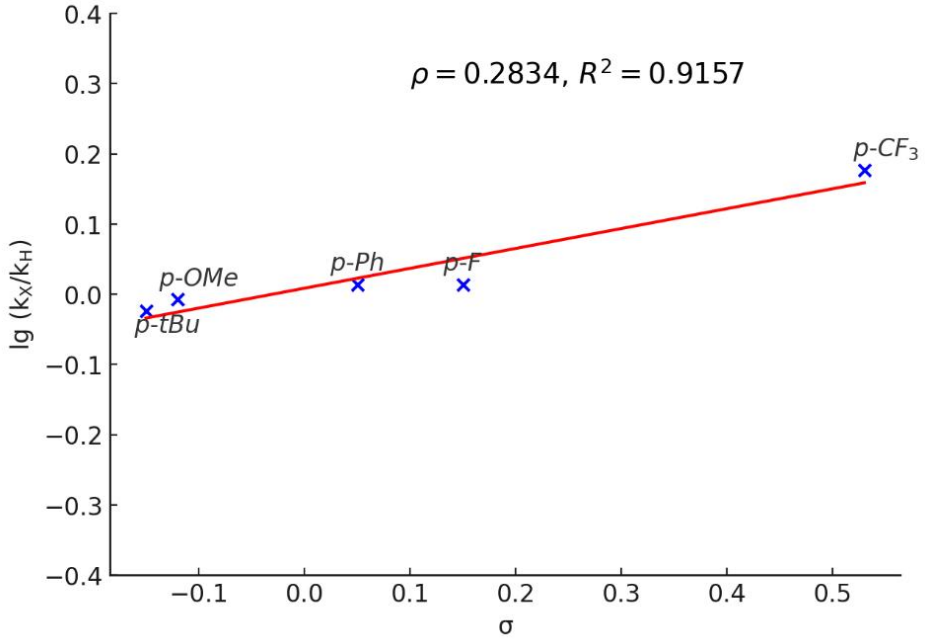
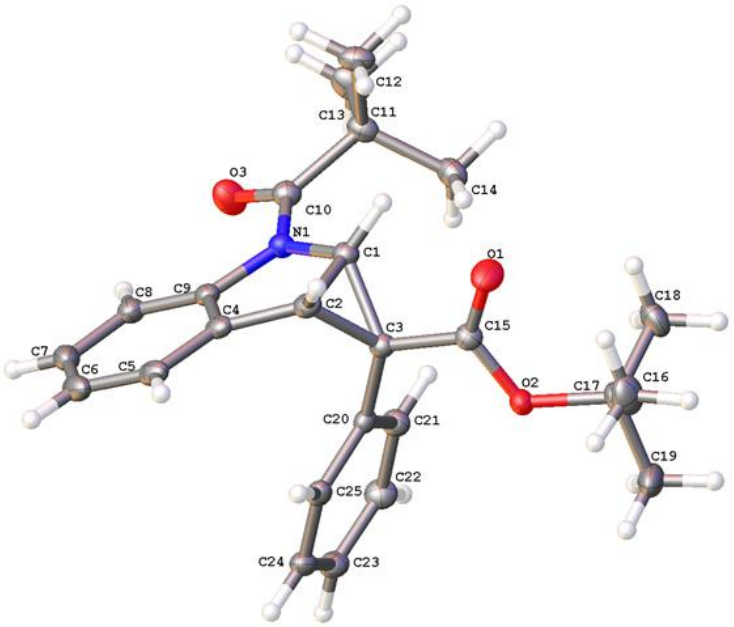
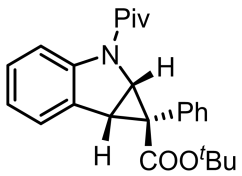


Figure S1 Hammett plot

6. X-ray crystallographic data for compound 3a

Sample preparation: Compound **3a** was recrystallized from petroleum ether by slowly evaporating the solvent at room temperature.





3a

Figure S2 Single-crystal structure of **3a** (CCDC: 2429515)

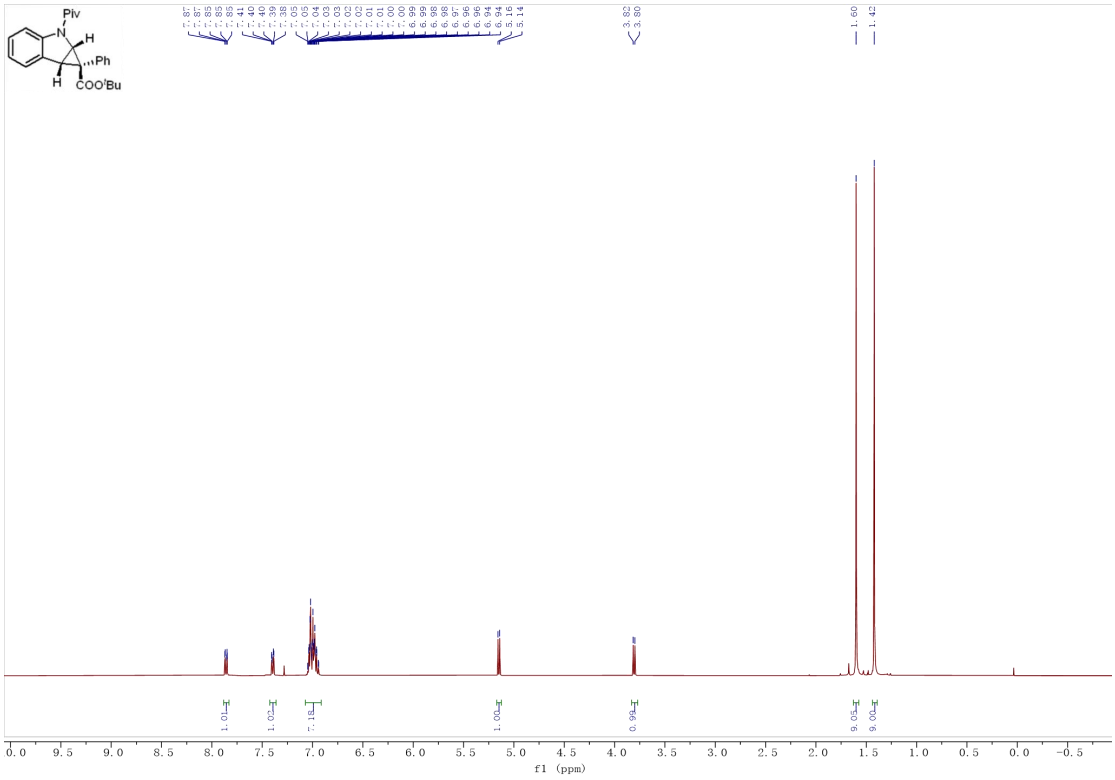
Crystal data and structure refinement for **3a**

Empirical formula	$C_{25}H_{29}NO_3$
Formula weight	391.49
Temperature/K	170.00
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.51040(10)
b/Å	17.6621(3)
c/Å	19.4925(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2241.39(6)
Z	4
ρ_{calc}g/cm^3	1.160
μ/mm^{-1}	0.381
F(000)	840.0
Crystal size/mm^3	0.17 × 0.17 × 0.05

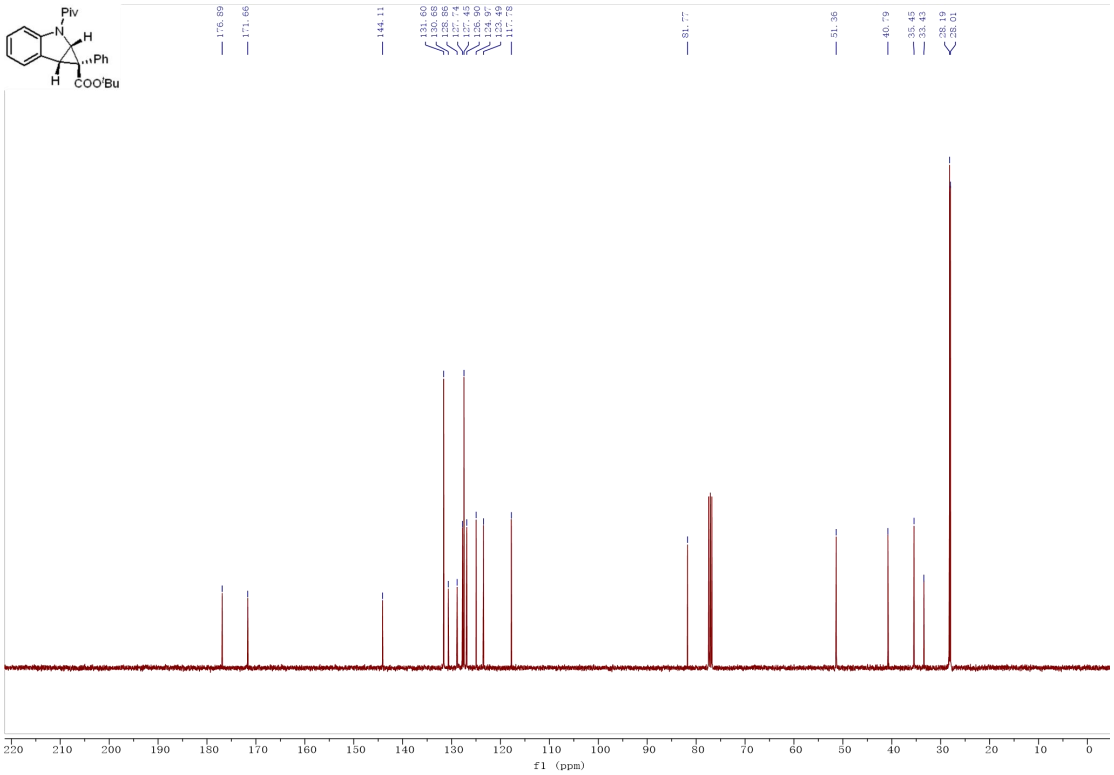
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	5.874 to 109.698
Index ranges	$-7 \leq h \leq 4$, $-21 \leq k \leq 21$, $-22 \leq l \leq 23$
Reflections collected	29089
Independent reflections	4230 [R_{int} = 0.0486, R_{sigma} = 0.0263]
Data/restraints/parameters	4230/0/268
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0309, wR_2 = 0.0736
Final R indexes [all data]	R_1 = 0.0345, wR_2 = 0.0755
Largest diff. peak/hole / e $Å^{-3}$	0.09/-0.17
Flack parameter	0.19(9)

7. NMR Spectra

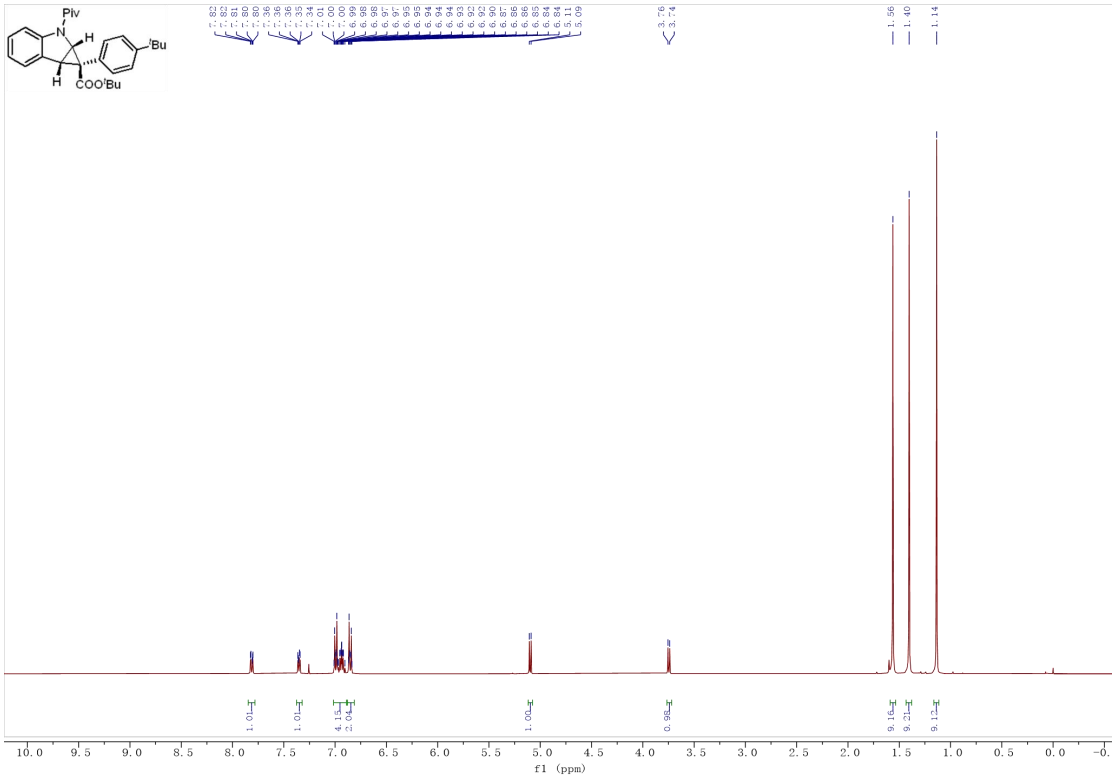
^{1}H NMR spectrum of **3a**:



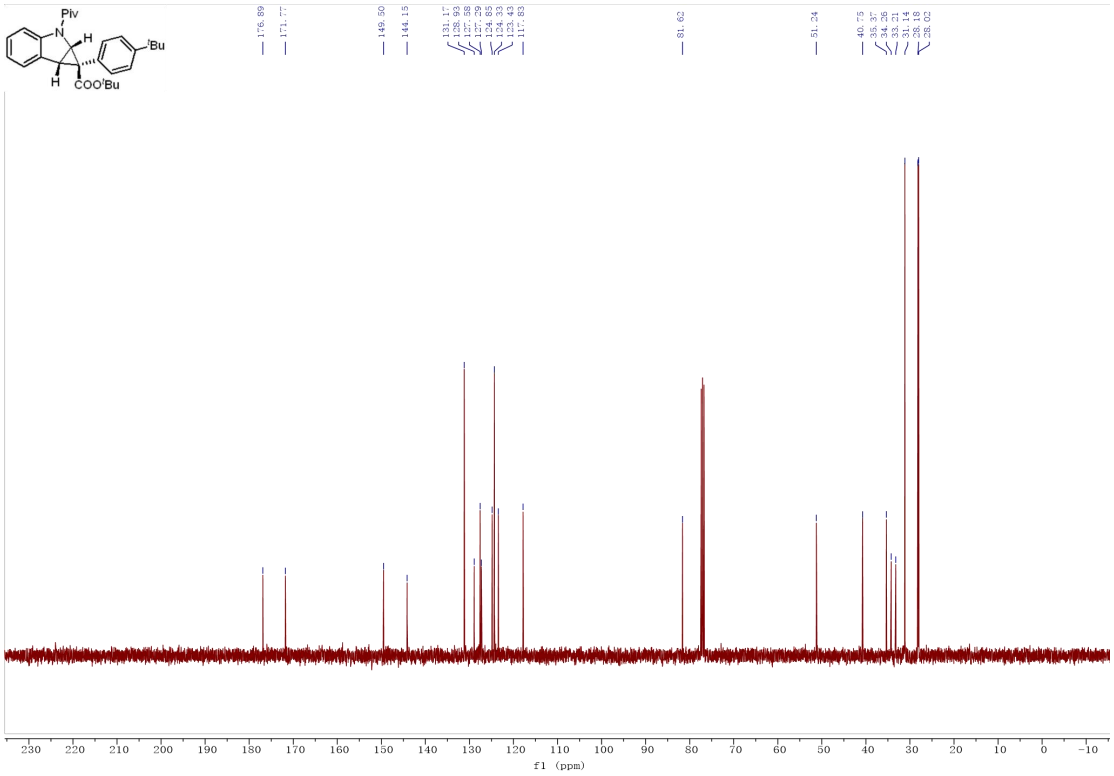
^{13}C NMR spectrum of **3a**



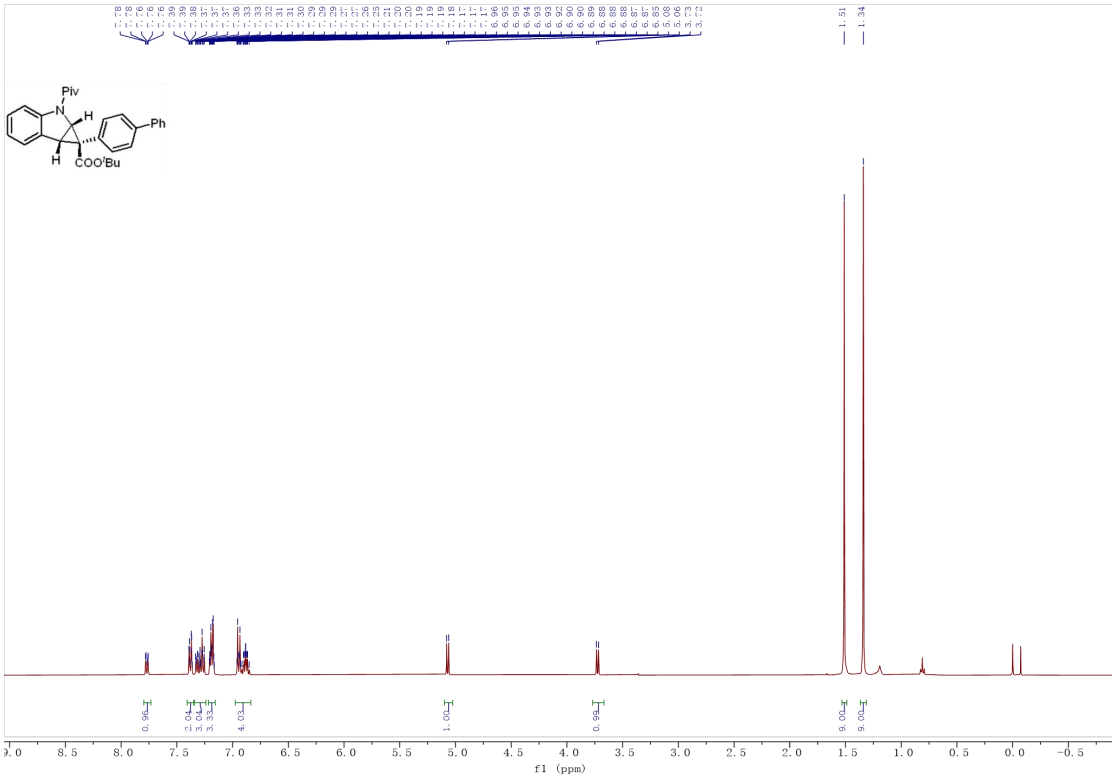
^{1}H NMR spectrum of **3b**



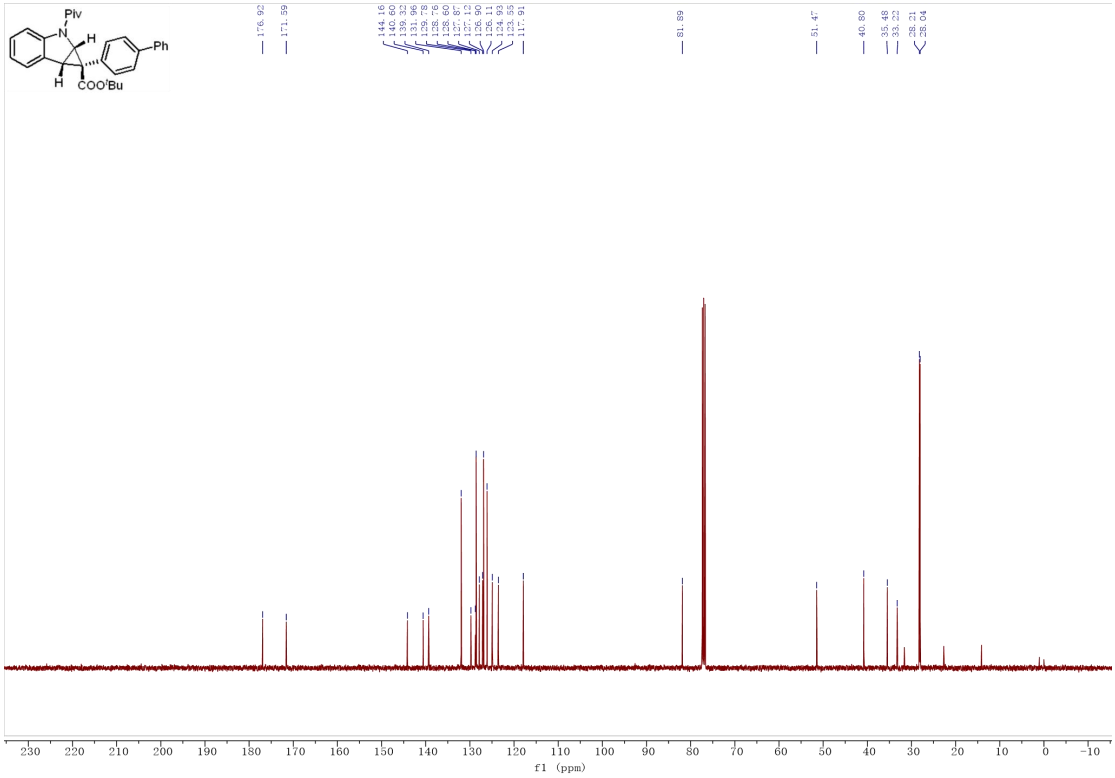
^{13}C NMR spectrum of **3b**



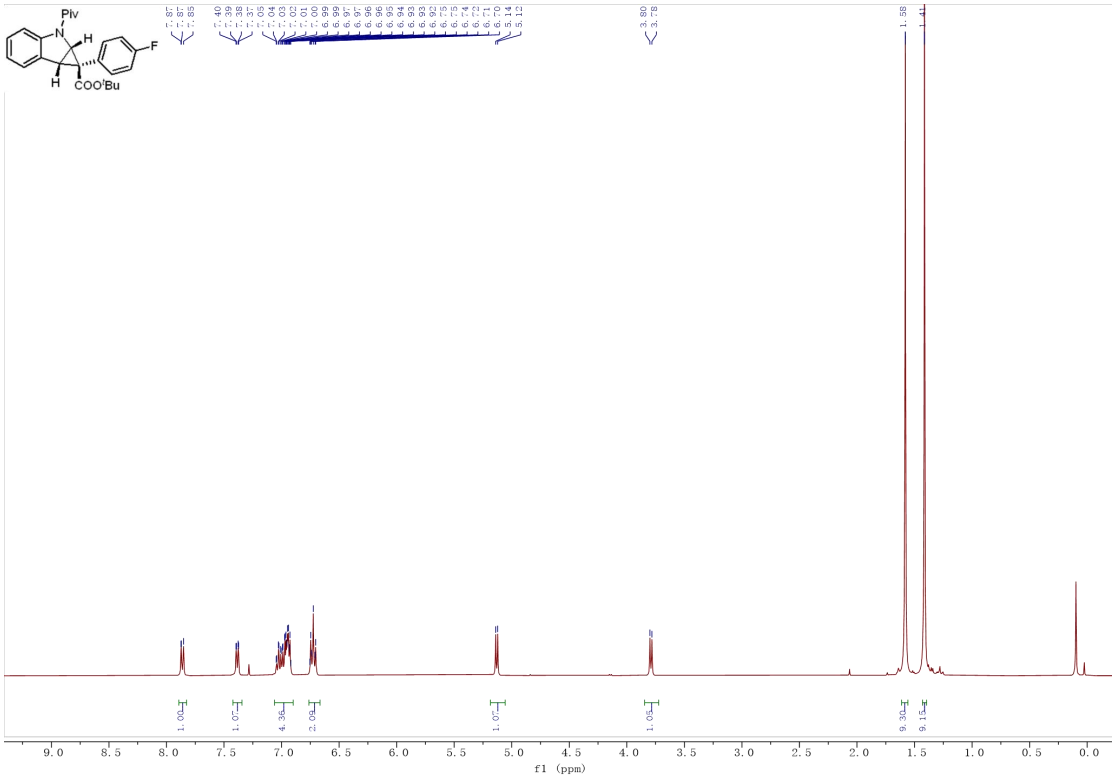
^{1}H NMR spectrum of **3c**



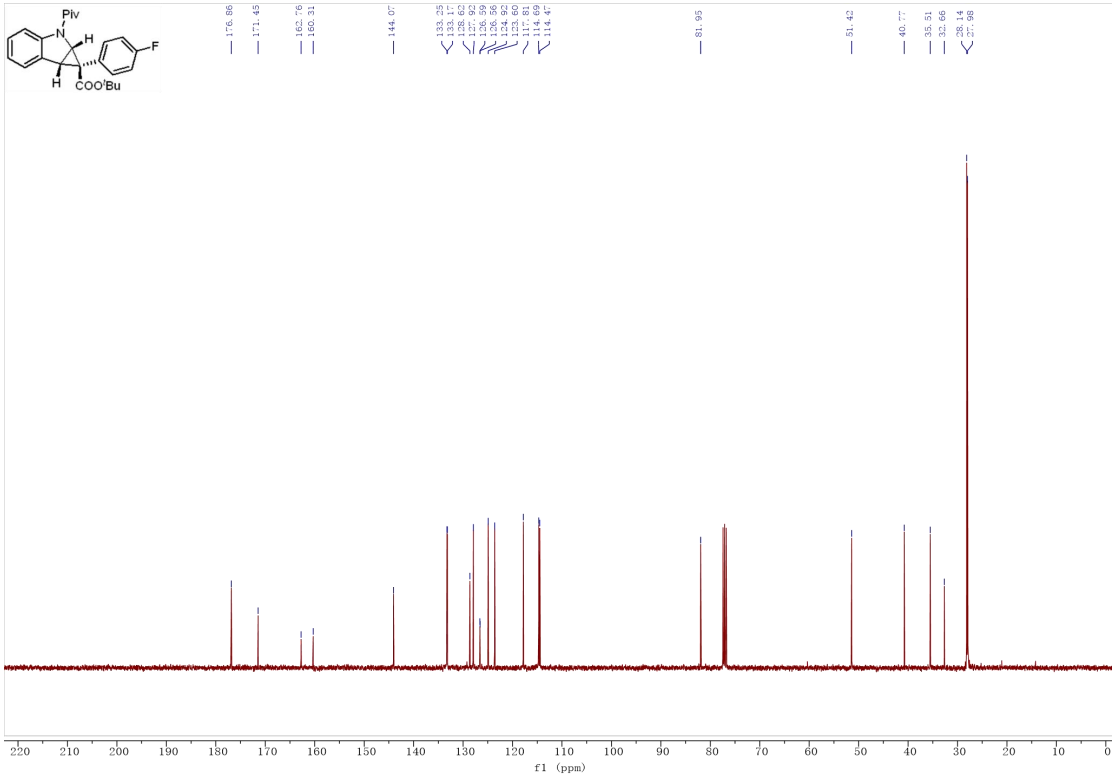
^{13}C NMR spectrum of **3c**



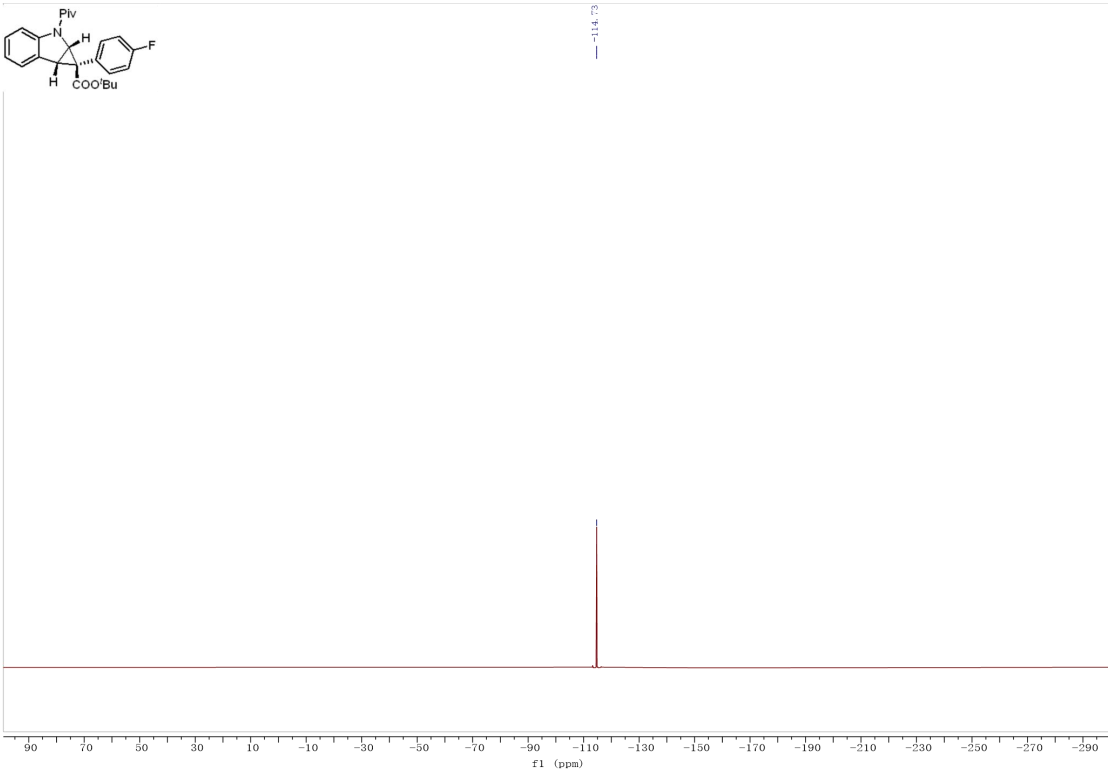
^{1}H NMR spectrum of **3d**



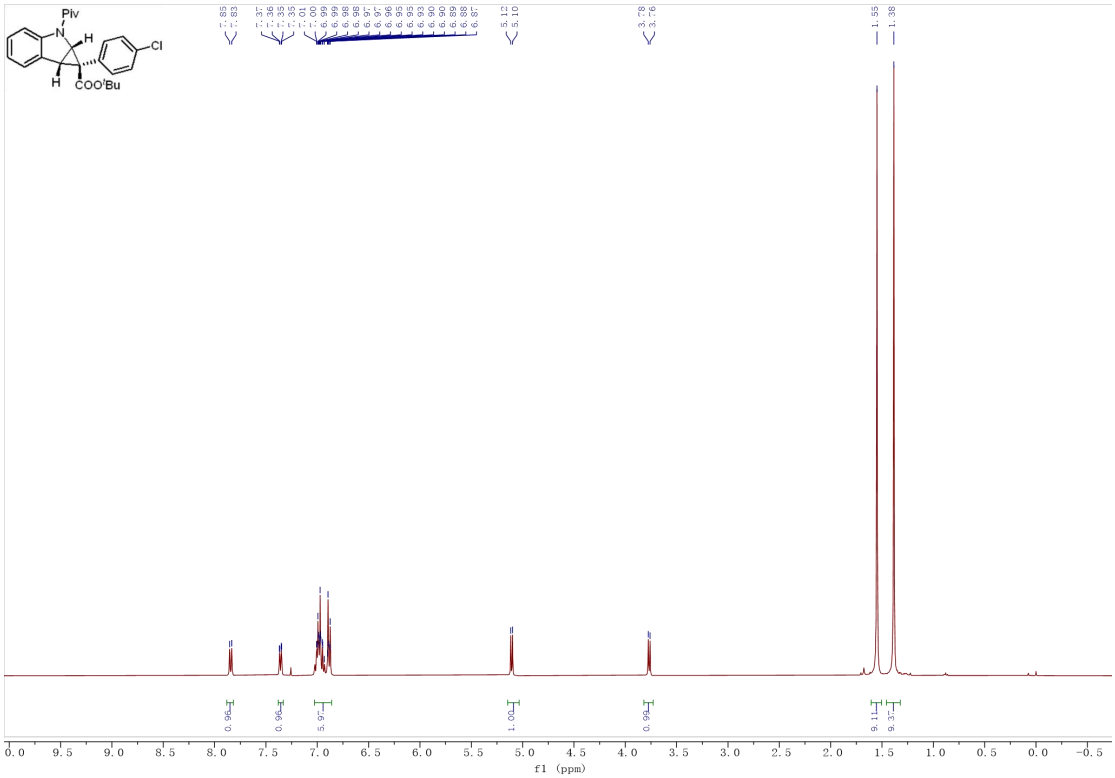
^{13}C NMR spectrum of **3d**



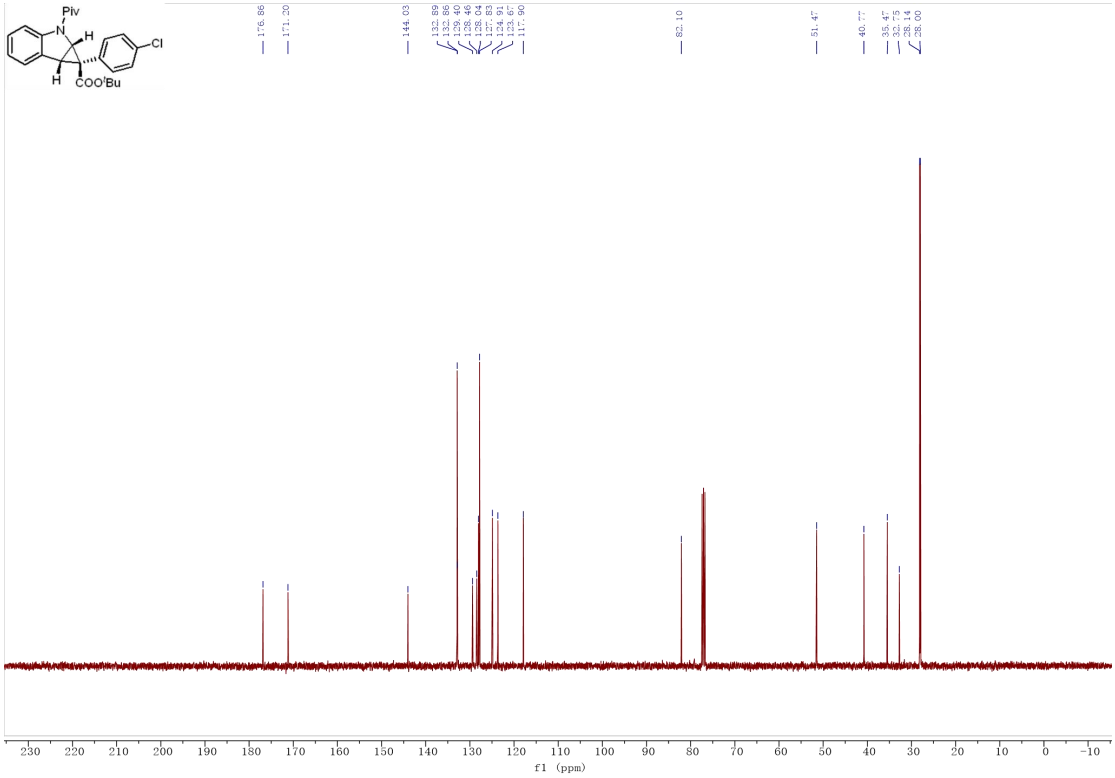
^{19}F NMR spectrum of **3d**



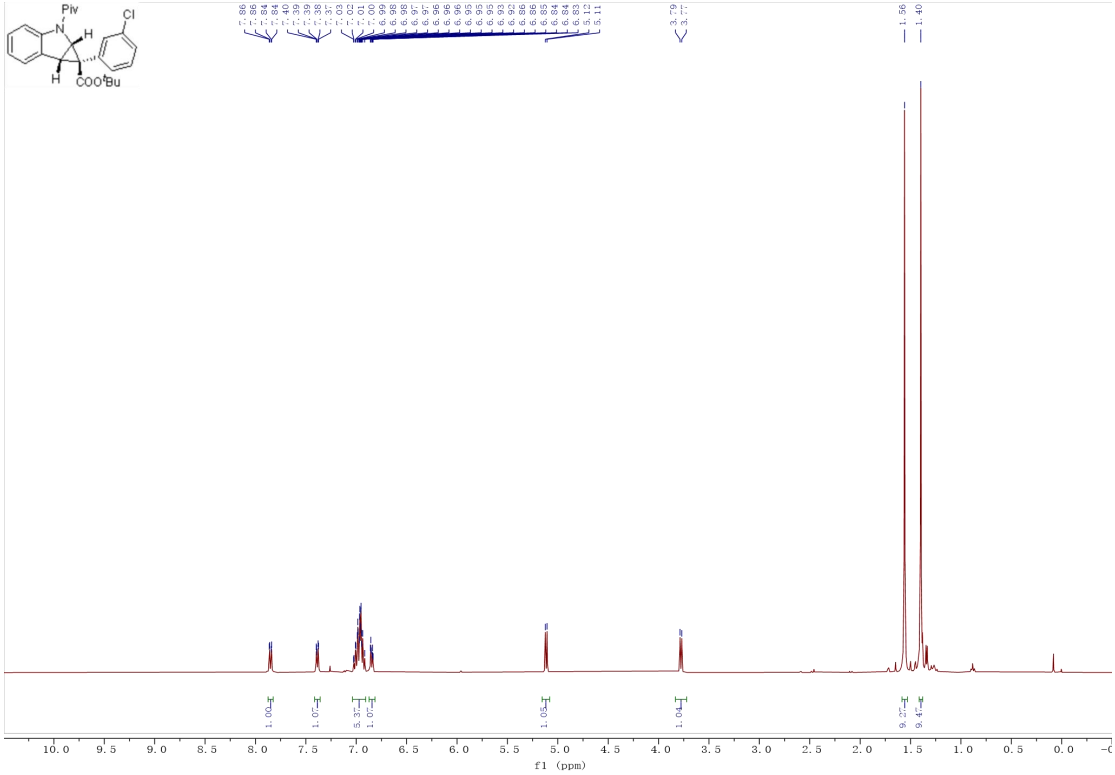
^{1}H NMR spectrum of **3e**



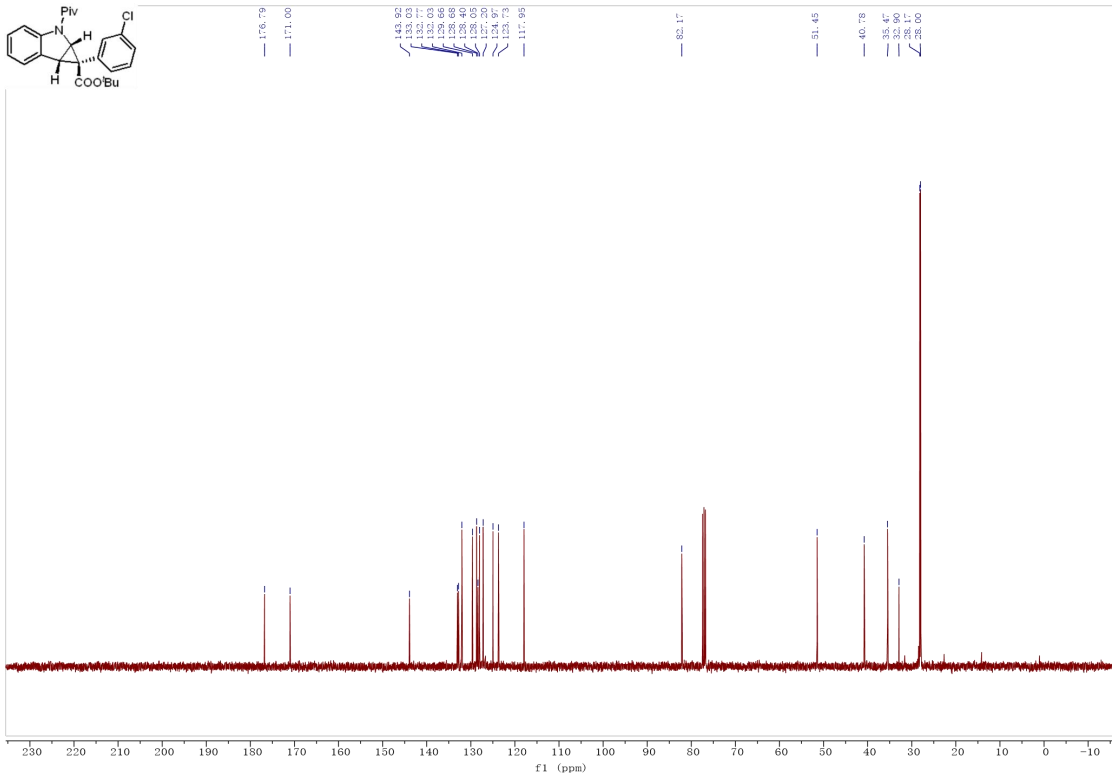
^{13}C NMR spectrum of **3e**



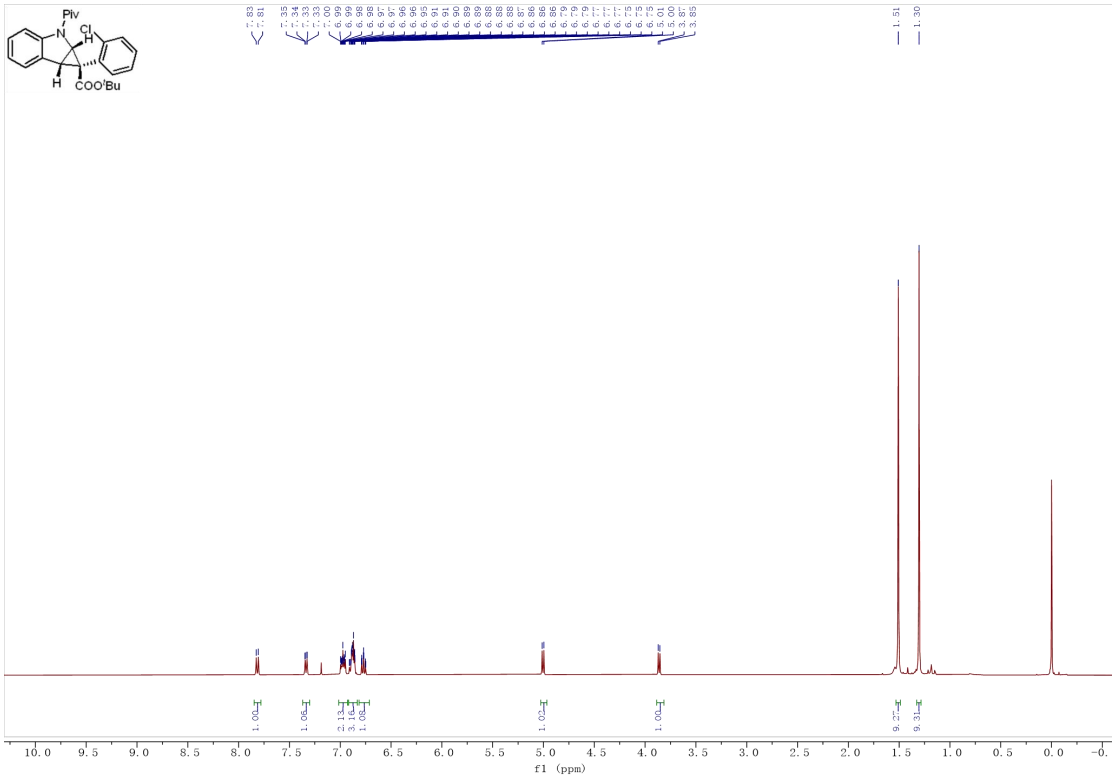
^{1}H NMR spectrum of **3f**



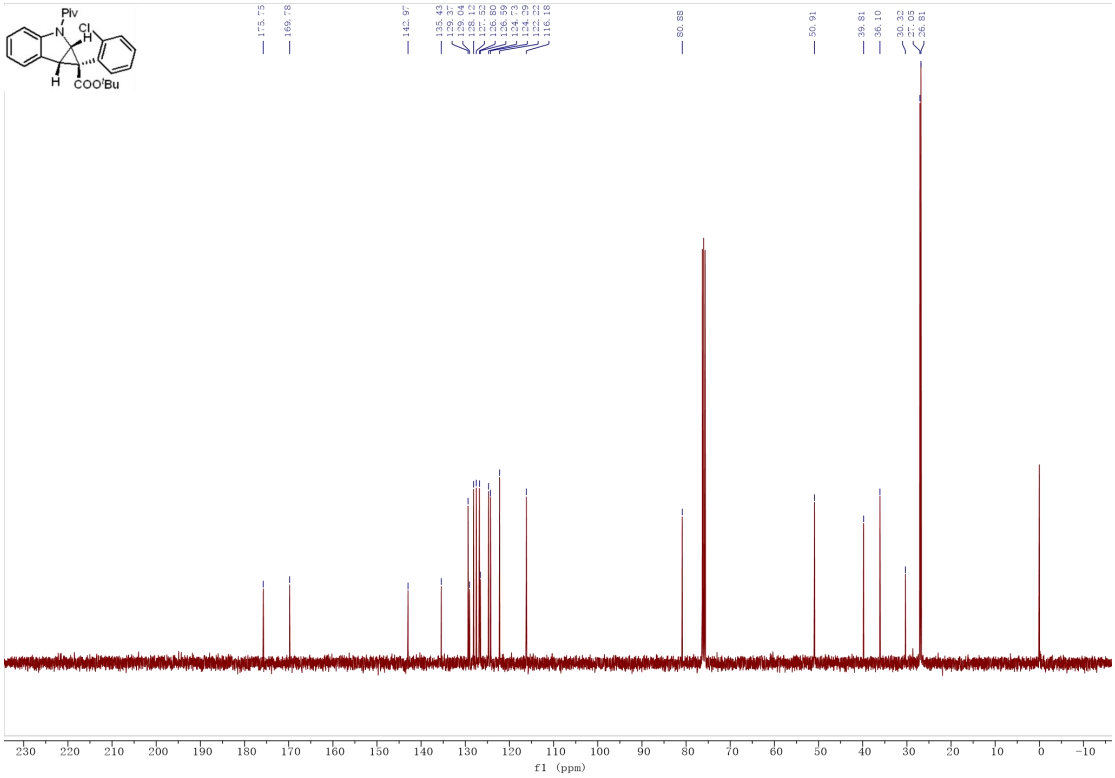
^{13}C NMR spectrum of **3f**



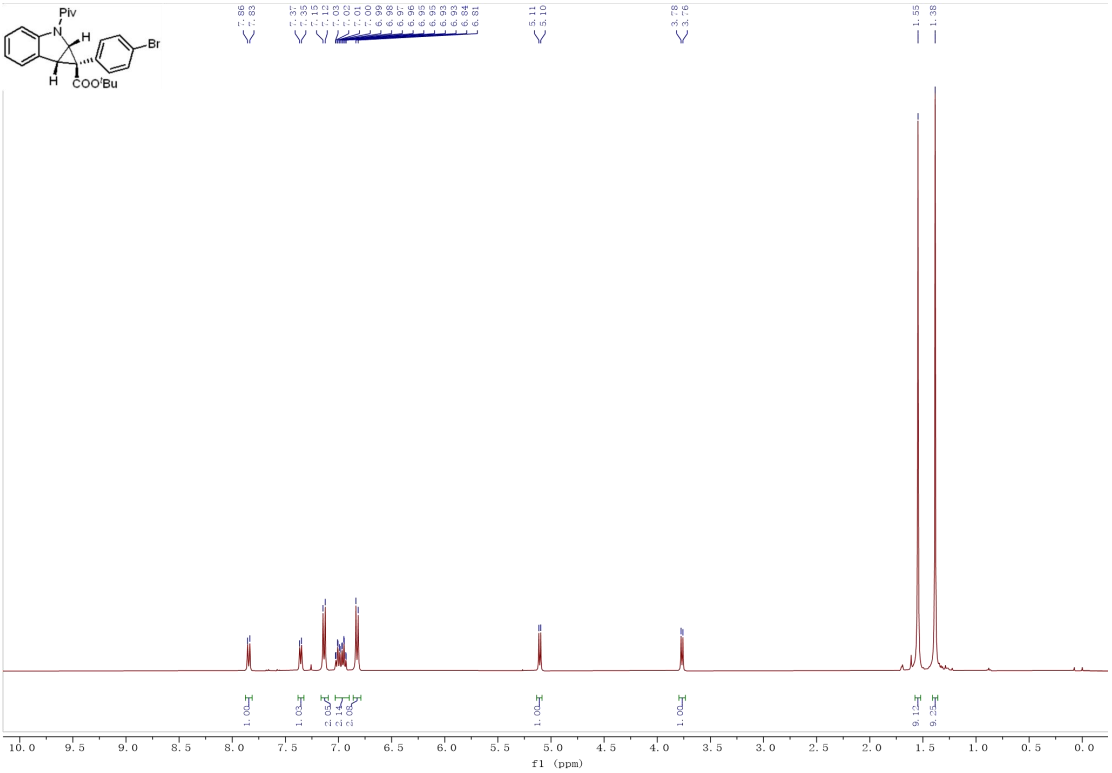
^{1}H NMR spectrum of **3g**



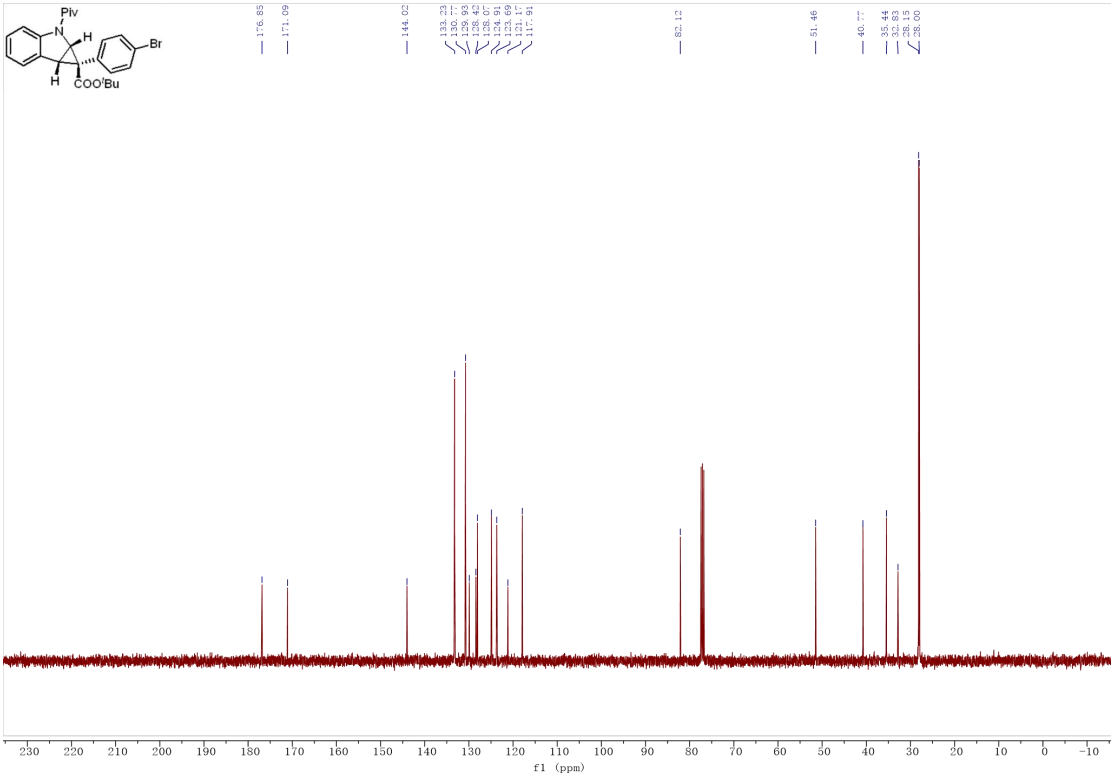
^{13}C NMR spectrum of **3g**



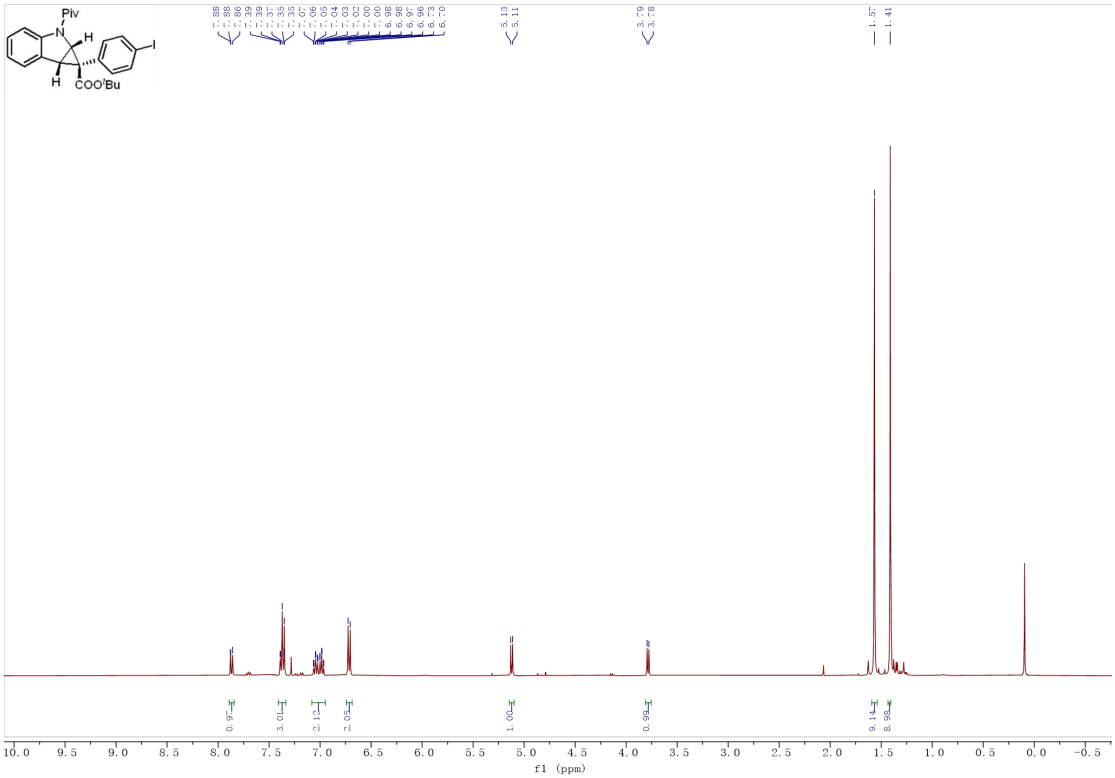
^{1}H NMR spectrum of **3h**



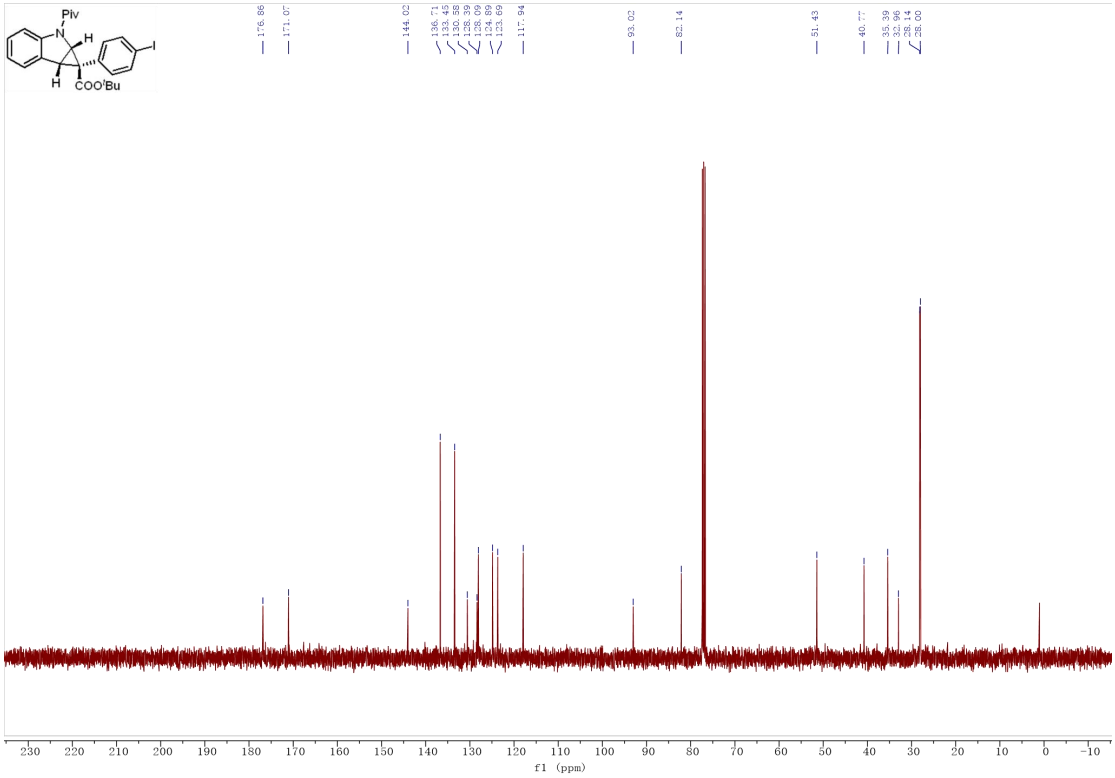
^{13}C NMR spectrum of **3h**



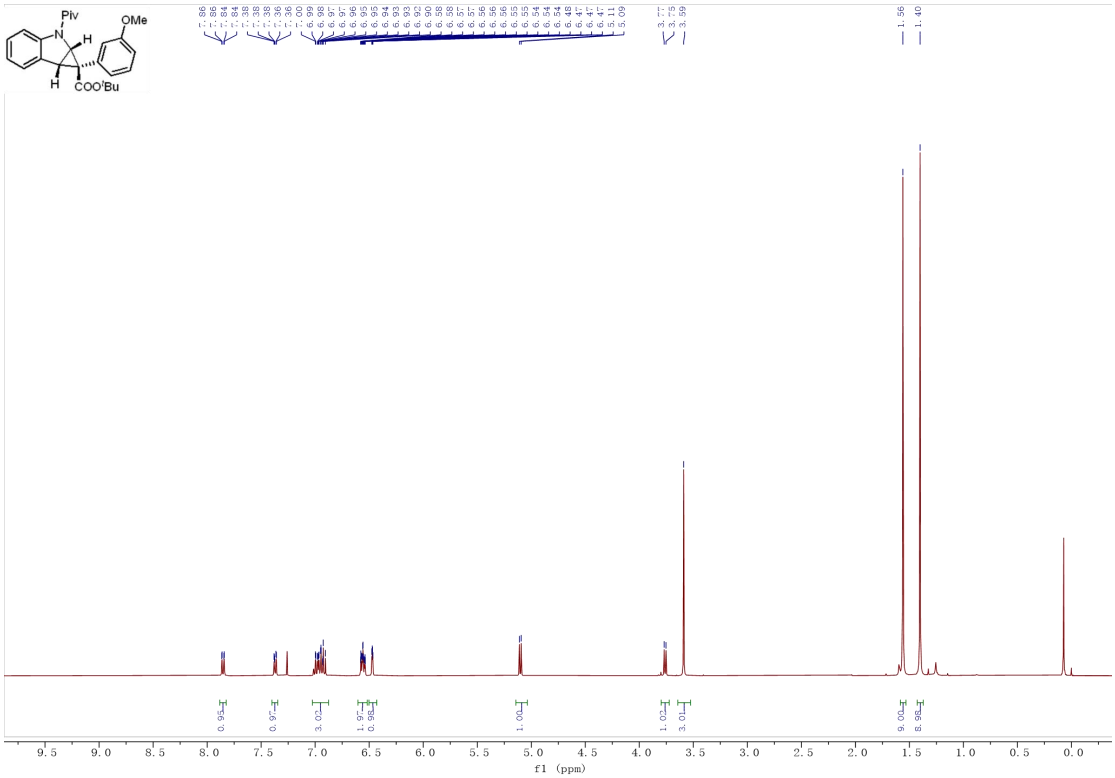
^{1}H NMR spectrum of **3i**



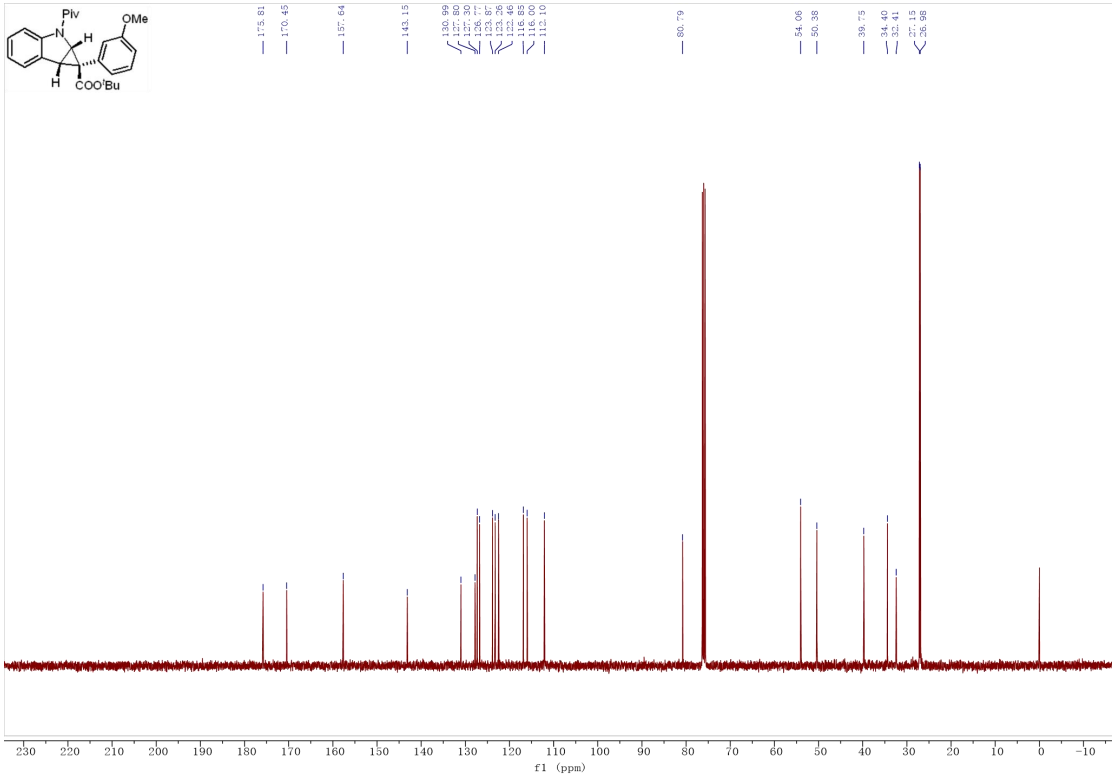
^{13}C NMR spectrum of **3i**



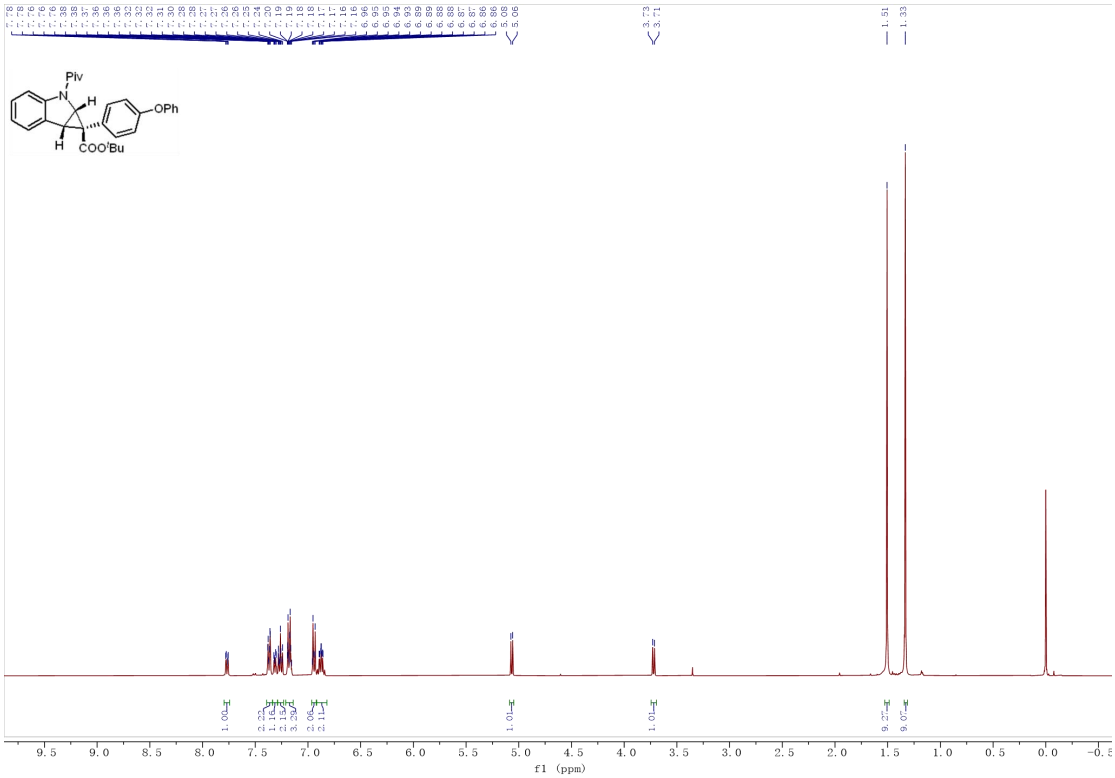
^{1}H NMR spectrum of **3j**



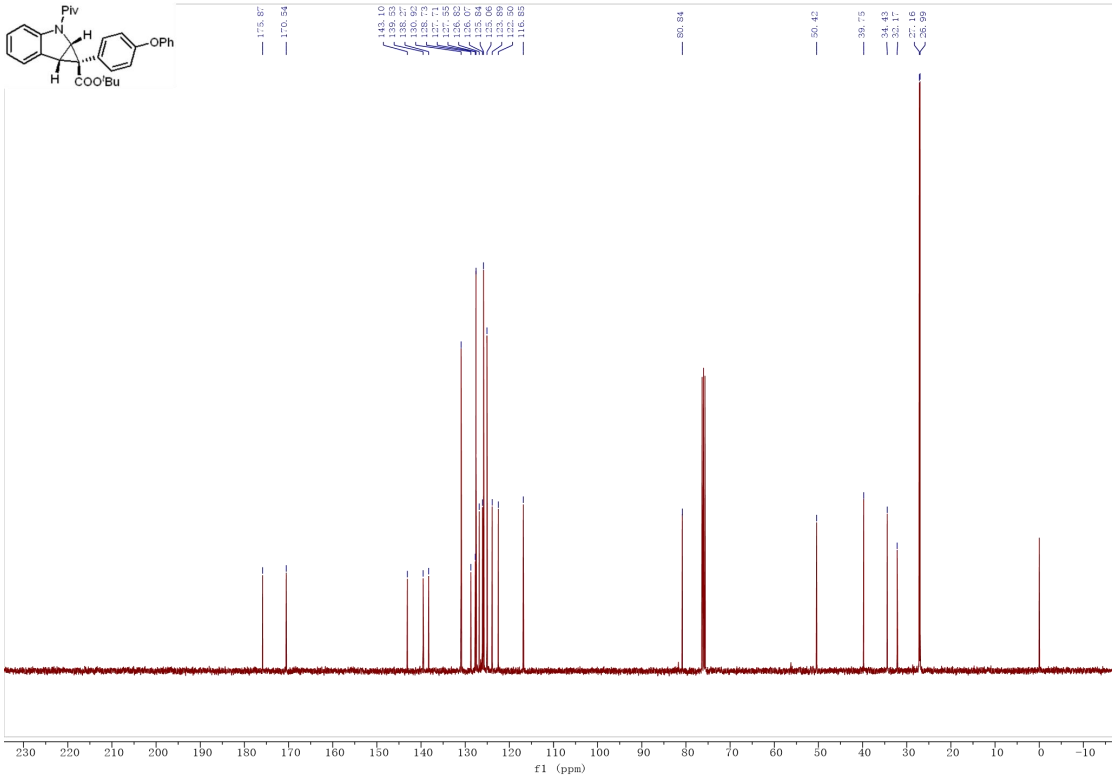
^{13}C NMR spectrum of **3j**



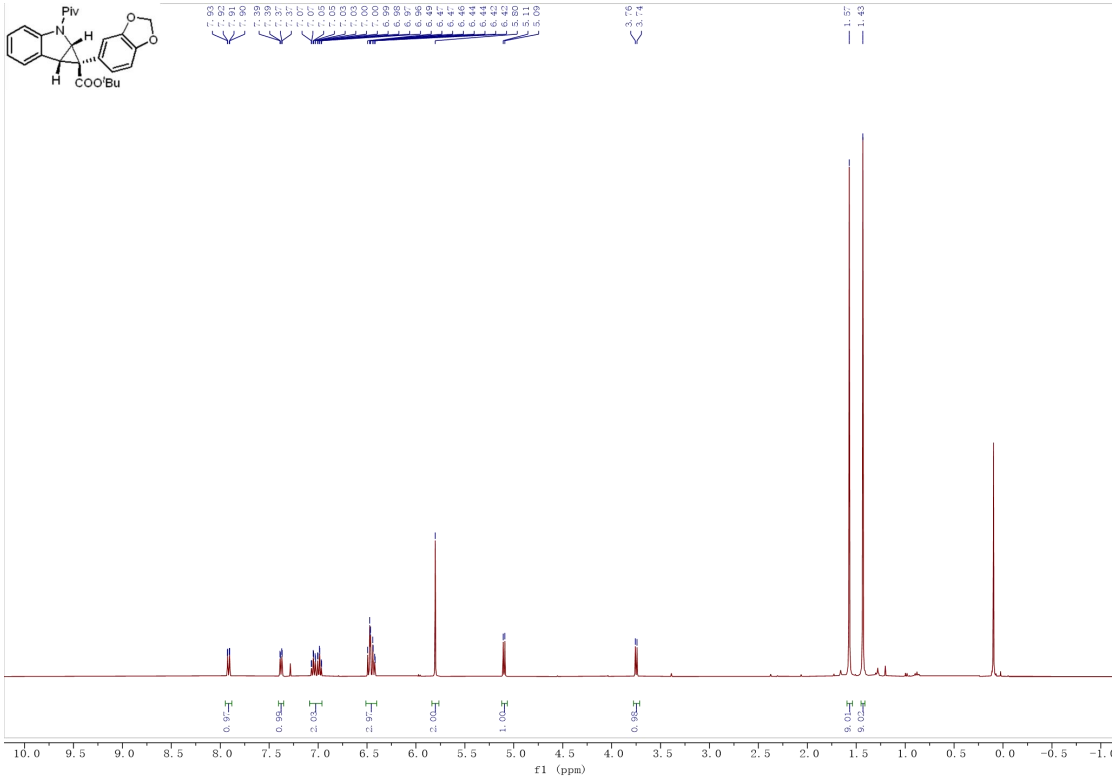
^{1}H NMR spectrum of **3k**



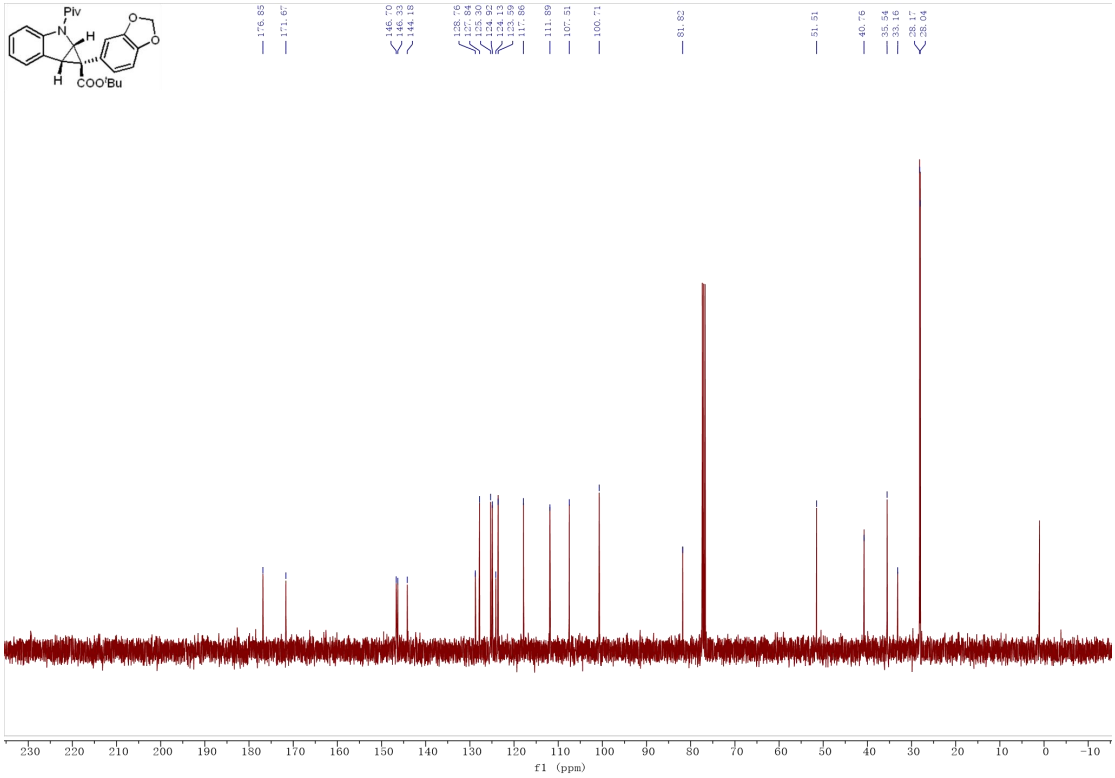
^{13}C NMR spectrum of **3k**



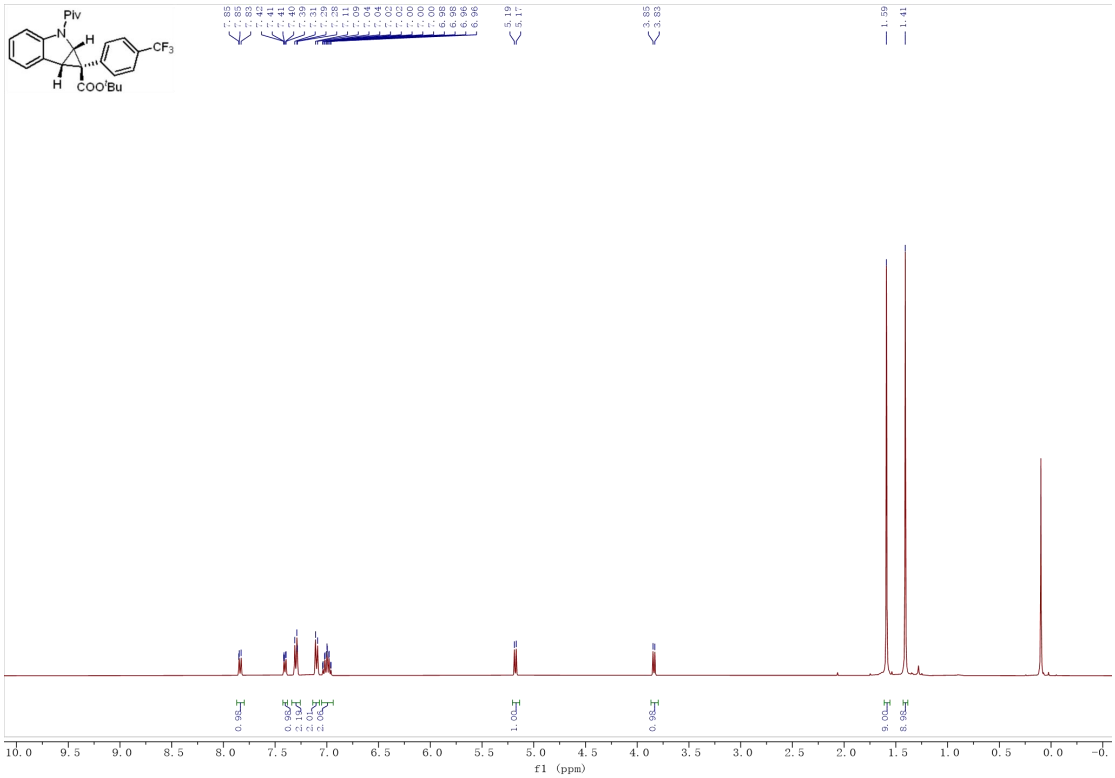
^{1}H NMR spectrum of **3l**



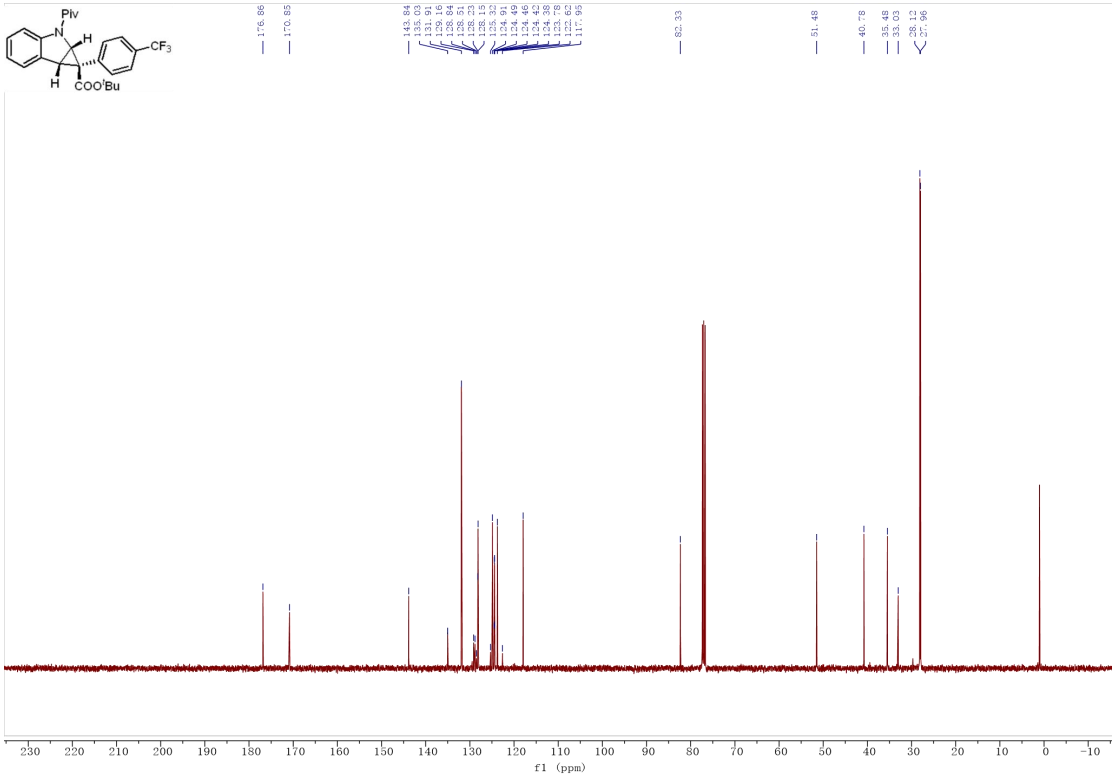
^{13}C NMR spectrum of **3l**



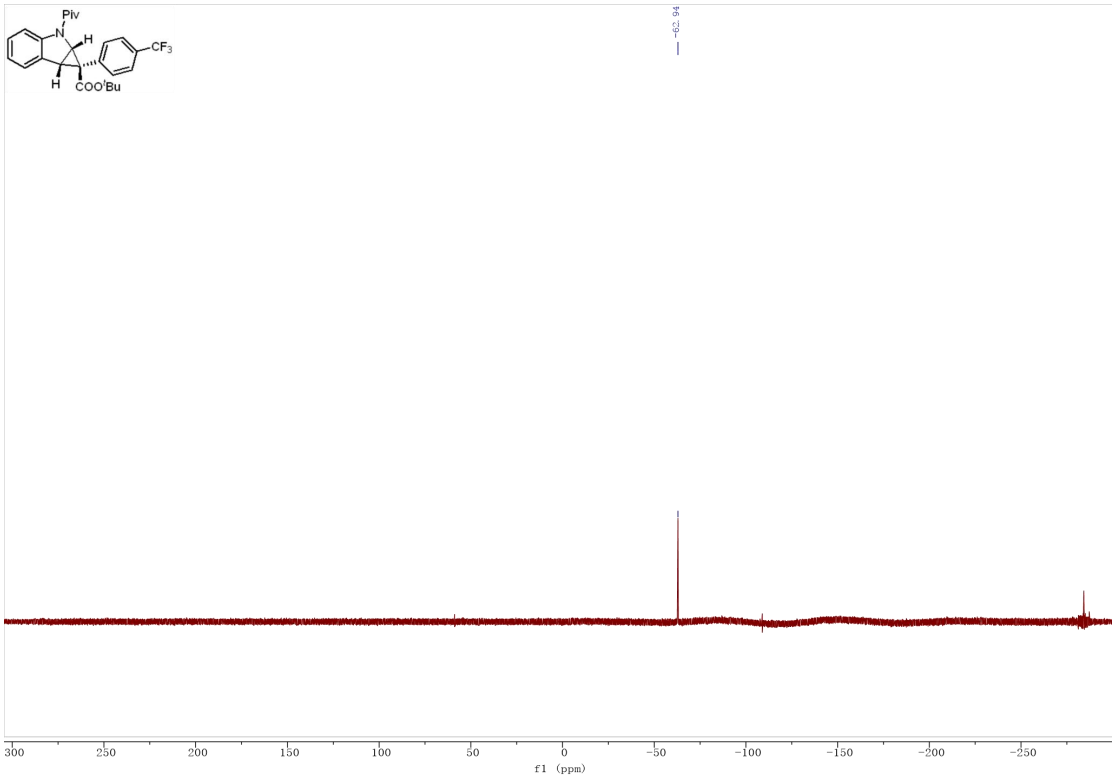
^{1}H NMR spectrum of **3m**



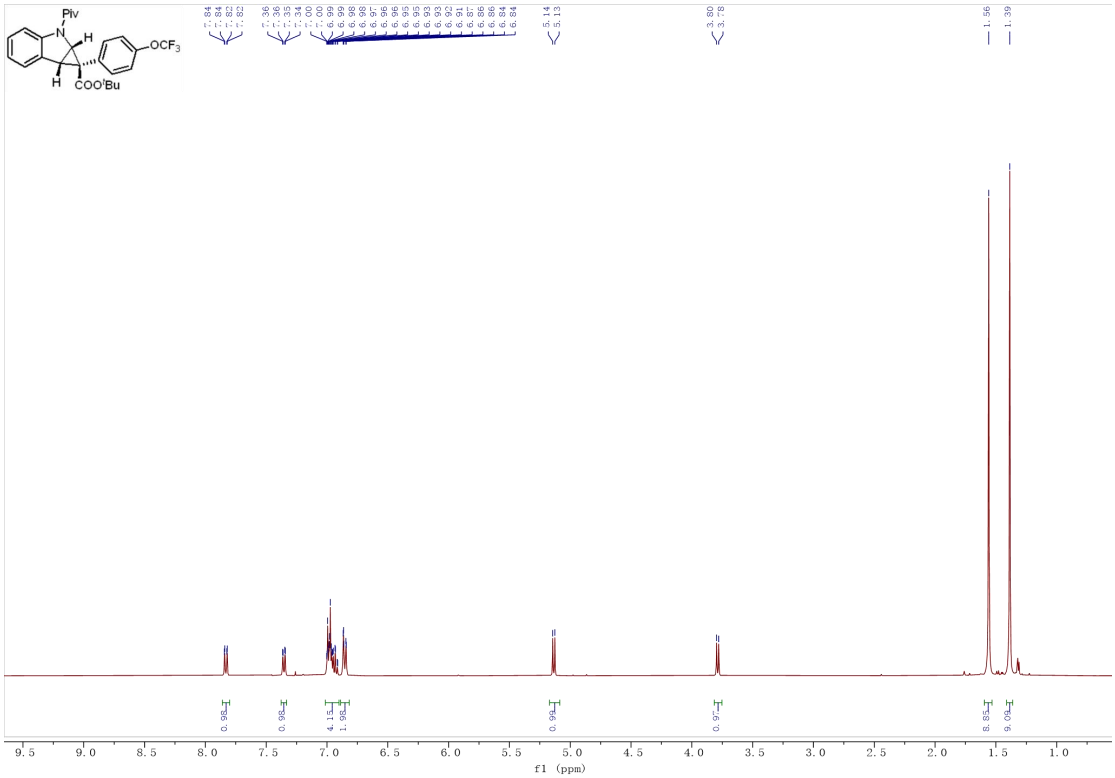
^{13}C NMR spectrum of **3m**



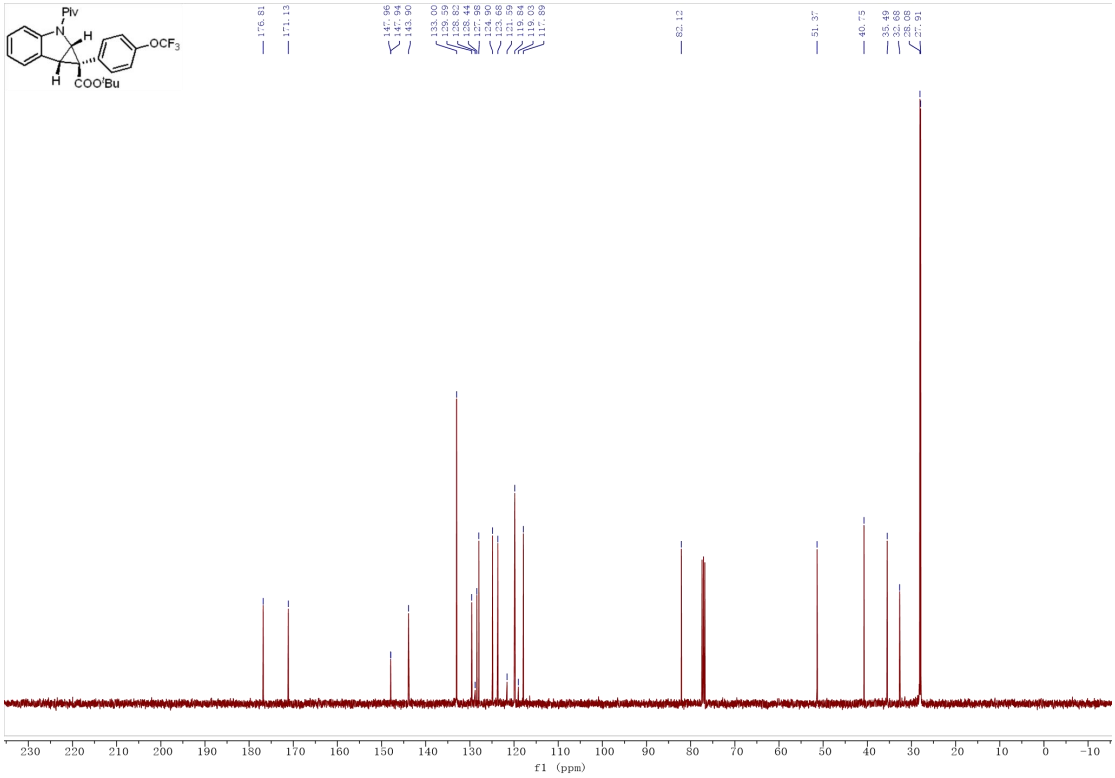
^{19}F NMR spectrum of **3m**



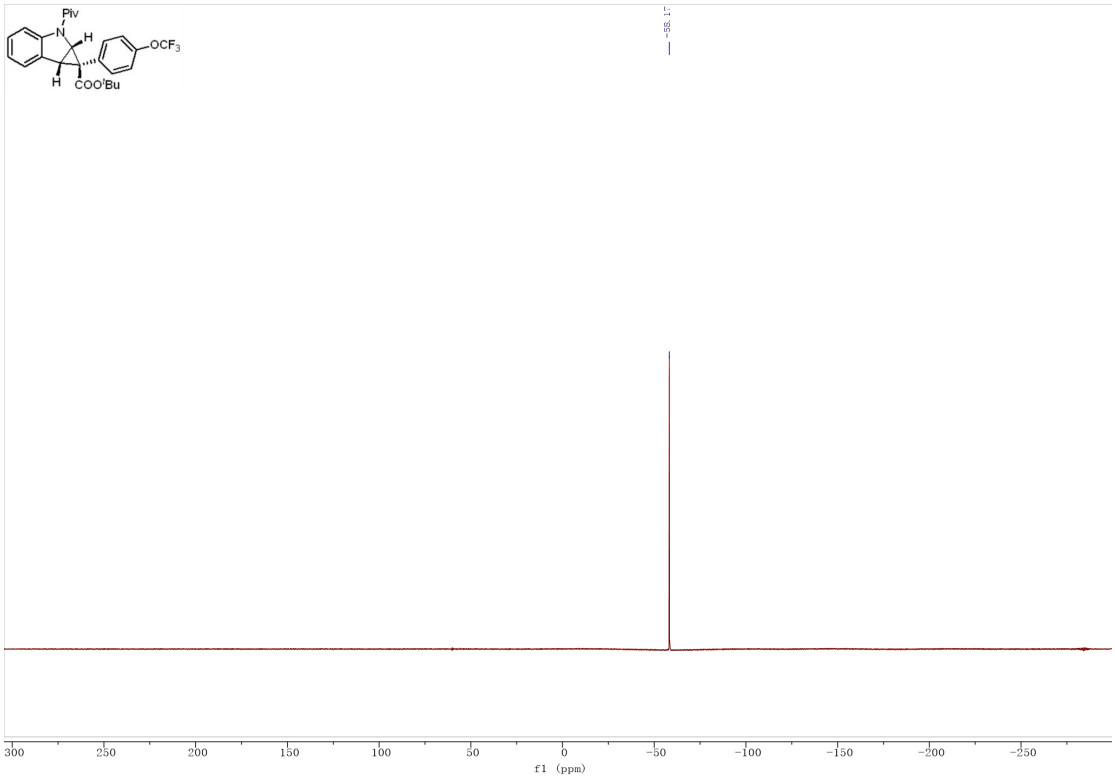
^{1}H NMR spectrum of **3n**



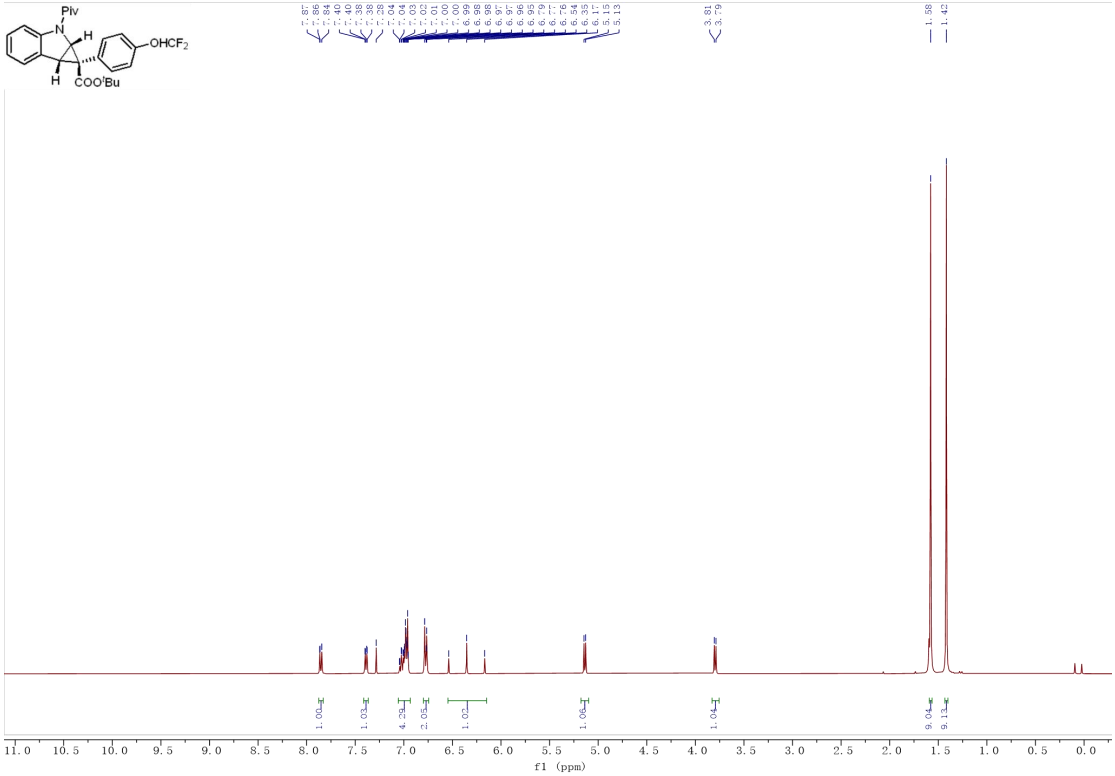
^{13}C NMR spectrum of **3n**



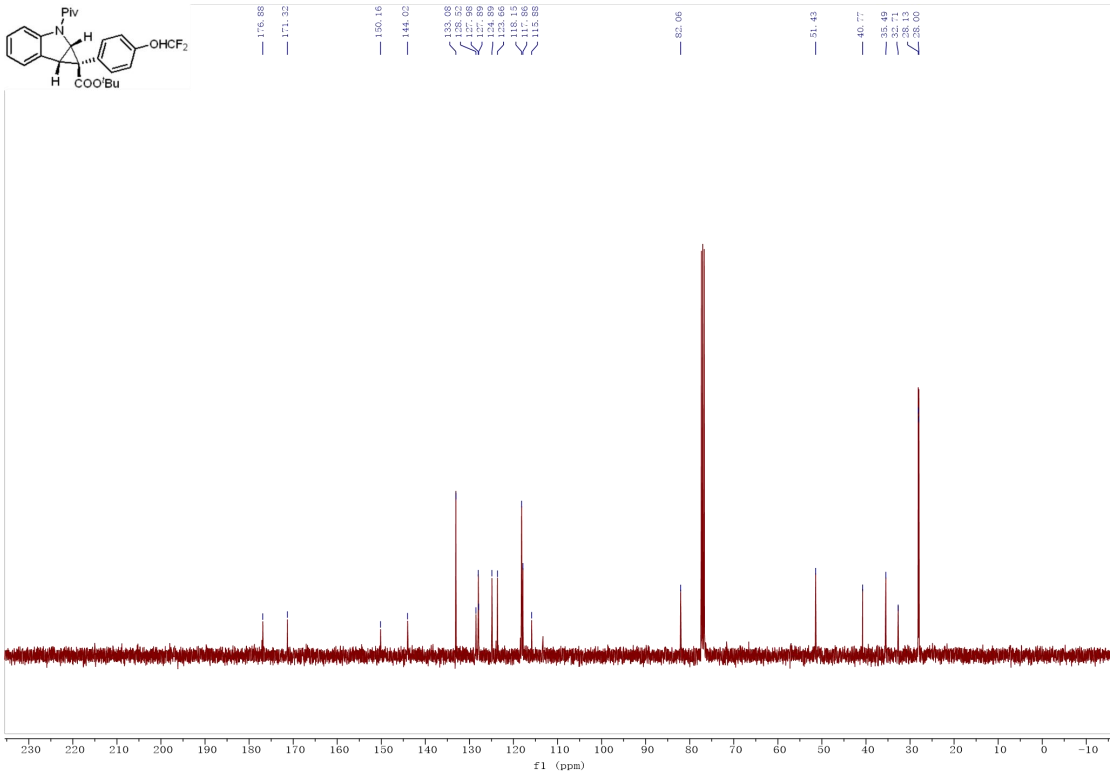
^{19}F NMR spectrum of **3n**



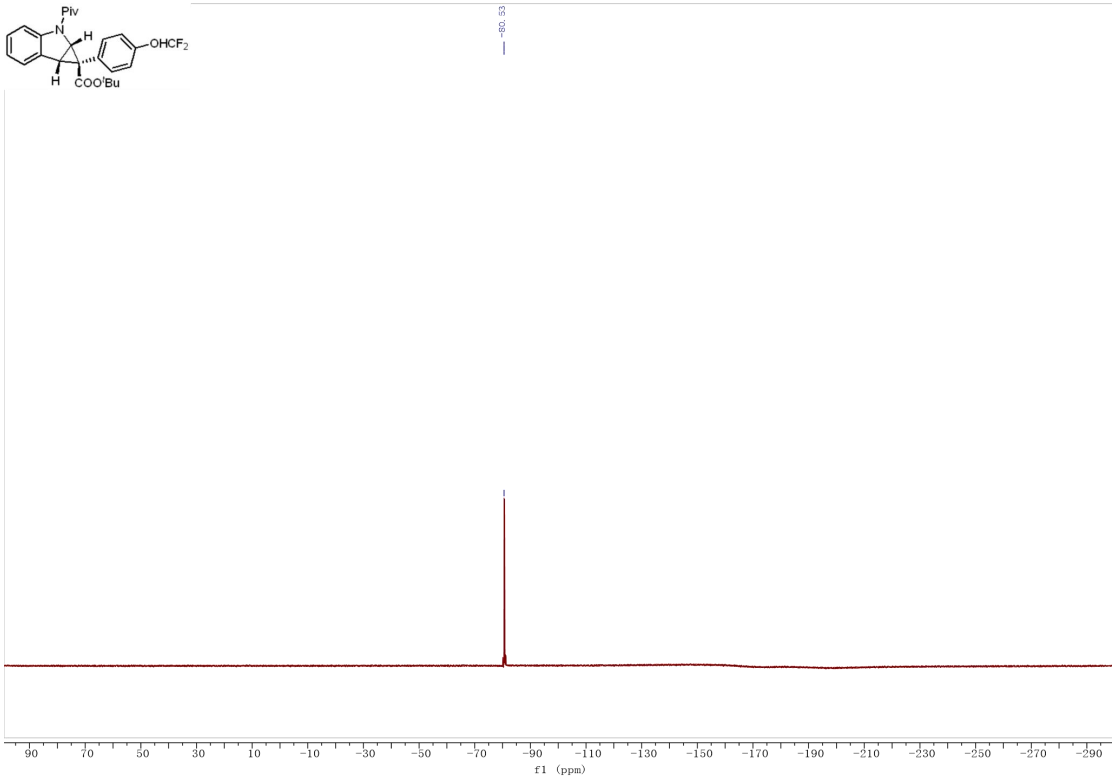
^{1}H NMR spectrum of **3o**



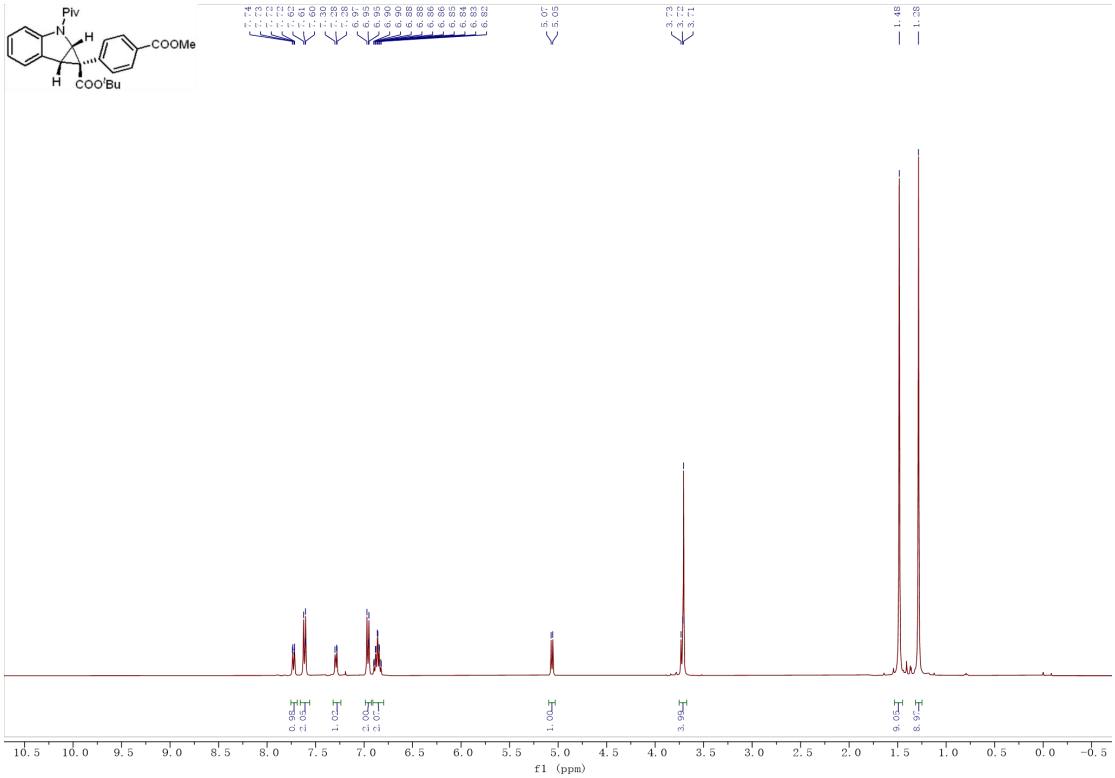
^{13}C NMR spectrum of **3o**



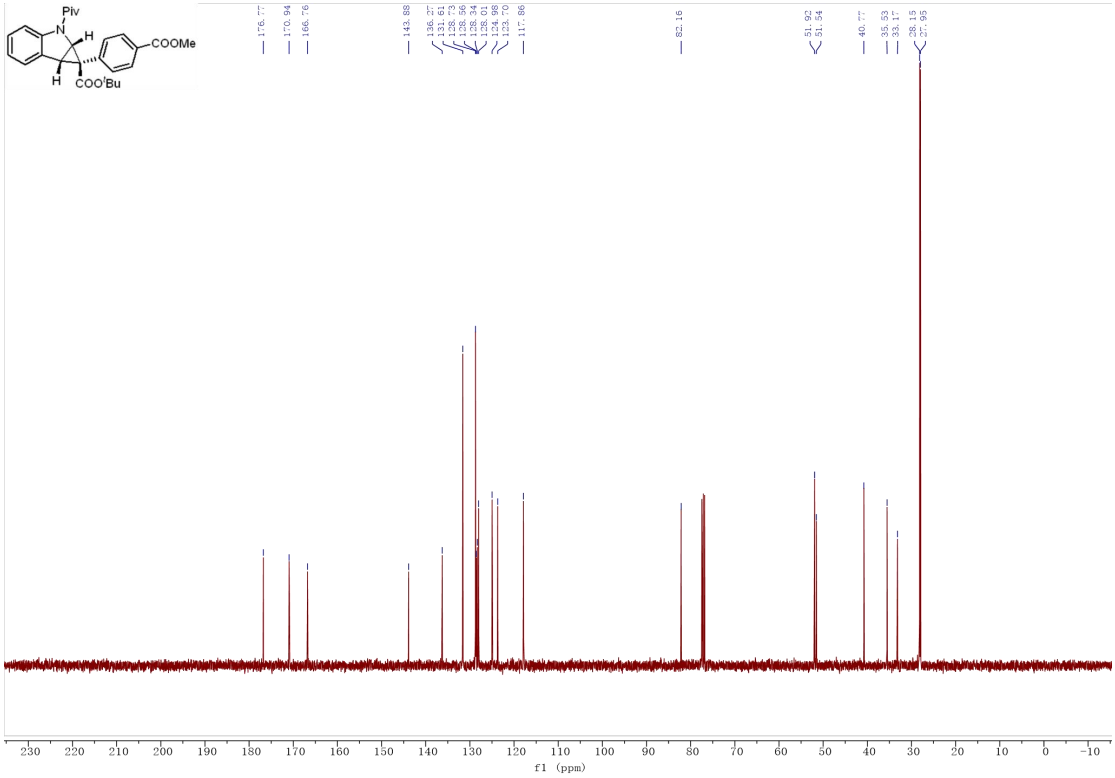
^{19}F NMR spectrum of **3o**



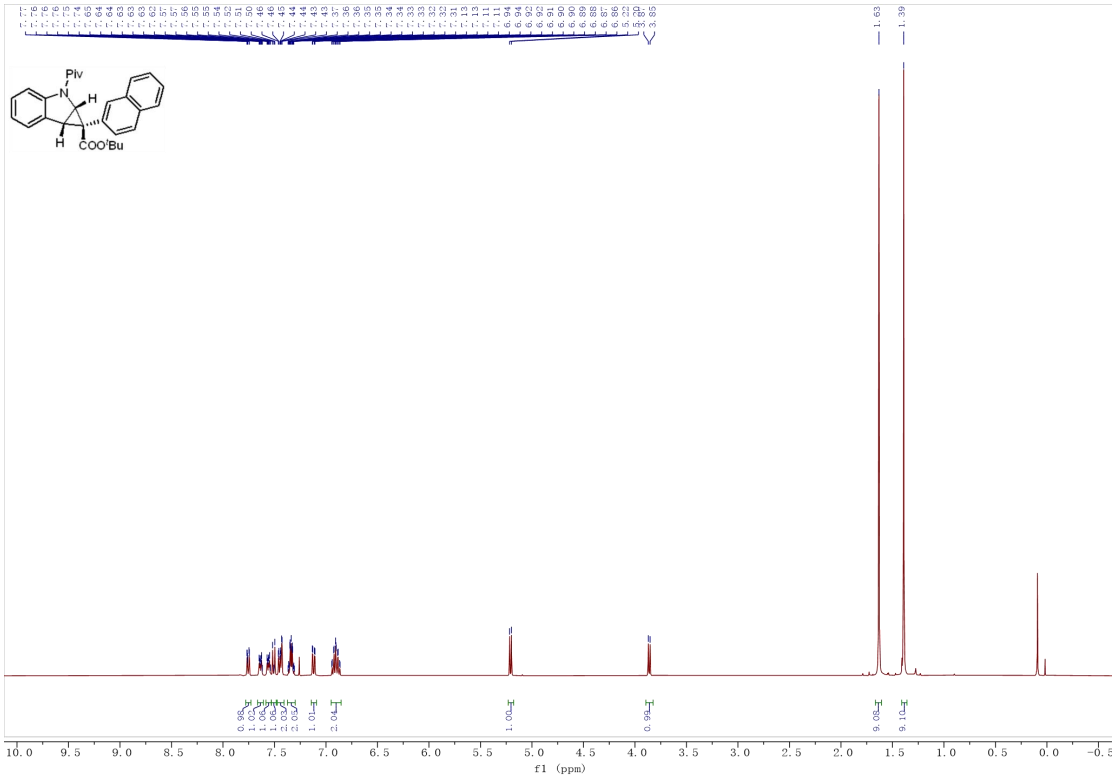
^{1}H NMR spectrum of **3p**



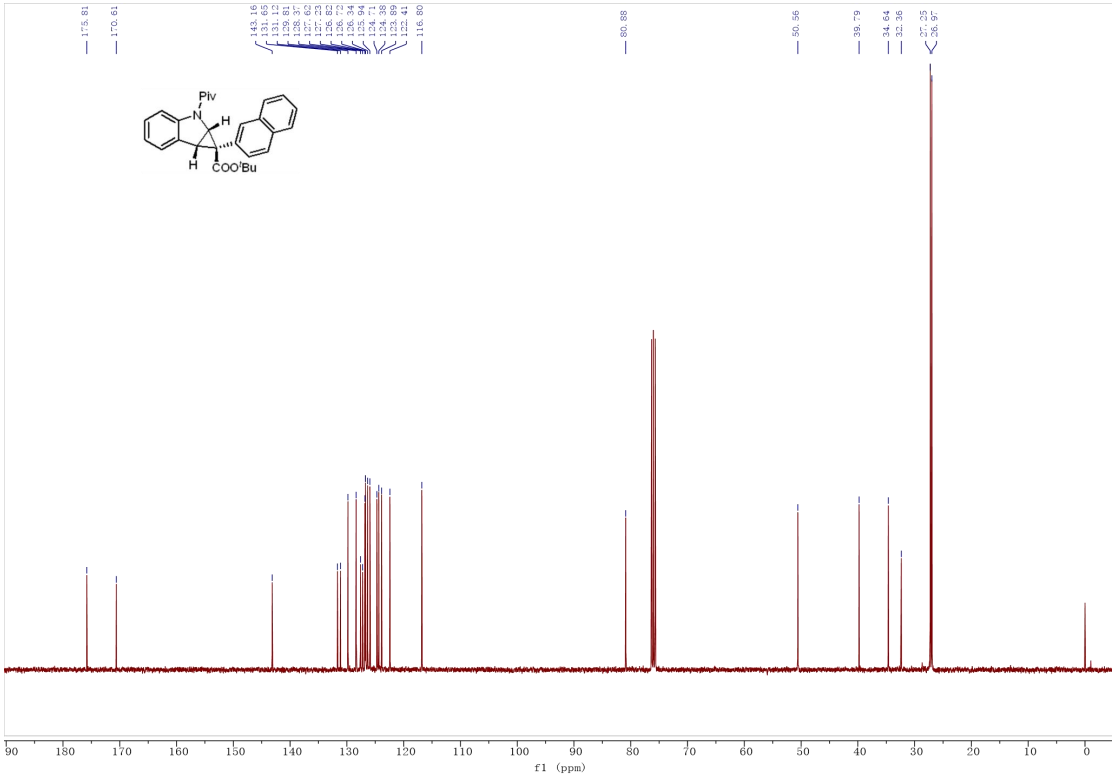
^{13}C NMR spectrum of **3p**



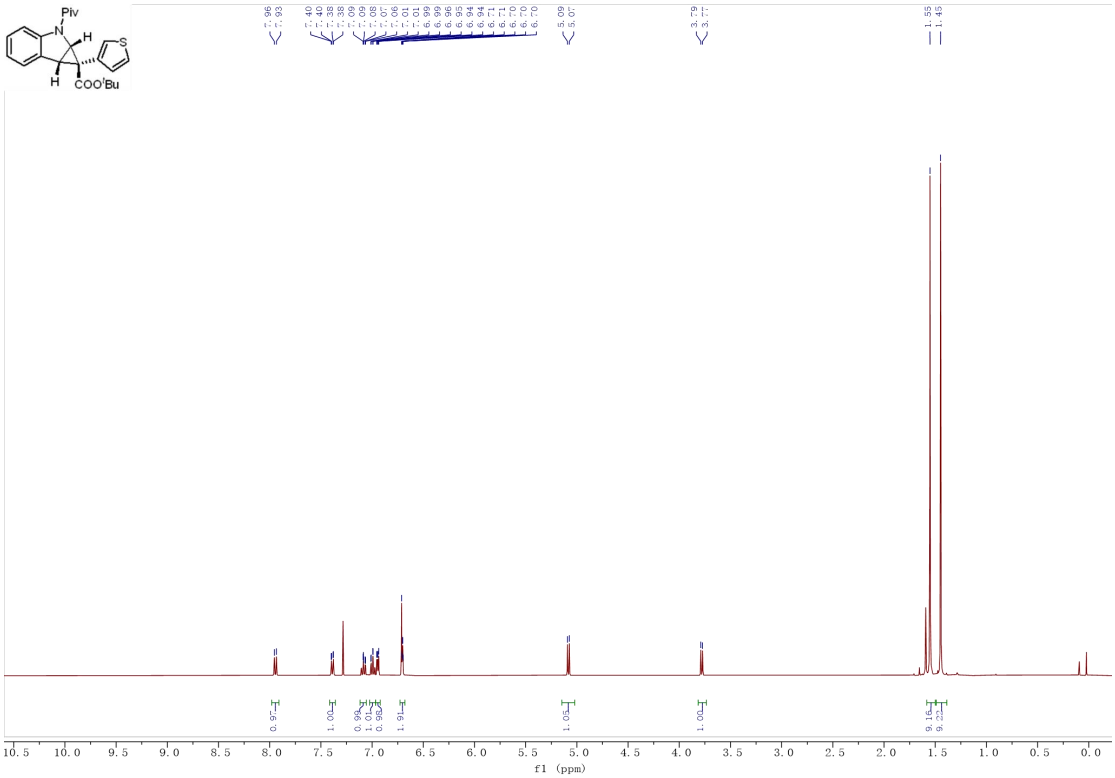
^{1}H NMR spectrum of **3q**



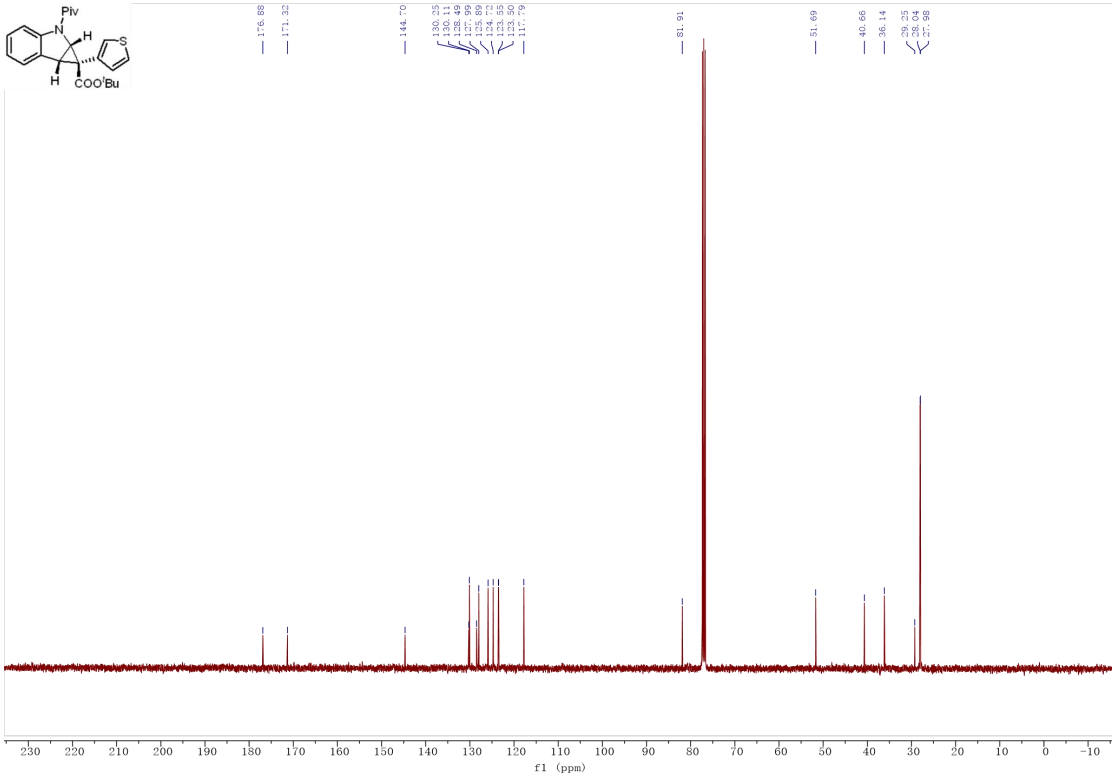
^{13}C NMR spectrum of **3q**



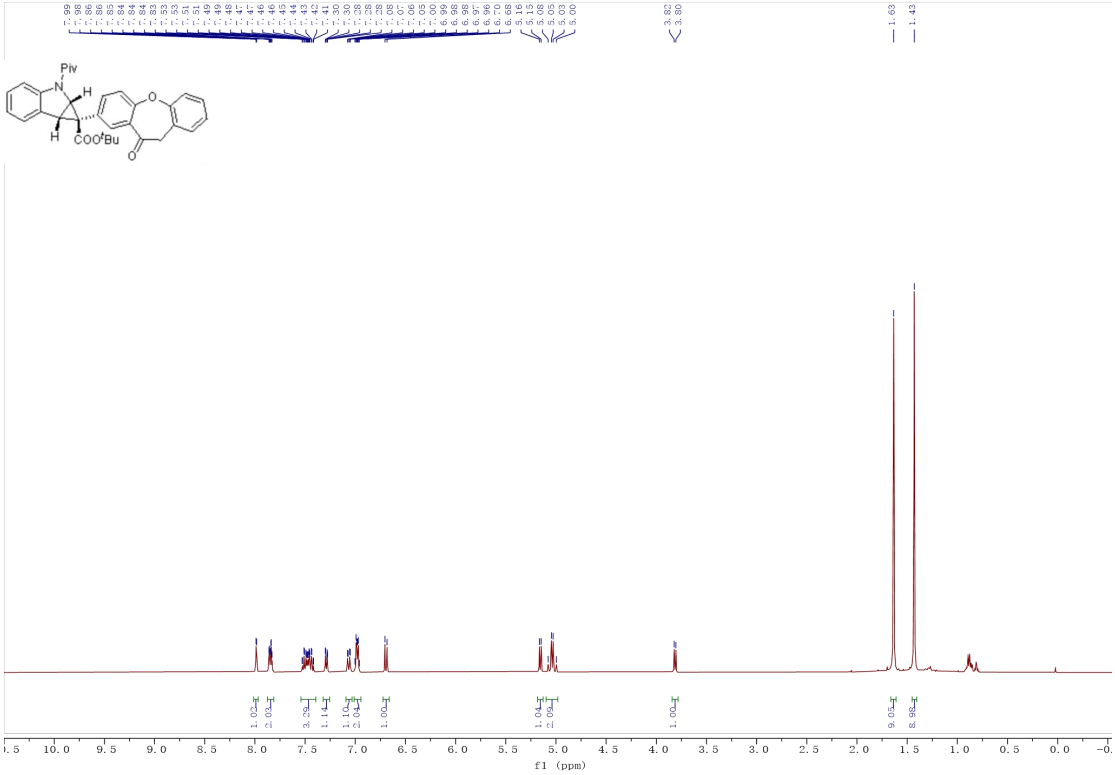
^{1}H NMR spectrum of **3r**



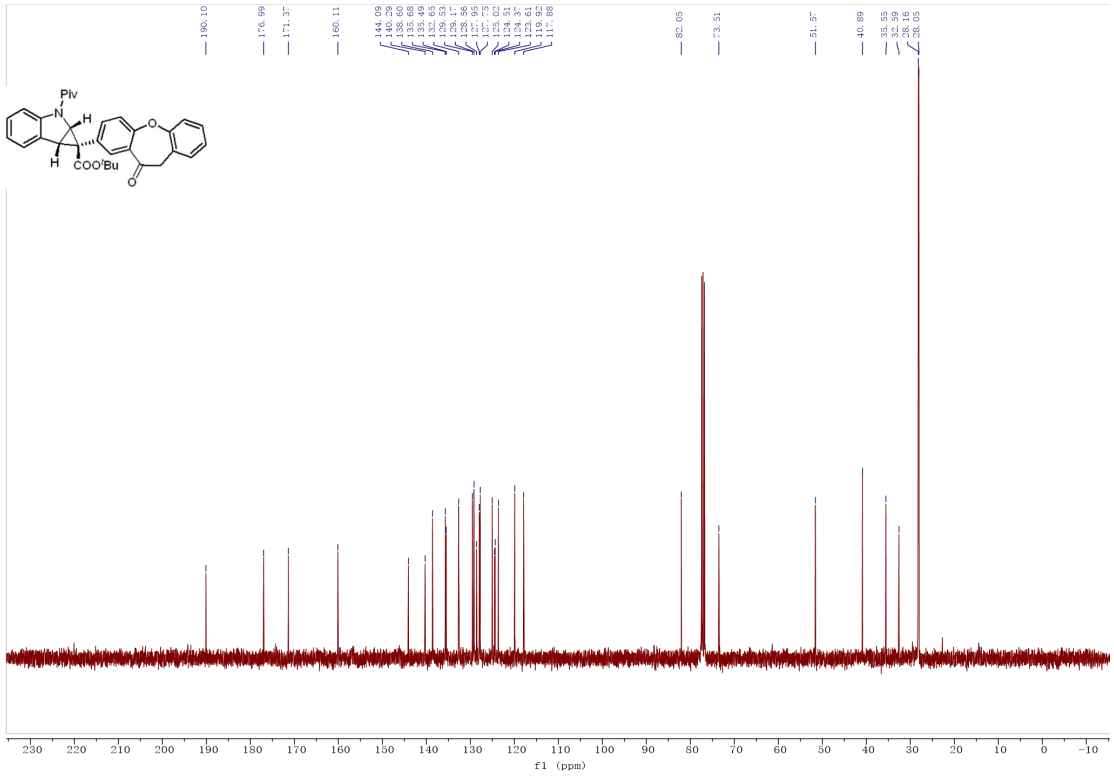
^{13}C NMR spectrum of **3r**



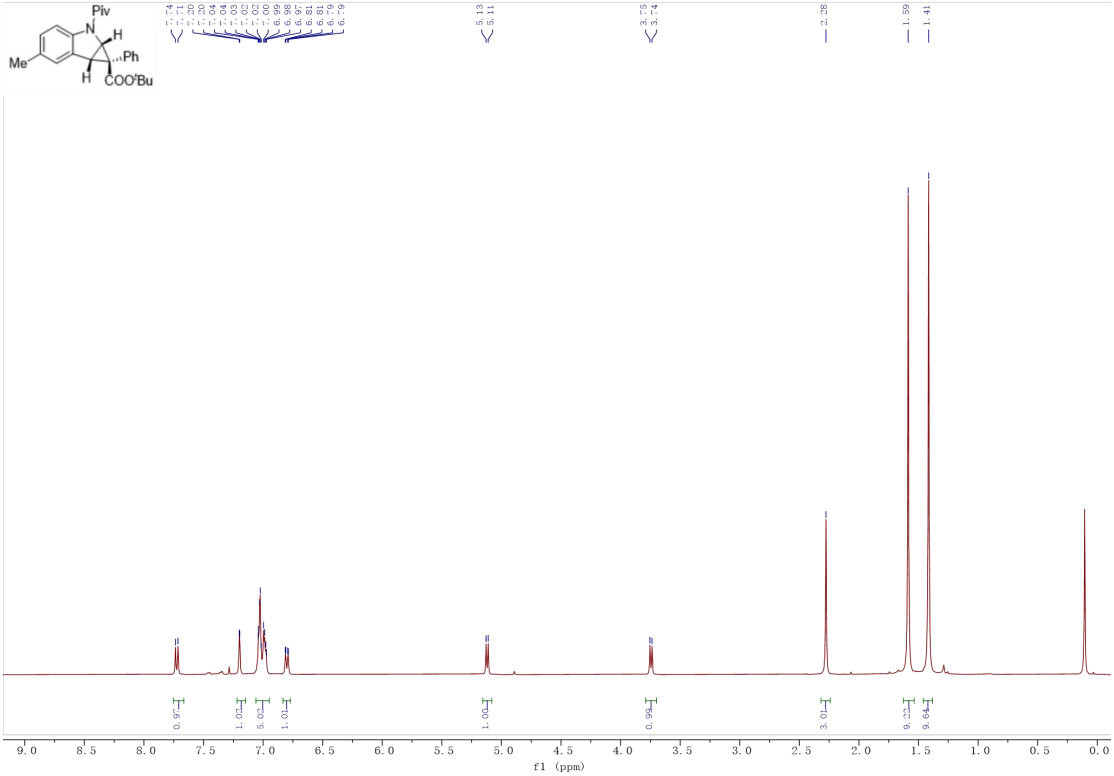
^{1}H NMR spectrum of **3s**



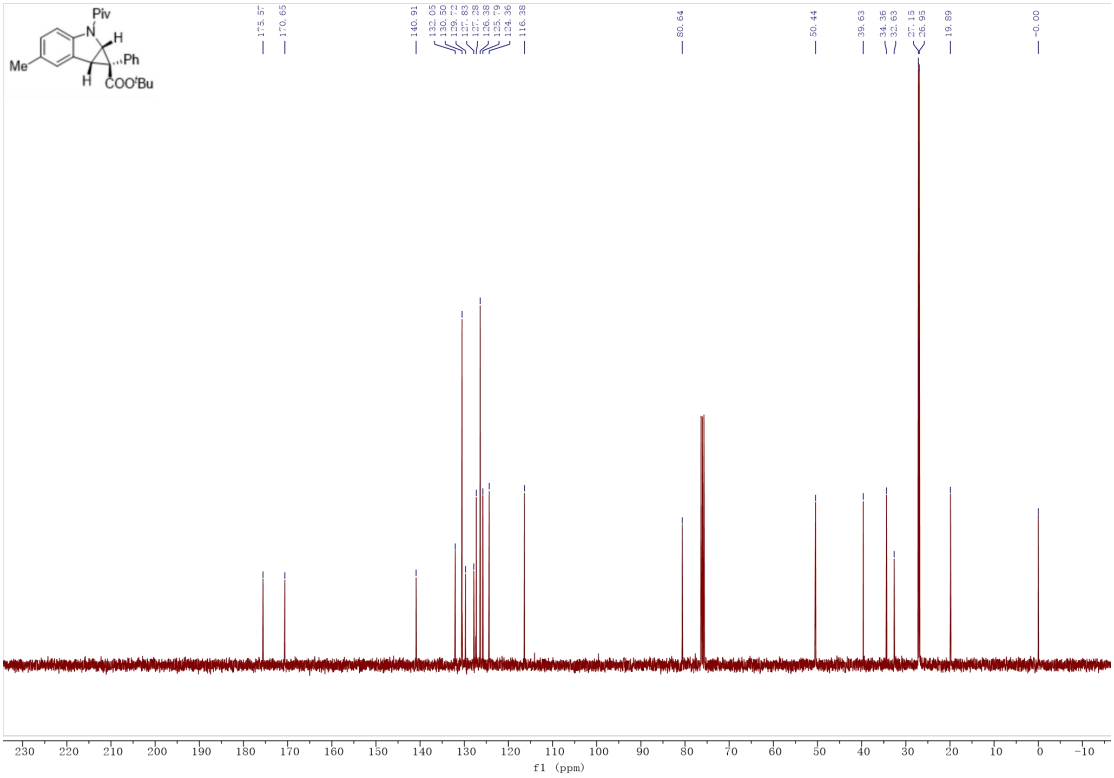
^{13}C NMR spectrum of **3s**



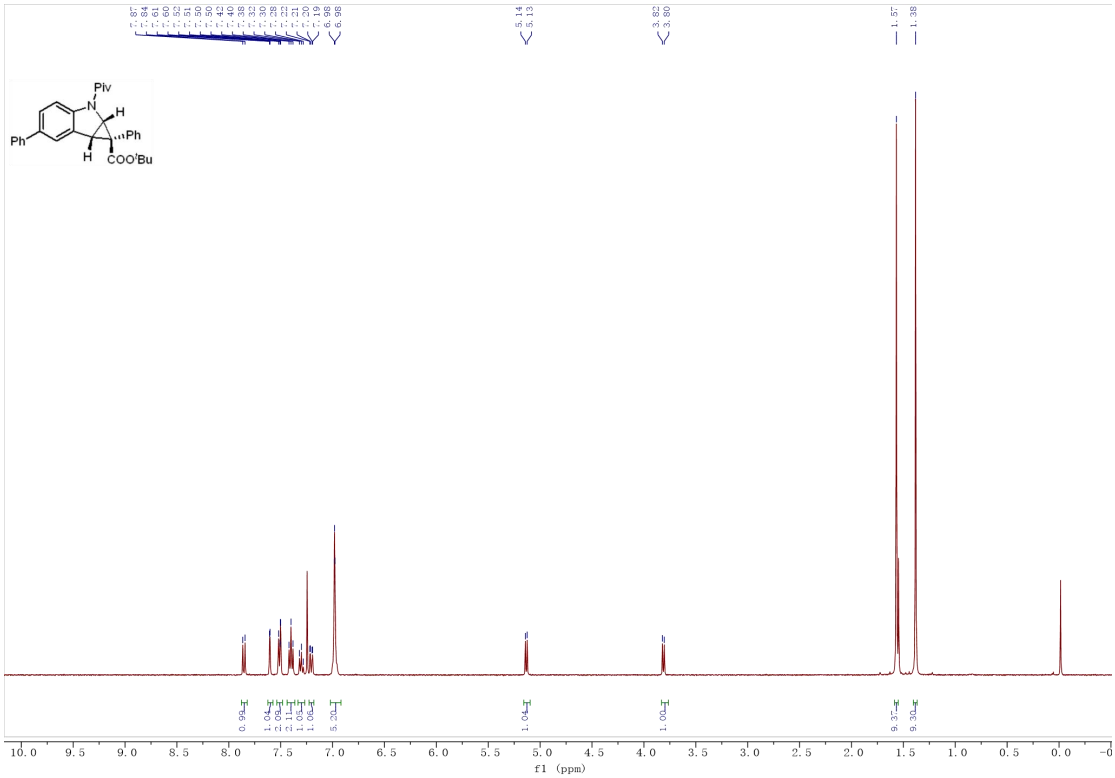
^{1}H NMR spectrum of **3t**



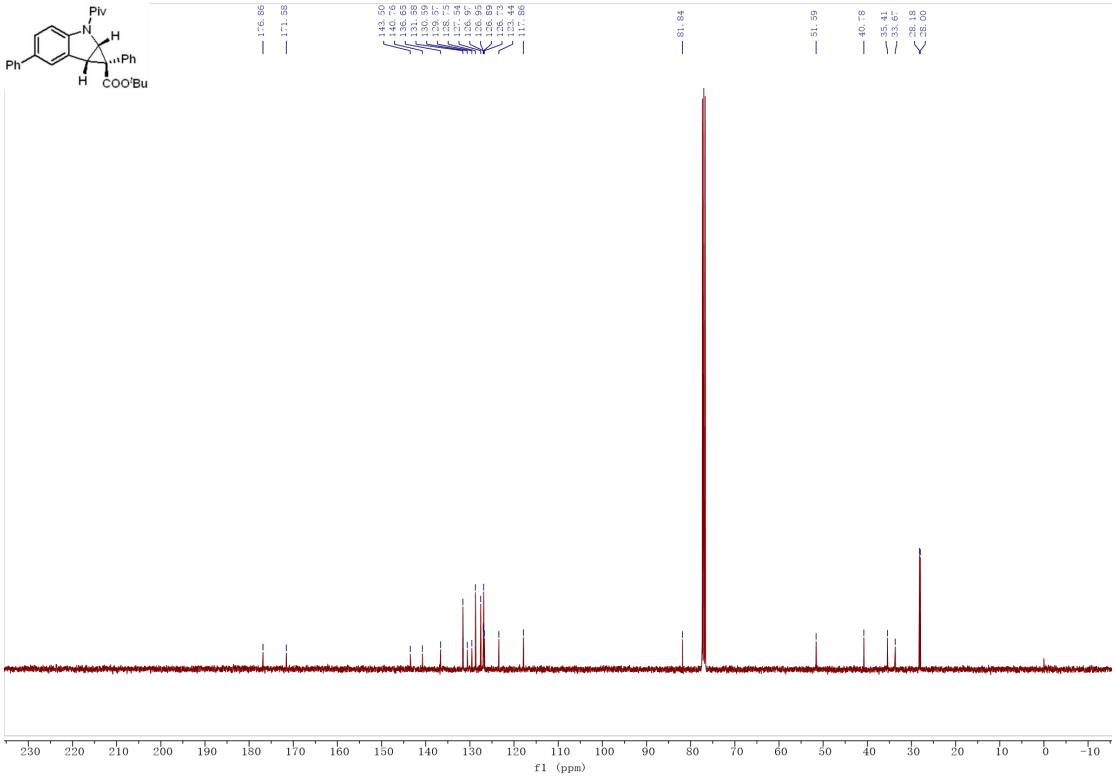
^{13}C NMR spectrum of **3t**



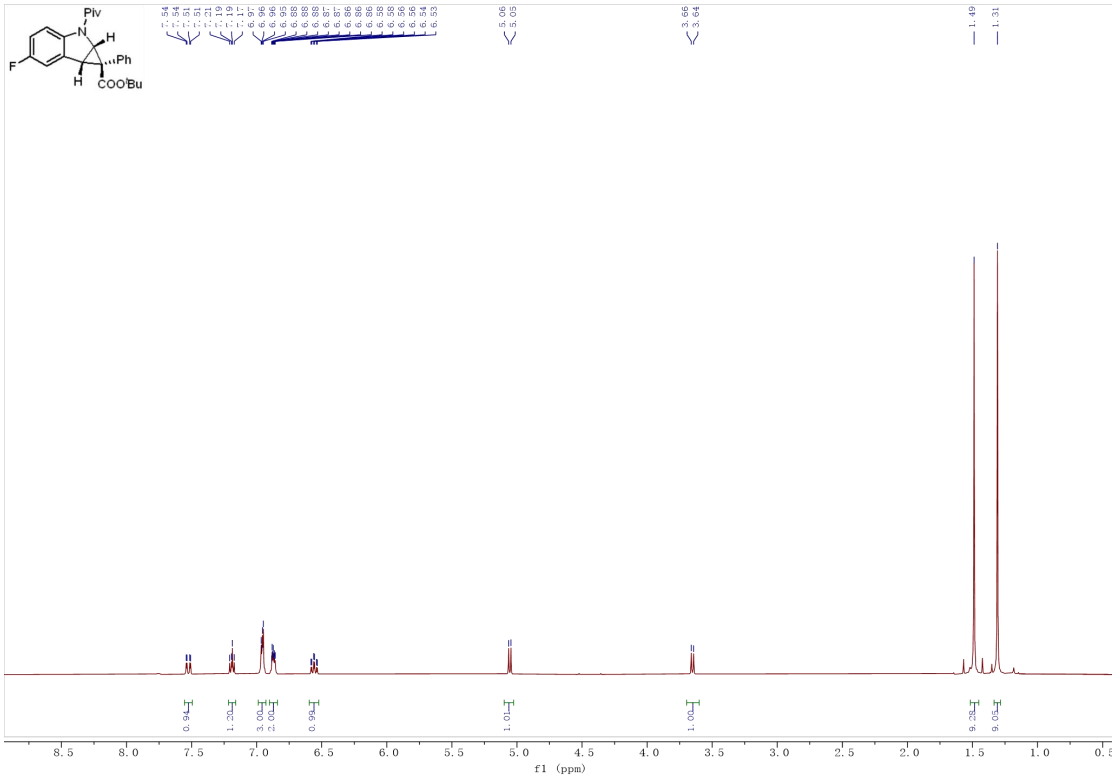
^{1}H NMR spectrum of **3u**



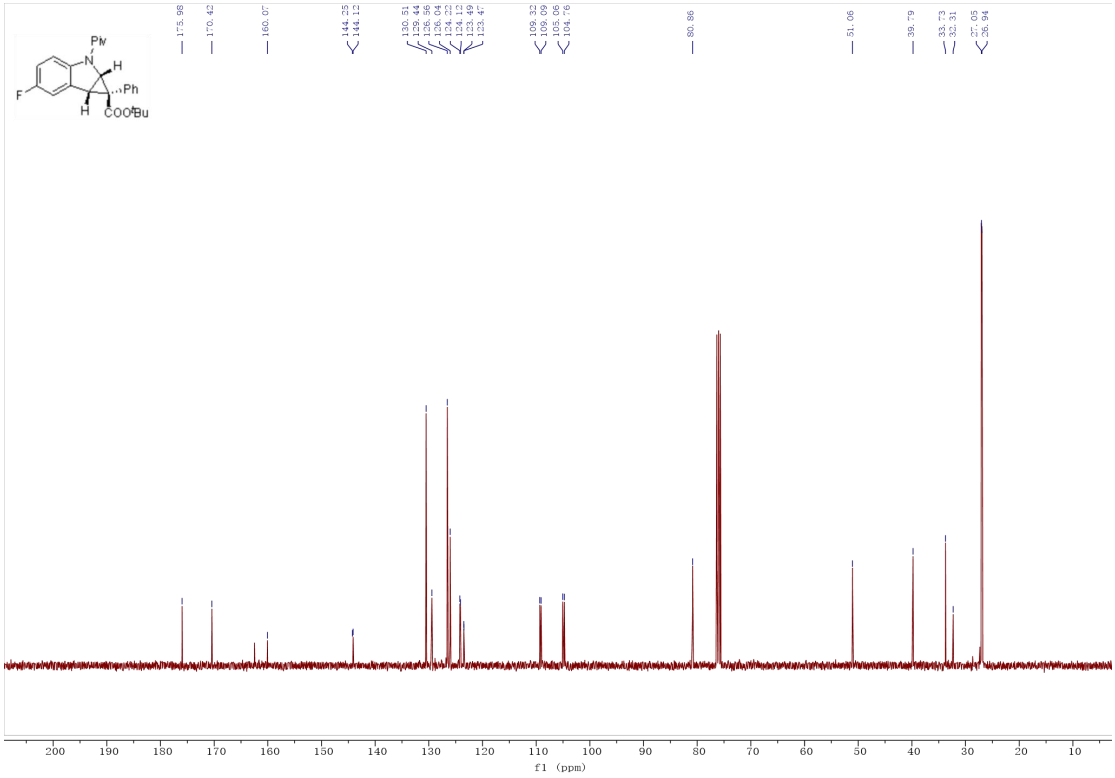
^{13}C NMR spectrum of **3u**



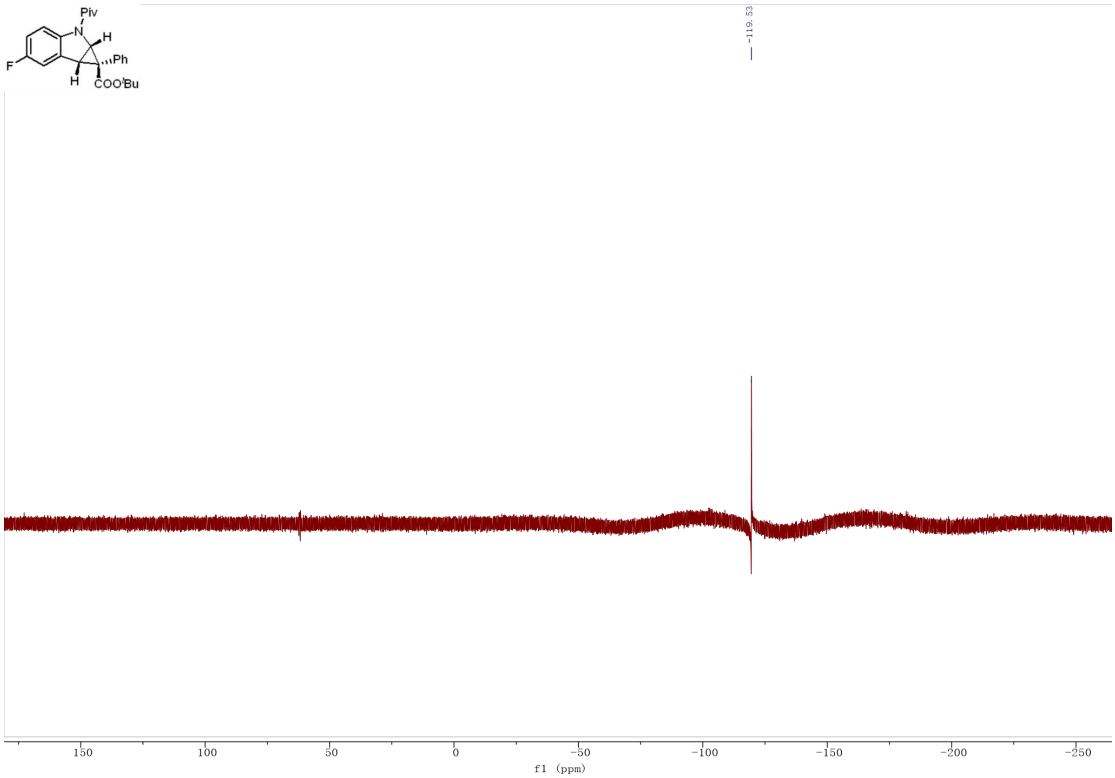
^{1}H NMR spectrum of **3v**



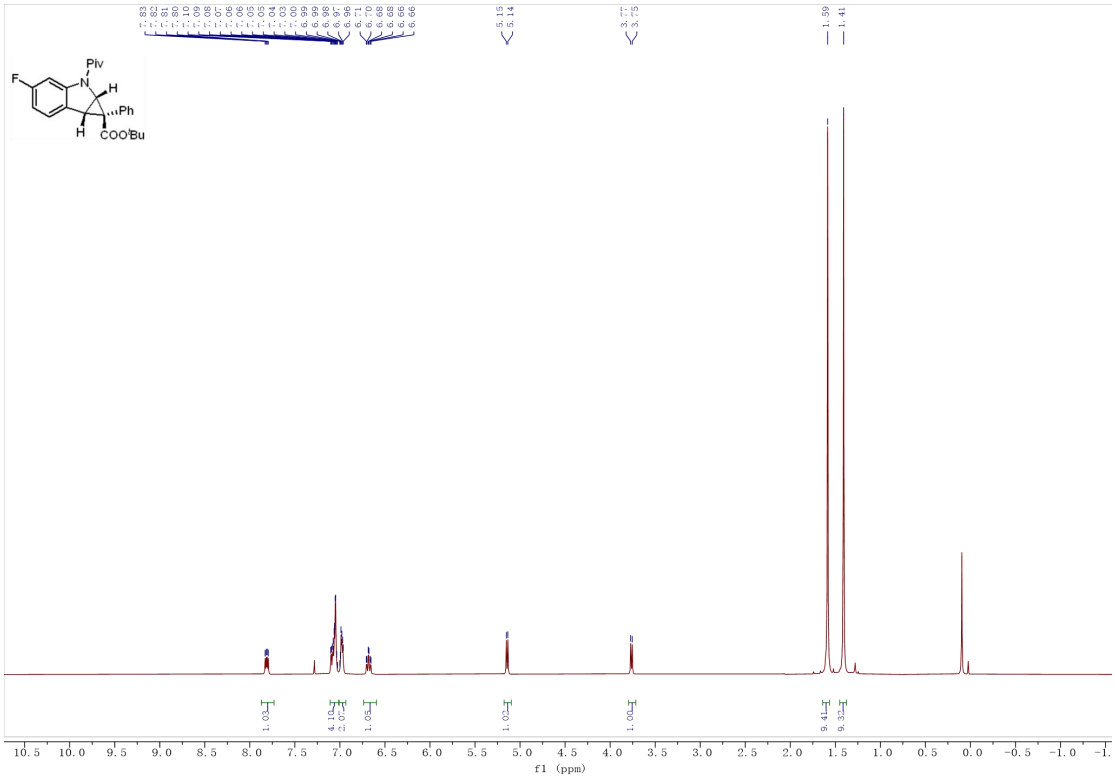
^{13}C NMR spectrum of **3v**



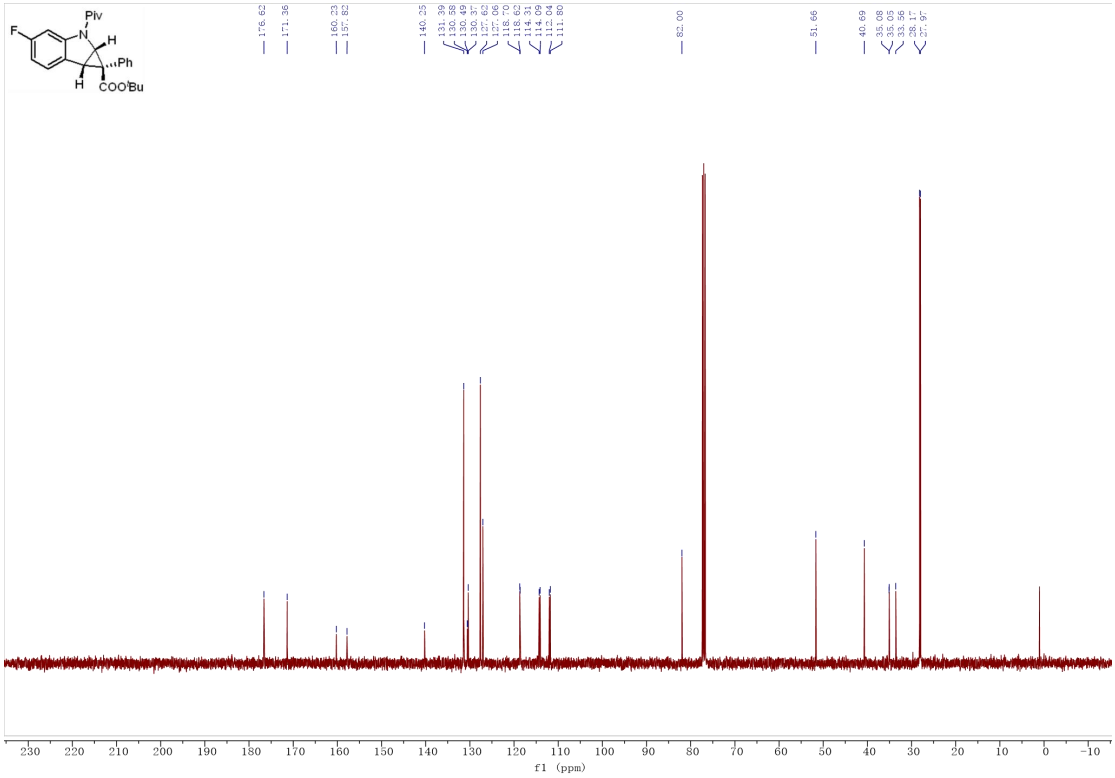
^{19}F NMR spectrum of **3v**



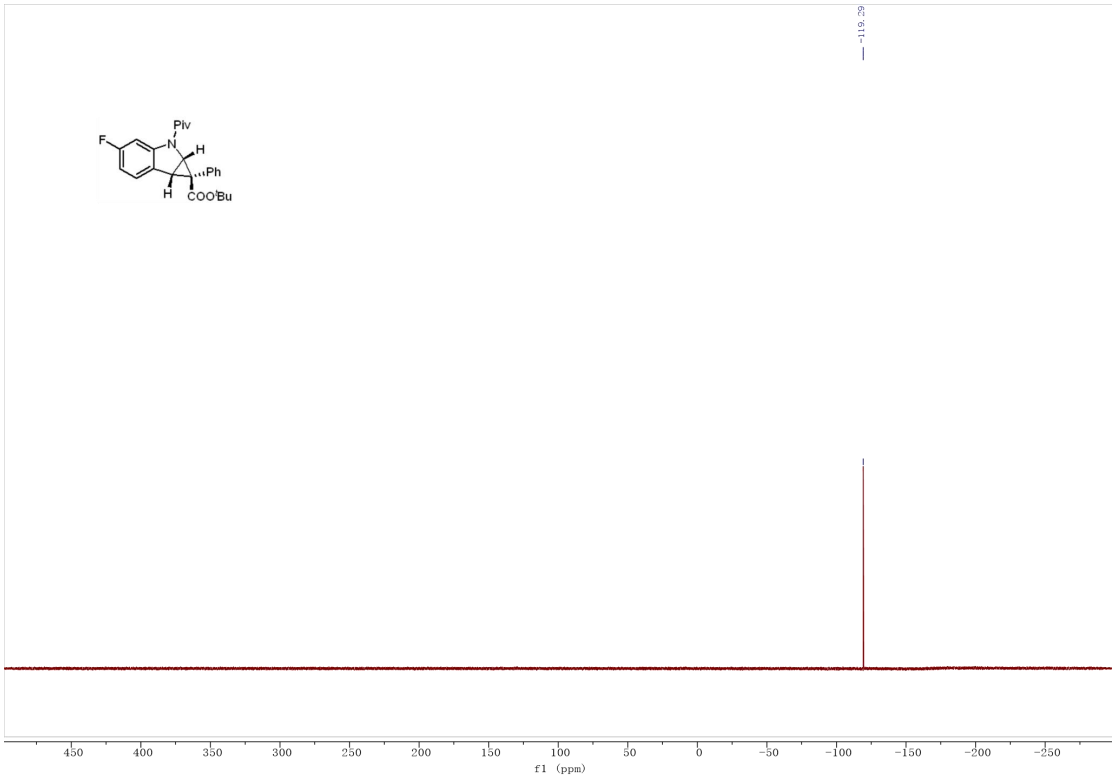
^{1}H NMR spectrum of **3w**



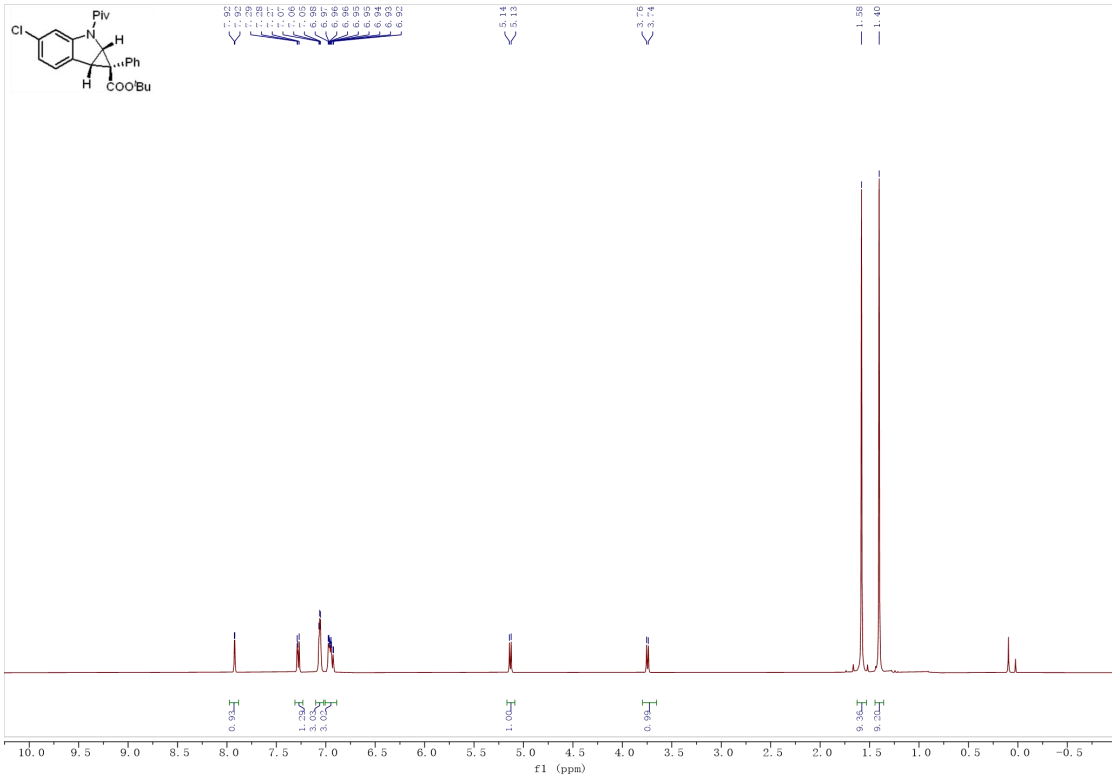
^{13}C NMR spectrum of **3w**



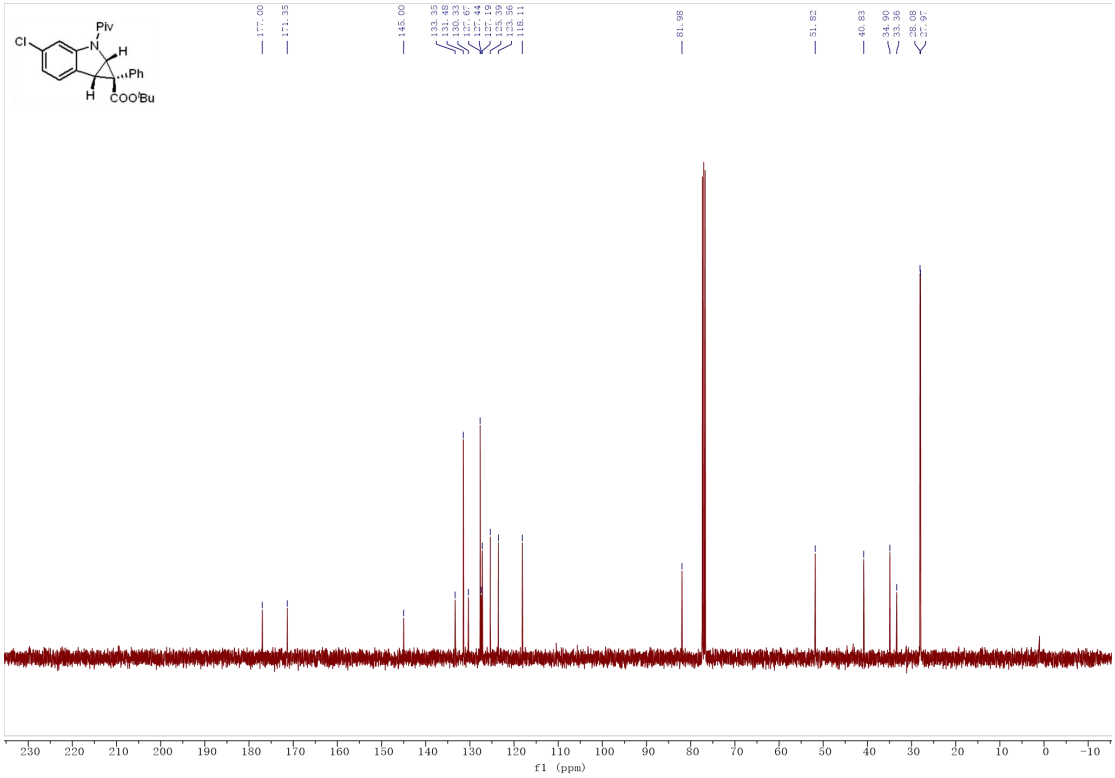
^{19}F NMR spectrum of **3w**



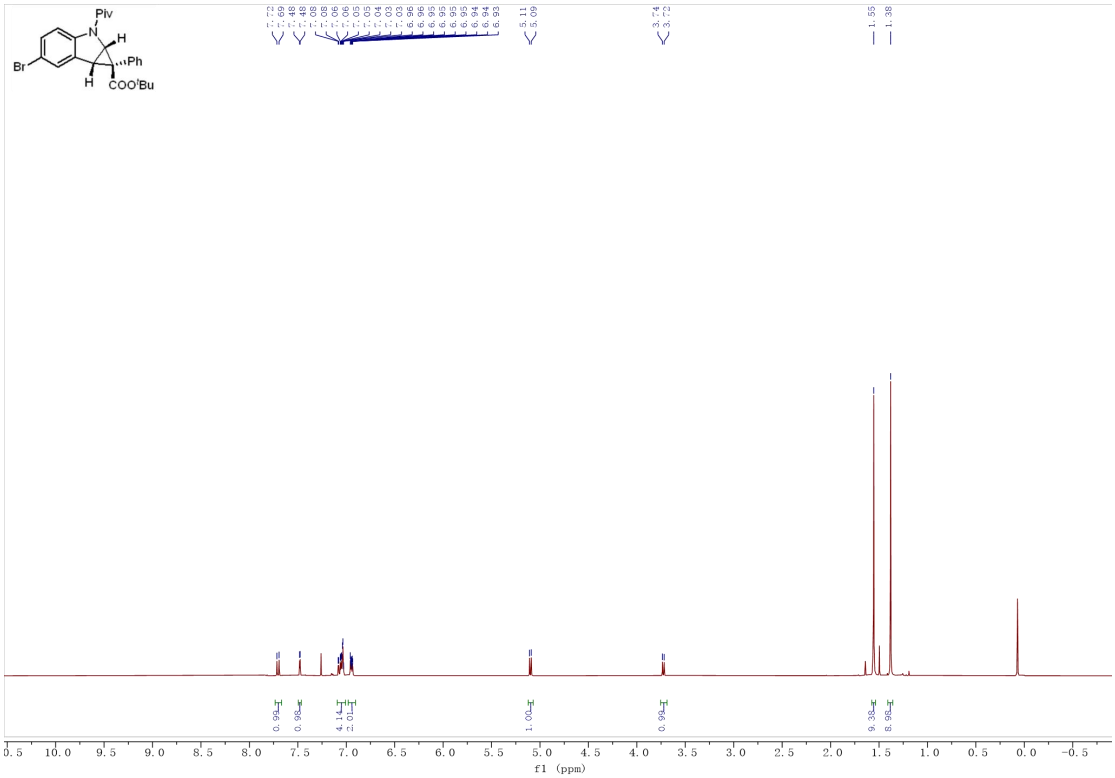
^{1}H NMR spectrum of **3x**



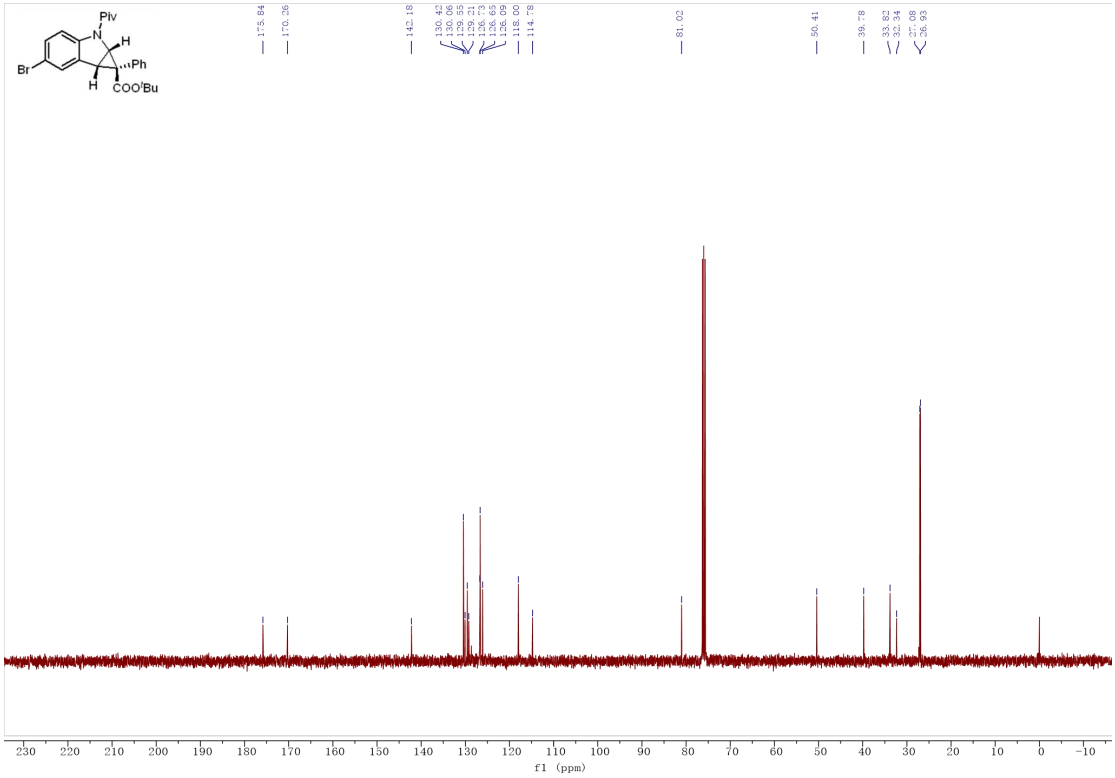
^{13}C NMR spectrum of **3x**



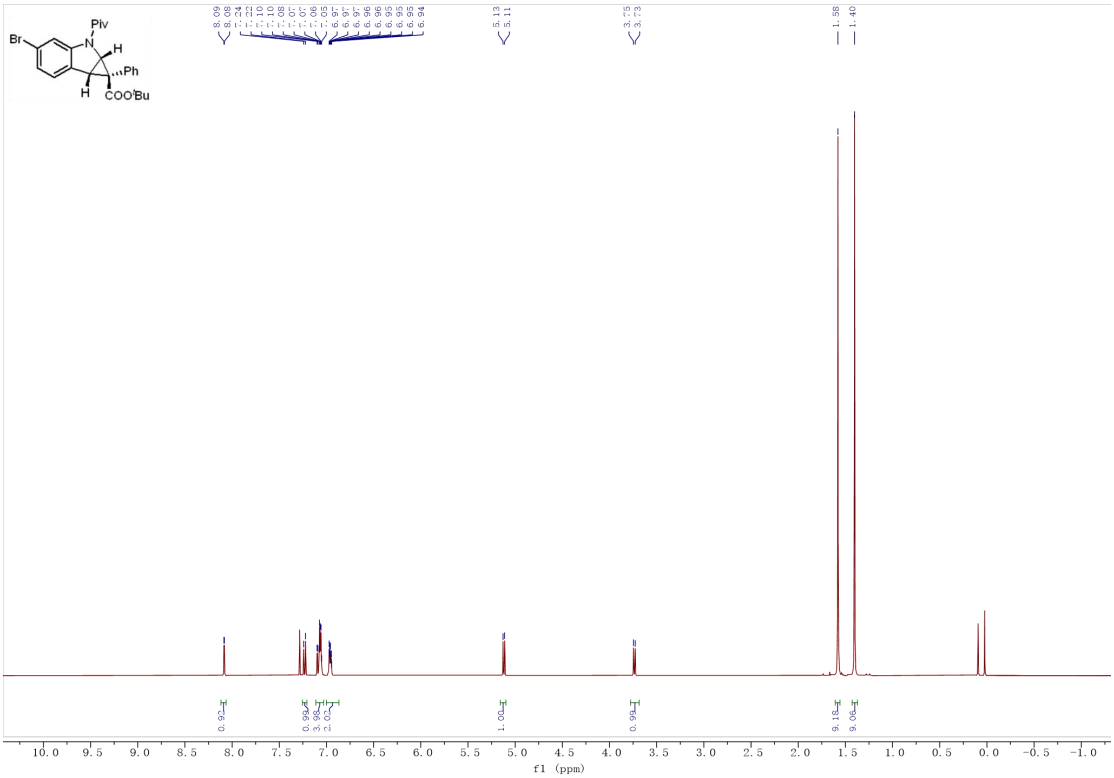
^{1}H NMR spectrum of **3y**



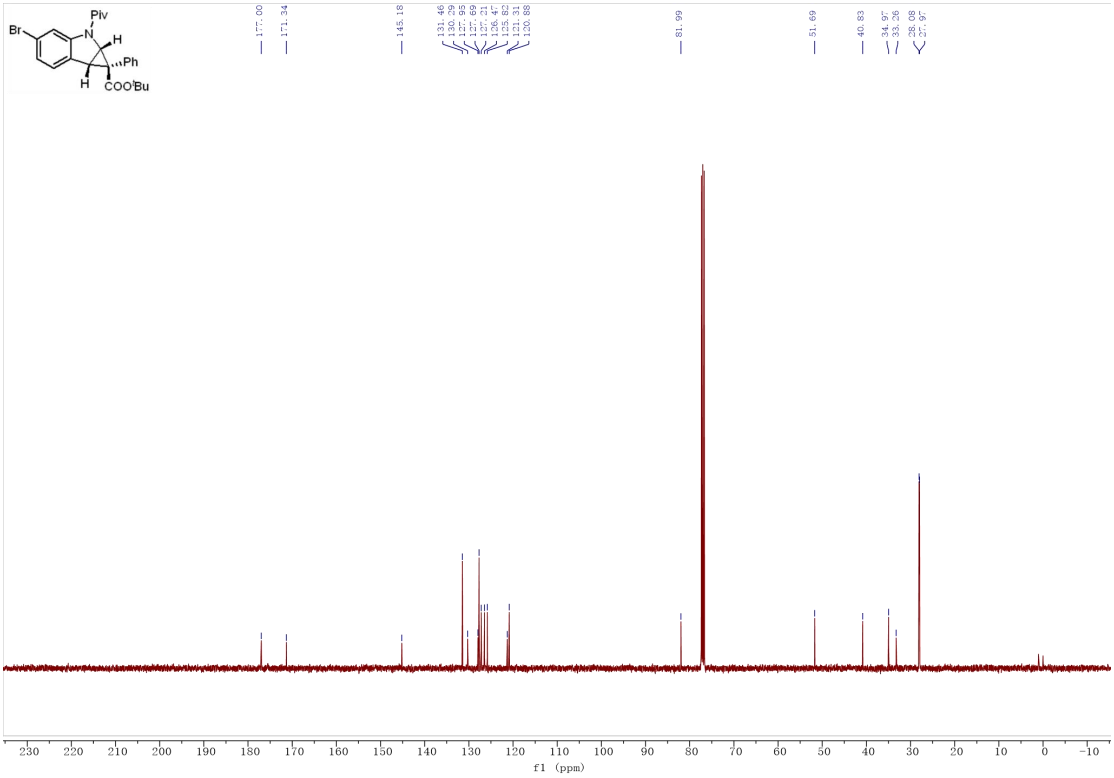
^{13}C NMR spectrum of **3y**



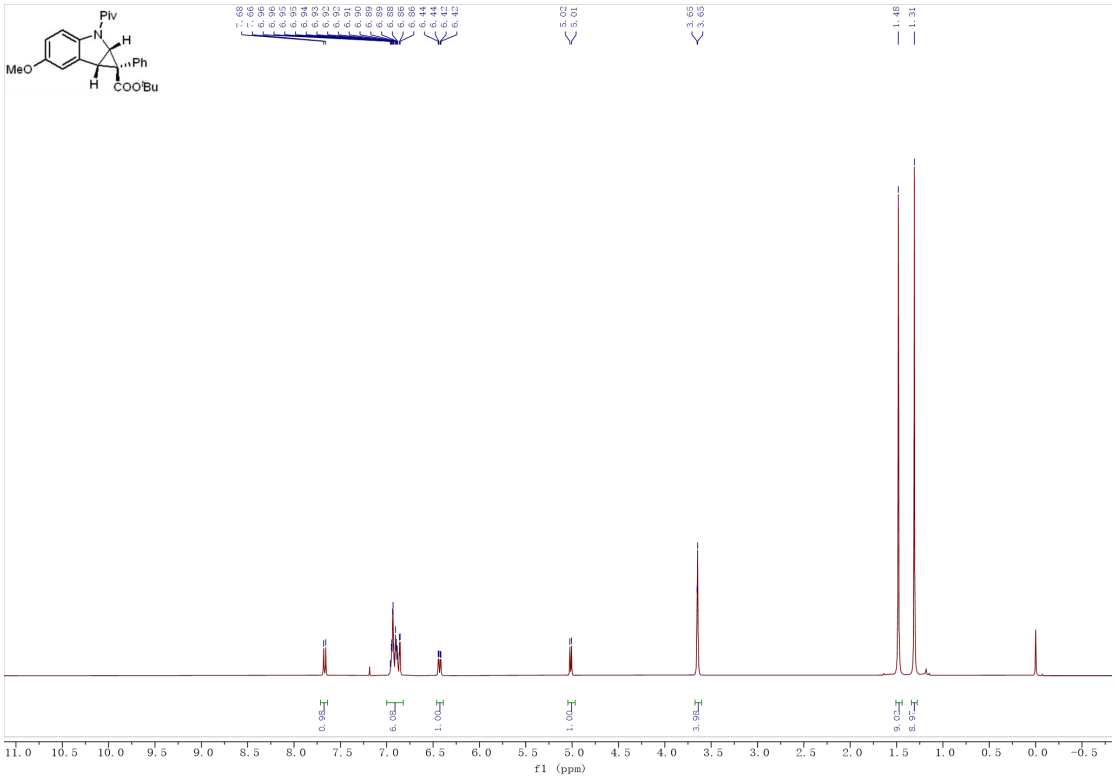
^{1}H NMR spectrum of **3z**



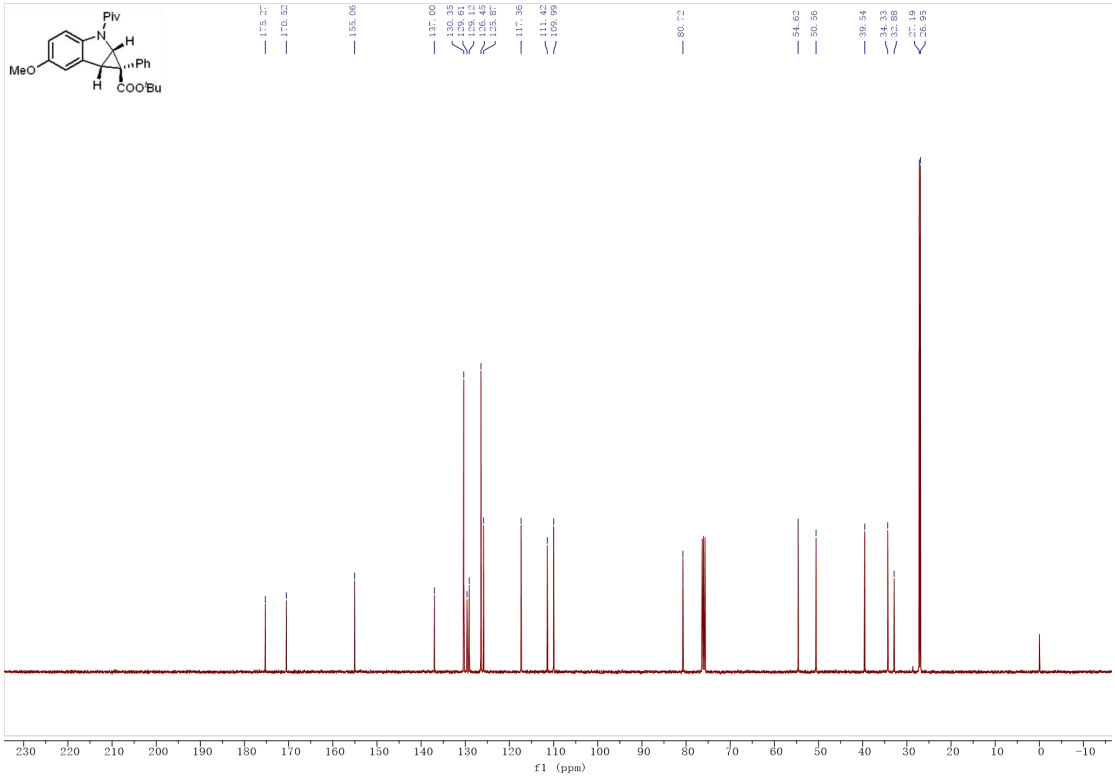
^{13}C NMR spectrum of **3z**



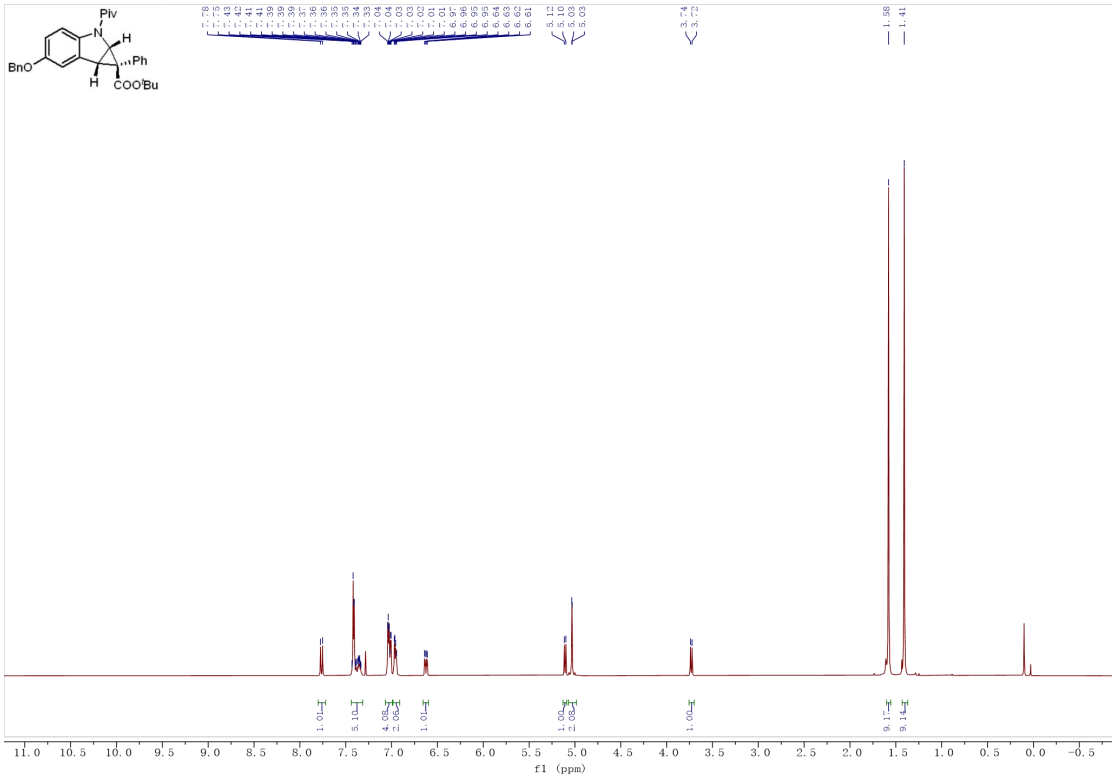
^{1}H NMR spectrum of **4a**



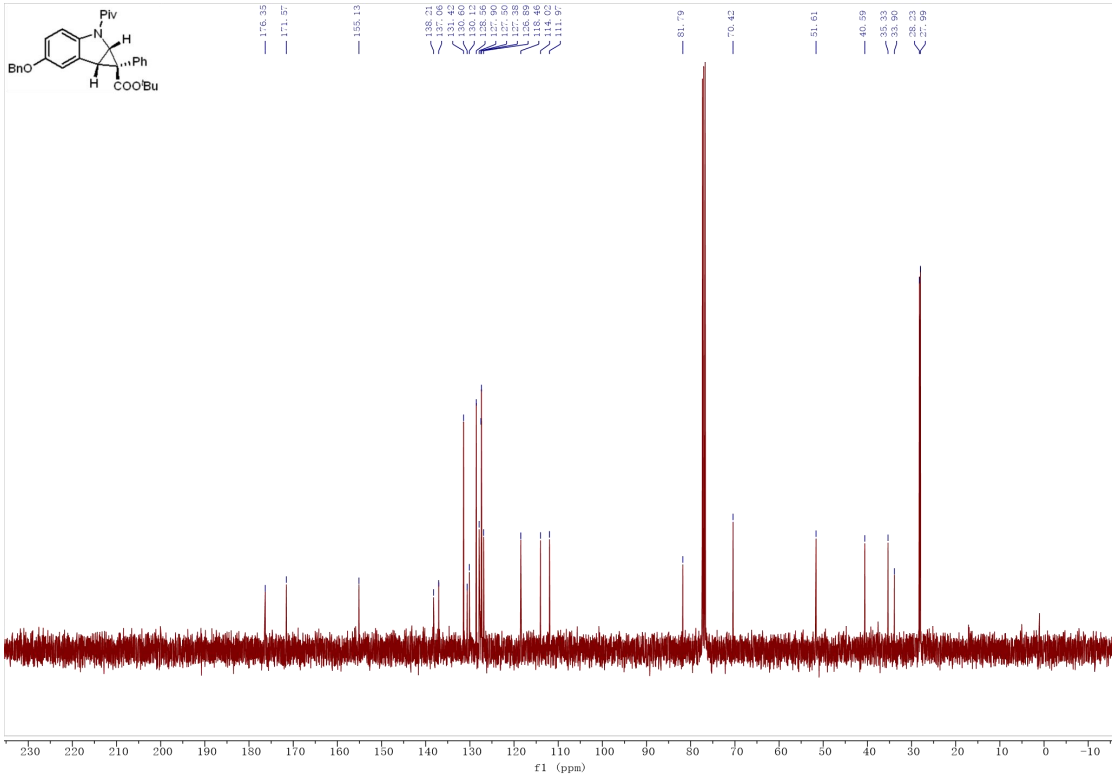
^{13}C NMR spectrum of **4a**



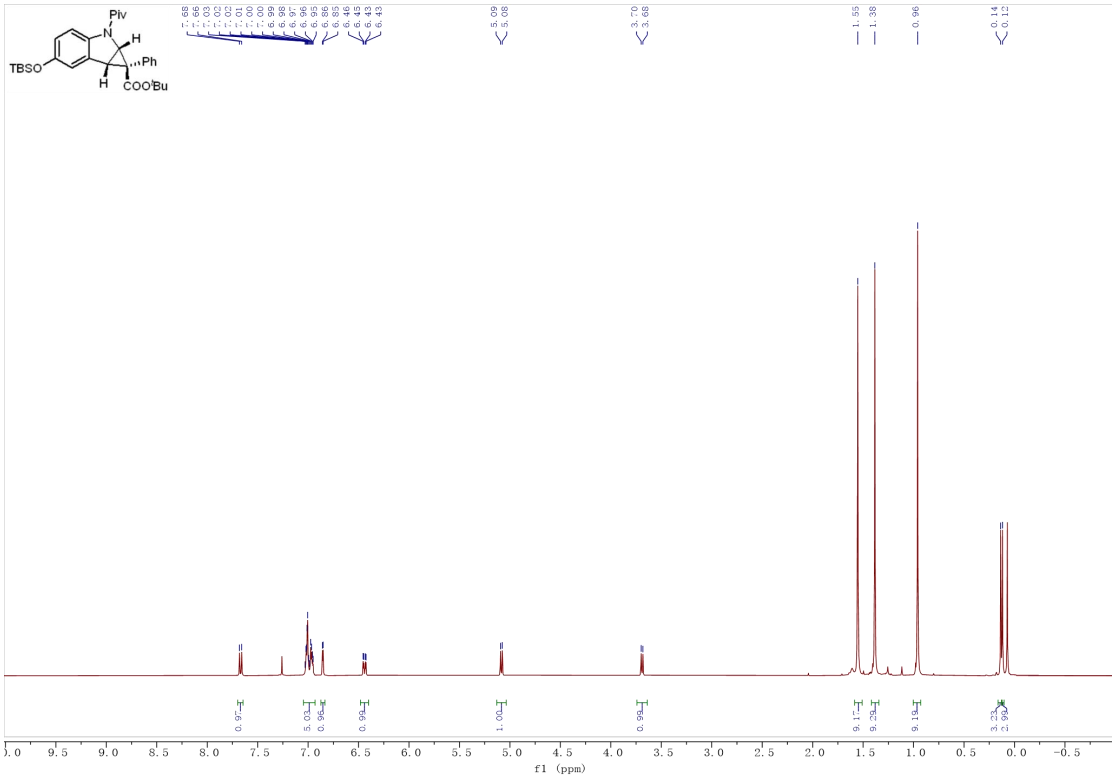
^{1}H NMR spectrum of **4b**



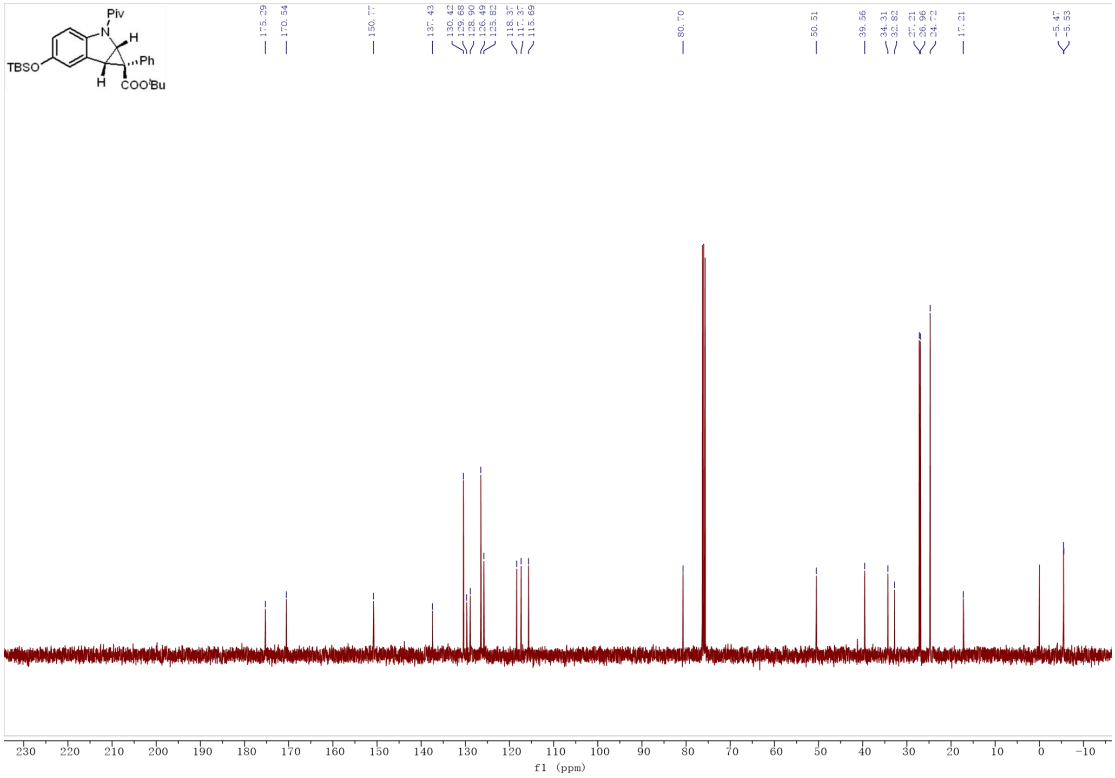
^{13}C NMR spectrum of **4b**



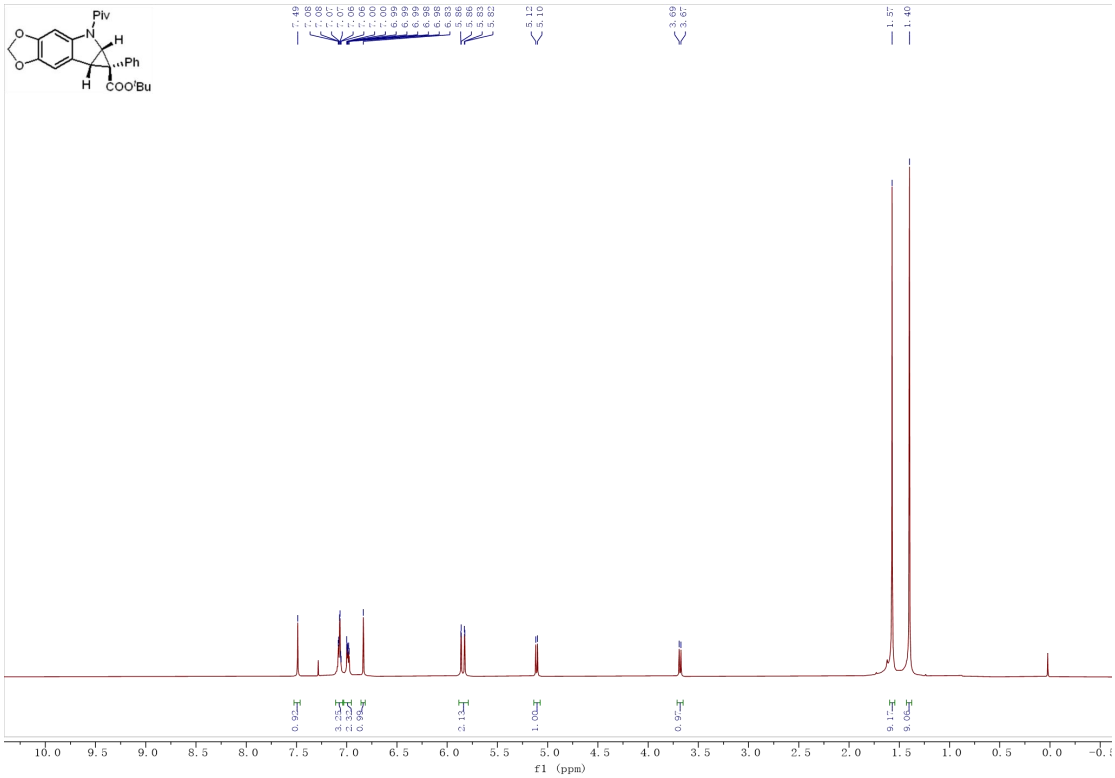
^{1}H NMR spectrum of **4c**



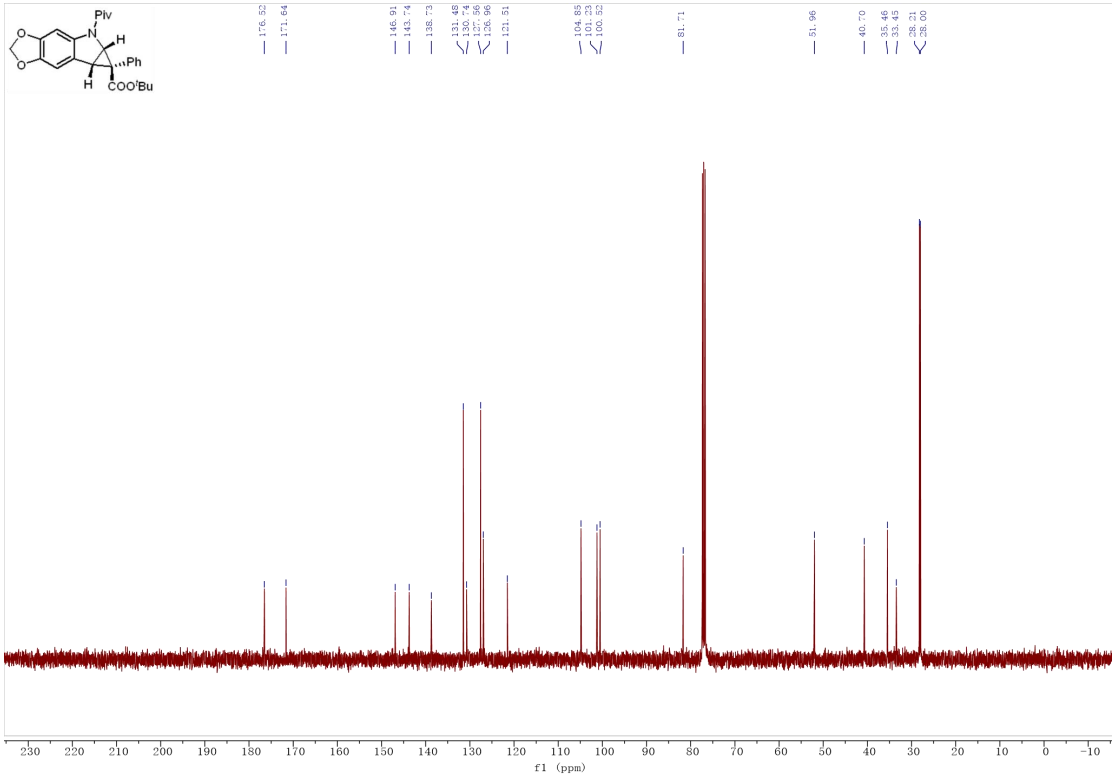
^{13}C NMR spectrum of **4c**



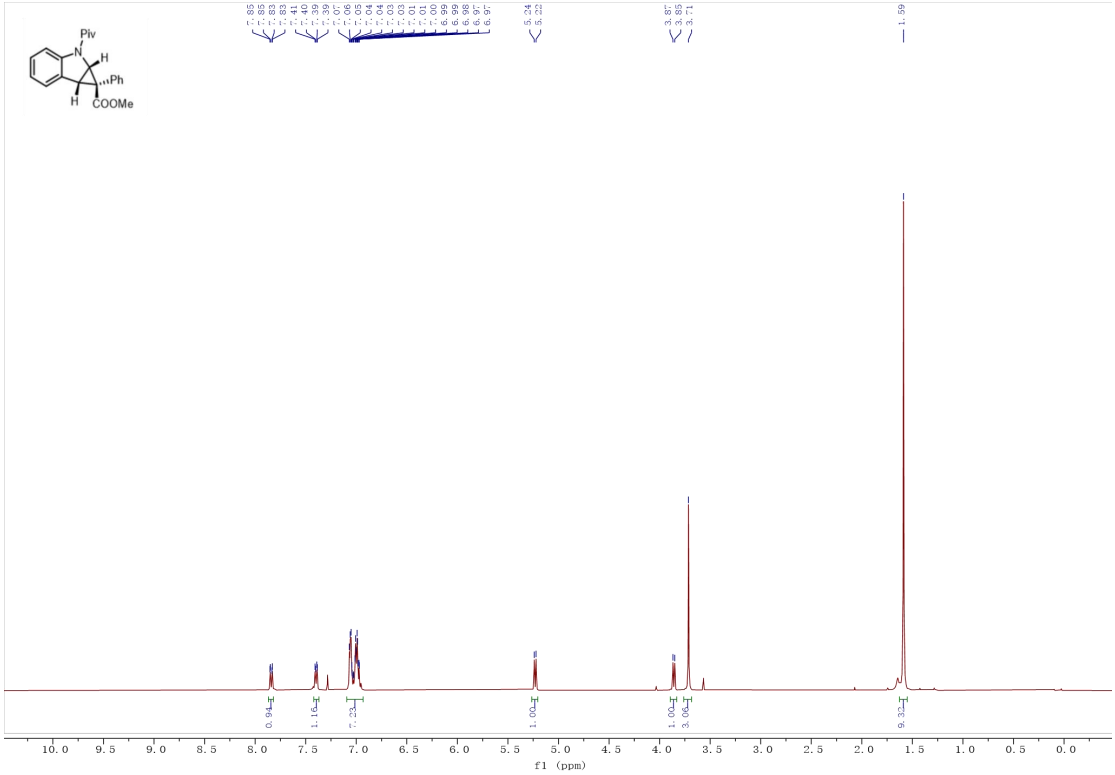
^{1}H NMR spectrum of **4d**



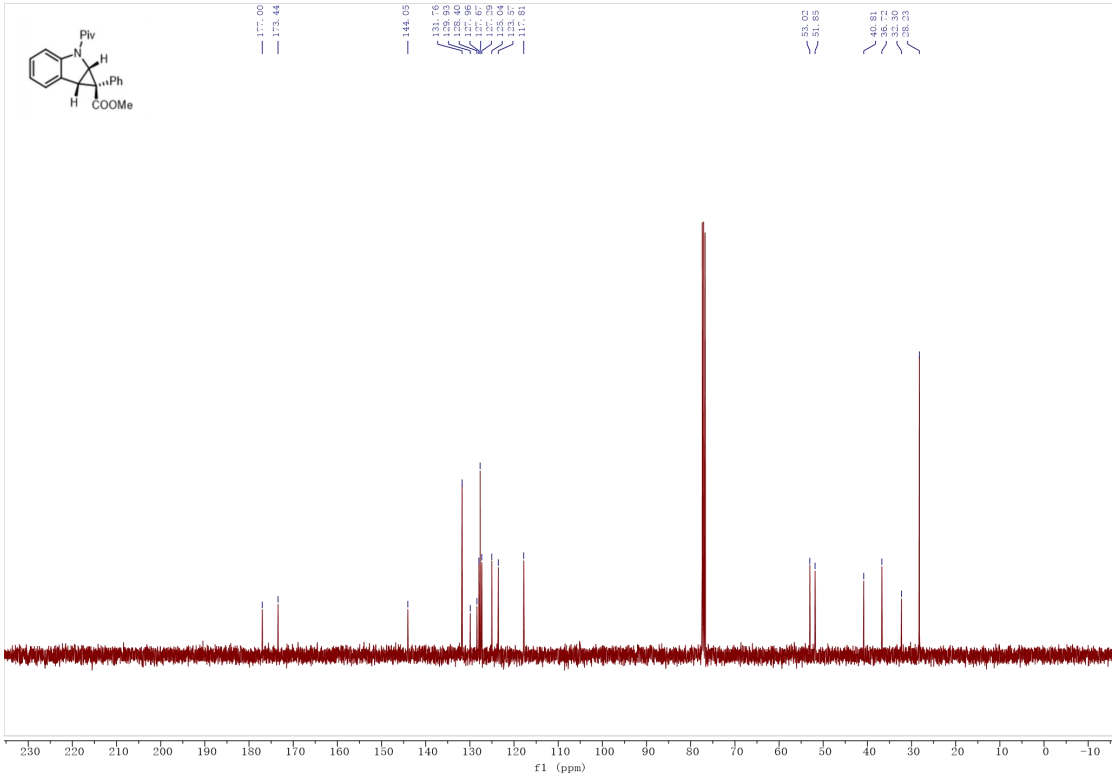
^{13}C NMR spectrum of **4d**



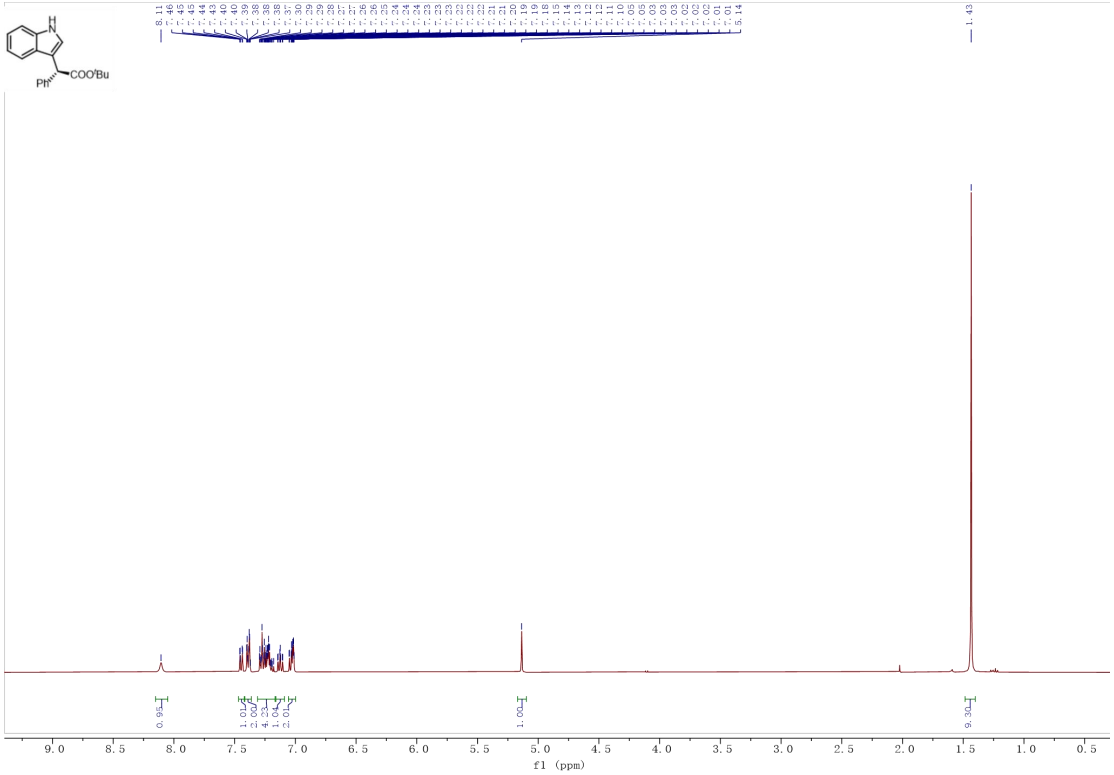
^{1}H NMR spectrum of **4e**



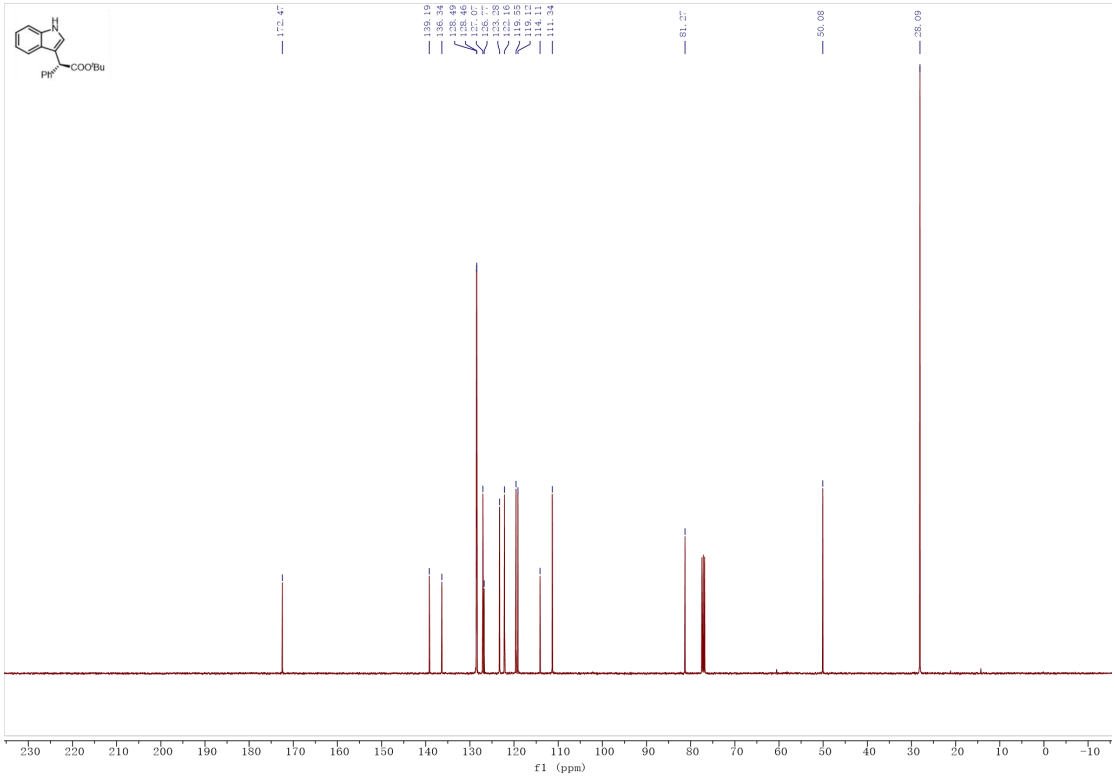
^{13}C NMR spectrum of **4e**



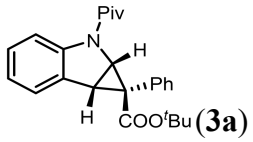
^{1}H NMR spectrum of **4f**



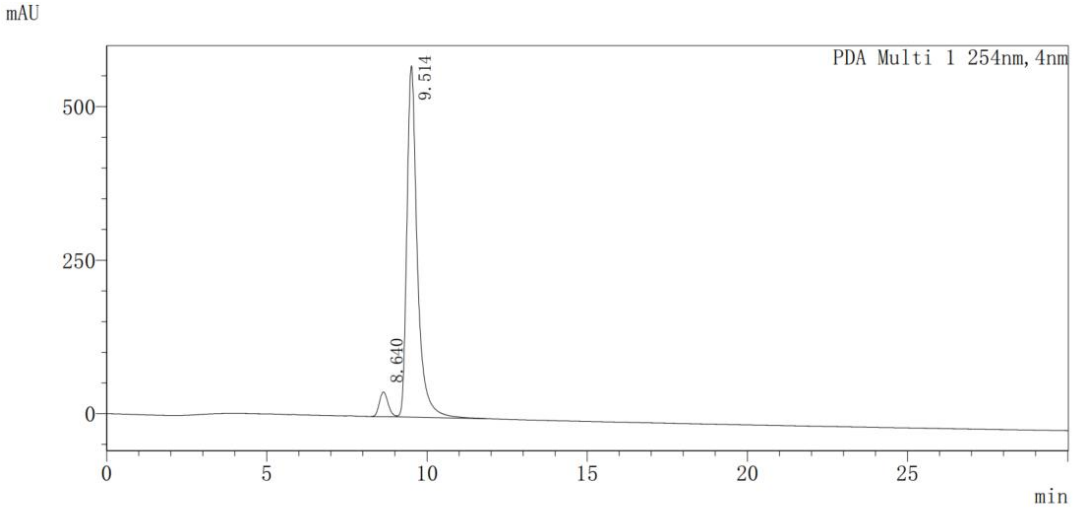
^{13}C NMR spectrum of **4f**



8. HPLC Traces

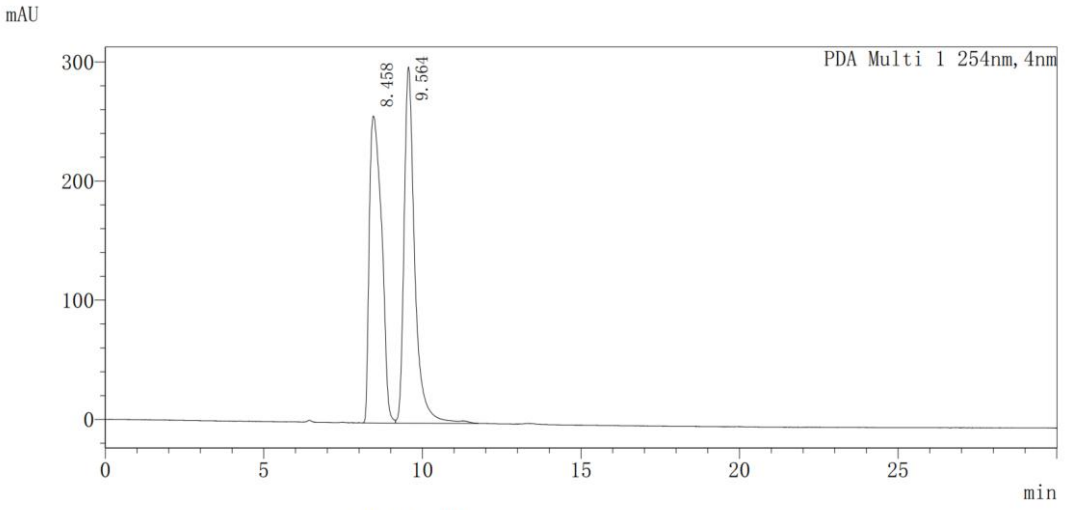


(3a)



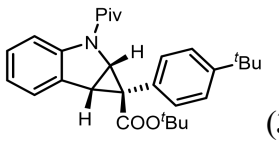
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.640	5.596
2	9.514	94.404

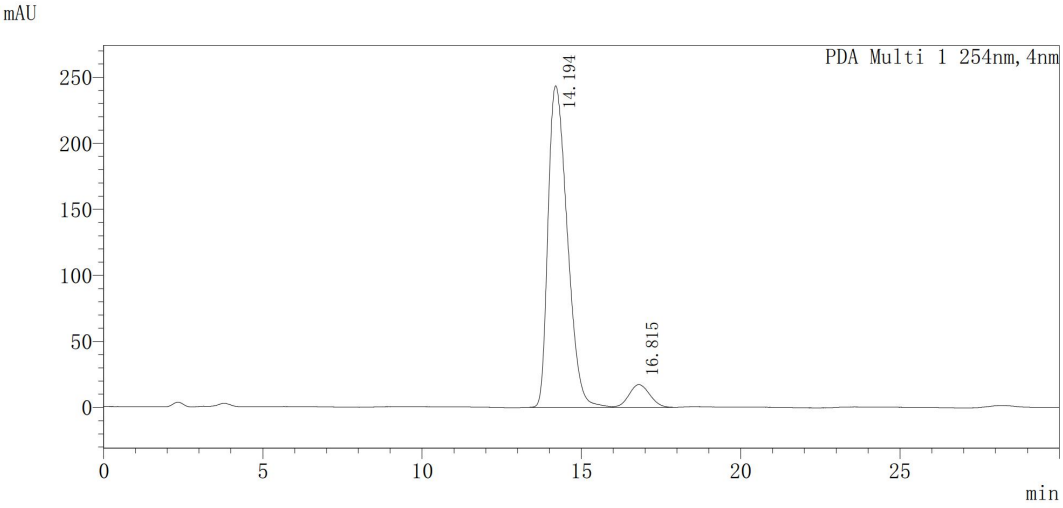


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.458	49.886
2	9.564	50.114

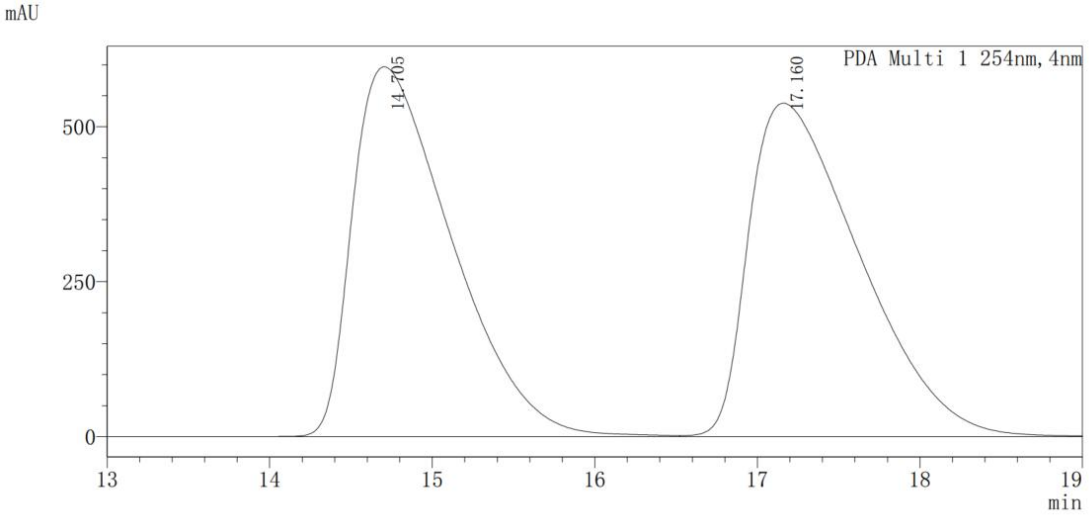


(3b)



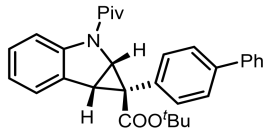
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.194	92.991
2	16.815	7.009

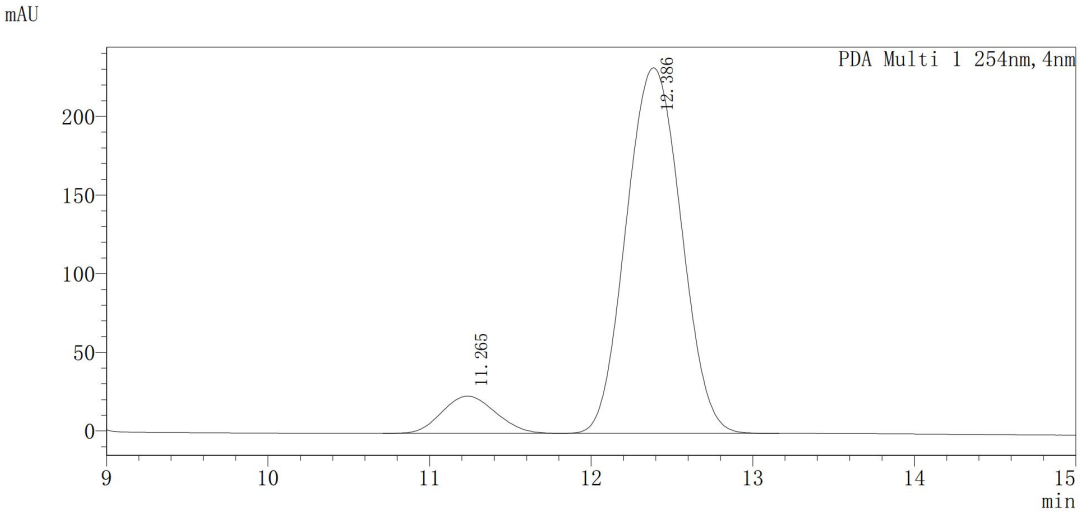


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.705	49.739
2	17.160	50.261

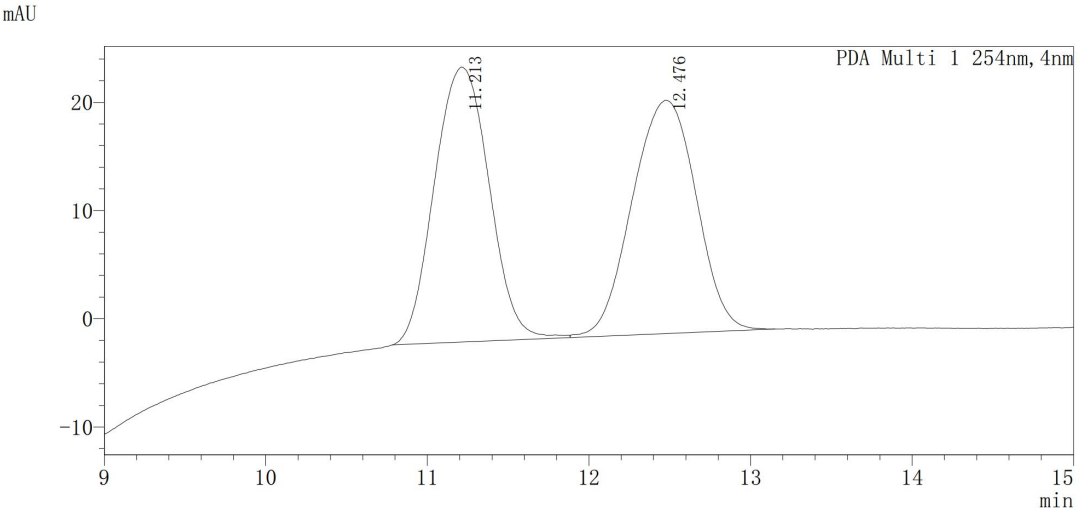


(3c)



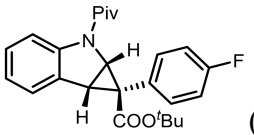
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	11.265	8.997
2	12.386	91.003

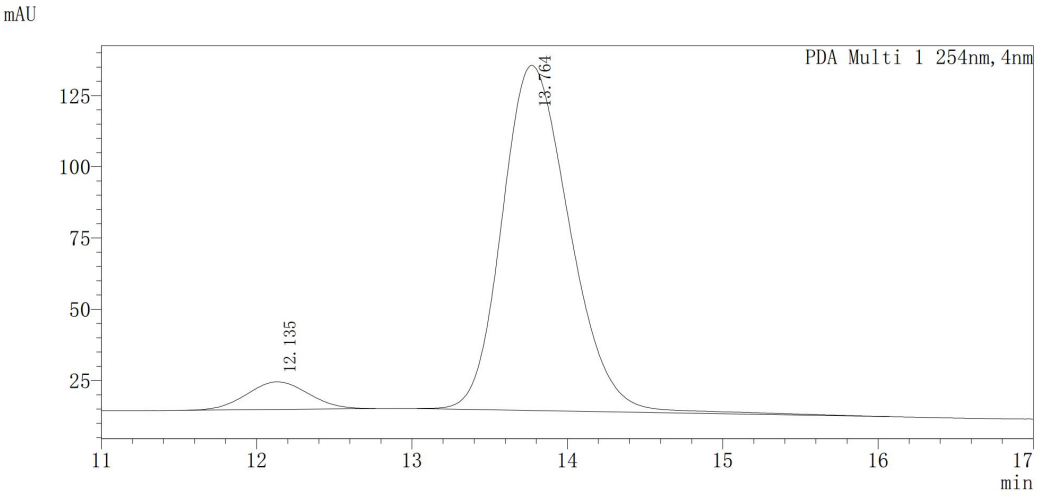


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	11.213	50.214
2	12.476	49.786

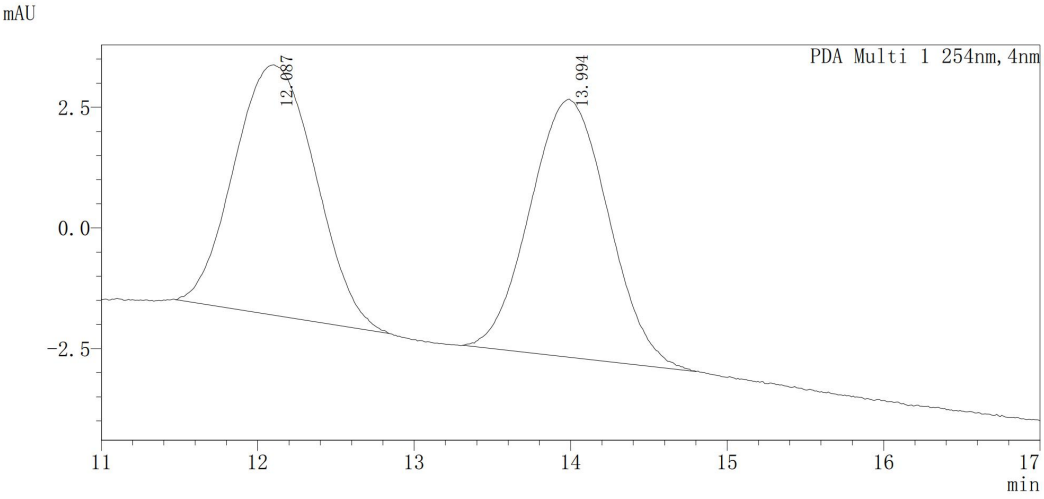


(3d)



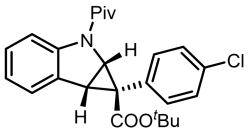
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	12.135	6.526
2	13.764	93.474

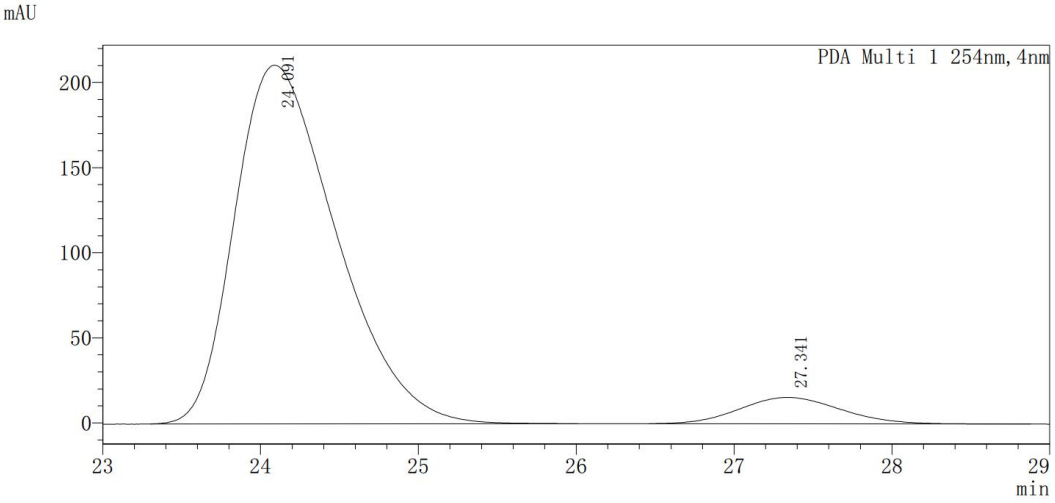


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	12.087	50.045
2	13.994	49.955

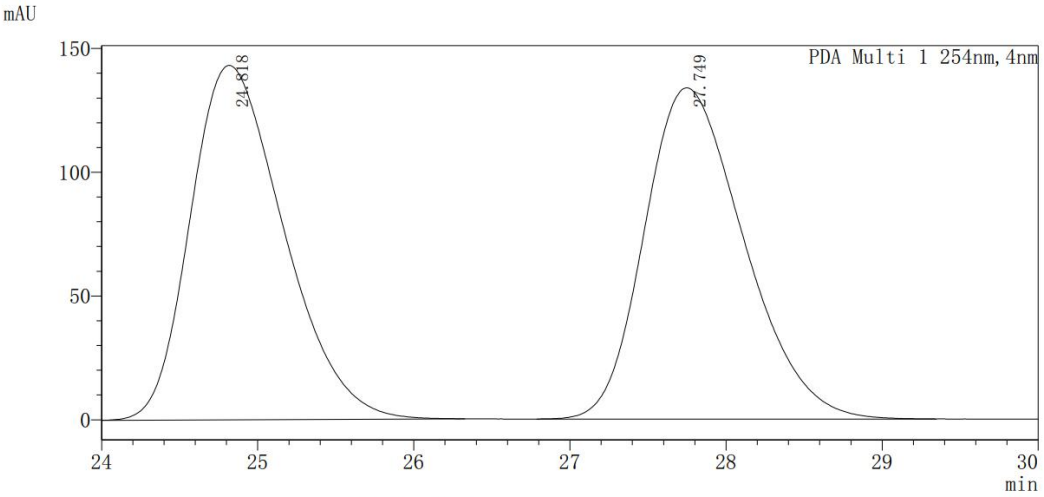


(3e)



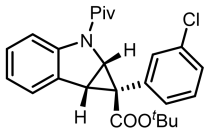
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	24.091	93.172
2	27.341	6.828

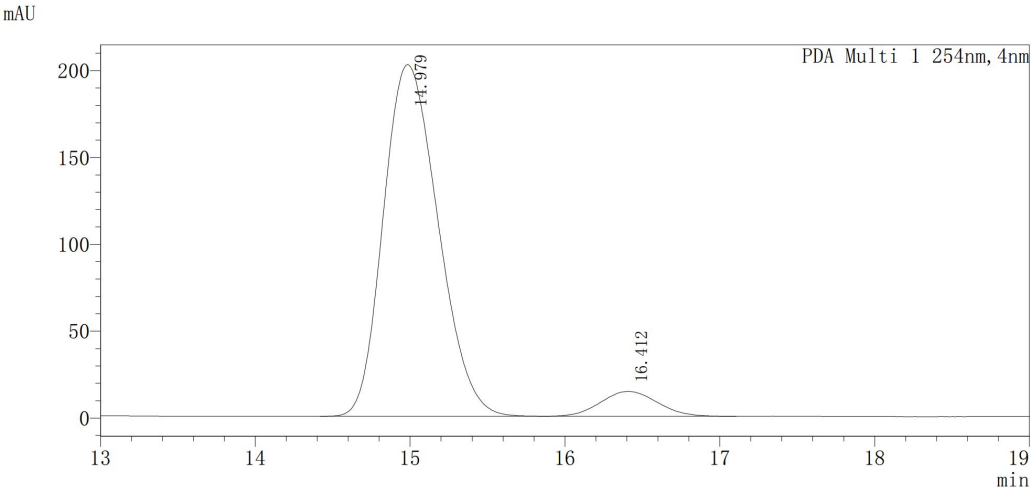


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	24.818	50.074
2	27.749	49.926

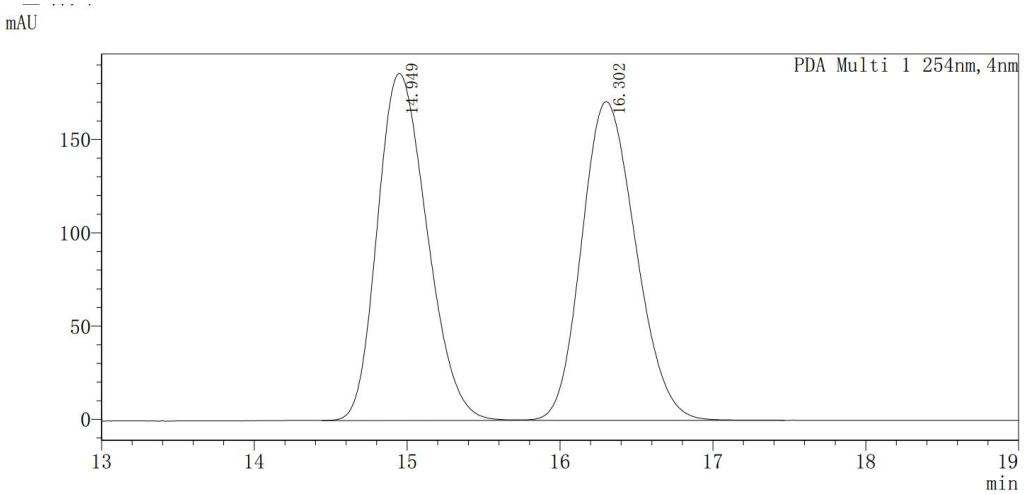


(3f)



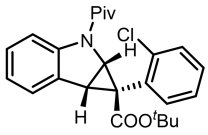
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.979	93.370
2	16.412	6.630

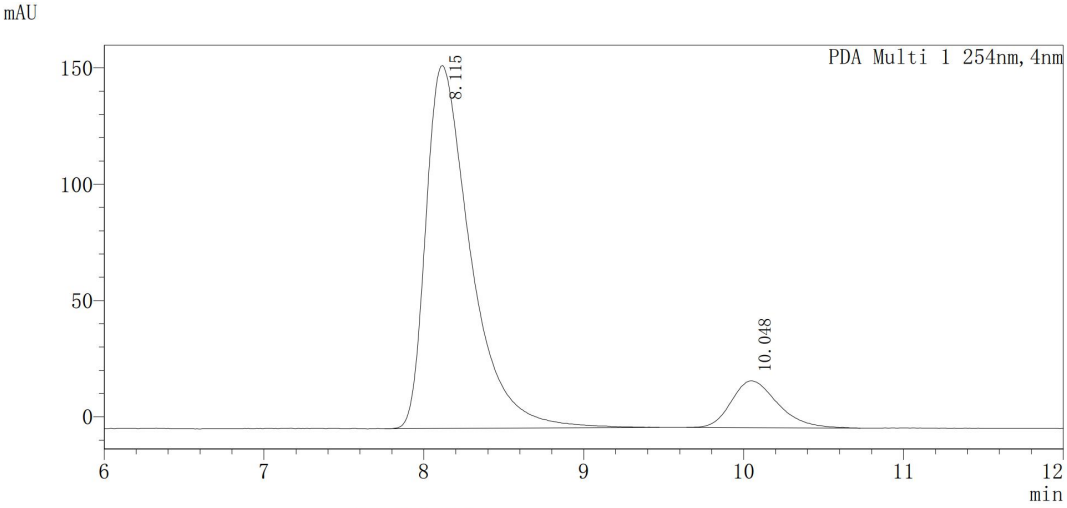


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.949	49.988
2	16.302	50.012

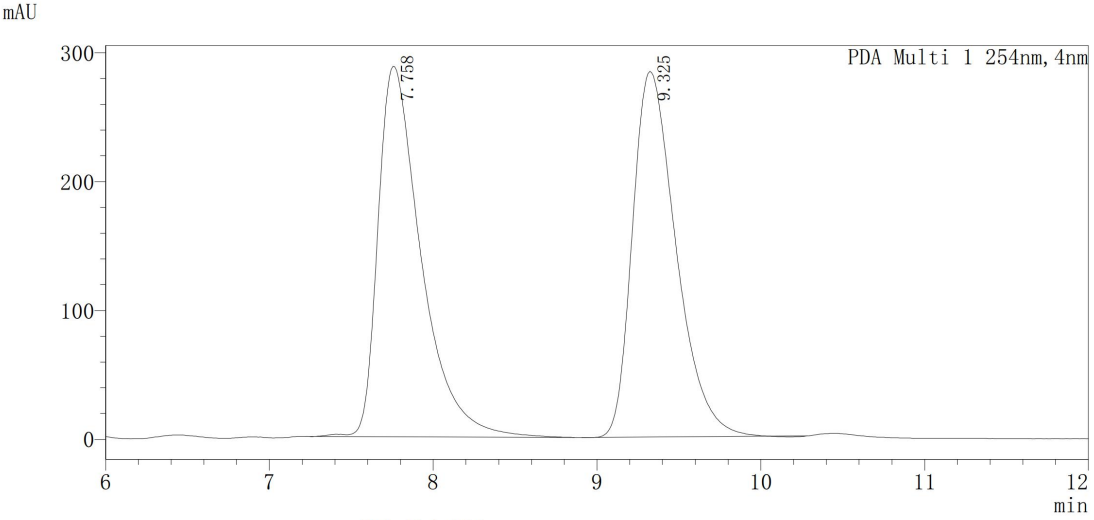


(3g)



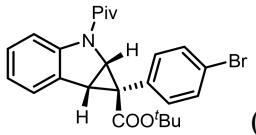
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.115	88.182
2	10.048	11.818

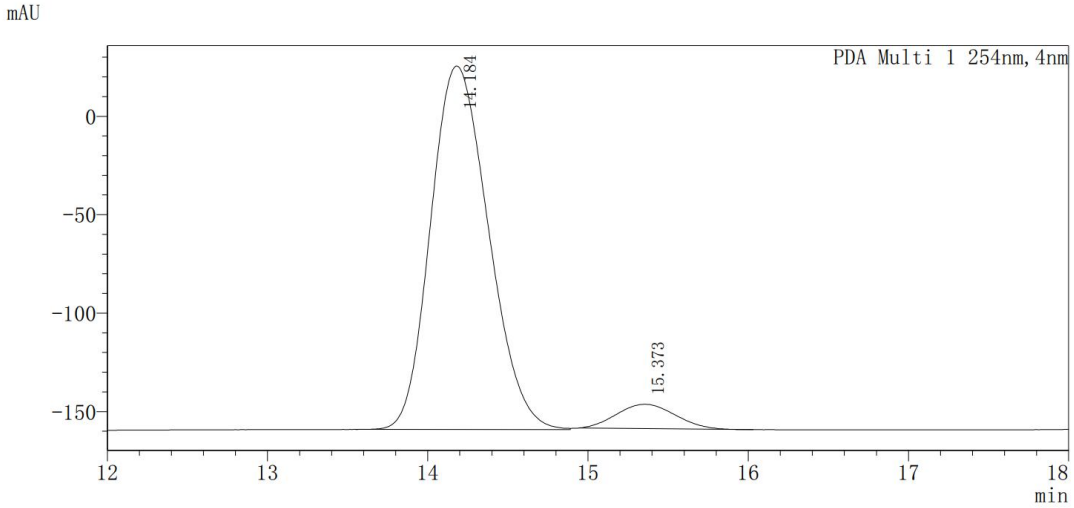


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	7.758	50.086
2	9.325	49.914

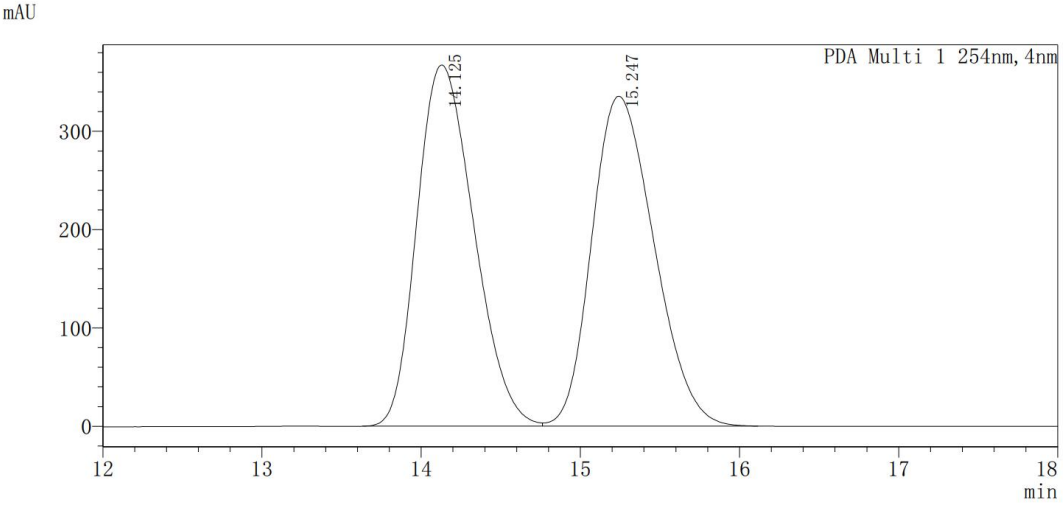


(3h)



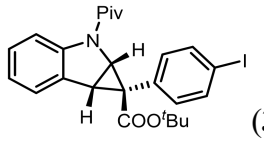
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.184	93.644
2	15.373	6.356

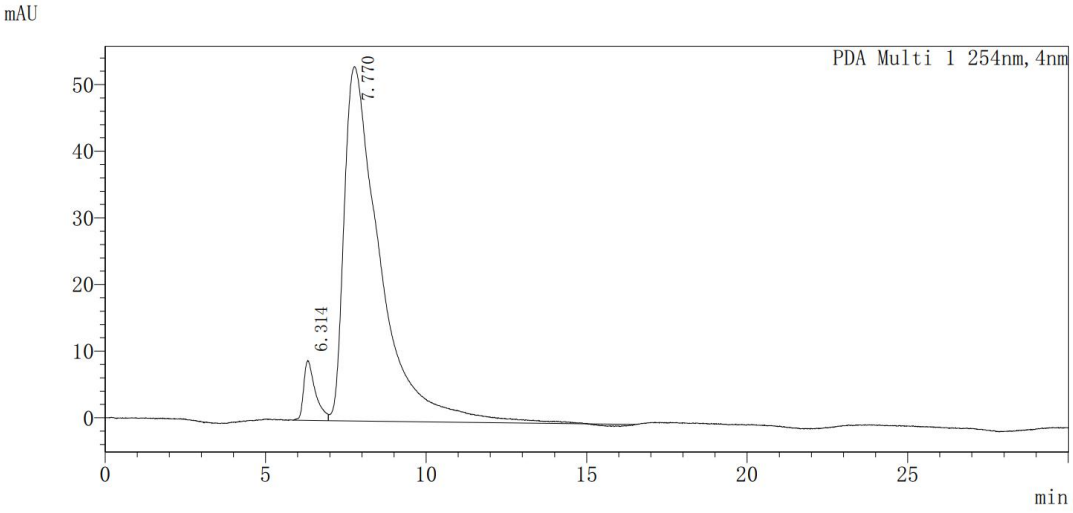


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.125	49.996
2	15.247	50.004

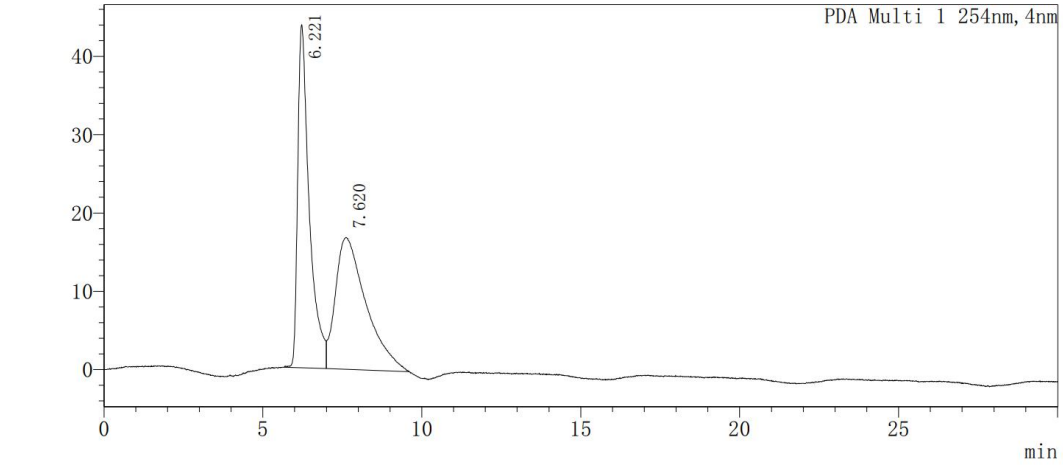


(3i)



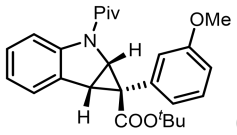
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.314	5.215
2	7.770	94.785

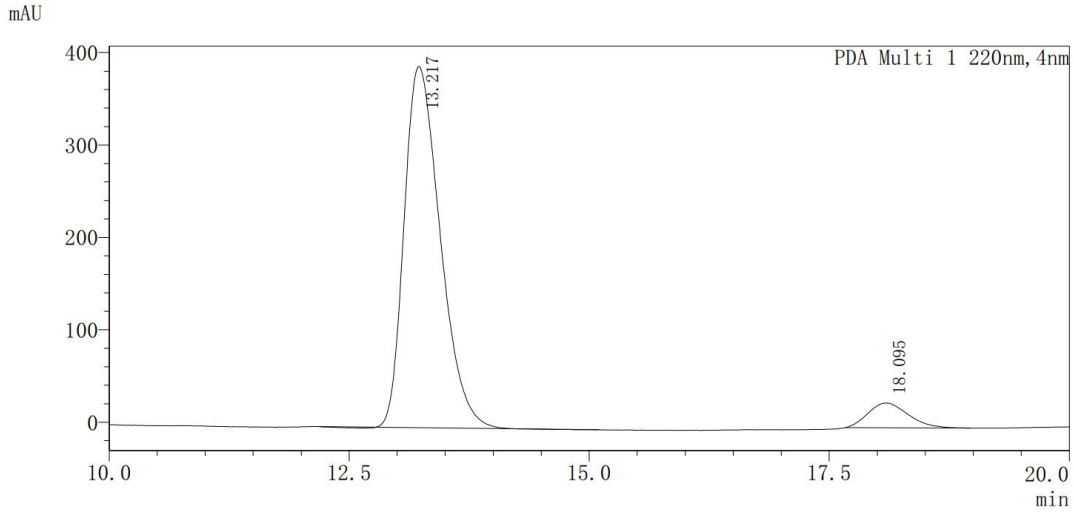


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.221	49.632
2	7.620	50.368

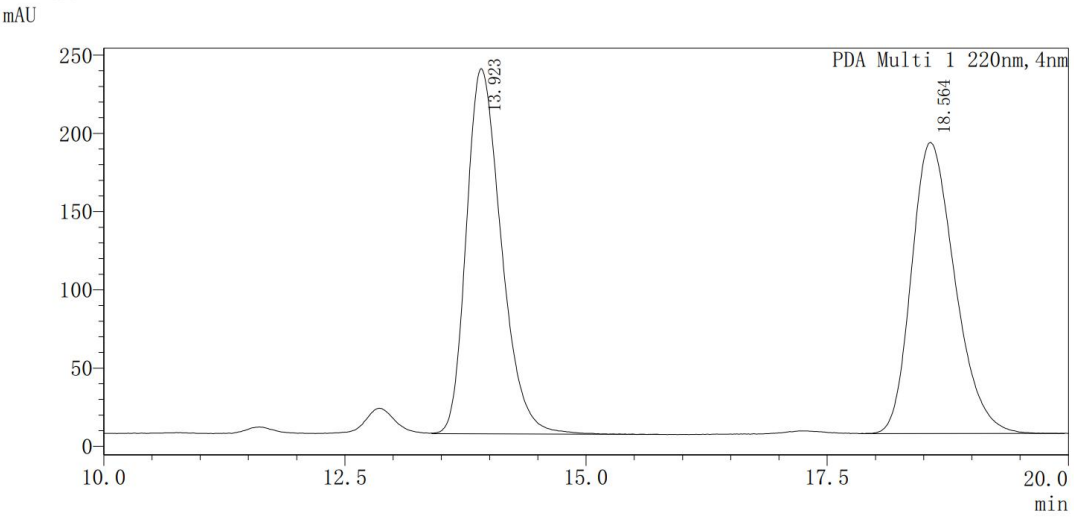


(3j)



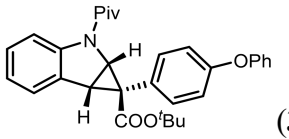
PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	13.217	93.257
2	18.095	6.743

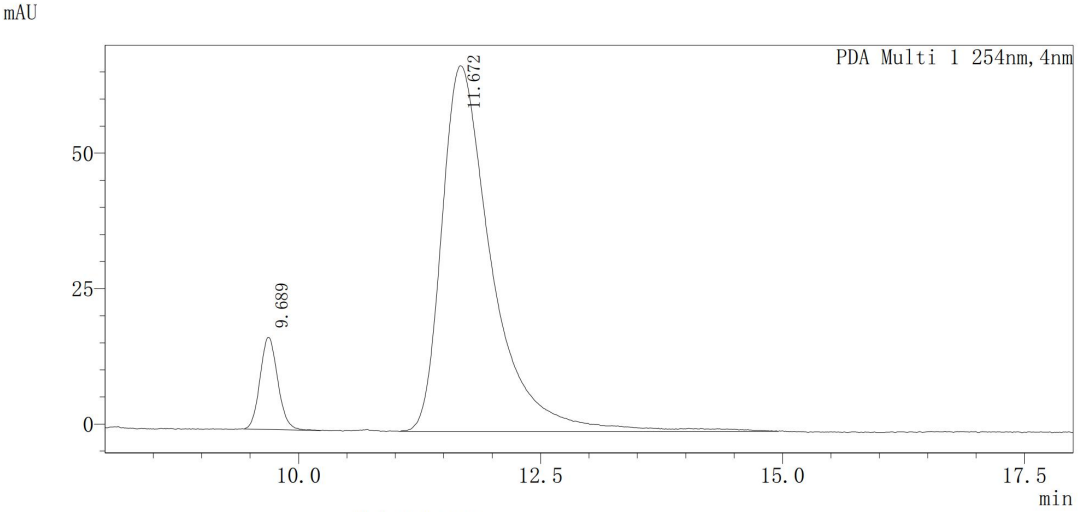


PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	13.923	50.063
2	18.564	49.937

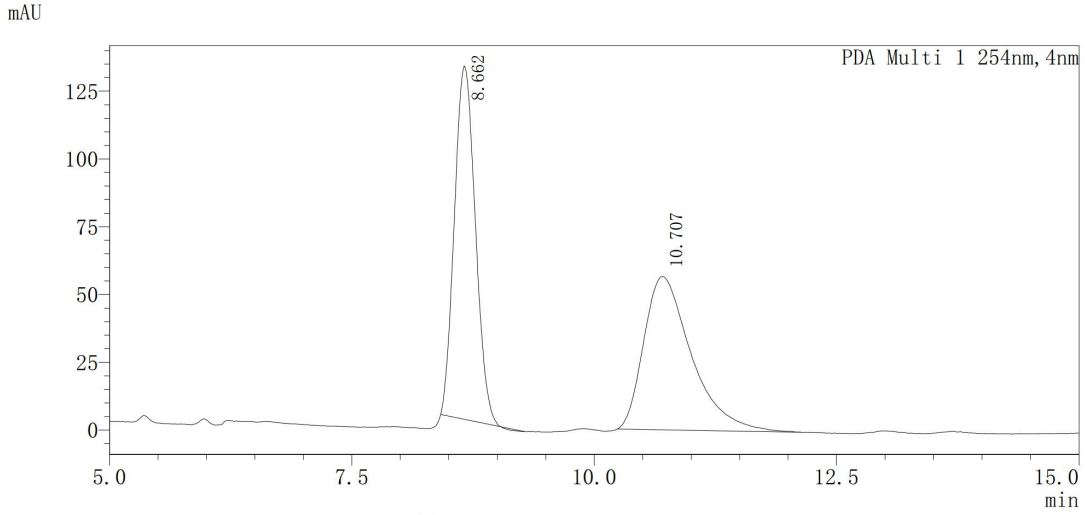


(3k)



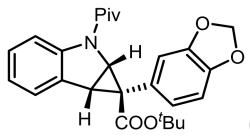
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	9.689	8.194
2	11.672	91.806

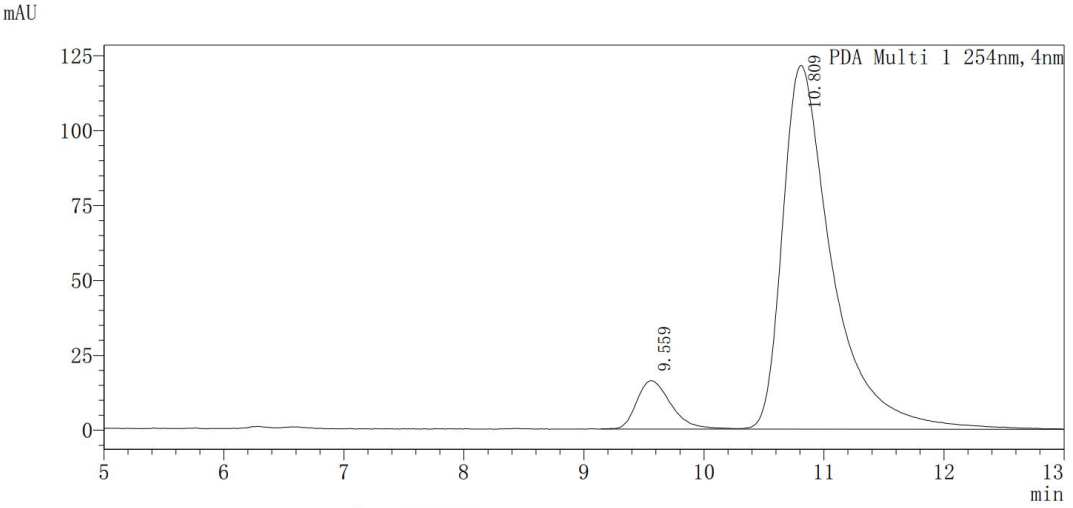


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.662	50.287
2	10.707	49.713

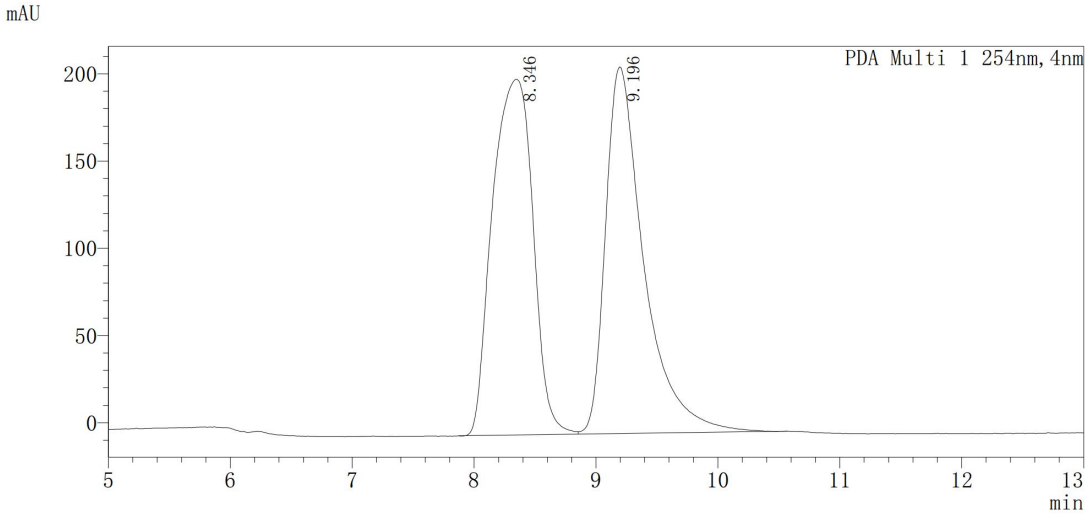


(3l)



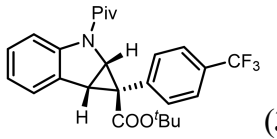
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	9.559	8.422
2	10.809	91.578

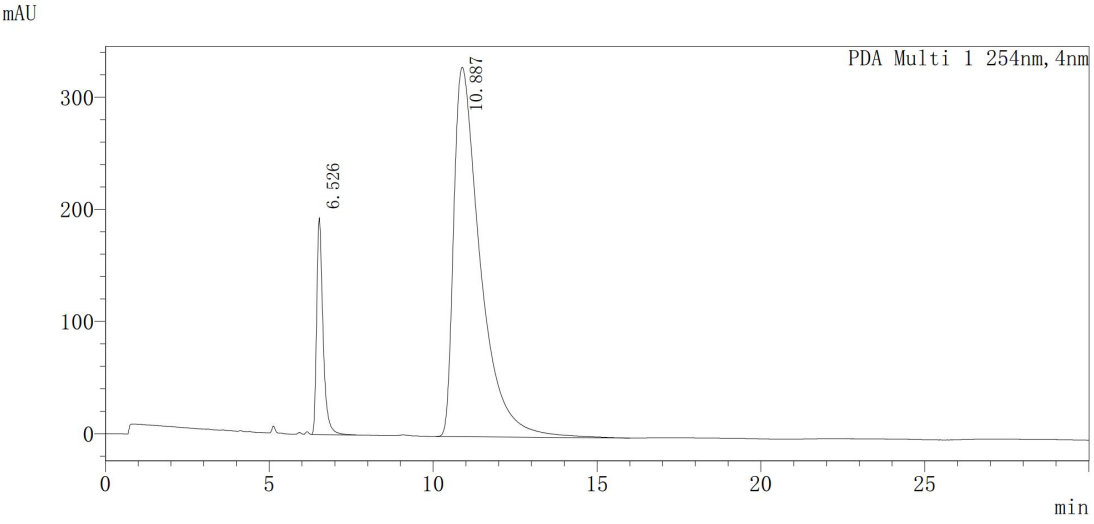


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.346	50.714
2	9.196	49.286

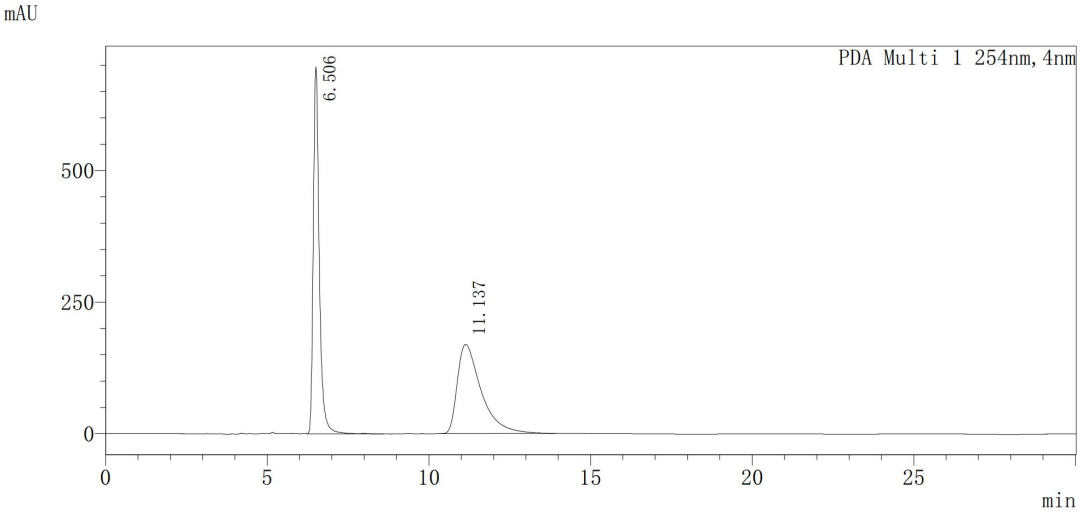


(3m)



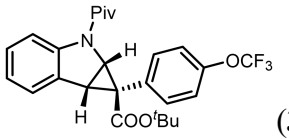
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.526	12.318
2	10.887	87.682

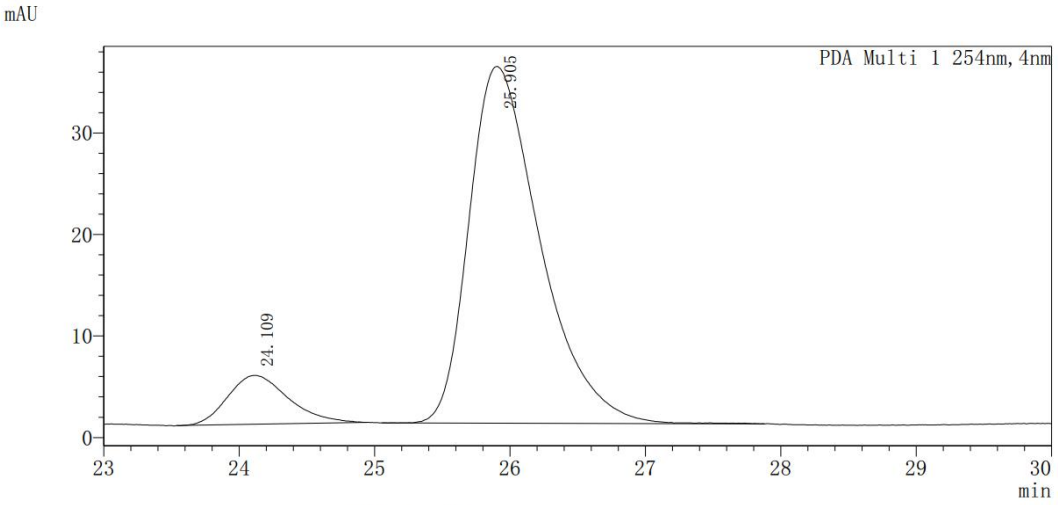


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.506	50.814
2	11.137	49.186

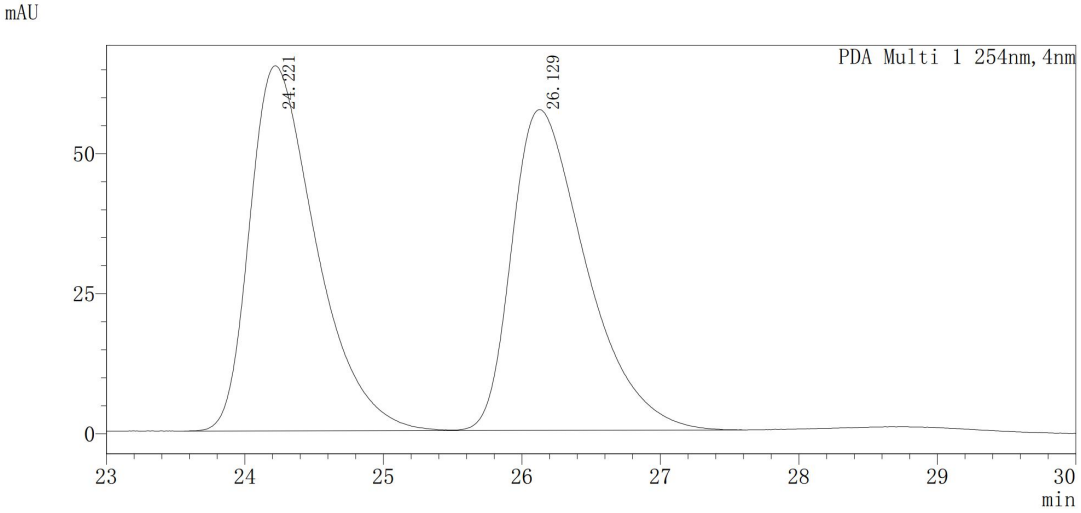


(**3n**)



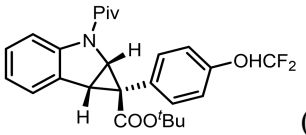
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	24.109	10.491
2	25.905	89.509

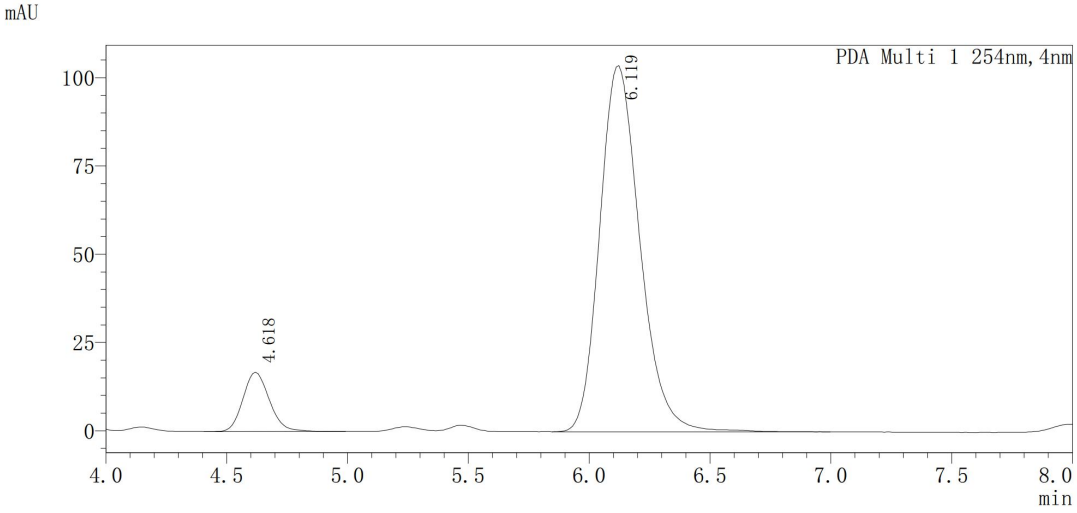


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	24.221	50.418
2	26.129	49.582

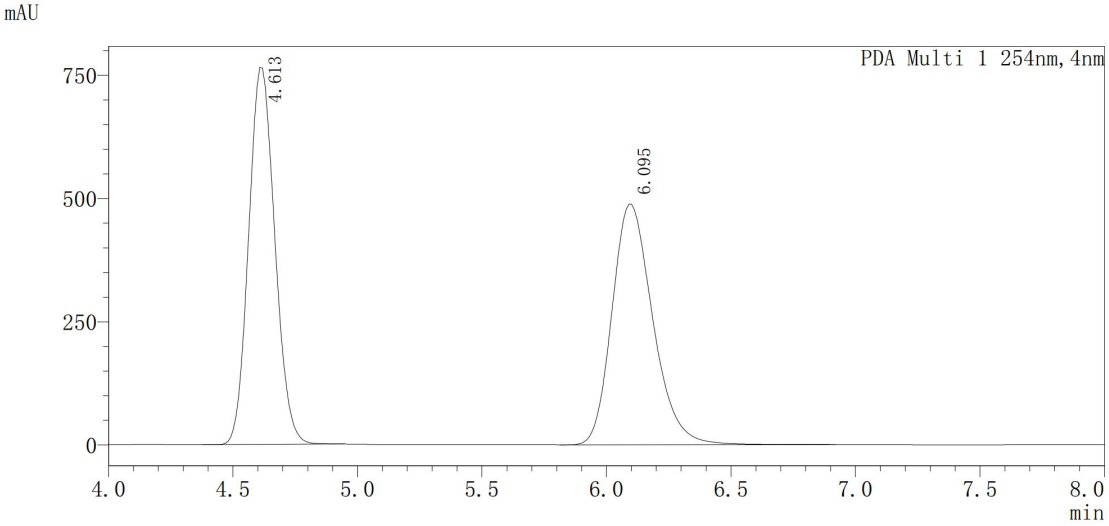


(3o)



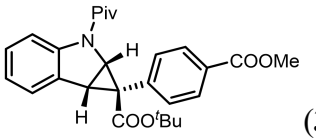
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	4.618	9.585
2	6.119	90.415

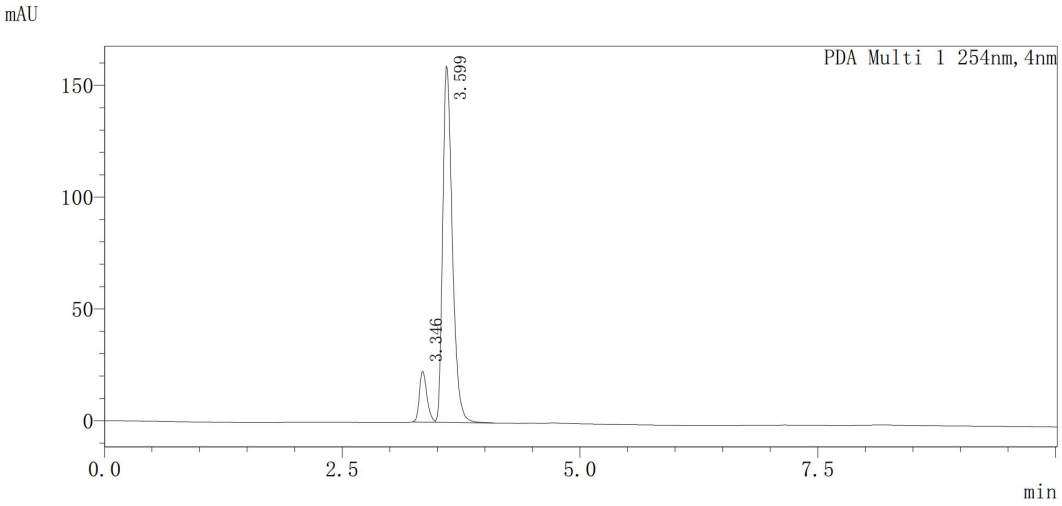


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	4.613	50.150
2	6.095	49.850

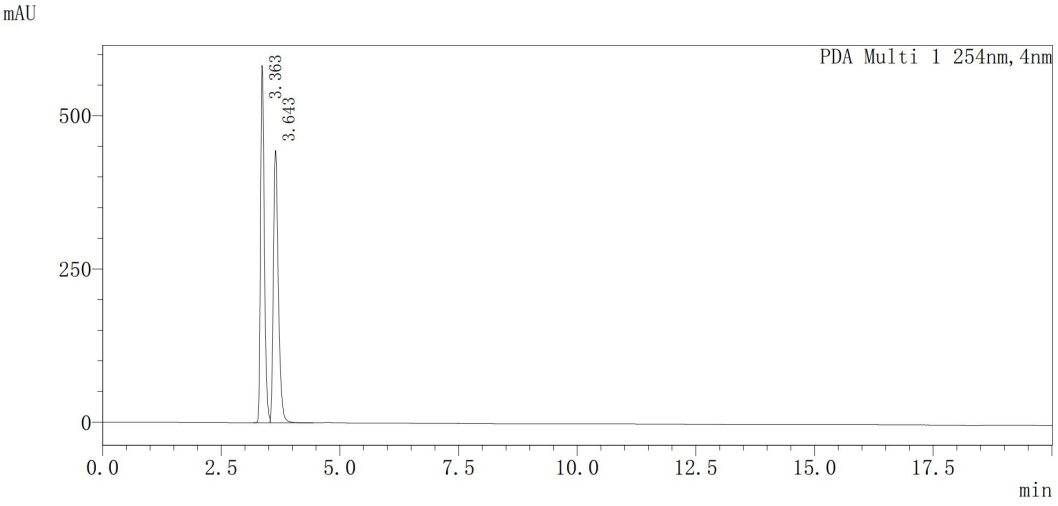


(3p)



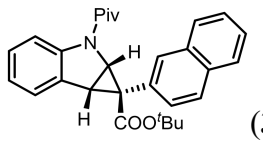
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	3.346	10.005
2	3.599	89.995

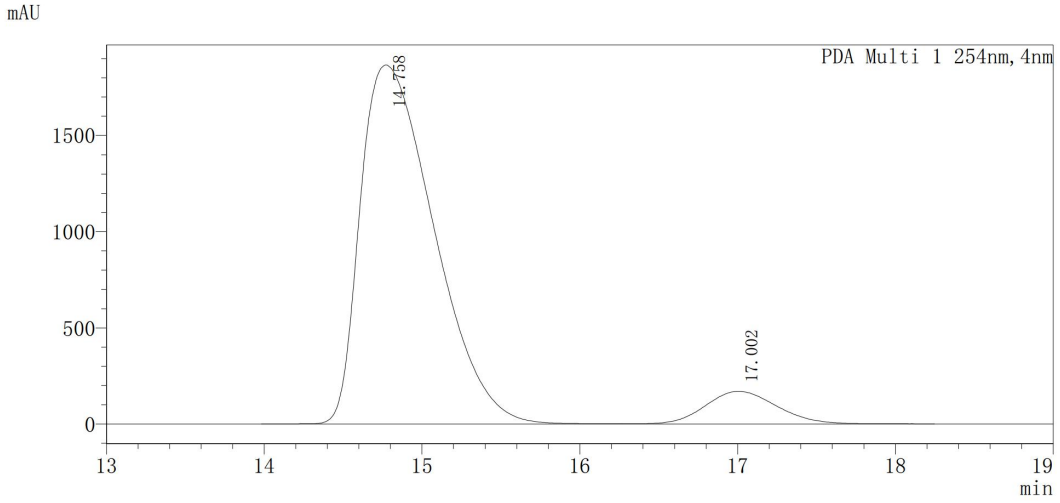


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	3.363	49.921
2	3.643	50.079

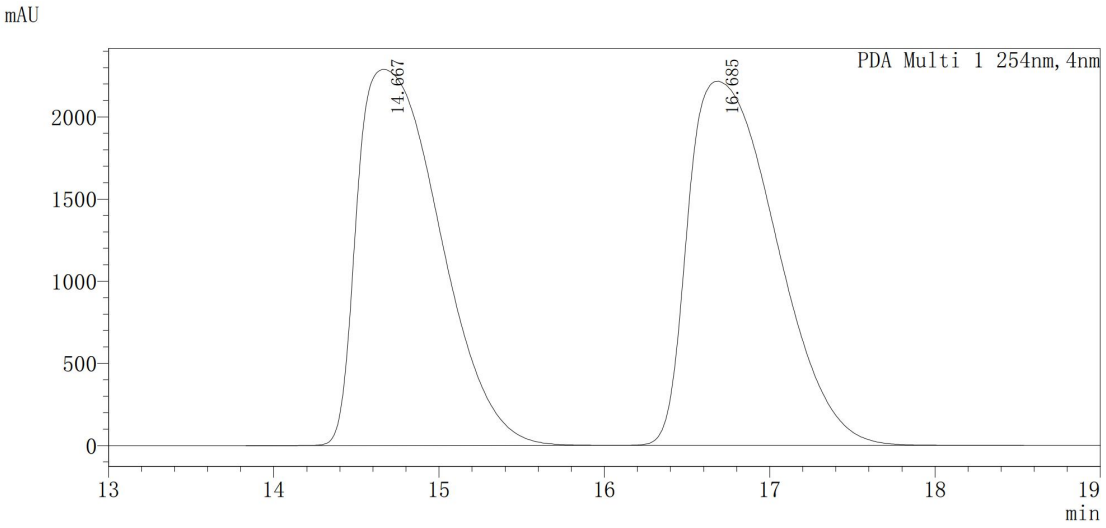


(3q)



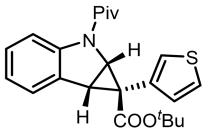
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.758	91.953
2	17.002	8.047

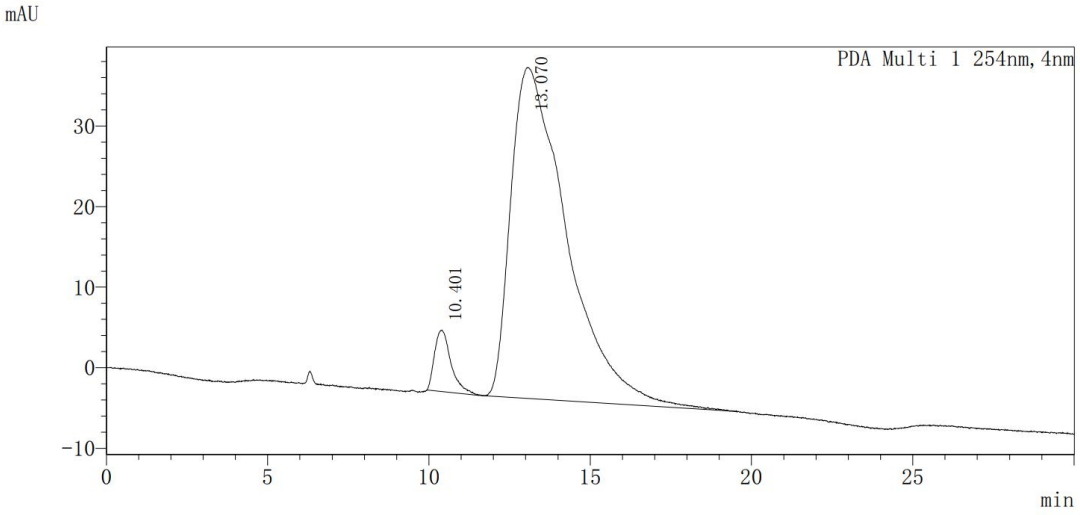


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	14.667	49.544
2	16.685	50.456

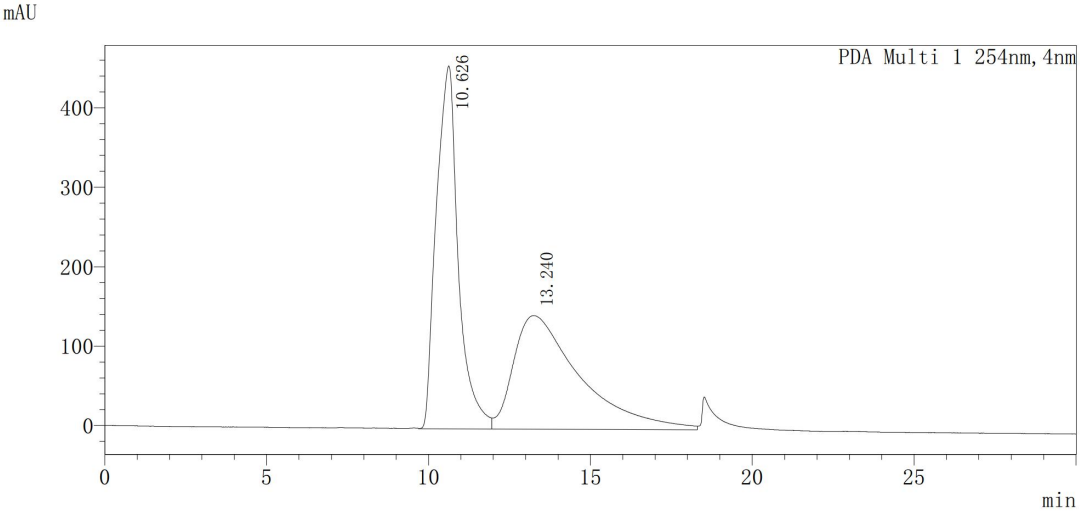


(3r)



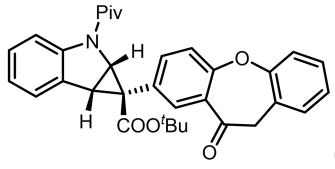
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	10.401	5.175
2	13.070	94.825

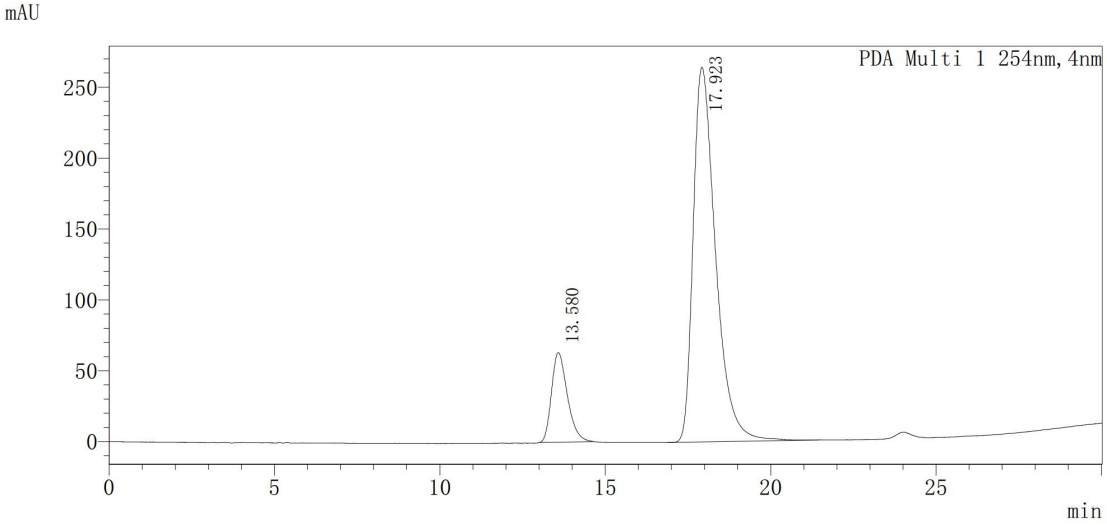


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	10.626	51.415
2	13.240	48.585

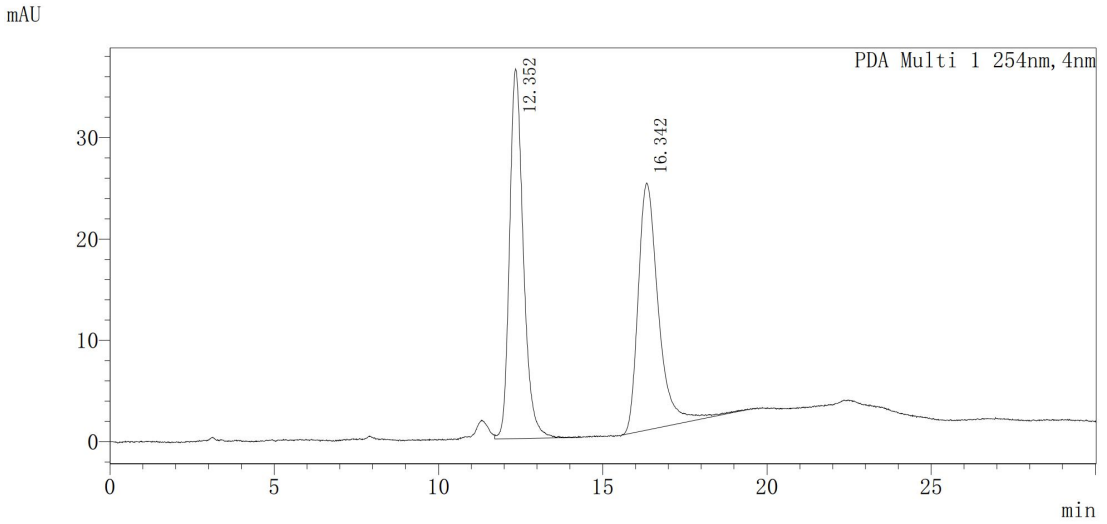


(3s)



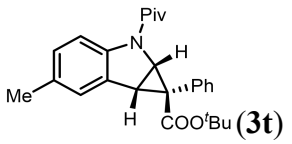
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	13.580	14.468
2	17.923	85.532

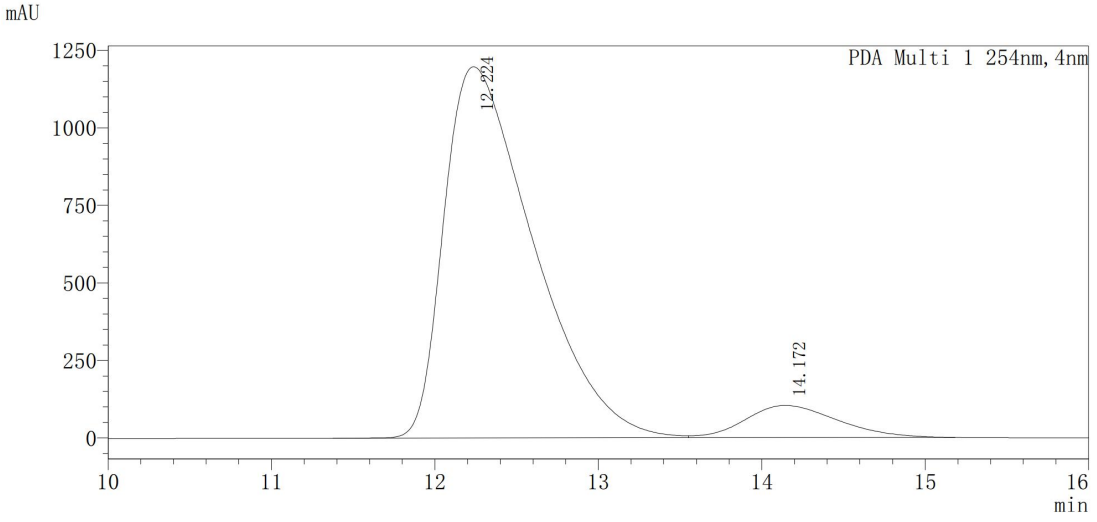


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	12.352	50.412
2	16.342	49.588

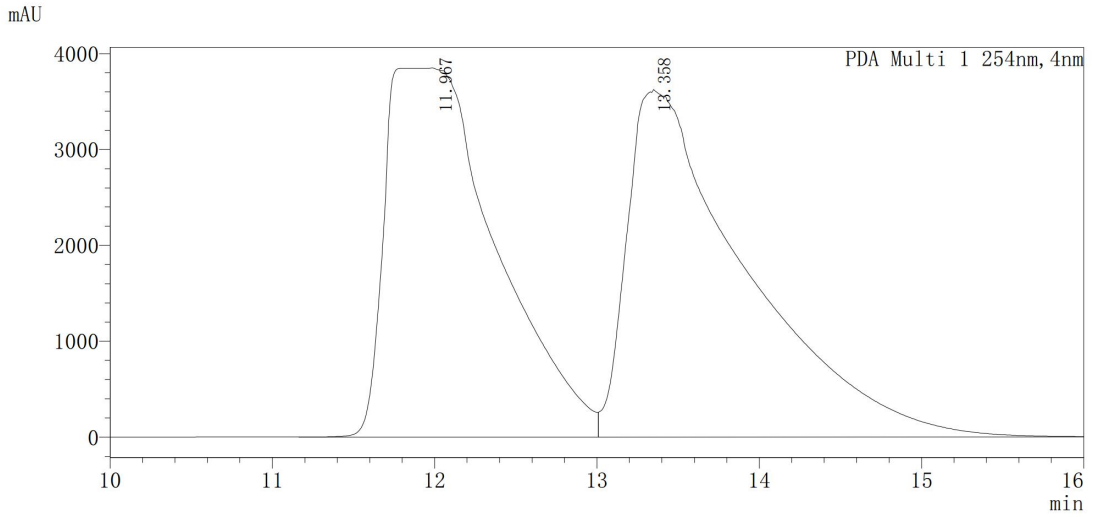


(3t)



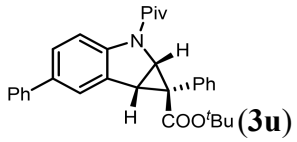
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	12.224	91.743
2	14.172	8.257

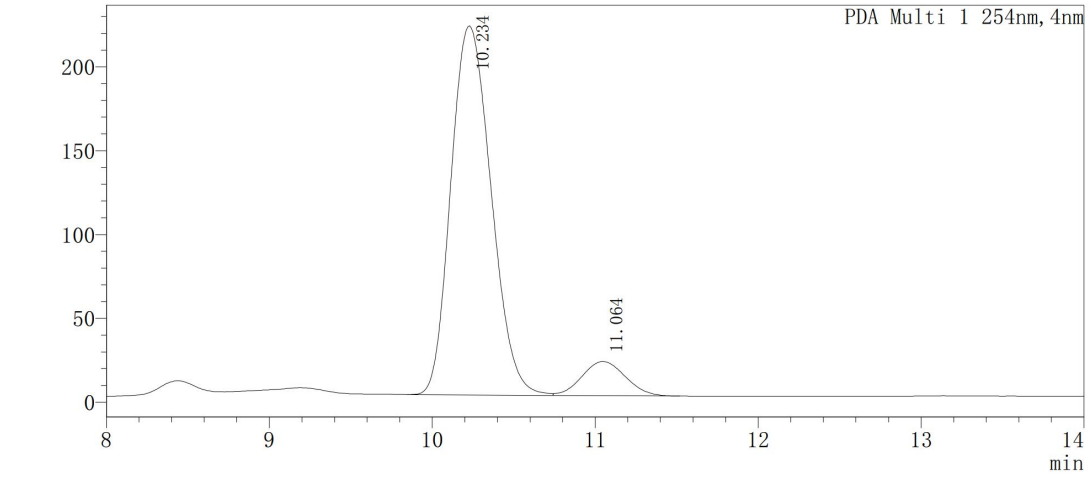


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	11.967	49.858
2	13.358	50.142

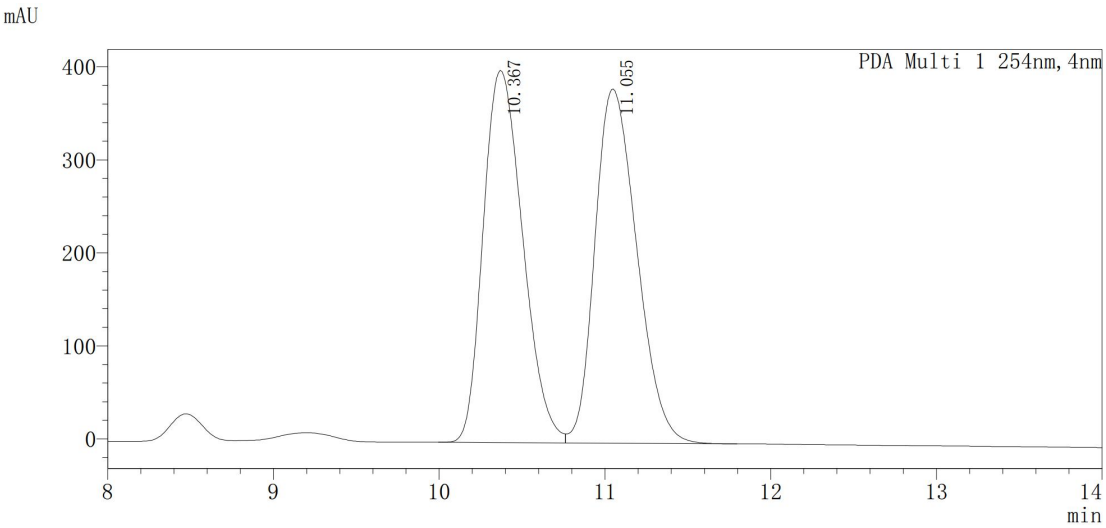


(3u)



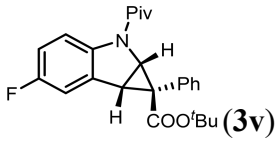
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	10.234	90.928
2	11.064	9.072

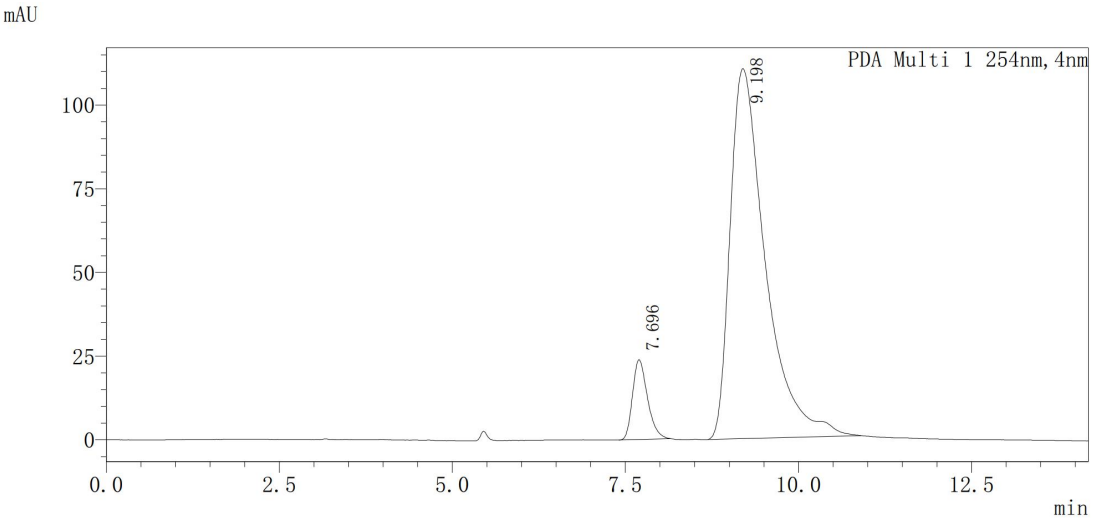


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	10.367	49.941
2	11.055	50.059

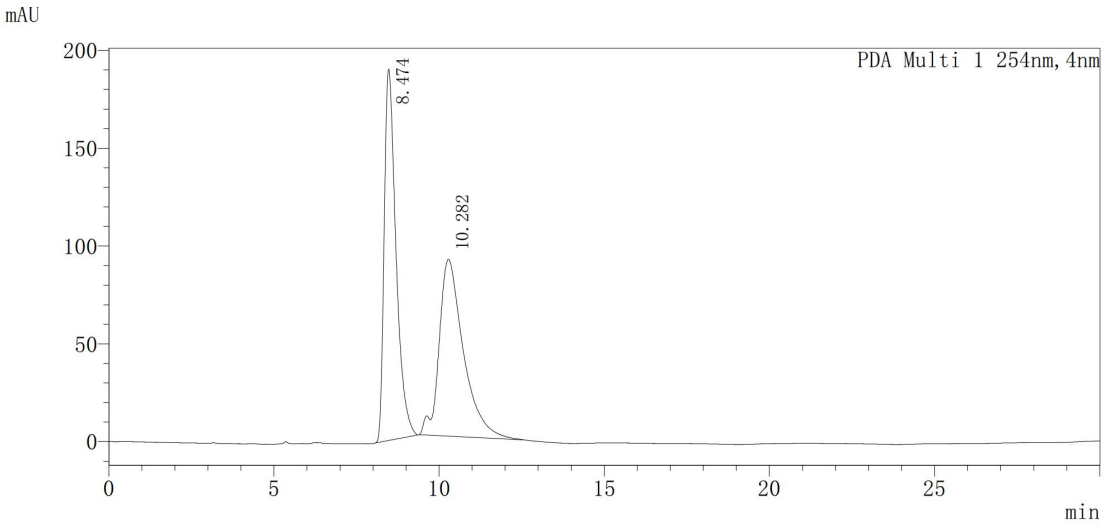


(3v)



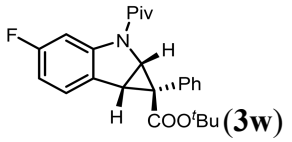
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	7.696	8.389
2	9.198	91.611

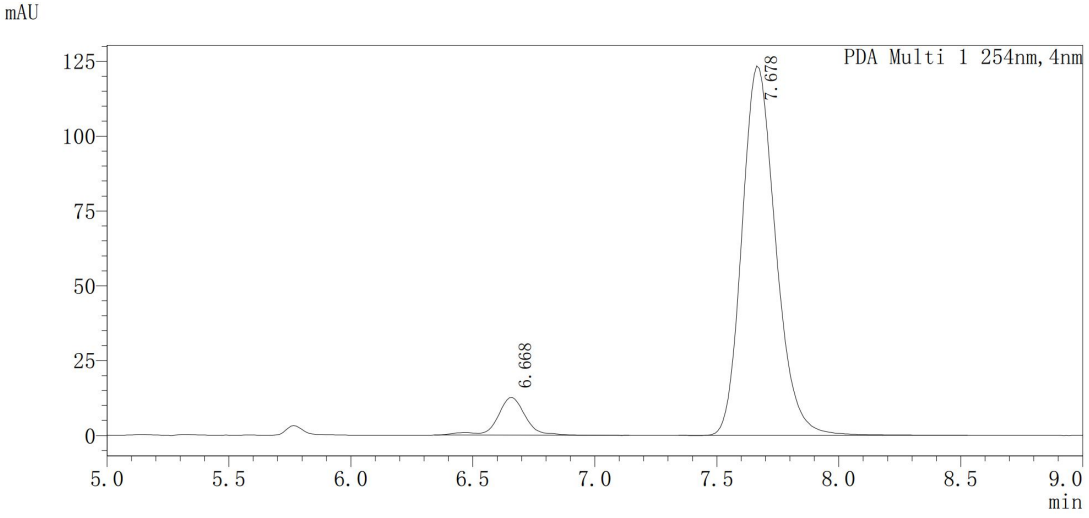


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.474	50.530
2	10.282	49.470

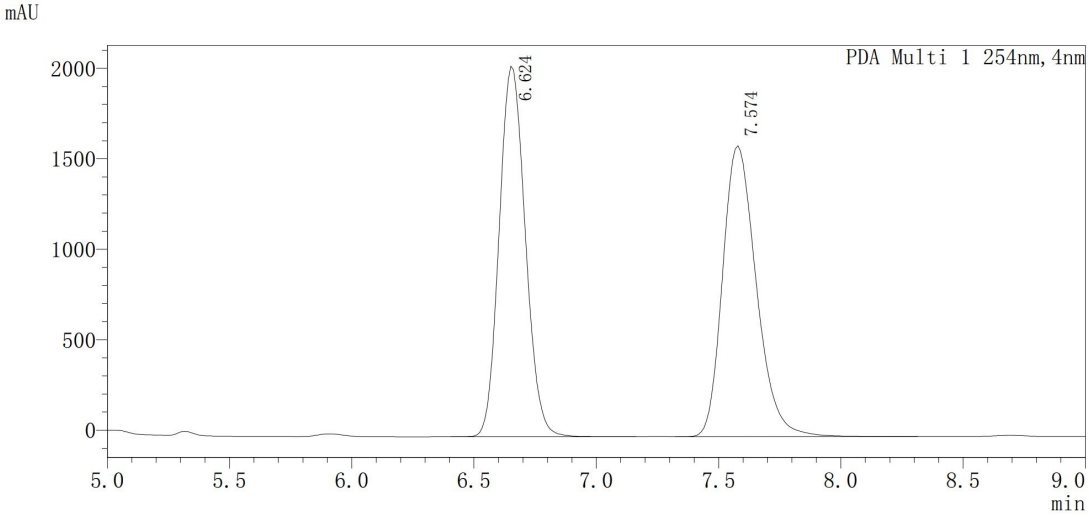


(3w)



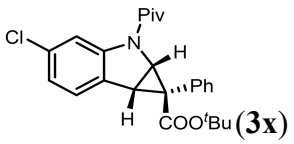
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.668	7.442
2	7.678	92.558

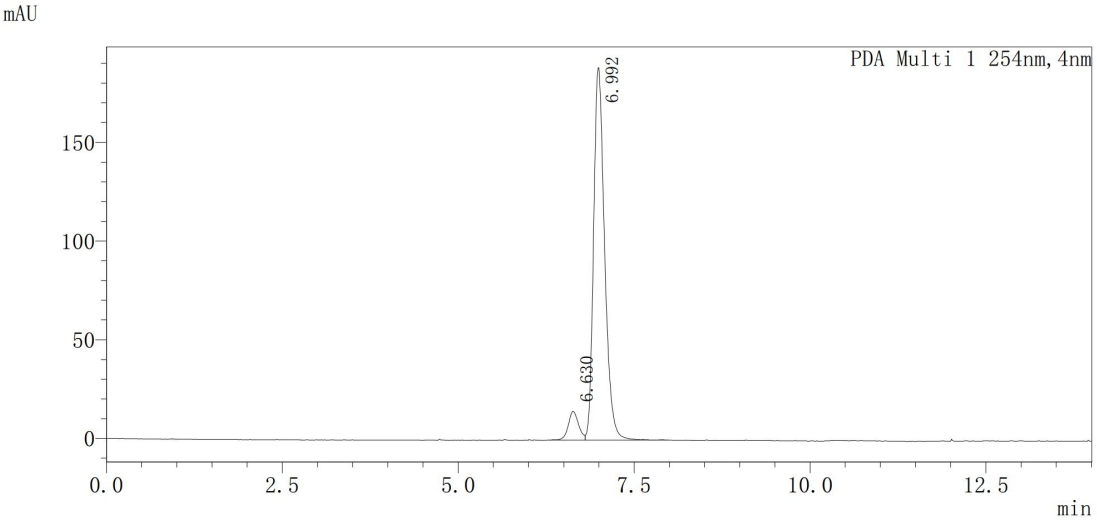


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.624	49.658
2	7.574	50.342

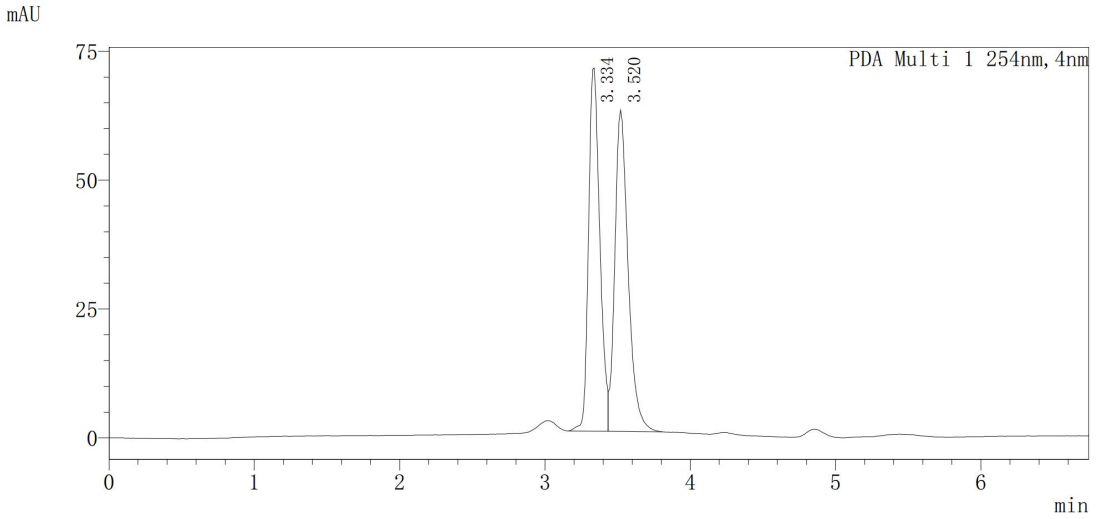


(3x)



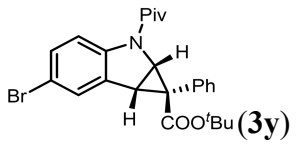
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.630	6.869
2	6.992	93.131

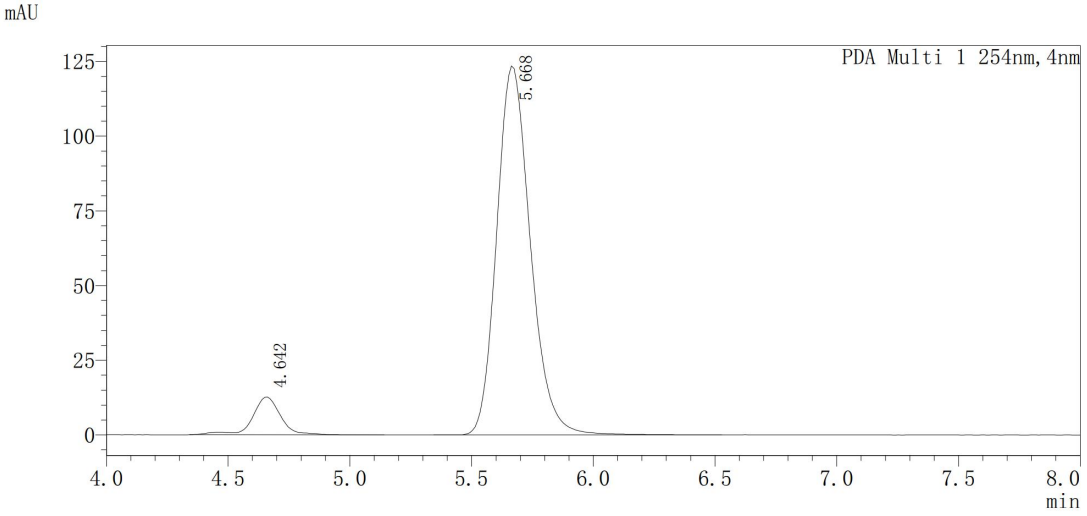


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	3.334	49.069
2	3.520	50.931

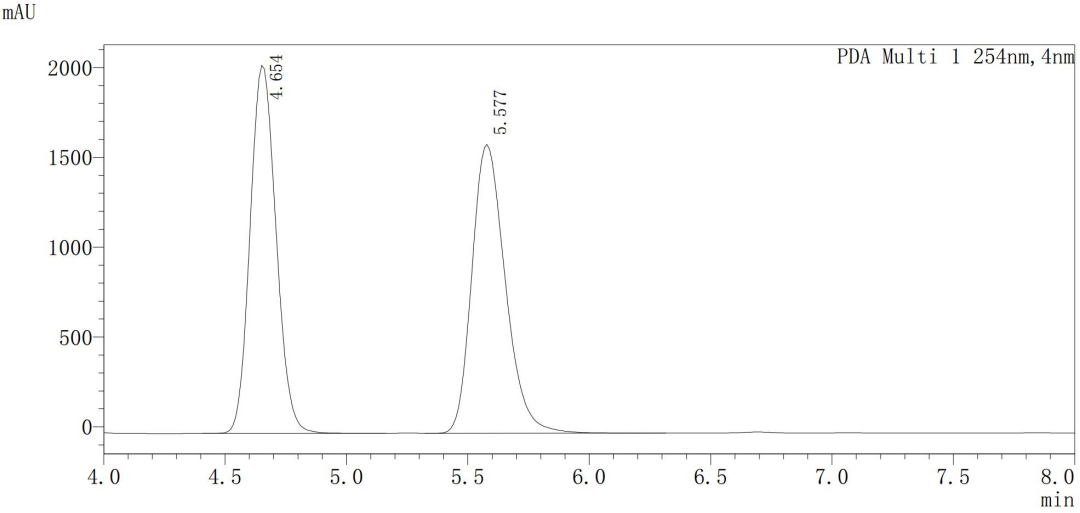


(3y)



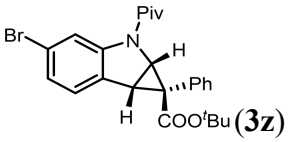
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	4.642	7.142
2	5.668	92.858

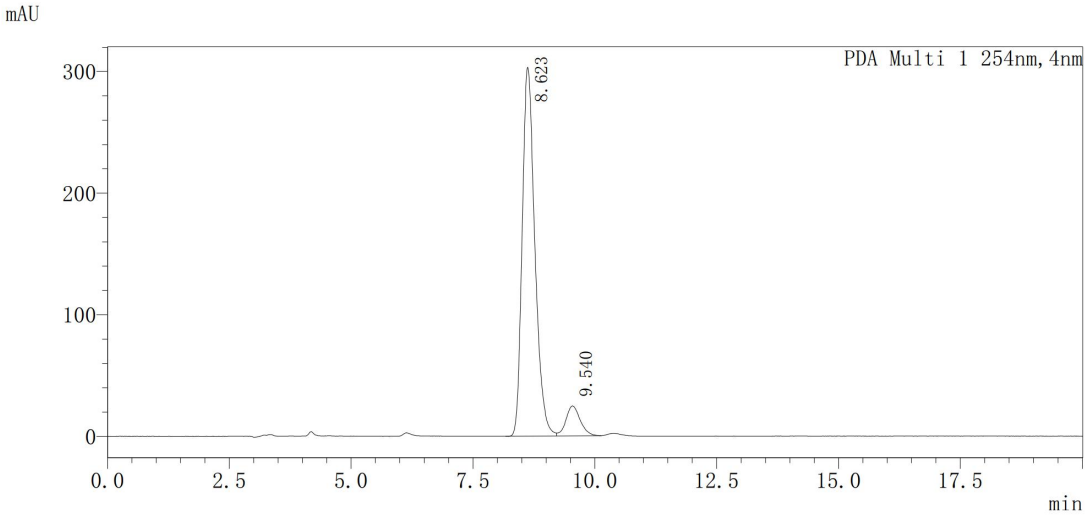


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	4.654	49.688
2	5.577	50.312

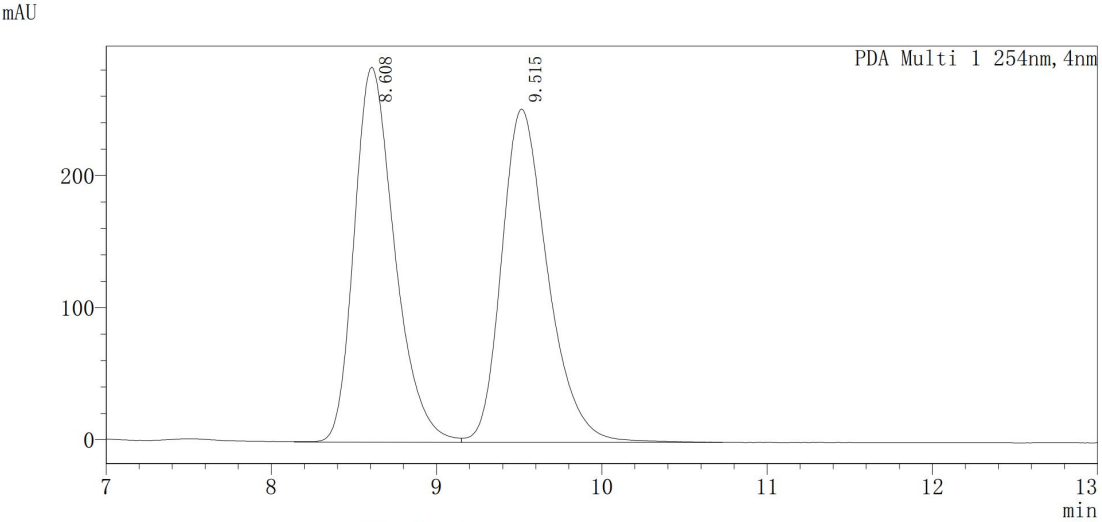


(3z)



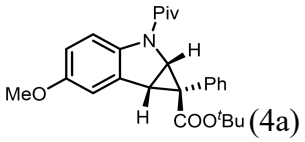
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.623	91.657
2	9.540	8.343

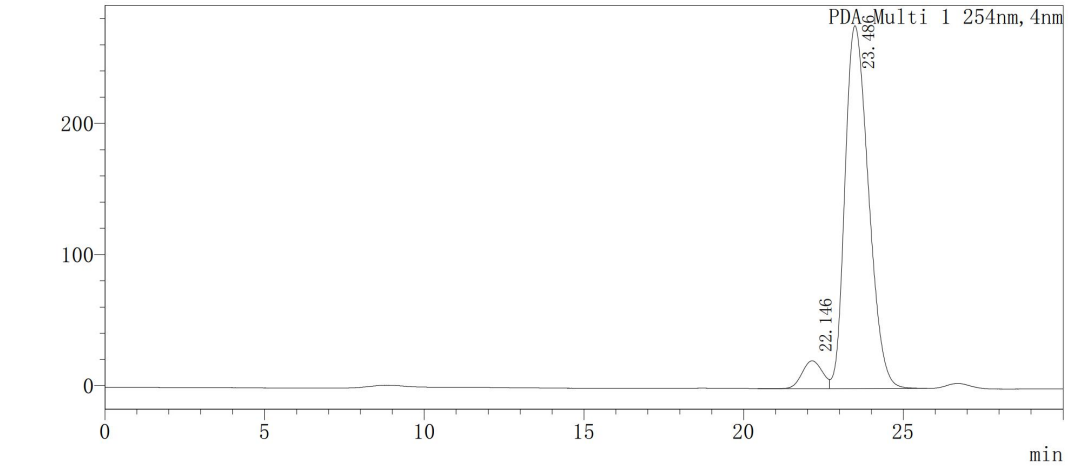


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.608	49.744
2	9.515	50.256

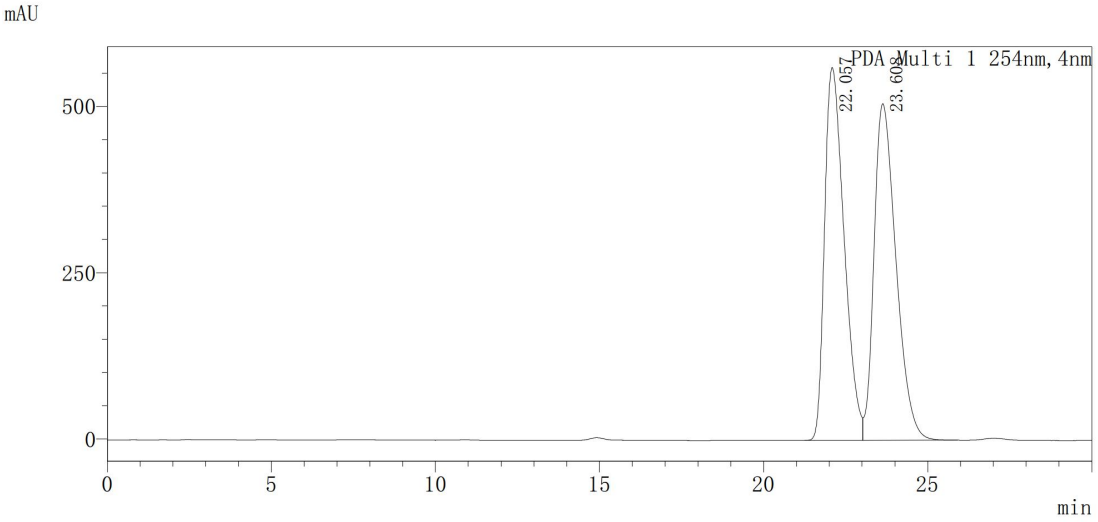


(4a)



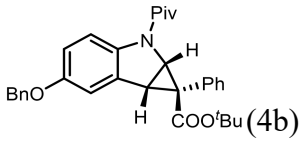
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	22.146	6.150
2	23.486	93.850

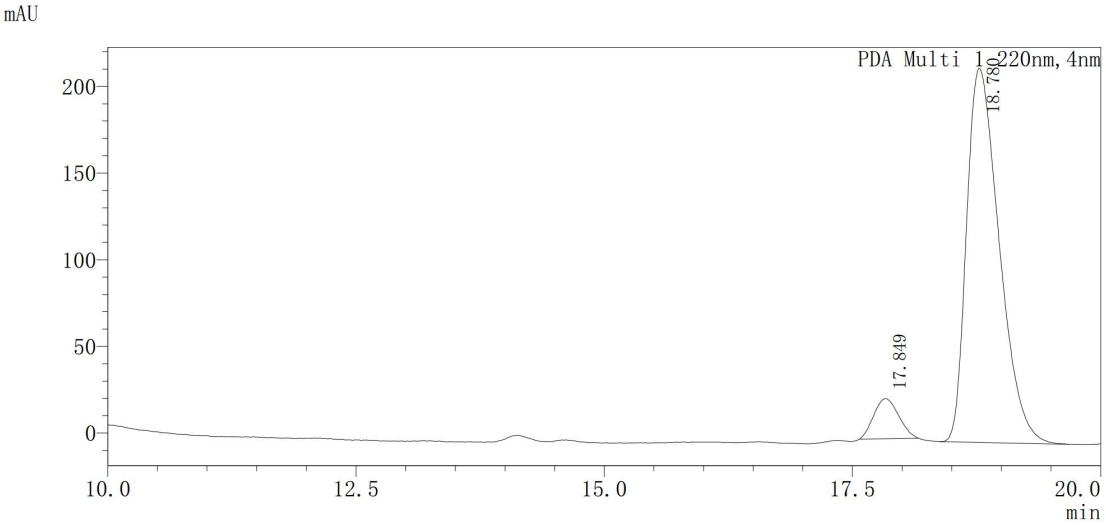


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	22.057	49.580
2	23.608	50.420

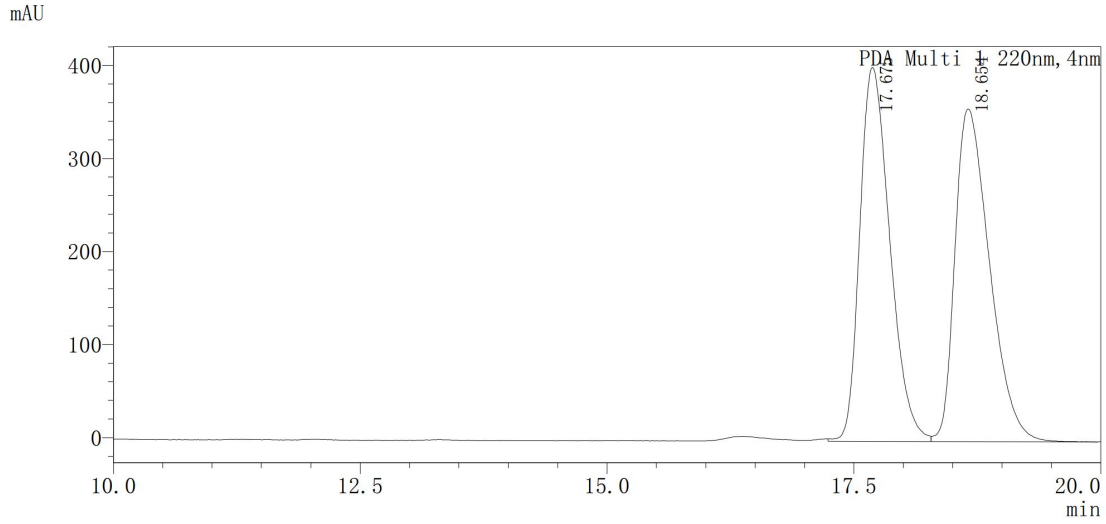


(4b)



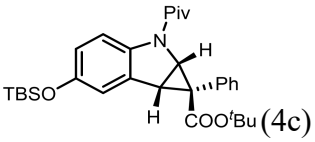
PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	17.849	7.442
2	18.780	92.558

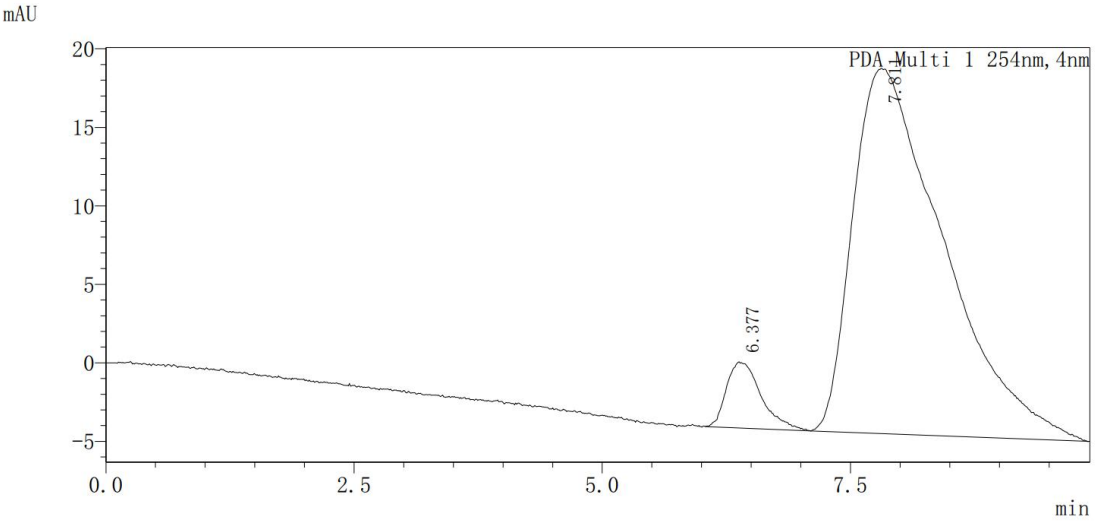


PDA Ch1 220nm

Peak No	Ret. time	Area/%
1	17.675	49.857
2	18.654	50.143

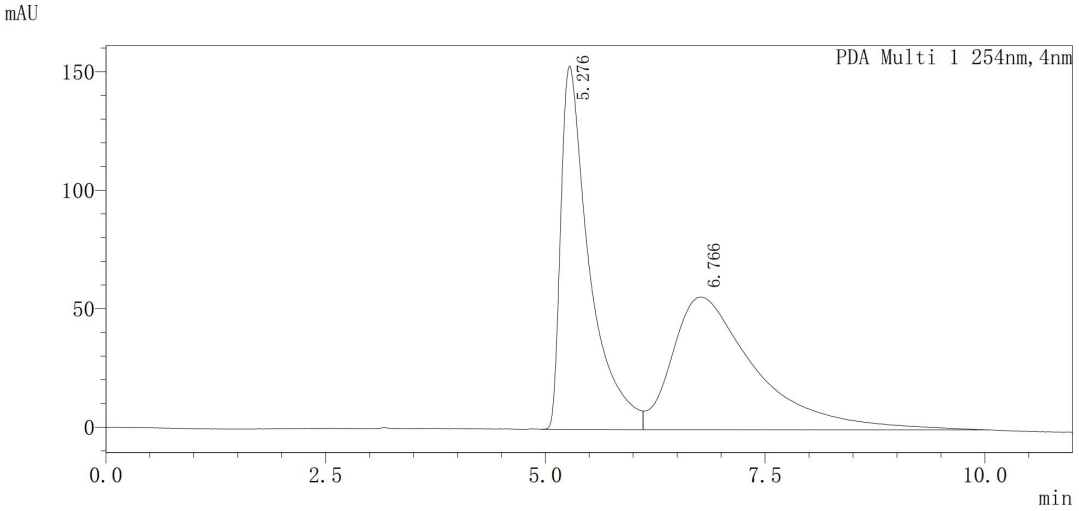


(4c)



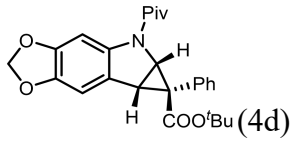
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	6.377	6.463
2	7.811	93.537

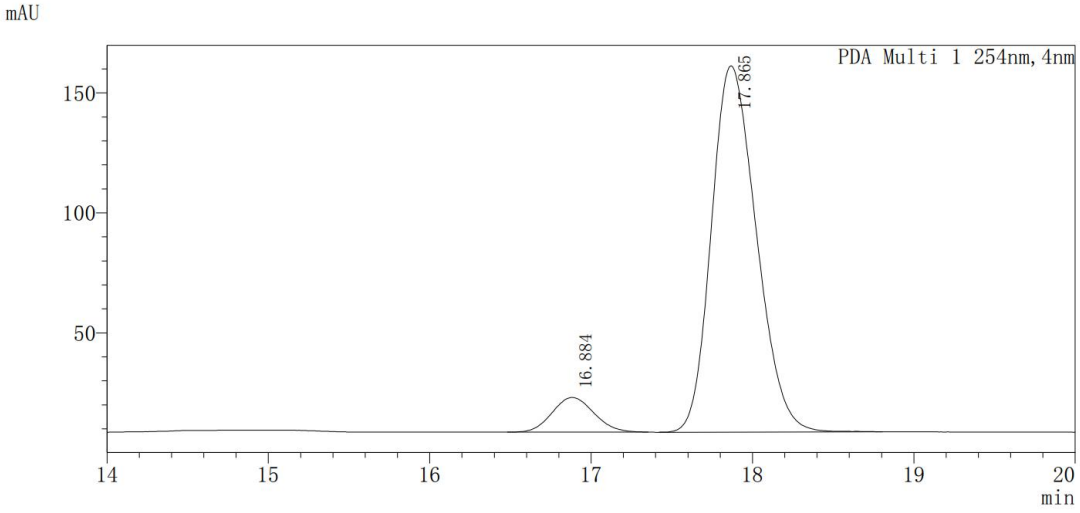


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	5.276	48.407
2	6.766	51.593

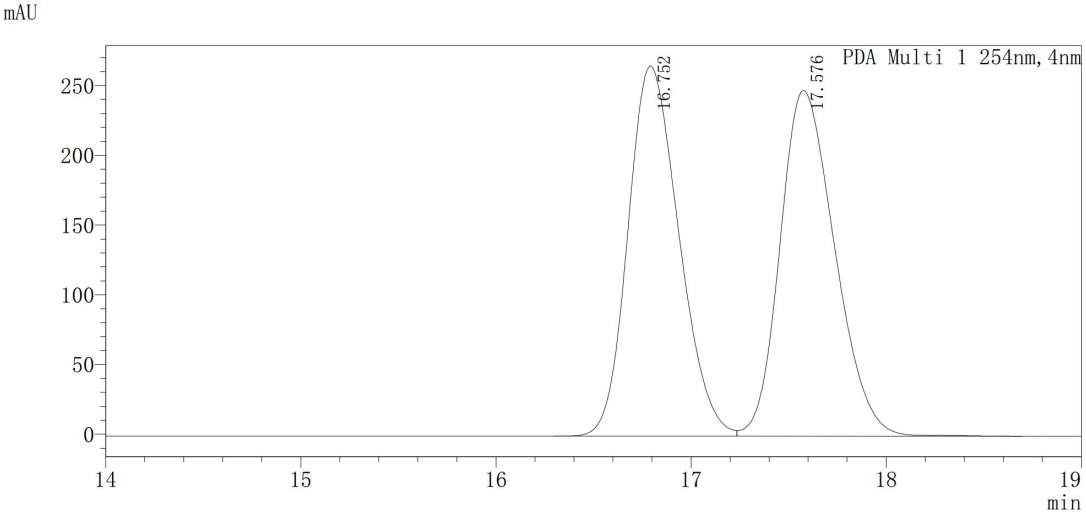


(4d)



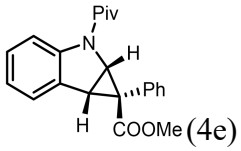
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	16.884	8.054
2	17.865	91.946

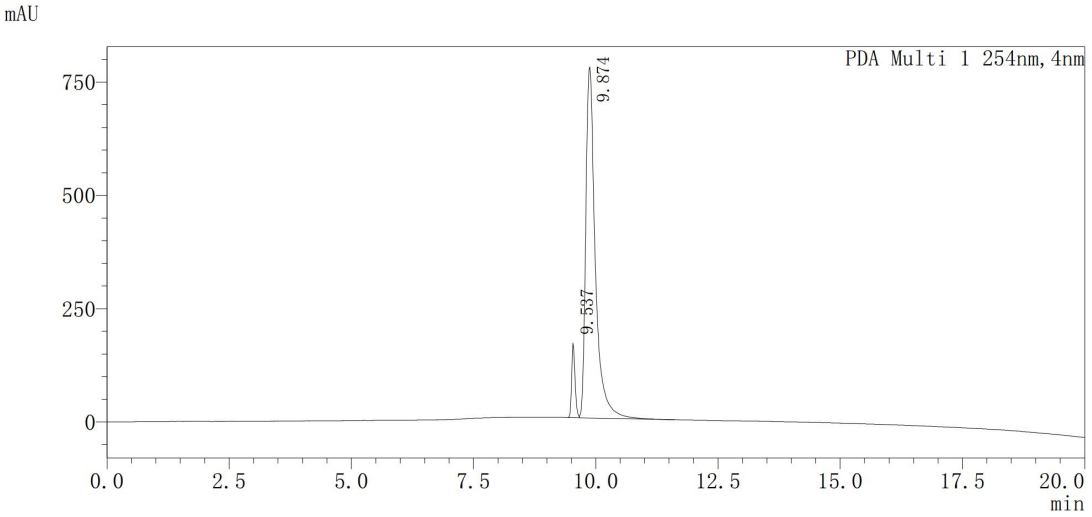


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	16.752	49.804
2	17.576	50.196

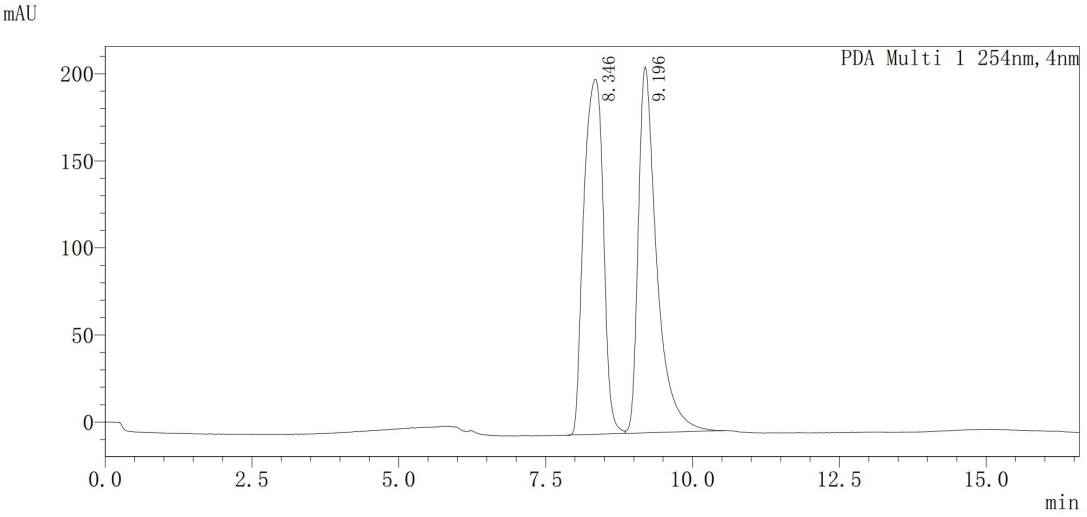


(4e)



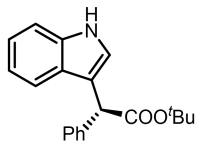
PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	9.537	7.036
2	9.874	92.964

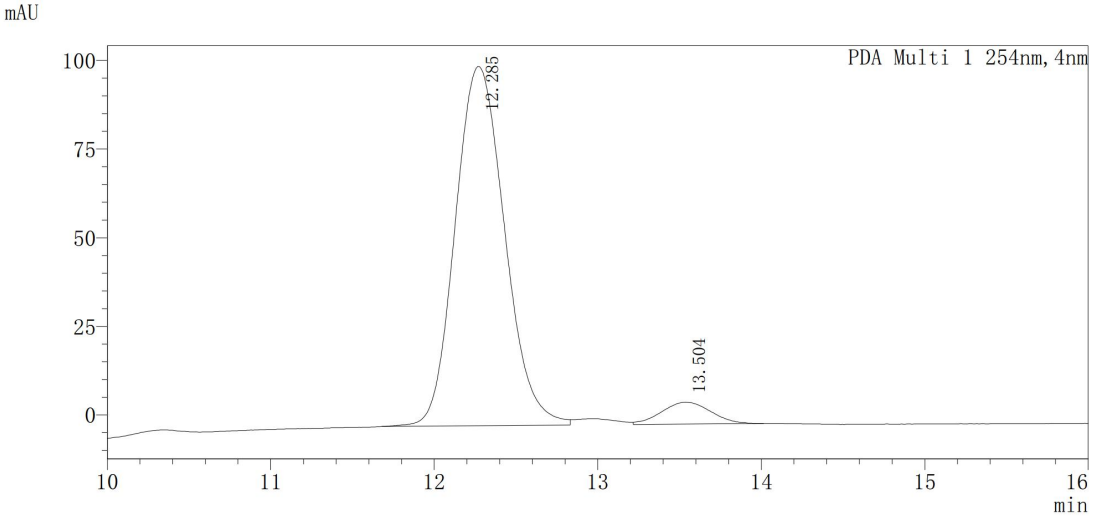


PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	8.346	50.714
2	9.196	49.286

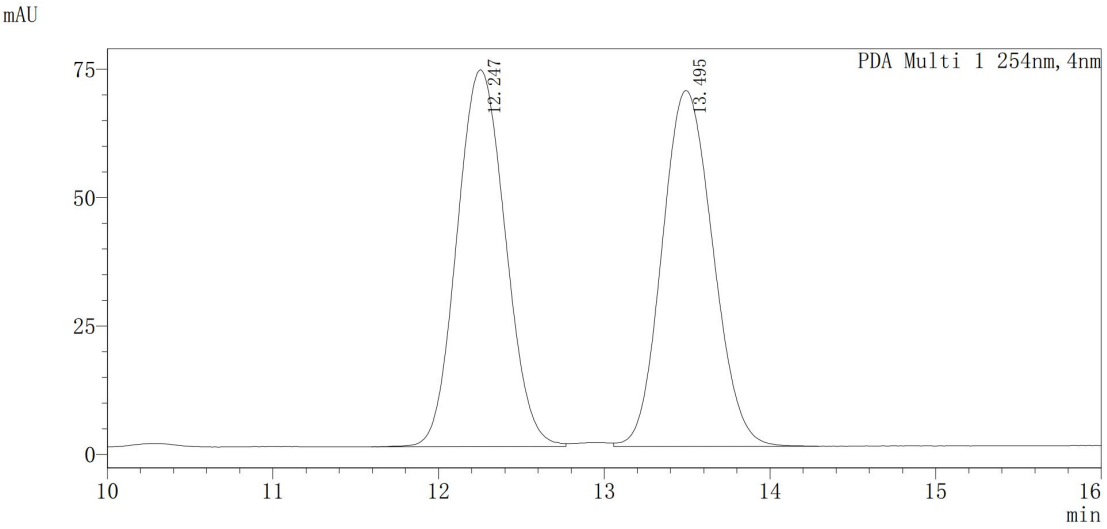


(4f)



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	12.285	94.547
2	13.504	5.453



PDA Ch1 254nm

Peak No	Ret. time	Area/%
1	12.247	50.152
2	13.495	49.848

9. References

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