Supplementary Information (SI) for Organic Chemistry Frontiers.


# Stable Sulfonate Esters as C1-Synthons for Cyclopropanation Reaction to Access Antimicrobial Active 3,3'-Spirocyclopropyloxindoles

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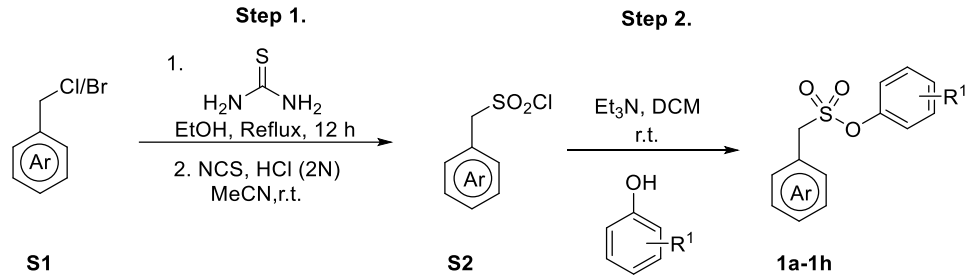
## 1. General information

Commercially available materials purchased from J&K or Aladdin were used as received. THF was distilled over sodium. Unless otherwise specified, all reactions were carried out under an atmosphere of nitrogen in 10.0 mL dry Schlenk tube. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer or on a JEOL-ECX-500 (500 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, $\delta$) relative to tetramethylsilane ($\delta$= 0.00) or chloroform ($\delta$ = 7.26, singlet). $^1$H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Fluorine ($^{19}$F) nuclear magnetic resonance ($^{19}$F NMR) spectra were recorded on a Bruker (AVANCE III HD 376 MHz) spectrometer. The melting points (m.p.) of the title compounds were determined when left untouched on a XT-4-MP apparatus from Beijing Tech. Instrument Co. (Beijing, China). High resolution mass spectral analysis (HRMS) was performed on a quadrupole/electrostatic field orbitrap mass spectrometer. Absolute configuration of the products was determined by X-ray crystallography. HPLC analyses were measured on Waters systems with Empower 3 system controller, Alliance 2695, and 2998 Diode Array Waters 2489 UV/Vis detector. Chiralcel brand chiral columns from Daicel Chemical Industries were used with models IA, IB, or IC or in 4.6 x 250 mm size. The racemic products used to determine the er values were synthesized using racemic catalyst. Optical rotations were measured on a Insmark IP-digi Polarimeter in a 1 dm cuvette at 25 ºC. The concentration (c) is given in g/100 mL. Analytical thin-layer chromatography (TLC) was carried out pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp [1].

## 2. Experimental Section

### (1) General procedure for preparation of substrates and products

**General procedure 1 for preparation of substrates 1:**



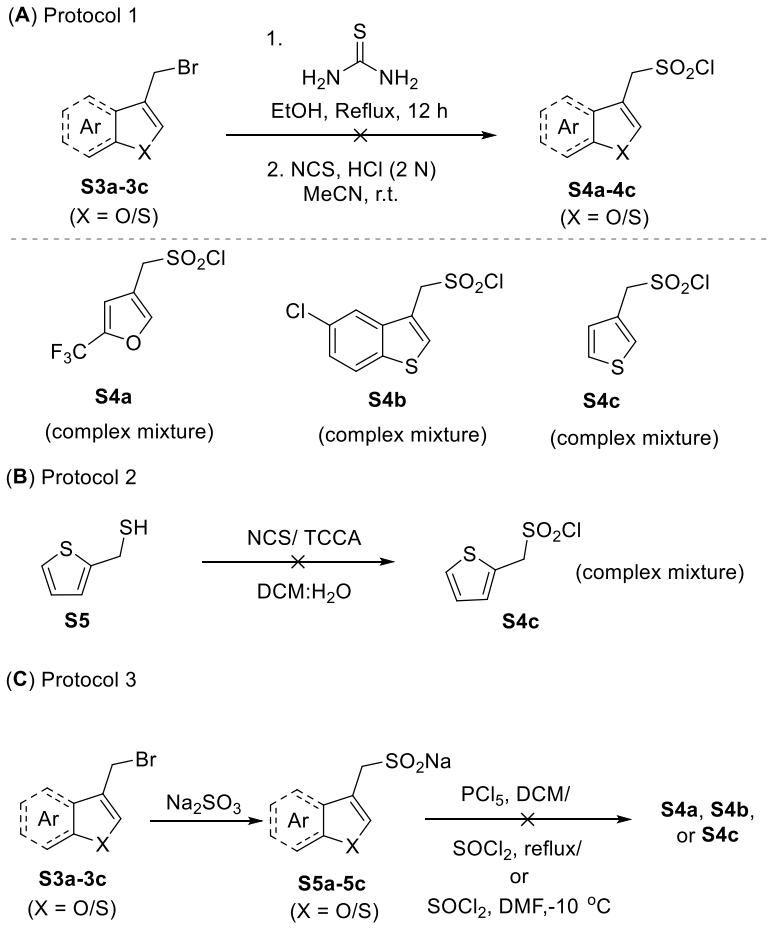

**Step 1.** An oven dried clean round bottom flask was charged with magnetic stir-bar, substituted benzyl chloride (10.0 mmol) and thiourea (10.0 mmol, 760 mg). 10.0 mL of Absolute ethanol was added and refluxed at 96 °C. After 3 h the reaction was taken out and the solvent was evaporated under reduced pressure to obtain a white solid (thiourea salt). The obtained solid salt was suspended in 14 mL of $CH_3CN$ and 3 mL 2N HCl was then added to it. The mixture was stirred at 0 °C for 15 min. N-chlorosuccinimide (NCS) (40.0 mmol, 5.34 g) was added in portions to the suspension in order to obtain a clear solution. The solution was stirred for another 30 min at room temperature. The solution was evaporated under reduced pressure to remove the $CH_3CN$. The remaining aqueous portion was extracted with ethyl acetate. The organic portion was dried over anhydrous $Na_2SO_4$ and the crude mixture was evaporated and purified by column chromatography over silica gel with ethyl acetate/petroleum ether as the eluent. Quantitative yield.

**Step 2.** To an ice-cold solution of 2-hydroxy-5-methoxybenzonitrile (5.0 mmol) and triethylamine (1.5 equiv., 1.04 mL) in 10 mL dichloromethane under nitrogen atmosphere, substituted benzyl sulfonyl chloride was added portionwise. Stirring was continued for additional 20 minutes, after that the ice bath was removed and the reaction mixture was left for vigorous stirring at room temperature for overnight. $CH_2Cl_2$ was removed under reduced pressure. The residual was diluted and extracted with ethyl acetate (3 × 20.0 mL) and brine solution (3 × 10.0 mL). The organic layer was collected and dried over anhydrous $Na_2SO_4$. After filtration and evaporation of the solvent, the

crude mixture was purified by column chromatography over neutral alumina with petroleum ether/ethyl acetate (85/15, v/v) as the eluent.

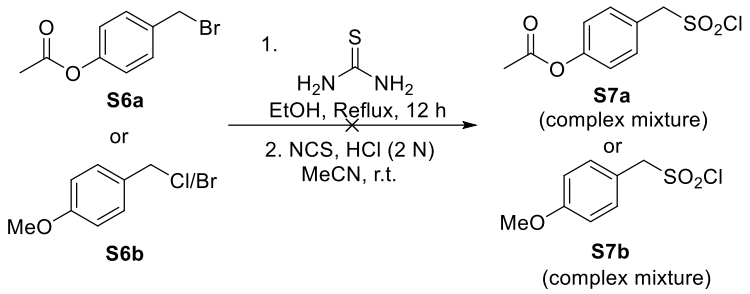
It is also worth noting that we failed to examine the scope with respect to sulfonates bearing heterocycles or electron-donating groups due to the difficulty to obtain these substrates **1**. The protocols to prepare the sulfonyl chlorides as key building blocks of sulfonates **1** were demonstrated as below.

**Attempts to prepare heterocyclic substrates S4a-4c:**

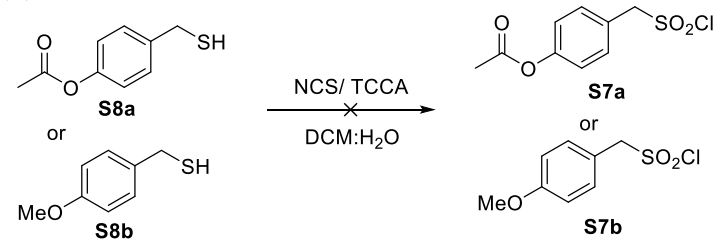


## Attempts to prepare substrates S7a-S7b with electron-donating groups:

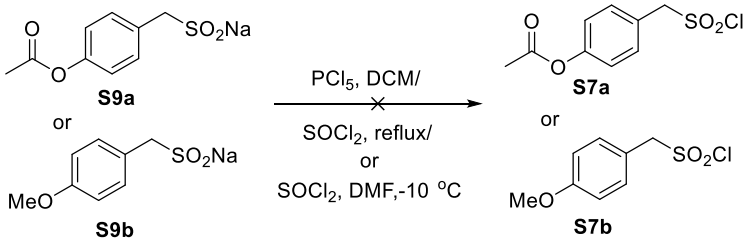
(**A**) Protocol 1



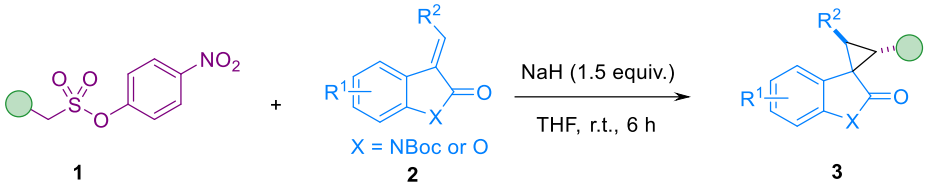

(**B**) Protocol 2




(**C**) Protocol 3

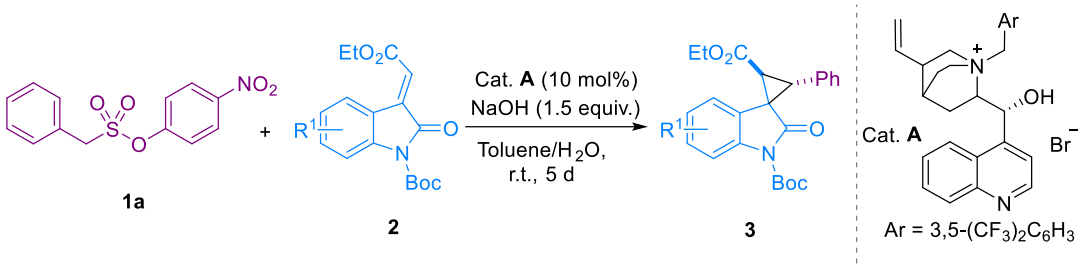


**General procedure 2 for preparation of products 3:**



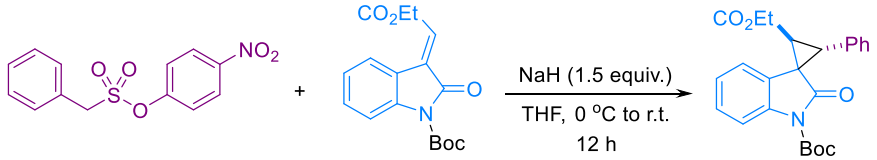

To an oven-dried 10.0 mL screw cap vial equipped with a magnetic stir bar were added **1** (0.11 mmol, 1.1 equiv.), **2** (0.1 mmol, 1.0 equiv.) and NaH (0.15 mmol, 1.5 equiv.) in THF (1.0 mL) and the reaction was stirred at r.t. for 6 h under nitrogen atmosphere. Then the mixture was concentrated under reduced pressure. The resulting crude residue was purified by column chromatography over silica gel (Petroleum ether / EtOAc = 30:1) to afford the desired products **3**.

**General procedure 3 for the catalytic asymmetric reactions:**




To an oven-dried 10.0 mL screw cap vial equipped with a magnetic stir bar were added **1a** (0.044 mmol, 1.1 equiv.), **2** (0.04 mmol, 1.0 equiv.), Cat. **A** (0.004 mmol, 10 mol%) and NaOH (0.06 mmol, 1.5 equiv.) in Toluene/$H_2O$ = 5:1 (1.0 mL) and the reaction was stirred at r.t. for 5 d under nitrogen atmosphere. Then the mixture was concentrated under reduced pressure. The resulting crude residue was purified by column chromatography over silica gel (Petroleum ether / EtOAc = 30:1) to afford the desired chiral products **3**.

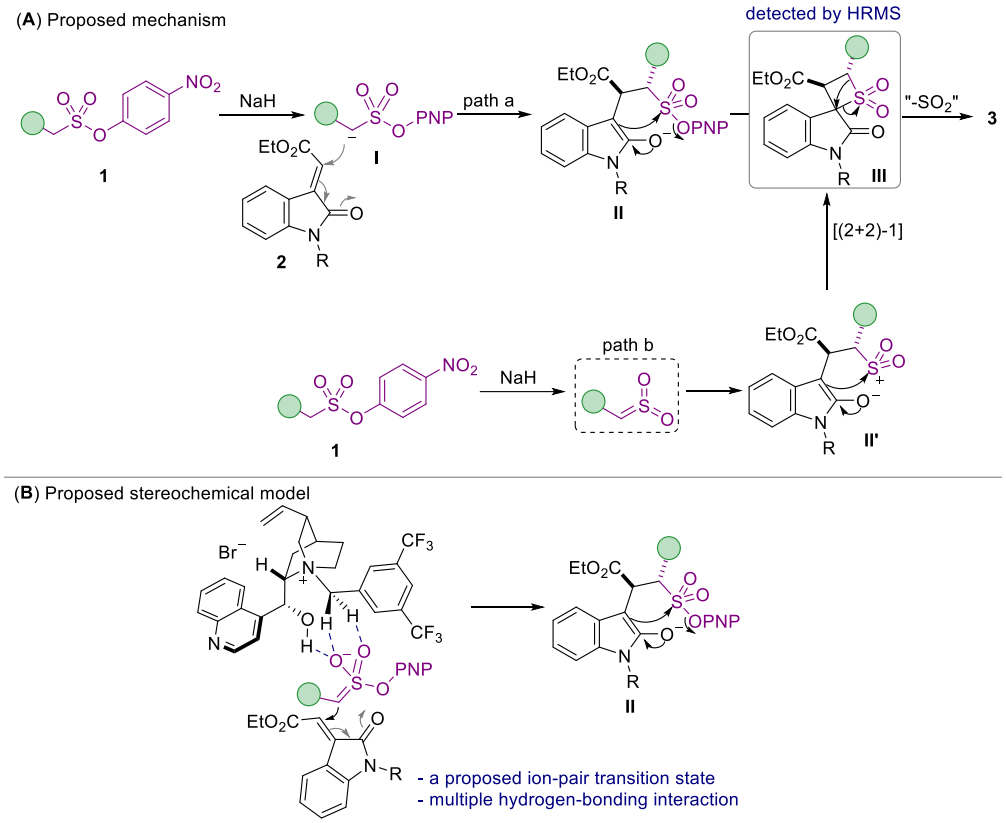
**Gram-scale synthesis of products 3a:**




**1a** **2a** *trans*-**3a**

To an oven-dried 100.0 mL screw cap vial equipped with a magnetic stir bar were added **1a** (3.52 mmol, 1.1 equiv.) in THF (35.0 mL). After cooling down to 0 °C, NaH (4.80 mmol, 1.5 equiv.) was added to the mixture in batches, followed by addition of **2a** (3.20 mmol, 1.0 equiv.) at 0 °C. Then, the reaction was stirred at r.t. for 12 h under nitrogen atmosphere. Then the mixture was concentrated under reduced pressure. The resulting crude residue was purified by column chromatography over silica gel (Petroleum ether / EtOAc = 20:1) to afford the desired products *trans*-**3a** (0.98 g, 75% yield, d.r. = 10:1).

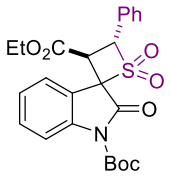
**Scheme S1.** Proposed mechanism




Building upon previous reports and our preliminary studies on the reaction (Figure S1), a plausible mechanism was illustrated in Scheme S1A. The process begins with the NaH-mediated formation of a carbon anion intermediate **I** from sulfonate **1**. Subsequently, a Michael addition to the alkylidene oxindole **2** would result in the formation of intermediate **II**. Annulation through intramolecular attack on the sulfonyl moiety and elimination of the phenolate anion would lead to intermediate **III**. Then a spontaneous $SO_2$ extrusion proceeds to produce the final product **3**, probably owing to the lability of the four-membered sulfonate (path a). In our preliminary mechanistic studies, the generation of the four-membered sultone intermediate **III** could be verified by HRMS detection of the reaction mixture during the progress of the model reaction. However, it should be noted that our attempts to isolate it were not successful. Notably, the formation of the 4-membered ring might also proceed through the formation of sulfene intermediates via path b, which were generated in situ under strong basic

conditions. Additionally, the stereochemical course of the observed diastereoselectivity could be explained by the favoured trans-configuration of the initial Michael addition.

Furthermore, based on previous studies on the PTC asymmetric catalysis,[2-4] a plausible stereochemical model to account for the developed enantioselective catalytic transformation of **1a** and **2** to form **3a-3d**, **3i** was illustrated in Scheme 1B. The transition state involved an ion-pair interaction between the substrate and PTC catalyst **A** through multiple hydrogen-bonding interactions.




**HRMS** (ESI, m/z): Calculated for $C_{24}H_{25}NaNO_7S^+$ $[M + Na]^+$, 494.1243, found: 494.1236.

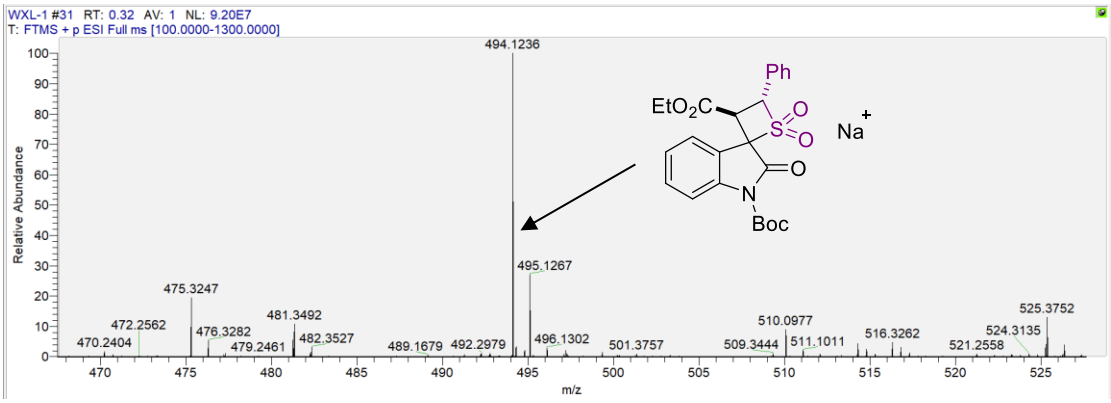
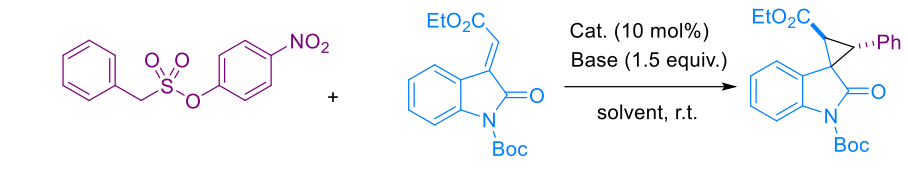



**Figure S1.** HRMS spectrum of intermediate **III**

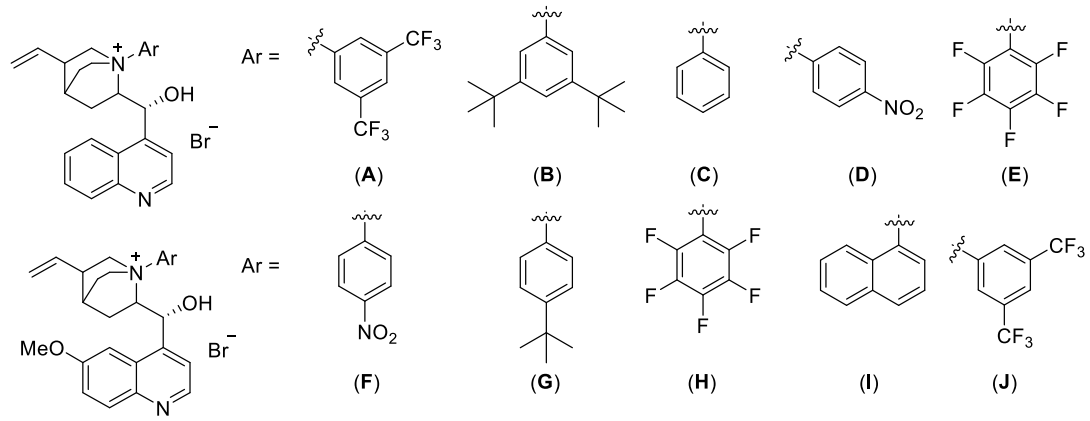
## (2) Supplementary results of condition optimization

**Table S1.** Condition optimization for the enantioselective synthesis of **3a**[a]




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

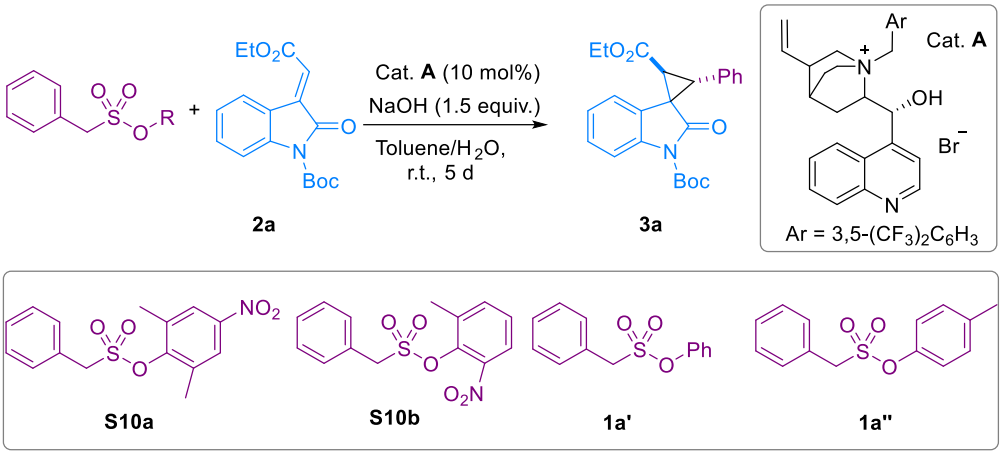
**Cat.**




| Entry | Cat. | Solvent | Base | Yield (%)[b] | E.r.[c] |
|---|---|---|---|---|---|
| 1 | **J** | toluene | NaOH | - | 35:65 |
| 2 | **J** | toluene | KOH | <10 | 37:63 |
| 3 | **J** | toluene:$H_2O$ (5:1) | NaOH | - | 30:70 |
| 4 | **A** | toluene:$H_2O$ (5:1) | NaOH | 58 | 79:21 |
| 5 | **B** | toluene:$H_2O$ (5:1) | NaOH | - | 62:38 |
| 6 | **C** | toluene:$H_2O$ (5:1) | NaOH | 20 | 69:31 |
| 7 | **D** | toluene:$H_2O$ (5:1) | NaOH | - | 70:30 |
| 8 | **E** | toluene:$H_2O$ (5:1) | NaOH | - | 65:35 |
| 9 | **F** | toluene:$H_2O$ (5:1) | NaOH | 39 | 67:33 |
| 10 | **G** | toluene:$H_2O$ (5:1) | NaOH | 14 | 68:32 |
| 11 | **H** | toluene:$H_2O$ (5:1) | NaOH | 64 | 75:25 |
| 12 | **I** | toluene:$H_2O$ (5:1) | NaOH | 75 | 38:62 |

[a]General conditions: **1a** (0.044 mmol, 1.1 equiv.), **2a** (0.04 mmol, 1.0 equiv.), Cat. (10 mol%), base (0.06 mmol, 1.5 equiv.), and solvent (1.0 mL) at r.t. for 5 d; [b]Determined by $^1$H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard, isolated yield of major isomer; [c]The e.r. values were determined via HPLC on chiral stationary phase.

**Table S2.** Screening of the enantioselective annulation with various sulfonates[a]



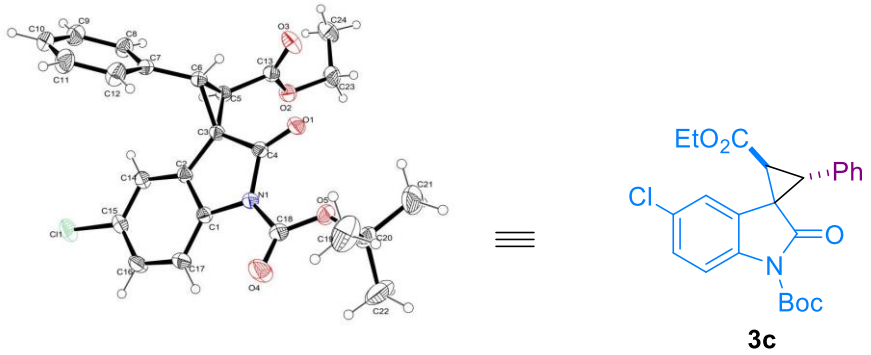

| Entry | Sulfonate | Yiled of **3a** (%) | D.r. of **3a**[b] | E.r. of **3a** (%)[c] |
|---|---|---|---|---|
| 1 | **S10a** | 22 | 2:1 | 88:12 |
| 2 | **S10b** | 35 | 2:1 | 63:37 |
| 3 | **1a'** | trace | n.d. | n.d. |
| 4 | **1a''** | trace | n.d. | n.d. |

[a]General conditions: sulfonates (0.044 mmol, 1.1 equiv.), **2a** (0.04 mmol, 1.0 equiv.), Cat. **A** (10 mol%), NaOH (0.06 mmol, 1.5 equiv.), and toluene/$H_2O$ (5:1, 1.0 mL) at r.t. for 5 d; [b]Determined by $^1H$ NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard, isolated yield of major isomer; [c]The e.r. values were determined via HPLC on chiral stationary phase.

**(3) Structure determination of 3c and 3f via X-ray crystallographic analysis.**

**(a) X-ray crystallographic analysis of 3c**

Product **3c** was crystallized as colorless crystal *via* evaporation of a petroleum ether / ethyl acetate solution, and its absolute configuration was determined by x-ray structure analysis. CCDC 2405965 (**3c**) contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.



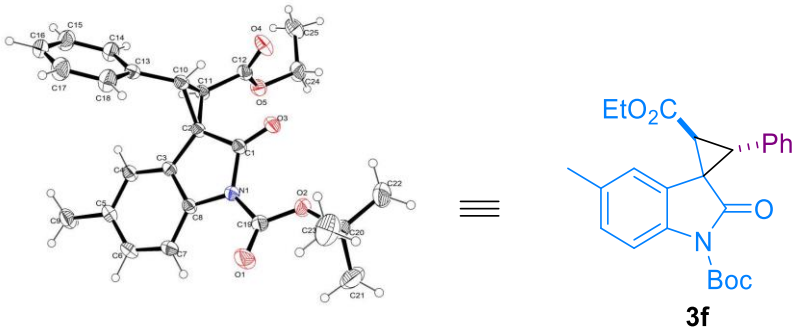

**3c**

| **Compound** | **3c** |
|---|---|
| **Empirical formula** | $C_{24}H_{24}ClNO_5$ |
| **Formula weight** | 441.89 |
| **Temperature/K** | 297 |
| **Crystal system** | monoclinic |
| **Space group** | $P2_1/c$ |
| **a/Å** | 10.2458(5) |
| **b/Å** | 9.6613(4) |
| **c/Å** | 22.6816(10) |
| **α/°** | 90 |
| **β/°** | 92.990(2) |
| **γ/°** | 90 |
| **Volume/Å$^3$** | 2242.14(17) |
| **Z** | 4 |
| **$\rho_{calc}$g/cm$^3$** | 1.309 |
| **μ/mm$^{-1}$** | 1.803 |

| | |
|---|---|
| **F(000)** | 928.0 |
| **Crystal size/mm$^3$** | 0.56 × 0.44 × 0.23 |
| **Radiation** | CuKα (λ = 1.54184) |
| **2Θ range for data collection/°** | 7.806 to 136.682 |
| **Index ranges** | $-12 \leq h \leq 12$, $-11 \leq k \leq 8$, $-27 \leq l \leq 27$ |
| **Reflections collected** | 19906 |
| **Independent reflections** | 4077 [$R_{int}$ = 0.0378, $R_{sigma}$ = 0.0337] |
| **Data/restraints/parameters** | 4077/0/285 |
| **Goodness-of-fit on F$^2$** | 1.091 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0414, $wR_2$ = 0.1144 |
| **Final R indexes [all data]** | $R_1$ = 0.0433, $wR_2$ = 0.1158 |
| **Largest diff. peak/hole / e Å$^{-3}$** | 0.24/-0.29 |
| **Flack parameter** | 0.02(6) |

**(b) X-ray crystallographic analysis of 3f**

Product **3f** was crystallized as colorless crystal *via* evaporation of a petroleum ether / ethyl acetate solution, and its absolute configuration was determined by x-ray structure analysis. CCDC 2405966 (**3f**) contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data request/cif.




**3f**

| **Compound** | **3f** |
|---|---|
| **Empirical formula** | $C_{25}H_{27}NO_5$ |
| **Formula weight** | 421.47 |
| **Temperature/K** | 297 |
| **Crystal system** | monoclinic |
| **Space group** | $P2_1/c$ |
| **a/Å** | 10.2635(4) |
| **b/Å** | 9.5914(4) |
| **c/Å** | 22.8353(9) |
| **α/°** | 90 |
| **β/°** | 93.370(2) |
| **γ/°** | 90 |
| **Volume/Å$^3$** | 2244.05(16) |
| **Z** | 4 |
| **$\rho_{calc}$g/cm$^3$** | 1.248 |
| **μ/mm$^{-1}$** | 0.706 |
| **F(000)** | 896.0 |
| **Crystal size/mm$^3$** | 0.65 × 0.33 × 0.25 |

| | |
|---|---|
| **Radiation** | CuKα (λ = 1.54184) |
| **2Θ range for data collection/°** | 11.95 to 136.59 |
| **Index ranges** | $-10 \leq h \leq 12$, $-11 \leq k \leq 11$, $-27 \leq l \leq 24$ |
| **Reflections collected** | 28723 |
| **Independent reflections** | 4070 [$R_{int}$ = 0.0436, $R_{sigma}$ = 0.0358] |
| **Data/restraints/parameters** | 4070/0/286 |
| **Goodness-of-fit on $F^2$** | 1.062 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0458, $wR_2$ = 0.1227 |
| **Final R indexes [all data]** | $R_1$ = 0.0472, $wR_2$ = 0.1238 |
| **Largest diff. peak/hole / e $Å^{-3}$** | 0.22/-0.18 |
| **Flack parameter** | 0.02(6) |

**(3) Biological activity studies.**

**Antibacterial activity of compounds 3a-w against *Xanthomonas oryzae* pv. *oryzae* (*Xoo*) and *Xanthomonas axonopodis.* pv. *citri* (*Xac*):**

Antibacterial activities of the title compounds against *Xoo* and *Xac* were evaluated by using the turbidimeter test. Thiodiazole-copper was used as the positive controls. The compound was dissolved in 150.0 $\mu$L of dimethylformamide and diluted with 0.1% (*V* / *V*) Tween-20 to prepare the solutions on a concentration of 100 $\mu$g/mL. 1.0 mL of the above solution was added to the non-toxic nutrient broth (NB: 1.5 g of beef extract, 2.5 g of peptone, 0.5 g of yeast powder, 5.0 g of glucose and 500 mL of distilled water, pH = 7.0 ~ 7.2) liquid medium in a 4.0 mL tube. Then, 40.0 $\mu$L of NB solution containing *Xanthomonas oryzae* pv. *oryzae* (*Xoo*) or *Xanthomonas axonopodis.* pv. *citri* (*Xac*) was added to 5.0 mL of the NB solution containing the test compound. The inoculated test tube was incubated at (28 ± 1) °C under continuous shaking at 200 rpm for 24 h. The culture growth was monitored by measuring the optical density at 595 nm ($OD_{595}$) and expressed as corrected turbidity. The relative inhibitory rate was calculated as follows:

$I$ (%) = ($C_{tur} - T_{tur}$) / $C_{tur}$ × 100%

$C_{tur}$: the corrected turbidity value of bacterial growth on untreated NB;

$T_{tur}$: the corrected turbidity value of bacterial growth on treated NB;

$I$: The relative inhibitory rate[5].

**Table S3.** Inhibition rate of compound **3** against *Xoo* and *Xac*[a]

| | Inhibition rate/% (100 $\mu$g/mL) | | | Inhibition rate/% (100 $\mu$g/mL) | |
|---|---|---|---|---|---|
| Compound | *Xoo* | *Xac* | Compound | *Xoo* | *Xac* |
| **3c** | 0 | 19.2 ± 3.4 | **3l** | 19.5 ± 6.1 | 32.1 ± 5.5 |
| **3d** | 0 | 43.1 ± 3.1 | **3n** | 0 | 51.1 ± 3.8 |
| **3f** | 0 | 48.6 ± 3.2 | **3y** | 23.9 ± 1.6 | 51.9 ± 5.0 |
| **3g** | 19.5 ± 3.2 | 41.1 ±5.3 | **3s** | **73.1 ± 1.6** | 36.6 ± 5.8 |
| **3h** | 30.3 ± 1.7 | 55.2 ± 1.3 | **3t** | 0 | 49.3 ± 6. 7 |
| **3i** | 51.2 ± 6.5 | **72.5 ± 1.2** | **3u** | 0 | 48.4 ± 4.1 |
| **3y** | 0 | 43.2 ± 6.9 | **3v** | 0 | 20.1 ± 3.2 |
| **3s** | 0 | 55.7 ± 4.6 | **3r** | 58.8 ± 1.1 | 55.9 ± 1.0 |
| **3z** | 0 | 60.4 ± 2.4 | **3z** | 0 | 16.2 ± 2.5 |
| **TC**[b] | 64.0 ± 1.9 | 40.6 ± 6.6 | **BT**[b] | 46.8 ± 6.0 | 49.4 ± 8.7 |

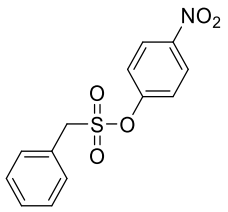
[a]All data were average data of three replicates; [b] Commercial bactericide, used as the positive control. TC = Thiodiazole-copper, BT = Bismerthiazol

## 3. Characterization data of the substrates 1 and products 3-4

### (1) Characterization of substrates products

(Note: substrates **2** were prepared according to previous reports[6])

**4-Nitrophenyl phenylmethanesulfonate (1a):**



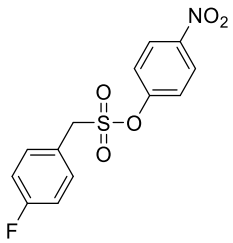
Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1), Colorless solid, m.p. 104.0-106.5 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.26 – 8.16 (m, 2H), 7.54 – 7.37 (m, 5H), 7.24 – 7.13 (m, 2H), 4.61 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 153.5, 146.1, 130.9, 129.7, 129.2, 126.6, 125.5, 122.7, 57.7.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_{11}NO_5S$ $[M-H]^+$, 292.0358; found 292.0285.

**4-Nitrophenyl (4-fluorophenyl)methanesulfonate (1b):**



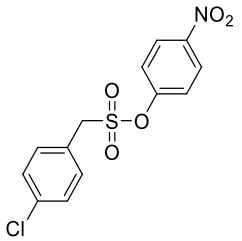
Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Colorless solid, m.p. 92.5-94.5 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.31 – 8.21 (m, 2H), 7.51 – 7.40 (m, 2H), 7.29 – 7.21 (m, 2H), 7.19 – 7.09 (m, 2H), 4.58 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 164.8, 162.3, 153.2, 146.2, 132.8, 132.7, 125.6, 122.7, 122.5, 122.4, 116.5, 116.3, 56.9.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_{10}FNO_5S$ $[M-H]^+$, 310.0264; found 310.0910.

**4-Nitrophenyl (4-chlorophenyl)methanesulfonate (1c):**



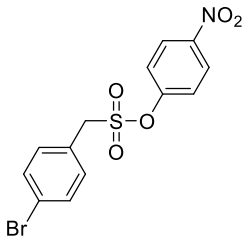

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Yellow solid, m.p. 85.1-90.8 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.30 – 8.21 (m, 2H), 7.47 – 7.37 (m, 4H), 7.29 – 7.24 (m, 2H), 4.57 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 153.2, 146.2, 136.1, 132.2, 129.5, 125.7, 125.7, 122.7, 56.9.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_9ClNO_5S$ $[M-H]^+$, 325.9968; found 325.9895.

**4-Nitrophenyl (4-bromophenyl)methanesulfonate (1d):**



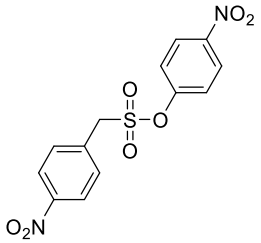

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Colorless solid, m.p. 117.5-121.2 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.31 – 8.20 (m, 2H), 7.65 – 7.52 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.21 (m, 2H), 4.55 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 153.2, 146.2, 132.5, 132.4, 125.7, 125.6, 124.3, 122.7, 57.0.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_{10}BrNO_5S$ $[M-H]^+$, 369.9463; found 369.9390.

**4-Nitrophenyl (4-nitrophenyl)methanesulfonate (1e):**



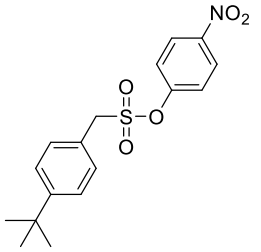
Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Yellow solid, m.p. 142.3-144.7 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.39 – 8.23 (m, 4H), 7.73 – 7.66 (m, 2H), 7.36 – 7.29 (m, 2H), 4.70 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 152.8, 148.7, 146.4, 133.5, 131.9, 125.8, 124.3, 122.7, 56.8.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_{10}N_2O_7S$ $[M-H]^+$, 337.0209; found 337.0140.

**4-Nitrophenyl (4-(tert-butyl)phenyl)methanesulfonate (1f):**



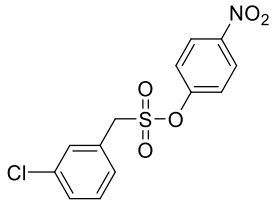
Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Colorless crystal, m.p. 103.6-105.2 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.23 – 8.15 (m, 2H), 7.47 – 7.42 (m, 2H), 7.42 – 7.35 (m, 2H), 7.21 – 7.13 (m, 2H), 4.58 (s, 2H), 1.33 (s, 9H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 153.7, 153.1, 146.0, 130.6, 126.2, 125.5, 123.4, 122.7, 57.5, 34.8, 31.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{17}H_{19}NO_5S$ $[M-H]^+$, 348.0984; found 348.0911.

**4-Nitrophenyl (3-chlorophenyl)methanesulfonate (1g):**



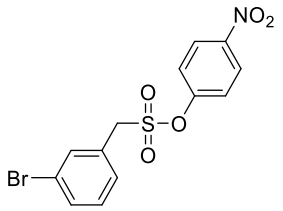
Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Colorless solid, m.p. 98.7-100.5 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.29 – 8.22 (m, 2H), 7.50 – 7.42 (m, 2H), 7.42 – 7.34 (m, 2H), 7.27 (dd, $J$ = 6.8, 2.4 Hz, 3H), 4.57 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 153.2, 135.1, 130.9, 130.5, 130.0, 129.0, 128.4, 125.7, 122.7, 57.0.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_{10}ClNO_5S$ $[M-H]^+$, 325.9968; found 325.9895.

**4-Nitrophenyl (3-bromophenyl)methanesulfonate (1h):**



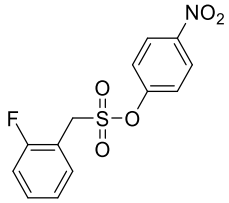
Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Colorless solid, m.p. 115.4-119.2 ℃.

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.29 – 8.21 (m, 2H), 7.64 – 7.56 (m, 2H), 7.41 (dt, $J$ = 7.7, 1.5 Hz, 1H), 7.32 (t, $J$ = 7.8 Hz, 1H), 7.29 – 7.23 (m, 2H), 4.56 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 153.2, 146.2, 133.8, 132.9, 130.7, 129.5, 128.7, 125.7, 123.0, 122.7, 57.0.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_{10}BrNO_5S$ $[M-H]^+$, 369.9463; found 369.9390.

**4-Nitrophenyl (2-fluorophenyl)methanesulfonate (1i):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 5/1). Colorless solid, m.p. 93.4-96.3 ℃.

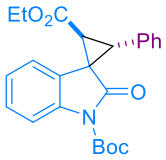
**$^{1}$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.32 – 8.17 (m, 2H), 7.60 – 7.40 (m, 2H), 7.36 – 7.11 (m, 4H), 4.69 (s, 2H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 162.49, 160.00, 153.41, 146.13, 132.68, 132.66, 131.96, 131.88, 125.58, 124.91, 124.87, 122.53, 116.23, 116.02, 114.48, 114.34, 50.81, 50.77.

**HRMS (ESI, m/z)**: Mass calculated for $C_{13}H_{10}FNO_5S$ $[M-H]^+$, 310.0264; found 310.0191.

**(2) Characterization of the products 3**

**1'-(Tert-butyl) 2-ethyl (*trans*)-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3a):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless crystal, m.p. 122.4-126.8 ℃, d.r. = 10:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (81%, 33.0 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.87 (dt, $J$ = 8.2, 0.8 Hz, 1H), 7.29 (dd, $J$ = 5.2, 1.9 Hz, 3H), 7.23 – 7.12 (m, 3H), 6.79 (td, $J$ = 7.6, 1.1 Hz, 1H), 5.95 (dd, $J$ = 7.6, 1.3 Hz, 1H), 4.36 – 4.18 (m, 2H), 3.98 – 3.89 (m, 1H), 3.06 (d, $J$ = 8.4 Hz, 1H), 1.66 (s, 9H), 1.30 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.5, 166.7, 149.2, 140.0, 132.6, 129.8, 128.6, 128.0, 127.7, 124.7, 123.6, 120.8, 114.8, 84.5, 61.7, 39.8, 38.5, 38.3, 28.2, 14.2.

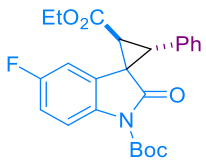
**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{25}NNaO_5$ $[M+Na]^+$, 430.1630; found 430.1625.

General procedure **3** for synthesis of chiral product **3a**, d.r. = 3:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), isolated yield of major isomer (58%, 9.5 mg).

$[\alpha]_D^{25}$ = +3.521 (c = 1.0 in $CHCl_3$).

**HPLC** analysis: 79:21 e.r. (Chiralcel OD-H, 2:98 *i*-PrOH/*n*-Hexane, 0.8 mL/min), Rt (major) = 12.1 min, Rt (minor) = 9.5 min.

**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-fluoro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3b):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl

acetate = 30/1). Colorless solid, m.p. 147.6-153.8 ℃, d.r. = 10:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (89%, 37.9 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.85 (dd, $J$ = 9.0, 4.6 Hz, 1H), 7.32 (dd, $J$ = 5.1, 1.9 Hz, 3H), 7.17 (ddd, $J$ = 6.3, 3.2, 1.5 Hz, 2H), 6.88 (td, $J$ = 9.0, 2.7 Hz, 1H), 5.67 (dd, $J$ = 8.2, 2.7 Hz, 1H), 4.39 – 4.19 (m, 2H), 3.97 (d, $J$ = 8.5 Hz, 1H), 3.05 (d, $J$ = 8.5 Hz, 1H), 1.65 (s, 9H), 1.30 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.05, 166.35, 160.39, 157.97, 149.12, 135.93, 135.91, 132.05, 129.66, 128.82, 128.36, 126.70, 126.61, 116.09, 116.01, 114.26, 114.03, 108.51, 108.25, 84.65, 61.79, 40.12, 38.71, 38.31, 38.29, 28.11, 14.16.

**$^{19}$F NMR (377 MHz, Chloroform-*d*)** $\delta$: -118.13.

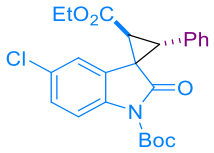
**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}FNNaO_5$ $[M+Na]^+$, 448.1536; found 448.1531.

General procedure **3** for synthesis of chiral product **3b**, d.r. = 5:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), isolated yield of major isomer (42%, 7.2 mg).

$[\alpha]_D^{25}$ = +3.421 (c = 1.0 in $CHCl_3$).

**HPLC** analysis: 82:18 e.r. (Chiralcel OD-H, 2:98 *i*-PrOH/*n*-Hexane, 0.8 mL/min), Rt (major) = 9.9 min, Rt (minor) = 12.5 min.

**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-chloro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3c):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 165.7-171.2 ℃, d.r. = 5:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (74%, 32.7 mg).

**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.82 (d, $J$ = 8.7 Hz, 1H), 7.33 (dd, $J$ = 5.1, 1.9 Hz, 3H), 7.21 – 7.12 (m, 3H), 5.89 (d, $J$ = 2.2 Hz, 1H), 4.28 (qd, $J$ = 7.2, 4.9

Hz, 2H), 3.96 (dd, *J* = 8.5, 1.1 Hz, 1H), 3.06 (d, *J* = 8.5 Hz, 1H), 1.65 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 170.8, 166.3, 149.0, 138.5, 132.0, 129.7, 129.2, 128.8, 128.4, 127.6, 126.5, 121.0, 116.0, 84.8, 61.8, 40.2, 38.7, 38.1, 28.1, 14.2.

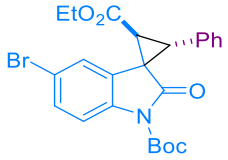
**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}ClNNaO_5$ $[M+Na]^+$, 464.1241; found 464.1235.

General procedure **3** for synthesis of chiral product **3c**, d.r. = 3:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), isolated yield of major isomer (46%, 8.1 mg).

$[\alpha]_D^{25}$ = +3.482 (c = 1.0 in $CHCl_3$).

**HPLC** analysis: 82:18 e.r. (Chiralcel OD-H, 2:98 *i*-PrOH/*n*-Hexane, 0.8 mL/min), Rt (major) = 9.9 min, Rt (minor) = 12.5 min.

**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-bromo-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3d):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow solid, m.p. 146.8-148.9 ℃, d.r. = 10:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (84%, 40.9 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.76 (d, *J* = 8.7 Hz, 1H), 7.41 – 7.29 (m, 4H), 7.22 – 7.11 (m, 2H), 6.02 (d, *J* = 2.1 Hz, 1H), 4.34 – 4.21 (m, 2H), 3.96 (d, *J* = 8.7 Hz, 1H), 3.06 (d, *J* = 8.4 Hz, 1H), 1.64 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 170.6, 166.3, 149.0, 138.9, 132.0, 130.5, 129.7, 128.8, 128.4, 126.9, 123.9, 116.7, 116.4, 84.9, 61.8, 40.2, 38.7, 37.9, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}BrNNaO_5$ $[M+Na]^+$, 508.0736; found 508.0730.

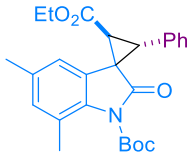
General procedure **3** for synthesis of chiral product **3d**, d.r. = 4:1(The d.r. value was determined via $^1$H NMR analysis of the crude mixture), isolated yield of major isomer

(52%, 10.1 mg).

$[\alpha]_D^{25}$ = +3.482 (c = 1.0 in $CHCl_3$).

**HPLC** analysis: 83:17 e.r. (Chiralcel OD-H, 2:98 *i*-PrOH/*n*-Hexane, 0.8 mL/min), Rt (major) = 10.2 min, Rt (minor) = 12.9 min.

**1'-(Tert-butyl) 2-ethyl (*trans*)-5',7'-dimethyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3e):**



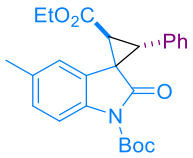

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 120.3-121.6 ℃, d.r. > 20:1, (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (56%, 24.4 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.33 – 7.27 (m, 3H), 7.22 – 7.13 (m, 2H), 6.80 (dt, *J* = 1.8, 0.8 Hz, 1H), 5.59 – 5.54 (m, 1H), 4.36 – 4.15 (m, 2H), 3.95 – 3.88 (m, 1H), 2.99 (d, *J* = 8.3 Hz, 1H), 2.21 (s, 3H), 1.98 (s, 3H), 1.64 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 166.8, 133.0, 132.8, 131.3, 129.9, 128.5, 127.9, 125.8, 123.0, 119.3, 84.7, 61.5, 39.3, 38.5, 38.4, 27.8, 20.8, 19.5, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{26}H_{29}NNaO_5$ $[M+Na]^+$, 458.1943; found 458.1938.

**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-methyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3f):**



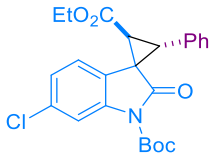

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 137.6-138.1 ℃, d.r. = 10:1, (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (67%, 28.2 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.72 (d, $J$ = 8.4 Hz, 1H), 7.30 (qd, $J$ = 4.9, 1.7 Hz, 3H), 7.22 – 7.11 (m, 2H), 7.02 – 6.94 (m, 1H), 5.76 – 5.69 (m, 1H), 4.27 (qt, $J$ = 7.1, 3.8 Hz, 2H), 3.93 (d, $J$ = 8.4 Hz, 1H), 3.02 (d, $J$ = 8.4 Hz, 1H), 2.02 (s, 3H), 1.65 (s, 9H), 1.30 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.6, 166.8, 149.2, 137.6, 133.2, 132.7, 129.8, 128.5, 128.1, 128.0, 124.6, 121.6, 114.6, 84.3, 61.7, 39.7, 38.4, 38.3, 28.2, 20.9, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{25}H_{27}NNaO_5$ $[M+Na]^+$, 444.1787; found 444.1781.

**1'-(Tert-butyl) 2-ethyl (*trans*)-6'-chloro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3g):**



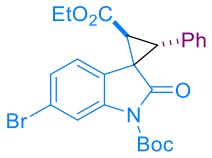

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow solid, m.p. 112.1-115.9 ℃, d.r. = 10:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (89%, 39.33 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.95 (d, $J$ = 1.9 Hz, 1H), 7.30 (dd, $J$ = 5.1, 1.9 Hz, 3H), 7.16 (ddd, $J$ = 6.4, 2.7, 0.9 Hz, 2H), 6.77 (dd, $J$ = 8.2, 2.0 Hz, 1H), 5.85 (d, $J$ = 8.1 Hz, 1H), 4.36 – 4.20 (m, 2H), 3.94 (dt, $J$ = 8.4, 0.9 Hz, 1H), 3.06 (d, $J$ = 8.4 Hz, 1H), 1.66 (s, 9H), 1.30 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.0, 166.4, 148.9, 140.8, 133.6, 132.3, 129.7, 128.8, 128.2, 123.7, 123.1, 121.5, 115.6, 85.0, 61.8, 40.0, 38.5, 38.0, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}ClNNaO_5$ $[M+Na]^+$, 464.1241; found 464.1235.

**1'-(Tert-butyl) 2-ethyl (*trans*)-6'-bromo-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3h):**



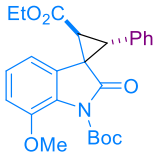

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow solid, m.p. 125.1-126.8 ℃, d.r. = 10:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (78 %, 37.9 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.10 (d, $J$ = 1.8 Hz, 1H), 7.30 (dd, $J$ = 5.1, 1.9 Hz, 3H), 7.20 – 7.11 (m, 2H), 6.92 (dd, $J$ = 8.2, 1.8 Hz, 1H), 5.79 (d, $J$ = 8.1 Hz, 1H), 4.28 (p, $J$ = 7.2 Hz, 2H), 3.97 – 3.91 (m, 1H), 3.06 (d, $J$ = 8.4 Hz, 1H), 1.66 (s, 9H), 1.30 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 170.8, 166.4, 148.9, 140.9, 132.2, 129.7, 128.8, 128.2, 126.6, 123.6, 121.9, 121.5, 118.4, 85.0, 61.8, 40.0, 38.5, 38.1, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}BrNNaO_5$ $[M+Na]^+$, 508.0736; found 508.0730.

**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-methoxy-2'-oxo-3 phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3i):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow oil, d.r. = 5:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (70%, 30.6 mg).

**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.35 – 7.27 (m, 3H), 7.22 – 7.16 (m, 2H), 6.80 – 6.68 (m, 2H), 5.59 (dd, $J$ = 7.2, 1.4 Hz, 1H), 4.34 – 4.16 (m, 2H), 3.97 – 3.91 (m, 1H), 3.84 (s, 3H), 3.04 (d, $J$ = 8.4 Hz, 1H), 1.62 (s, 9H), 1.28 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.6, 166.6, 145.6, 132.8, 129.8, 128.6, 128.0, 126.8, 124.1, 113.7, 111.5, 84.4, 61.6, 55.8, 39.2, 38.6, 38.2, 27.7, 14.2.

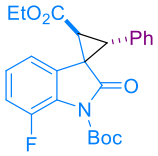
**HRMS (ESI, m/z)**: Mass calculated for $C_{25}H_{27}NNaO_6$ $[M+Na]^+$, 460.1736; found 460.1731.

General procedure **3** for synthesis of chiral product **3f**, d.r. = 2:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), isolated yield of major isomer (47%, 8.22 mg).

$[\alpha]_D^{25}$ = +3.541 (c = 1.0 in $CHCl_3$).

**HPLC** analysis: 79:21 e.r. (Chiralcel OD-H, 2:98 *i*-PrOH/*n*-Hexane, 0.8 mL/min), Rt (major) = 23.3 min, Rt (minor) = 29.4 min.

**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-fluoro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3j):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 132.9-137.8 ℃, d.r. = 8:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (78%, 33.2 mg).

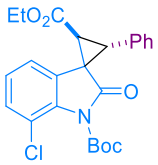
**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.31 (dd, $J$ = 5.1, 2.0 Hz, 3H), 7.18 (ddd, $J$ = 6.5, 2.7, 0.9 Hz, 2H), 6.95 (ddd, $J$ = 11.3, 8.5, 1.1 Hz, 1H), 6.75 (ddd, $J$ = 8.4, 7.6, 4.4 Hz, 1H), 5.75 (dd, $J$ = 7.6, 1.1 Hz, 1H), 4.36 – 4.20 (m, 2H), 3.97 (dt, $J$ = 8.5, 1.0 Hz, 1H), 3.08 (d, $J$ = 8.4 Hz, 1H), 1.63 (s, 9H), 1.30 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 170.91, 166.30, 149.71, 147.55, 147.22, 132.28, 129.77, 128.69, 128.19, 127.97, 127.94, 126.74, 126.64, 124.61, 124.54, 116.75, 116.71, 116.20, 116.00, 85.11, 61.84, 40.06, 38.74, 27.73, 14.16.

**$^{19}$F NMR (377 MHz, Chloroform-*d*)** $\delta$: -119.90.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}FNNaO_5$ $[M+Na]^+$, 448.1536; found 448.1531.

**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-chloro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3k):**



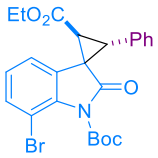

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 107.7-109.9 ℃, d.r. = 12:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (79%, 34.9 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.30 (dd, $J$ = 5.1, 1.9 Hz, 3H), 7.22 – 7.13 (m, 3H), 6.71 (dd, $J$ = 8.2, 7.6 Hz, 1H), 5.84 (dd, $J$ = 7.6, 1.1 Hz, 1H), 4.36 – 4.17 (m, 2H), 4.00 – 3.94 (m, 1H), 3.08 (d, $J$ = 8.4 Hz, 1H), 1.65 (s, 9H), 1.29 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.4, 166.2, 148.1, 137.0, 132.2, 129.8, 129.4, 128.7, 128.2, 128.0, 124.2, 119.4, 118.3, 85.6, 61.8, 39.7, 38.6, 38.3, 27.7, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}ClNNaO_5$ $[M+Na]^+$, 464.1241; found 464.1235.

**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-bromo-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3l):**



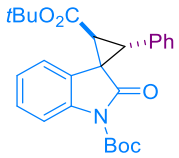

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 95.5-96.9 ℃, d.r. > 20:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (72%, 35.0 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.34 (dd, $J$ = 8.2, 1.1 Hz, 1H), 7.30 (dd, $J$ = 5.1, 1.9 Hz, 3H), 7.18 (ddd, $J$ = 6.4, 3.3, 1.6 Hz, 2H), 6.64 (t, $J$ = 7.9 Hz, 1H), 5.88 (dd, $J$ = 7.6, 1.1 Hz, 1H), 4.37 – 4.17 (m, 2H), 3.97 (dd, $J$ = 8.5, 1.1 Hz, 1H), 3.07 (d, $J$ = 8.4 Hz, 1H), 1.66 (s, 9H), 1.29 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.6, 166.2, 148.0, 138.6, 132.6, 132.2, 129.8, 128.7, 128.3, 128.2, 124.5, 119.9, 106.1, 85.6, 61.8, 39.8, 38.6, 38.4, 27.8, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}BrNNaO_5$ $[M+Na]^+$, 508.0736; found 508.0730.

**Di-tert-butyl (*trans*)-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3m):**



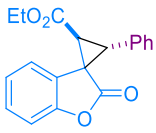

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow oil, d.r. = 5:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (91%, 36.0 mg).

**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.87 (dt, $J$ = 8.3, 0.8 Hz, 1H), 7.30 – 7.11 (m, 6H), 6.78 (td, $J$ = 7.6, 1.0 Hz, 1H), 5.93 (dd, $J$ = 7.7, 1.3 Hz, 1H), 3.88 (dd, $J$ = 8.4, 0.9 Hz, 1H), 2.99 (d, $J$ = 8.5 Hz, 1H), 1.65 (s, 9H), 1.50 (s, 9H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 165.7, 132.9, 129.8, 128.6, 127.9, 127.5, 123.5, 120.8, 114.7, 84.2, 82.2, 39.9, 39.7, 38.3, 28.2, 28.1.

**HRMS (ESI, m/z)**: Mass calculated for $C_{26}H_{29}NNaO_5$ $[M+Na]^+$, 458.1938; found 458.1938.

**Ethyl (*trans*)-2-oxo-3'-phenyl-2H-spiro[benzofuran-3,1'-cyclopropane]-2'-carboxylate (3n):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow solid, m.p. 94.5-96.6 ℃, d.r. = 3:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (62%, 17.4 mg).

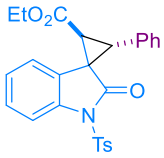
**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.33 (dd, $J$ = 5.0, 1.9 Hz, 3H), 7.20 (ddt, $J$ = 6.5, 3.6, 1.8 Hz, 3H), 7.13 (dd, $J$ = 8.1, 1.1 Hz, 1H), 6.81 (td, $J$ = 7.6, 1.1 Hz,

1H), 5.99 (dd, *J* = 7.6, 1.3 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.01 (dd, *J* = 8.3, 1.1 Hz, 1H), 3.13 (d, *J* = 8.3 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** *δ*: 173.0, 166.1, 153.8, 129.6, 128.8, 128.4, 128.4, 123.7, 121.3, 110.6, 62.0, 39.5, 38.2, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{19}H_{16}NaO_4$ $[M+H]^+$, 331.0946; found 331.0941.

**Ethyl (*trans*)-2'-oxo-3-phenyl-1'-tosylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (3o):**



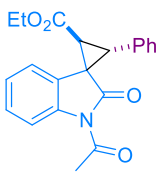

Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 30/1). Colorless crystal, m.p. 218.7-219.6 ℃, d.r. >10:1, (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (60%, 27.7mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** *δ*: 7.90 (dd, *J* = 14.4, 8.2 Hz, 3H), 7.27 – 7.12 (m, 6H), 7.03 – 6.97 (m, 2H), 6.72 (t, *J* = 7.6 Hz, 1H), 5.84 (d, *J* = 7.7 Hz, 1H), 4.07 (qd, *J* = 7.1, 4.3 Hz, 2H), 3.79 (d, *J* = 8.4 Hz, 1H), 2.93 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** *δ*: 171.59, 166.32, 145.87, 139.63, 135.61, 132.29, 129.99, 129.96, 128.92, 128.45, 128.36, 128.28, 124.95, 124.33, 121.52, 113.82, 61.96, 40.20, 38.11, 21.97, 14.27, 1.29.

**HRMS (ESI, m/z)**: Mass calculated for $C_{26}H_{23}NNaO_5S$ $[M+Na]^+$, 484.1189; found 484.1190.

**Ethyl (*trans*)-1'-acetyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (3p):**




Purification by flash column chromatography on silica gel (petroleum ether / ethyl

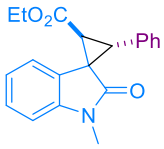
acetate = 30/1). Colorless crystal, m.p. 85.8-88.2 ℃, d.r. = 5:1, (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (64%, 22.36mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.29 – 8.13 (m, 1H), 7.26 – 7.06 (m, 6H), 6.77 (td, $J$ = 7.7, 1.1 Hz, 1H), 5.90 (dd, $J$ = 7.7, 1.3 Hz, 1H), 4.21 (qd, $J$ = 7.2, 2.2 Hz, 2H), 3.88 (d, $J$ = 8.4 Hz, 1H), 3.03 (d, $J$ = 8.5 Hz, 1H), 2.65 (s, 3H), 1.24 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 173.24, 166.33, 154.06, 132.18, 129.87, 129.04, 128.67, 128.62, 123.92, 121.61, 110.91, 62.27, 39.72, 38.47, 36.13, 14.44.

**HRMS (ESI, m/z)**: Mass calculated for $C_{21}H_{19}NNaO_4$ $[M+Na]^+$, 372.1206; found 372.1206.

**Ethyl (*trans*)-1'-methyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (3q):**



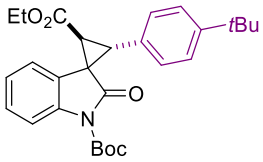

Purification by flash column chromatography on silica gel (petroleum ether / ethyl acetate = 30/1). Colorless crystal, m.p. 110.3-112.8 ℃, d.r. = 4:1, (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (70%, 22.5 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.34 – 7.23 (m, 3H), 7.18 (ddd, $J$ = 7.6, 4.4, 1.2 Hz, 3H), 6.86 (d, $J$ = 7.7 Hz, 1H), 6.70 (td, $J$ = 7.6, 1.0 Hz, 1H), 5.99 (dd, $J$ = 7.6, 1.2 Hz, 1H), 4.26 (qd, $J$ = 7.1, 4.2 Hz,2H), 3.92 (d, $J$ = 8.2 Hz, 1H), 3.07 (d, $J$ = 8.3 Hz, 3H), 1.30 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 172.63, 166.79, 143.62, 132.93, 129.29, 128.14, 127.40, 127.09, 125.29, 121.30, 120.68, 107.61, 61.12, 37.71, 37.54, 36.62, 26.26, 13.82.

**HRMS (ESI, m/z)**: Mass calculated for $C_{20}H_{19}NNaO_3$ $[M+Na]^+$, 344.1257; found 344.1256.

**1'-(Tert-butyl) 3-ethyl (*trans*)-2-(4-(tert-butyl)phenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',3-dicarboxylate (3r):**



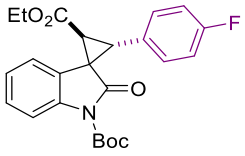

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow solid, m.p. 132.7-137.4 ℃, d.r. = 5:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (53 %, 24.6 mg).

**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.89 – 7.83 (m, 1H), 7.34 – 7.28 (m, 2H), 7.19 (td, $J$ = 7.9, 1.3 Hz, 1H), 7.13 – 7.07 (m, 2H), 6.79 (td, $J$ = 7.6, 1.0 Hz, 1H), 6.00 (dd, $J$ = 7.7, 1.3 Hz, 1H), 4.36 – 4.18 (m, 2H), 3.91 (d, $J$ = 8.4 Hz, 1H), 3.05 (d, $J$ = 8.4 Hz, 1H), 1.66 (s, 9H), 1.29 (s, 9H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.5, 166.8, 151.1, 149.2, 140.0, 129.5, 129.4, 127.6, 125.5, 124.8, 123.6, 120.9, 114.8, 84.4, 61.6, 39.7, 38.6, 38.4, 34.6, 31.3, 28.2, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{28}H_{33}NNaO_5$ $[M+Na]^+$, 486.2256; found 486.2251.

**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(4-fluorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3s):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow solid, m.p. 108.4-112.6 ℃, d.r. = 4:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (75%, 31.9 mg).

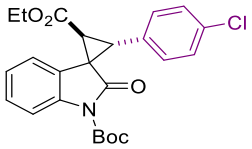
**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.88 (dt, $J$ = 8.2, 0.8 Hz, 1H), 7.22 (td, $J$ = 7.9, 1.3 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.04 – 6.95 (m, 2H), 6.82 (td, $J$ = 7.6, 1.0 Hz, 1H), 5.94 (dd, $J$ = 7.7, 1.3 Hz, 1H), 4.36 – 4.18 (m, 2H), 3.88 (dq, $J$ = 8.3, 1.1 Hz, 1H), 3.01 (d, $J$ = 8.4 Hz, 1H), 1.66 (s, 9H), 1.30 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.30, 166.51, 163.59, 161.13, 149.13, 140.02, 131.54, 131.45, 128.50, 128.47, 127.84, 124.38, 123.71, 120.78, 115.77, 115.55, 114.92, 84.56, 61.75, 38.93, 38.63, 38.23, 28.13, 14.17.

**$^{19}$F NMR (377 MHz, Chloroform-*d*)** $\delta$: -113.45.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}FNNaO_5$ $[M+Na]^+$, 448.1536; found 448.1531.

**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(4-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3t):**



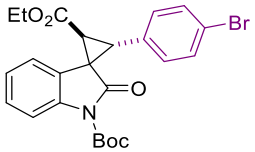

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Pink solid, m.p. 154.2-157.9 ℃, d.r. = 7:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (73%, 32.26 mg).

**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.88 (dt, $J$ = 8.2, 0.8 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.22 (td, $J$ = 7.9, 1.3 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.84 (td, $J$ = 7.6, 1.0 Hz, 1H), 5.96 (dd, $J$ = 7.7, 1.3 Hz, 1H), 4.35 – 4.18 (m, 2H), 3.90 – 3.83 (m, 1H), 3.01 (d, $J$ = 8.3 Hz, 1H), 1.66 (s, 9H), 1.30 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.2, 166.4, 149.1, 140.0, 134.0, 131.2, 131.2, 128.9, 127.9, 124.3, 123.8, 120.8, 115.0, 84.6, 61.8, 38.9, 38.4, 38.2, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}ClNNaO_5$ $[M+Na]^+$, 464.1241; found 464.1235.

**1'-(Tert-butyl) 3-ethyl (*trans*)-2-(4-bromophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',3-dicarboxylate (3u):**



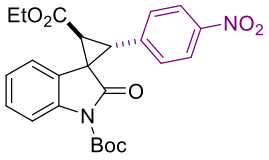
Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 159.8-161.9 ℃, d.r. = 4:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (84%, 40.9 mg).

**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.88 (dt, $J$ = 8.2, 0.8 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.22 (td, $J$ = 7.9, 1.3 Hz, 1H), 7.12 – 7.00 (m, 2H), 6.84 (td, $J$ = 7.6, 1.0 Hz, 1H), 5.97 (dd, $J$ = 7.7, 1.3 Hz, 1H), 4.35 – 4.19 (m, 2H), 3.85 (dd, $J$ = 8.4, 1.0 Hz, 1H), 3.01 (d, $J$ = 8.4 Hz, 1H), 1.65 (s, 9H), 1.30 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.2, 166.4, 149.1, 140.0, 131.8, 131.8, 131.5, 127.9, 124.2, 123.8, 122.1, 120.8, 115.0, 84.6, 61.8, 39.0, 38.4, 38.2, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}BrNNaO_5$ $[M+Na]^+$, 508.0736; found 508.0730.

**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(4-nitrophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3v):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless solid, m.p. 132.6-135.6 ℃, d.r. = 4:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (85%, 38.5 mg).

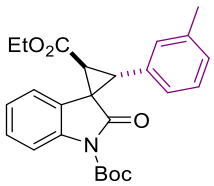
**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 8.18 (d, $J$ = 8.7 Hz, 2H), 7.90 (dt, $J$ = 8.3, 0.8 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.24 (td, $J$ = 7.9, 1.3 Hz, 1H), 6.83 (td, $J$ = 7.6, 1.0 Hz, 1H), 5.92 (dd, $J$ = 7.7, 1.3 Hz, 1H), 4.39 – 4.21 (m, 2H), 3.99 – 3.89 (m, 1H), 3.09 (d, $J$ = 8.4 Hz, 1H), 1.66 (s, 9H), 1.31 (t, $J$ = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 170.8, 166.0, 149.0, 147.6, 140.2, 140.2, 130.9, 128.3, 123.9, 123.9, 123.6, 120.5, 115.2, 84.8, 62.0, 38.7, 38.3, 38.0, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}N_2NaO_7$ $[M+Na]^+$, 475.1481; found 475.1475.

**1'-(Tert-butyl) 2-ethyl (*trans*)-2'-oxo-3-(m-tolyl)spiro[cyclopropane-1,3'**

**indoline]-1',2-dicarboxylate (3w):**



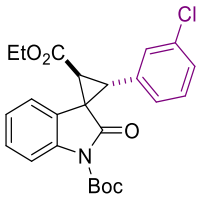

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow oil, d.r. = 9:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (70%, 29.5 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.87 (dt, $J$ = 8.3, 0.7 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.09 (ddd, $J$ = 7.6, 2.0, 1.1 Hz, 1H), 7.00 (dq, $J$ = 1.9, 1.0 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.80 (td, $J$ = 7.6, 1.1 Hz, 1H), 5.99 (dd, $J$ = 7.6, 1.3 Hz, 1H), 4.37 – 4.16 (m, 2H), 3.99 – 3.81 (m, 1H), 3.04 (d, $J$ = 8.4 Hz, 1H), 2.29 (s, 3H), 1.66 (s, 9H), 1.30 (t, $J$ = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.5, 166.8, 149.2, 140.0, 138.3, 132.5, 130.5, 128.8, 128.5, 127.6, 126.8, 124.8, 123.6, 120.9, 114.8, 84.4, 61.7, 39.8, 38.5, 38.3, 28.2, 21.3, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{25}H_{27}NNaO_5$ $[M+Na]^+$, 444.1787; found 444.1781.

**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(3-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3x):**



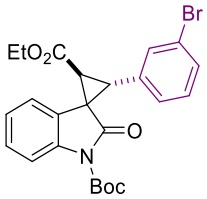

Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless oil, d.r. = 8:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (68%, 30.1 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.94 – 7.81 (m, 1H), 7.30 – 7.17 (m, 4H), 7.03 (dq, *J* = 7.4, 1.3 Hz, 1H), 6.84 (td, *J* = 7.6, 1.0 Hz, 1H), 5.99 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.27 (qd, *J* = 7.1, 4.9 Hz, 2H), 3.94 – 3.81 (m, 1H), 3.03 (d, *J* = 8.3 Hz, 1H), 1.66 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 166.3, 134.7, 134.5, 129.9, 129.8, 128.3, 128.1, 128.0, 124.2, 123.8, 120.8, 115.0, 84.6, 61.8, 39.0, 38.2, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}ClNNaO_5$ $[M+Na]^+$, 464.1241; found 464.1235.

**1'-(Tert-butyl) 3-ethyl (*trans*)-2-(3-bromophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',3-dicarboxylate (3y):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Yellow oil, d.r. = 5:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (77%, 37.5 mg).

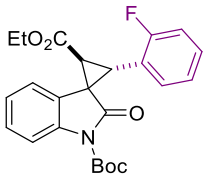
**Major isomer: $^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.88 (dt, *J* = 8.3, 0.7 Hz, 1H), 7.43 (ddt, *J* = 8.0, 1.9, 0.9 Hz, 1H), 7.37 (q, *J* = 1.5 Hz, 1H), 7.23 (td, *J* = 7.9, 1.3 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.07 (ddt, *J* = 7.7, 1.9, 1.0 Hz, 1H), 6.84 (td, *J* = 7.6, 1.0 Hz,

1H), 5.99 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.27 (qd, *J* = 7.1, 4.5 Hz, 2H), 3.88 (dd, *J* = 8.3, 0.9 Hz, 1H), 3.02 (d, *J* = 8.3 Hz, 1H), 1.66 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.1, 166.3, 149.1, 140.0, 135.0, 132.7, 131.2, 130.2, 128.6, 128.0, 124.1, 123.8, 122.6, 120.8, 115.0, 84.6, 61.8, 38.9, 38.2, 38.2, 28.1, 14.2.

**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}BrNNaO_5$ $[M+Na]^+$, 508.0736; found 508.0730.

**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(2-fluorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3z):**




Purification by flash column chromatography over silica gel (petroleum ether / ethyl acetate = 30/1). Colorless oil, d.r. > 20:1 (The d.r. value was determined via $^1$H NMR analysis of the crude mixture), combined yield (75%, 31.9 mg).

**$^1$H NMR (400 MHz, $CDCl_3$)** $\delta$: 7.88 (dt, *J* = 8.2, 0.7 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.18 (dtd, *J* = 24.0, 7.5, 1.3 Hz, 2H), 6.94 (ddd, *J* = 9.6, 8.4, 1.2 Hz, 1H), 6.79 (td, *J* = 7.6, 1.0 Hz, 1H), 5.96 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.29 (qd, *J* = 7.1, 4.5 Hz, 2H), 3.79 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.05 (d, *J* = 8.4 Hz, 1H), 1.66 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** $\delta$: 171.16, 166.48, 163.30, 160.82, 149.14, 140.06, 130.82, 130.78, 130.12, 130.04, 127.87, 124.57, 124.15, 124.12, 123.64, 120.48, 120.34, 119.85, 115.84, 115.63, 114.96, 84.47, 61.77, 37.77, 37.75, 37.70, 34.40, 34.38, 28.14, 14.17.

**$^{19}$F NMR (377 MHz, Chloroform-*d*)** $\delta$: -114.20.

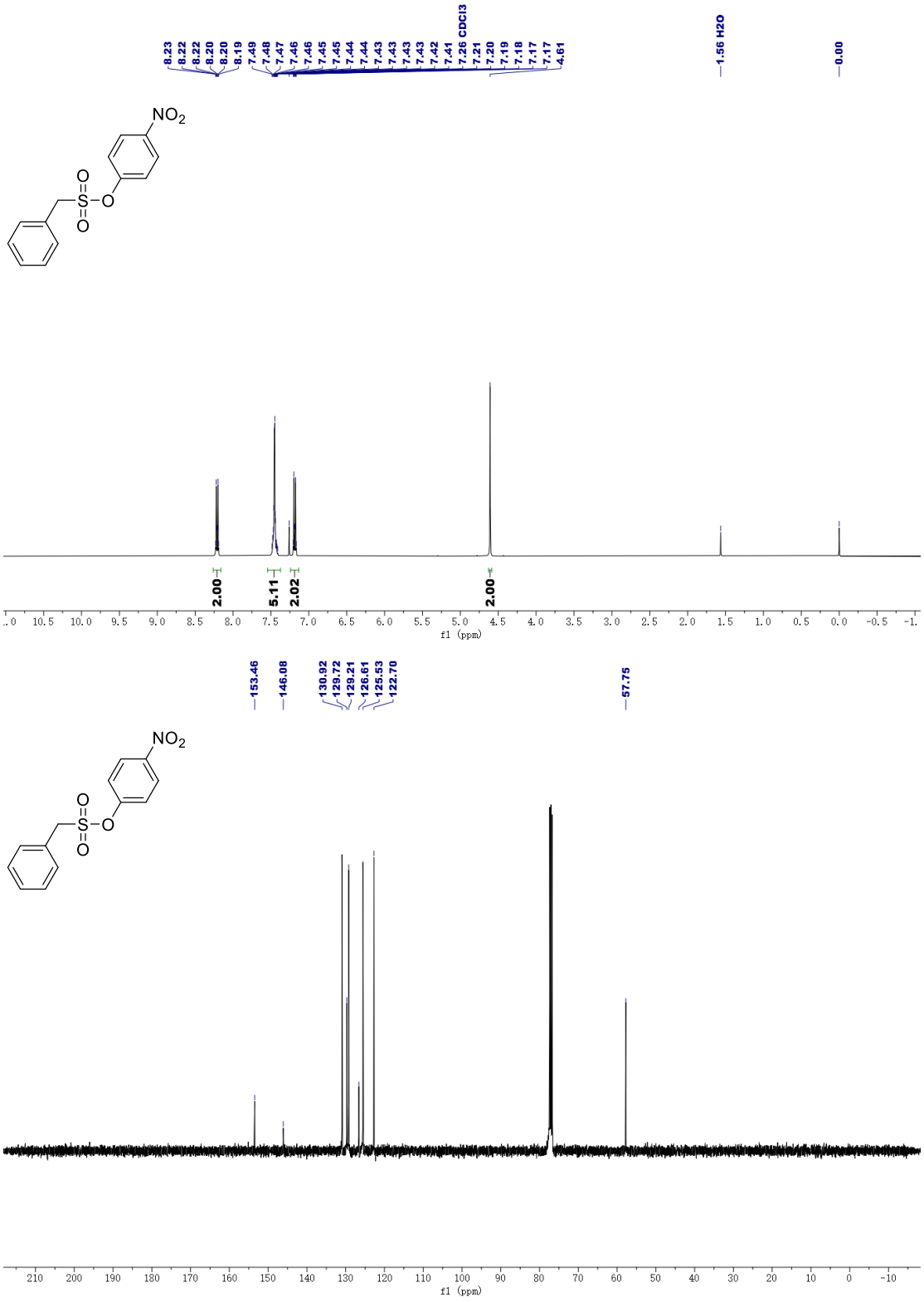
**HRMS (ESI, m/z)**: Mass calculated for $C_{24}H_{24}FNaNO_4$ $[M+Na]^+$, 448.1531; found 448.1532.

**References**

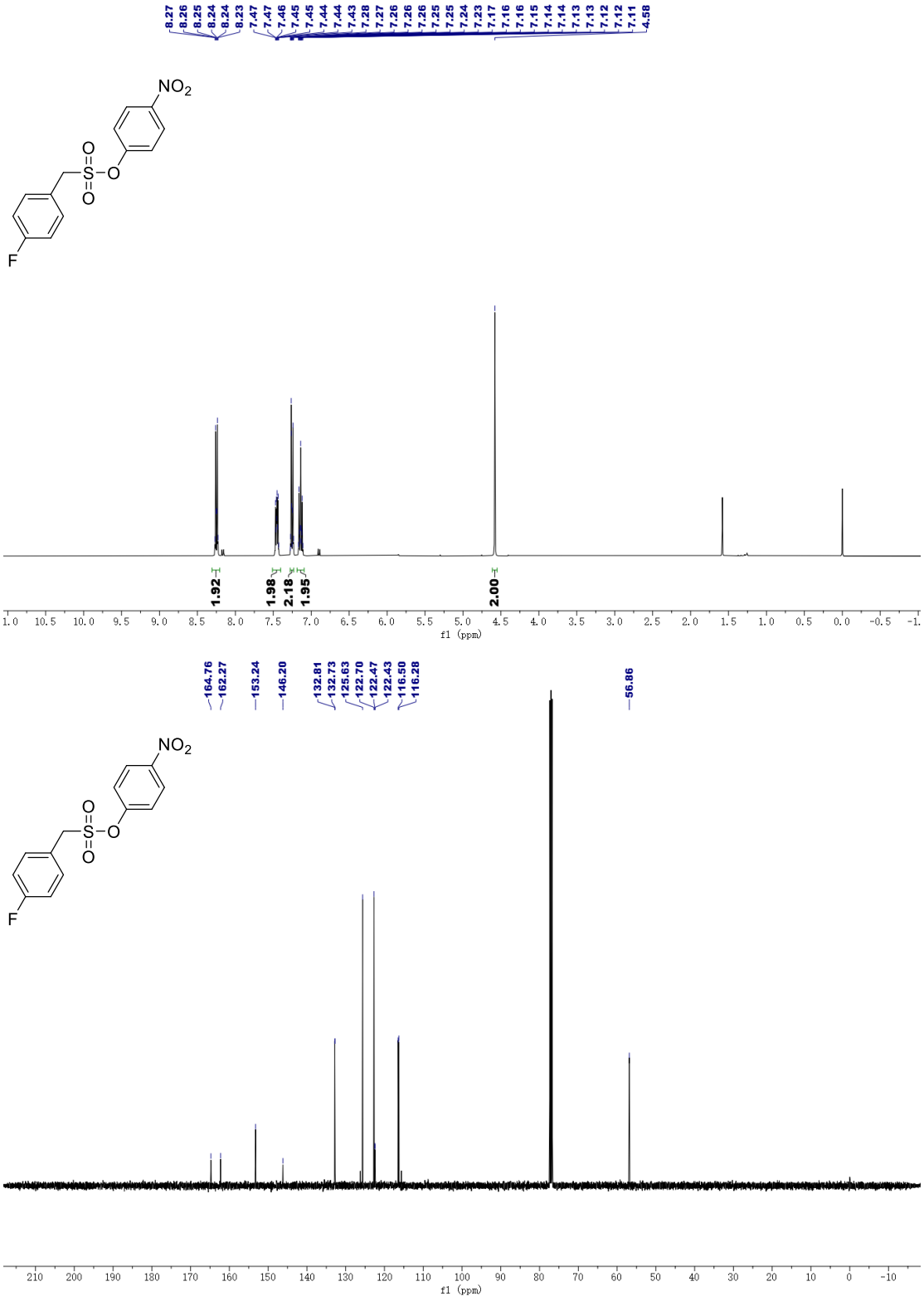

1. M.-M. Zhou, J.-J. Liu, R. Deng, Q.-Y. Wang, S.-Q. Wu, P. Zheng, and Y. R. Chi, Construction of Tetrasubstituted Silicon-Stereogenic Silanes via Conformational Isomerization and N-Heterocyclic Carbene Catalyzed Desymmetrization. *ACS Catal.* **2022**, *12*, 7781.
2. Y. Wang, S. Wang, P. Qiu, L. Fang, K. Wang, Y. Zhang, C. Zhang and T. Zhao, Asymmetric α-Electrophilic Difluoromethylation of β-keto Esters by Phase Transfer Catalysis. *Org. Biomol. Chem*., **2021**, *19*, 4788
3. C. Yang, W. Zhang, Y. Li, X. Xue, X. Li and J. Cheng, Origin of Stereoselectivity of the Photoinduced Asymmetric Phase-Transfer-Catalyzed Perfluoroalkylation of β-Ketoesters, *J. Org. Chem*., **2017**, *82*, 9321.
4. Y. Wang, Z. Zheng, M. Lian, H. Yin, J. Zhao, Q. Meng and Z. Gao, Photo-Organocatalytic Enantioselective α-hydroxylation of β-keto Esters and β-keto Amides withOxygen under Phase Transfer Catalysis, *Green Chem*., **2016**, *18*, 5493.
5. Y.-L. Chen, T.-T. Li, Z.-C. Jin and Y. R. Chi, New Axially Chiral Molecular Scaffolds with Antibacterial Activities against Xanthomonas oryzae pv. oryzae for Protection of Rice. *J. Agric. Food Chem.* **2022**, *70*, 6050
6. Q. Liu and K. P. Teng, Facile Approach for the Oxidative Enolate Activation of Aliphatic Aldehydes. *J. Org. Chem,* **2023**, *88*, 2404.

# 4. Copies of $^{1}H$, $^{19}F$ and $^{13}C$ NMR spectra

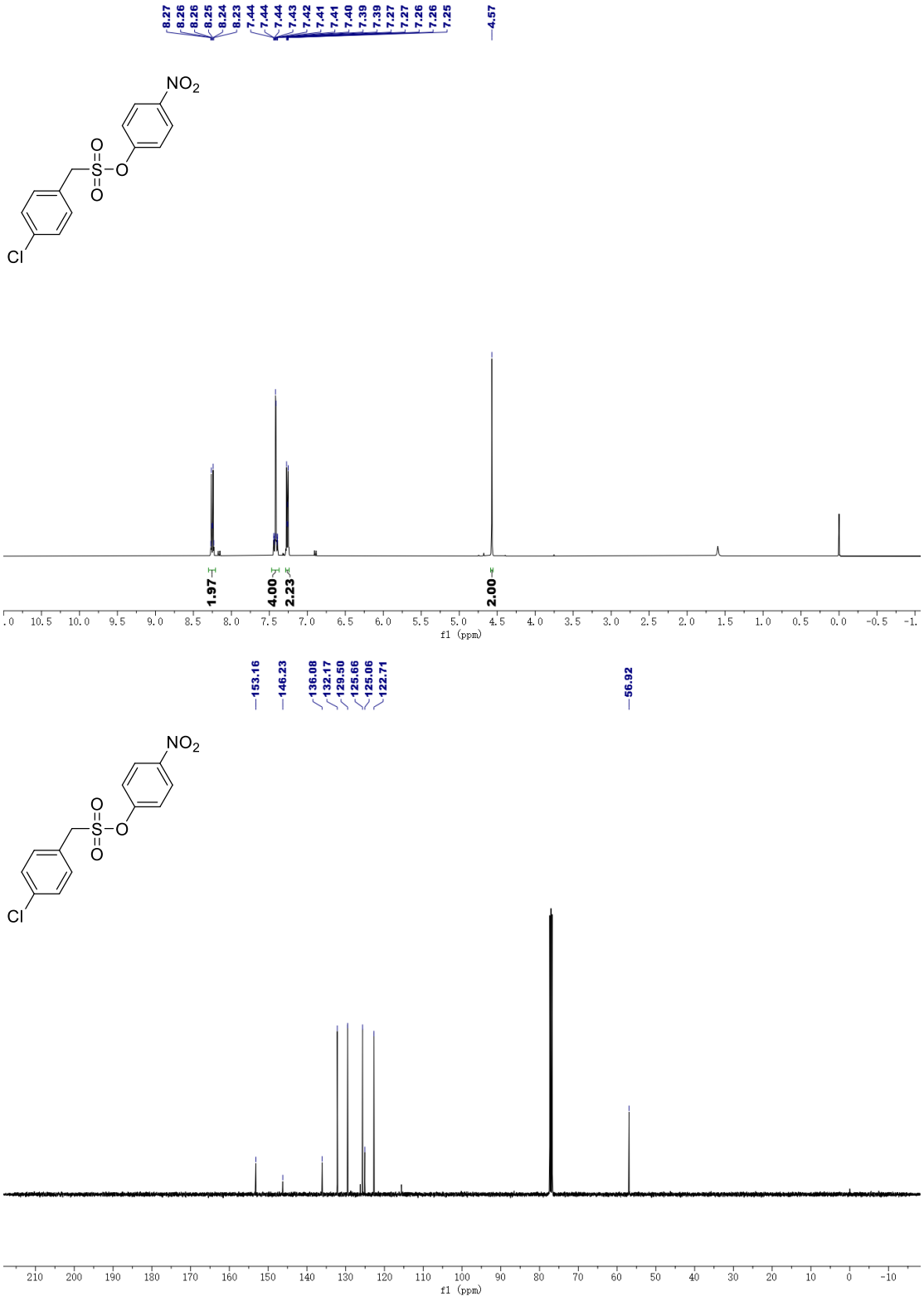
## 4-Nitrophenyl phenylmethanesulfonate (1a):



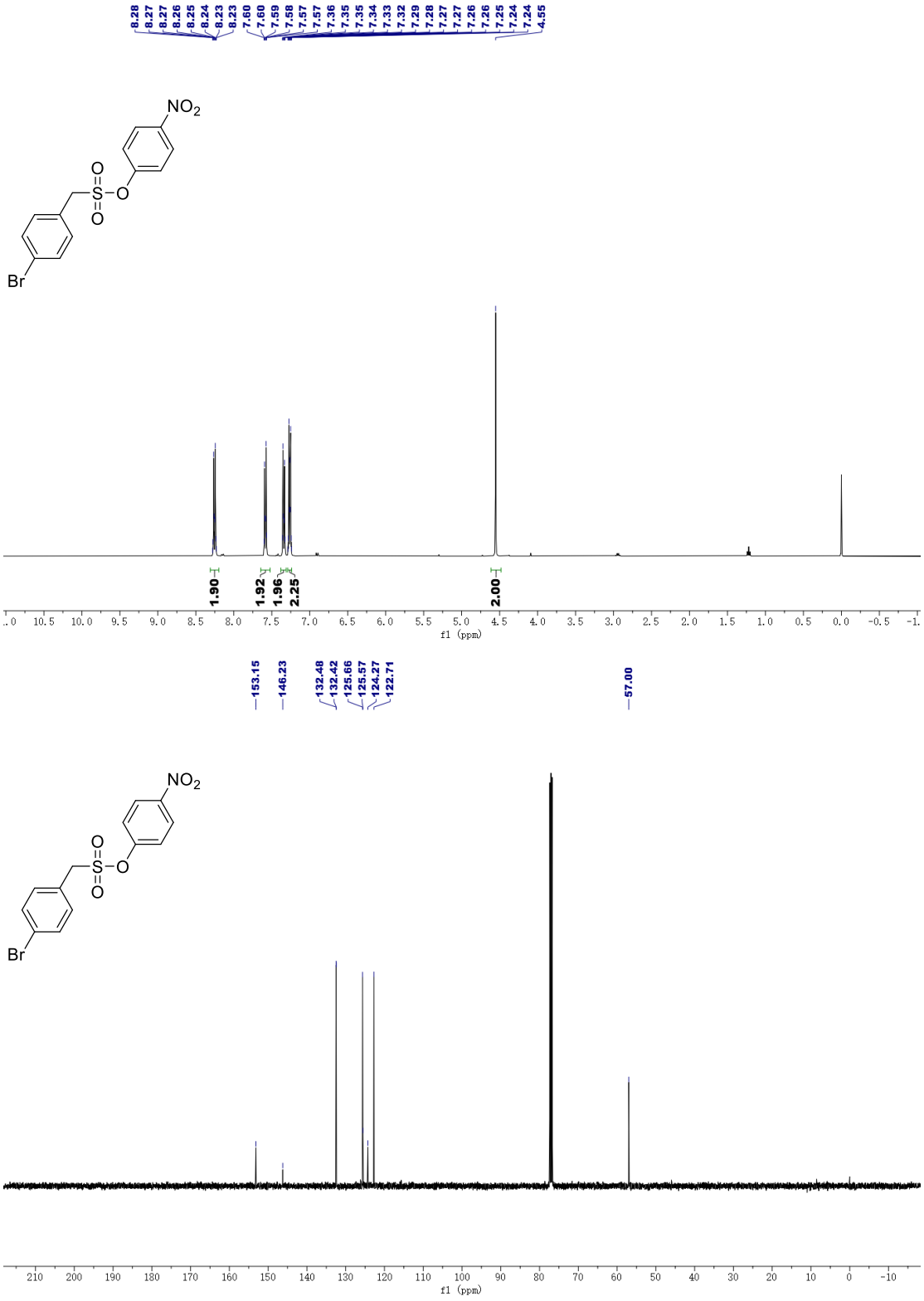
## 4-Nitrophenyl (4-fluorophenyl)methanesulfonate (1b):



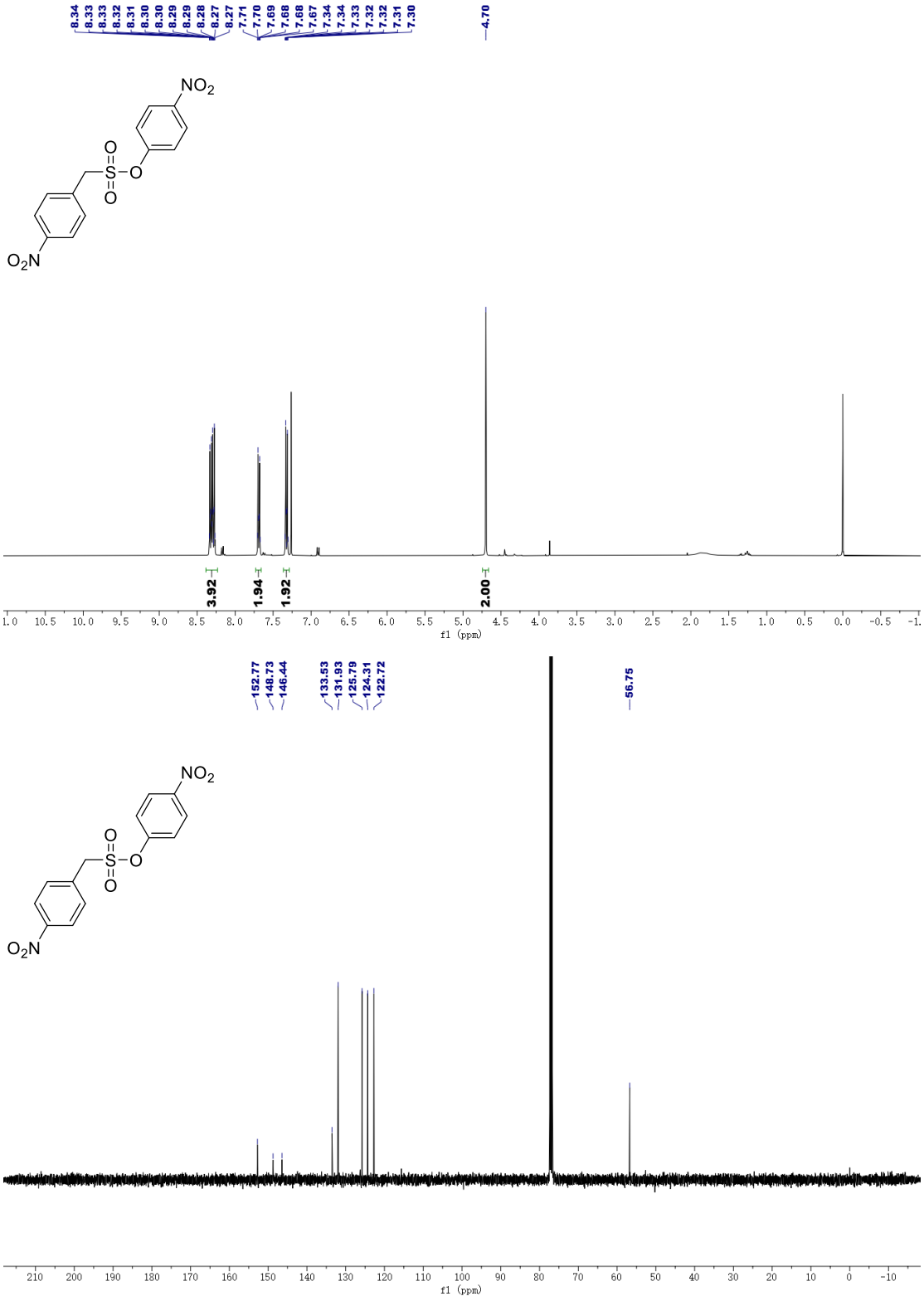
**4-Nitrophenyl (4-chlorophenyl)methanesulfonate (1c):**



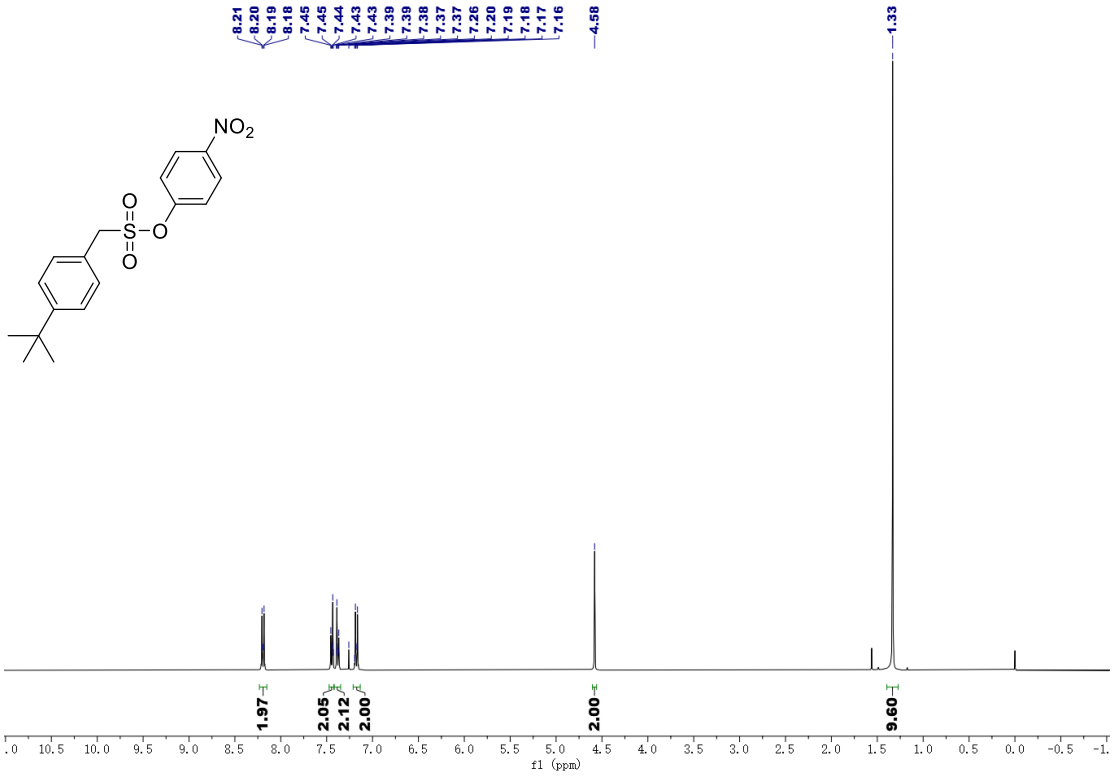
**4-Nitrophenyl (4-bromophenyl)methanesulfonate (1d):**

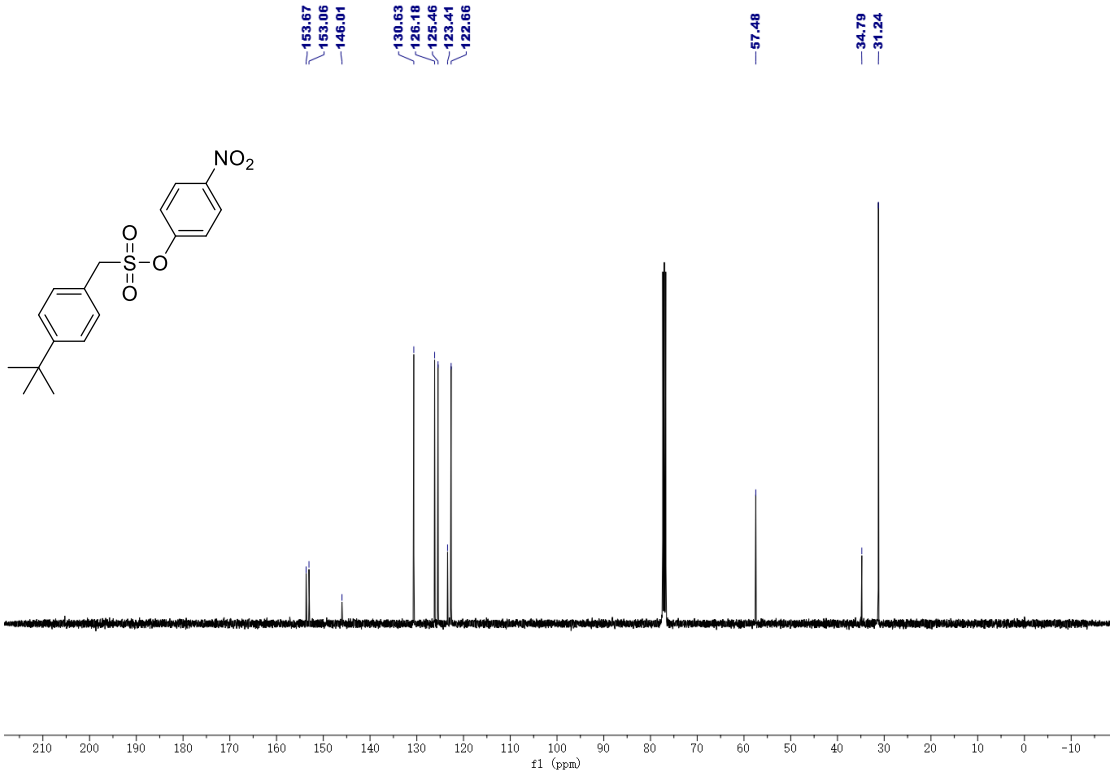


**4-Nitrophenyl (4-nitrophenyl)methanesulfonate (1e):**

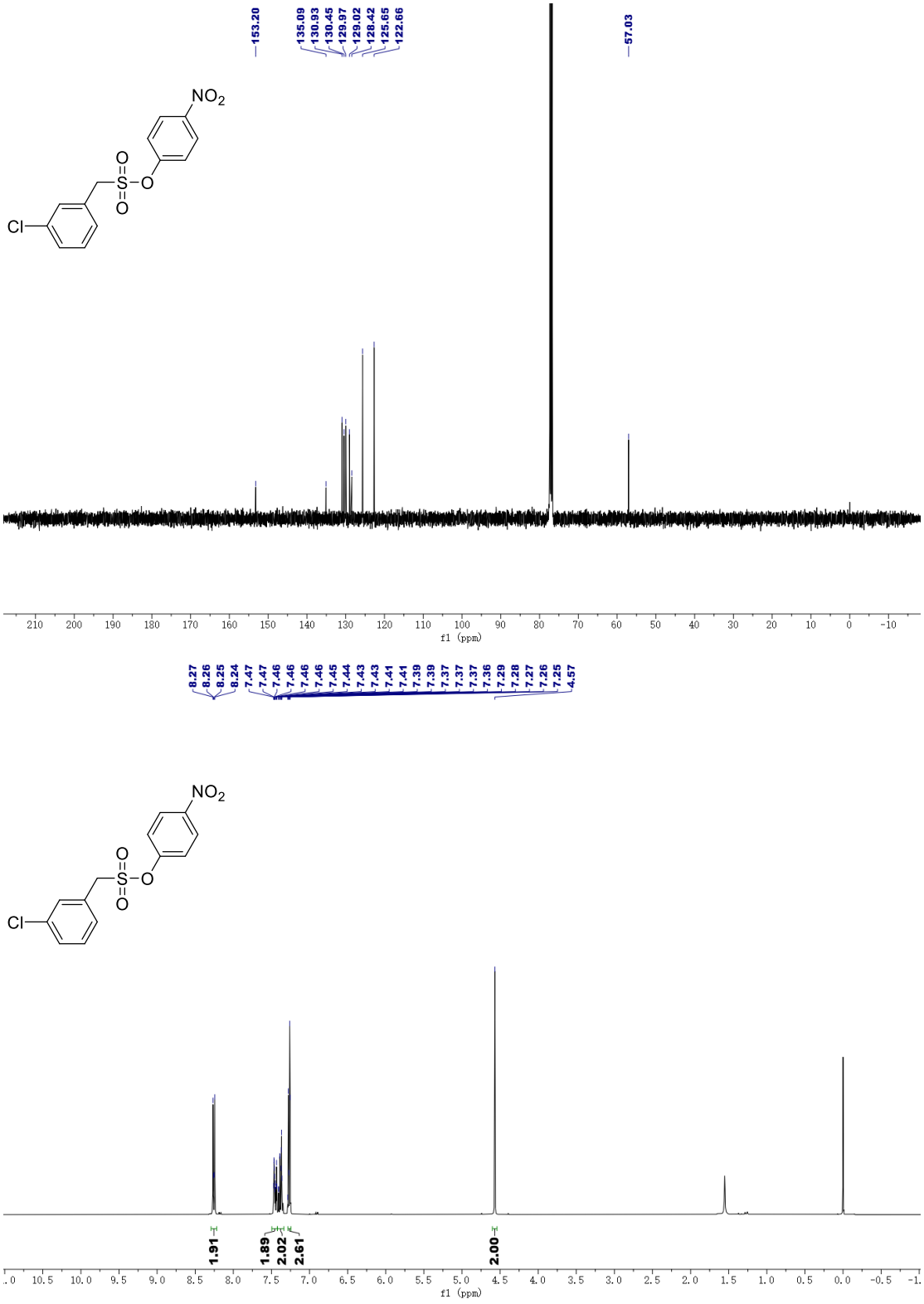


**4-Nitrophenyl (4-(tert-butyl)phenyl)methanesulfonate (1f):**

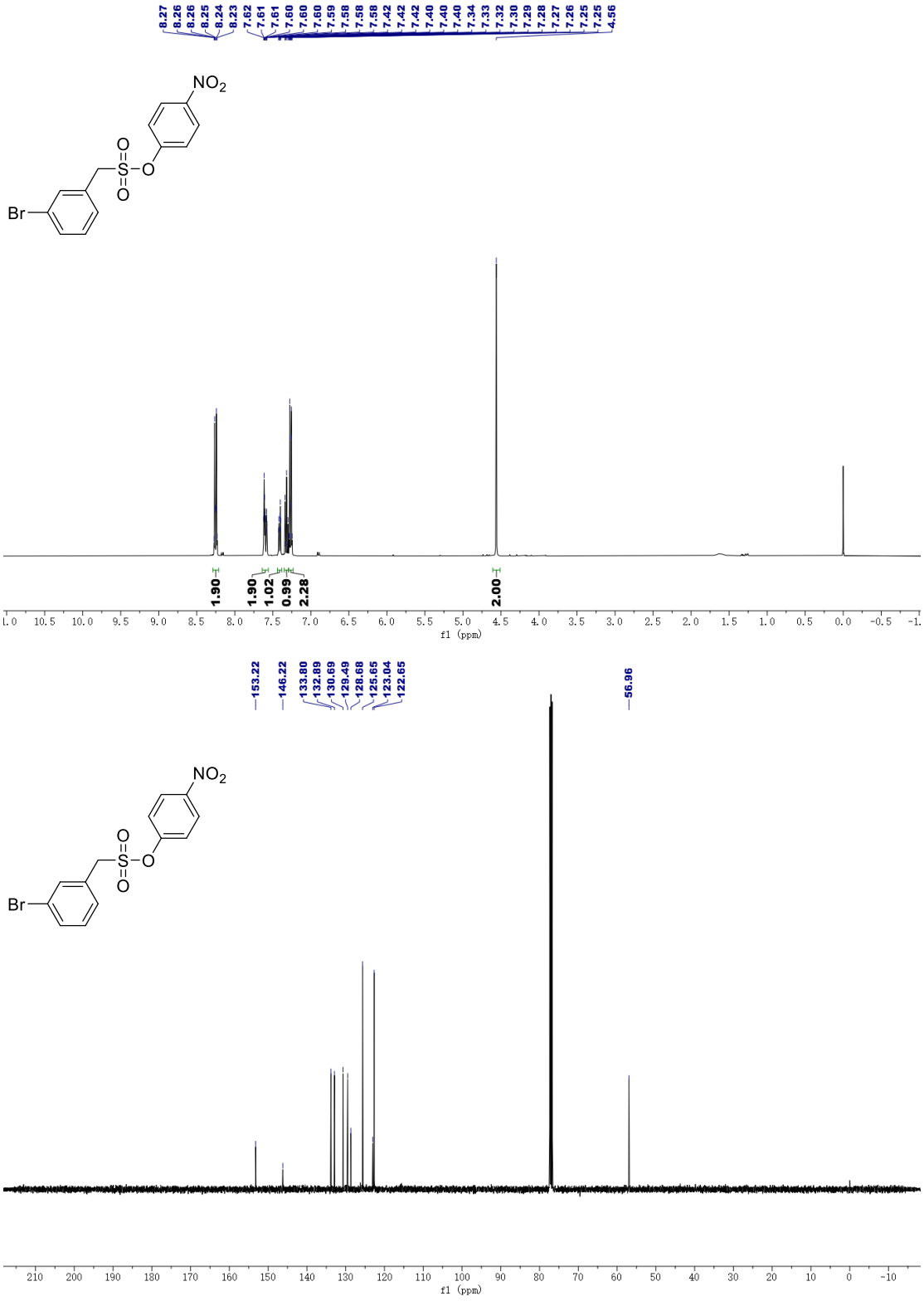


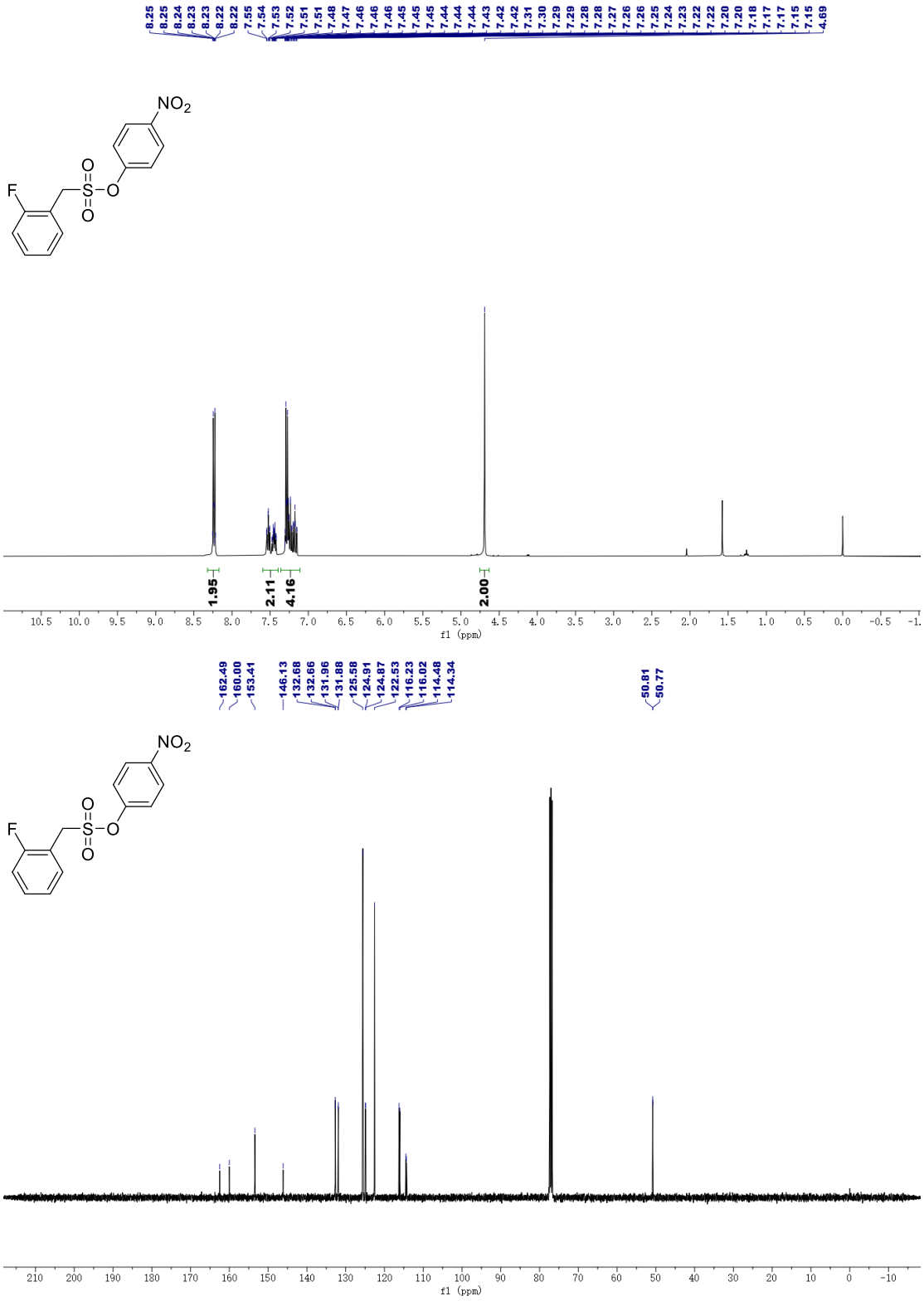
**4-Nitrophenyl (3-chlorophenyl)methanesulfonate (1g):**



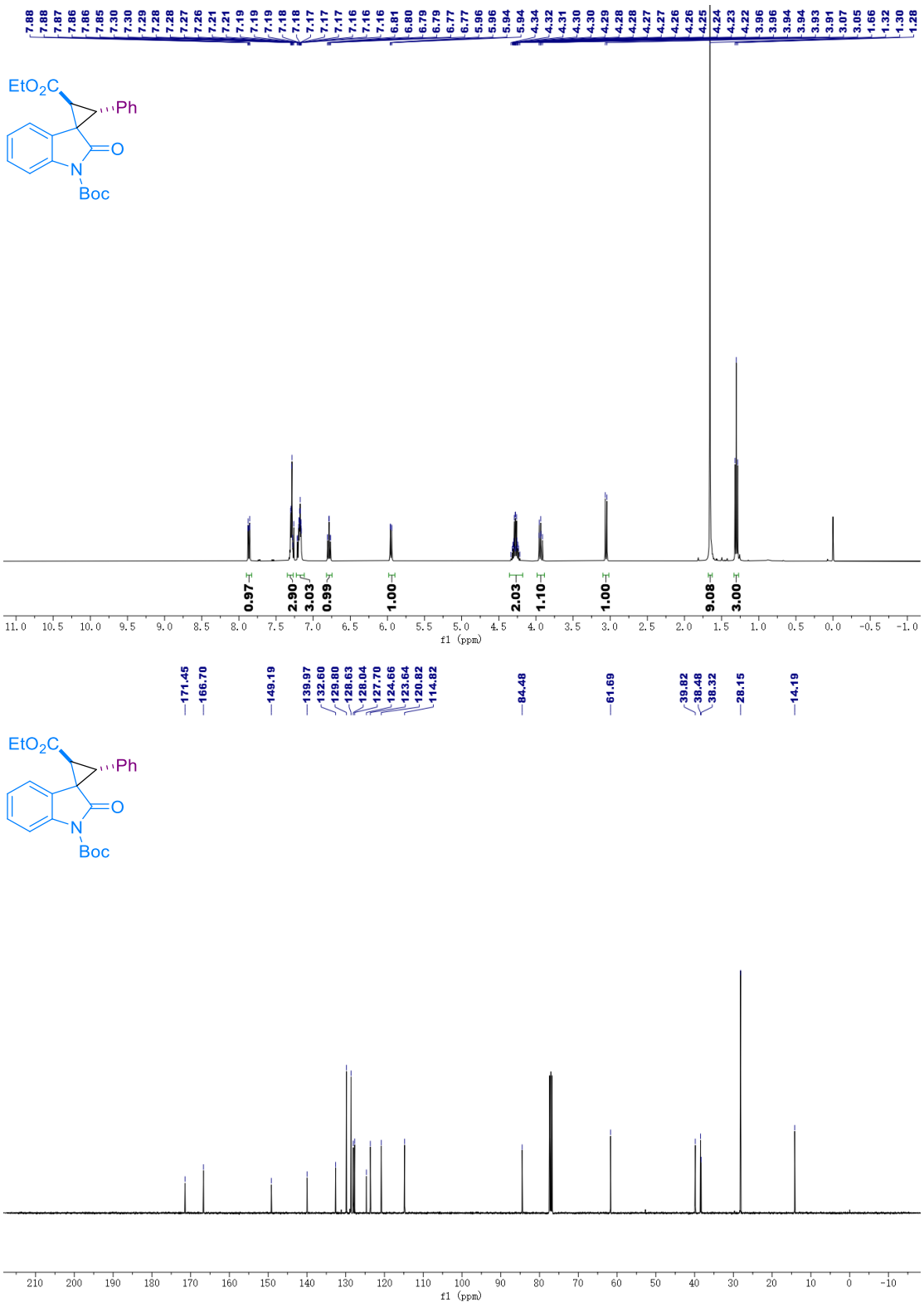
**4-Nitrophenyl (3-bromophenyl)methanesulfonate (1h):**



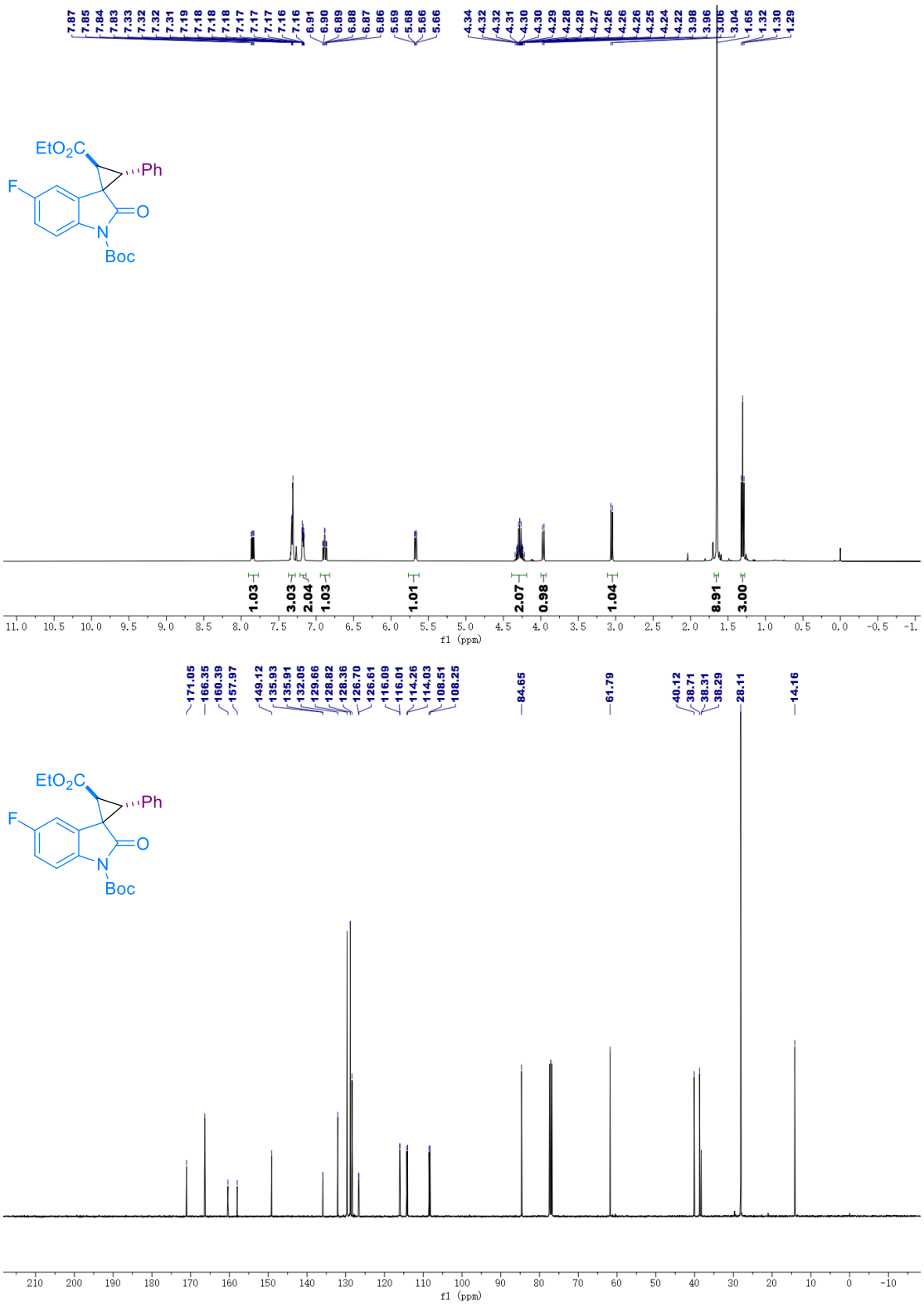
**4-Nitrophenyl (2-fluorophenyl)methanesulfonate (1i):**

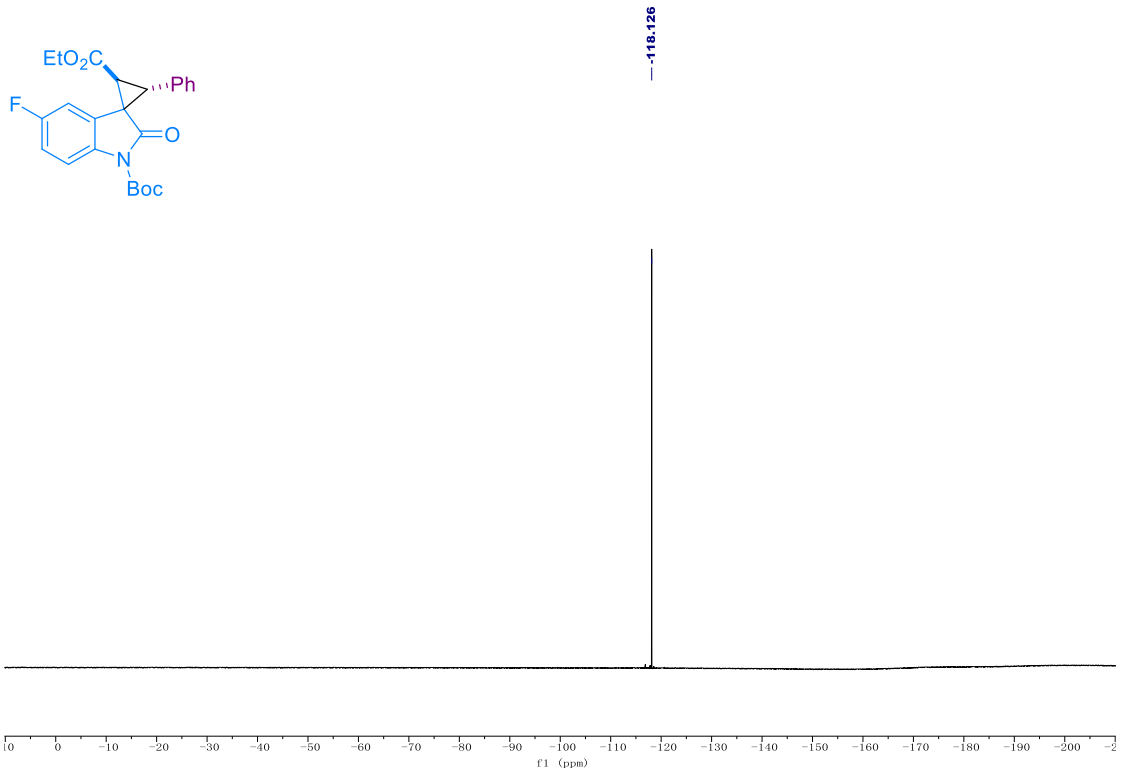


**1'-(Tert-butyl) 2-ethyl (*trans*)-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3a):**



**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-fluoro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3b):**




EtO2C
Ph
F
O
N
Boc
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0
-10
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-30
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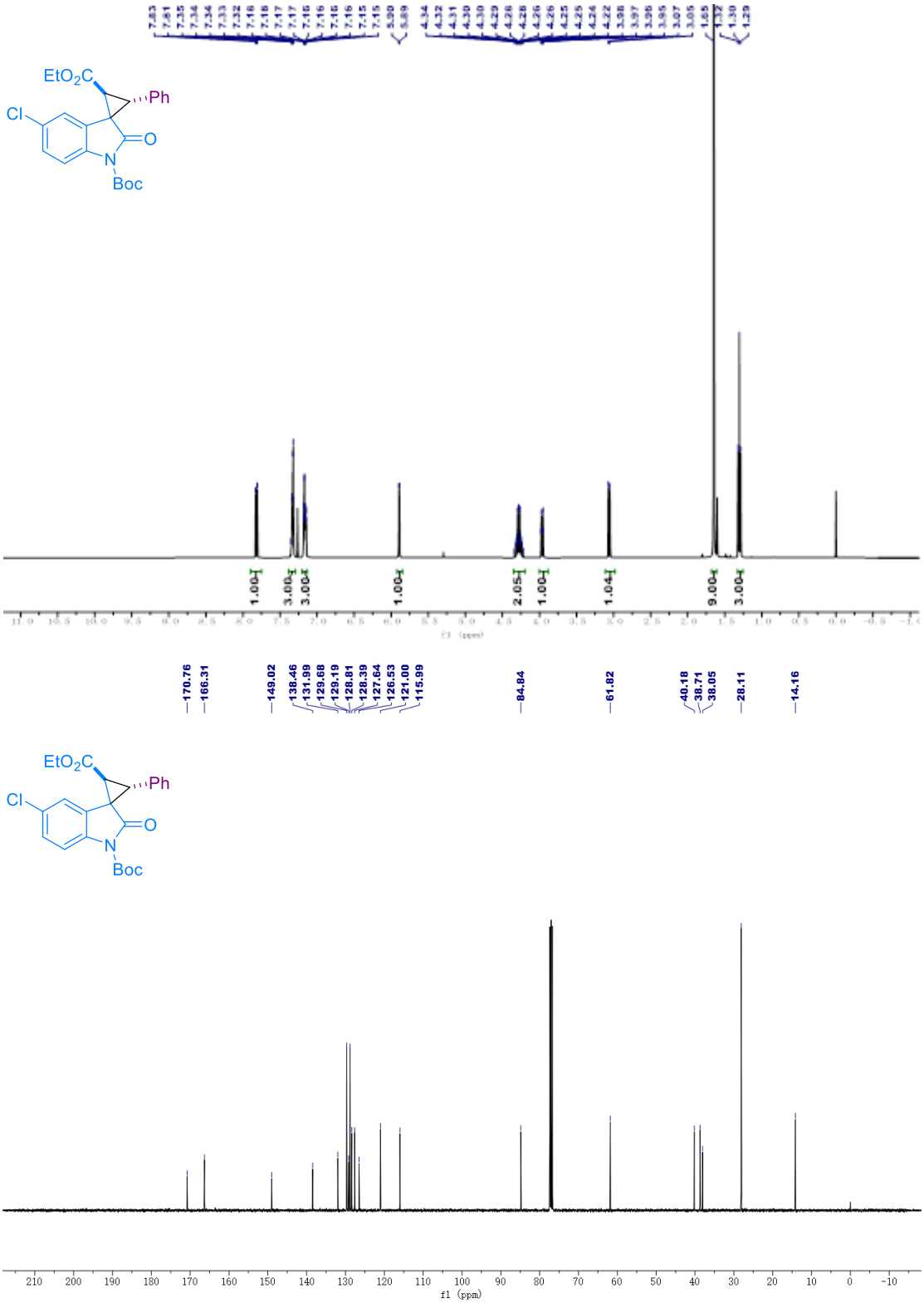
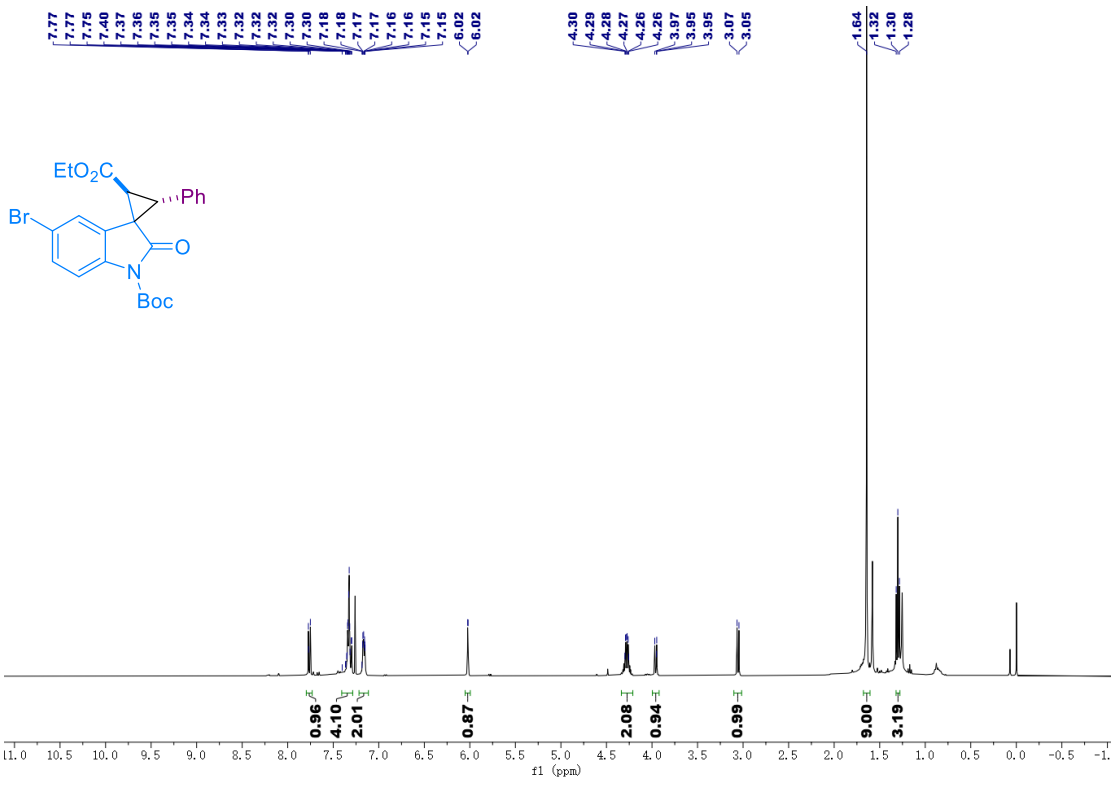
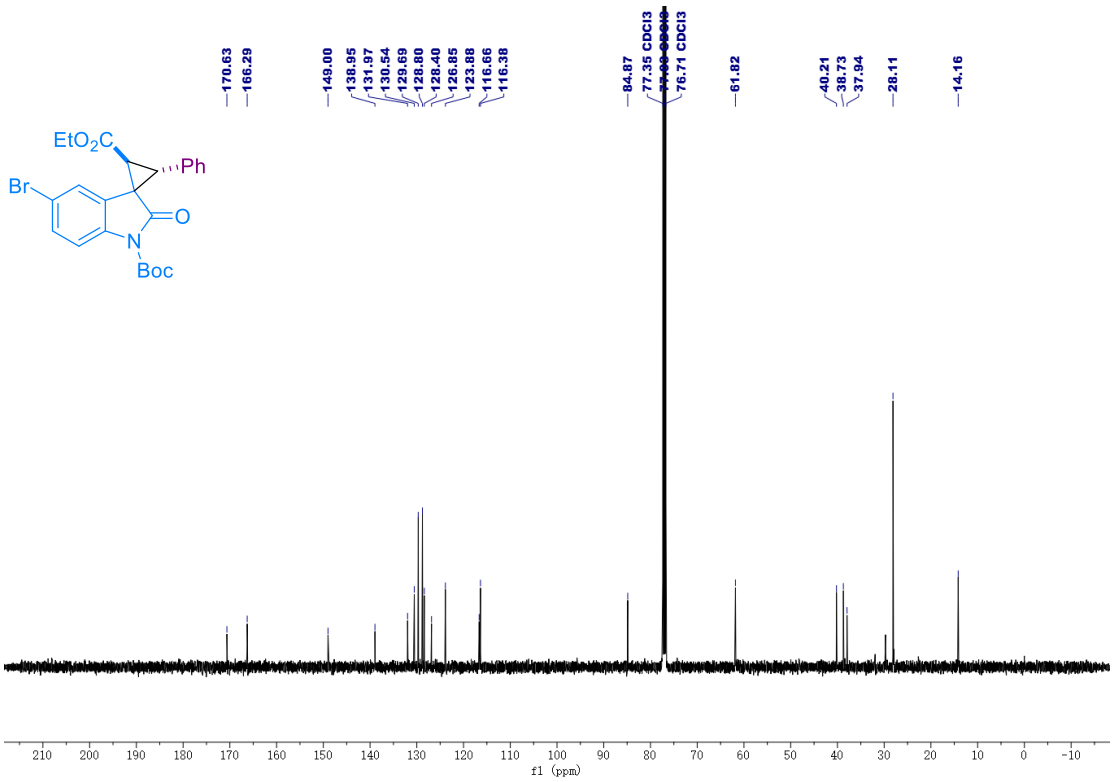
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-chloro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3c):**

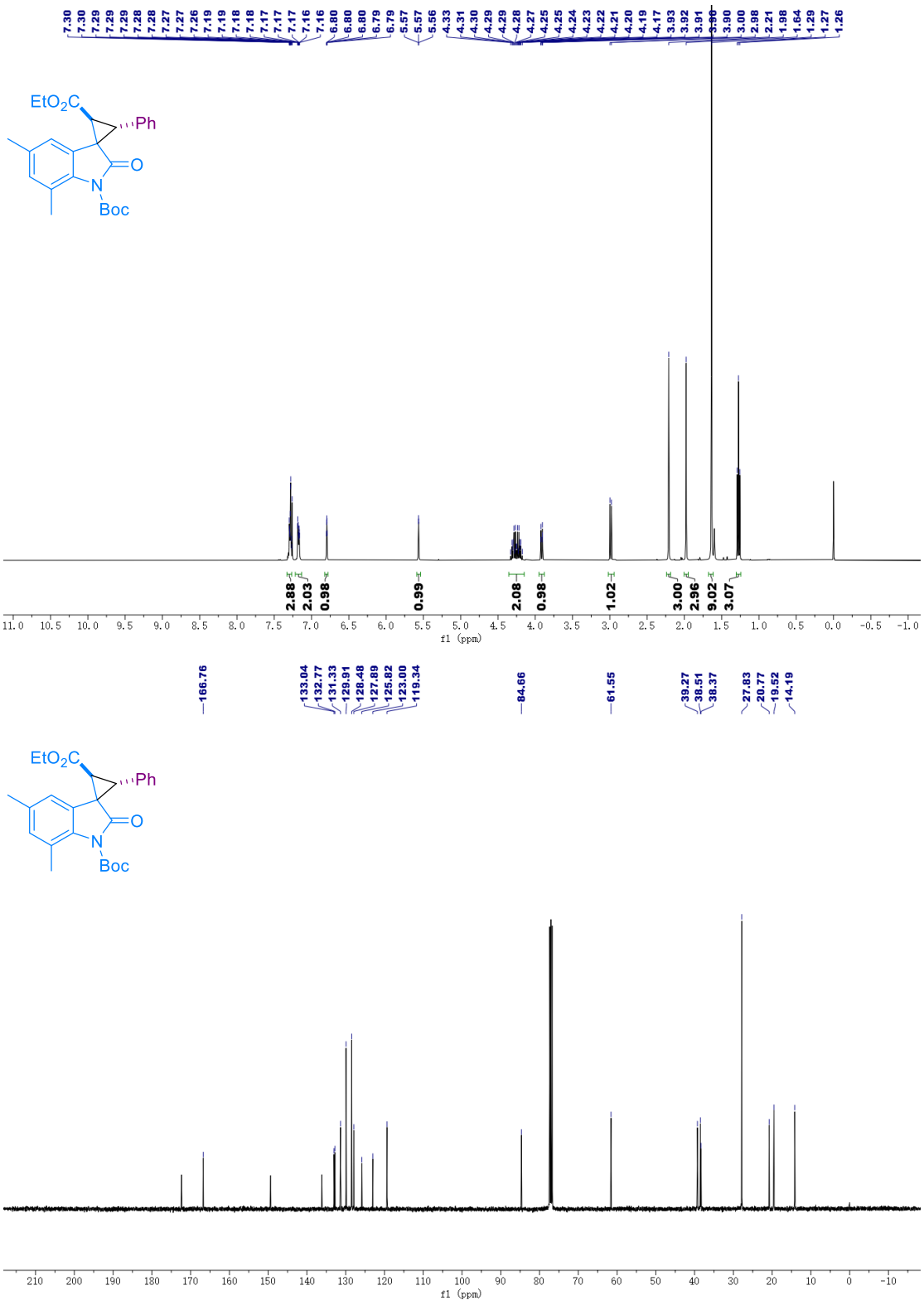


**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-bromo-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3d):**

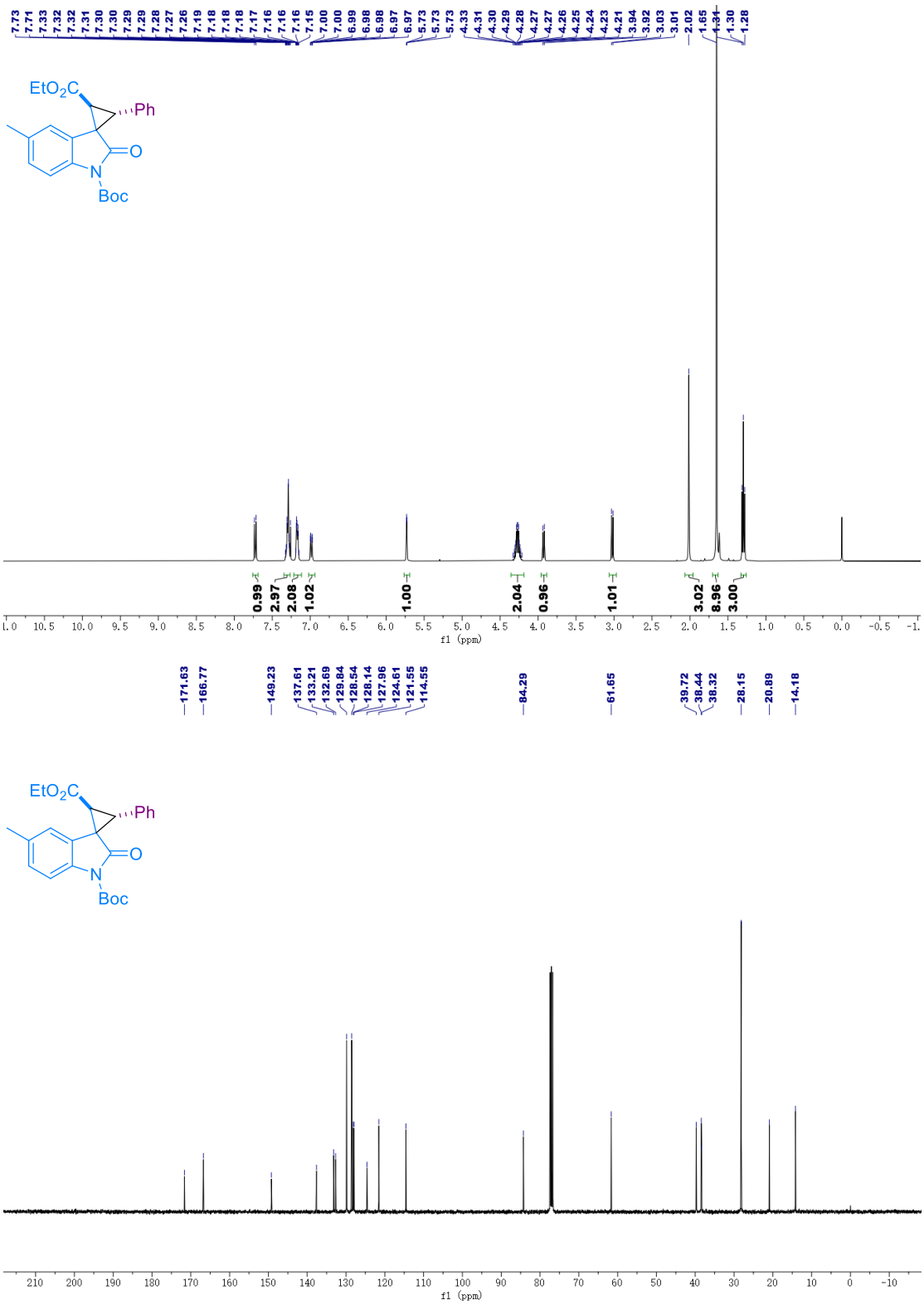


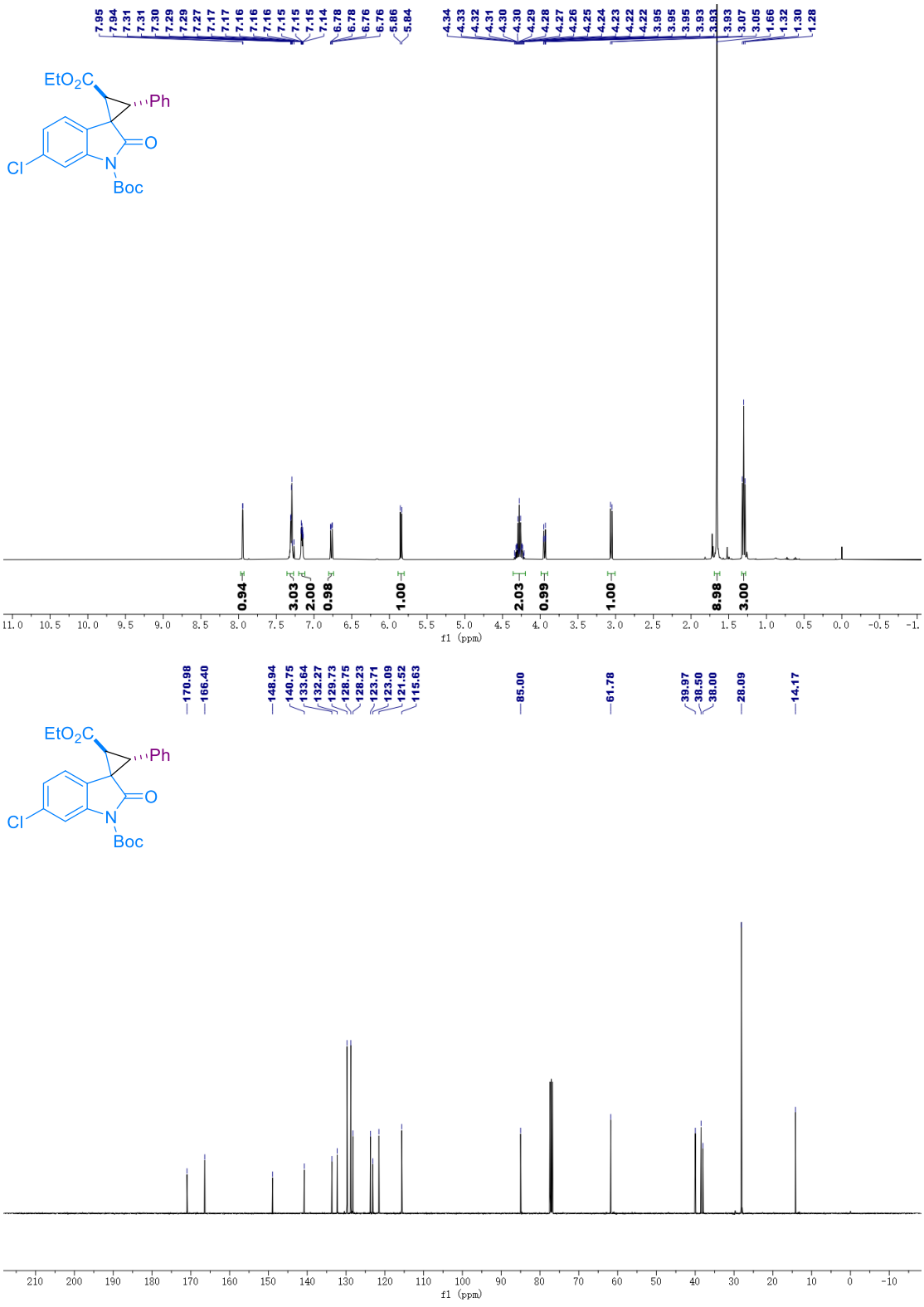
**1'-(Tert-butyl) 2-ethyl (*trans*)-5',7'-dimethyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3e):**



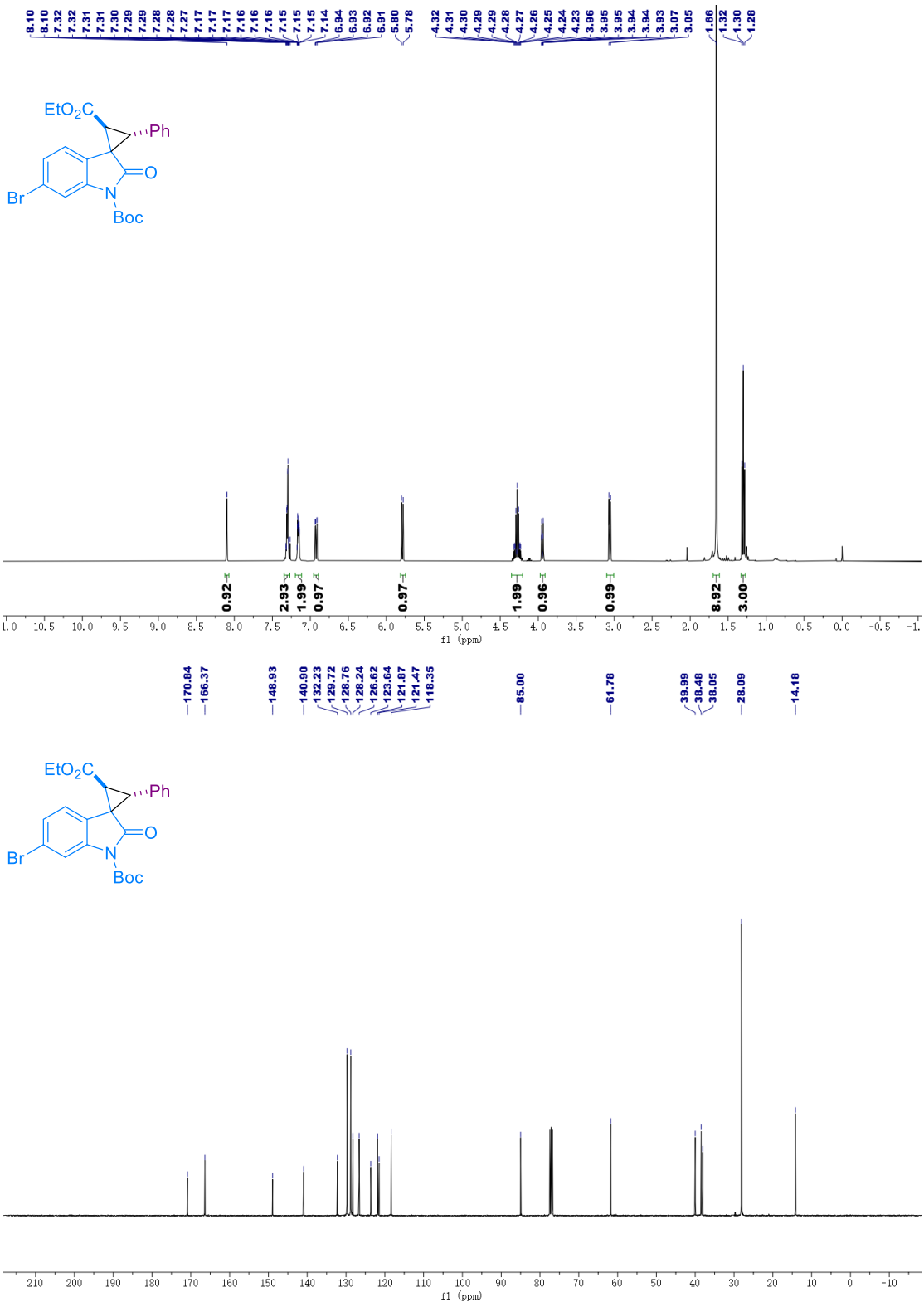
**1'-(Tert-butyl) 2-ethyl (*trans*)-5'-methyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3f):**



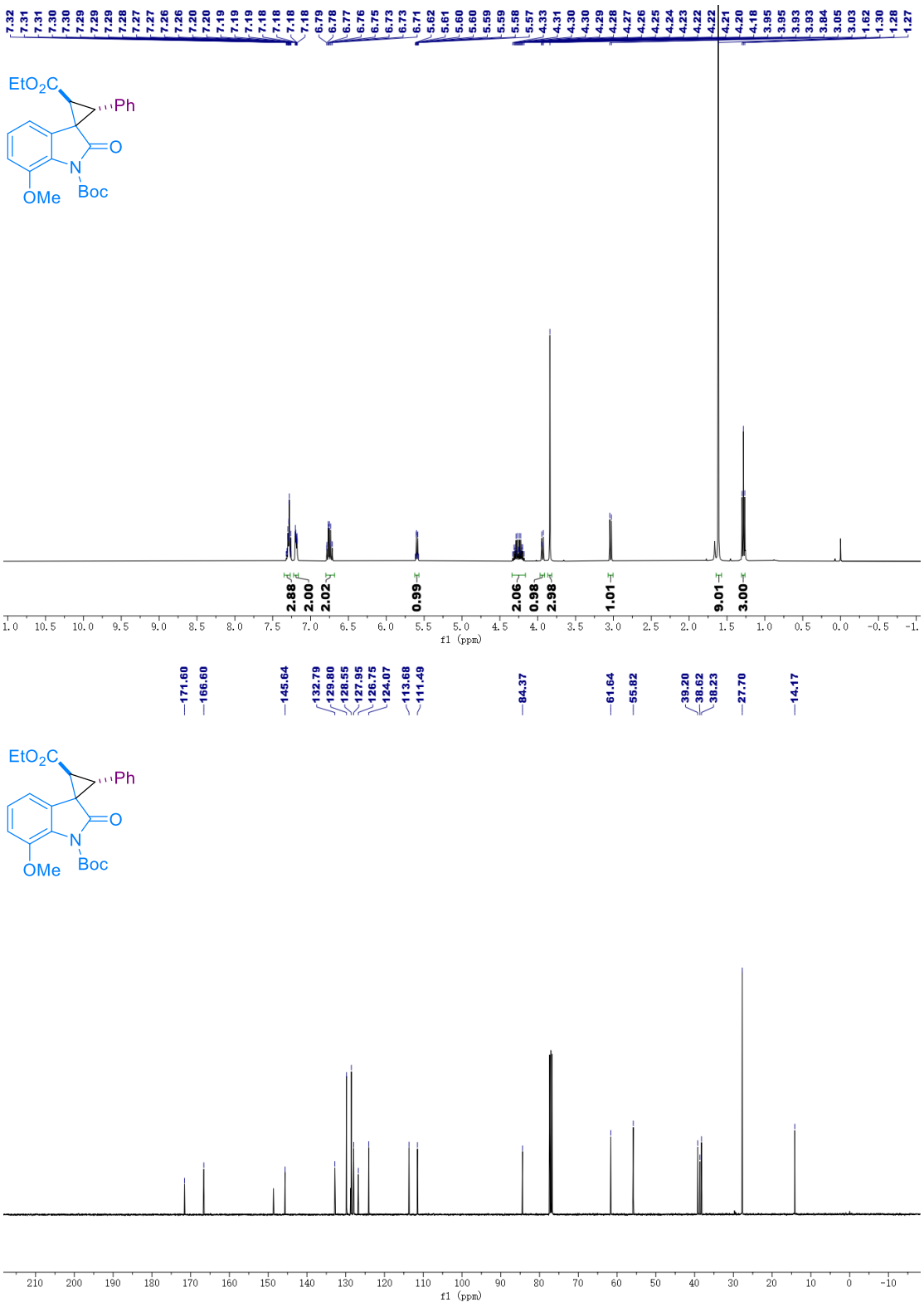
**1'-(Tert-butyl) 2-ethyl (*trans*)-6'-chloro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3g):**



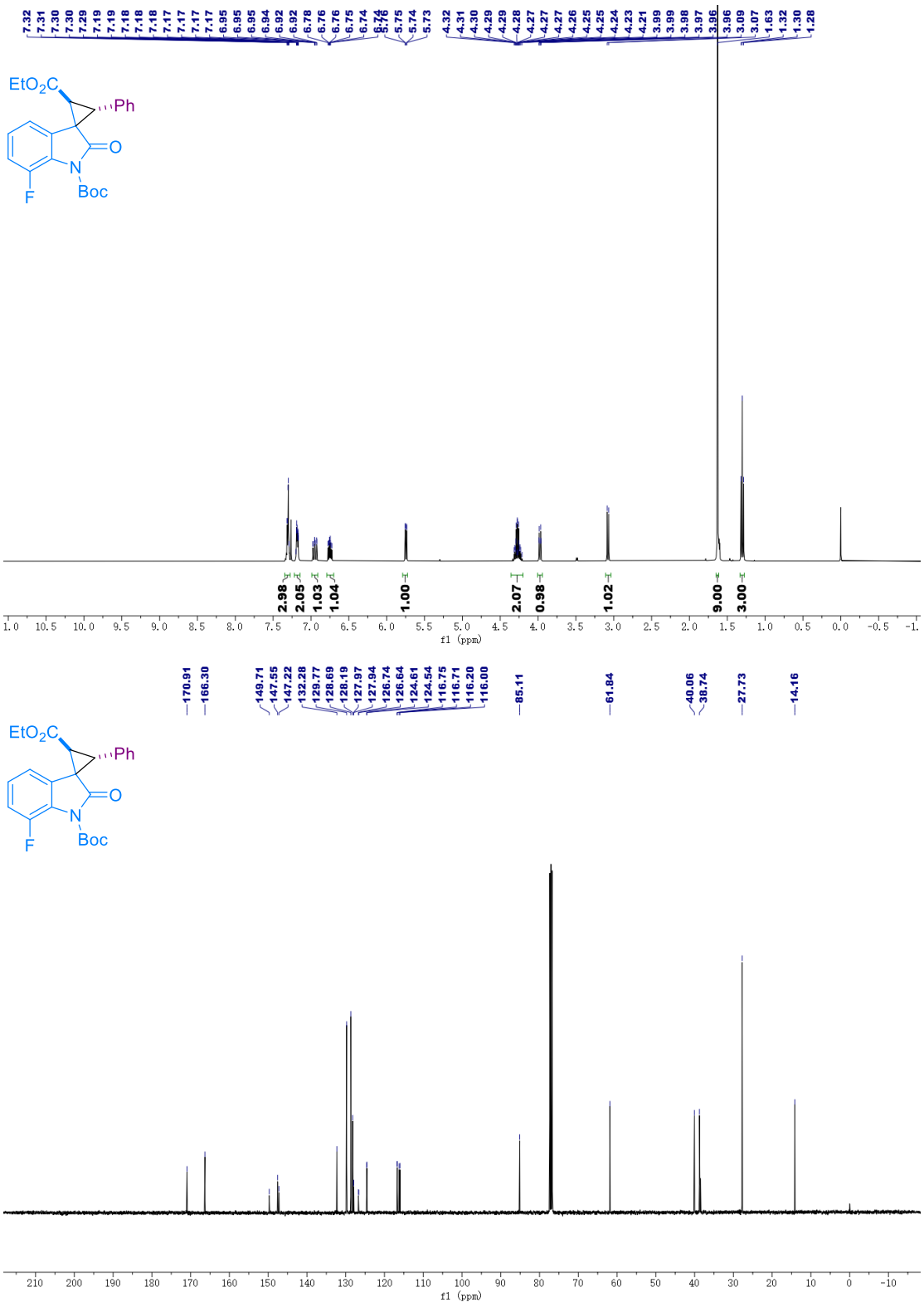
**1'-(Tert-butyl) 2-ethyl (*trans*)-6'-bromo-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3h):**

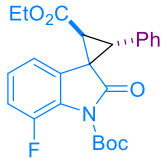


**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-methoxy-2'-oxo-3 phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3i):**



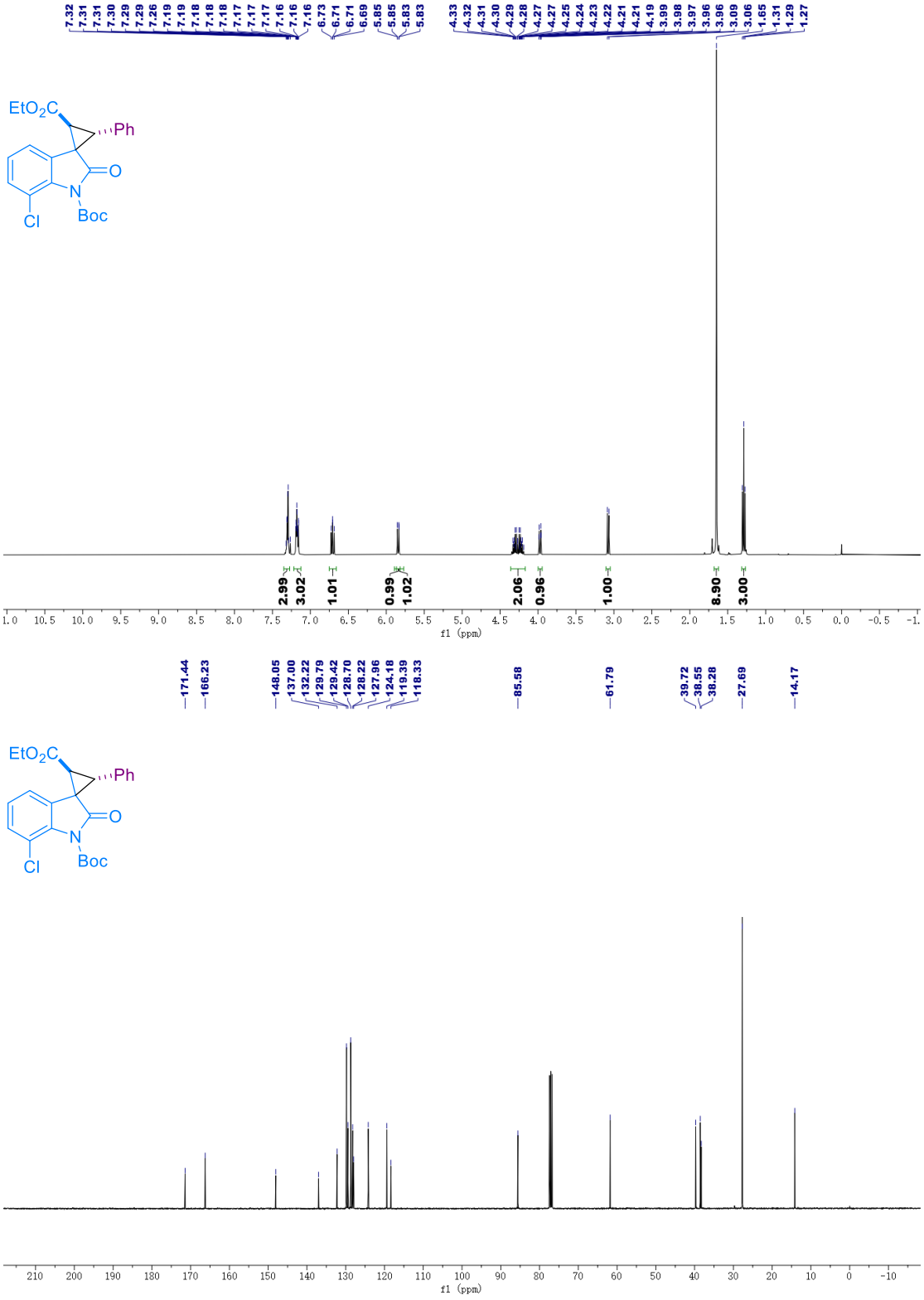
**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-fluoro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3j):**



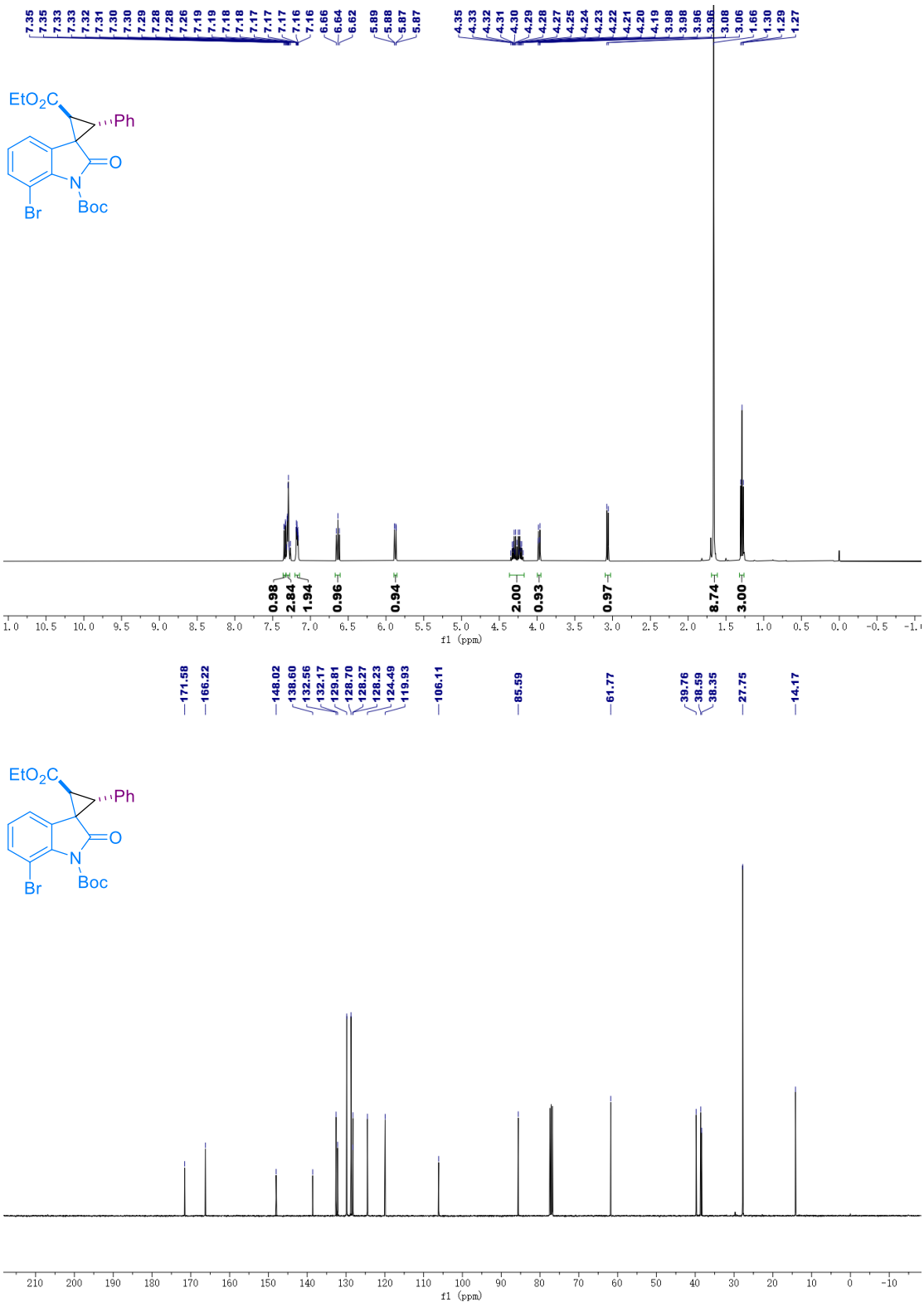

EtO2C
Ph
O
N
Boc
F


-119.900
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

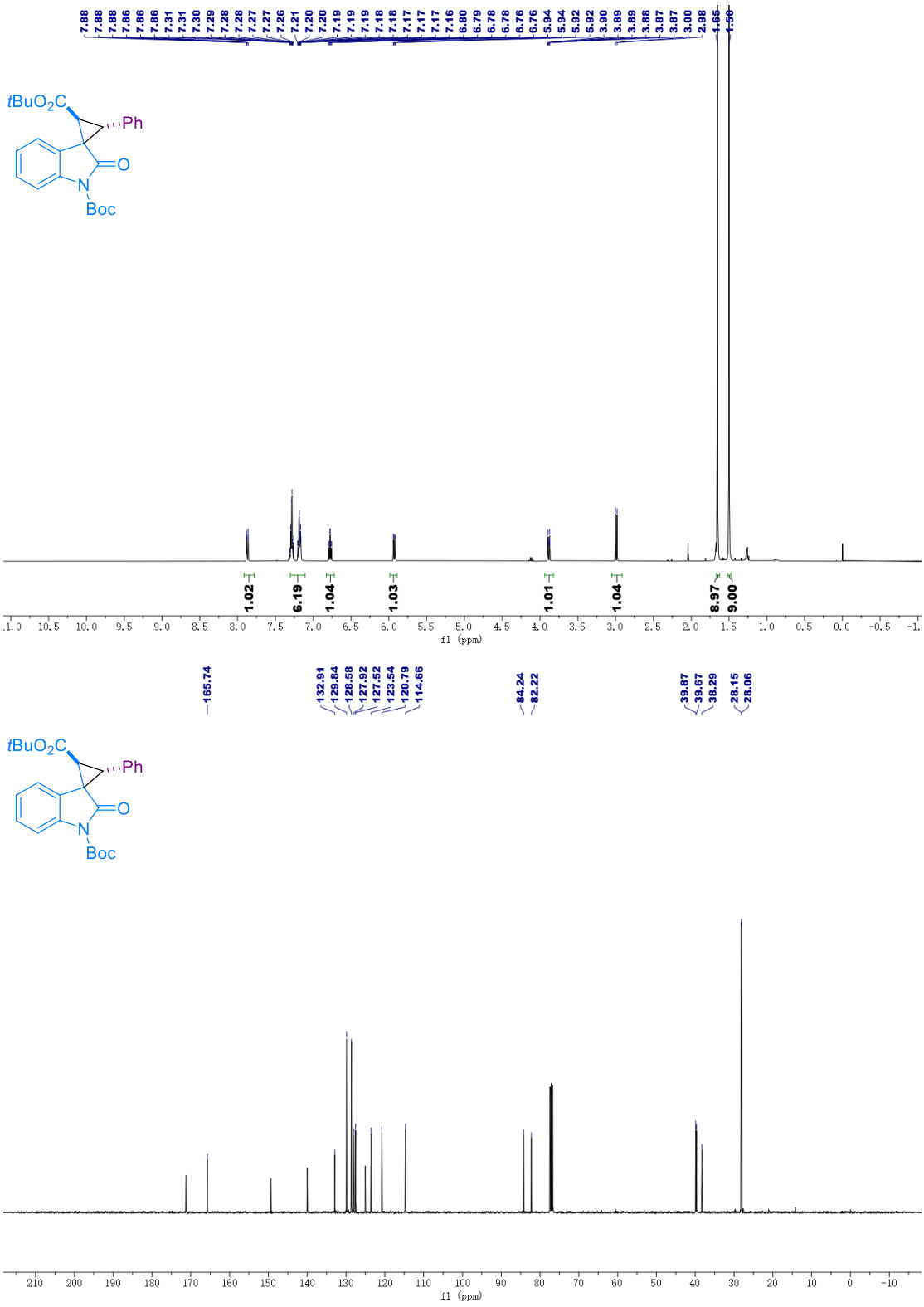
**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-chloro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3k):**



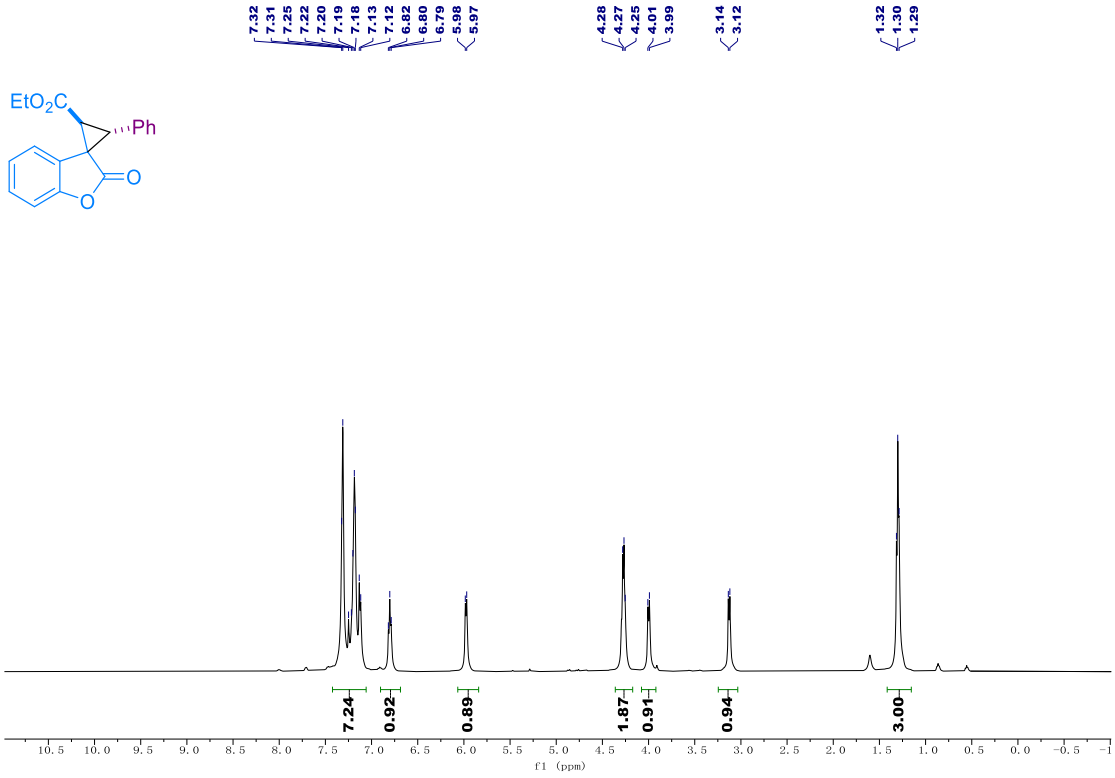
**1'-(Tert-butyl) 2-ethyl (*trans*)-7'-bromo-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3l):**

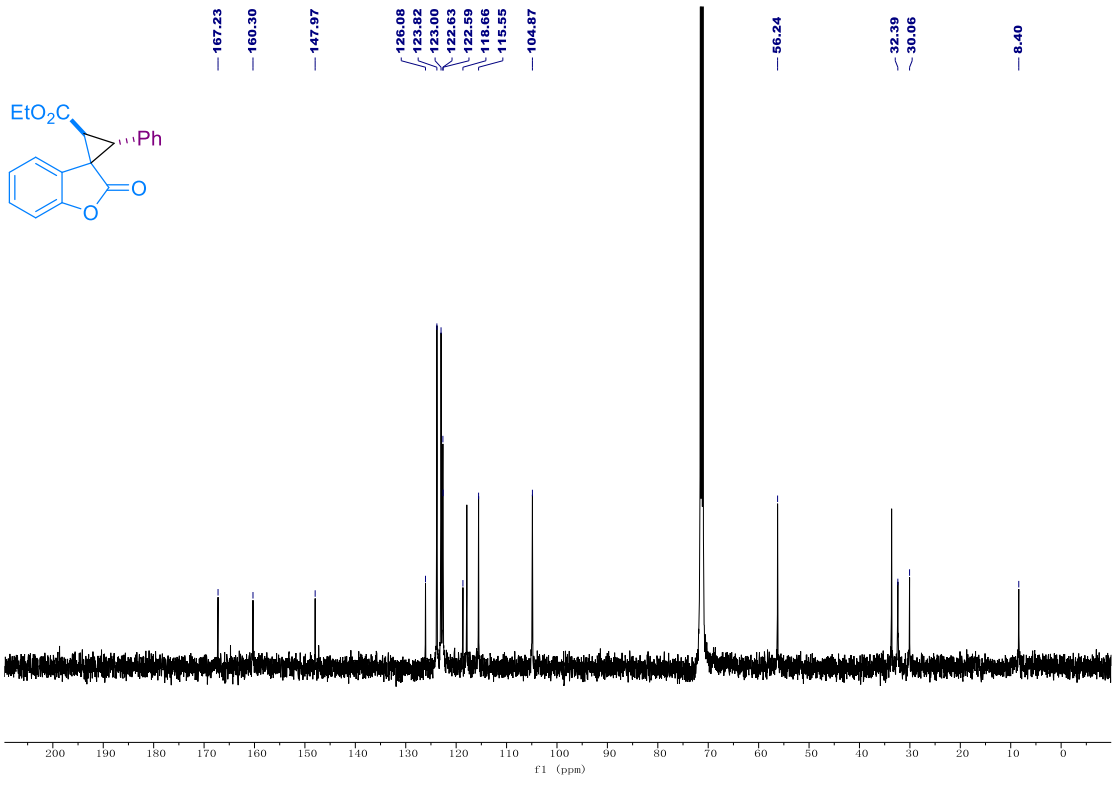


**Di-tert-butyl (*trans*)-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3m):**

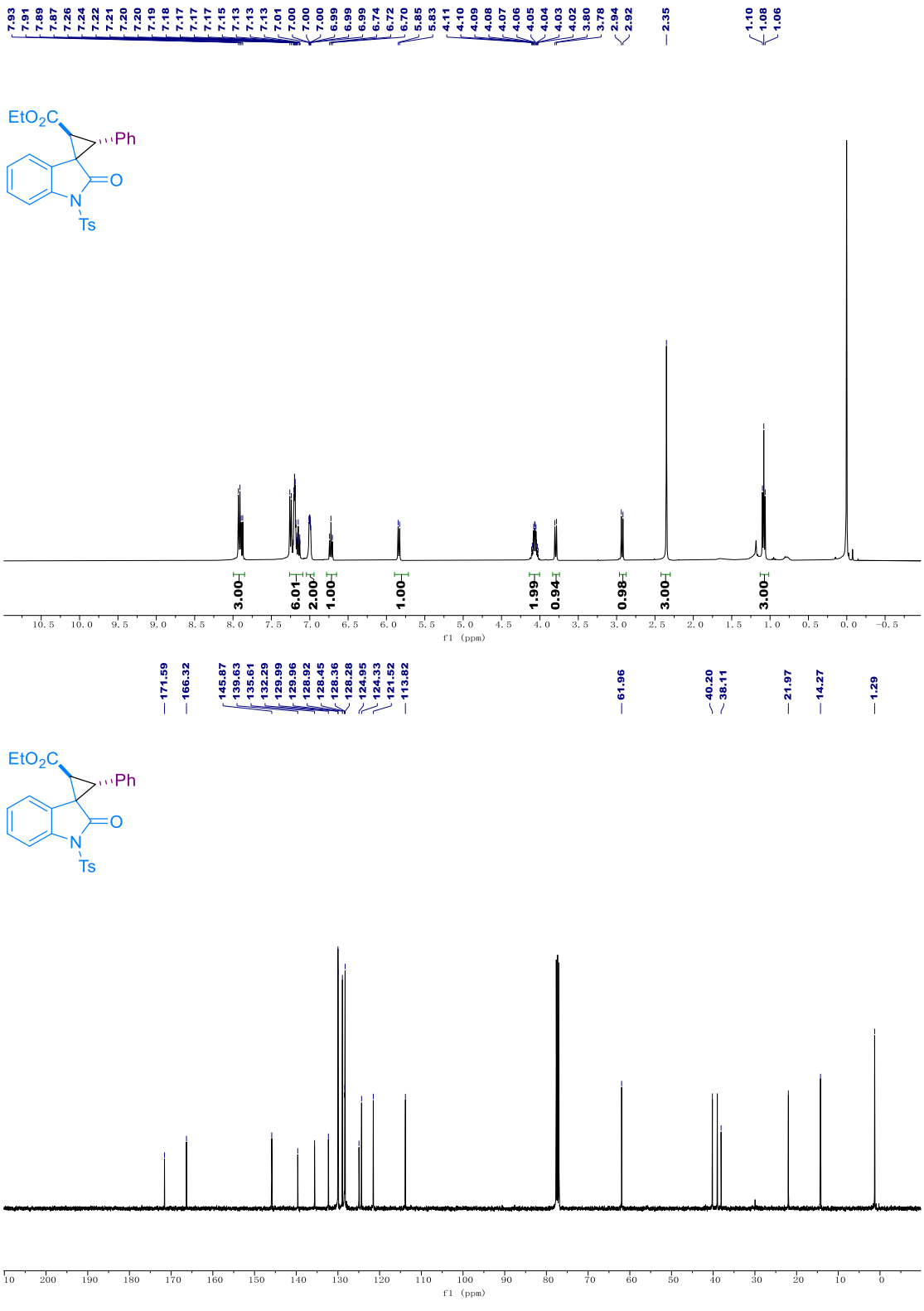


**Ethyl (*trans*)-2-oxo-3'-phenyl-2H-spiro[benzofuran-3,1'-cyclopropane]-2'-carboxylate (3n):**

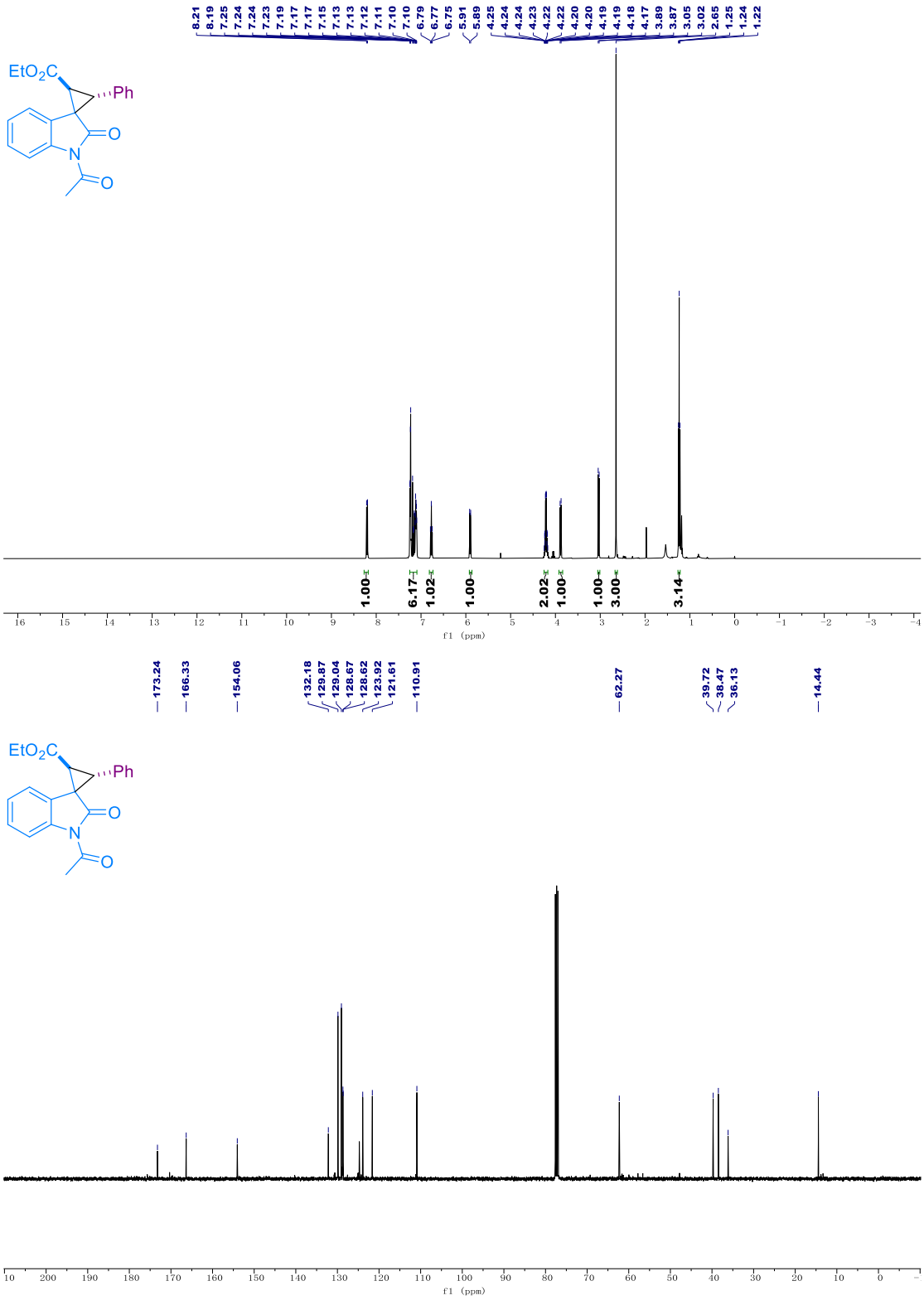


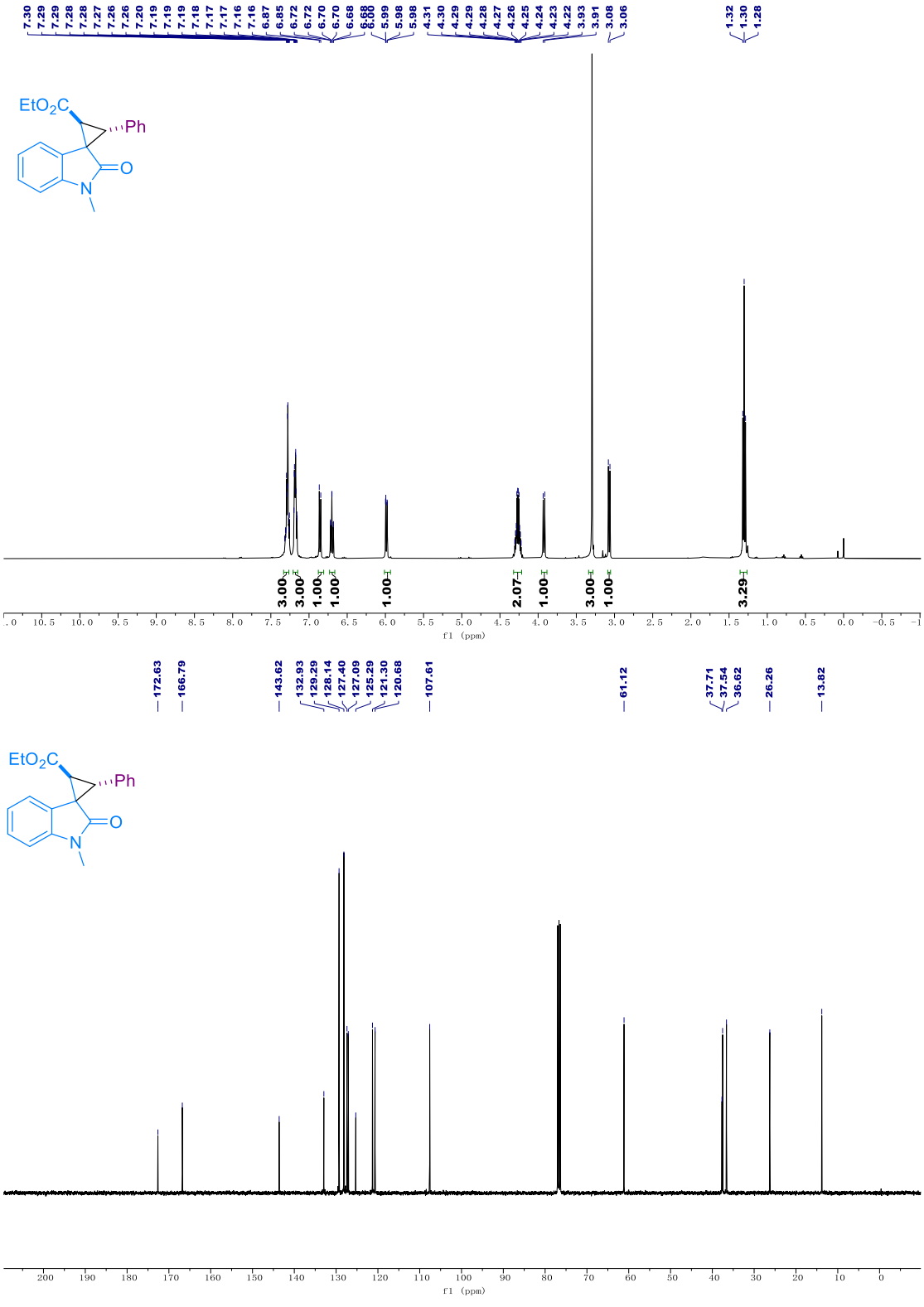
**Ethyl (*trans*)-2'-oxo-3-phenyl-1'-tosylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (3o):**



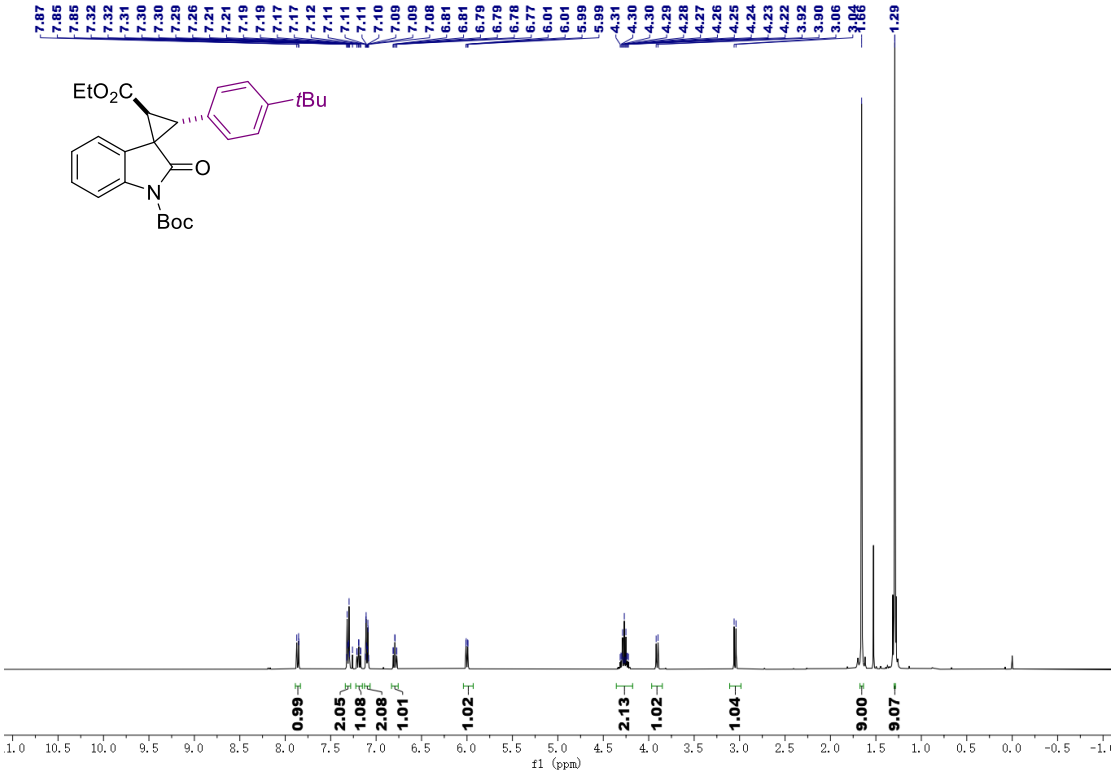
**Ethyl (*trans*)-1'-acetyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (3p):**

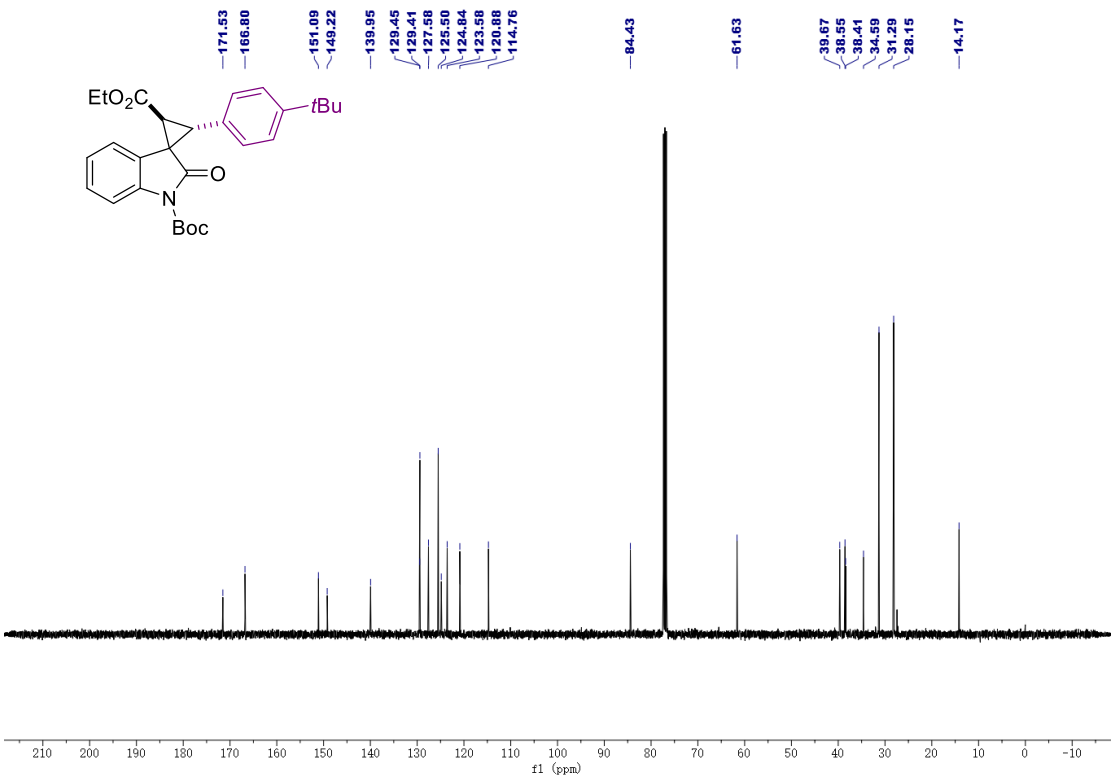


**Ethyl (*trans*)-1'-methyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-2-carboxylate (3q):**

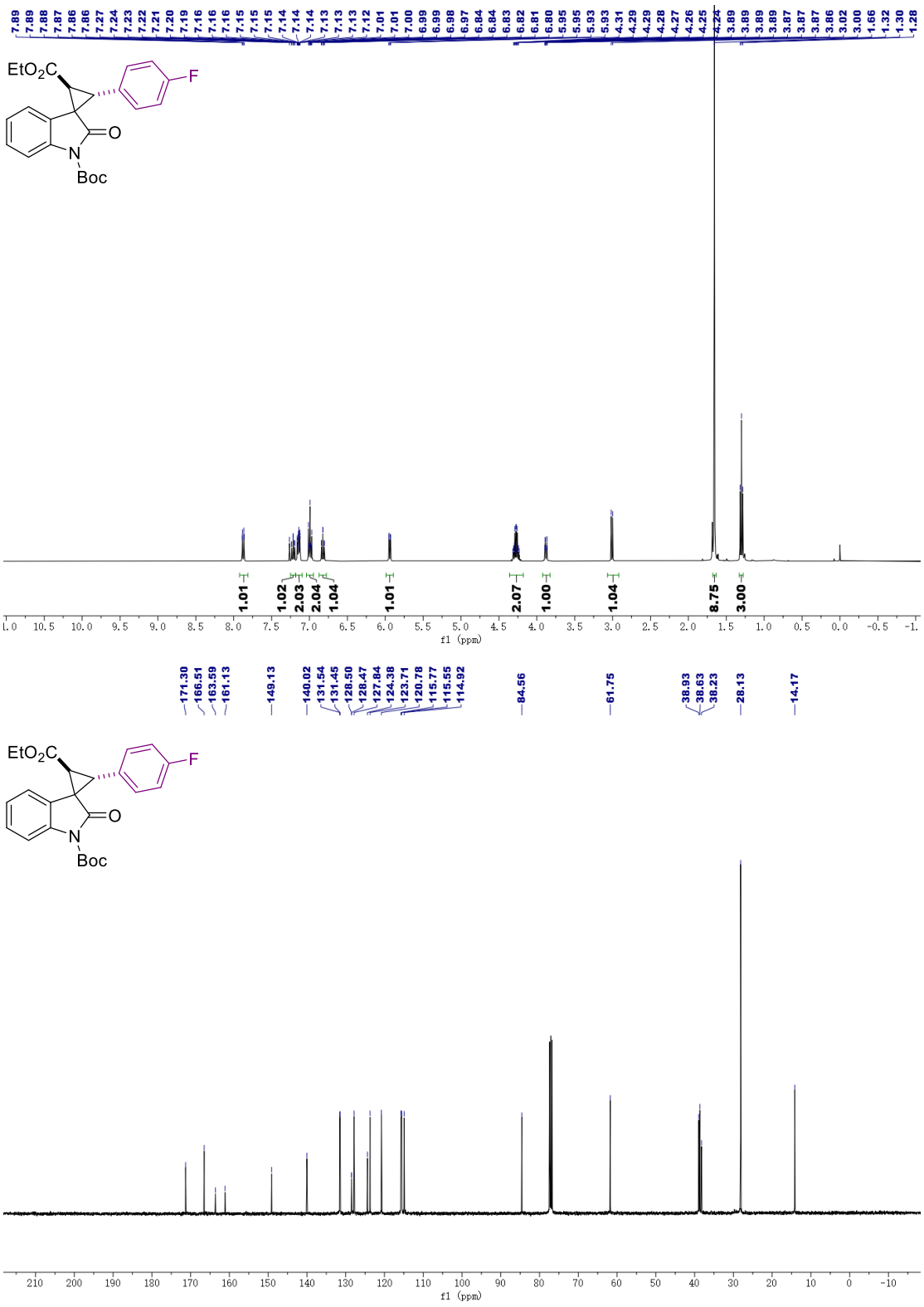


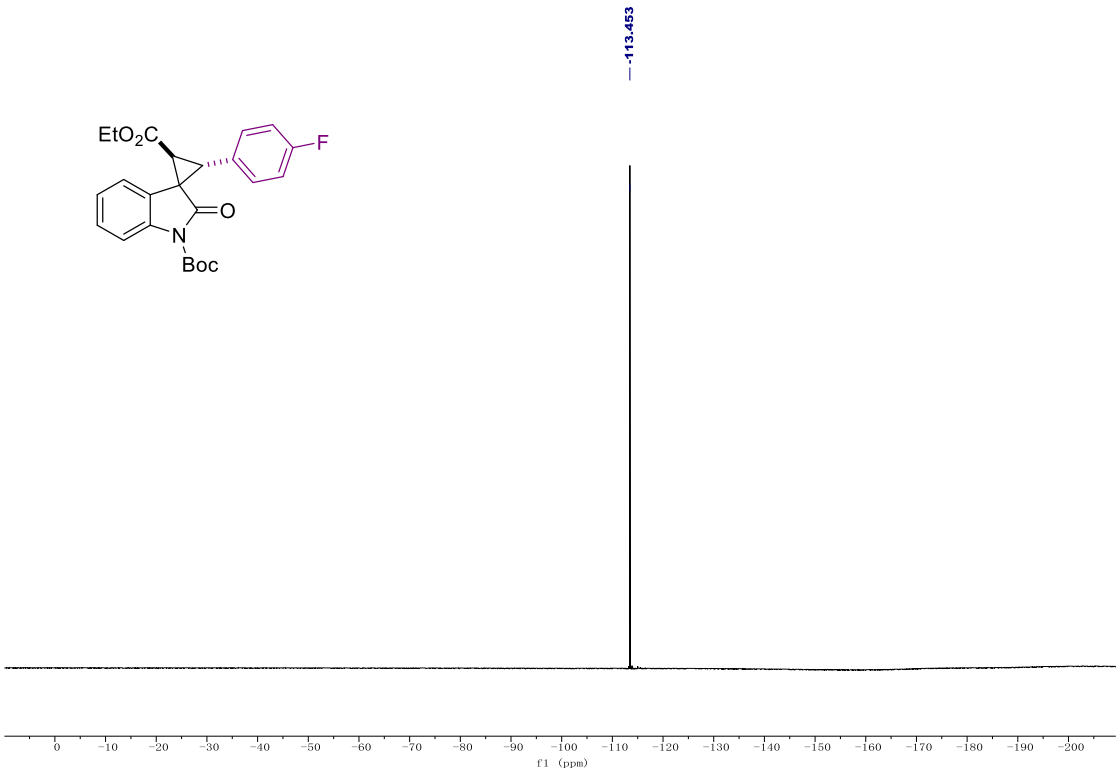
**1'-(Tert-butyl) 3-ethyl (*trans*)-2-(4-(tert-butyl)phenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',3-dicarboxylate (3r):**



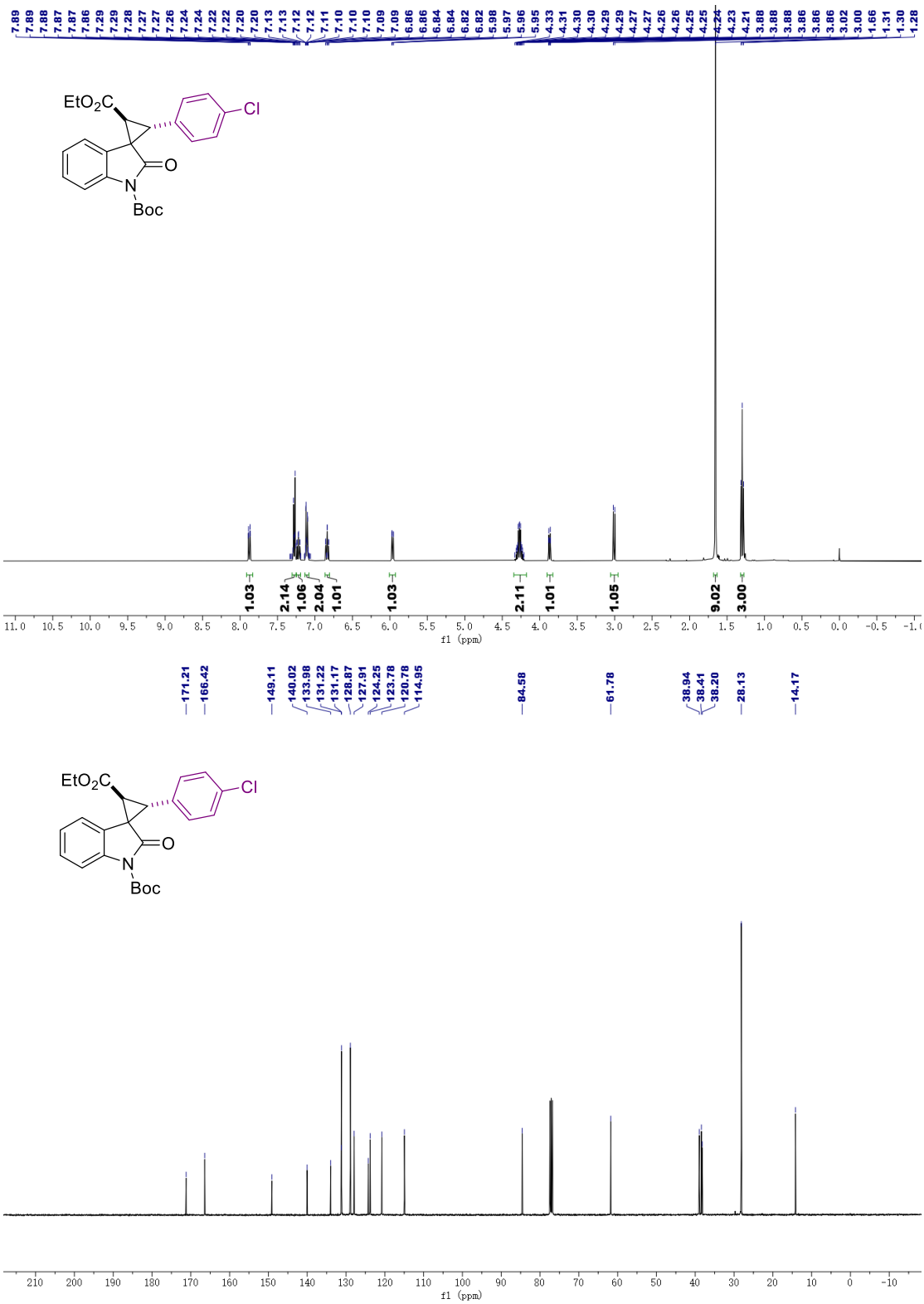



**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(4-fluorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3s):**

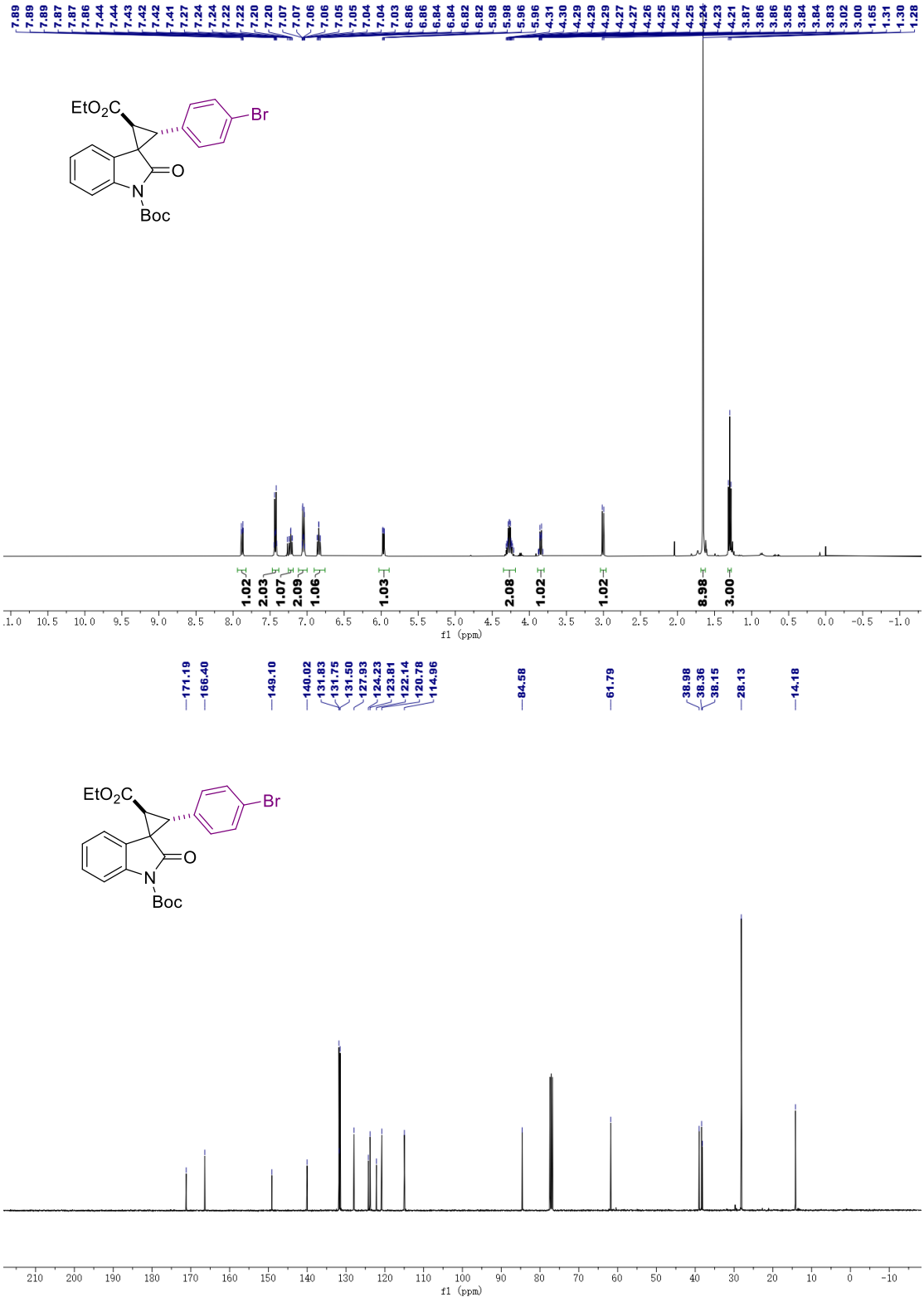



-113.453
EtO2C
F
O
N
Boc
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

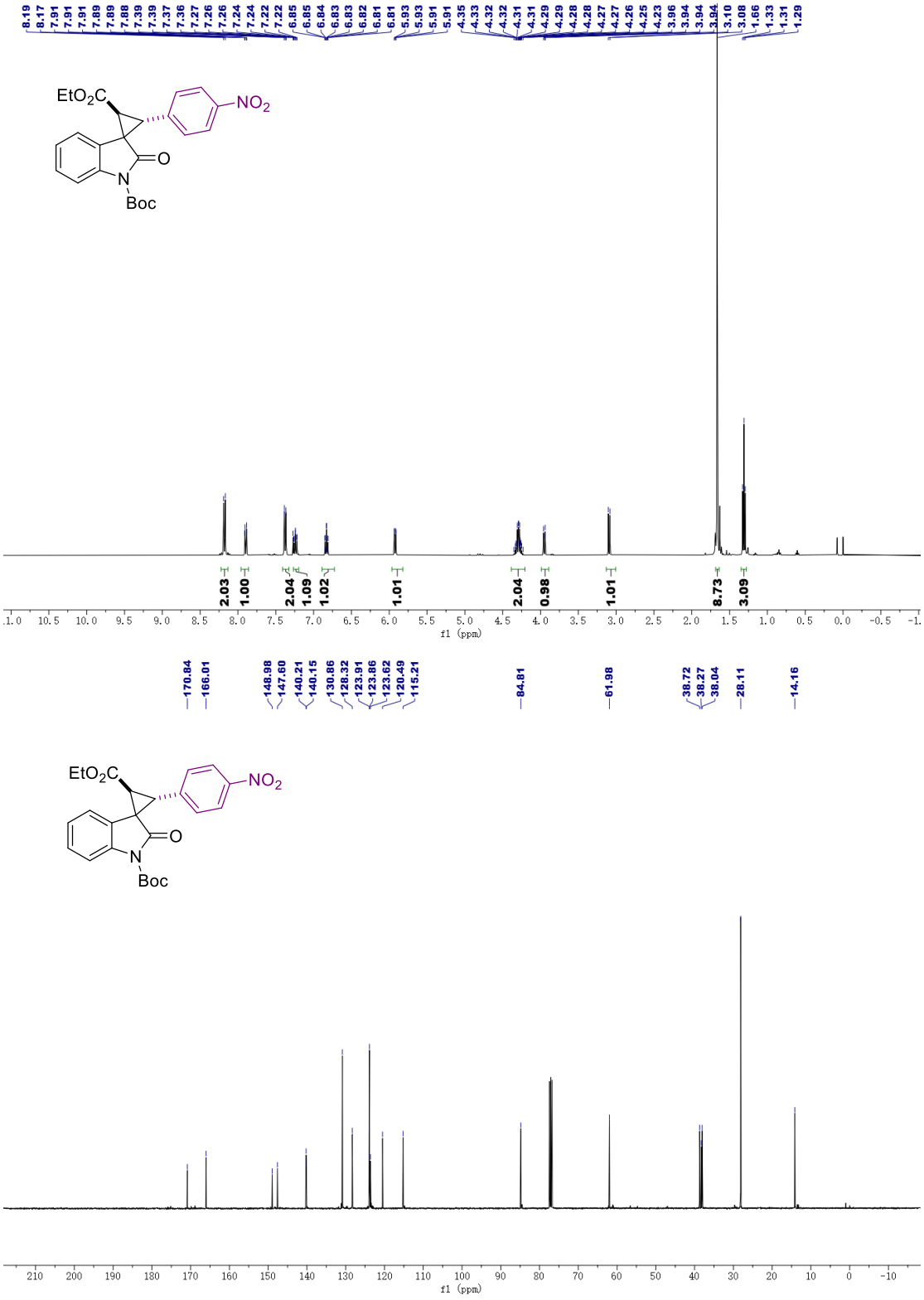
**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(4-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3t):**



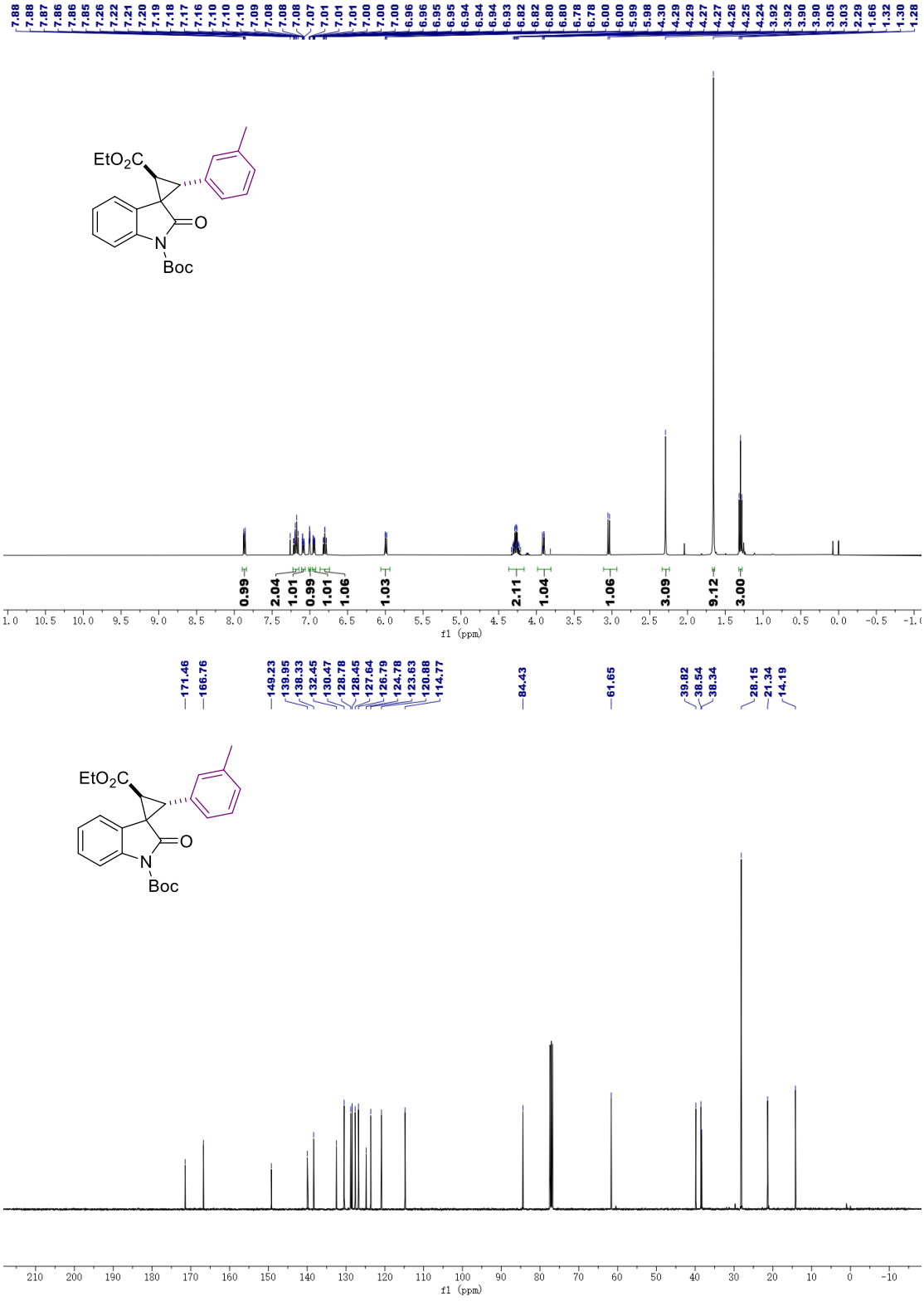
**1'-(Tert-butyl) 3-ethyl (*trans*)-2-(4-bromophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',3-dicarboxylate (3u):**



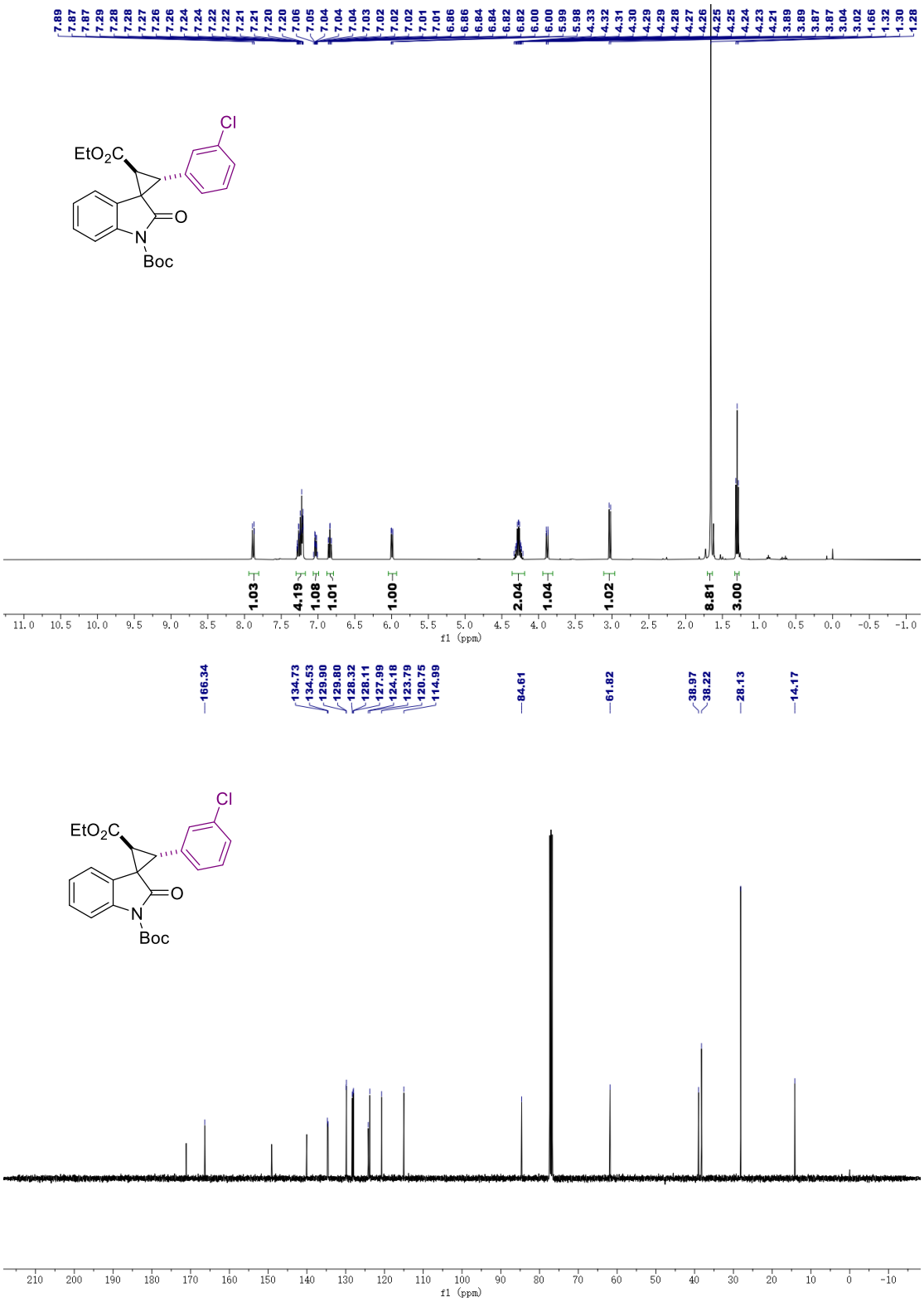
**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(4-nitrophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3v):**



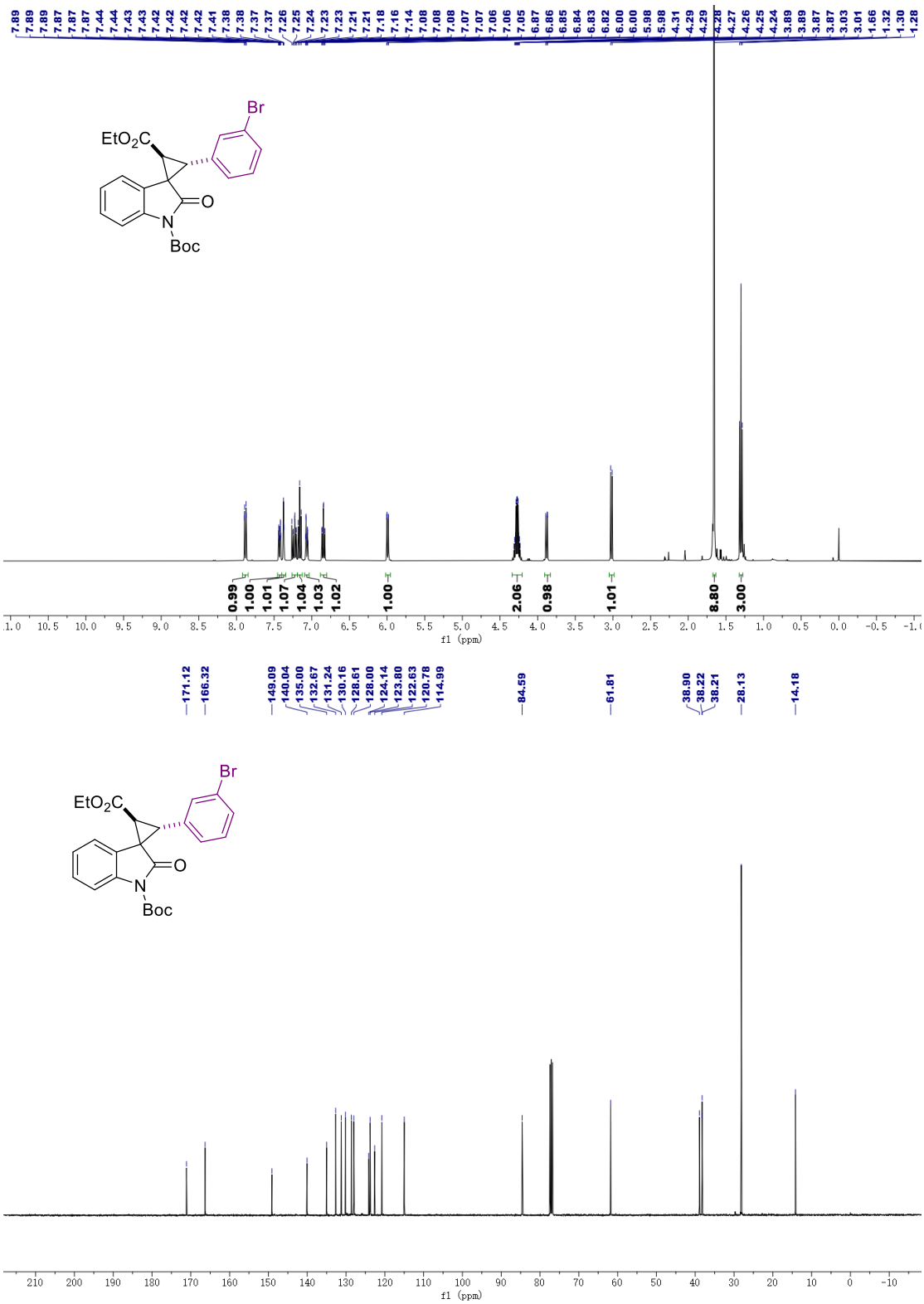
**1'-(Tert-butyl) 2-ethyl (*trans*)-2'-oxo-3-(m-tolyl)spiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3w):**



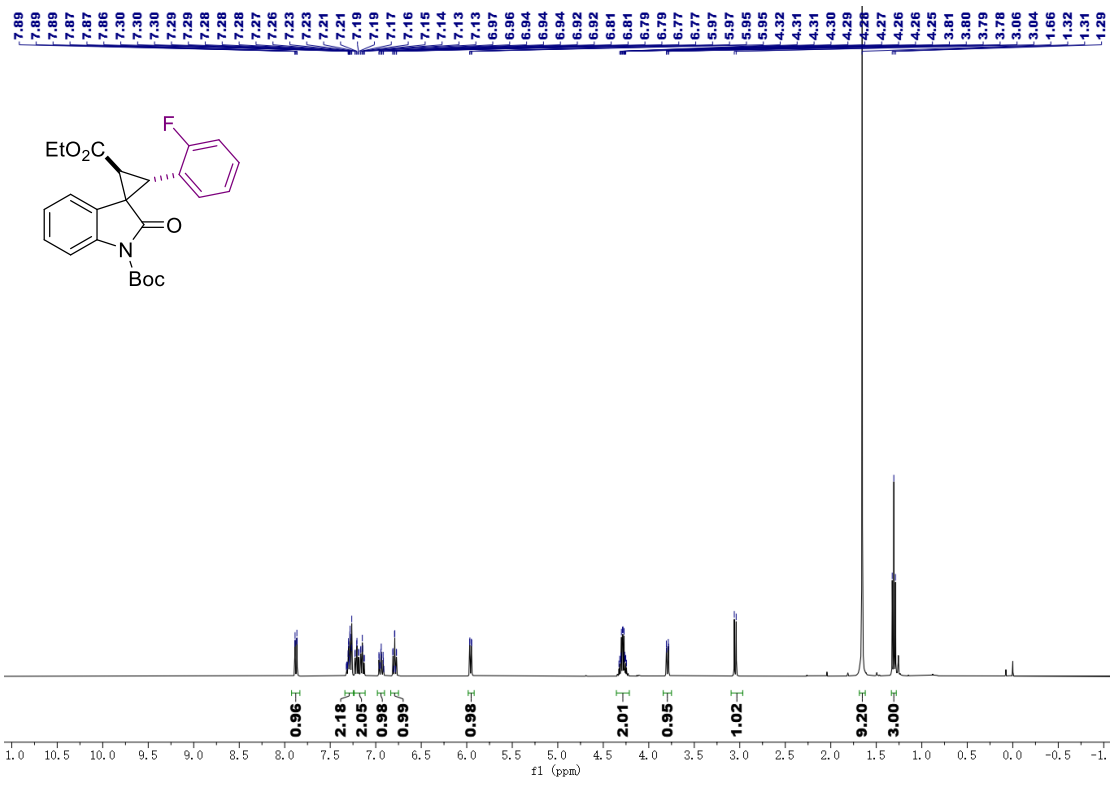
**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(3-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3x):**

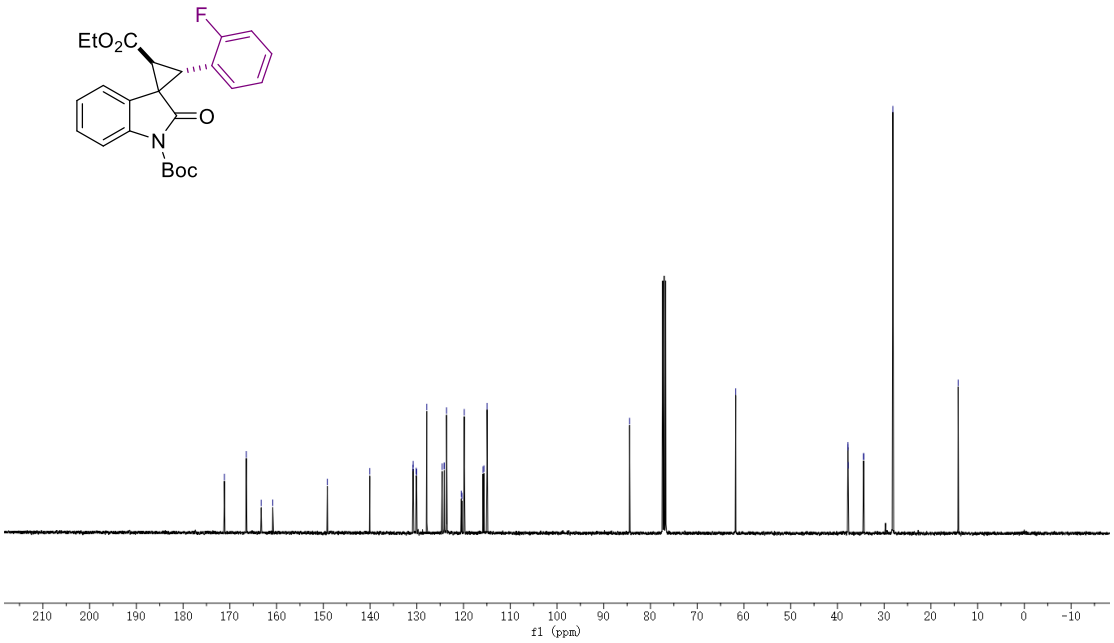


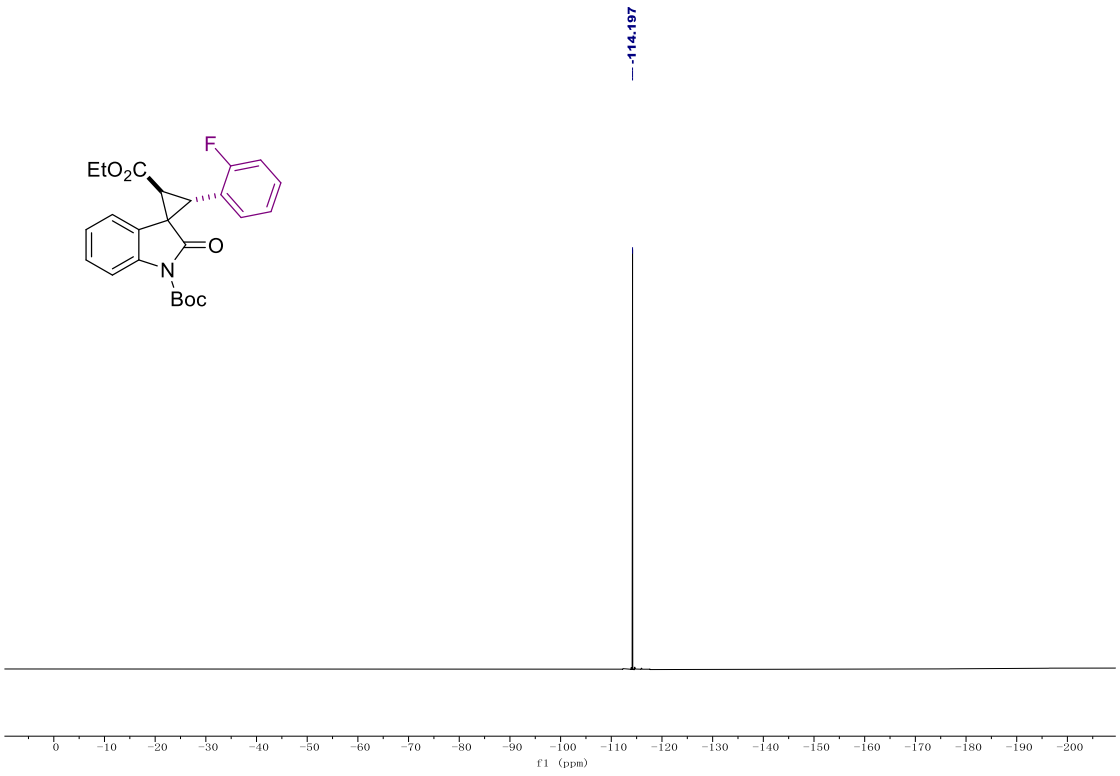
**1'-(Tert-butyl) 3-ethyl (*trans*)-2-(3-bromophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',3-dicarboxylate (3y):**



**1'-(Tert-butyl) 2-ethyl (*trans*)-3-(2-fluorophenyl)-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3z):**

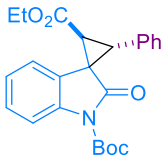



-114.197
F
EtO2C
O
N
Boc
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

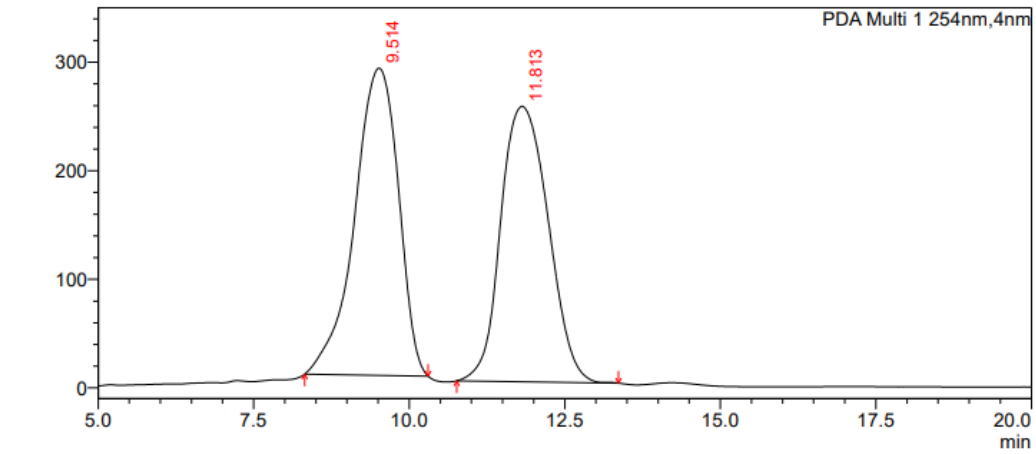
## 5. HPLC traces of the obtained chiral products

### (+)-1'-(Tert-butyl) 2-ethyl-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3a)




**HPLC conditions:** Chiralcel OD-H (i-PrOH/n-Hexane, 2:98), Flow: 0.8 mL.min-1, Temp: 40 °C.

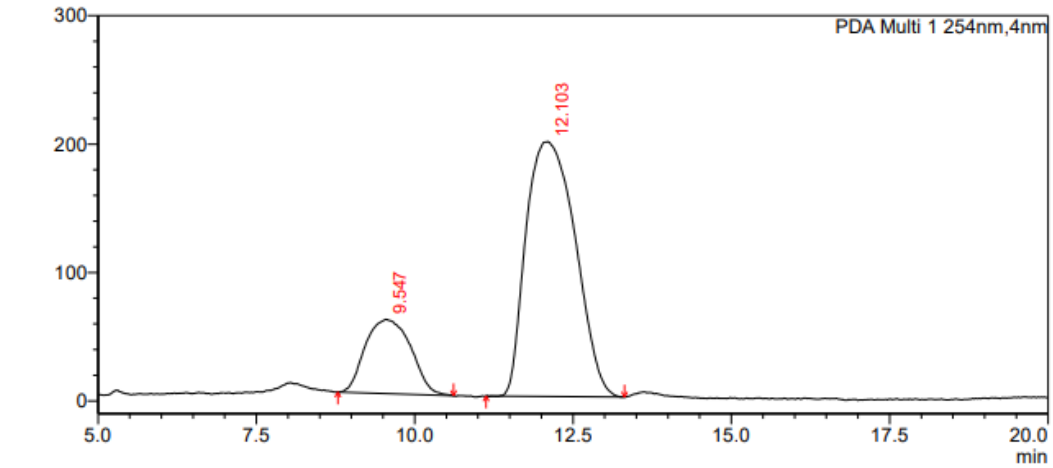
**<Chromatogram>**




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.514 | 13886837 | 282999 | 50.732 |
| 2 | 11.813 | 13486354 | 253594 | 49.268 |
| Total | | 27373191 | 536592 | 100.000 |

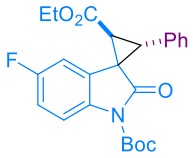
**<Chromatogram>**



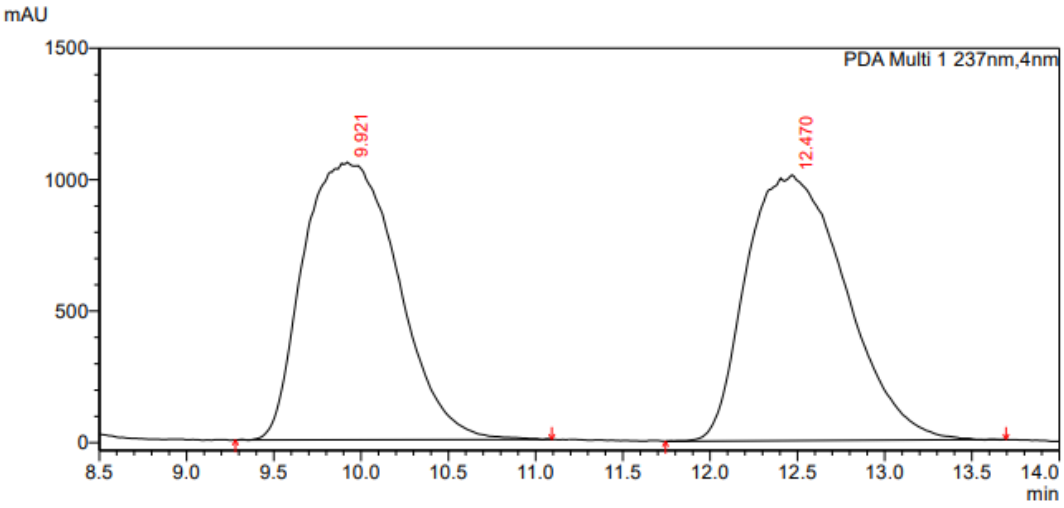

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.547 | 2883020 | 57736 | 21.146 |
| 2 | 12.103 | 10751105 | 198372 | 78.854 |
| Total | | 13634124 | 256108 | 100.000 |

**(+)-1'-(Tert-butyl) 2-ethyl-5'-fluoro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3b):**

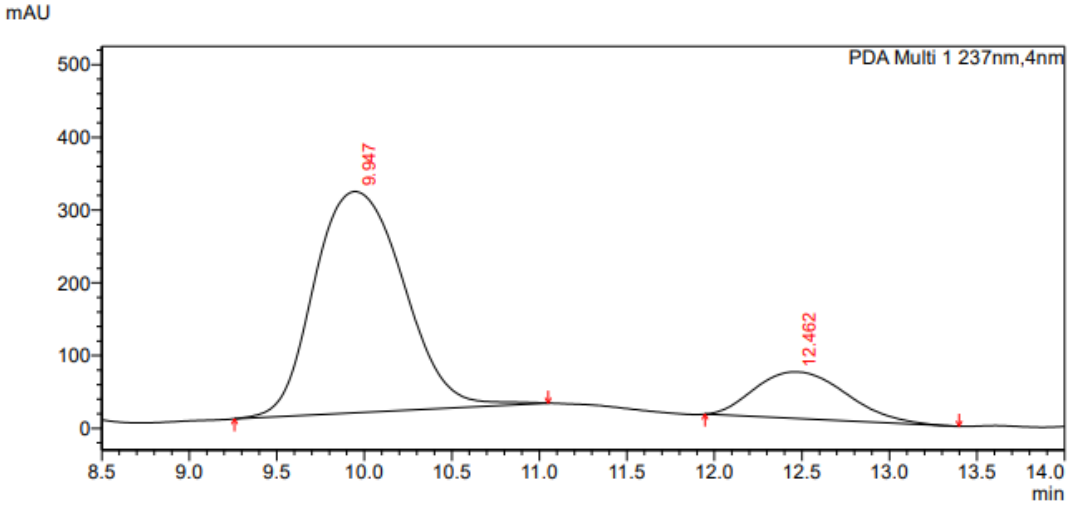



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 2:98), Flow: 0.8 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 237nm

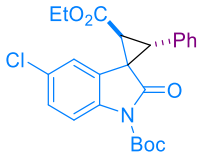
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.921 | 39943118 | 1055801 | 49.864 |
| 2 | 12.470 | 40160469 | 1010405 | 50.136 |
| Total | | 80103587 | 2066206 | 100.000 |



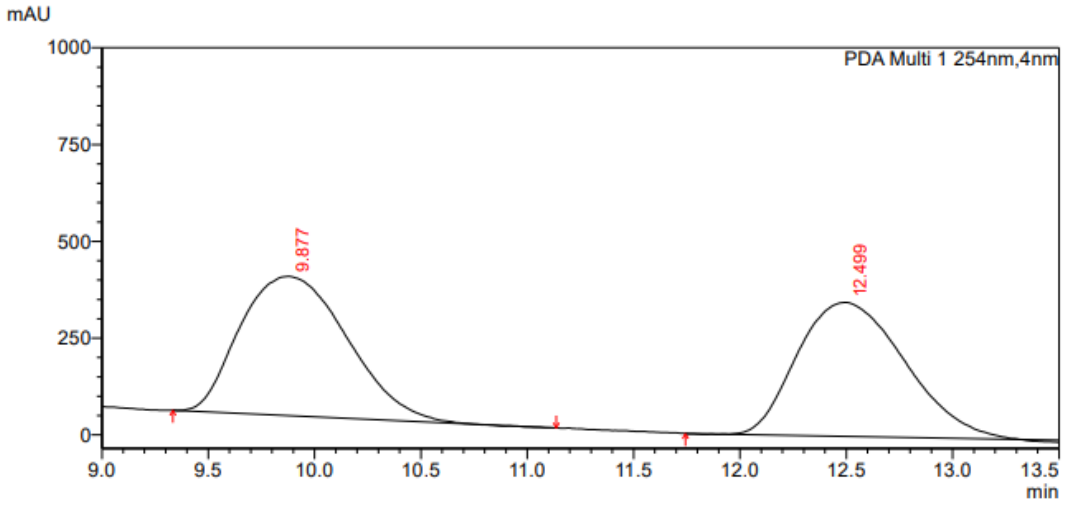

PDA Ch1 237nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.947 | 10808136 | 304088 | 82.198 |
| 2 | 12.462 | 2340710 | 64050 | 17.802 |
| Total | | 13148846 | 368139 | 100.000 |

**(+)-1'-(Tert-butyl) 2-ethyl-5'-chloro-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3c):**

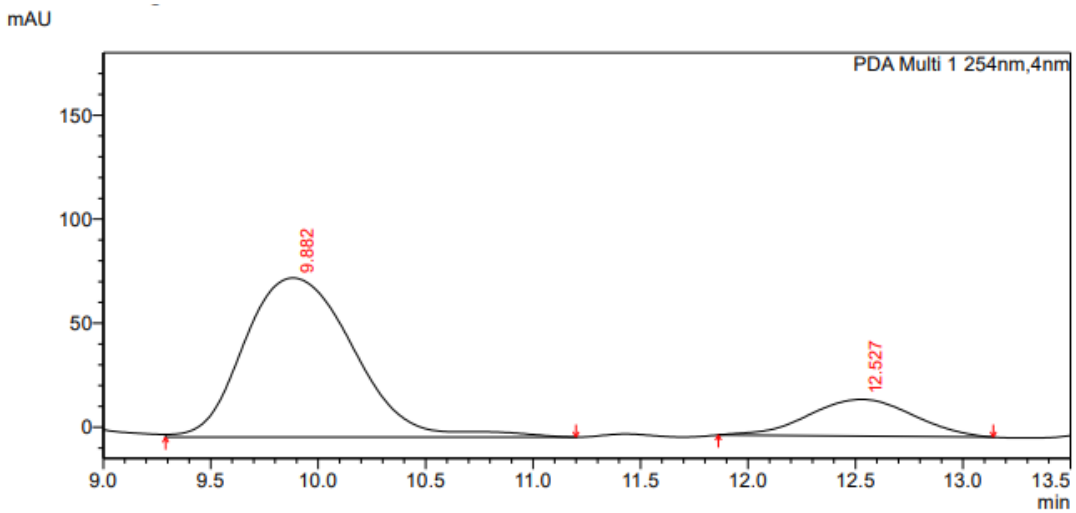



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 2:98), Flow: 0.8 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 254nm

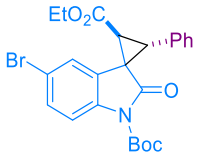
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.877 | 12590107 | 359792 | 50.977 |
| 2 | 12.499 | 12107548 | 345853 | 49.023 |
| Total | | 24697655 | 705646 | 100.000 |



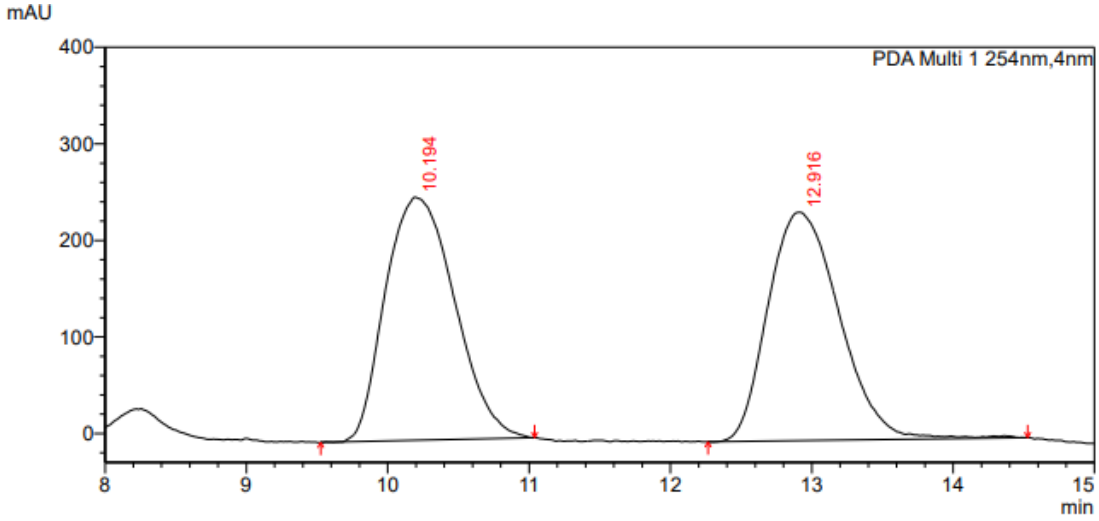

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 9.882 | 2723978 | 76539 | 81.975 |
| 2 | 12.527 | 598965 | 17667 | 18.025 |
| Total | | 3322943 | 94206 | 100.000 |

**(+)-1'-(Tert-butyl) 2-ethyl-5'-bromo-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3d):**

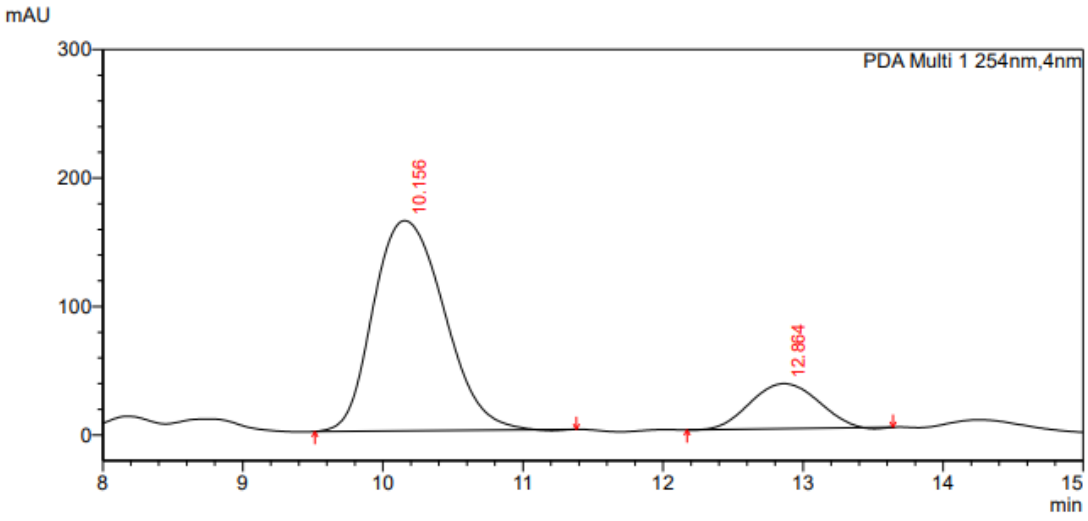



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 2:98), Flow: 0.8 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 254nm

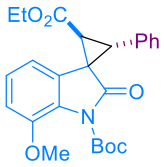
| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 10.194 | 8589833 | 251790 | 50.777 |
| 2 | 12.916 | 8327074 | 236598 | 49.223 |
| Total | | 16916907 | 488388 | 100.000 |



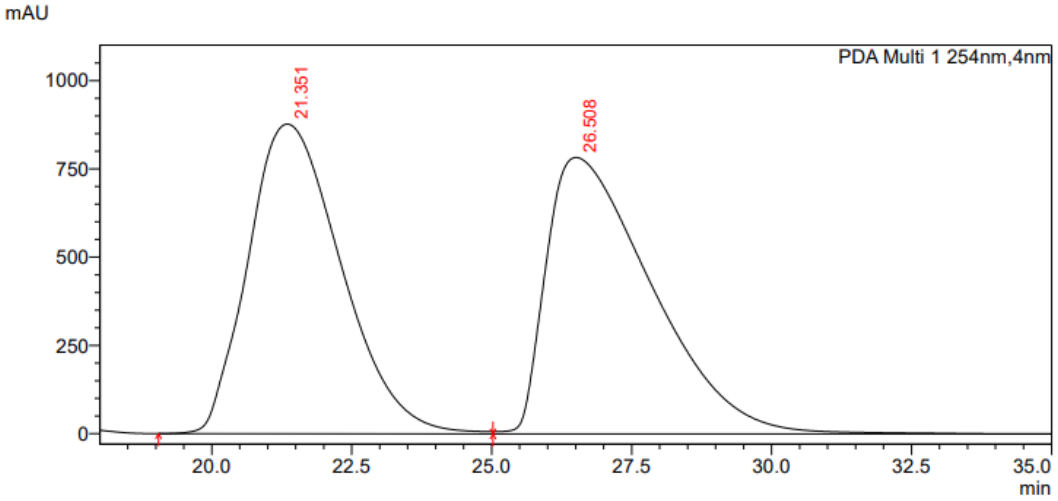

PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 10.156 | 5748026 | 163577 | 82.978 |
| 2 | 12.864 | 1179108 | 35070 | 17.022 |
| Total | | 6927134 | 198647 | 100.000 |

**(+)-1'-(Tert-butyl) 2-ethyl-7'-methoxy-2'-oxo-3 phenylspiro[cyclopropane-1,3'-indoline]-1',2-dicarboxylate (3i):**

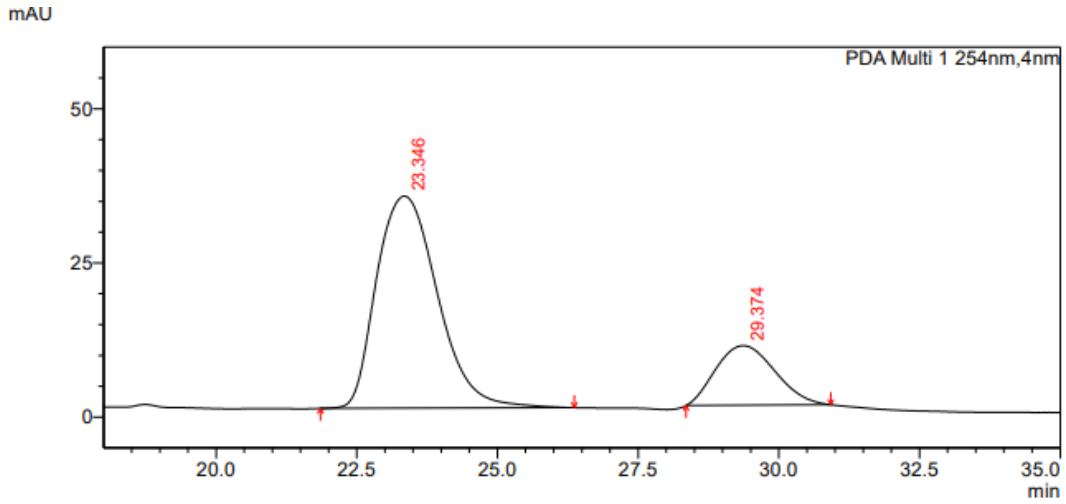



**HPLC conditions**: Chiralcel OD-H (*i*-PrOH/*n*-Hexane, 2:98), Flow: 0.8 mL.min$^{-1}$, Temp: 40 °C.




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 21.351 | 101518681 | 876770 | 49.706 |
| 2 | 26.508 | 102717603 | 782586 | 50.294 |
| Total | | 204236285 | 1659357 | 100.000 |




PDA Ch1 254nm

| Peak# | Ret. Time | Area | Height | Area% |
|---|---|---|---|---|
| 1 | 23.346 | 2598623 | 34402 | 78.606 |
| 2 | 29.374 | 707267 | 9662 | 21.394 |
| Total | | 3305891 | 44064 | 100.000 |