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Electronic Supplementary Information

Visible Light Induced One-pot Synthesis of Spirocyclopropyl Oxoindoles from Isatin Derivatives and Glycine Ester Hydrochloride

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1.General Information:

All reactions were performed in oven-dried glassware under open-air atmosphere unless otherwise stated. Liquids and solutions were transferred with syringes. Solvents used were dried and purified by following standard procedures. Technical grade solvents for extraction or chromatography (ethyl acetate, and Hexane) were distilled prior to use. Used chemicals were purchased from Sigma-Aldrich, TCI, Alfa-Aesar used without further purification. All the liquid chemicals distilled freshly prior to use. Analytical thin-layer chromatography (TLC) was performed on using pre-coated aluminium-backed plates (Merck Kieselgel 60 F254) and visualized by UV radiation, basic aqueous potassium permangante ($KMnO_4$), p-anisaldehyde stains and heat as developing agents. Column chromatography was performed on silica gel 60-120 mesh, using the indicated solvents. Organic solutions were concentrated under reduced pressure on Heidolph rotary evaporator. NMR spectra were acquired on a Bruker AVANCE 400 MHz FT-NMR instrument running at 400 MHz for ^{1}H, 101 MHz ^{13}C and 376 MHz for ^{19}F respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet), coupling constants (Hz), and integration. MS analyses were carried out using an Agilent 6540 accurate-mass Q-TOF LC/MS (Agilent Technologies, U.S.A.). MS analyses were performed under the following operation parameters: dry gas temperature 350 °C, dry gas (N_2) flow rate 10 L/min, nebulizer pressure 30 psi, Vcap 4000, and fragmentor voltage 110 V. Mass spectra were acquired in the positive ion mode by scanning from 100 to 1500 in the mass-to-charge ratio (m/z). The mobile-phase composition used for UHPLC-QTOF MS comprises H_2O (A) and ACN (B), with optimized linear gradient elution. The injection volume was 0.5-1 µL. The flow rate was set at 0.3 mL/min. Accurate mass analysis calibration was carried out by ESI-low concentration tuning mix solution provided by Agilent Technologies, U.S.A. The accuracy error threshold was set at 5 ppm.

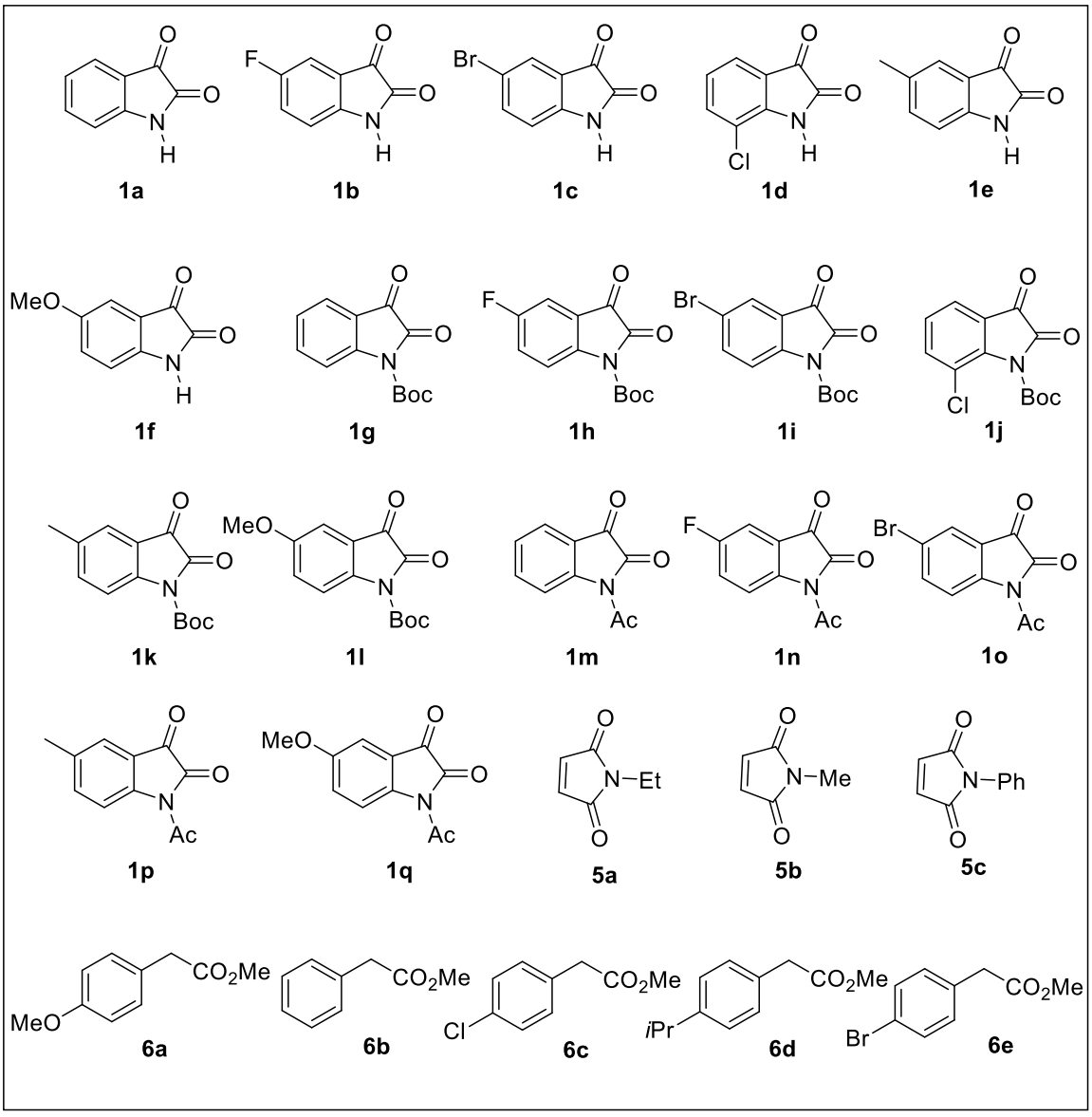
2. Photoreactor Setup:

Photochemical reactions were carried out in 20 ml borosilicate glass vials in a Penn Phd Photoreactor m2 composed of cooling block and LED plate connected to AC/DC input 100 - 240 V AC, 50/60 Hz power supply (Figure 1). The instrument details from the manufacturer as follows **AC/DC input** 100 - 240 V AC, 50/60 Hz; **feature** thermocouple type K-Type Thermocouple (Touch Screen: 3.5" TFT LCD; 320 x 480 resolution); **reaction suitability** reaction type: Photocatalysis reagent type: catalyst; **parameter** (Variable stir bar control 100 - 2000 RPM) 0-95% RH at 10-40 °C; **W × H × D** 11.4 cm × 27.2 cm × 27.9 cm 4.5 in. × 10.7 in. × 11.0 in. All the reaction was set using stir rate of magnetic stir ber 400 rpm, using 75% LED source and fan rotation speed 4500 rpm.

Instrument details available at: https://www.pennphd.com/product/5

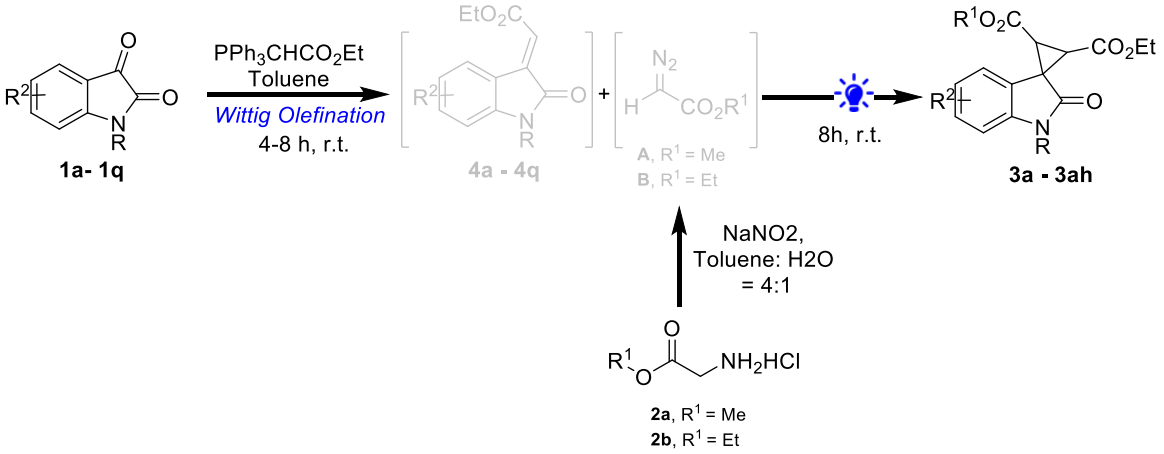
Figure S1: Blue LED Reaction Set-up for this synthesis.

3. General procedure:



Scheme S1: Structure of substrate used in this study.

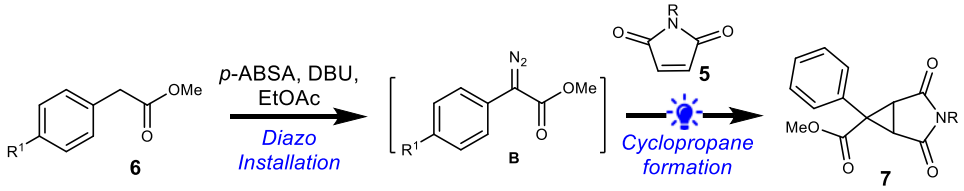
General procedure-A for the preparation spirocyclopropyl oxindole (3a- 3ah):



To an oven-dried 20 mL vial containing a magnetic stir bar, appropriate isatin derivative **1a – q** (0.679 mmol, 1 equiv.) and ethyl 2-(triphenyl-l5-phosphanylidene)acetate (0.747 mmol, 1.1 equiv.) dissolved in 7-8 mL toluene. The reaction mixture was stirred at room temperature for 4- 8h (depending on substitution). After 4-8 h a biphasic solution (toluene: H_2O = 4:1) of glycine alkyl ester hydrochloride **2a-b** (2.037 mmol, 3.0 equiv.) and sodium nitrite (2.45 mmol, 3.6 equiv.) was added into the reaction mixture and stirred the reaction mixture for an additional 8h under blue LED.

Upon completion, the reaction progress was confirmed by thin-layer chromatography (TLC). The crude reaction mixture was concentrated by using rota-vap. Purified by silica gel column chromatography (eluent: 95:5 to 80:20 hexane/ethyl acetate) to afford the desired products **3a-3ah**.

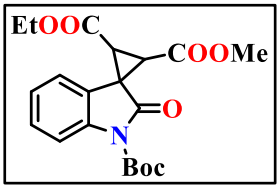
General procedure-B for the reaction of N- alkyl/aryl malimides with methyl 2-arylacetate:



To an oven-dried 20 mL vial containing a magnetic stir bar were added methyl 2-arylacetate 6 a-e (0.84 mmol, 1.4 equiv.), p-ABSA (0.72 mmol, 1.2 equiv.), and DBU (0.84 mmol, 1.4 equiv.) dissolved in 10 mL of EtOAc. The reaction mixture was stirred at room temperature for 6–8 h. After this period, the corresponding maleimide 5a–c (0.6 mmol, 1.0 equiv.) was added, and the reaction mixture was stirred for an additional 8 h under blue LED irradiation. Upon completion of the reaction, as confirmed by thin-layer chromatography (TLC), the crude mixture was concentrated using a rotary evaporator and purified by silica gel column chromatography (eluent: 95:5 to 80:20 hexane/ethyl acetate) to afford the desired products 7a–7f.

3.1. Characterization data:

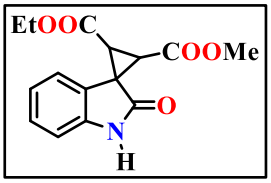
1'-(tert-butyl) 2-ethyl 3-methyl 2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3a):



Prepared according to the general procedure using tert-butyl 2,3-dioxoindoline-1-carboxylate **1g** (167.9 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column

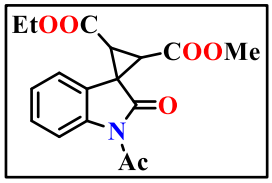
chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3a** was obtained as a yellowish solid (216.8 mg, 82% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.33-7.31 (m, 2H), 7.15-7.13 (m, 1H), 4.24-4.21 (m, 1H), 4.17-4.10 (m, 1H), 3.79 (s, 3H), 3.69 (s, 2H), 1.63 (s, 9H), 1.20 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.3, 167.2, 166.6, 166.0, 165.4, 148.9, 140.5, 140.5, 128.8, 124.5, 124.4, 123.3, 123.2, 122.3, 122.3, 115.1, 84.9, 84.9, 62.0, 52.9, 52.7, 38.0, 37.3, 37.1, 36.2, 35.9, 28.2, 28.2, 14.2 ppm. **HRMS (ESI) m/z**: $[M+K]^+$ calcd for $C_{20}H_{23}NO_7K$ 428.1106 found 428.1137. Diastereomeric ratio = 52: 48.

2-ethyl 3-methyl 2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3b):



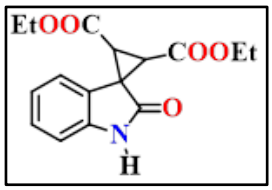
Prepared according to the general procedure using indoline-2,3-dione **1a** (100 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3b** was obtained as a yellowish semi solid (169.1 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.33 (s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.01-6.97 (m, 2H), 4.21-4.09 (m, 2H), 3.73 (s, 3H), 3.32 (d, J = 8.0 Hz, 1H), 3.26 (d, J = 8.0 Hz, 1H), 1.21 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 174.2, 167.1, 166.5, 141.8, 128.6, 124.7, 122.9, 122.5, 122.5, 110.4, 61.9, 52.8, 38.0, 35.6, 14.2 ppm. **HRMS (ESI) m/z**: $[M+K]^+$ calcd for $C_{15}H_{15}NO_5K$ 328.0582 found 328.0576. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 1'-acetyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3c):



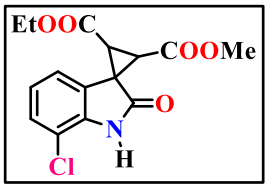
Prepared according to the general procedure using 1-acetylindoline-2,3-dione **1m** (128.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3c** was obtained as a yellowish solid (155.2 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8 Hz, 1H), 7.36-7.33 (m, 2H), 7.20-7.17 (m, 1H), 4.26-4.19 (m,1H), 4.17-4.09 (m, 1H), 3.77 (s, 3H), 3.71 (s, 2H), 2.66 (s, 3H), 1.21 (t, J = 8.0 Hz,3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.8, 172.7, 170.6, 166.9, 166.3, 165.9, 165.3, 140.8, 140.8, 129.1, 125.3, 125.2, 123.5, 123.4, 122.1, 122.1, 116.6, 62.1, 62.1, 52.9, 52.8, 38.1, 38.1, 37.4, 37.2, 36.5, 36.2, 26.9, 26.8, 14.2, 14.2 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for 332.1129 found 332.1141. Diastereomeric ratio = 50: 50.

diethyl 2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate(3d):



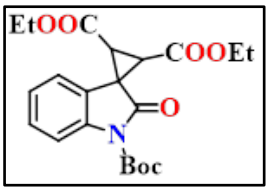
Prepared according to the general procedure using indoline-2,3-dione **1a** (100 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3d** was obtained as a yellowish solid (162.8 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 6.0 Hz, 1H), 7.02-6.97 (m, 2H), 4.22-4.12 (m, 4H), 3.29 (q, J = 9.3 Hz, 2H), 1.25 (t, J = 6.0 Hz, 3H) 1.21 (t, J = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 174.3, 167.2, 165.9, 141.8, 128.5, 124.9, 122.9, 122.4, 110.4, 61.8, 38.1, 35.6, 35.4, 14.2, 14.2 ppm. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{16}H_{18}NO_5$ 304.1179 found 304.1181. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 7'-chloro-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3e):



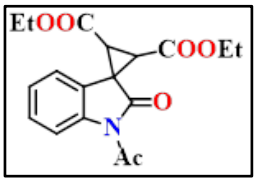
Prepared according to the general procedure using 7-chloroindoline-2,3-dione **1d** (123.3 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3e** was obtained as a yellowish solid (195.6 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 – 8.86 (m, 1H), 7.23 (d, J = 8.0 Hz, 2H), 6.97-6.93 (m, 1H), 4.22-4.09 (m, 2H), 3.75 (s, 3H), 3.33-3.28 (m, 2H), 1.22 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 173.0, 167.4, 166.9, 166.0, 165.4, 139.3, 128.5, 126.2, 126.2, 123.4, 121.4, 121.4, 115.4, 62.0, 52.9, 38.5, 36.0, 35.8, 35.5, 14.2 ppm. HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{15}H_{14}ClNO_5K$ 362.0192 found 362.0198. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2,3-diethyl 2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3f):



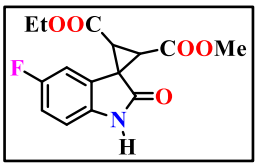
Prepared according to the general procedure using tert-butyl 2,3-dioxoindoline-1-carboxylate **1g** (167.9 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3f** was obtained as a yellowish solid (232.8 mg, 85% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 1H), 4.24-4.10 (m, 4H), 3.27 (s, 2H), 1.63 (s, 9H), 1.26 (t, J = 6.0 Hz, 3H), 1.20 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.2, 166.6, 165.5, 148.9, 140.5, 128.8, 124.4, 123.4, 122.3, 115.0, 84.8, 61.9, 38.0, 37.2, 36.2, 28.1, 14.1 ppm. HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{21}H_{25}NO_7K$ 442.1263 found 442.1278. Diastereomeric ratio = 1:1.

diethyl 1'-acetyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate(3g):



Prepared according to the general procedure using 1-acetylindoline-2,3-dione **1m** (128.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3g** was obtained as a yellowish solid (166.4 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.0 Hz, 1H), 7.37-7.33 (m, 2H), 7.19 – 7.15 (m, 1H), 4.25-4.12 (m, 4H), 3.33 (d, J = 8.0 Hz, 1H), 3.28 (d, J = 8.0 Hz, 1H), 2.65 (s, 3H), 1.27 (t, J = 6.0 Hz, 3H), 1.21 (t, J = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.7, 170.6, 166.4, 165.4, 140.7, 129.0, 125.2, 123.5, 122.1, 116.6, 62.1, 62.0, 38.1, 37.4, 36.4, 26.8, 14.2, 14.1 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}NO_6$ 346.1285 found 346.1302. Diastereomeric ratio = 1:1.

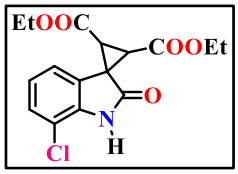
2-ethyl 3-methyl 5'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3h):



Prepared according to the general procedure using 5-fluoroindoline-2,3-dione **1b** (112.1 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel

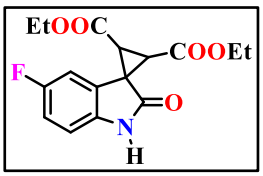
[SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3h** was obtained as a reddish liquid (187.7 mg, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.13-7.10 (m, 1H), 6.96-6.93 (m, 2H), 4.24-4.12 (m, 2H), 3.73 (s, 3H), 3.29 (d, *J* = 8.0 Hz, 1H), 3.25 (d, *J* = 8.0 Hz, 1H), 1.23 (t, *J* = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 174.2, 166.9, 166.2, 160.1, 157.7, 137.8, 137.8, 126.3, 126.2, 115.2, 115.0, 111.3, 111.1, 111.0, 62.1, 60.5, 52.8, 38.2, 38.2, 35.7, 35.6, 14.2 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.8 ppm. HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{15}H_{14}FNO_5K$ 346.0488 found 346.0498. Diastereomeric ratio = 1:1.

diethyl 7'-chloro-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate(3i):



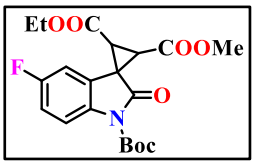
Prepared according to the general procedure using 7-chloroindoline-2,3-dione **1d** (123.3 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3i** was obtained as a white solid (204.1 mg, 89% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.96 (t, *J* = 8.0 Hz, 1H), 4.24-4.12 (m, 4H), 3.29 (q, *J* = 5.3 Hz, 2H), 1.26 (t, *J* = 6.0 Hz, 3H), 1.22 (t, *J* = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.7, 167.0, 165.5, 139.2, 128.5, 126.3, 123.4, 121.4, 115.4, 62.0, 62.0, 38.5, 36.0, 35.8, 14.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{16}H_{16}ClNO_5Na$ 360.0609 found 360.0622. Diastereomeric ratio = 1:1.

diethyl 5'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate(3j):



Prepared according to the general procedure using 5-fluoroindoline-2,3-dione **1b** (112.1 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3j** was obtained as a reddish solid (198.5 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 7.11 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.95-6.92 (m, 2H), 4.23-4.14 (m, 4H), 3.25 (d, *J* = 4.0 Hz, 2H), 1.25-1.21 (m, 6H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 174.3, 171.3, 167.0, 165.6, 160.1, 157.7, 137.8, 137.8, 126.4, 126.3, 115.1, 114.9, 111.3, 111.0, 110.9, 62.0, 61.9, 38.2, 38.2, 35.8, 35.6, 14.2, 14.1 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.9 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}FNO_5$ 322.1085 found 322.1099. Diastereomeric ratio = 1:1.

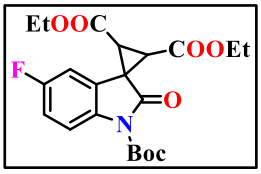
1'-(tert-butyl) 2-ethyl 3-methyl 5'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate(3k):



Prepared according to the general procedure using tert-butyl 5-fluoro-2,3-dioxoindoline-1-carboxylate **1h** (180.1 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3k** was obtained as a yellowish solid (240.7 mg, 87% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.86 (m, 1H), 7.12 (dd, J_1 = 4.0 Hz, J_2 = 1.2 Hz 1H), 7.05-7.00 (m, 1H), 4.22-4.11 (m, 2H), 3.76 (s, 3H), 3.28 (dd, J_1 = 12 Hz, J_2 = 8.0 Hz, 2H), 1.62 (s, 9H), 1.23 (t, *J* = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 169.9,

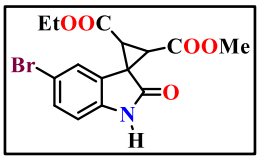
166.4, 165.7, 161.0, 158.5, 148.8, 136.5, 125.1, 125.0, 116.4, 116.3, 115.5, 115.3, 110.4, 110.1, 85.1, 62.2, 53.0, 37.4, 36.3, 28.2, 14.2 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.14 ppm. HRMS (ESI) m/z: $[M+K]^+$ calcd for $C_{20}H_{22}FNO_7K$ 446.1012 found 446.1032. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2,3-diethyl 5'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3l):



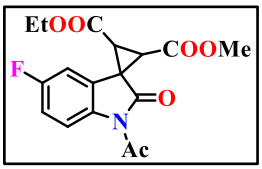
Prepared according to the general procedure using tert-butyl 5-fluoro-2,3-dioxoindoline-1-carboxylate **1h** (180.1 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3l** was obtained as a yellowish solid (246.1 mg, 86% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.85 (m, 1H), 7.11 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.04-6.99 (m, 1H), 4.26-4.10 (m, 4H), 3.26 (q, J = 6.7 Hz, 2H), 1.61 (s, 9H), 1.27 – 1.20 (m, 6H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 169.8, 166.5, 165.2, 160.9, 158.5, 148.9, 136.5, 136.5, 125.2, 125.1, 116.3, 116.2, 115.4, 115.2, 110.3, 110.1, 85.0, 62.1, 62.0, 37.9, 37.9, 37.3, 36.6, 28.1, 14.1 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ – 117.19 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{24}FNO_7Na$ 444.1429 found 444.1435. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 5'-bromo-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3m):



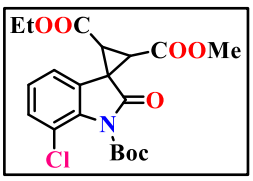
Prepared according to the general procedure using 5-bromoindoline-2,3-dione **1c** (153.5 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3m** was obtained as a yellowish semi solid (227.5 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.47 (d, J = 1.2 Hz, 1H), 7.38 (dd, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 4.21-4.18 (m, 2H), 3.74 (s, 3H), 3.30-3.24 (m, 2H), 1.25 (t, J = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 173.5, 167.4, 166.8, 166.1, 165.5, 140.7, 131.5, 126.8, 126.8, 126.3, 126.3, 115.3, 115.3, 111.7, 62.2, 62.0, 52.9, 52.8, 37.8, 37.7, 35.9, 35.9, 35.6, 14.2, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}BrNO_5$ 368.0128 found 368.0129. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 1'-acetyl-5'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3n):



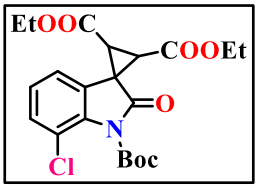
Prepared according to the general procedure using 1-acetyl-5-fluoroindoline-2,3-dione **1n** (140.7 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3n** was obtained as a yellowish solid (142.3 mg, 60% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29-8.25 (m, 1H), 7.12 (dd, J = 8.0Hz, J2 = 4.0 Hz, 1H), 7.07-7.01 (m, 1H), 4.24-4.12 (m, 2H), 3.76 (s, 3H), 3.31 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 2.64 (s, 3H), 1.23 (t, J = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.5, 170.4, 166.2, 165.6, 161.3, 158.9, 136.8, 125.4, 125.3, 118.0, 117.9, 115.7, 115.4, 110.2, 109.9, 62.3, 53.0, 37.9, 37.9, 37.5, 36.6, 26.7, 14.2 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.54ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}FNO_6Na$ 372.0854 found 372.0857. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2-ethyl 3-methyl 7'-chloro-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3o):



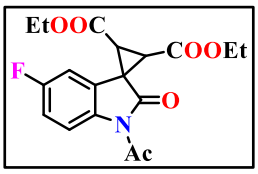
Prepared according to the general procedure using tert-butyl 7-chloro-2,3-dioxoindoline-1-carboxylate **1j** (191.27 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3o** was obtained as a yellowish solid (224.5 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2H), 7.08-7.03 (m, 1H), 4.24-4.19 (m, 1H), 4.16-4.11 (m, 1H), 3.75 (s, 3H), 3.30 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 1.63 (s, 9H), 1.23 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.4, 167.2, 166.6, 165.7, 165.1, 147.9, 137.6, 130.6, 126.7, 125.1, 121.3, 121.2, 118.8, 86.2, 62.3, 62.2, 53.1, 52.9, 38.1, 37.3, 37.0, 36.6, 36.3, 31.6, 27.8, 14.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}ClNO_7Na$ 446.0977 found 446.0975. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2,3-diethyl 7'-chloro-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3p):



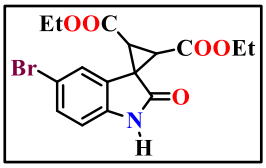
Prepared according to the general procedure using tert-butyl 7-chloro-2,3-dioxoindoline-1-carboxylate **1j** (191.27 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3p** was obtained as a yellowish solid (240.8 mg, 81% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 7.05 (t, J = 8.0 Hz, 1H), 4.24-4.12 (m, 4H), 3.29 (dd, J_1 = 12.0 Hz, J_2 = 8.0 2H), 1.62 (s, 9H), 1.23 (t, J = 8.0 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.2, 166.6, 165.1, 147.8, 137.5, 130.5, 126.7, 125.0, 121.1, 118.6, 86.0, 62.1, 62.1, 38.0, 37.1, 36.4, 27.7, 14.1 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{24}ClNO_7Na$ 460.1134 found 460.1133. Diastereomeric ratio = 1:1.

diethyl 1'-acetyl-5'-fluoro-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3q):



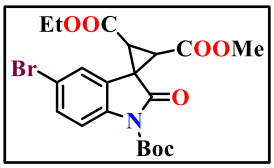
Prepared according to the general procedure using 1-acetyl-5-fluoroindoline-2,3-dione **1n** (140.7 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3q** was obtained as a white solid (150.5 mg, 61% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29-8.26 (m, 1H), 7.13 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.06-7.01 (m, 1H), 4.25-4.14 (m, 4H), 3.29 (d, J = 4.0 Hz, 2H), 2.64 (s, 3H), 1.28 (t, J = 8Hz, 3H), 1.23 (t, J = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.4, 170.4, 166.2, 165.0, 161.3, 158.9, 136.8, 136.8, 125.6, 125.5, 118.0, 117.9, 115.6, 115.4, 110.2, 109.9, 62.3, 62.2, 37.9, 37.9, 37.5, 36.8, 26.7, 14.2, 14.2 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -115.57 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{18}FNO_6Na$ 386.101 found 386.1010. Diastereomeric ratio = 1:1.

diethyl 5'-bromo-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3r):



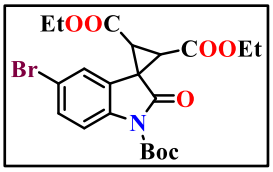
Prepared according to the general procedure using 5-bromoindoline-2,3-dione **1c** (153.5 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3r** was obtained as a reddish semi solid (207.6 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.48 (d, J = 4.0 Hz, 1H), 7.38 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 4.22-4.17(m, 4H), 3.27 (q, J = 6.7 Hz,2H), 1.25 (t, J = 8.0 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 173.6, 166.9, 165.5, 140.7, 131.5, 126.9, 126.3, 115.3, 111.7, 62.2, 62.0, 37.8, 35.9, 35.8, 14.2, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{17}BrNO_5$ 382.0285 found 382.0278. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2-ethyl 3-methyl 5'-bromo-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3s):



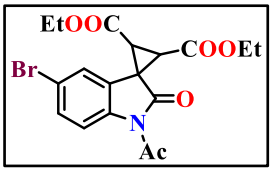
Prepared according to the general procedure using tert-butyl 5-bromo-2,3-dioxoindoline-1-carboxylate **1i** (221.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3s** was obtained as a yellowish liquid (289.3 mg, 91% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.48-7.45 (m, 2H), 4.24-4.21 (m, 2H), 3.73 (s, 3H), 3.27 (d, J = 1.2 Hz, 2H), 1.61 (s, 9H), 1.26 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 169.4, 166.9, 165.0, 148.7, 139.5, 131.8, 125.5, 125.4, 117.6, 116.6, 85.3, 62.1, 53.0, 52.9, 37.6, 37.2, 36.6, 28.1, 14.1 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{20}H_{22}BrNO_7Na$ 490.0472 found 490.0466. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2,3-diethyl 5'-bromo-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3t):



Prepared according to the general procedure using tert-butyl 5-bromo-2,3-dioxoindoline-1-carboxylate **1i** (221.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3t** was obtained as a yellowish solid (304.5 mg, 93% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 7.48-7.44 (m, 2H), 4.23-4.15 (m, 4H), 3.26 (s, 2H), 1.61 (s, 9H), 1.26 (t, J = 6.0 Hz, 3H), 1.23 (t, J = 4.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 169.4, 166.4, 165.1, 148.7, 139.5, 131.7, 125.5, 117.5, 116.6, 85.2, 62.2, 62.1, 37.6, 37.4, 36.5, 28.1, 14.2, 14.1 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{24}BrNO_7Na$ 504.0628 found 504.0631. Diastereomeric ratio = 1:1.

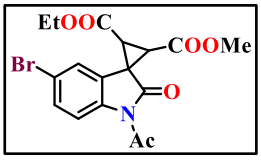
diethyl 1'-acetyl-5'-bromo-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3u):



Prepared according to the general procedure using 1-acetyl-5-bromoindoline-2,3-dione **1o** (182.0 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column

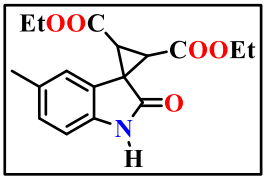
chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3u** was obtained as a white semi solid (198.7 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 12.0 Hz, 1H), 7.51-7.46 (m, 2H), 4.22 (q, *J* = 6.7 Hz, 4H), 3.30 (q, *J* = 8.0 Hz, 2H), 2.65 (s, 3H), 1.27 (t, *J* = 8.0 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.0, 170.4, 166.2, 165..0, 139.7, 131.9, 125.7, 125.3, 118.4, 118.1, 62.4, 62.2, 37.6, 36.8, 26.8, 14.2, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{19}BrNO_6$ 424.039 found 424.0396. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 1'-acetyl-5'-bromo-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3v):



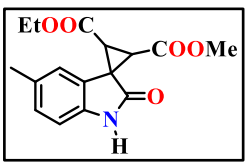
Prepared according to the general procedure using 1-acetyl-5-bromoindoline-2,3-dione **1o** (182.0 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3v** was obtained as a white solid (197.7 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 2H), 4.25-4.17 (m, 2H), 3.75 (d, *J* = 8 Hz, 3H), 3.34-3.27 (m, 2H), 2.64 (s, 3H), 1.25 (t, *J* = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.1, 172.0, 170.4, 166.7, 166.1, 165.5, 164.9, 139.7, 132.0, 125.6, 125.5, 125.4, 125.3, 118.4, 118.4, 118.1, 62.4, 62.2, 53.0, 37.7, 37.6, 37.6, 37.4, 36.9, 36.5, 26.8, 14.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{17}H_{16}BrNO_6Na$ 432.0053 found 432.0043. Diastereomeric ratio = 1:1.

diethyl 5'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate(3w):



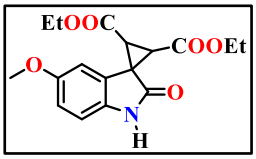
Prepared according to the general procedure using 5-methylindoline-2,3-dione **1e** (109.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3w** was obtained as a reddish solid (170.2 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.12 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 4.22-4.14 (m, 4H), 3.28-3.23 (m, 2H), 2.30 (s, 3H), 1.23 (q, *J* = 8.0 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 174.1, 167.2, 166.0, 139.3, 132.0, 128.9, 124.9, 123.6, 110.0, 61.8, 61.8, 38.1, 35.5, 35.5, 21.3, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}NO_5$ 318.1336 found 318.1338. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 5'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3x):



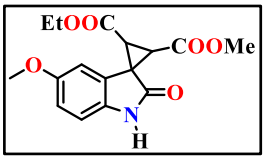
Prepared according to the general procedure using 5-methylindoline-2,3-dione **1e** (109.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3x** was obtained as a reddish solid (205.9 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.12 (s, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 4.22-4.10 (m, 2H), 3.73 (s, 3H), 3.29-3.23 (m, 2H), 2.29 (s, 3H), 1.22 (t, *J* = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 174.1, 167.1, 166.5, 139.3, 132.0, 128.9, 124.8, 123.6, 110.1, 61.8, 52.7, 38.1, 35.5, 35.2, 21.3, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{18}NO_5$ 304.1179 found 304.1181. Diastereomeric ratio = 1:1.

diethyl 5'-methoxy-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3y):



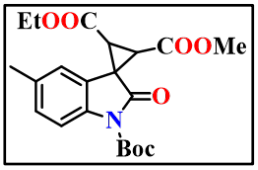
Prepared according to the general procedure using 5-methoxyindoline-2,3-dione **1f** (120.3 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3y** was obtained as a reddish solid (178.8 mg, 79% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 6.96 (d, *J*=2.26 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.80-6.77 (m, 1H), 4.22-4.15 (m, 4H), 3.75 (s, 3H), 3.25 (q, *J* = 5.3 Hz, 2H), 1.23 (t, *J* = 8.0 Hz, 6H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 174.0, 167.2, 165.9, 155.7, 135.1, 126.1, 113.9, 110.7, 109.7, 61.9, 61.9, 55.9, 38.4, 35.6, 35.6, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}NO_6$ 334.1285 found 334.1284. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 5'-methoxy-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3z):



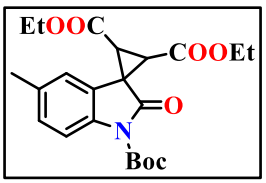
Prepared according to the general procedure using 5-methoxyindoline-2,3-dione **1f** (120.3 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3z** was obtained as a reddish semi solid (179.9 mg, 83% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 6.96 (d, *J* = 2.43, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.80-6.77 (m, 1H), 4.20-4.10 (m, 2H), 3.76 (s, 3H), 3.74 (s, 3H), 3.29-3.24 (m, 2H), 1.23 (t, *J* = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 173.9, 167.1, 166.4, 155.8, 135.0, 126.0, 113.9, 110.7, 109.7, 61.9, 55.9, 52.8, 38.3, 35.6, 35.4, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{18}NO6$ 320.1129 found 320.1128. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2-ethyl 3-methyl 5'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3aa):



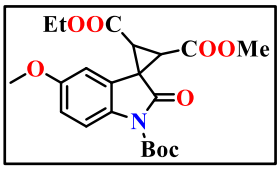
Prepared according to the general procedure using tert-butyl 5-methyl-2,3-dioxoindoline-1-carboxylate **1k** (177.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3aa** was obtained as a white solid (191.7 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.13-7.11 (m, 2H), 4.20-4.08 (m, 2H), 3.75 (s, 3H), 3.26 (s, 2H), 2.31 (s, 3H), 1.62 (s, 9H), 1.20 (t, *J* = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.4, 166.5, 166.0, 148.9, 138.1, 134.1, 129.3, 123.1, 122.8, 114.8, 84.7, 61.9, 52.8, 38.0, 37.3, 35.9, 28.2, 21.2, 14.1 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}NO_7Na$ 426.1523 found 426.1518. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2,3-diethyl 5'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3ab):



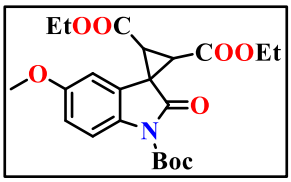
Prepared according to the general procedure using tert-butyl 5-methyl-2,3-dioxoindoline-1-carboxylate **1k** (177.4 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3ab** was obtained as a yellowish solid (226.7 mg, 80% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 1H), 7.13-7.11 (m, 2H), 4.22-4.11 (m, 4H), 3.27-3.23 (m, 2H), 2.31 (s, 3H), 1.61 (s, 9H), 1.25 (t, J = 8.0 Hz, 3H), 1.20 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.3, 166.6, 165.5, 148.9, 138.1, 134.1, 129.2, 123.3, 122.8, 114.8, 84.6, 61.9, 38.0, 37.2, 36.1, 28.1, 21.2, 14.1 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{27}NO_7Na$ 440.168 found 440.1678. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2-ethyl 3-methyl 5'-methoxy-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3ac):



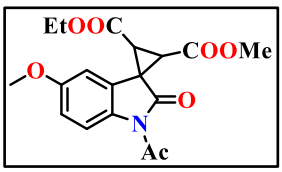
Prepared according to the general procedure using tert-butyl 5-methoxy-2,3-dioxoindoline-1-carboxylate **1l** (188.3 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3ac** was obtained as a white solid (213.6 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 2.64 Hz, 1H), 6.85 (dd, J_1 = 10Hz, J_2 = 2.0 Hz, 1H), 4.20-4.09 (m, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 3.27 (s, 2H), 1.62 (s, 9H), 1.21 (t, J = 6.0Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.4, 166.6, 166.0, 156.8, 149.0, 133.9, 124.5, 116.0, 114.2, 108.2, 84.7, 62.0, 55.8, 52.9, 38.2, 37.3, 36.1, 28.2, 14.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{25}NO_8Na$ 442.1472 found 442.1472. Diastereomeric ratio = 1:1.

1'-(tert-butyl) 2,3-diethyl 5'-methoxy-2'-oxospiro[cyclopropane-1,3'-indoline]-1',2,3-tricarboxylate (3ad):



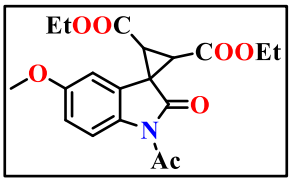
Prepared according to the general procedure using tert-butyl 5-methoxy-2,3-dioxoindoline-1-carboxylate **1l** (188.3 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3ad** was obtained as a white solid (229.6 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 4.0 Hz,1H), 6.86 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 4.24-4.12 (m, 4H), 3.78 (s, 3H), 3.28-3.24 (m, 2H), 1.62 (s, 9H), 1.26 (t, J = 6.0 Hz, 3H), 1.22 (t, J = 6.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 170.3, 166.7, 165.5, 156.8, 149.0, 133.9, 124.7, 116.0, 114.2, 108.2, 84.6, 62.0, 62.0, 55.8, 38.2, 37.2, 36.4, 28.2, 14.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{27}NO_8Na$ 456.1629 found 456.1640. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 1'-acetyl-5'-methoxy-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3ae):



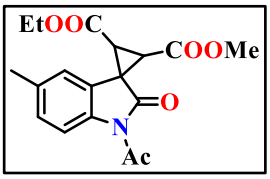
Prepared according to the general procedure using 1-acetyl-5-methoxyindoline-2,3-dione **1q** (148.8 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3ae** was obtained as a white solid (159.4 mg, 65% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz,1H), 6.93 (d, J = 4.0 Hz, 1H), 6.86 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 4.22-4.10 (m, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.30 (q, J = 9.3 Hz, 2H), 2.63 (s, 3H), 1.22 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.8, 170.3, 166.3, 165.8, 157.2, 134.2, 124.7, 117.6, 114.1, 108.0, 62.2, 55.7, 52.9, 38.2, 37.3, 36.3, 26.7, 14.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{19}NO_7Na$ 384.1054 found 384.1054. Diastereomeric ratio = 1:1.

diethyl 1'-acetyl-5'-methoxy-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3af):



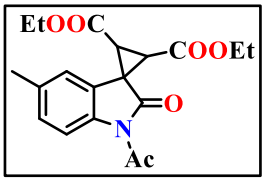
Prepared according to the general procedure using 1-acetyl-5-methoxyindoline-2,3-dione **1q** (148.8 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3af** was obtained as a white solid (173.3 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 6.93 (d, J = 4.0 Hz, 1H), 6.85 (dd, J_1 = 10 Hz, J_2 = 2.0 Hz, 1H), 4.25-4.10 (m, 4H), 3.77 (s, 3H), 3.28 (q, J = 8.0 Hz, 2H), 2.63 (s, 3H), 1.26 (t, J = 8.0 Hz, 3H), 1.22 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.7, 170.3, 166.4, 165.3, 157.2, 134.2, 124.9, 117.5, 114.0, 108.0, 62.1, 62.0, 55.7, 38.2, 37.3, 36.5, 26.6, 14.2, 14.2 ppm. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{19}H_{21}NO_7Na$ 398.121 found 398.1208. Diastereomeric ratio = 1:1.

2-ethyl 3-methyl 1'-acetyl-5'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3ag):



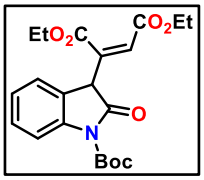
Prepared according to the general procedure using 1-acetyl-5-methylindoline-2,3-dione **1p** (137.9 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine methyl ester hydrochloride **2a** (255.7 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3ag** was obtained as a yellowish semi solid (164.0 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 1H), 7.16-7.13 (m, 2H), 4.22-4.11 (m, 2H), 3.76 (s, 3H), 3.30 (q, J = 9.3 Hz, 2H), 2.65 (s, 3H), 2.33 (s, 3H), 1.22 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 173.0, 170.5, 166.3, 166.0, 138.5, 135.0, 129.6, 123.4, 122.6, 122.5, 116.4, 62.1, 52.9, 38.1, 37.4, 36.2, 26.8, 21.3, 14.2 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}NO_6$ 346.1285 found 346.1290. Diastereomeric ratio = 1:1.

diethyl 1'-acetyl-5'-methyl-2'-oxospiro[cyclopropane-1,3'-indoline]-2,3-dicarboxylate (3ah):



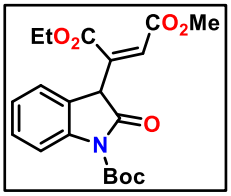
Prepared according to the general procedure using 1-acetyl-5-methylindoline-2,3-dione **1p** (137.9 mg, 0.679 mmol, 1 equiv.), ethyl 2-(triphenyl-l5-phosphanylidene)acetate (260.2 mg, 0.747 mmol, 1.1 equiv.), glycine ethyl ester hydrochloride **2b** (284.3 mg, 2.037 mmol, 3.0 equiv.) and sodium nitrite (169.0 mg, 2.45 mmol, 3.6 equiv.). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20) R_f= 0.3], the expected product **3ah** was obtained as a yellowish semi solid (173.1 mg, 71% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.0 Hz, 1H), 7.15-7.13 (m, 2H), 4.24-4.13 (m, 4H), 3.28 (q, J = 8.0 Hz, 2H), 2.63 (s, 3H), 2.32 (s, 3H), 1.26 (t, J = 6.0 Hz, 3H), 1.21 (t, J = 8.0 Hz, 3H) ppm; **^{13}C{^{1}H} NMR** (100MHz, $CDCl_3$) δ 172.8, 170.4, 166.4, 165.4, 138.4, 134.9, 129.4, 123.5, 122.5, 116.3, 62.09, 62.0, 38.1, 37.3, 36.4, 26.7, 21.3, 14.2, 14.1 ppm. . HRMS (ESI) m/z: $[M+H]^+$ calcd for C19H22NO6 360.1442 found 360.1441. Diastereomeric ratio = 1:1.

diethyl 2-(1-(tert-butoxycarbonyl)-2-oxoindolin-3-yl)fumarate (3f'):



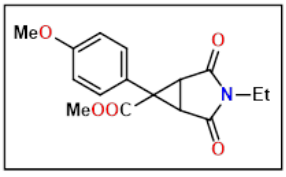
3f' was prepared using **3f** (100 mg, 0.247 mmol, 1equiv) and pyridine(2 equiv.) in DCM solvent for 24-30h at room temperature . The crude product was purified by column chromatography (SiO_2, hexane/EtOAc = 80:20, R_f = 0.3) to afford pure (53 mg, 53% yield) as yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.89− 7.86 (d, J = 12 Hz, 1H), 7.41−7.37 (m, 1H), 7.30−7.28 (m, 1H), 7.17−7.13 (td, J = 16 Hz, 1H), 4.63 (s, 1H), 4.35−4.33 (q, J = 8 Hz, 2H), 3.85−3.80 (q, J = 20 Hz, 2H), 1.64 (s, 9H), 1.37−1.33 (t, J = 16 Hz, 3H), 0.87−0.83 (t, J = 16 Hz, 3H) ppm. ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ_C 174.2, 166.3, 161.5, 149.1, 140.1, 139.5, 131.7, 126.1, 125.6, 125.5, 124.7, 123.5, 116.0, 115.8, 85.8, 73.3, 62.6, 62.1, 62.1, 60.5, 29.8, 28.5, 14.6, 14.0 ppm. HRMS (ESI+) m/z: $[M + H]^+$ calcd. for $C_{21}H_{26}NO_7$, 404.1709; found, 404.1712. Diastereomeric ratio = 1:1.

1-ethyl 4-methyl 2-(1-(tert-butoxycarbonyl)-2-oxoindolin-3-yl)fumarate (3a'):



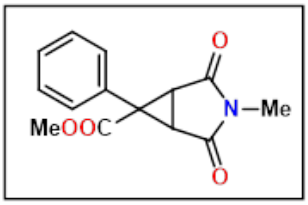
3a' was prepared using **3a** (96.2 mg, 0.247 mmol, 1 equiv.) and pyridine in DCM solvent for 24-30h at room temperature. The crude product was purified by column chromatography (SiO_2, hexane/EtOAc = 80:20, R_f = 0.3) to afford pure (64.4 mg, 67% yield) as a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.89−7.86 (dd, J = 12 Hz, 1H), 7.41−7.37 (td, J = 16 Hz, 1H), 7.29−7.27 (d, J = 8 Hz, 1H), 7.17−7.13 (td, J = 16 Hz, 1H), 4.62 (s, 1H), 3.87 (s, 3H), 3.85−3.80 (q, J = 20 Hz, 2H), 1.64 (s, 9H), 0.86−0.82 (t, J = 16 Hz, 3H) ppm. ^{13}C{1H} NMR (100 MHz, $CDCl_3$): δ_C 174.1, 166.3, 161.9, 149.1, 140.1, 139.1, 131.7, 131.4, 126.1, 125.6, 125.4, 124.7, 123.5, 116.0, 115.8, 85.8, 85.5, 73.5, 73.4, 62.6, 62.2, 62.1, 60.3, 53.0, 28.5, 14.0 ppm. HRMS s(ESI+) m/z: $[M + H]^+$ calcd. for $C_{20}H_{24}NO_7$, 390.1553; found, 390.1551. Diastereomeric ratio = 1:1.

methyl 3-ethyl-6-(4-methoxyphenyl)-2,4-dioxo-3-azabicyclo[3.1.0]hexane-6-carboxylate, 7a:



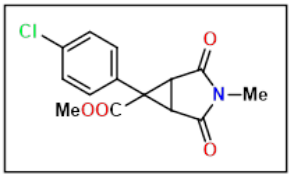
7a was prepared according to the general procedure-B using **5a** (0.6 mmol, 75 mg), **6a** (0.84 mmol, 151.37 mg), p-ABSA (0.72 mmol, 172.9 mg) and DBU (0.84 mmol, 127.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **7a** was obtained as a yellowish white viscous liquid. (140 mg, 77%) ***^{1}H* NMR** ($CDCl_3$, 400 MHz) δ_H 7.23 (d, J = 8Hz, 2H), 6.83 (d, J = 8Hz, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 3.22 (s, 2H), 3.05 (q, J = 8Hz, 2H), 0.28 (t, J = 8Hz, 3H) ppm. ***^{13}C* {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ_C 171.7, 169.7, 160.3, 131.9, 122.6, 114.4, 55.5, 53.7, 44.9, 33.0, 32.6, 11.4 ppm. HRMS (ESI) m/z calcd for $C_{16}H_{18}NO_5$ $[M + H]^+$ 304.1179, found 304.1173. Diastereomeric ratio = 1:1.

methyl 3-methyl-2,4-dioxo-6-phenyl-3-azabicyclo[3.1.0]hexane-6-carboxylate, 7b:



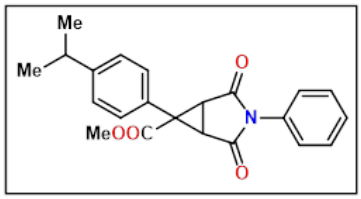
7b was prepared according to the general procedure-B using **BQ** (0.6 mmol, 66.8 mg), **6b** (0.84 mmol, 126 mg), p-ABSA (0.72 mmol, 172.9 mg) and DBU (0.84 mmol, 127.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **7b** was obtained as a yellowish white viscous liquid. (115.5 mg, 74%). ^{1}***H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 7.33-7.30 (m, 5H), 3.68 (s, 3H), 3.29 (s, 2H), 2.30 (s, 3H) ppm. ^{13}***C*** $\{^{1}$***H***$\}$ **NMR** ($CDCl_3$, 100 MHz) δ_C 190.8, 166.7, 138.4, 134.4, 132.5, 130.6, 123.7, 53.6, 47.6, 36.6 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{14}NO_4$ $[M + H]^+$ 260.0917, found 260.0916. Diastereomeric ratio = 1:1.

methyl 6-(4-chlorophenyl)-3-methyl-2,4-dioxo-3-azabicyclo[3.1.0]hexane-6-carboxylate, 7c:



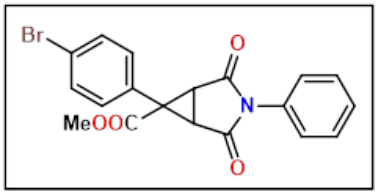
7c was prepared according to the general procedure-B using **5b** (0.6 mmol, 66.8 mg), **6c** (0.84 mmol, 155.1 mg), p-ABSA (0.72 mmol, 172.9 mg) and DBU (0.84 mmol, 127.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **7c** was obtained as a yellowish white viscous liquid. (119.9 mg, 68%). ^{1}***H*** **NMR** ($CDCl_3$, 400 MHz) δ_H : 7.31 (d, *J* = 8Hz, 2H), 7.23 (d, *J* = 8Hz, 2H), 3.68 (s, 3H), 3.29 (s, 2H), 2.36 (s, 3H) ppm. ^{13}***C*** $\{^{1}$***H***$\}$ **NMR** ($CDCl_3$, 100 MHz) δ_C 191.4, 170.1, 139.2, 132.7, 132.3, 130.2, 123.3, 54.0, 42.3, 36.7 ppm. HRMS (ESI) m/z calcd for $C_{14}H_{13}ClNO_4$ $[M + H]^+$ 294.0528, found 294.0523. Diastereomeric ratio = 1:1.

methyl 6-(4-isopropylphenyl)-2,4-dioxo-3-phenyl-3-azabicyclo[3.1.0]hexane-6-carboxylate, 7d:



7d was prepared according to the general procedure-B using **5c** (0.6 mmol, 103.9 mg), **6d** (0.84 mmol, 214.3 mg), p-ABSA (0.72 mmol, 172.9 mg) and DBU (0.84 mmol, 127.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **7d** was obtained as a yellowish white viscous liquid. (172.6 mg, 79%). ^{1}***H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 7.34 (d, *J* = 8Hz, 2H), 7.25-7.20 (m, 3H), 7.19-7.15 (m, 2H), 6.20 (d, *J* = 8Hz, 2H), 3.71 (s, 3H), 3.43 (s, 2H), 2.93 (sep, *J* = 6.67Hz, 1H), 1.26 (s, 3H), 1.24 (s, 3H) ppm. ^{13}***C*** $\{^{1}$***H***$\}$ **NMR** ($CDCl_3$, 100 MHz) δ_C 172.0, 157.6, 155.5, 131.0, 128.6, 123.4, 121.2, 120.5, 113.9, 111.0, 70.8, 55.6, 55.4, 36.2, 28.1, 19.2, 19.1 ppm. HRMS (ESI) m/z calcdfor $C_{22}H_{22}NO_4$ $[M + H]^+$ 364. 1543, found 364. 1546. Diastereomeric ratio = 1:1.

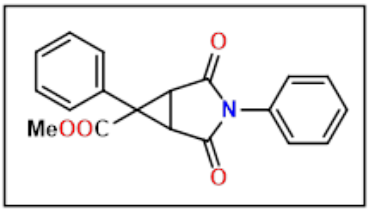
methyl 6-(4-bromophenyl)-2,4-dioxo-3-phenyl-3-azabicyclo[3.1.0]hexane-6-carboxylate, 7e:



7e was prepared according to the general procedure-B using **5c** (0.6 mmol, 103.9 mg), **6e** (0.84 mmol, 192.4 mg), p-ABSA (0.72 mmol, 172.9 mg) and DBU (0.84 mmol, 127.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **7e** was obtained as a yellowish white viscous liquid. (170.4 mg, 71%). ^{1}***H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 7.55 (d, *J* = 8Hz, 2H), 7.45 (d, *J* = 8Hz, 2H), 7.40 (d, *J* = 8Hz, 3H), 7.27 (m, 1H), 7.25 (m, 1H), 3.68 (s, 3H), 3.11 (s, 2H)

ppm. ***^{13}C {^{1}H}*** **NMR** ($CDCl_3$, 100 MHz) δ_C 170.2, 132.5, 130.7, 129.4, 128.8, 126.4, 54.0, 32.1 ppm. HRMS (ESI) m/z calcd for $C_{19}H_{15}BrNO_4$ $[M + H]^+$ 400.0179, found 400.0176. Diastereomeric ratio = 1:1.

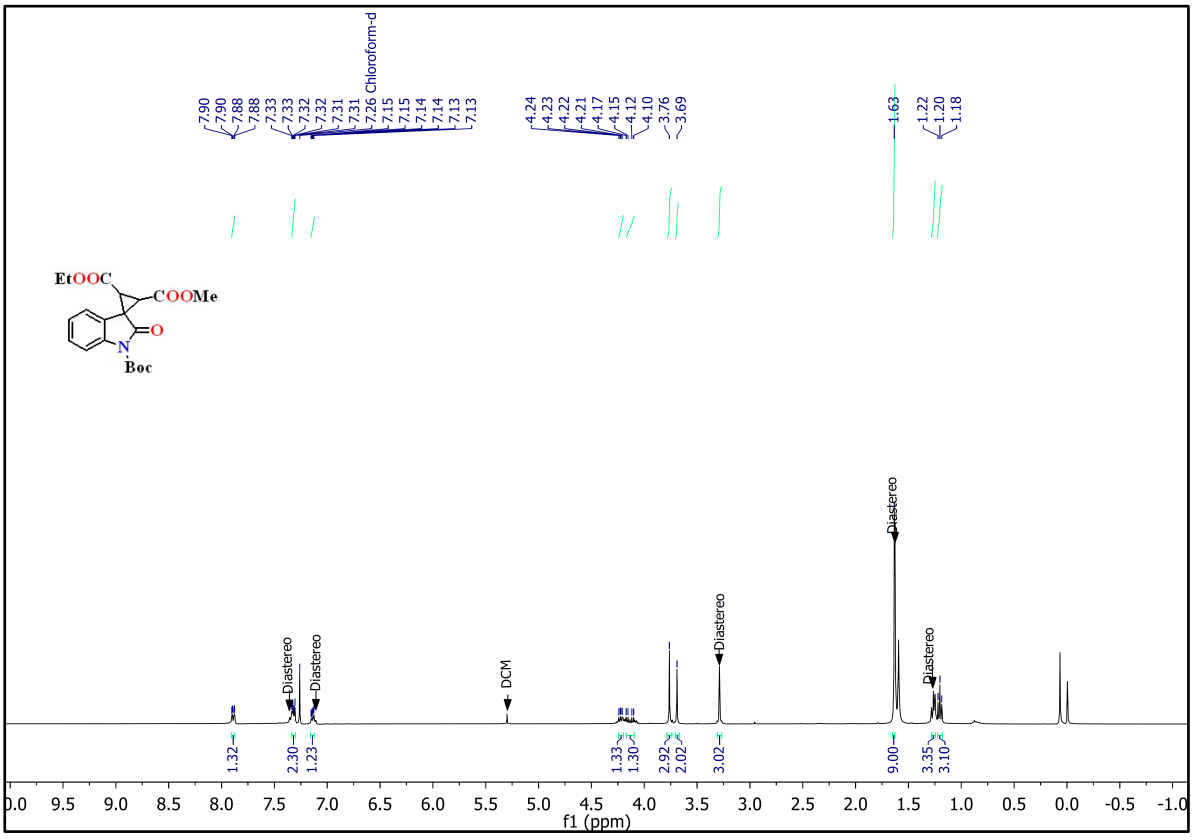
methyl 2,4-dioxo-3,6-diphenyl-3-azabicyclo[3.1.0]hexane-6-carboxylate, 7f:



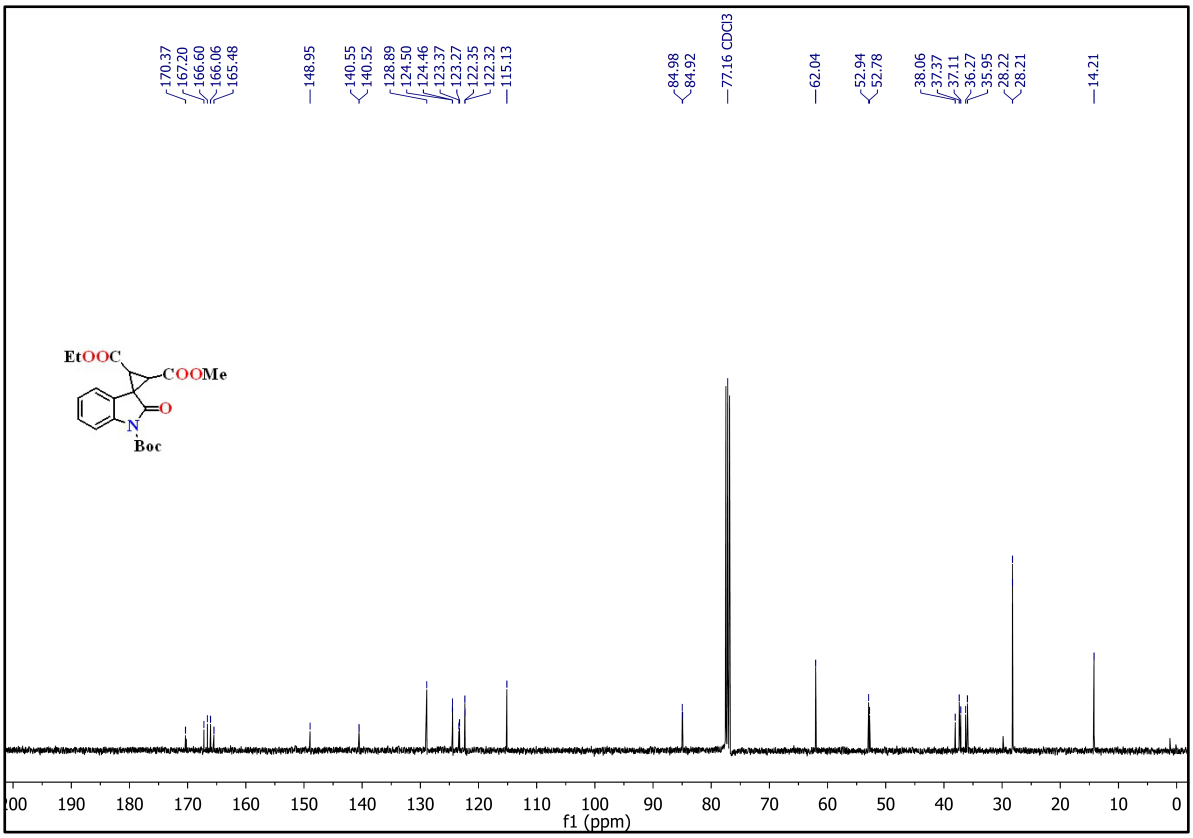
7f was prepared according to the general procedure-B using **5c** (0.6 mmol, 103.9 mg), **6b** (0.84 mmol, 126 mg), p-ABSA (0.72 mmol, 172.9 mg) and DBU (0.84 mmol, 127.9 mg). After column chromatography on silica gel [SiO_2, Hexane/EtOAc (95:5 to 80:20)], the expected product **7f** was obtained as a yellowish white viscous liquid. (125.2 mg, 65%). ***^{1}H*** **NMR** ($CDCl_3$, 400 MHz) δ_H 7.46-7.42 (m, 3H), 7.41-7.38 (m, 3H), 7.22-7.18 (m, 2H), 6.27 (dd, ^{1}J=6.8Hz, ^{2}J=1.8Hz, 2H), 3.71 (s, 3H), 3.45 (s, 2H) ppm. ***^{13}C {^{1}H}*** **NMR** ($CDCl_3$, 100 MHz) δ_C 170.9, 170.6, 169.3, 130.8, 129.4, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 126.5, 126.4, 53.8, 45.2, 32.7, 32.1 ppm. HRMS (ESI) m/z calcd for $C_{19}H_{16}NO_4$ $[M + H]^+$ 322.1074, found 322.1079. Diastereomeric ratio = 70: 30.

Spectral Images:

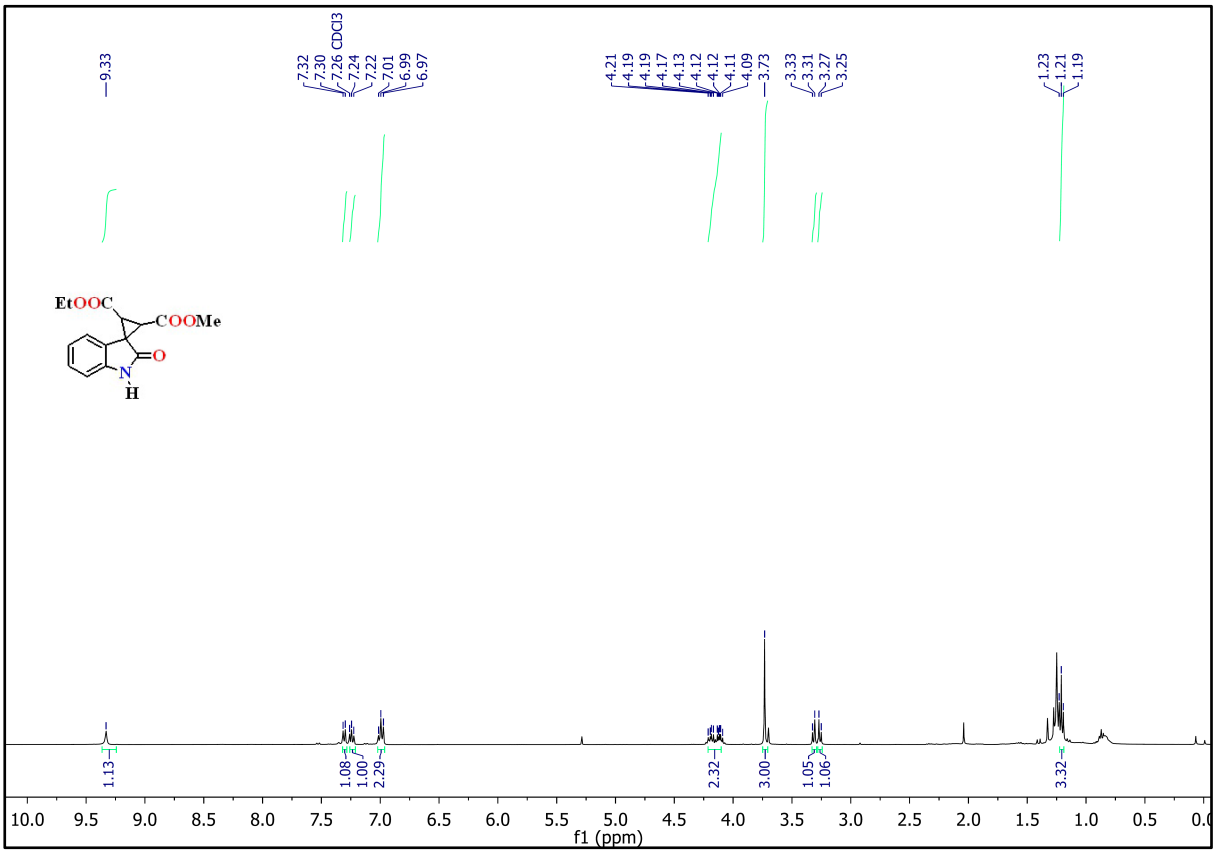
^{1}H NMR (400 MHz) of **3a** in CDCl3:



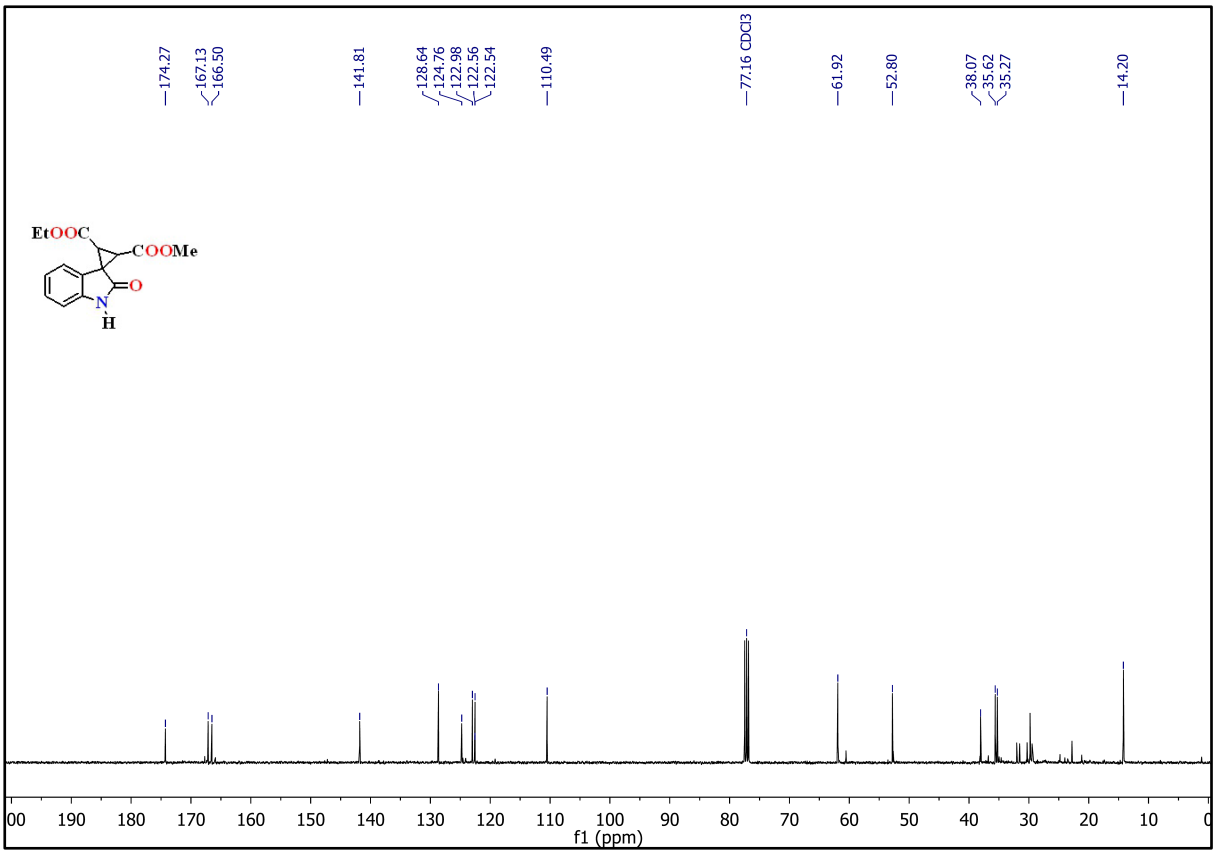
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3a** in CDCl3:



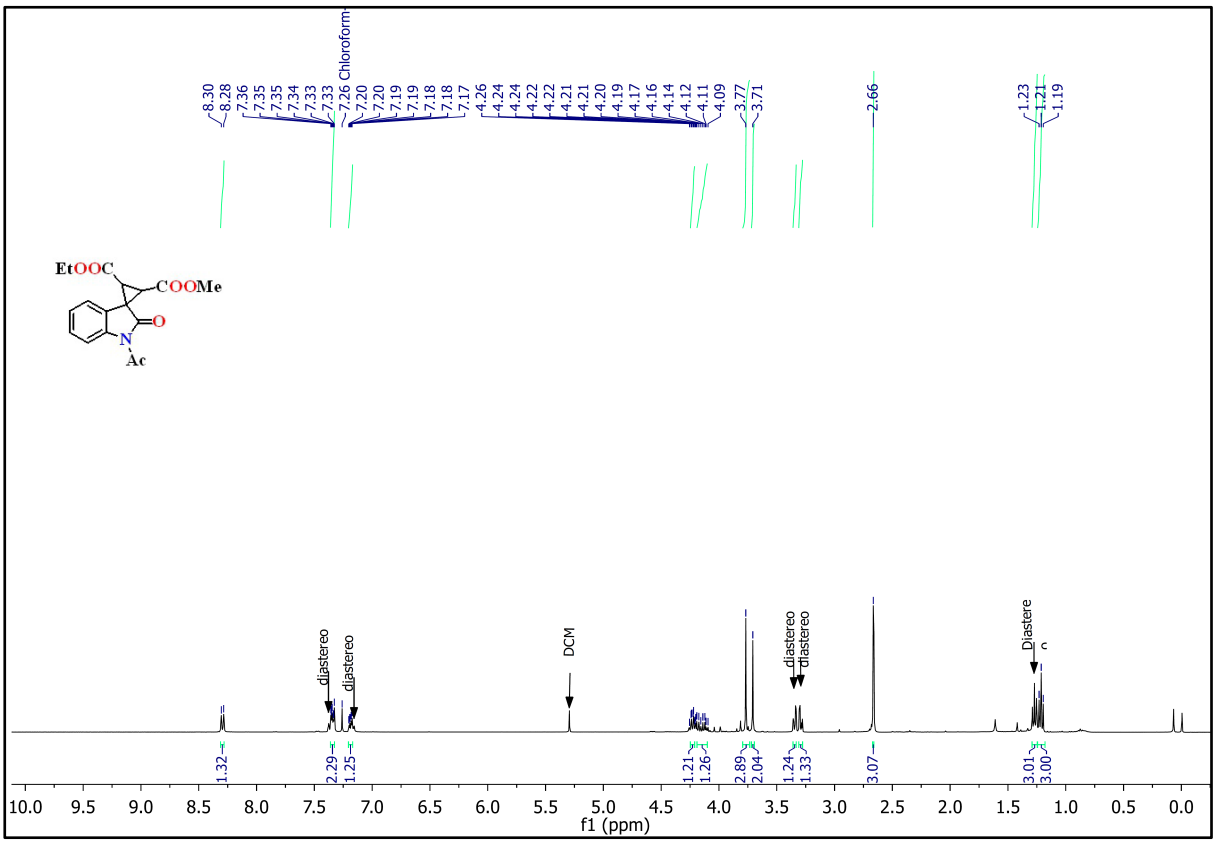
^{1}H NMR (400 MHz) of **3b** in CDCl3:



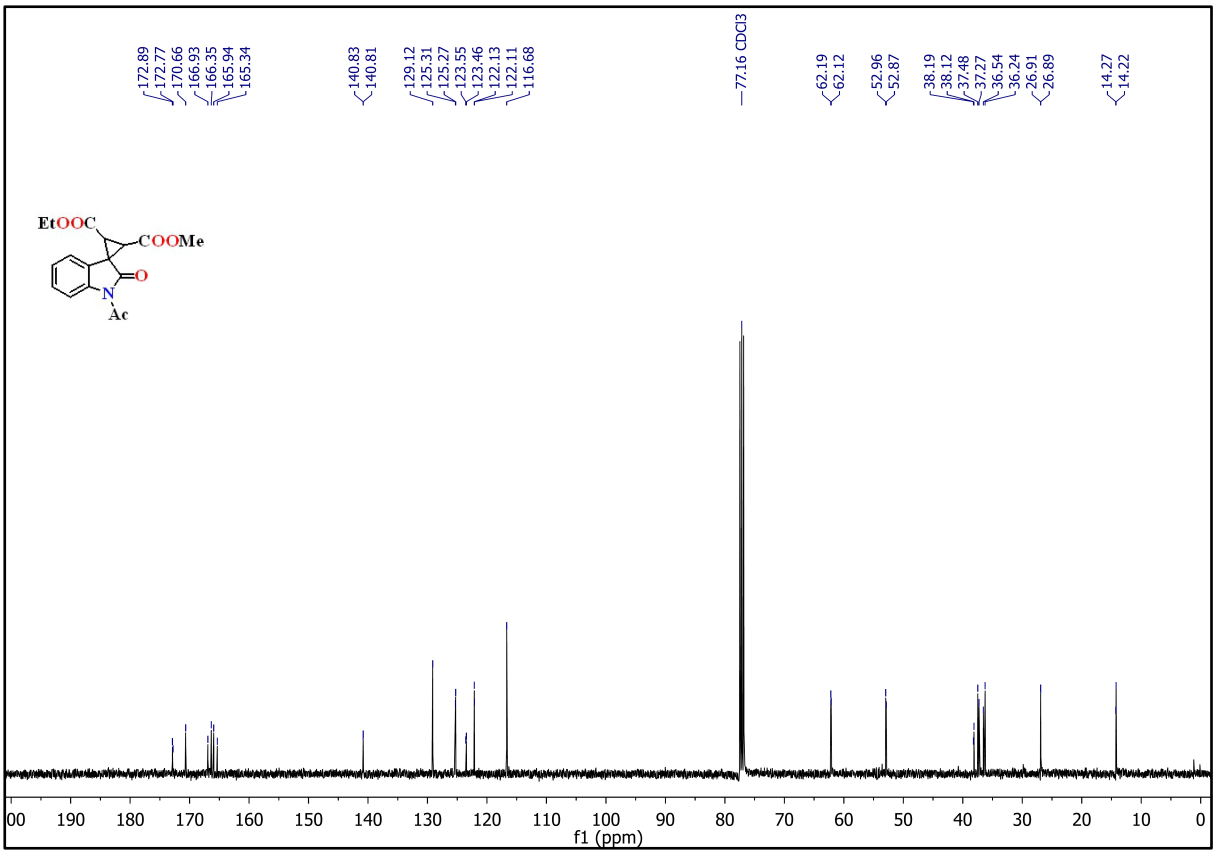
^{13}C{^{1}H} NMR (100 MHz) of **3b** in CDCl3:



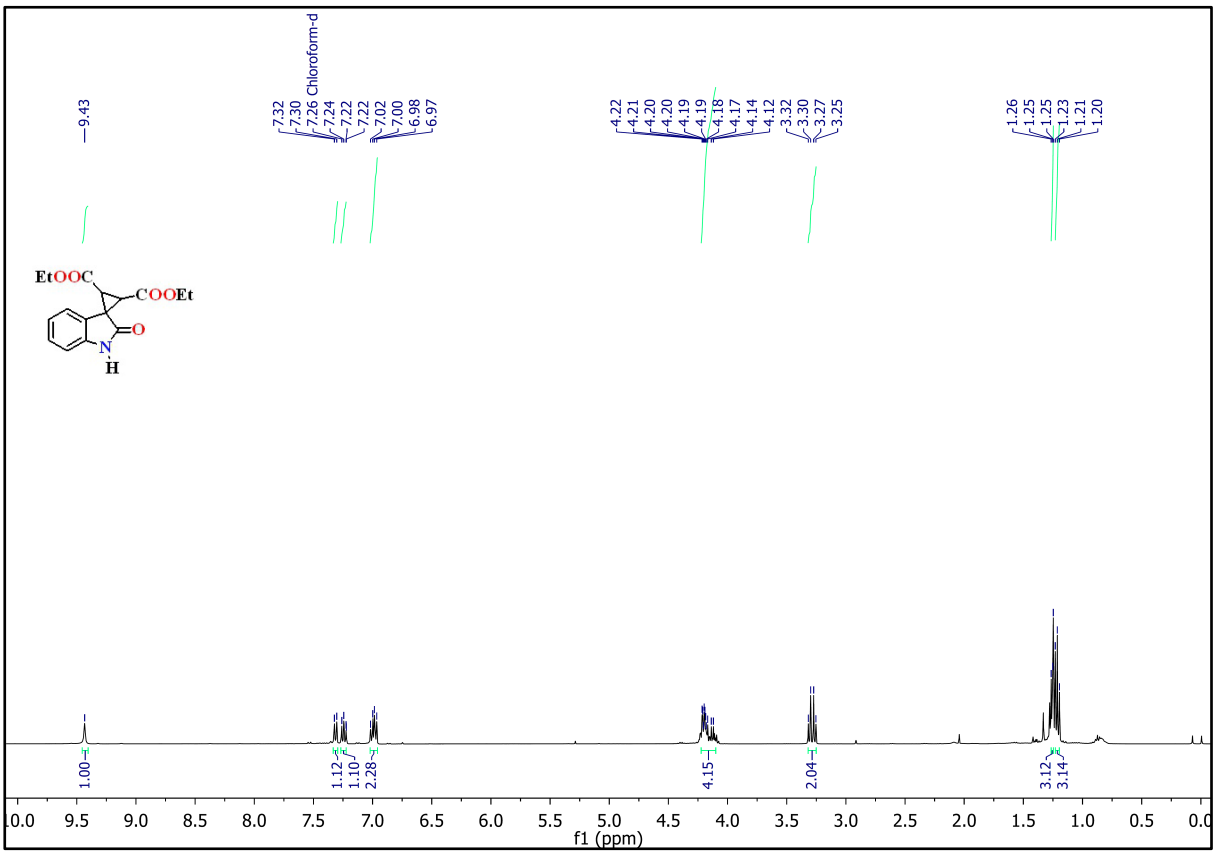
^{1}H NMR (400 MHz) of **3c** in CDCl3:



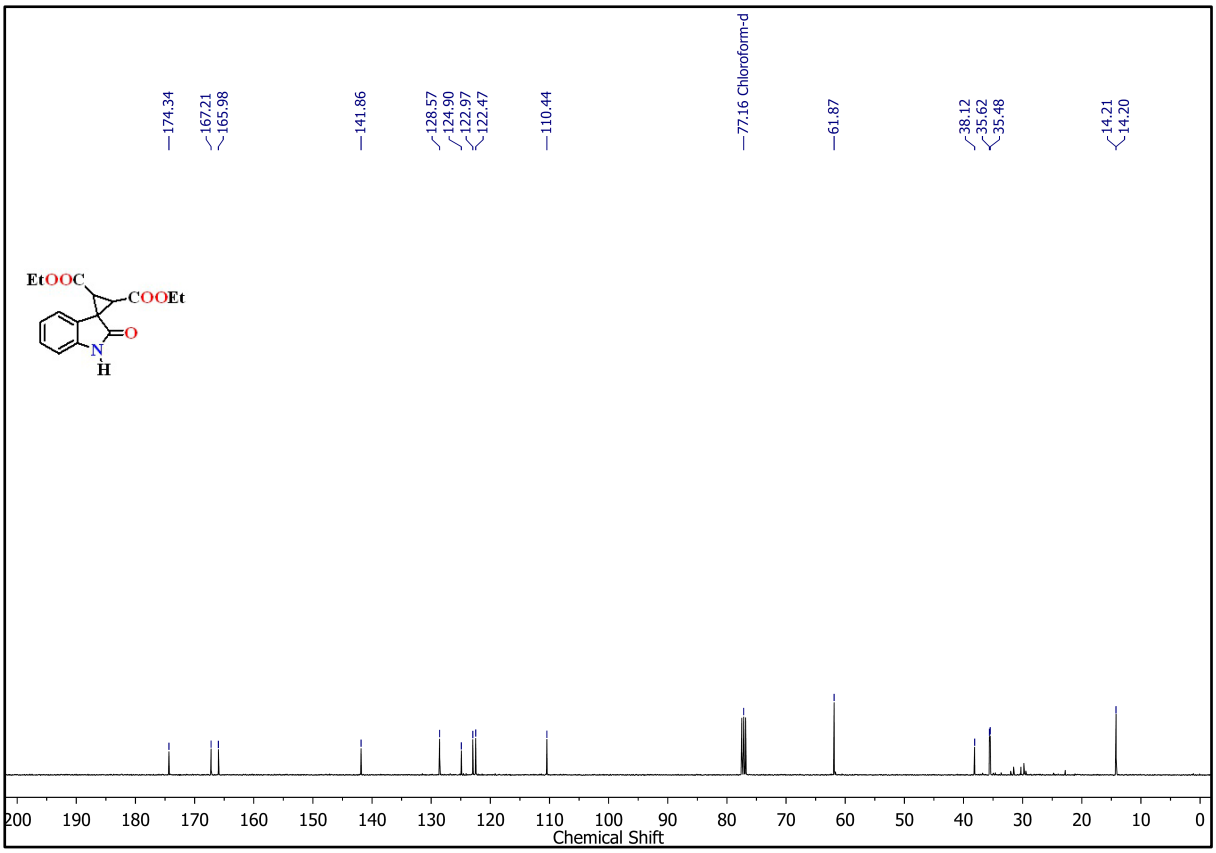
^{13}C{^{1}H} NMR (100 MHz) of **3c** in CDCl3:



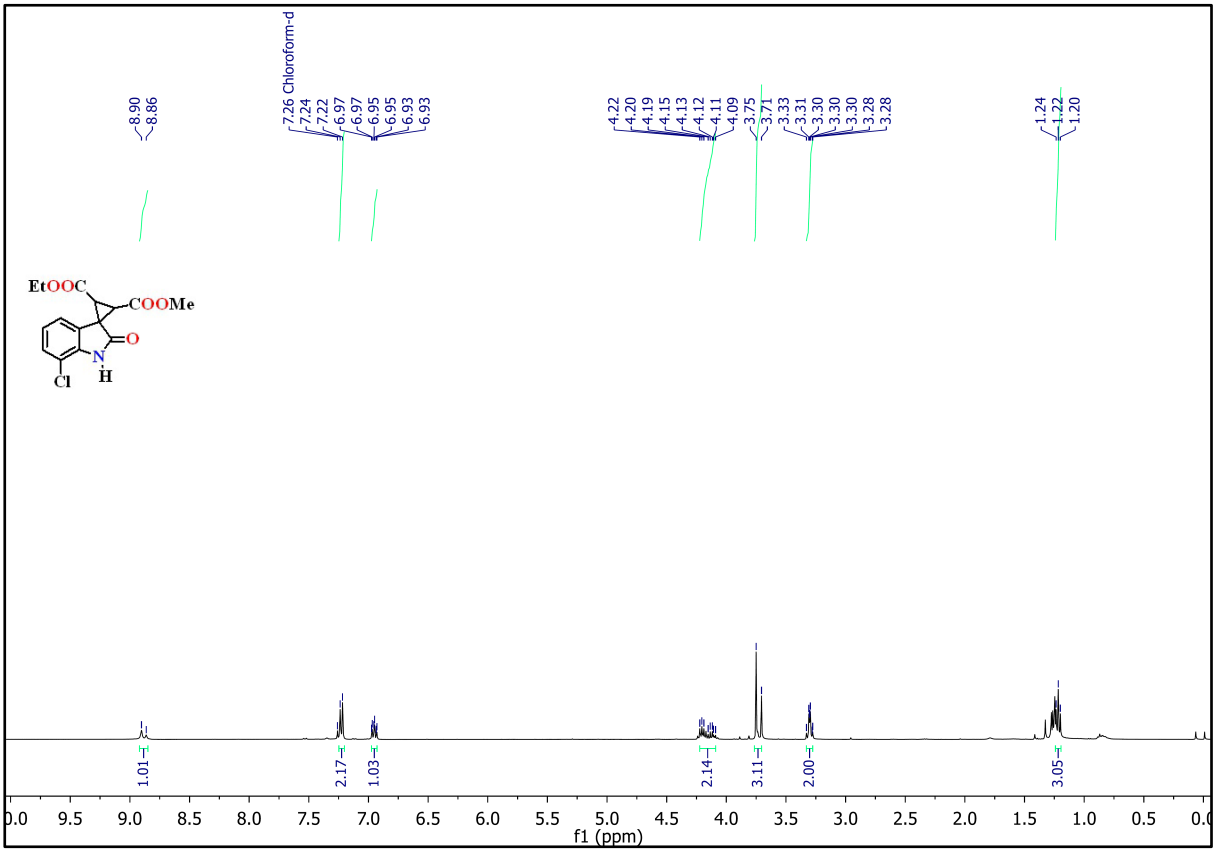
^{1}H NMR (400 MHz) of **3d** in CDCl3:



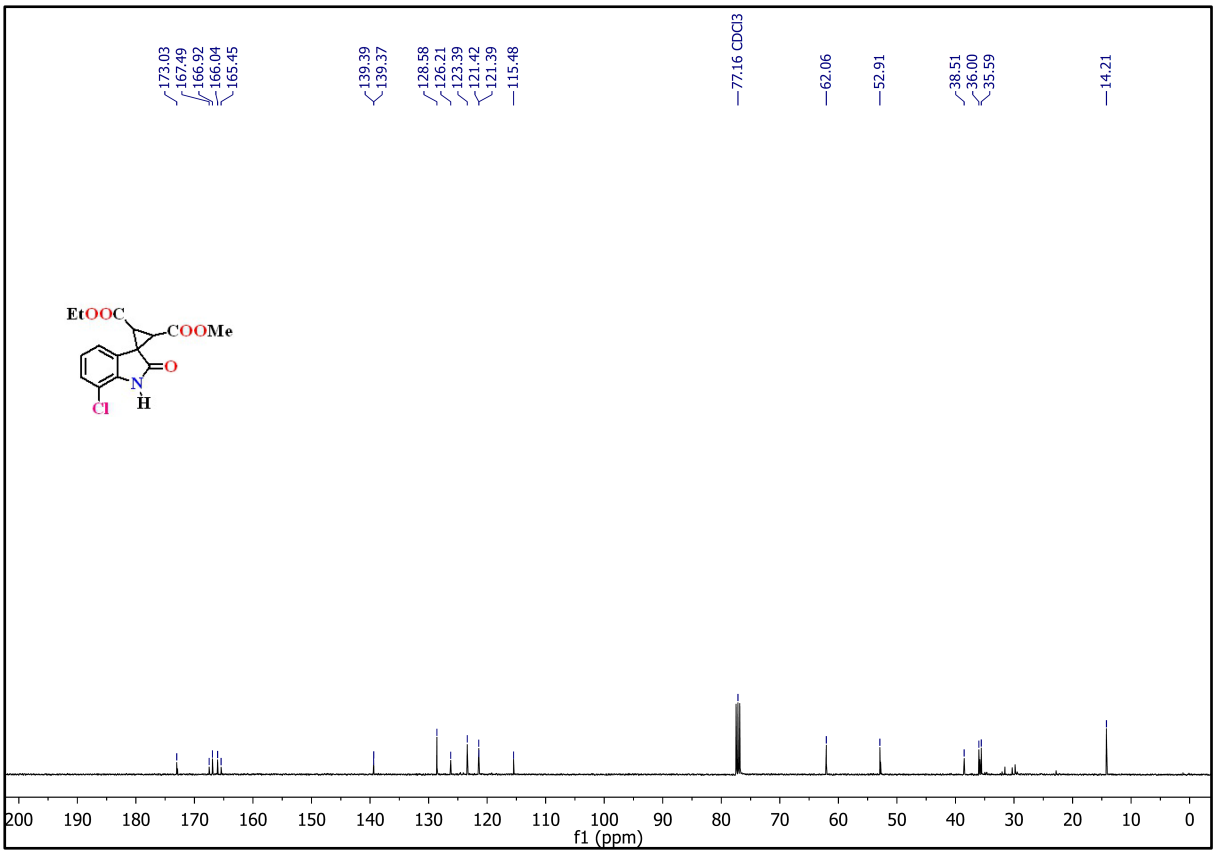
^{13}C{^{1}H} NMR (100 MHz) of **3d** in CDCl3:



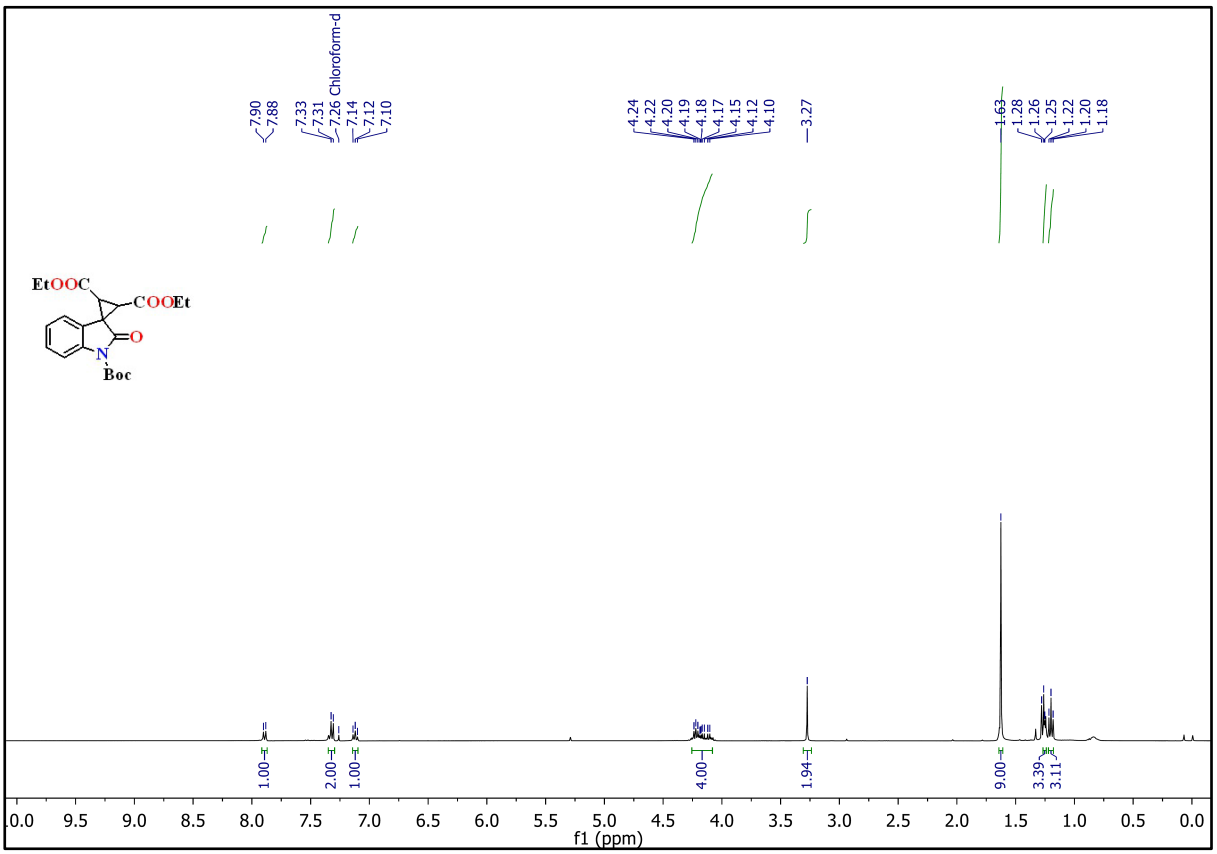
^{1}H NMR (400 MHz) of **3e** in CDCl3:



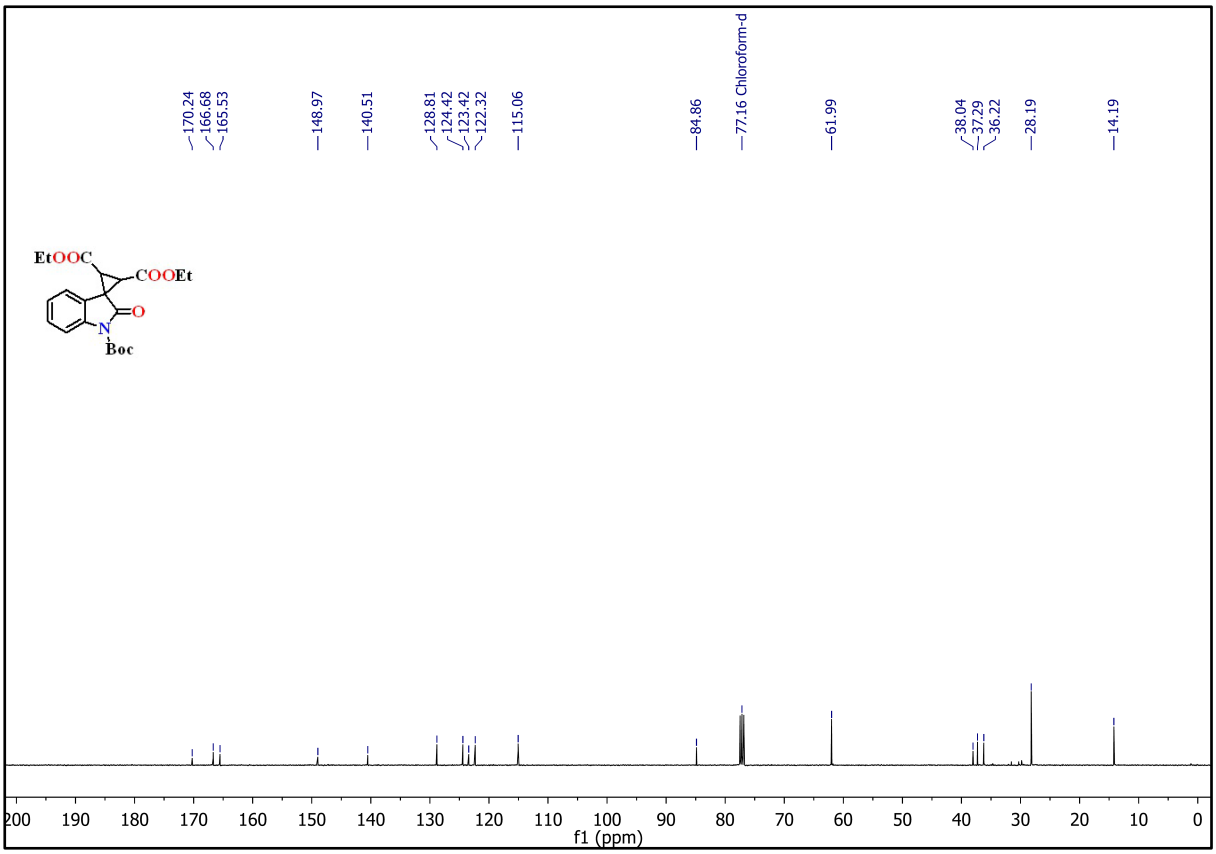
^{13}C{^{1}H} NMR (100 MHz) of **3e** in CDCl3:



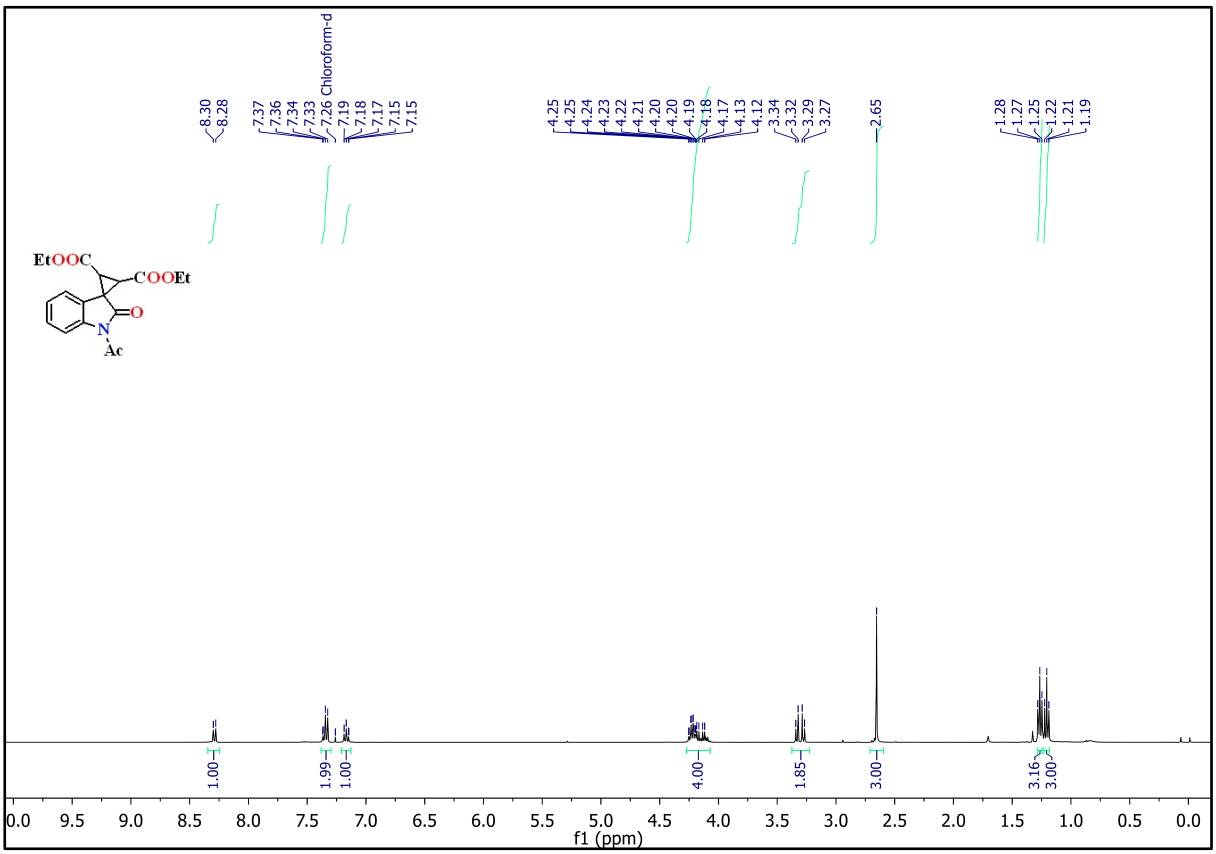
^{1}H NMR (400 MHz) of **3f** in CDCl3:



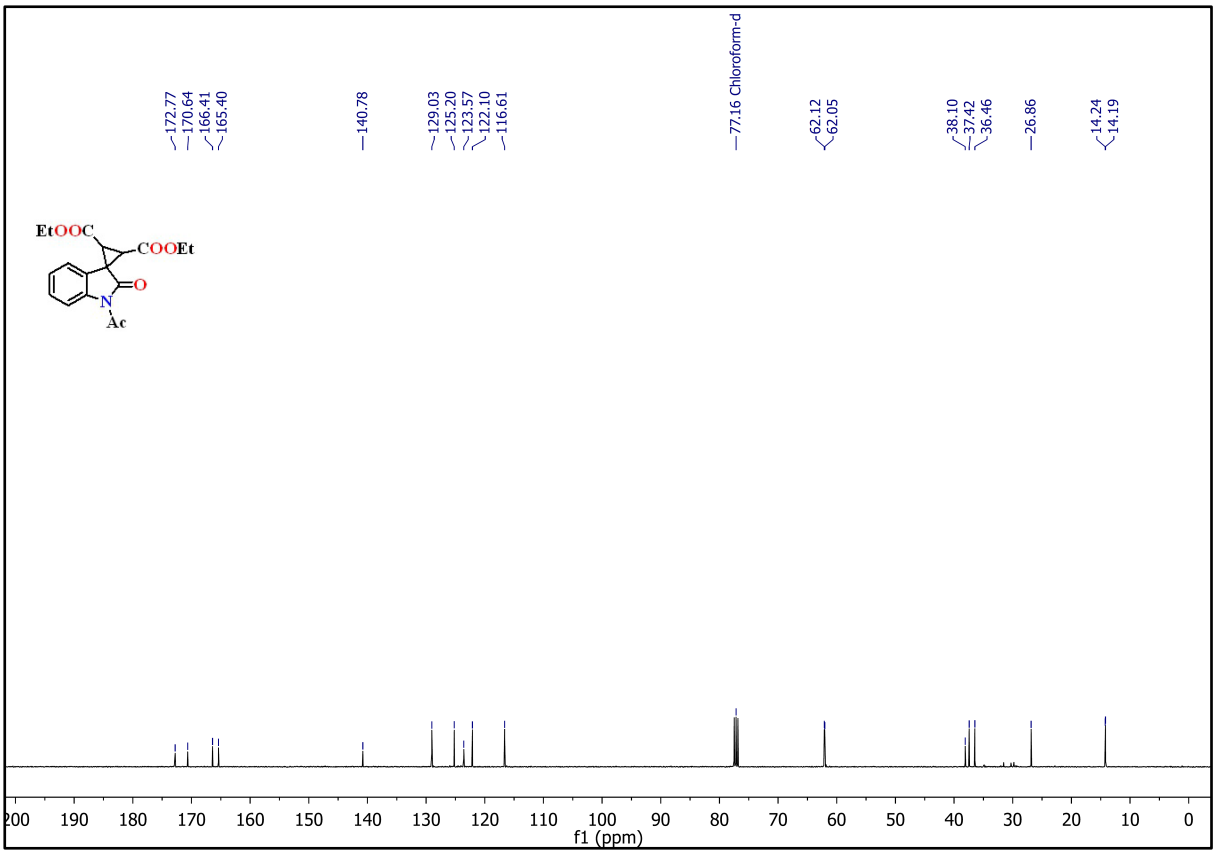
^{13}C{^{1}H} NMR (100 MHz) of **3f** in CDCl3:



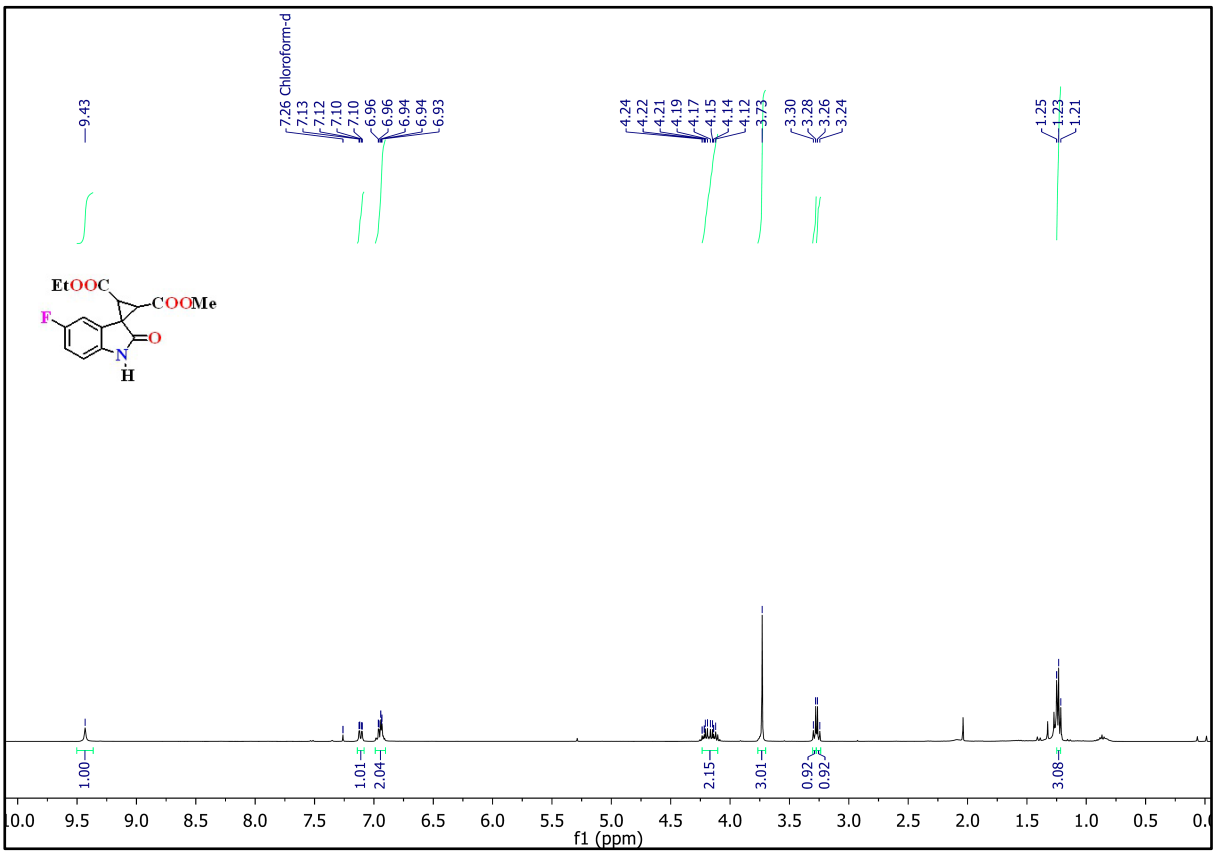
^{1}H NMR (400 MHz) of **3g** in CDCl3:



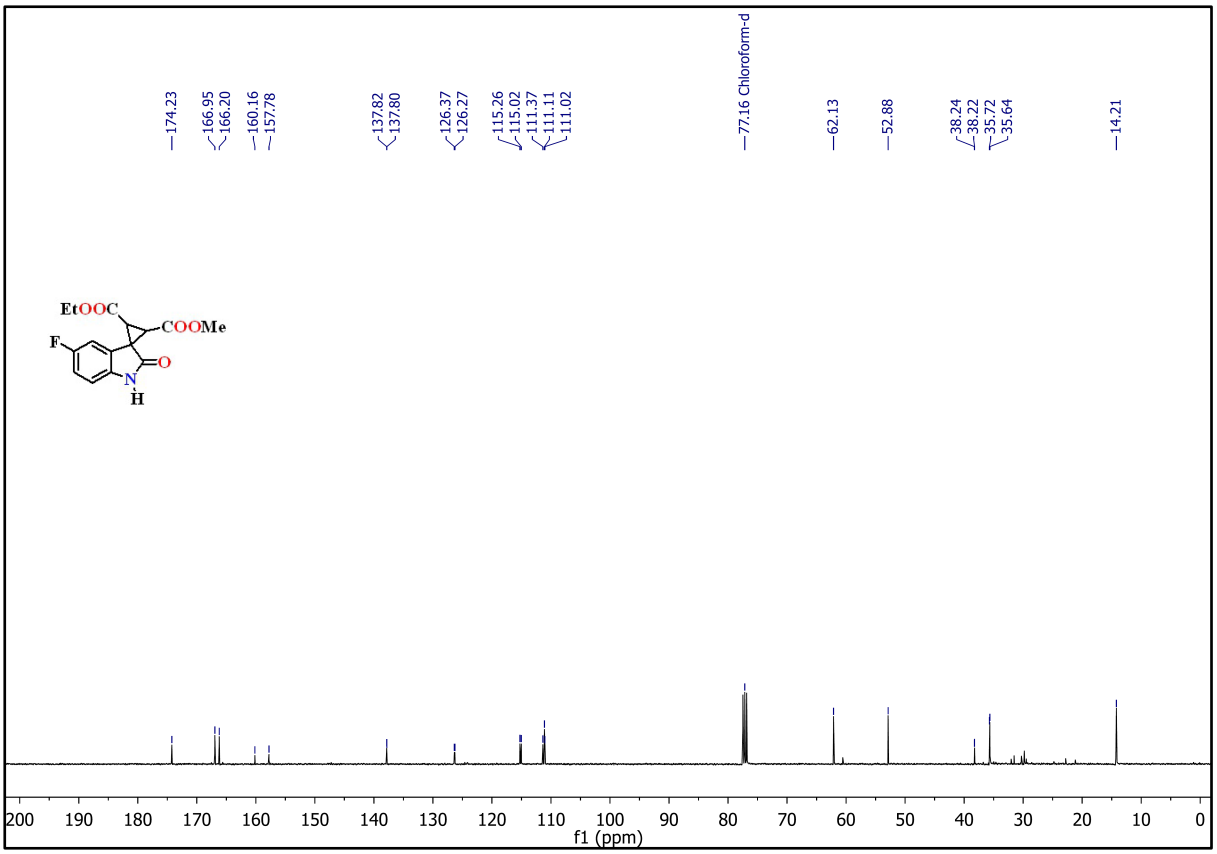
^{13}C{^{1}H} NMR (100 MHz) of **3g** in CDCl3:



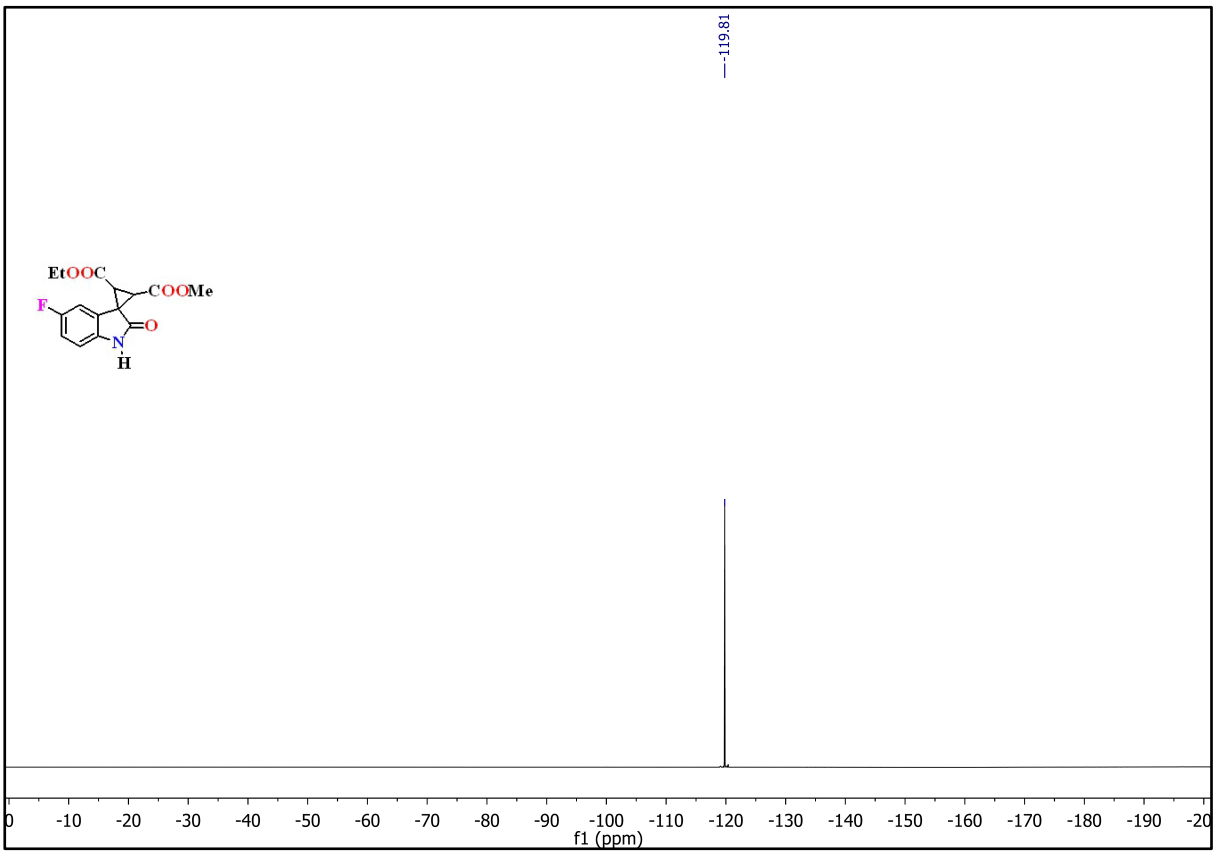
^{1}H NMR (400 MHz) of **3h** in CDCl3:



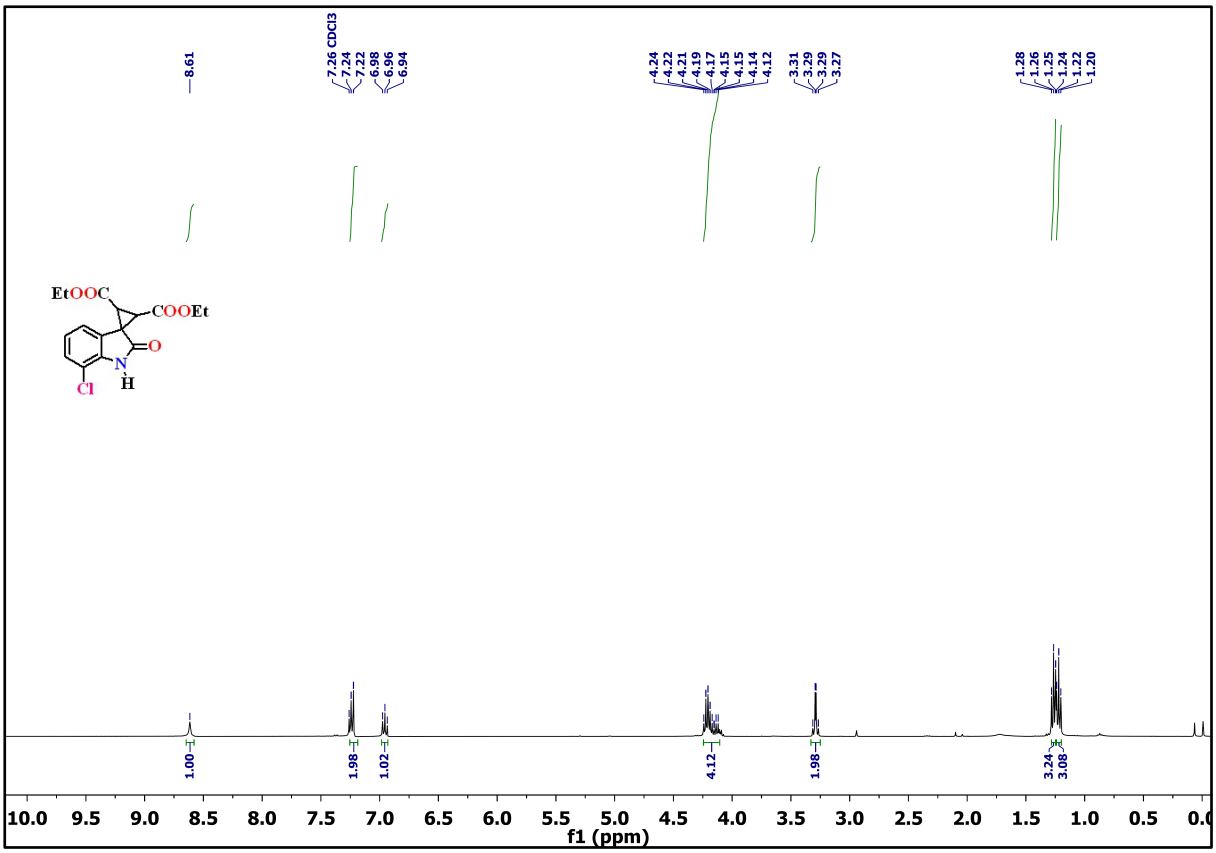
^{13}C{^{1}H} NMR (100 MHz) of **3h** in CDCl3:



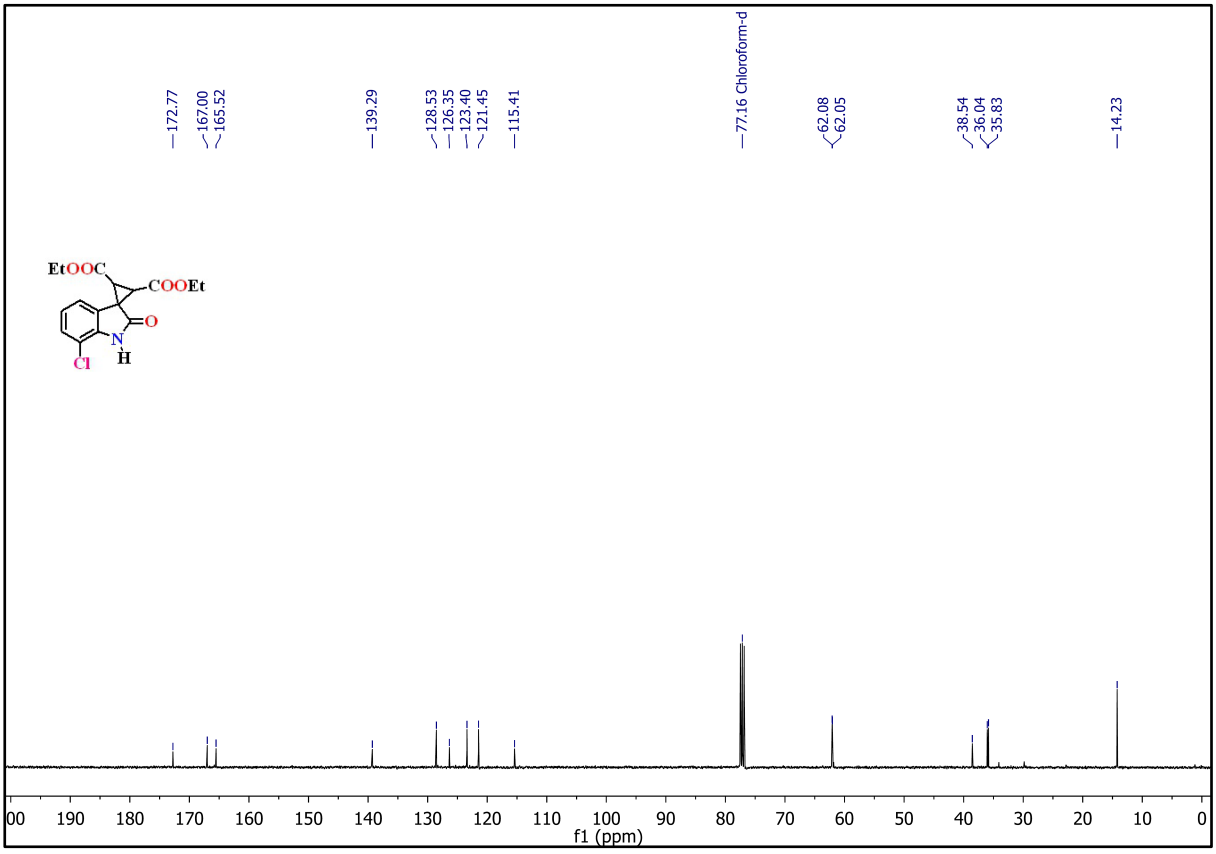
^{19}F NMR (376 MHz) of **3h** in $CDCl_3$:



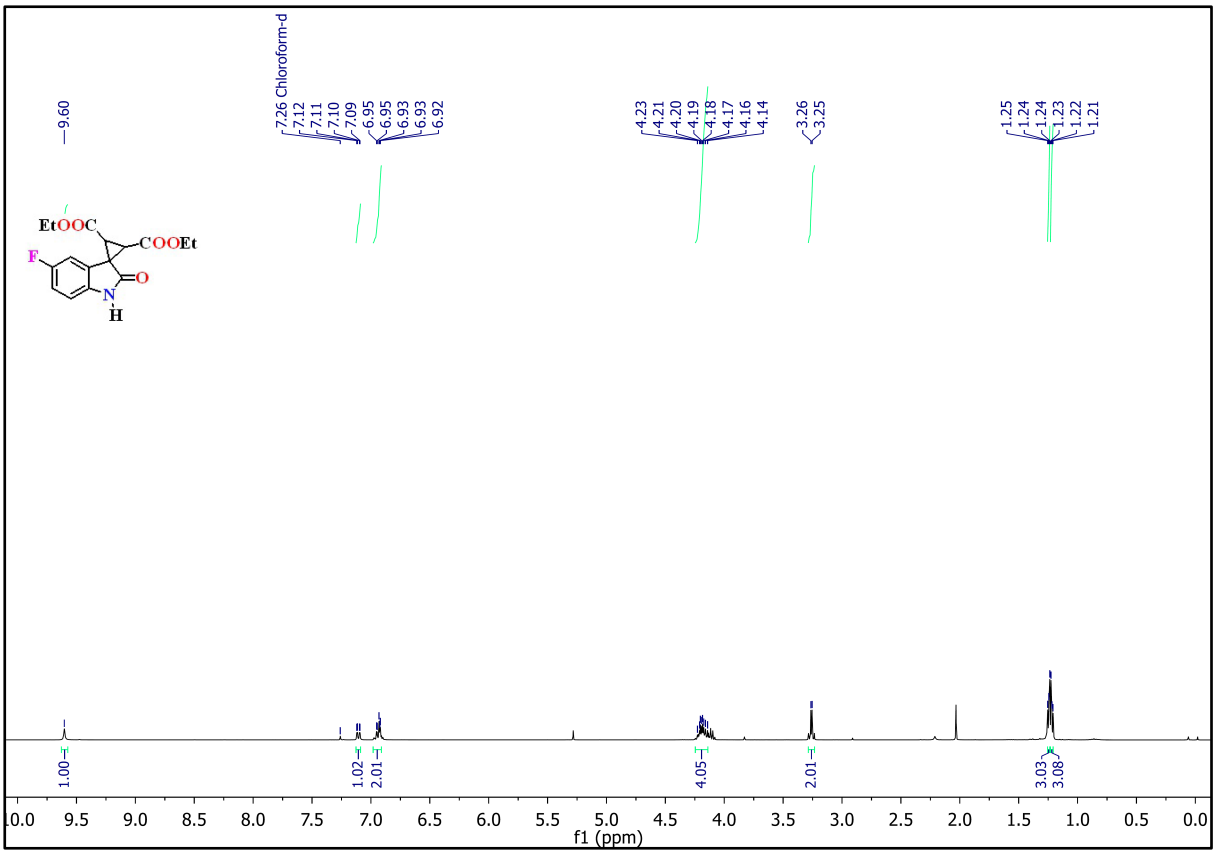
^{1}H NMR (400 MHz) of **3i** in CDCl3:



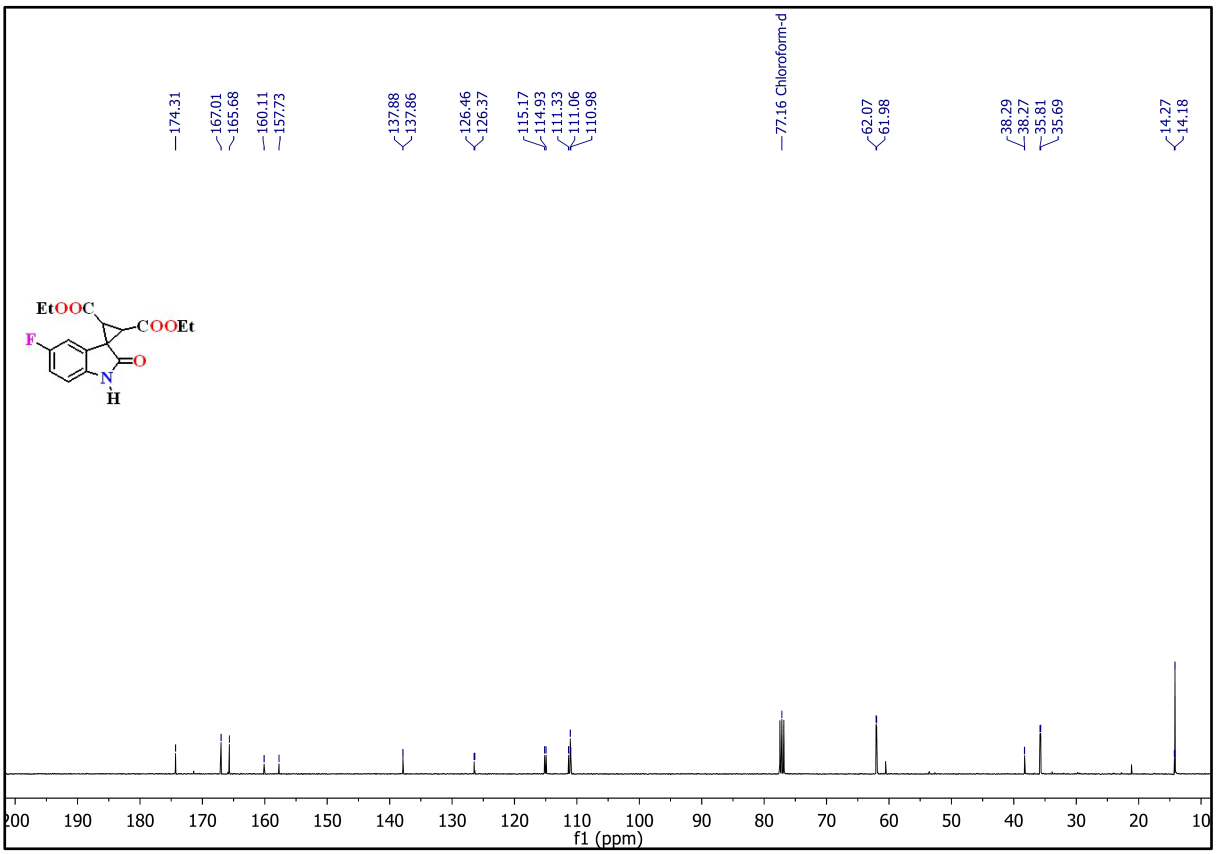
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3i** in CDCl3:



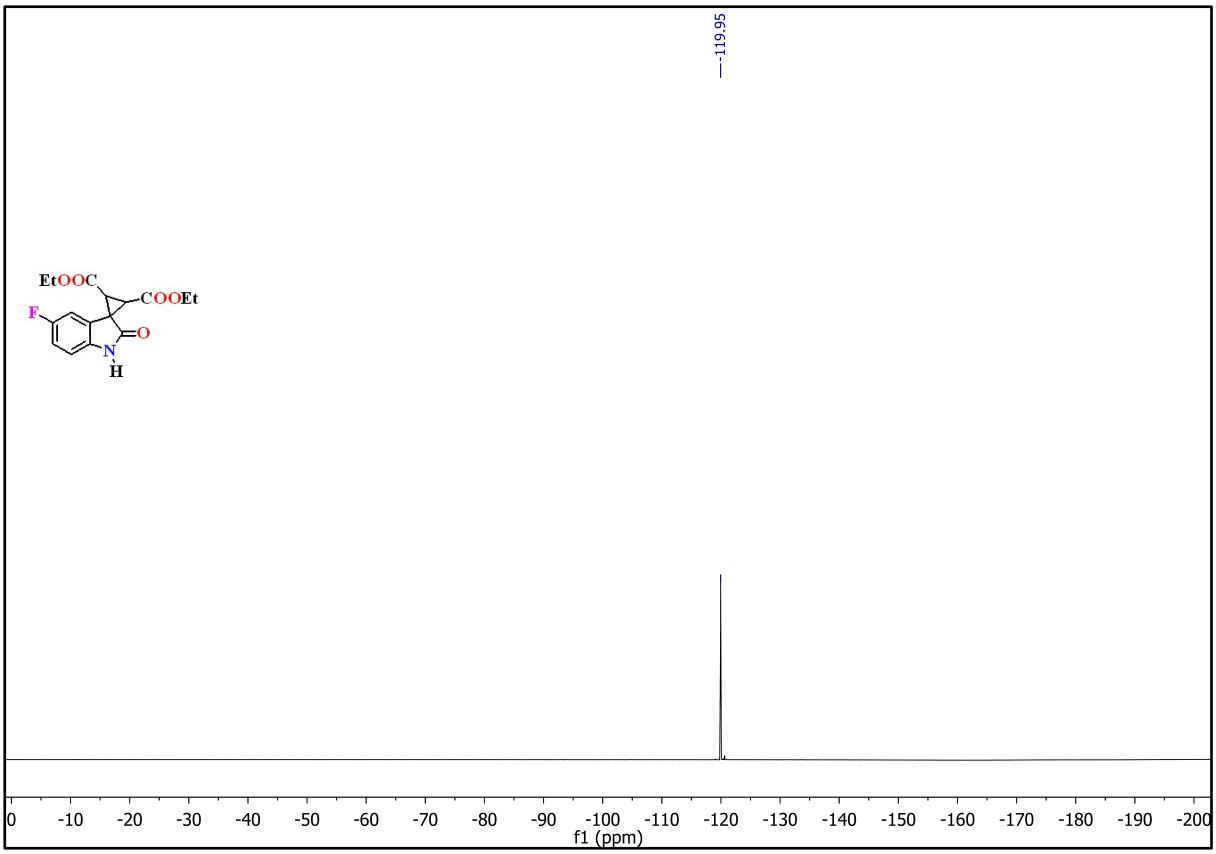
^{1}H NMR (400 MHz) of **3j** in CDCl3:



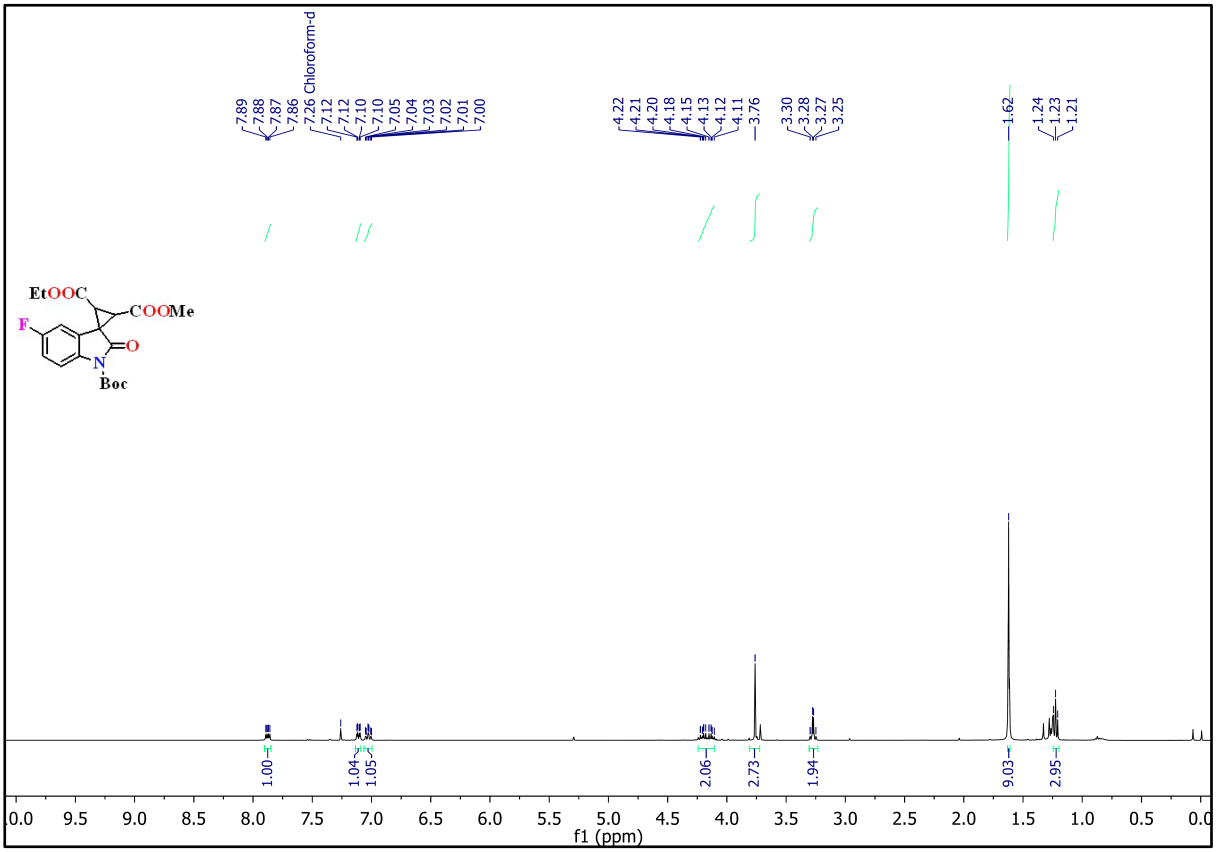
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3j** in CDCl3:



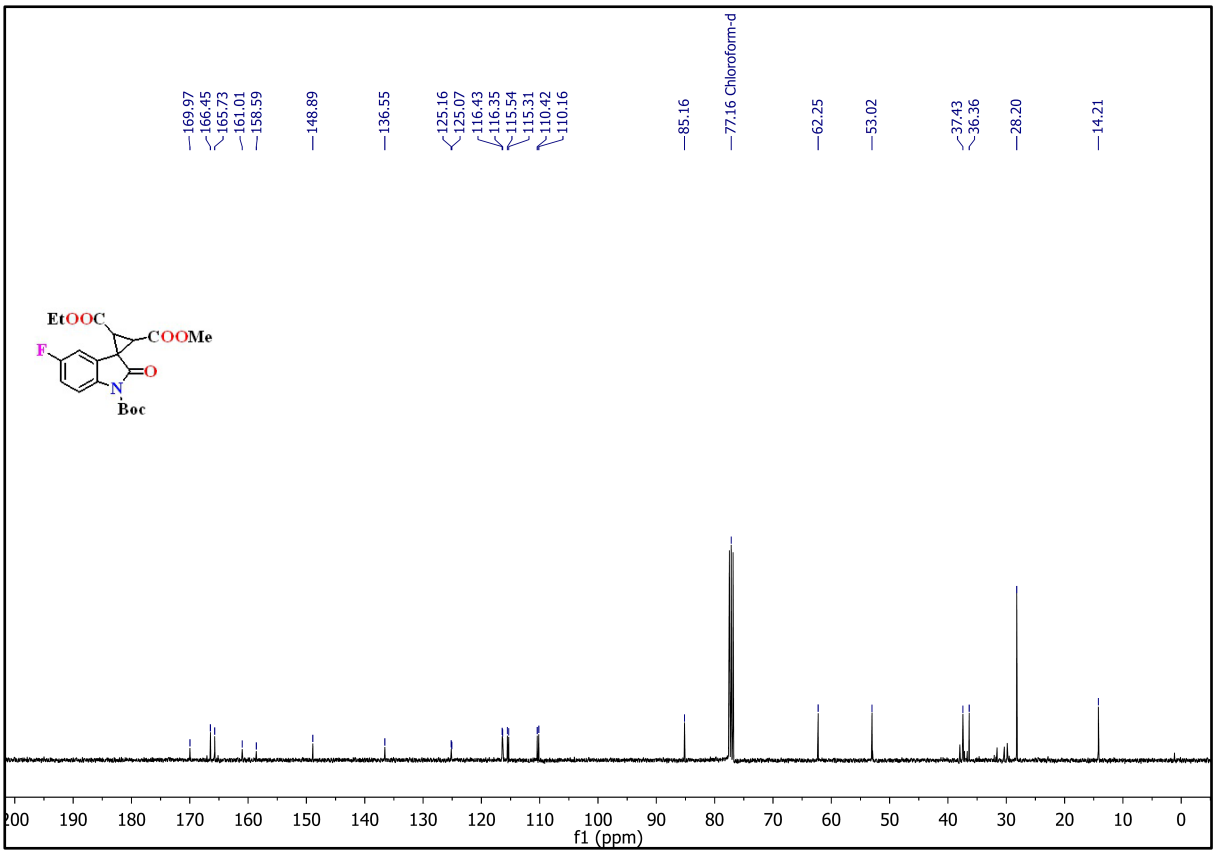
^{19}F NMR (376 MHz) of **3j** in $CDCl_3$:



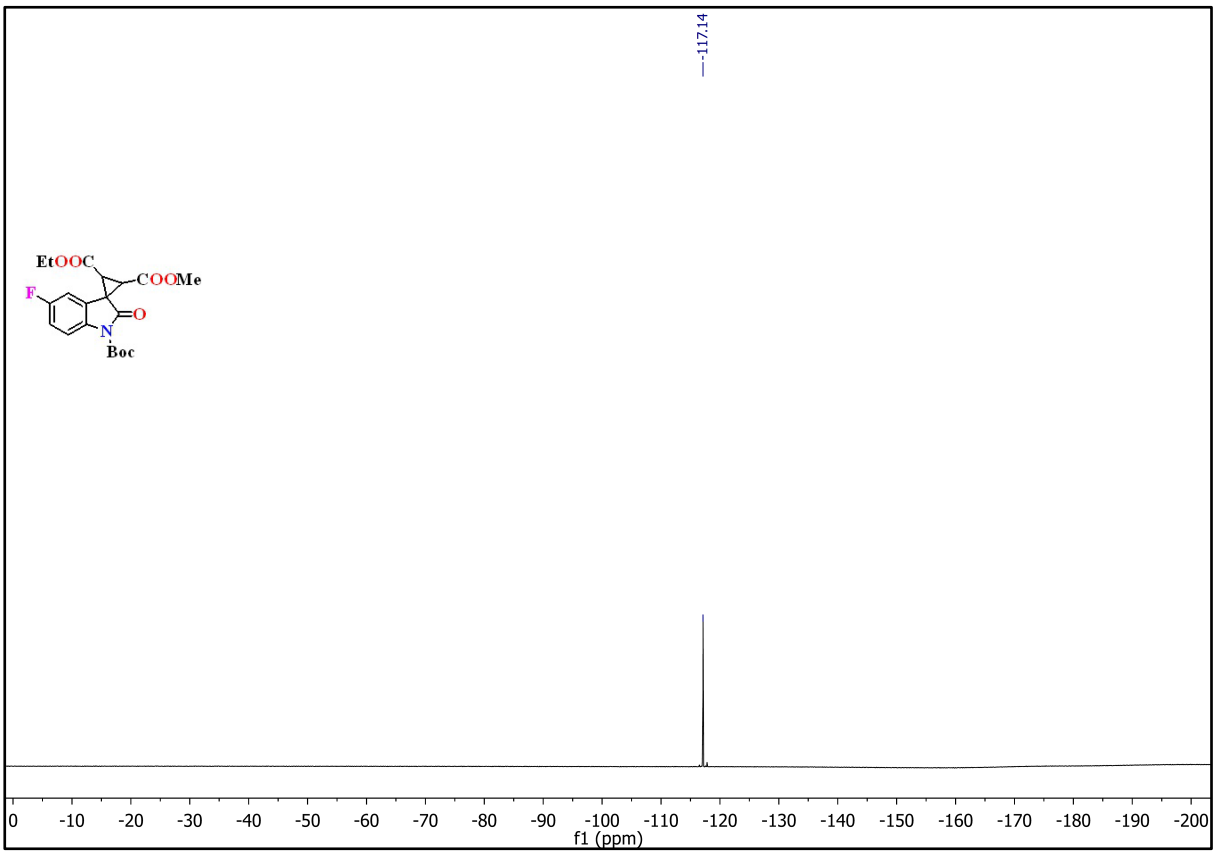
^{1}H NMR (400 MHz) of **3k** in CDCl3:



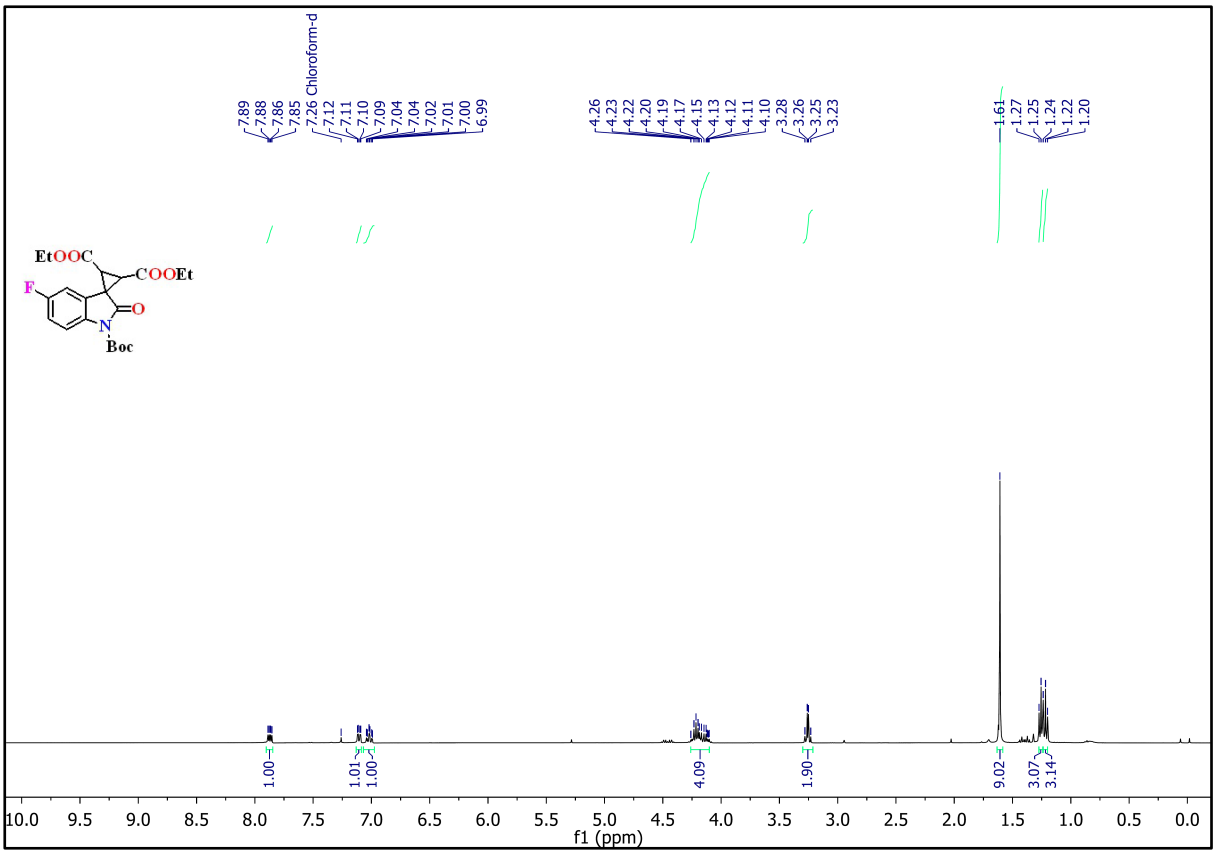
^{13}C{^{1}H} NMR (100 MHz) of **3k** in CDCl3:



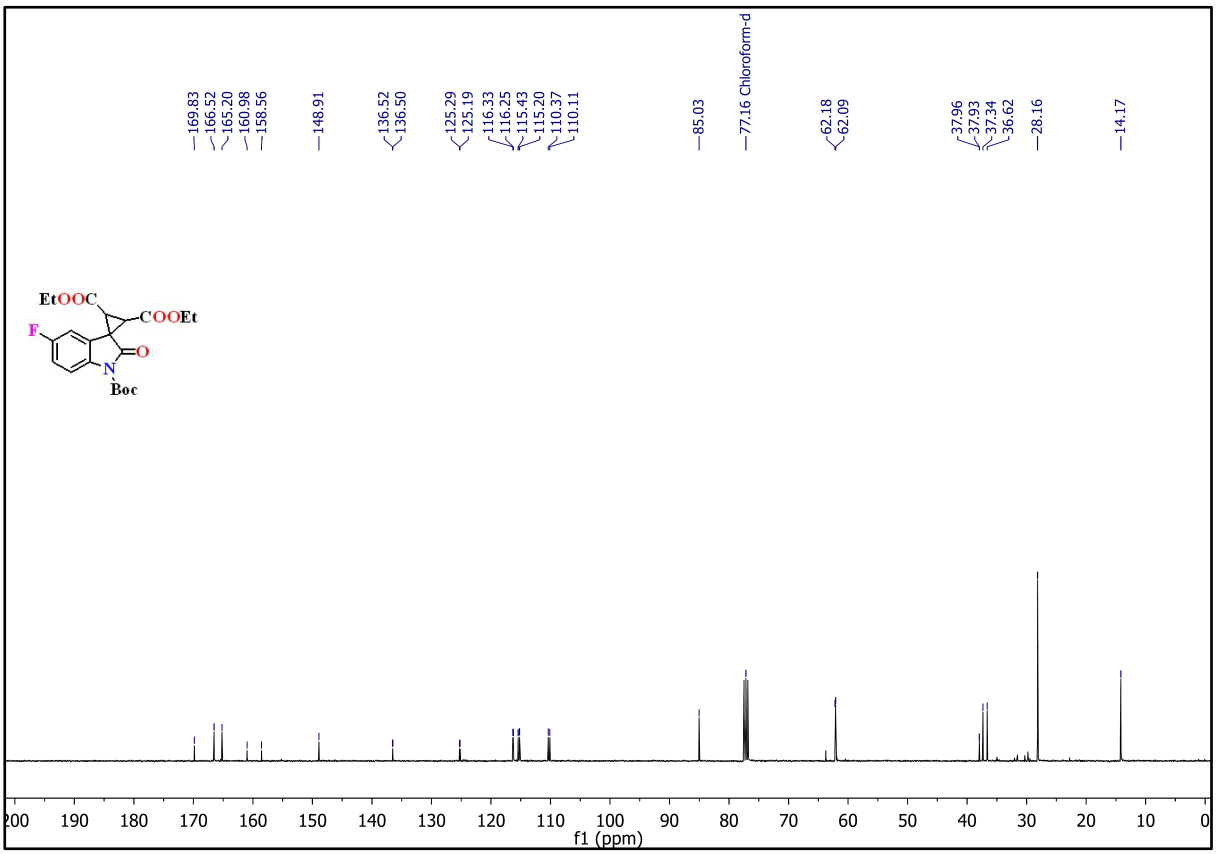
^{19}F NMR (376 MHz) of **3k** in $CDCl_3$:



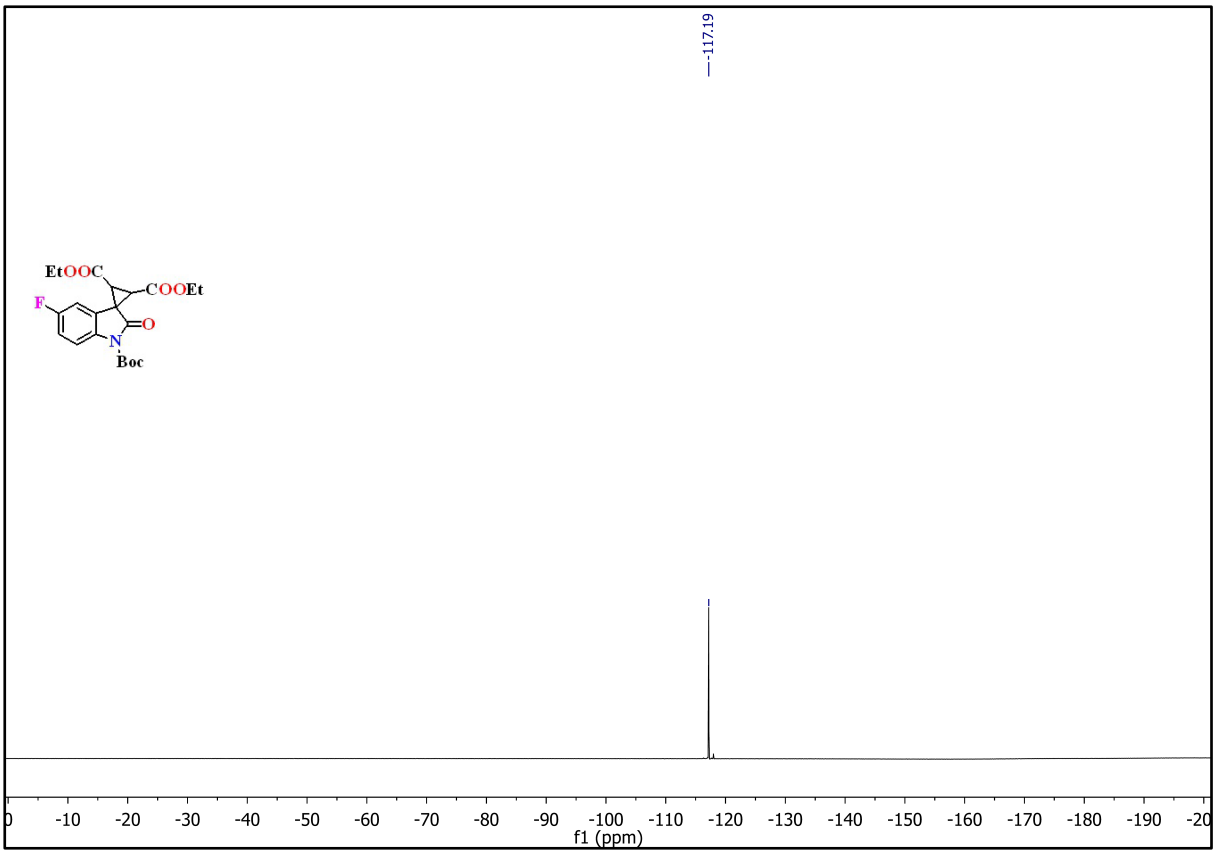
^{1}H NMR (400 MHz) of **3l** in CDCl3:



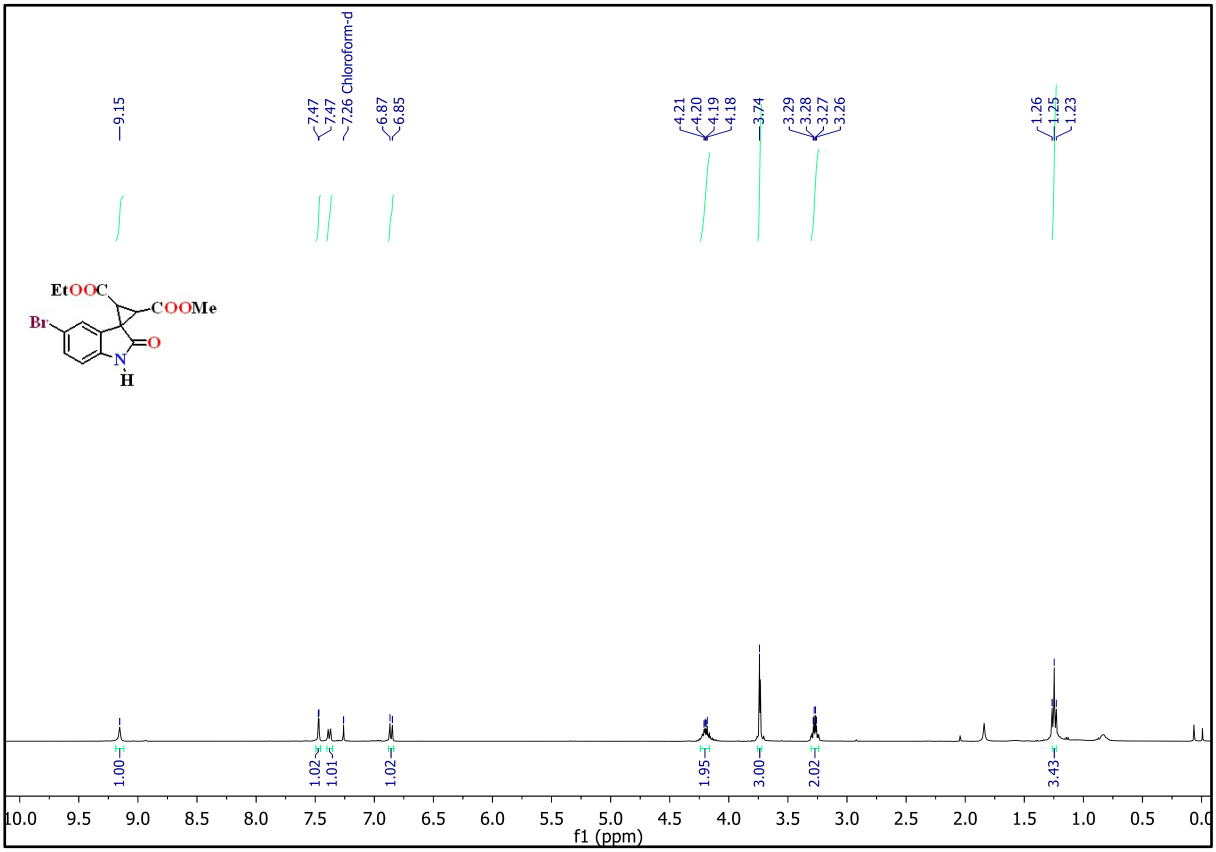
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3l** in CDCl3:



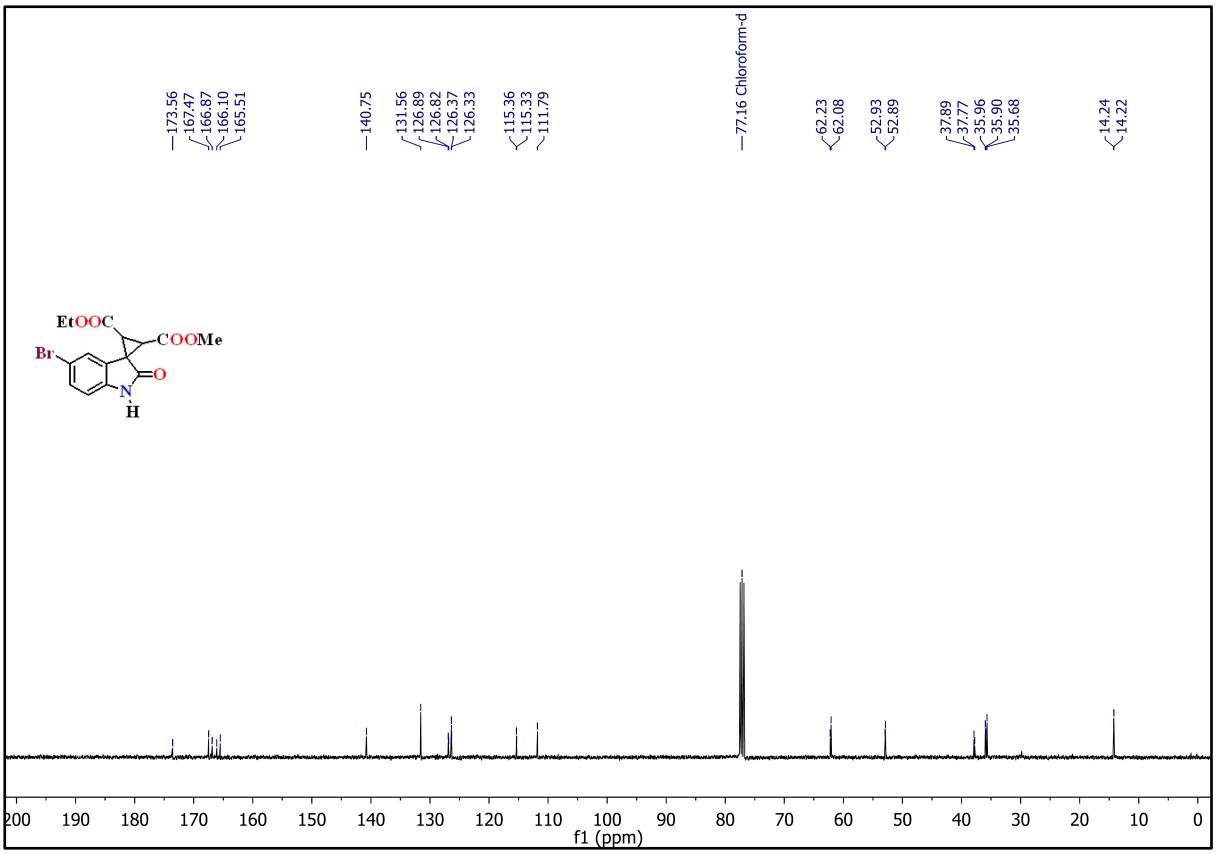
^{19}F NMR (376 MHz) of **3l** in $CDCl_3$:



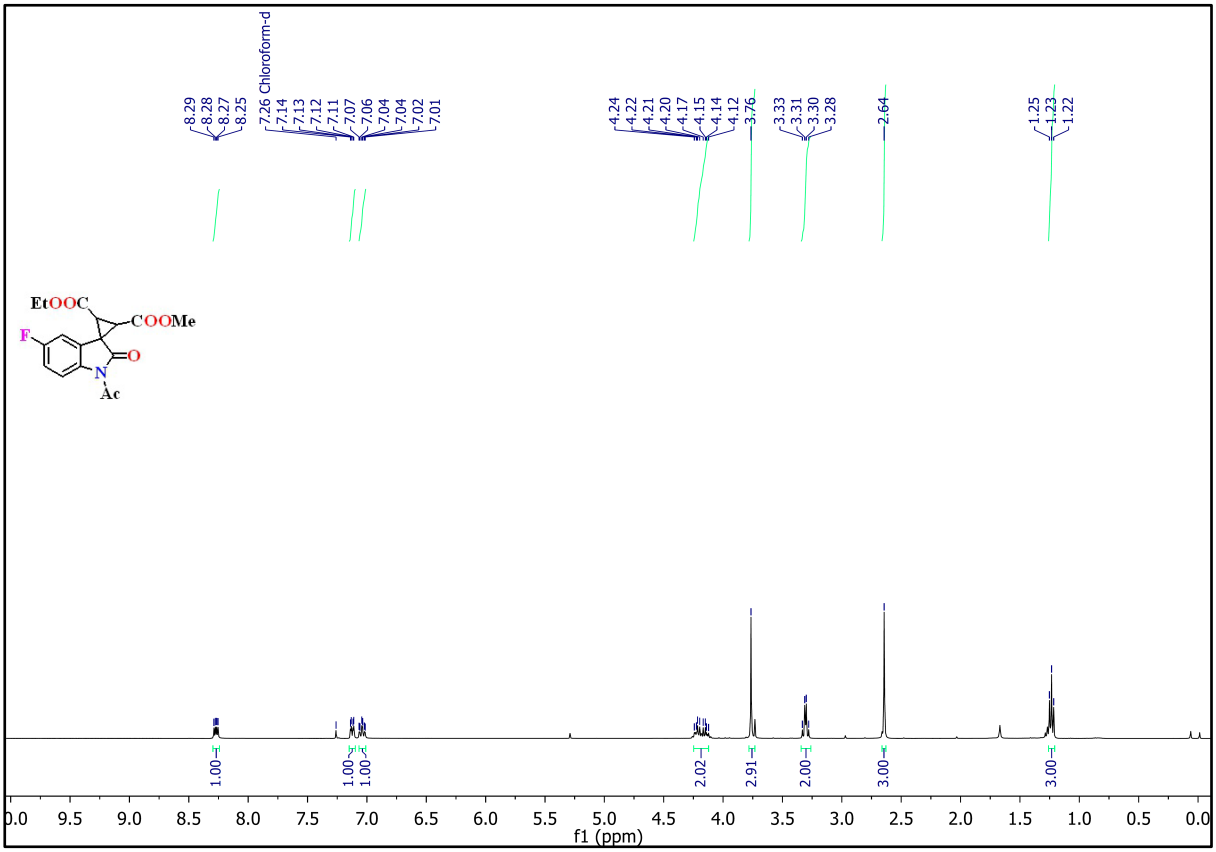
^{1}H NMR (400 MHz) of **3m** in CDCl3:



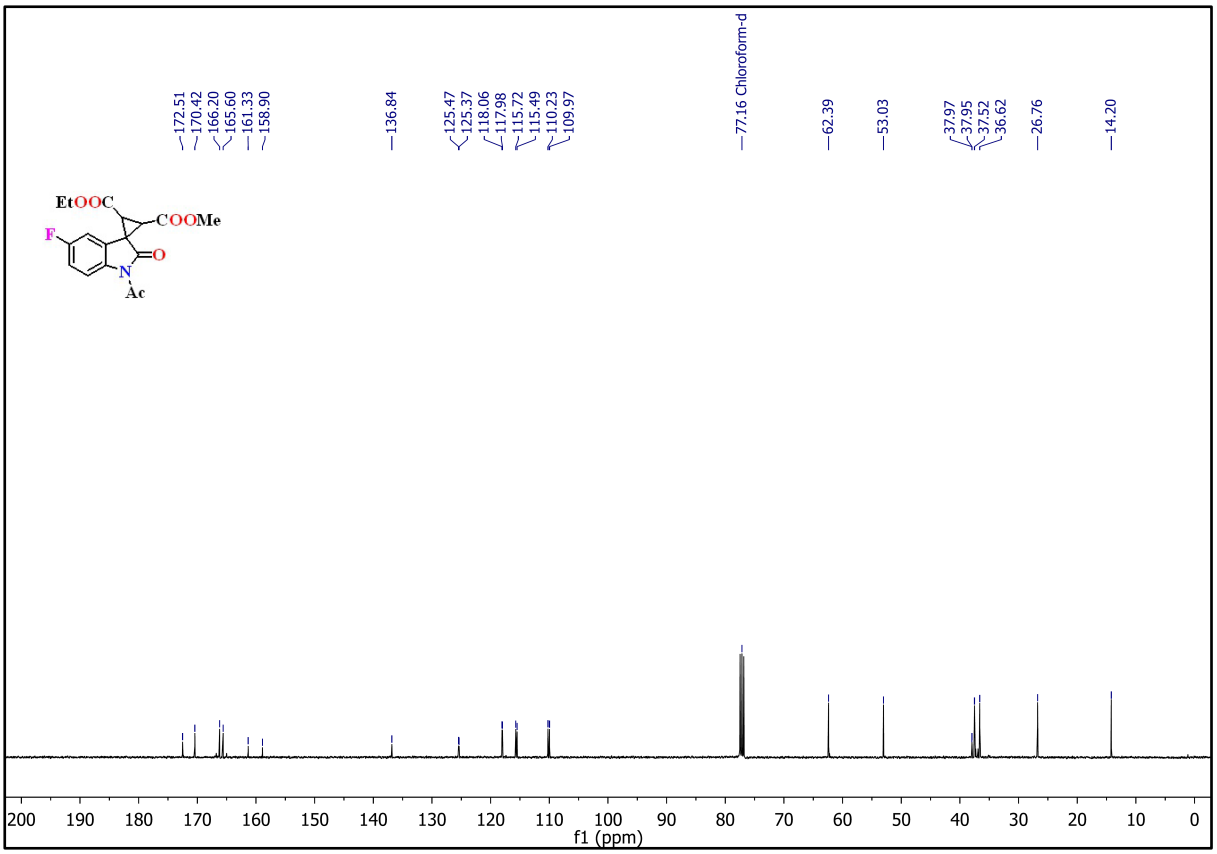
^{13}C{^{1}H} NMR (100 MHz) of **3m** in CDCl3:



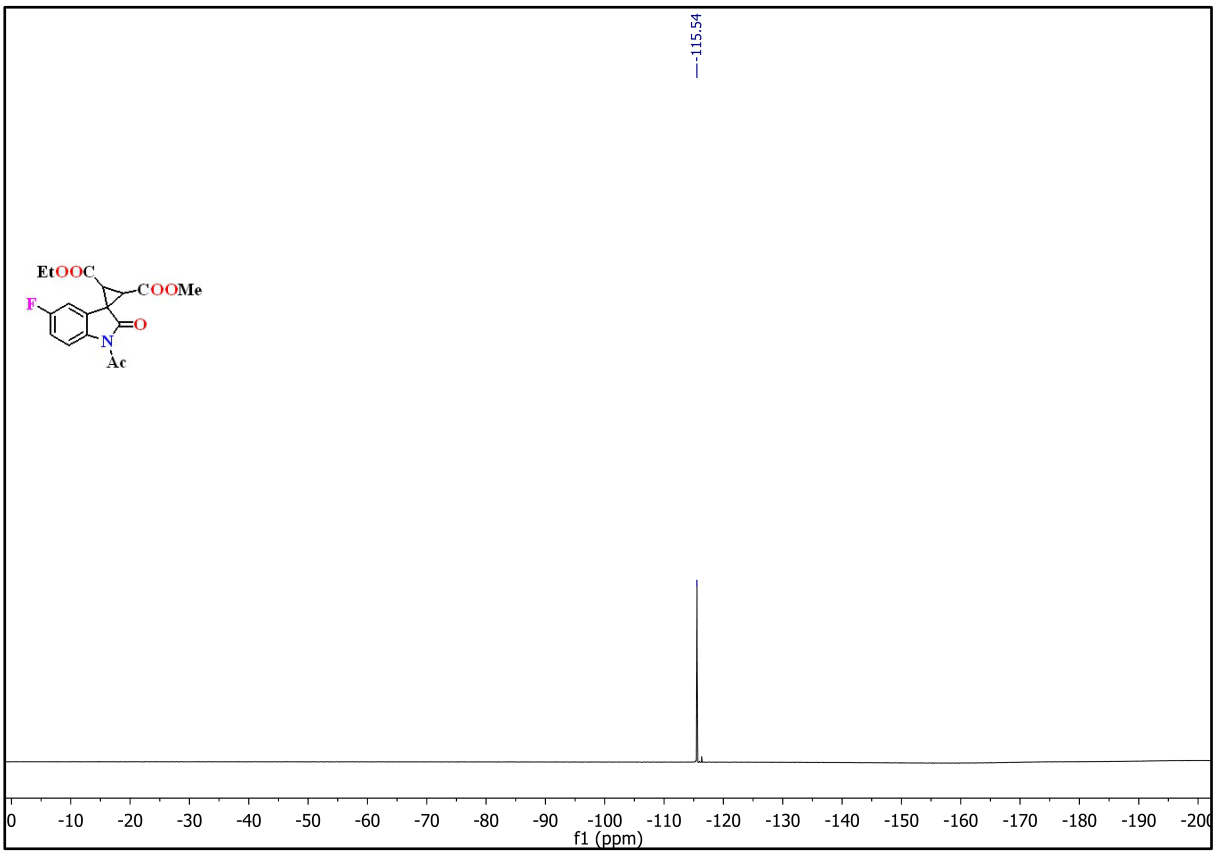
^{1}H NMR (400 MHz) of **3n** in CDCl3:



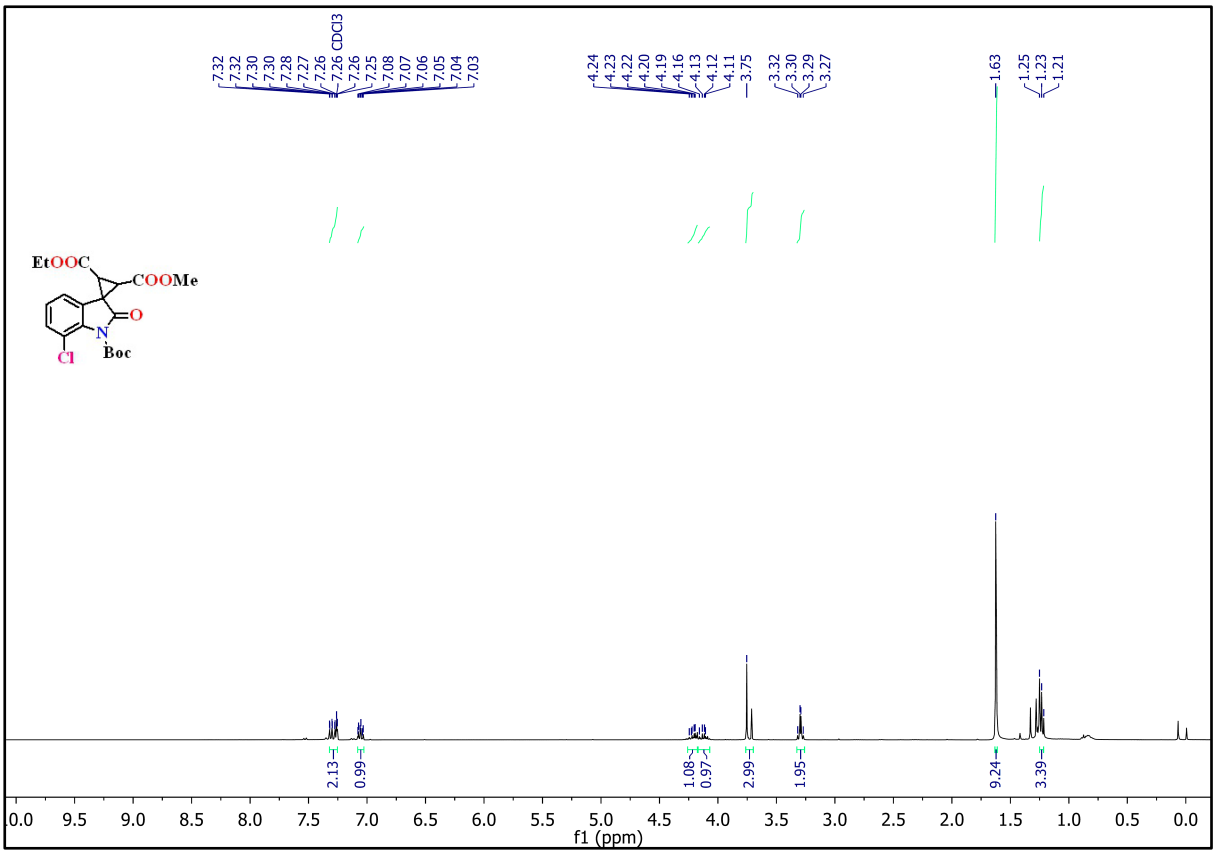
^{13}C{^{1}H} NMR (100 MHz) of **3n** in CDCl3:



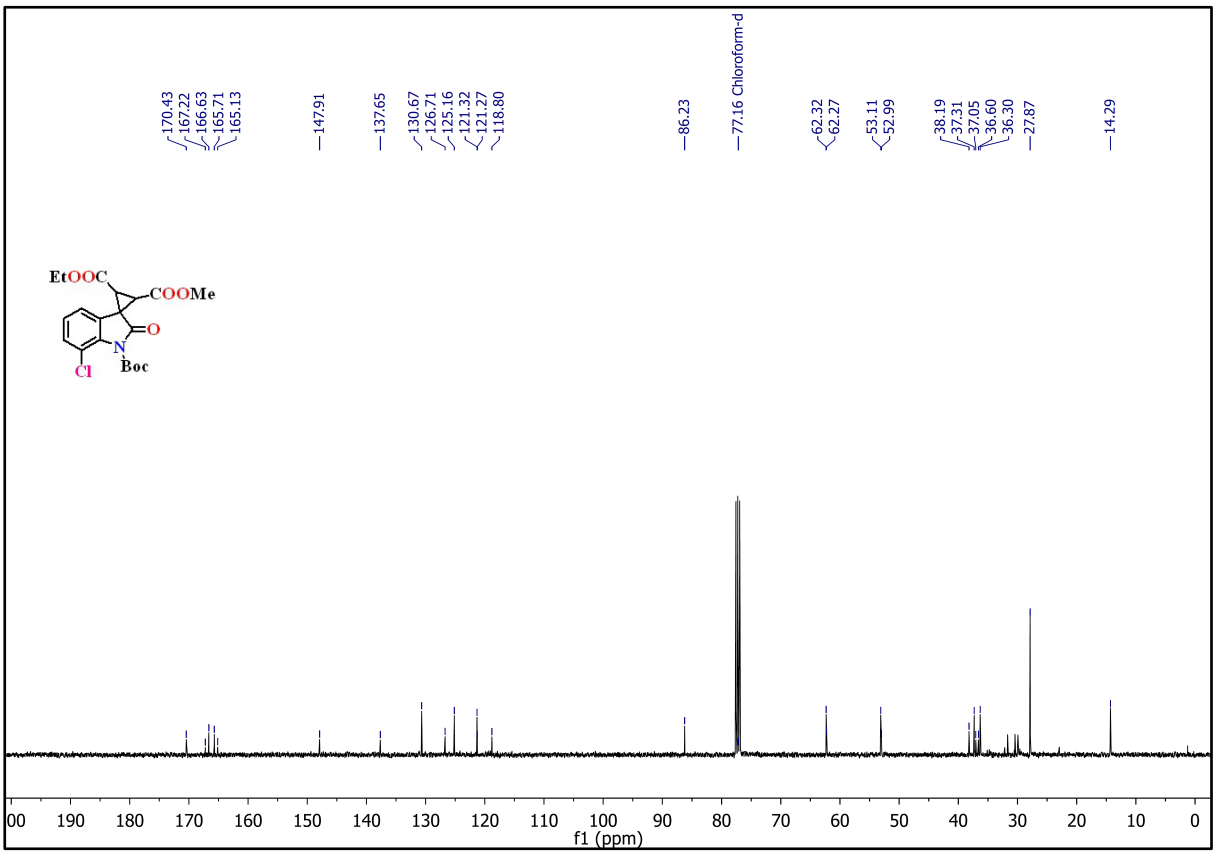
^{19}F NMR (376 MHz) of **3n** in $CDCl_3$:



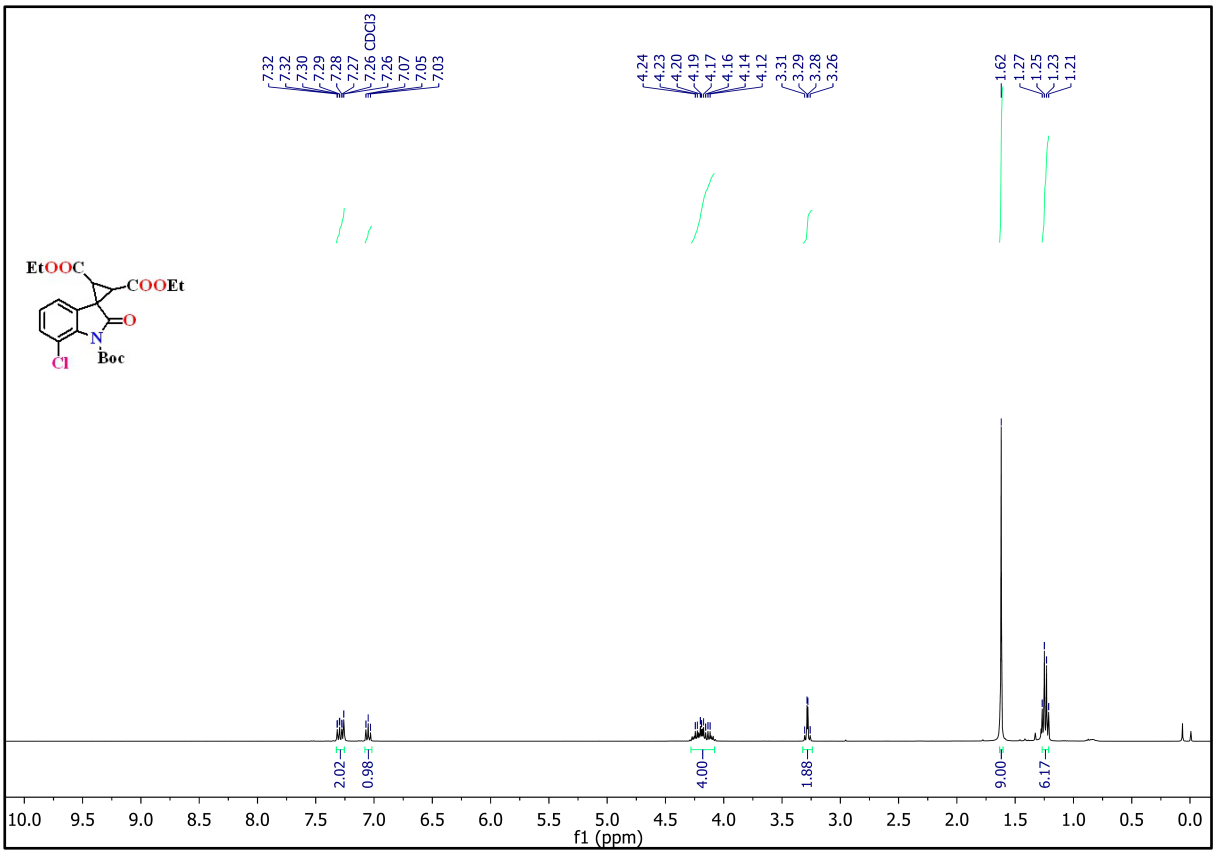
^{1}H NMR (400 MHz) of **3o** in CDCl3:



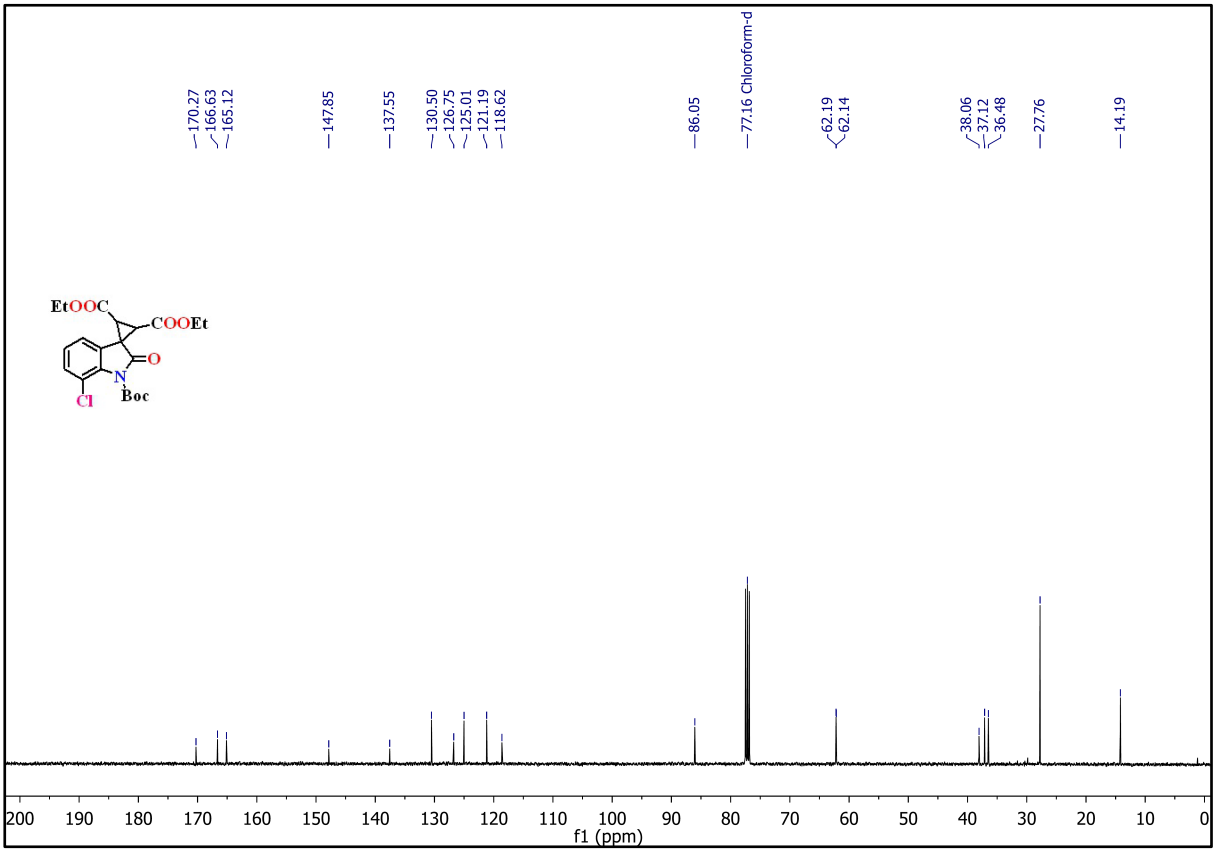
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3o** in CDCl3:



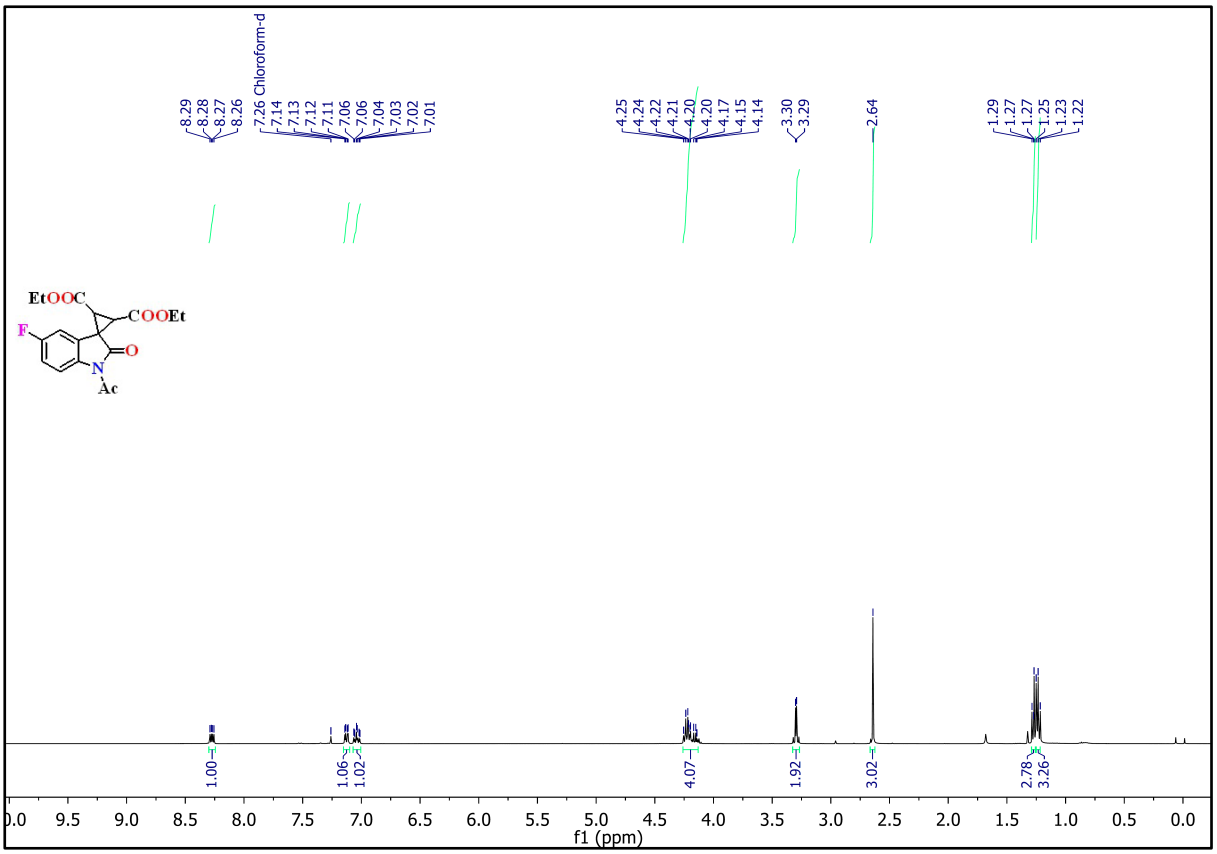
^{1}H NMR (400 MHz) of **3p** in CDCl3:



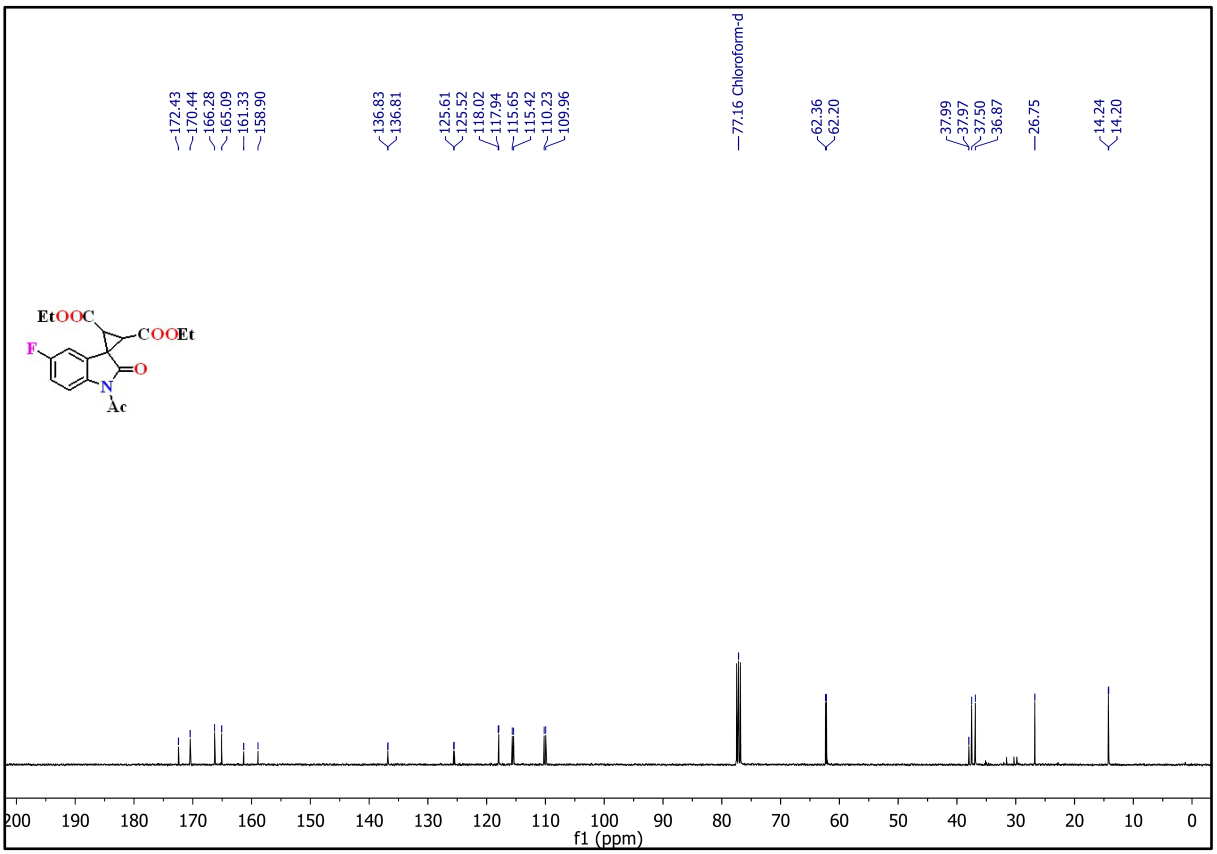
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3p** in CDCl3:



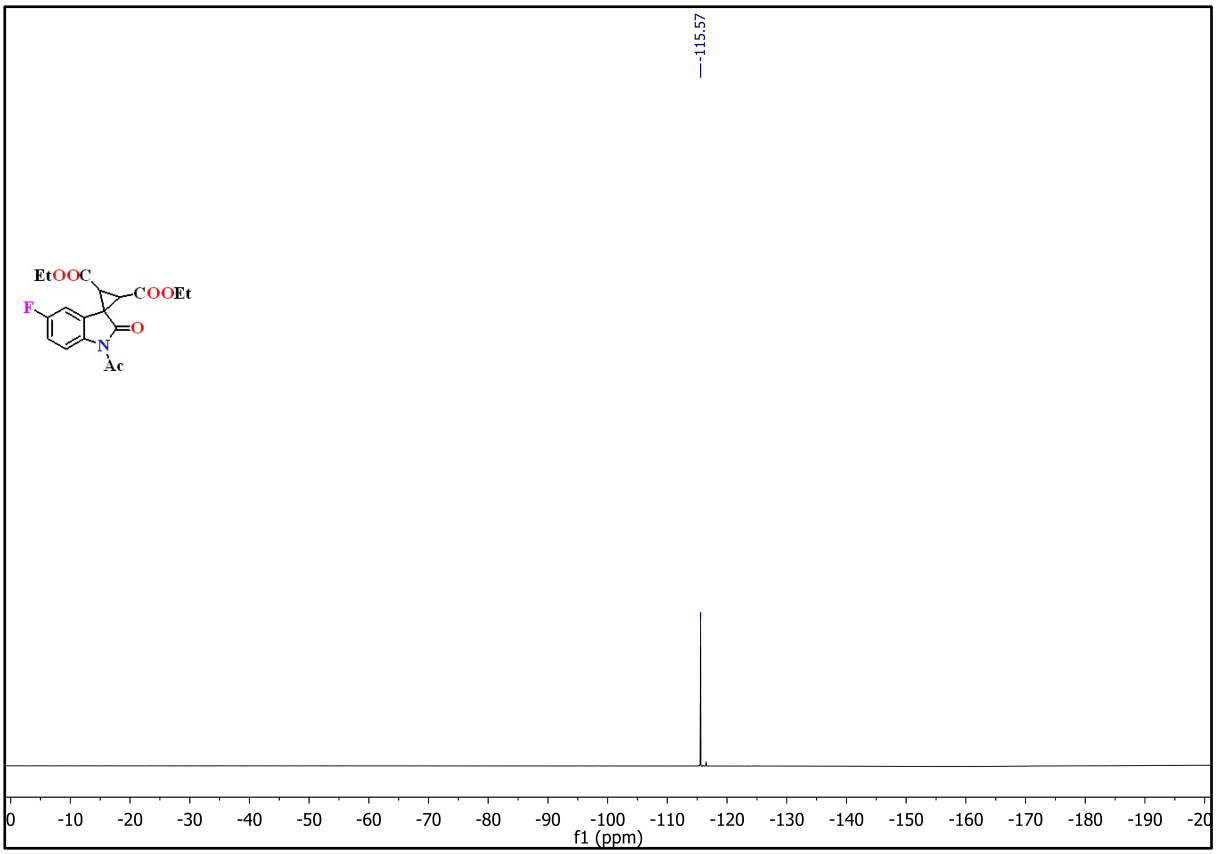
^{1}H NMR (400 MHz) of **3q** in CDCl3:



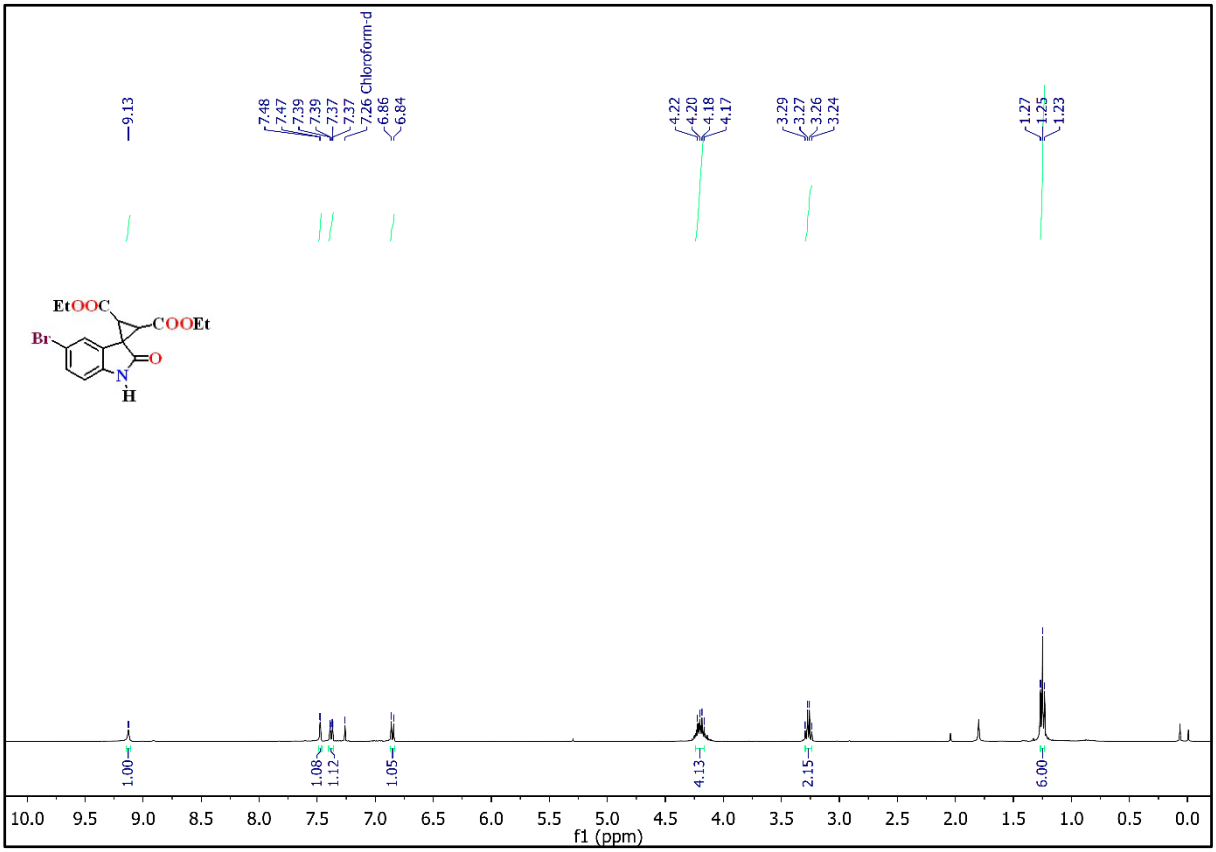
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3q** in CDCl3:



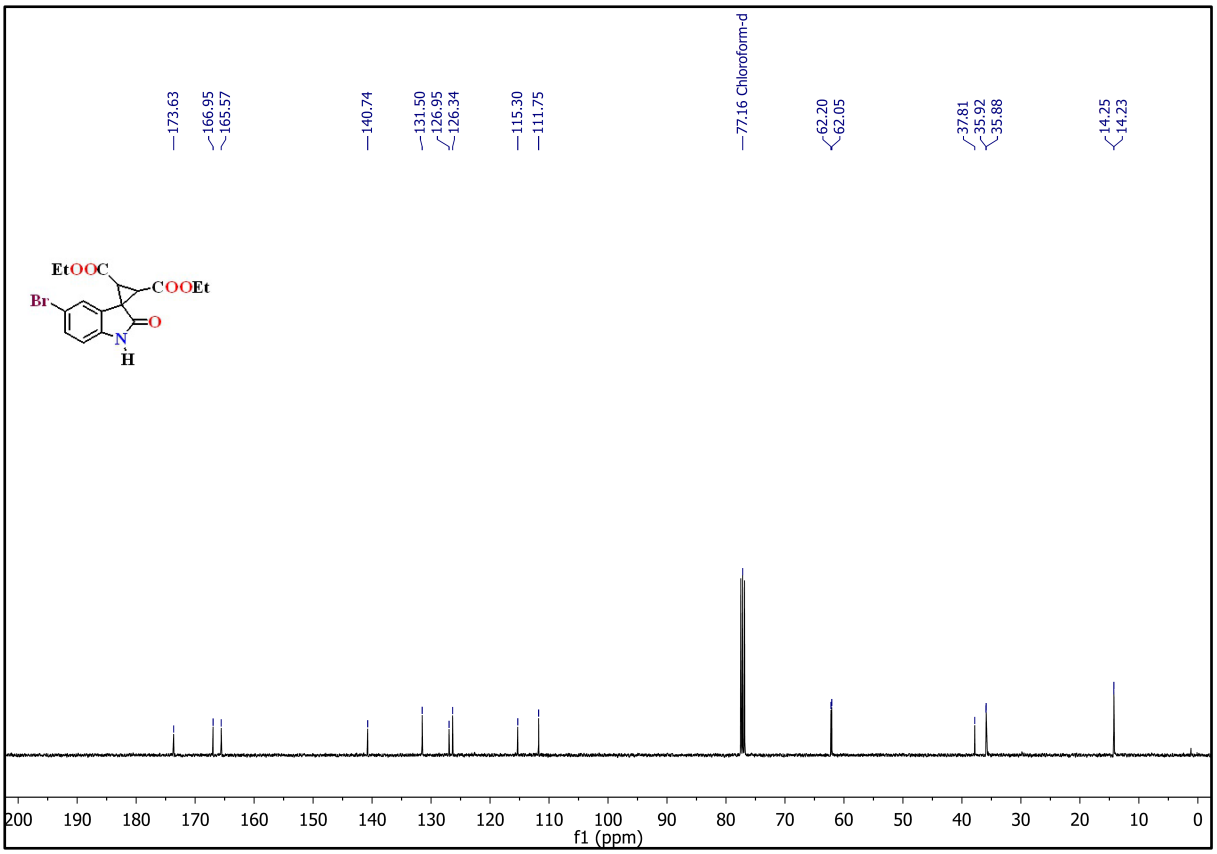
^{19}F NMR (376 MHz) of **3q** in $CDCl_3$:



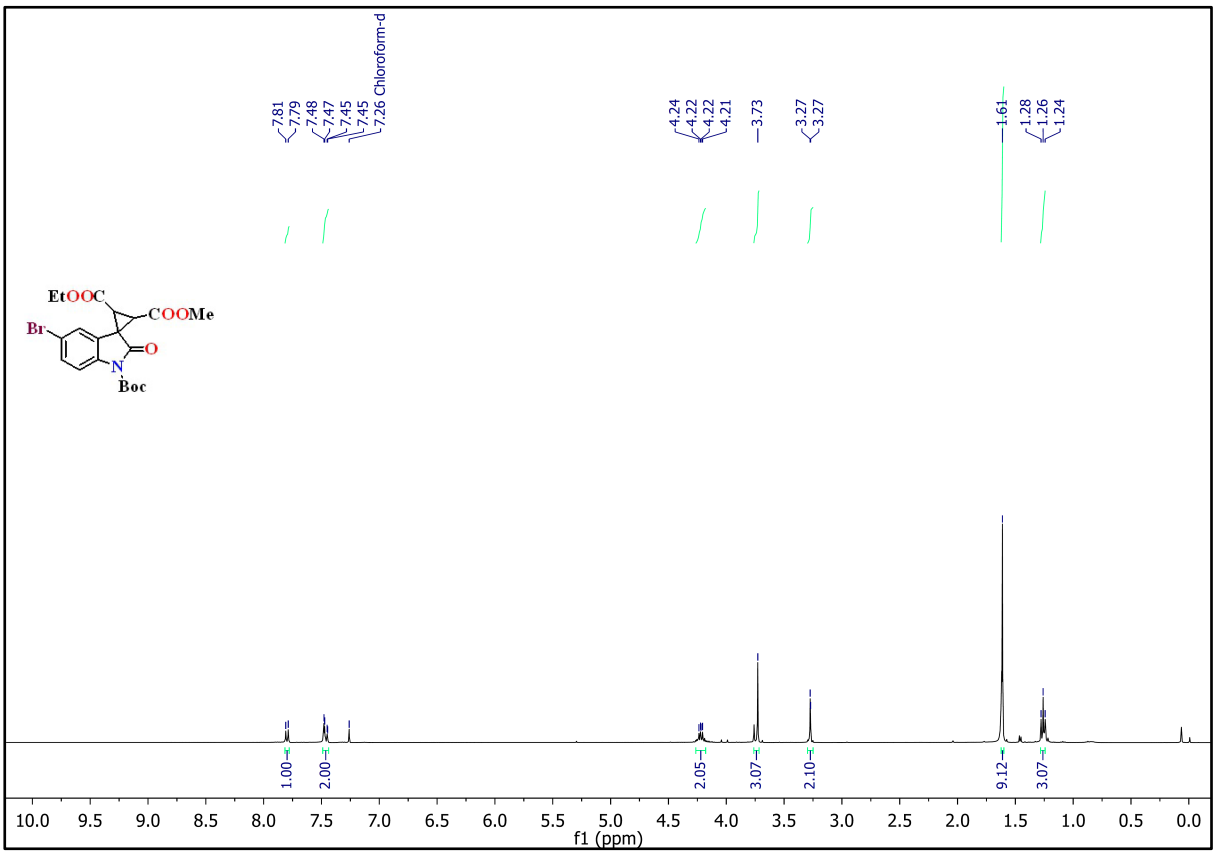
^{1}H NMR (400 MHz) of **3r** in CDCl3:



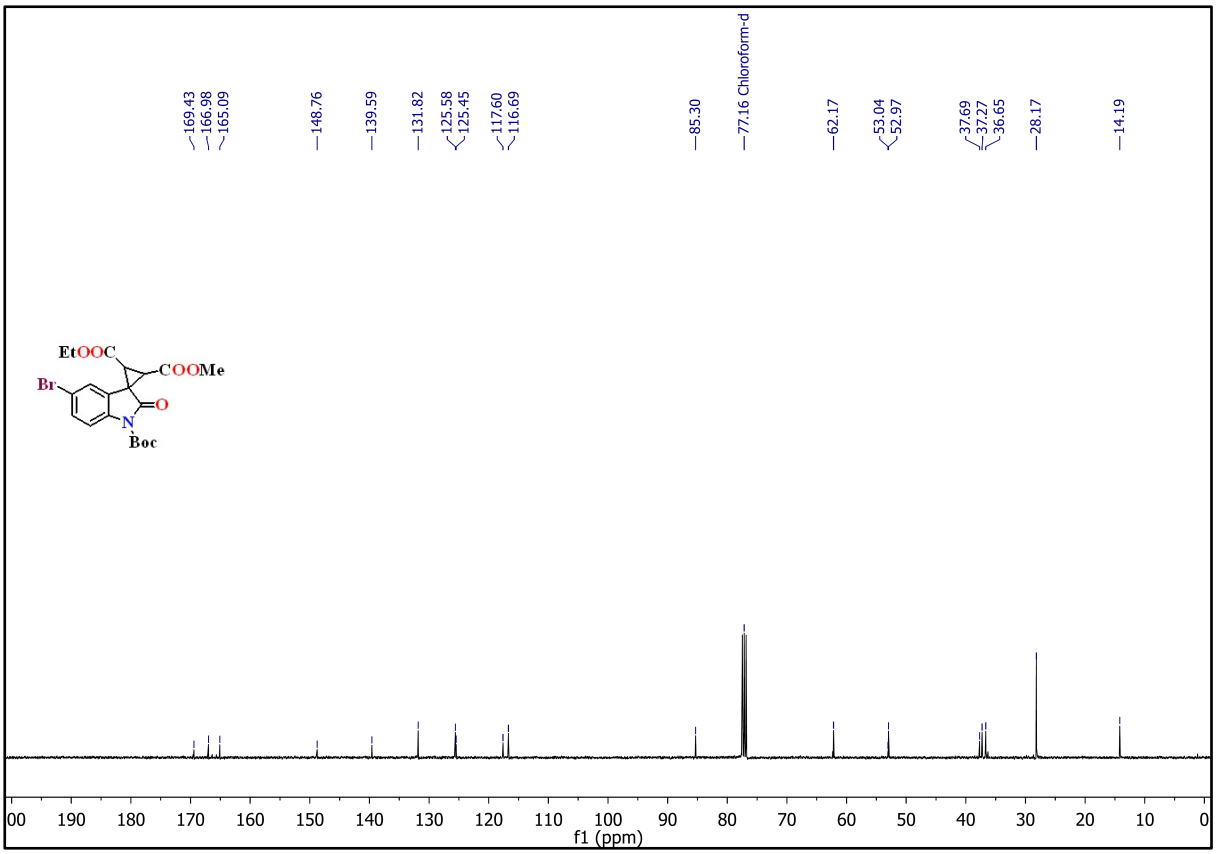
^{13}C{^{1}H} NMR (100 MHz) of **3r** in CDCl3:



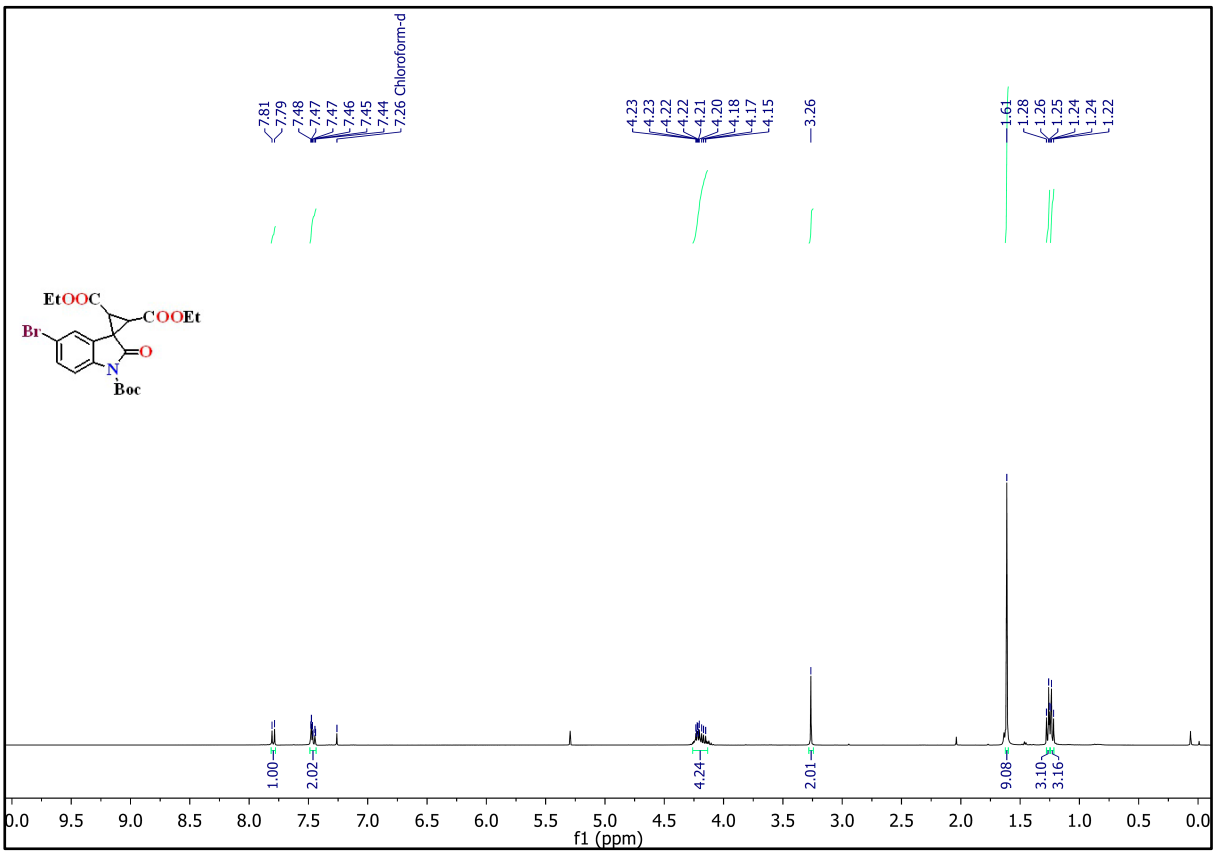
^{1}H NMR (400 MHz) of **3s** in CDCl3:



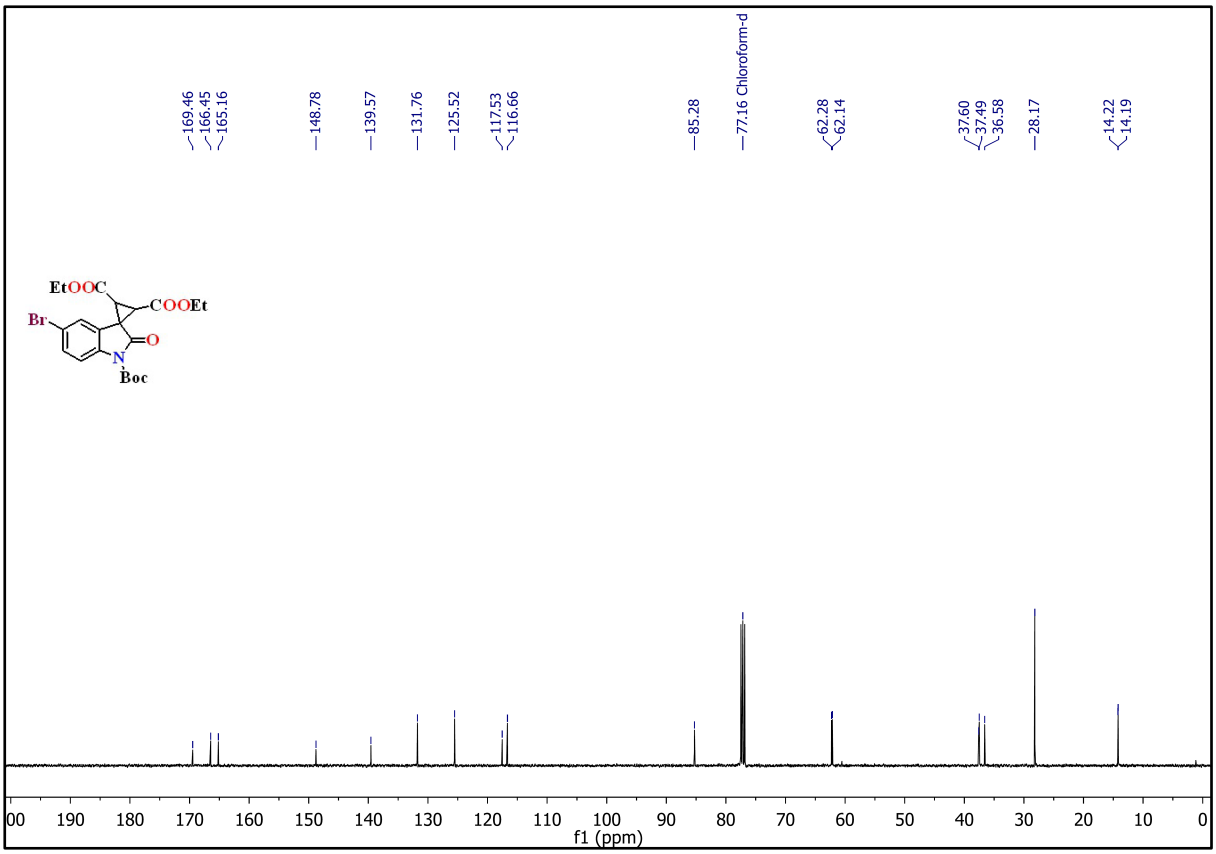
^{13}C{^{1}H} NMR (100 MHz) of **3s** in CDCl3:



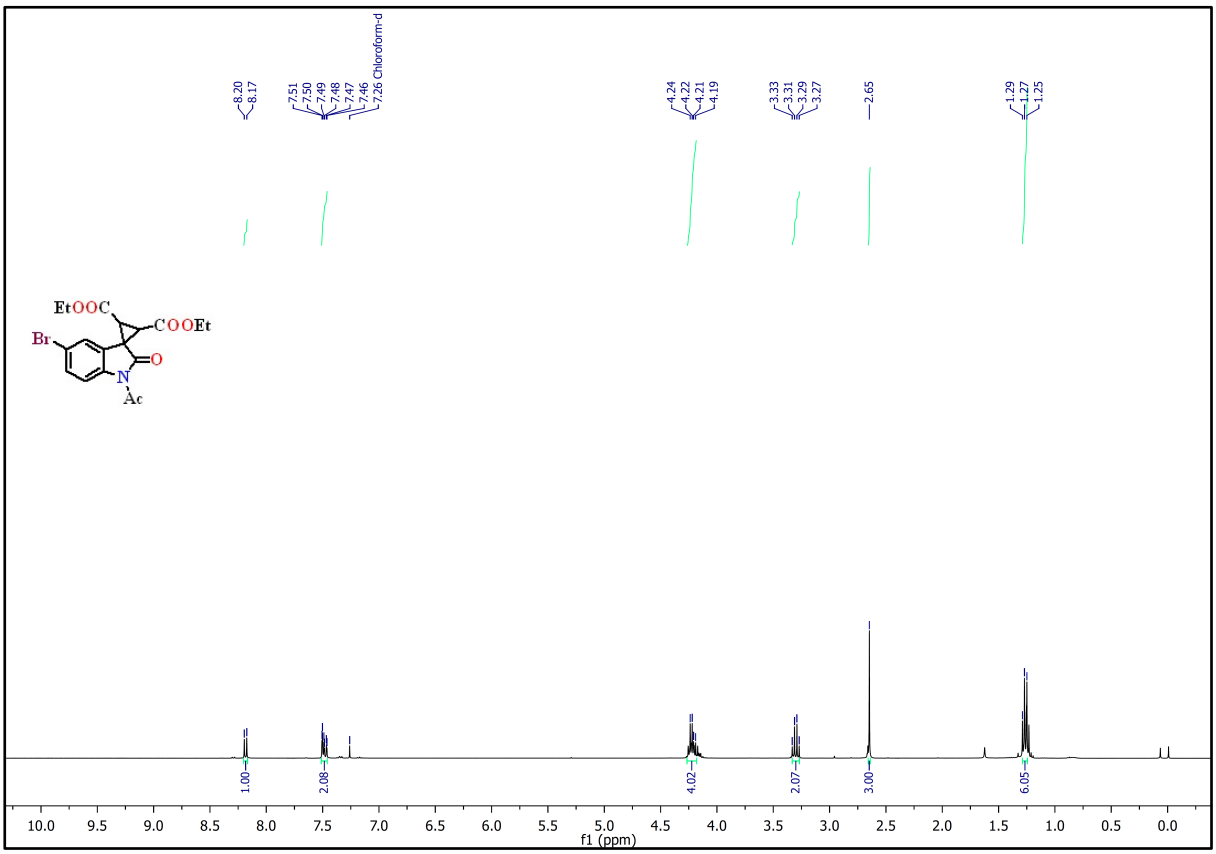
^{1}H NMR (400 MHz) of **3t** in CDCl3:



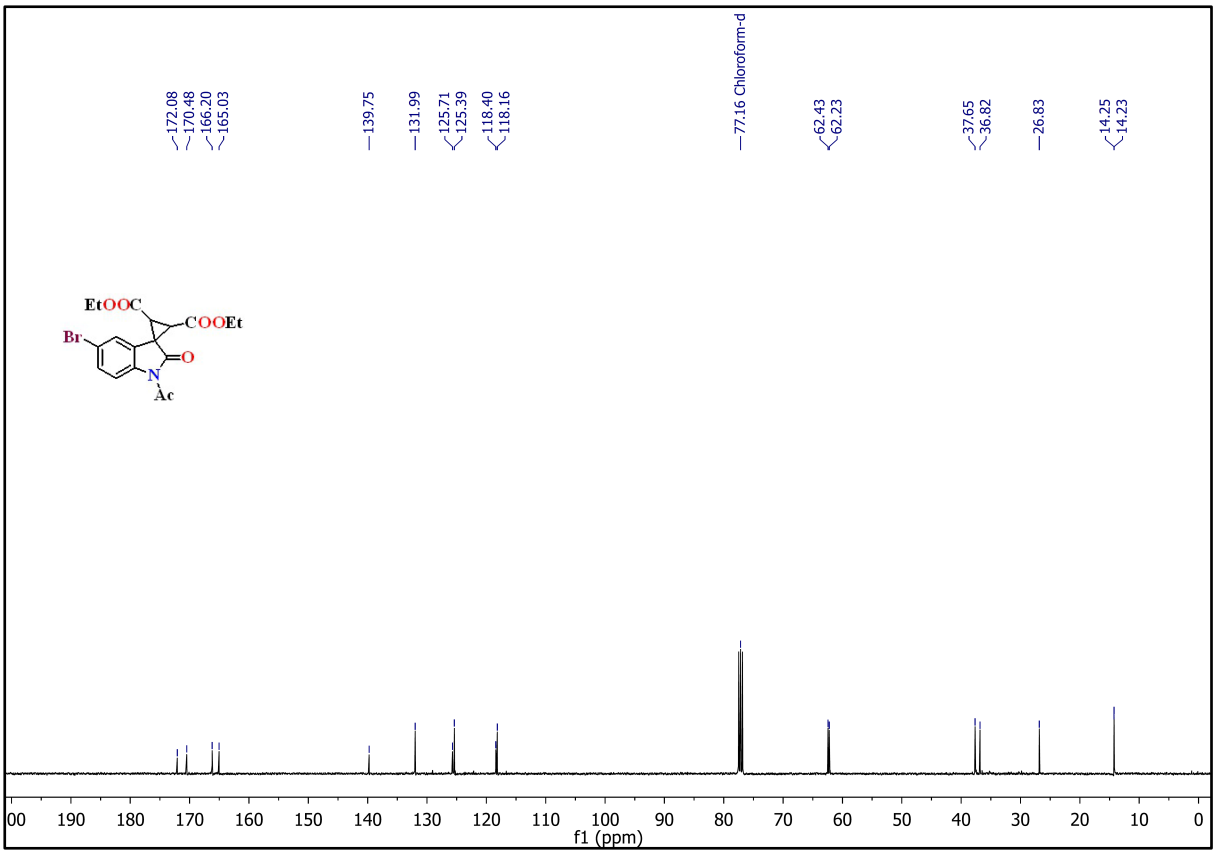
^{13}C{^{1}H} NMR (100 MHz) of **3t** in CDCl3:



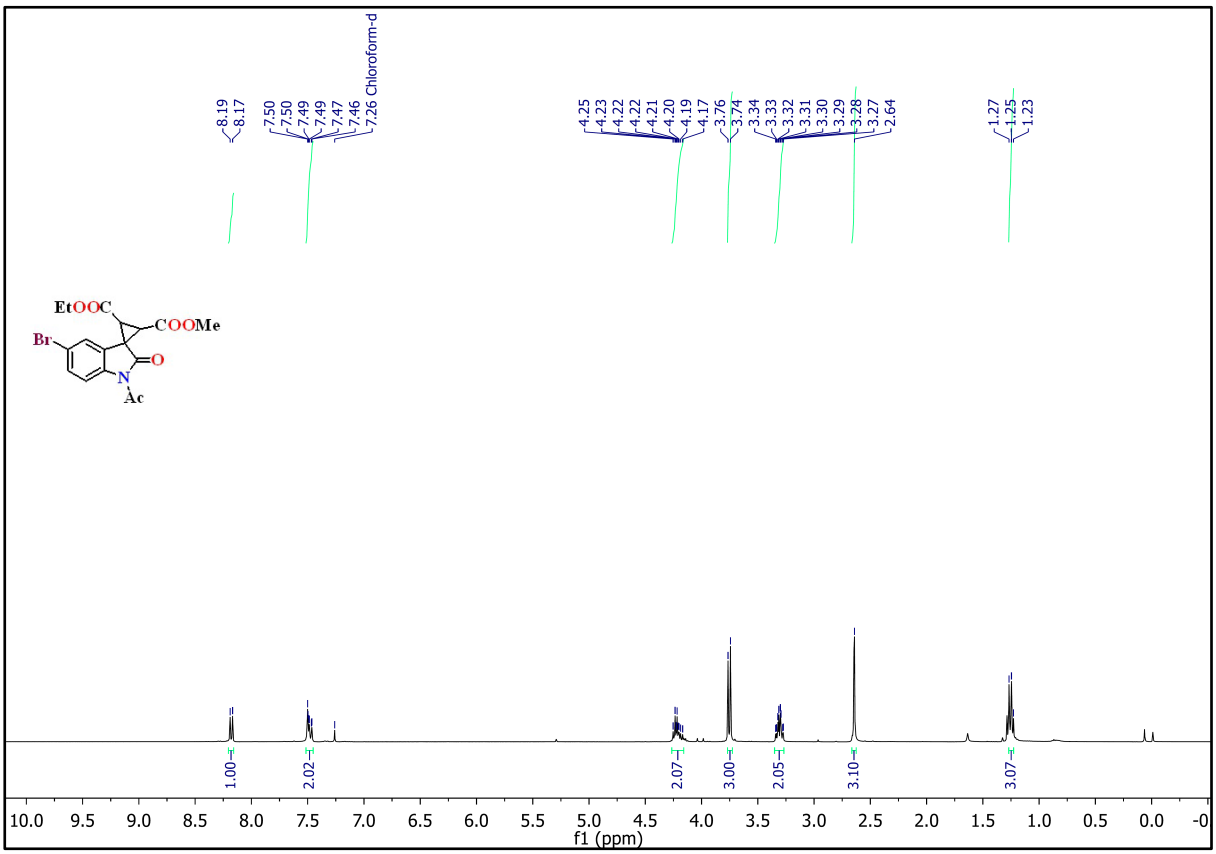
^{1}H NMR (400 MHz) of **3u** in CDCl3:



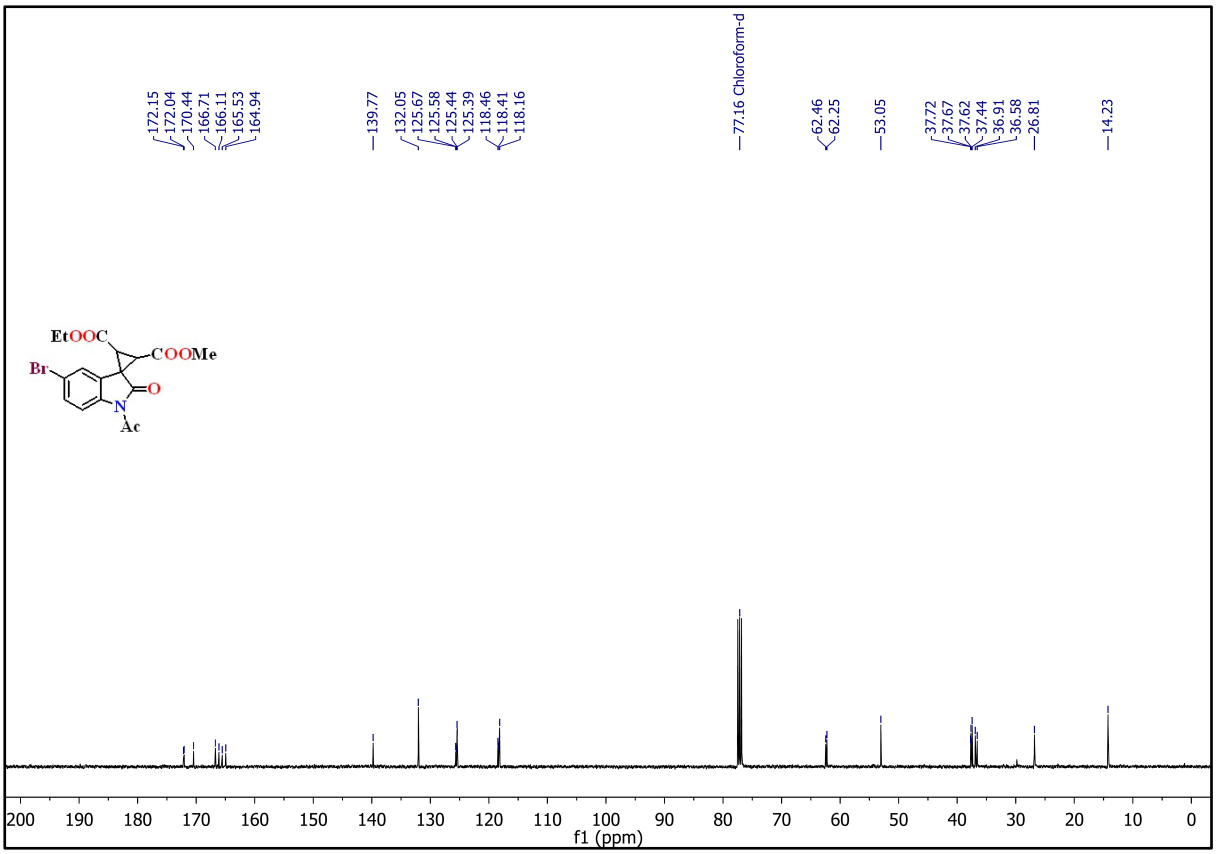
^{13}C{^{1}H} NMR (100 MHz) of **3u** in CDCl3:



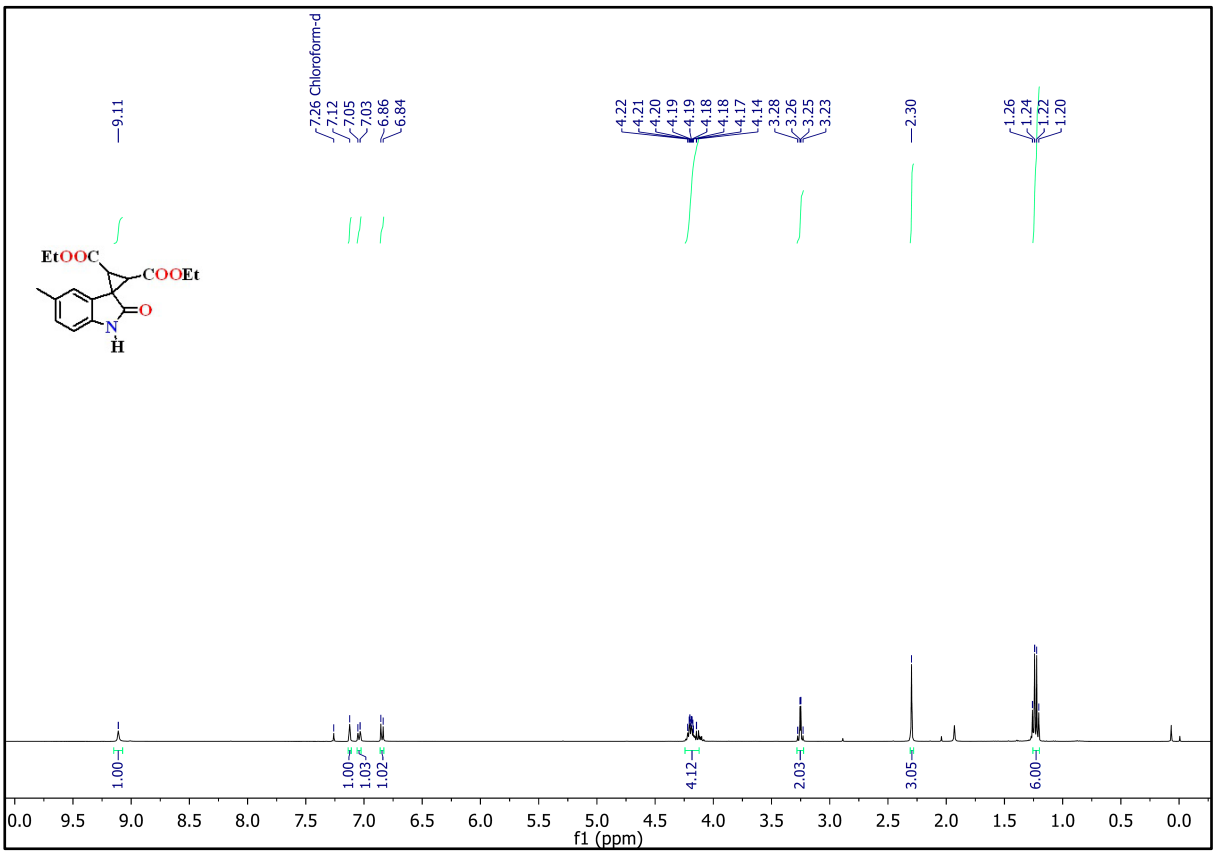
^{1}H NMR (400 MHz) of **3v** in CDCl3:



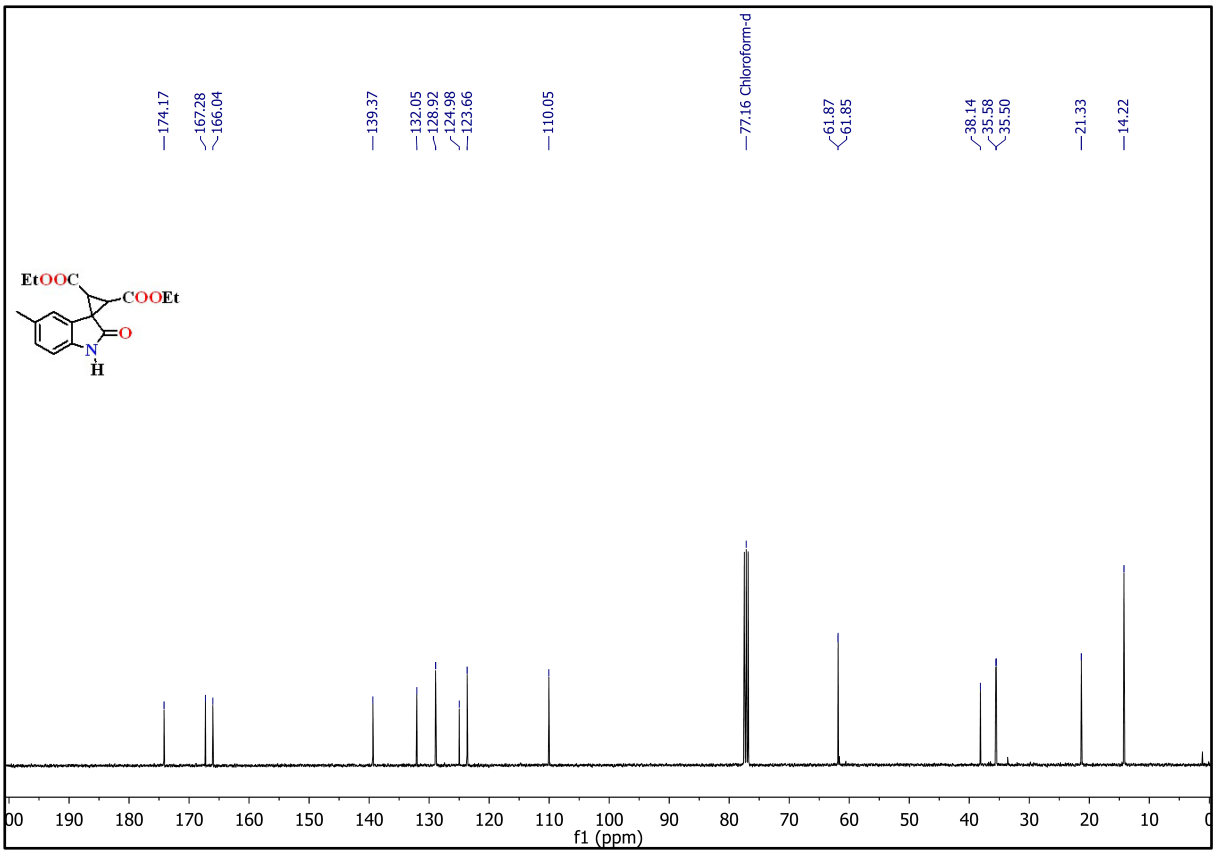
^{13}C{^{1}H} NMR (100 MHz) of **3v** in CDCl3:



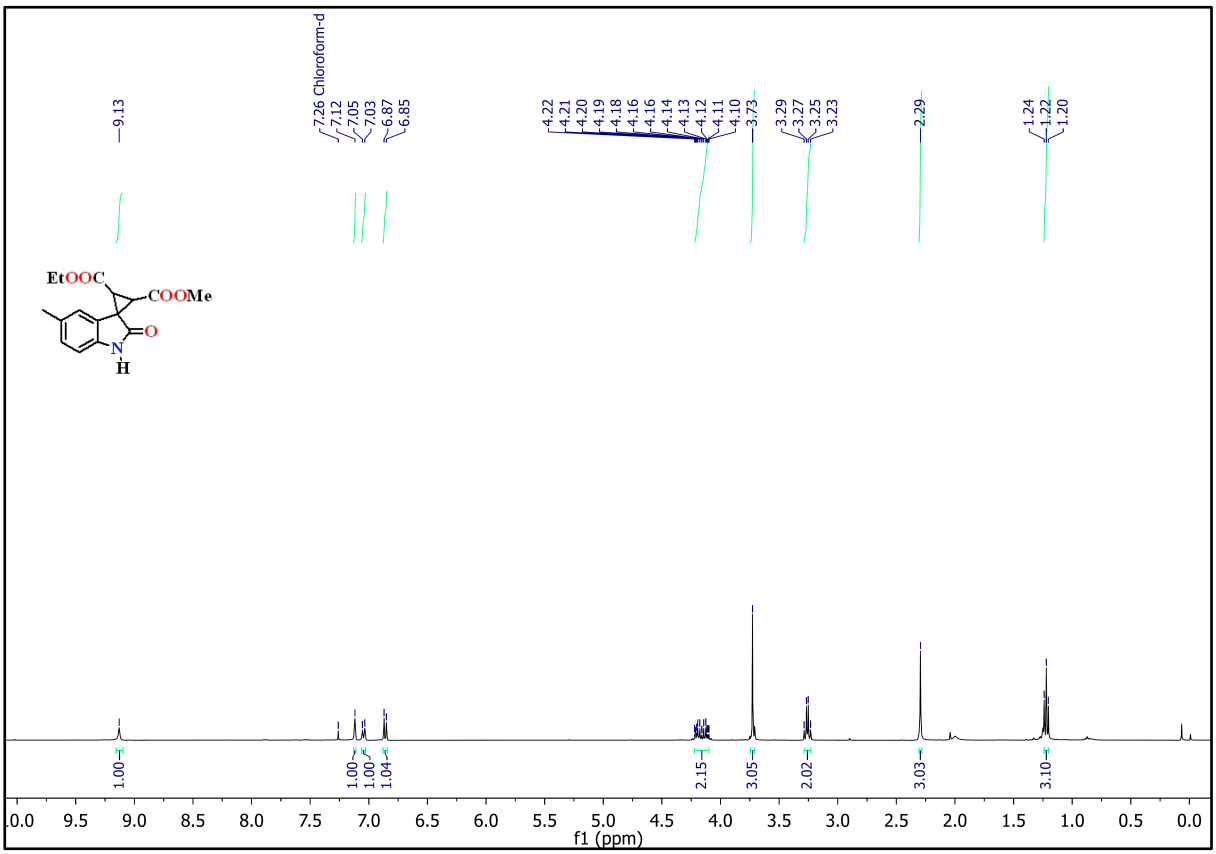
^{1}H NMR (400 MHz) of **3w** in CDCl3:



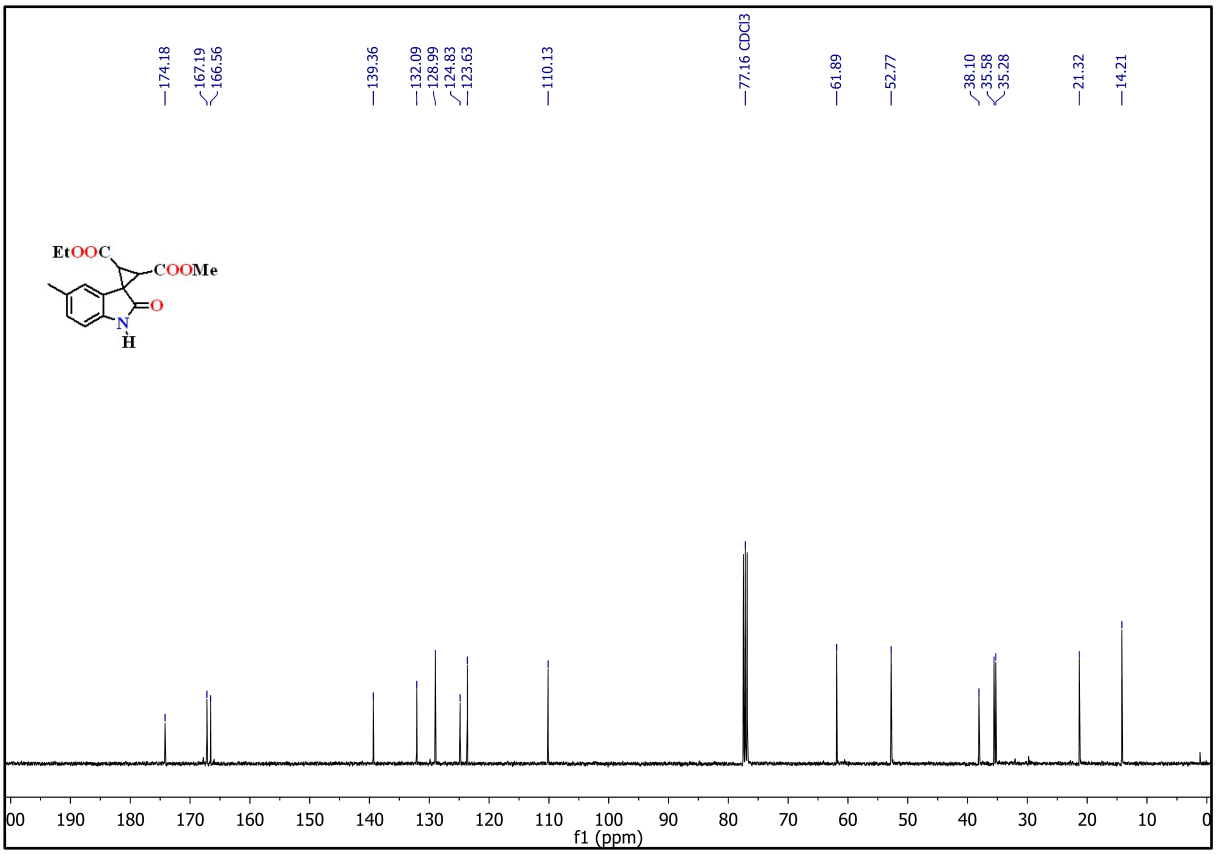
^{13}C{^{1}H} NMR (100 MHz) of **3w** in CDCl3:



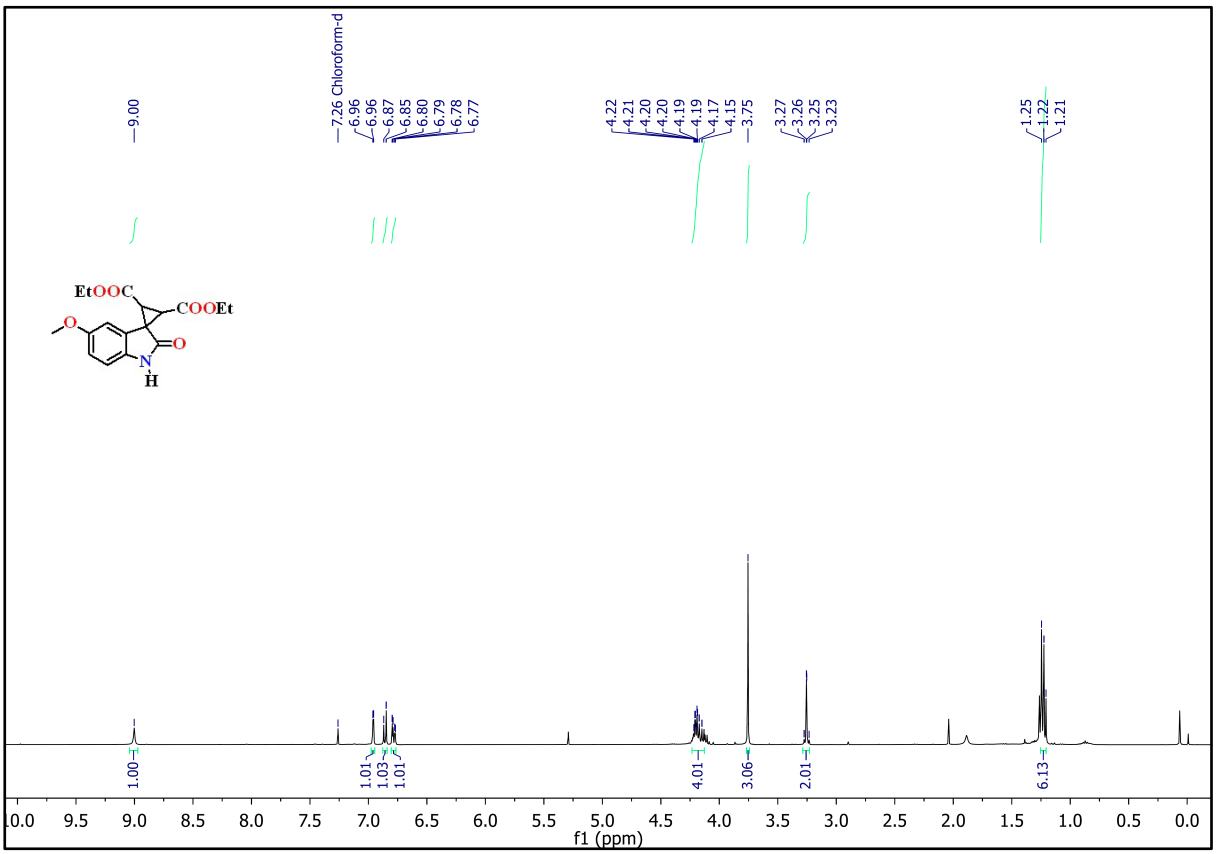
^{1}H NMR (400 MHz) of **3x** in CDCl3:



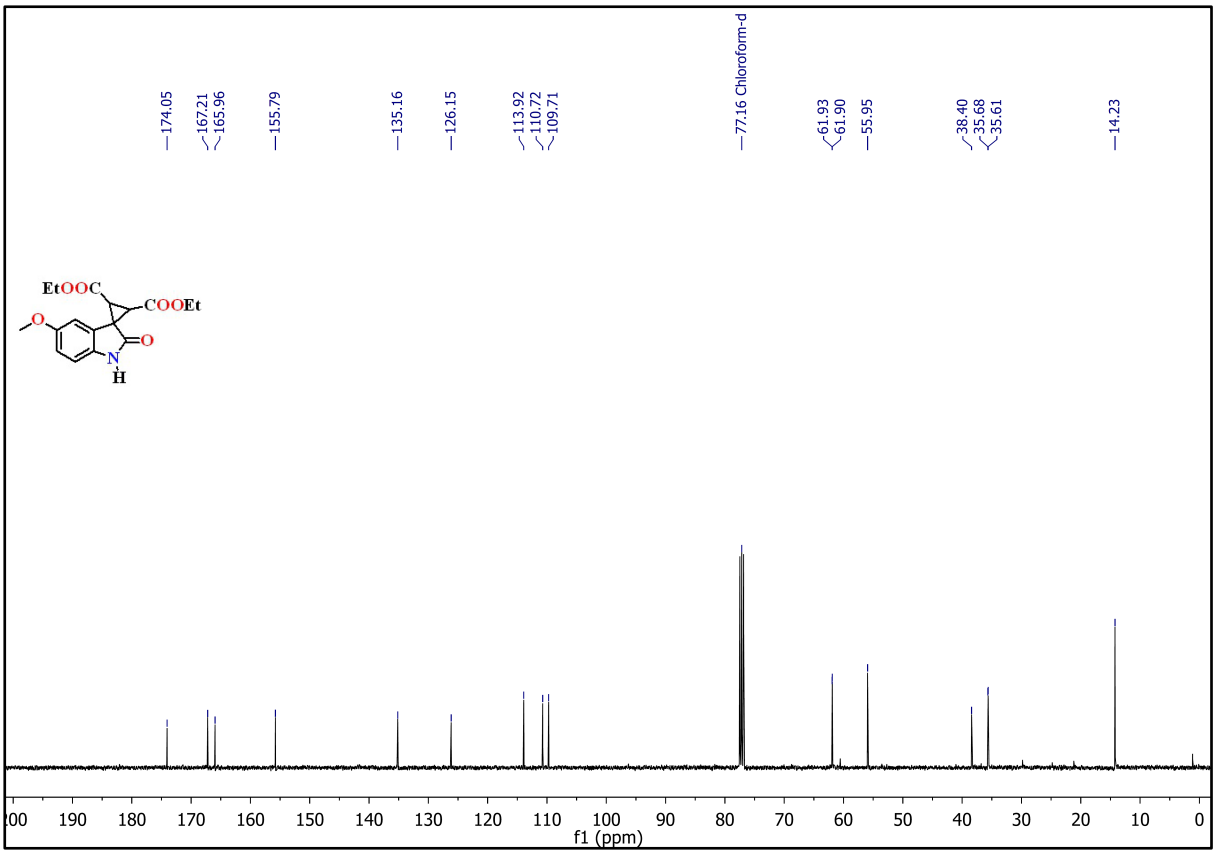
^{13}C{^{1}H} NMR (100 MHz) of **3x** in CDCl3:



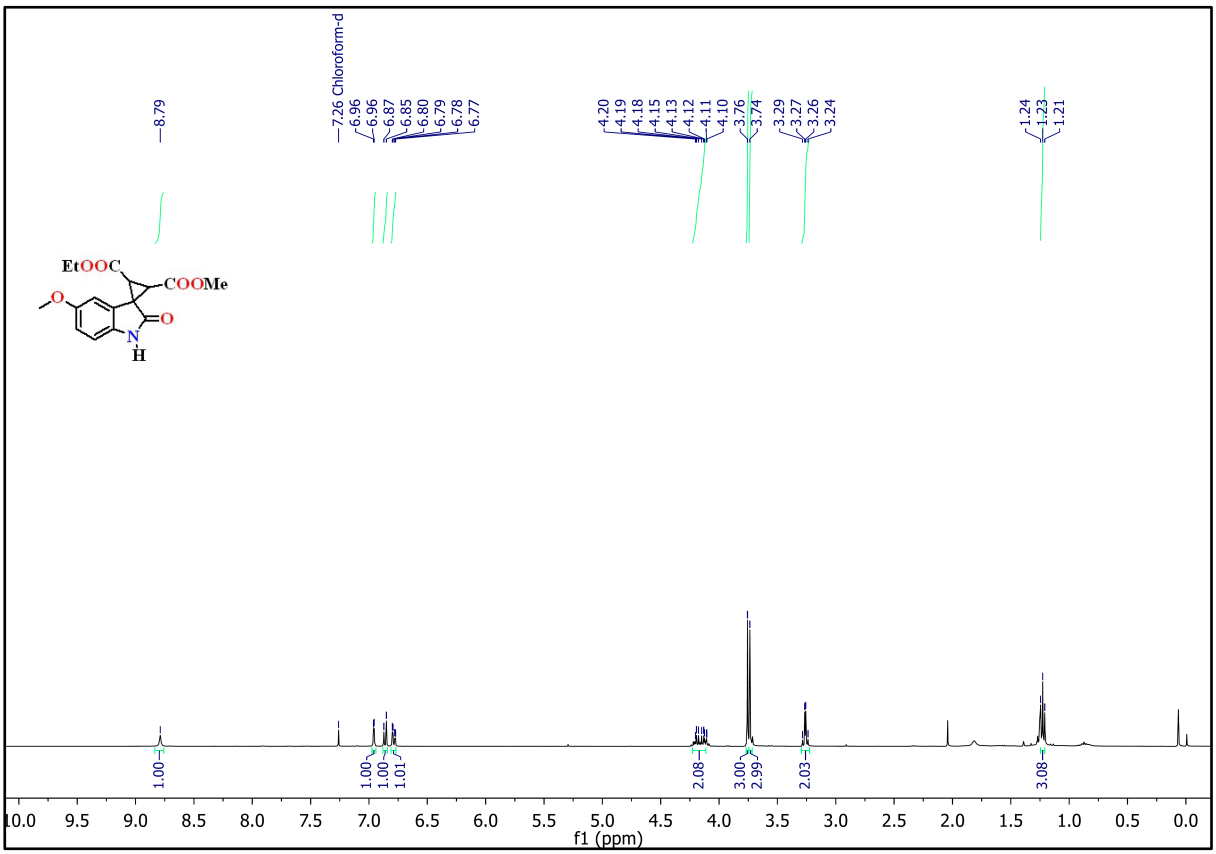
^{1}H NMR (400 MHz) of **3y** in CDCl3:



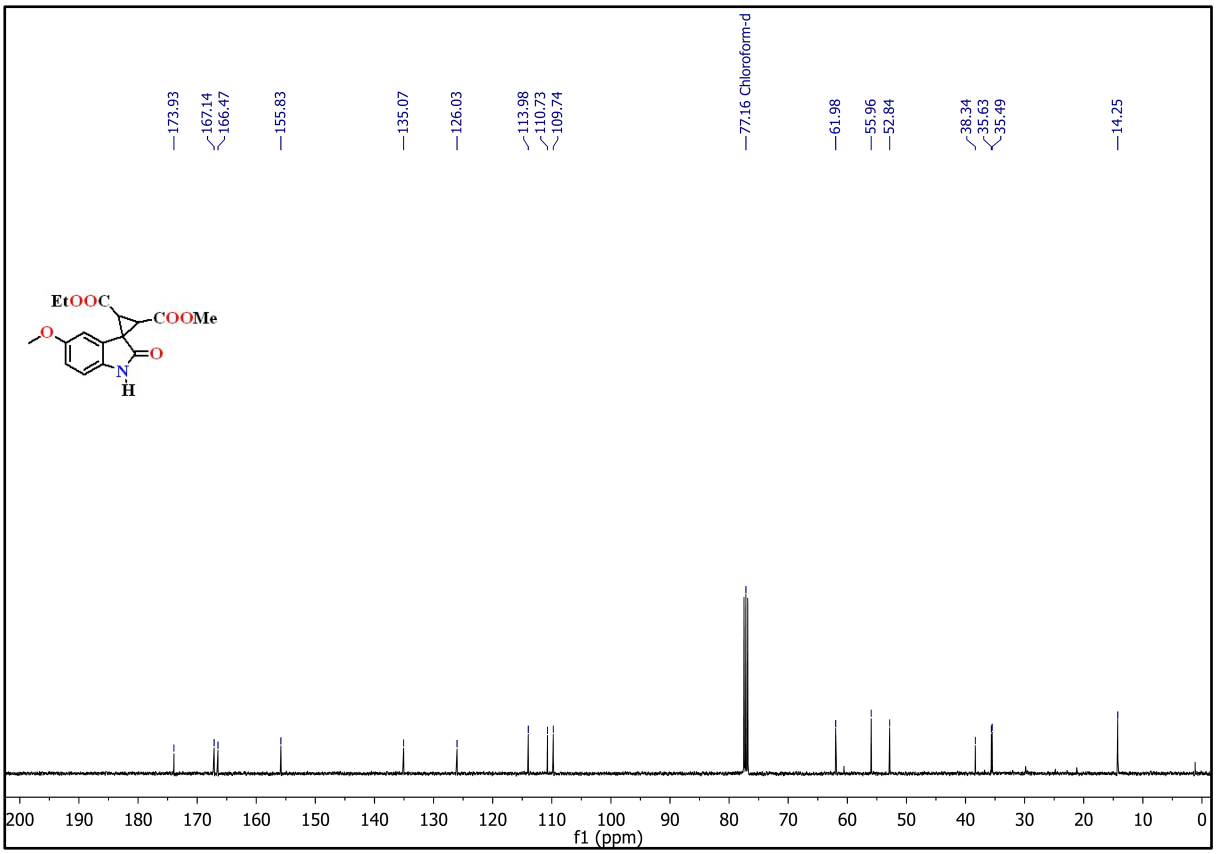
^{13}C{^{1}H} NMR (100 MHz) of **3y** in CDCl3:



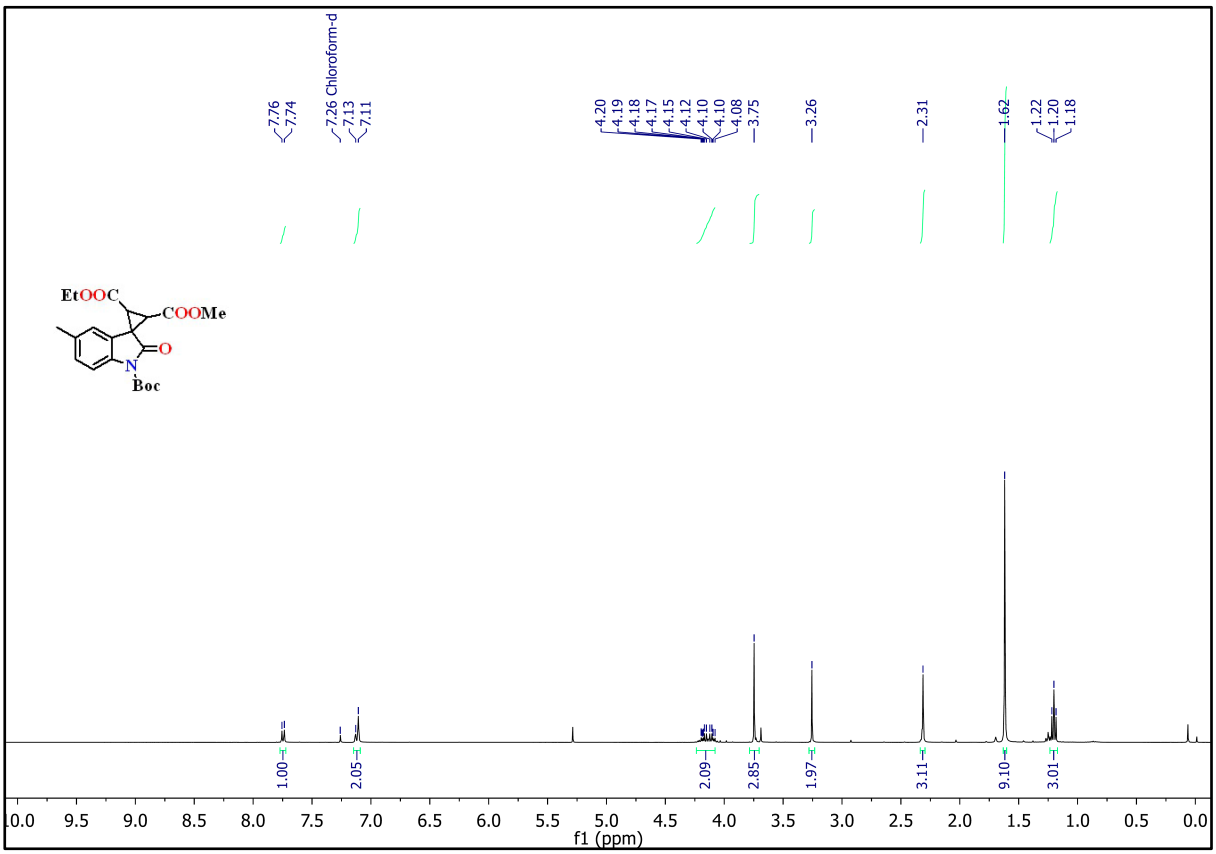
^{1}H NMR (400 MHz) of **3z** in CDCl3:



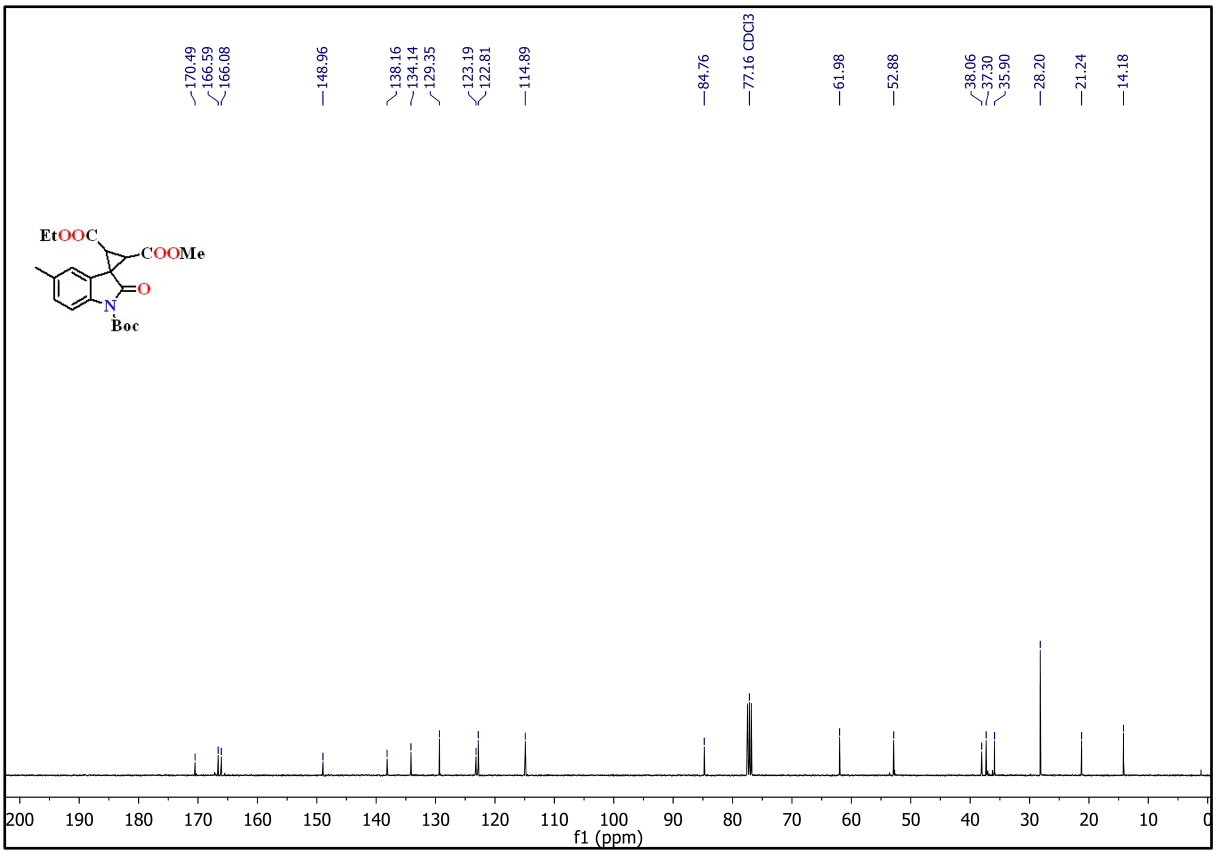
^{13}C{^{1}H} NMR (100 MHz) of **3z** in CDCl3:



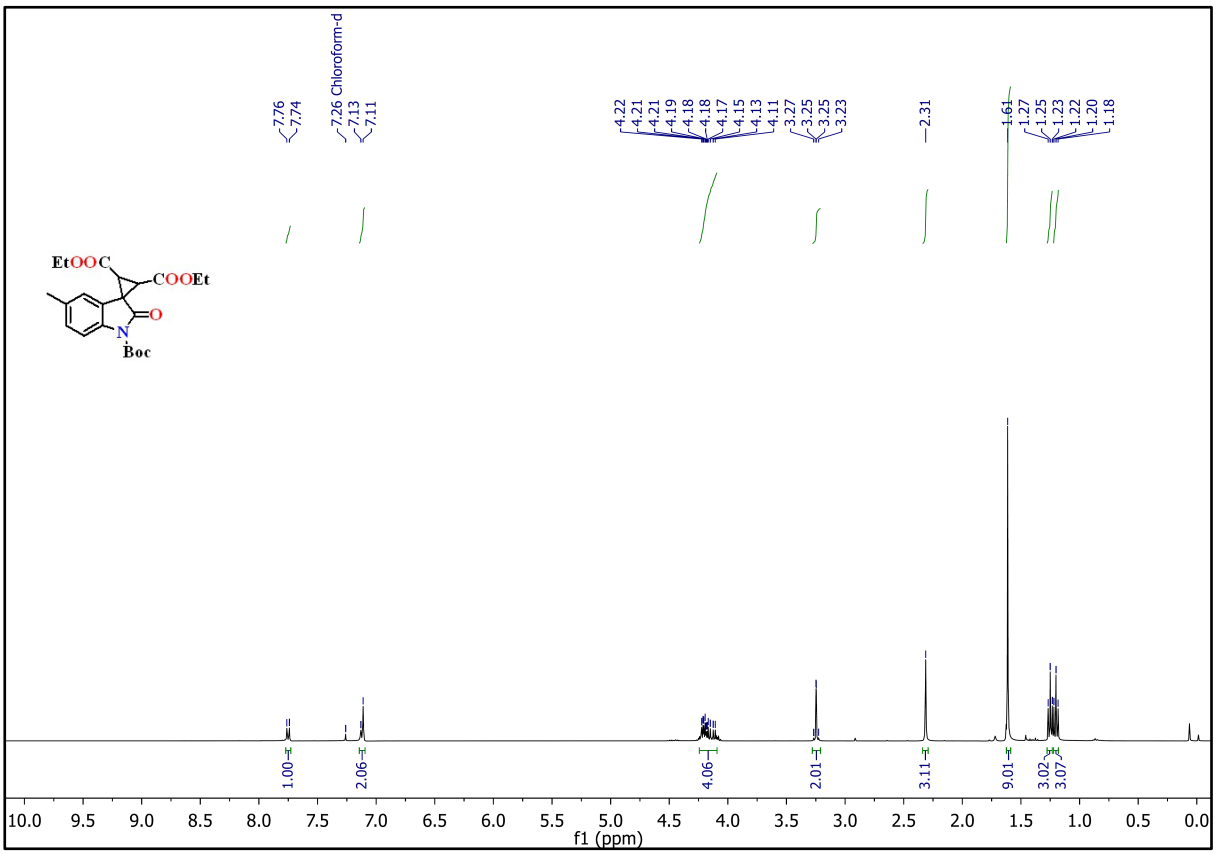
^{1}H NMR (400 MHz) of **3aa** in CDCl3:



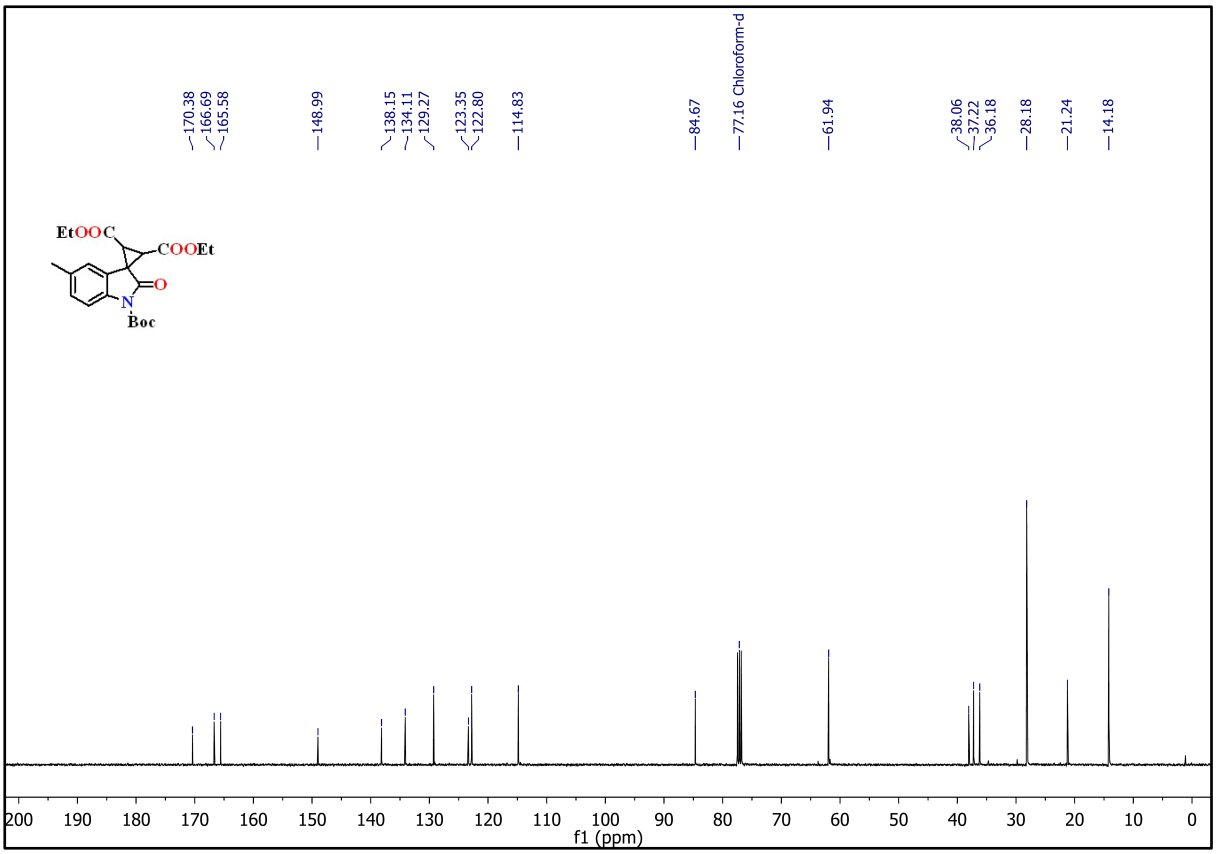
^{13}C{^{1}H} NMR (100 MHz) of **3aa** in CDCl3:



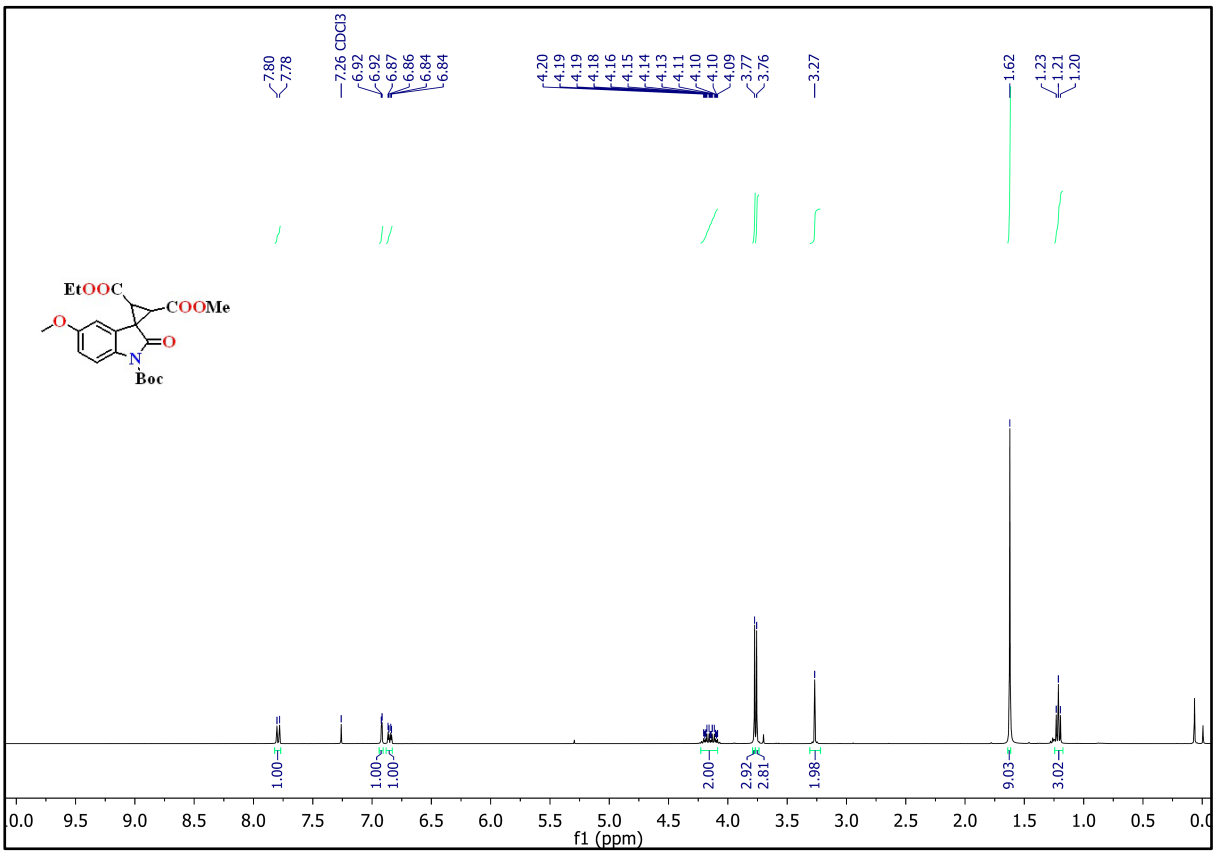
^{1}H NMR (400 MHz) of **3ab** in CDCl3:



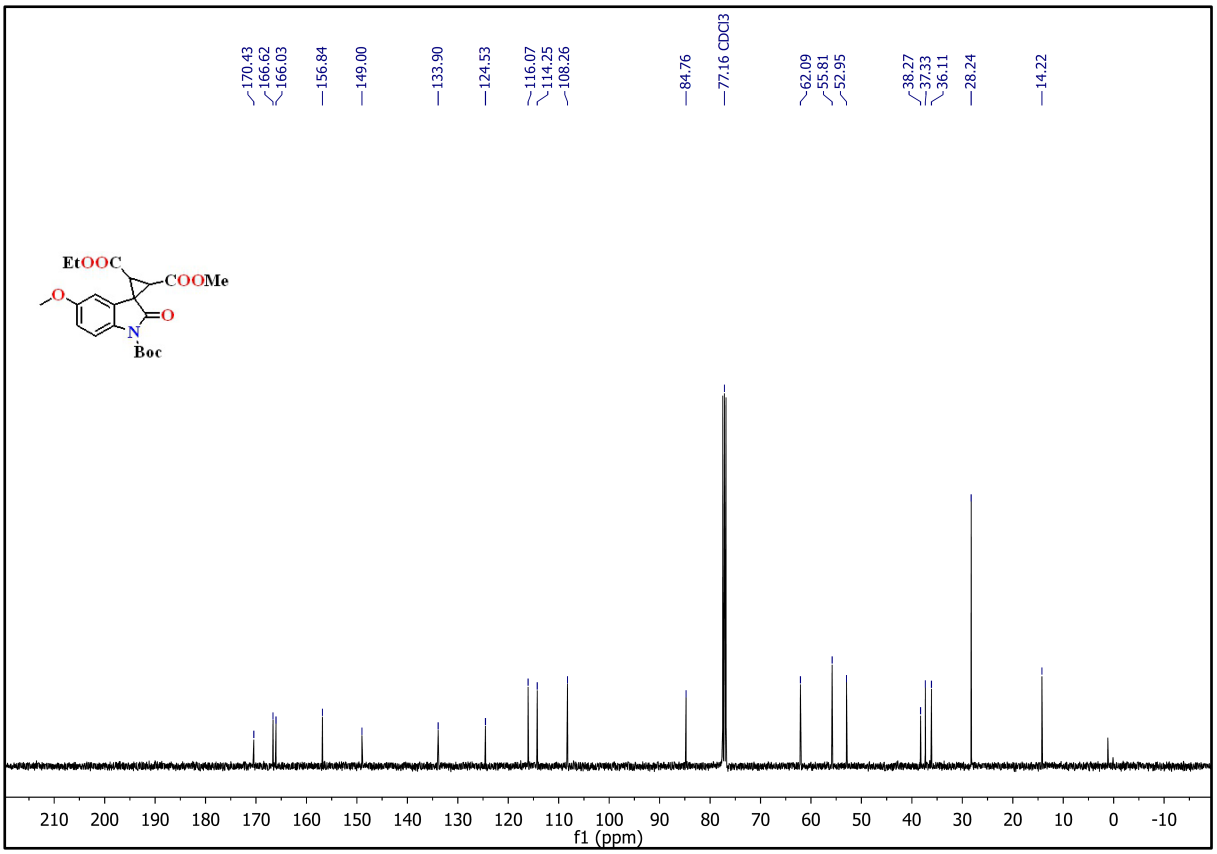
^{13}C{^{1}H} NMR (100 MHz) of **3ab** in CDCl3:



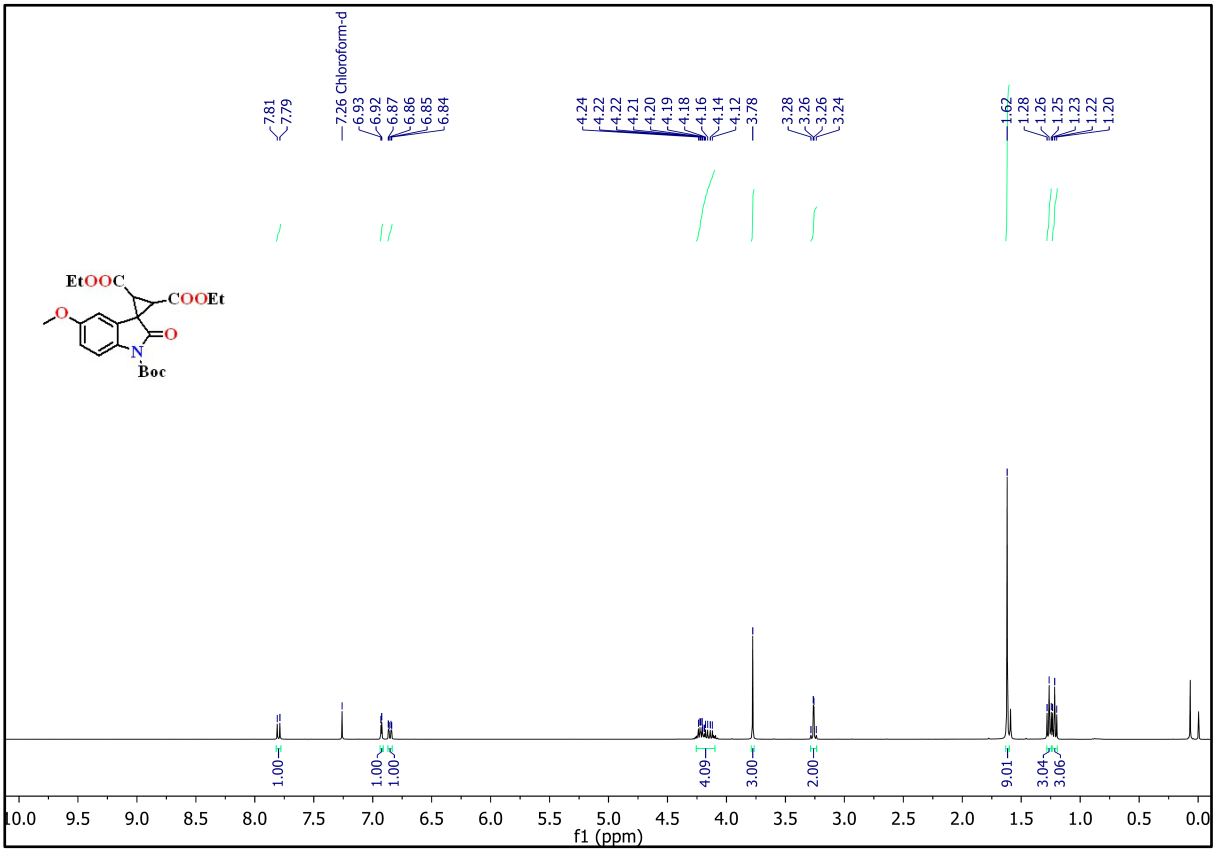
^{1}H NMR (400 MHz) of **3ac** in CDCl3:



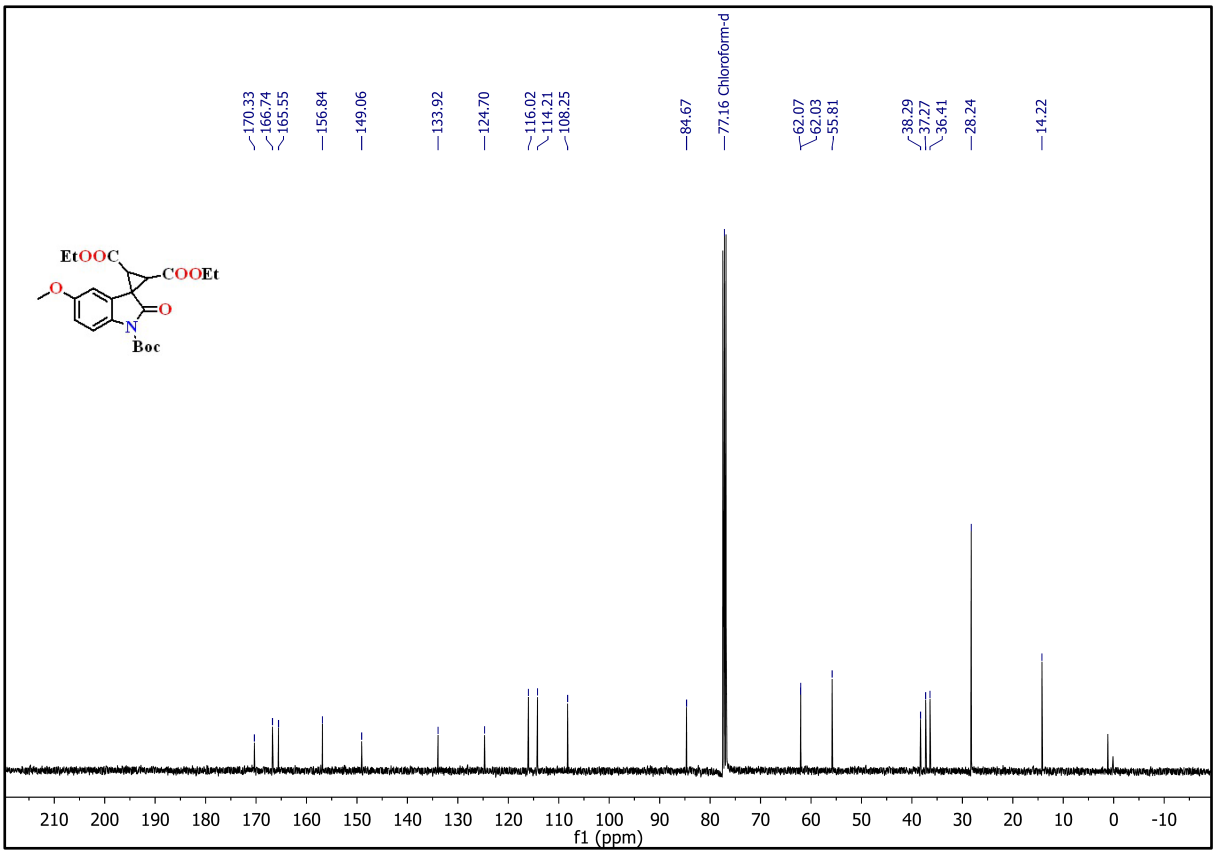
^{13}C{^{1}H} NMR (100 MHz) of **3ac** in CDCl3:



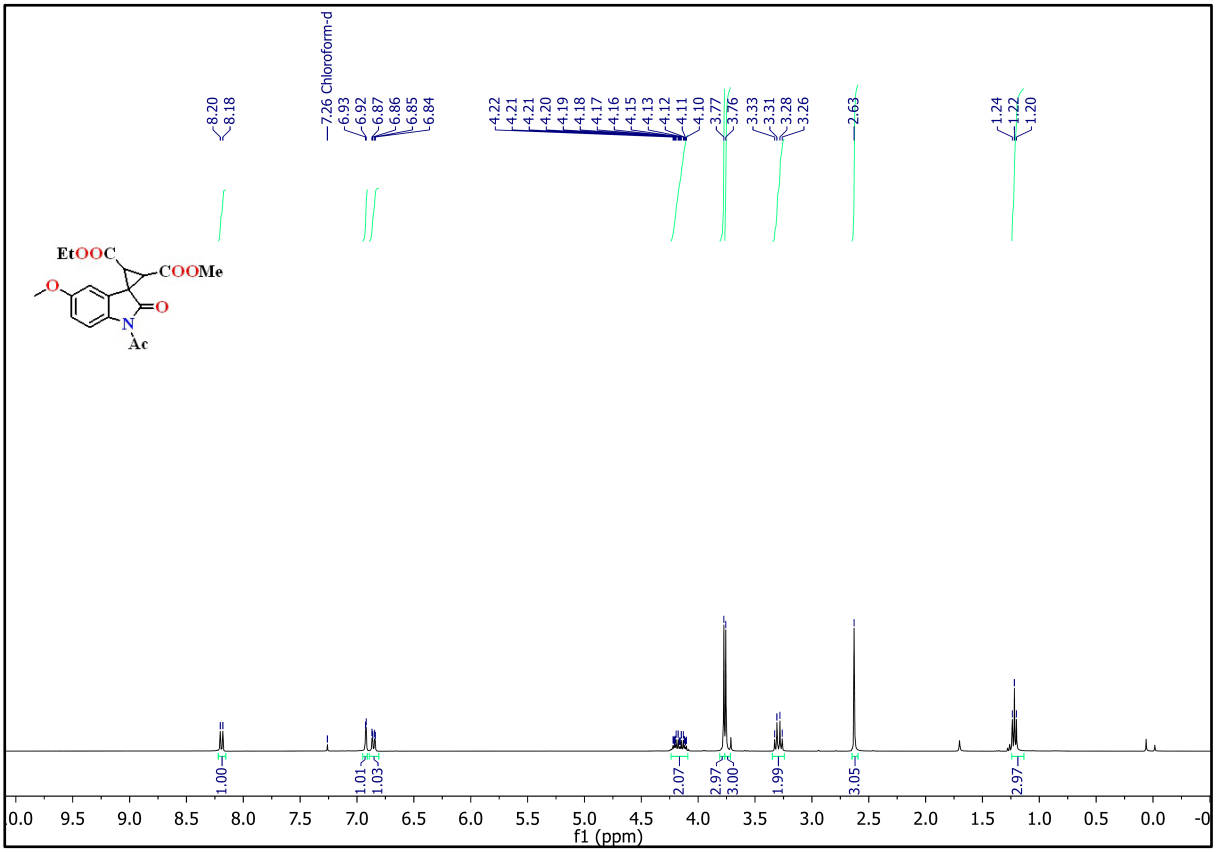
^{1}H NMR (400 MHz) of **3ad** in CDCl3:



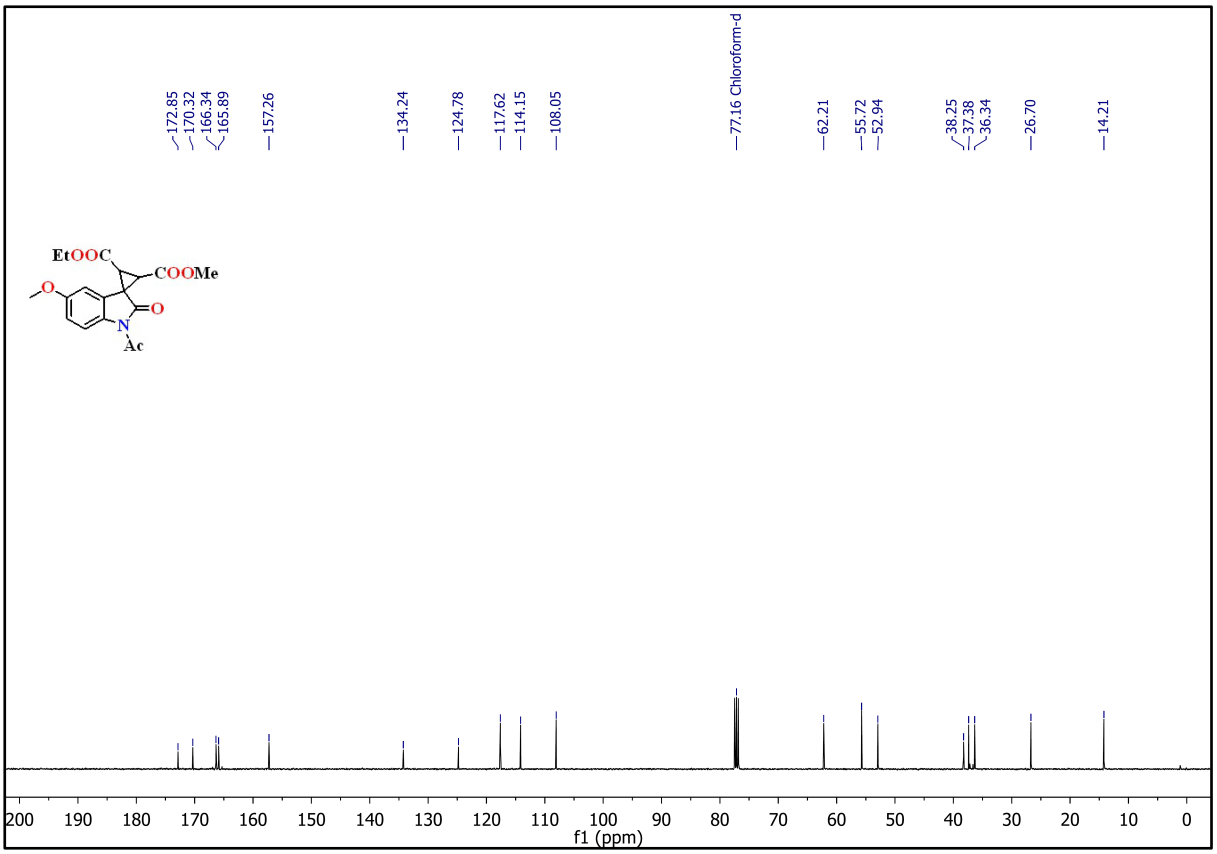
^{13}C{^{1}H} NMR (100 MHz) of **3ad** in CDCl3:



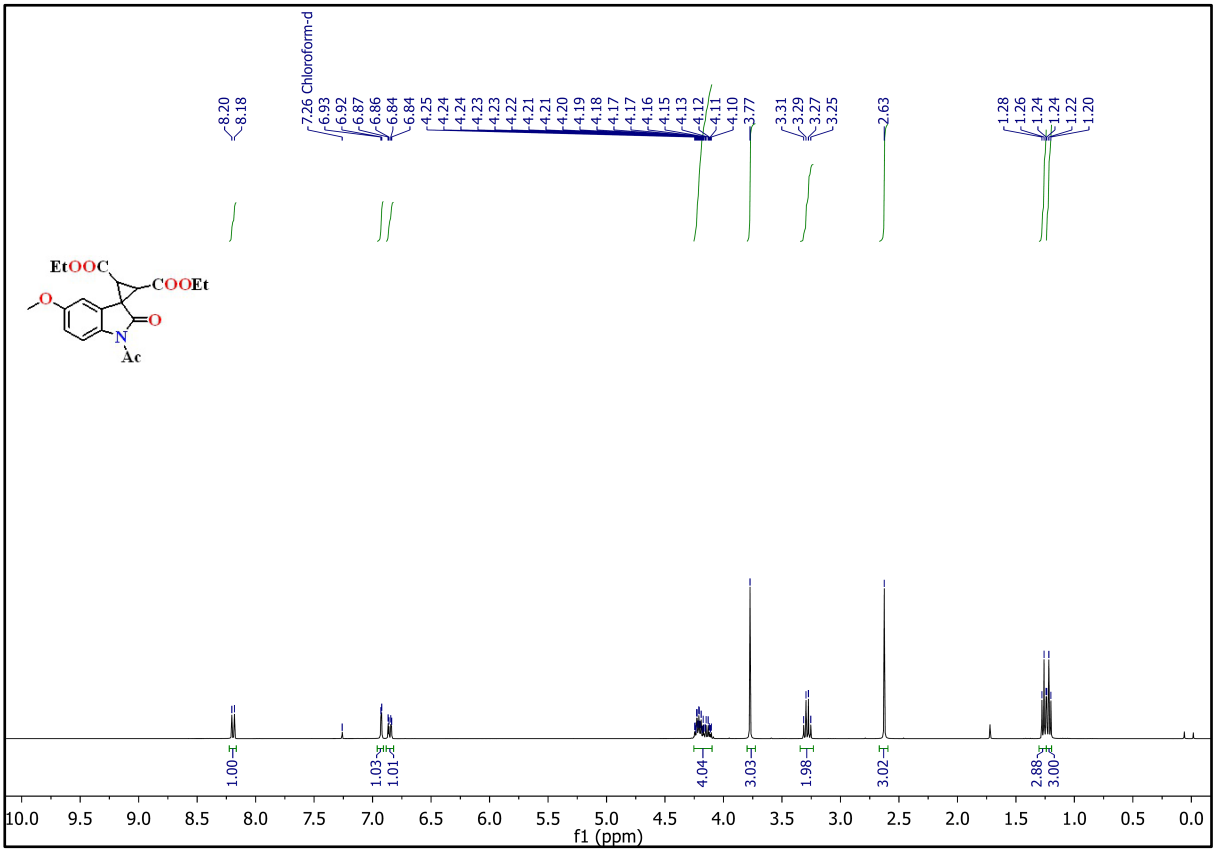
^{1}H NMR (400 MHz) of **3ae** in CDCl3:



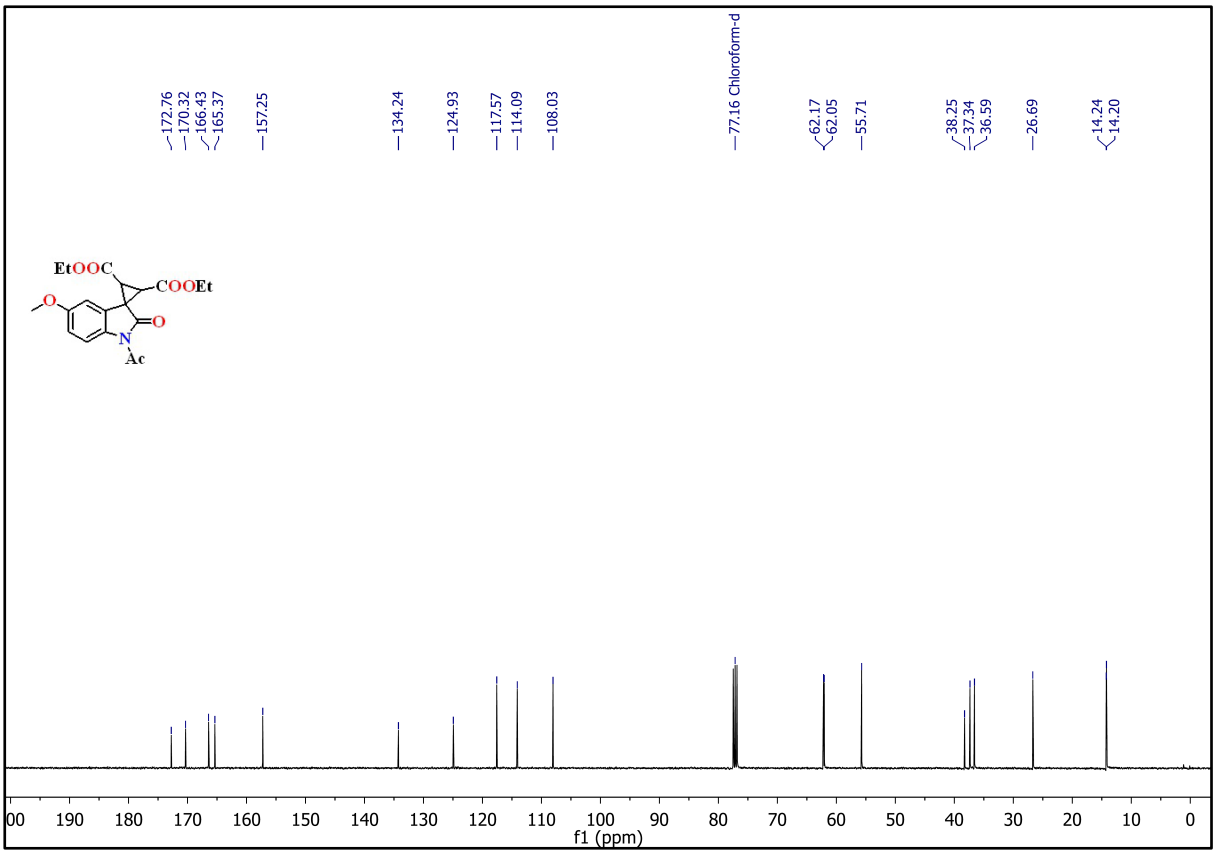
^{13}C{^{1}H} NMR (100 MHz) of **3ae** in CDCl3:



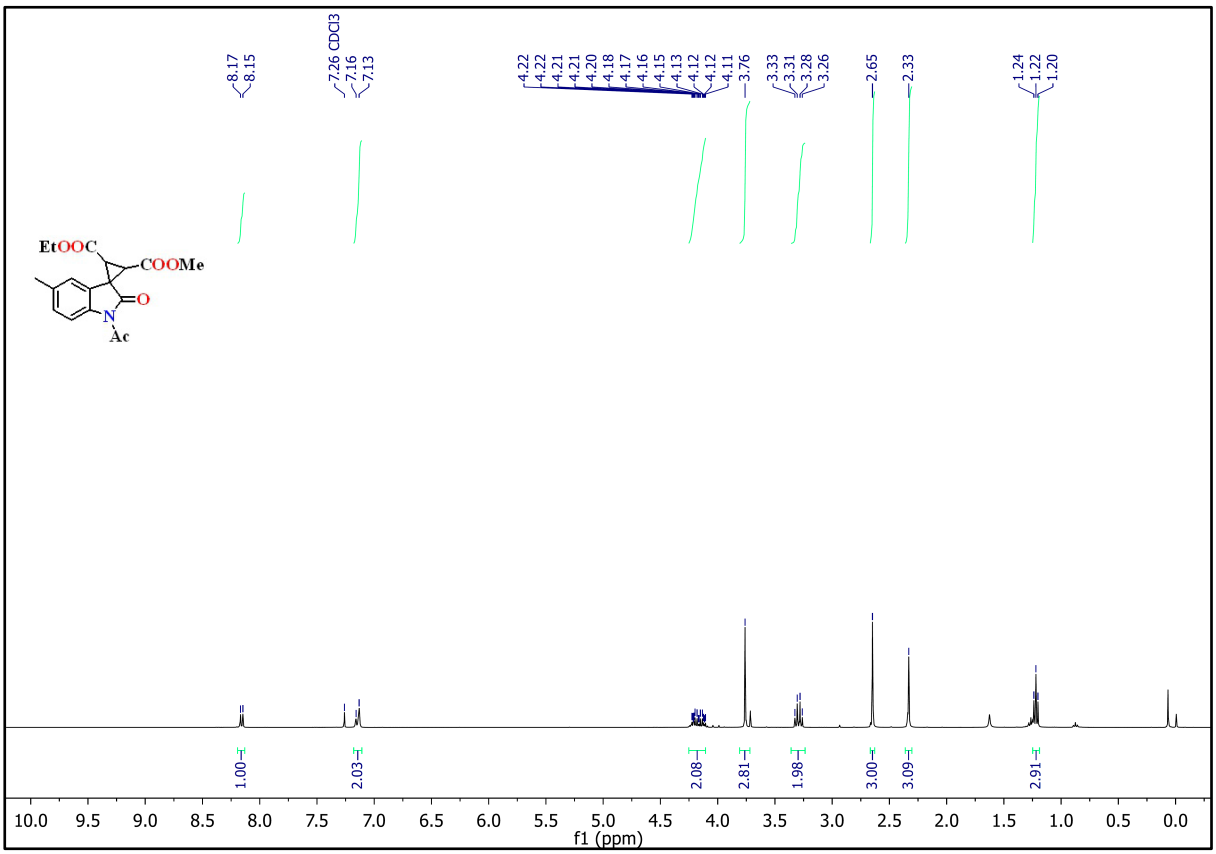
^{1}H NMR (400 MHz) of **3af** in CDCl3:



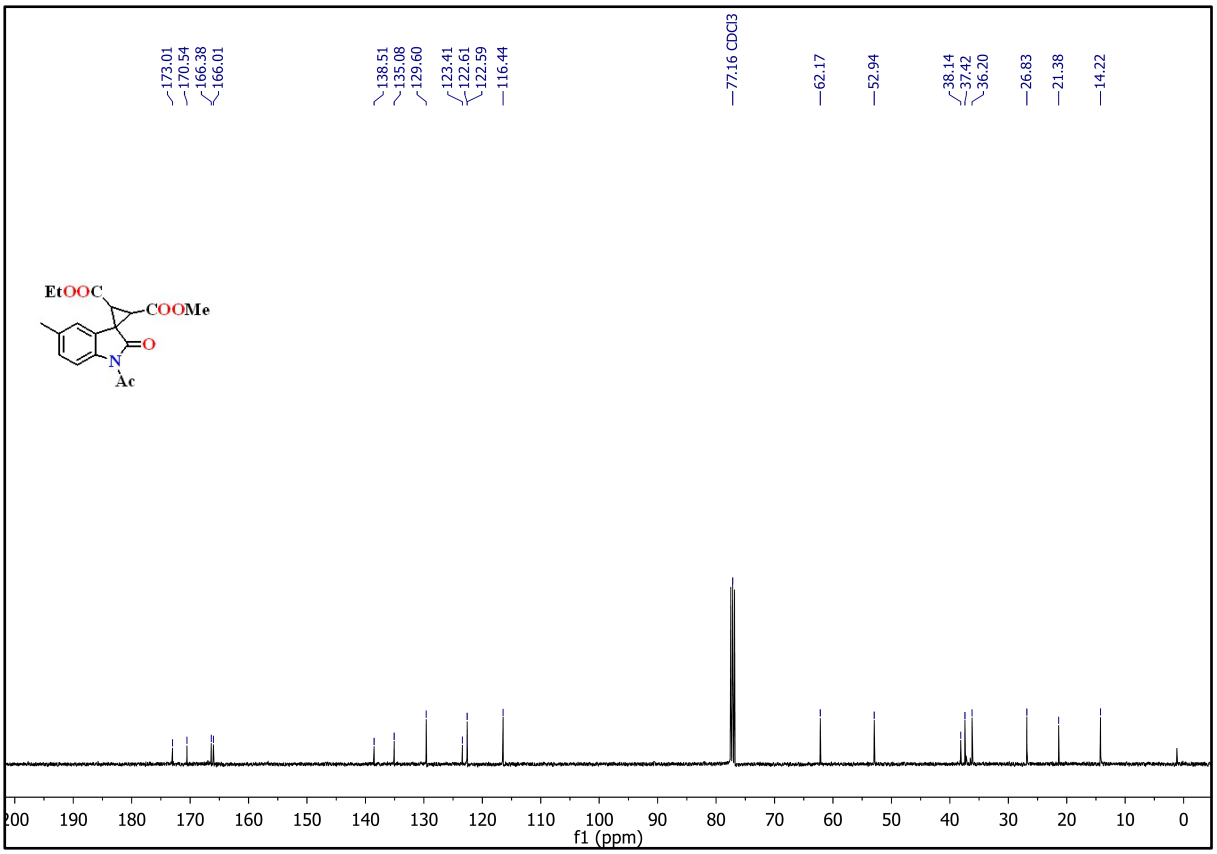
^{13}C{^{1}H} NMR (100 MHz) of **3af** in CDCl3:



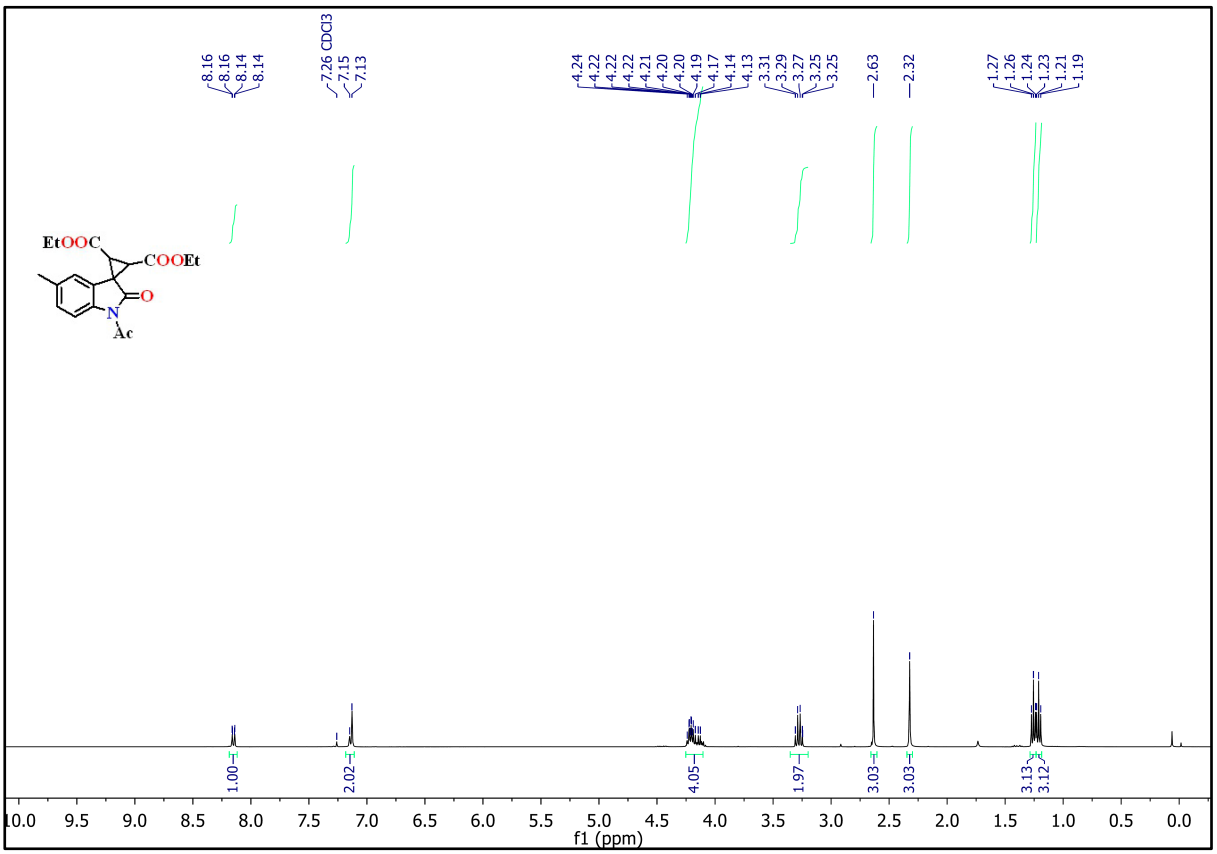
^{1}H NMR (400 MHz) of **3ag** in CDCl3:



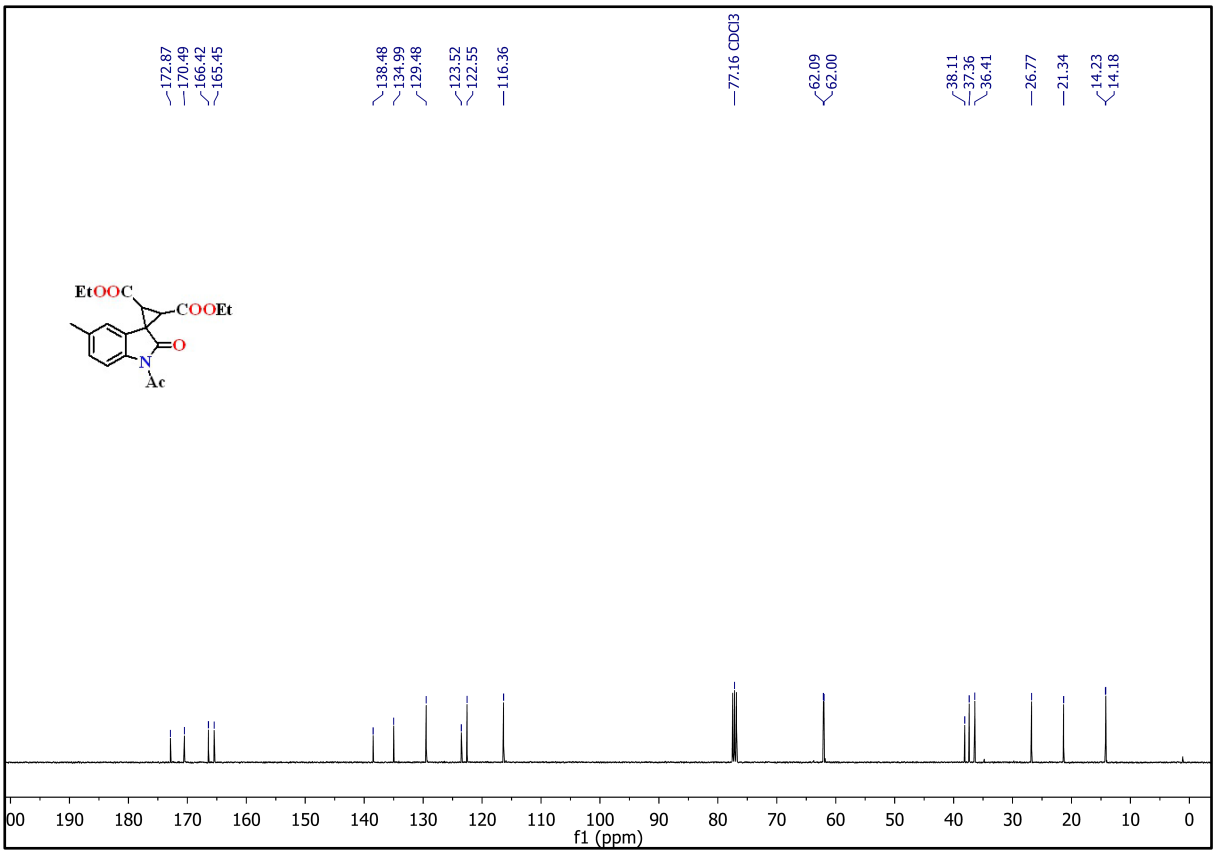
^{13}C{^{1}H} NMR (100 MHz) of **3ag** in CDCl3:



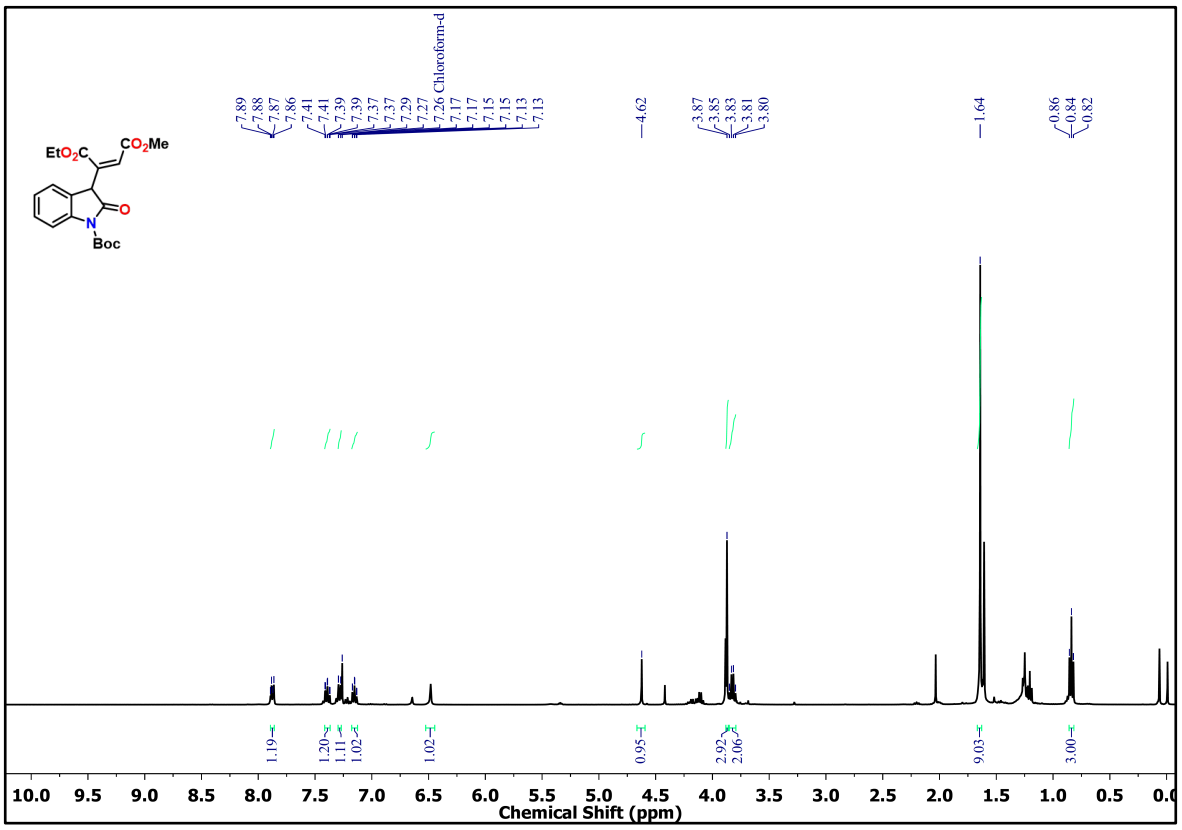
^{1}H NMR (400 MHz) of **3ah** in CDCl3:



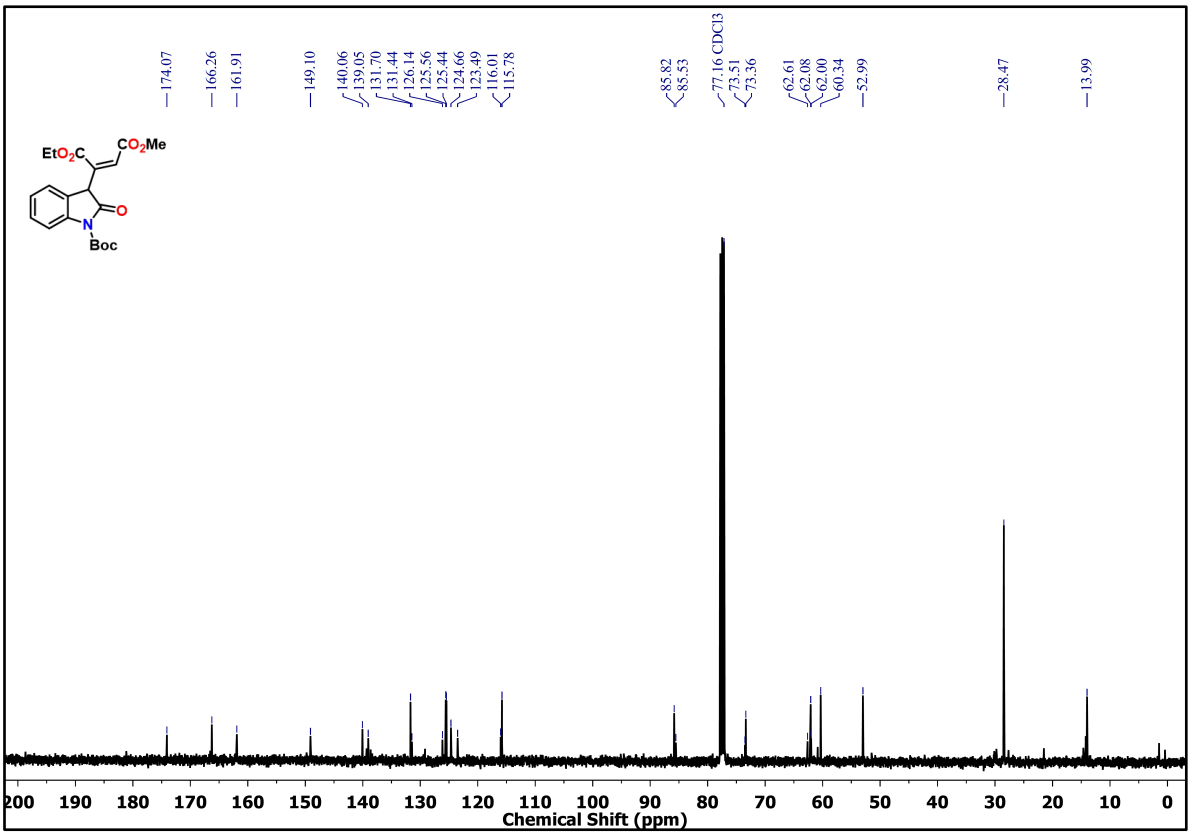
^{13}C{^{1}H} NMR (100 MHz) of **3ah** in CDCl3:



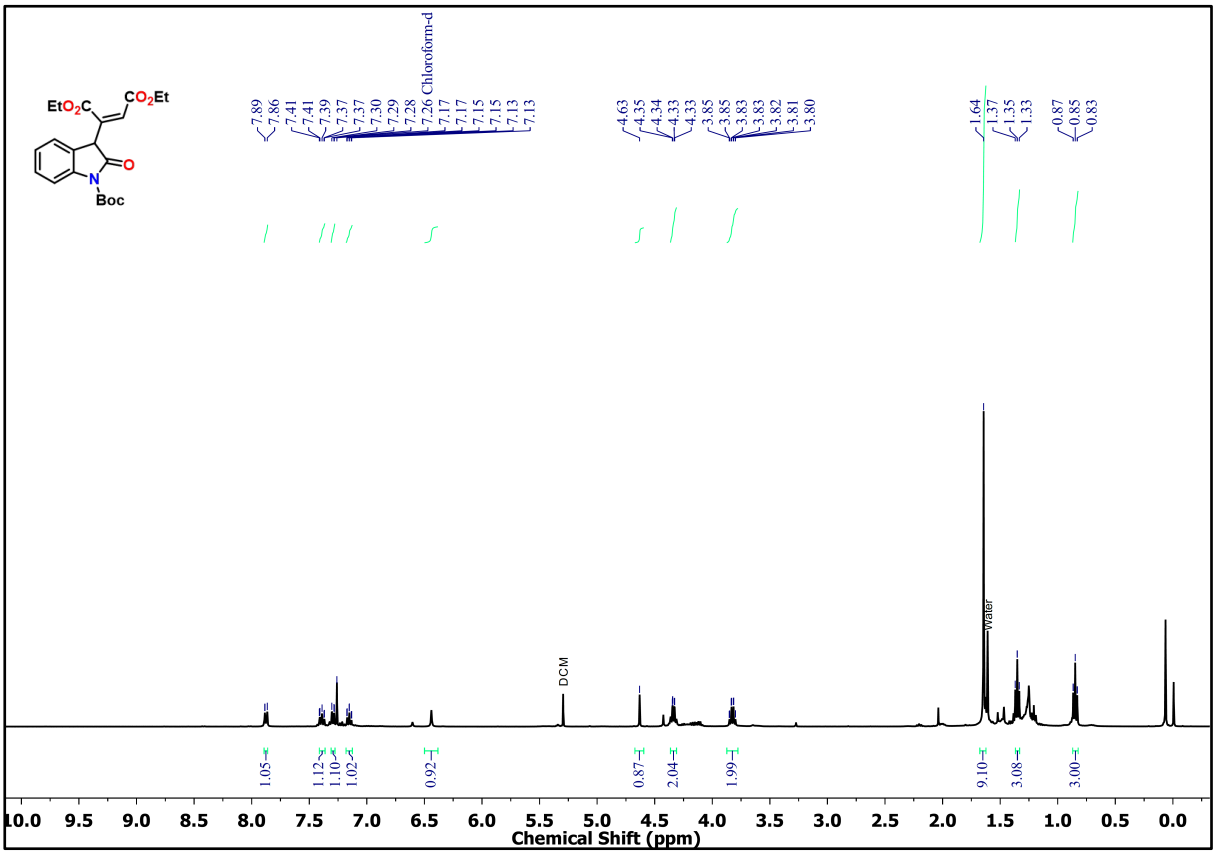
^{1}H NMR (400 MHz) of **3a'** in CDCl3:



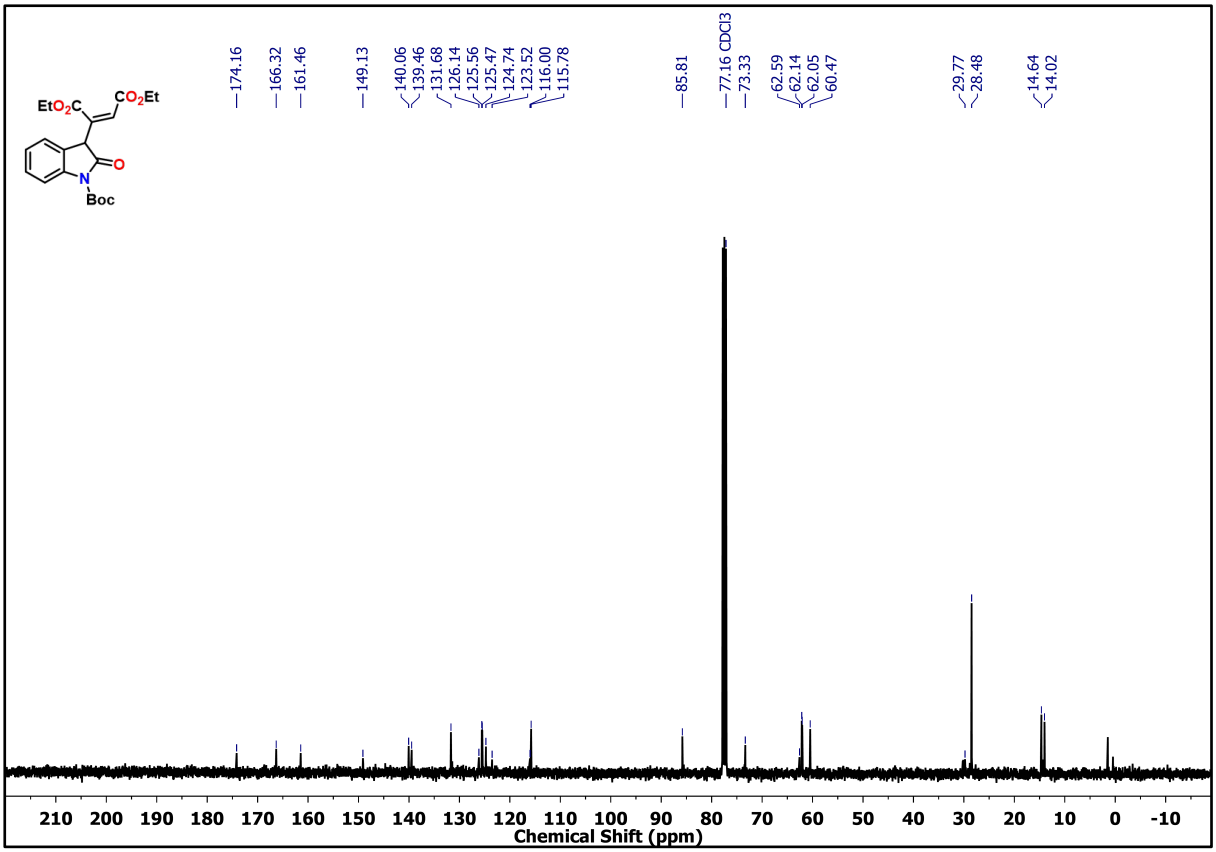
^{13}C{^{1}H} NMR (100 MHz) of **3a'** in CDCl3:



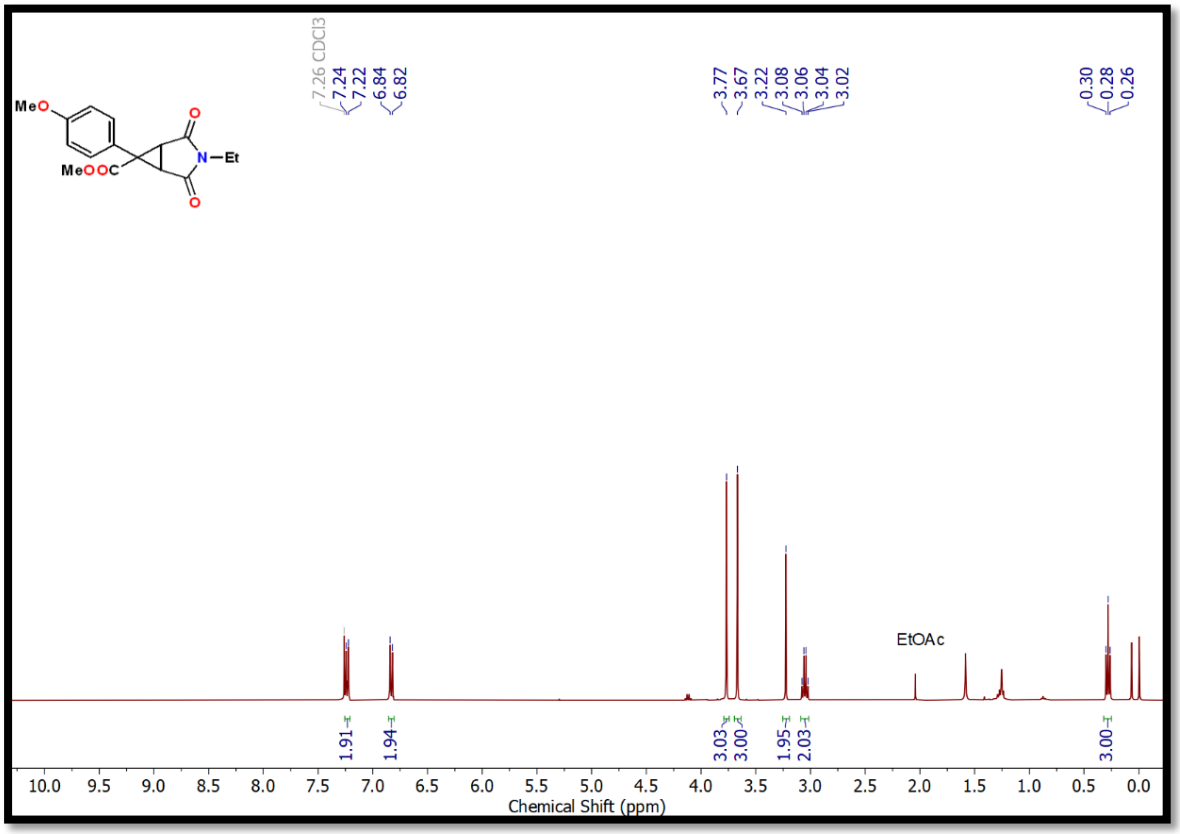
^{1}H NMR (400 MHz) of **3f'** in CDCl3:



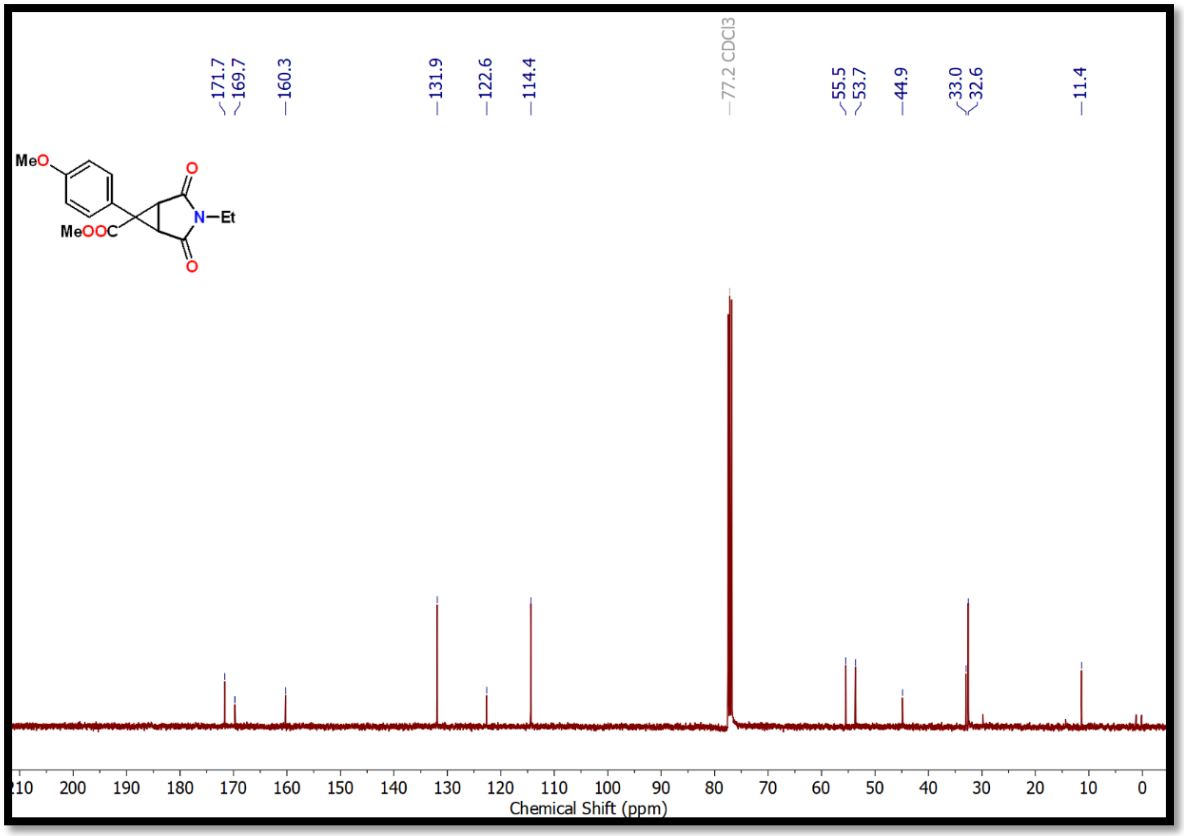
$^{13}C\{^{1}H\}$ NMR (100 MHz) of **3f'** in CDCl3:



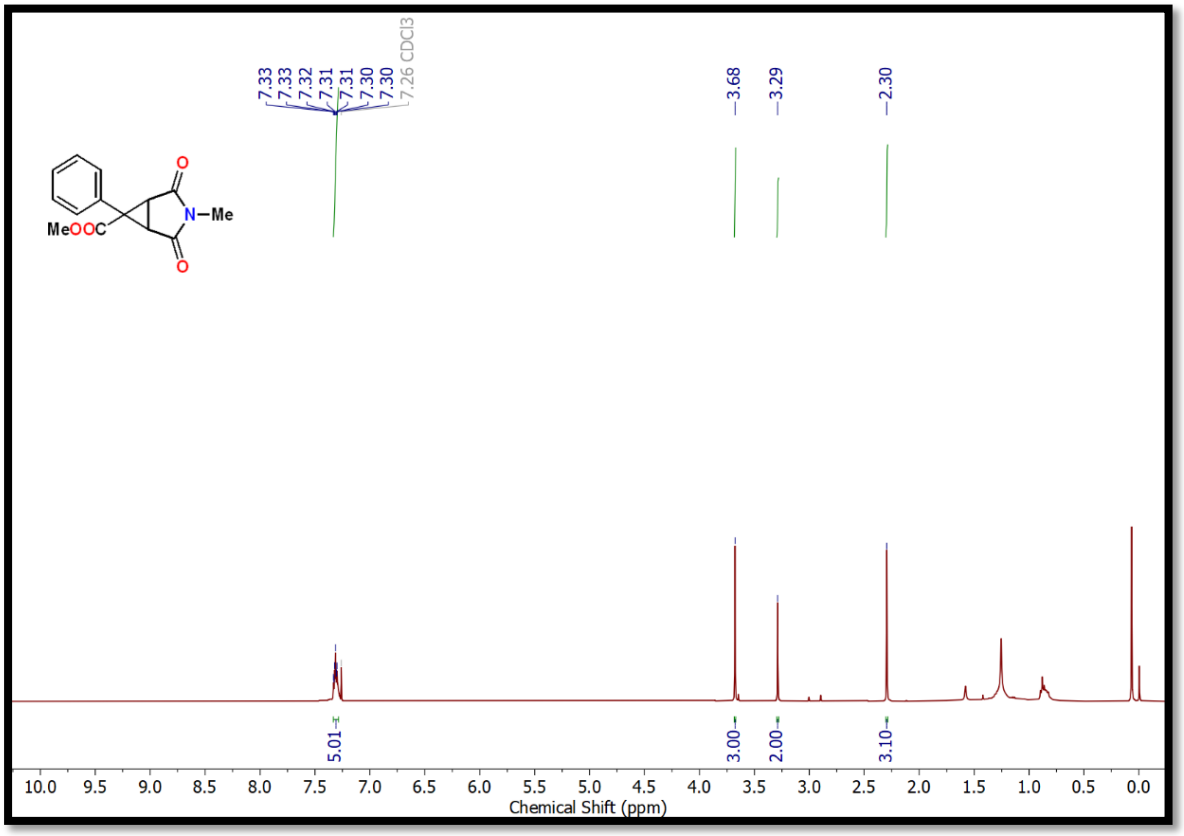
1H NMR (400 MHz) of **7a** in $CDCl_3$



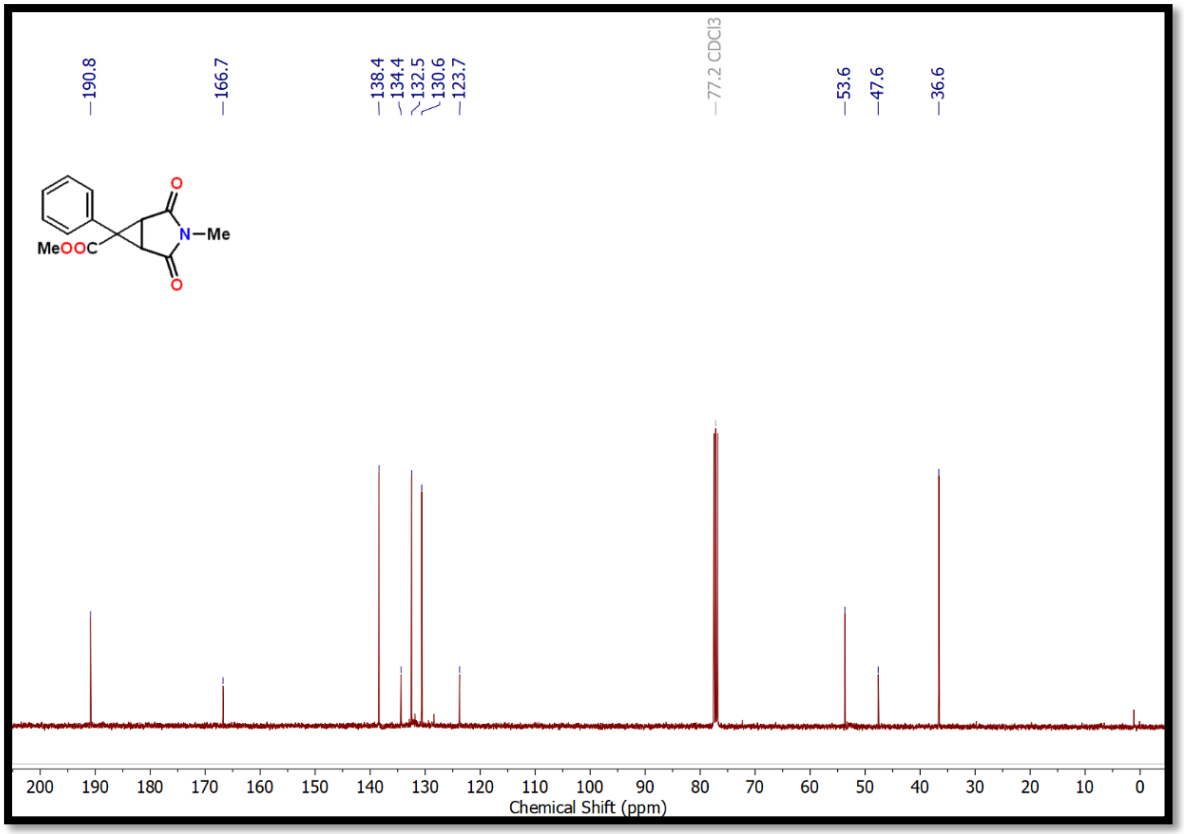
^{13}C NMR (100 MHz) of **7a** in $CDCl_3$



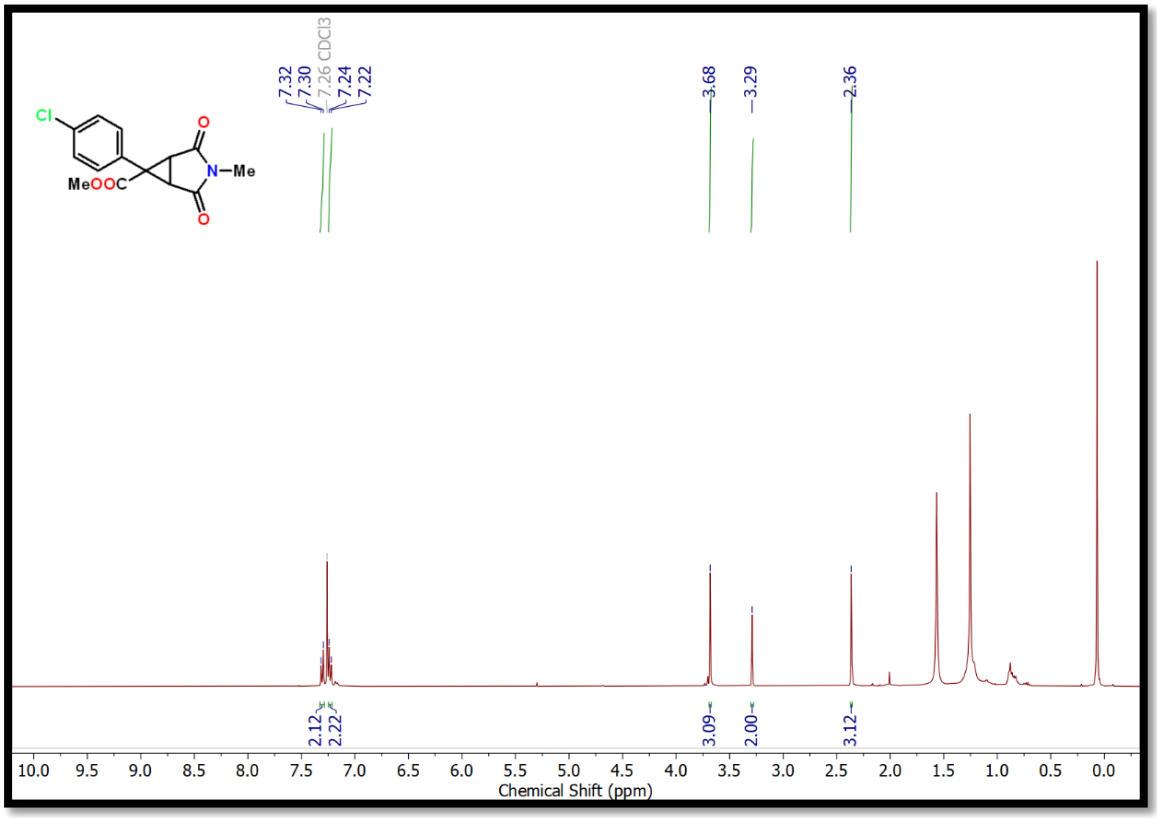
^{1}H NMR (400 MHz) of **7b** in $CDCl_3$



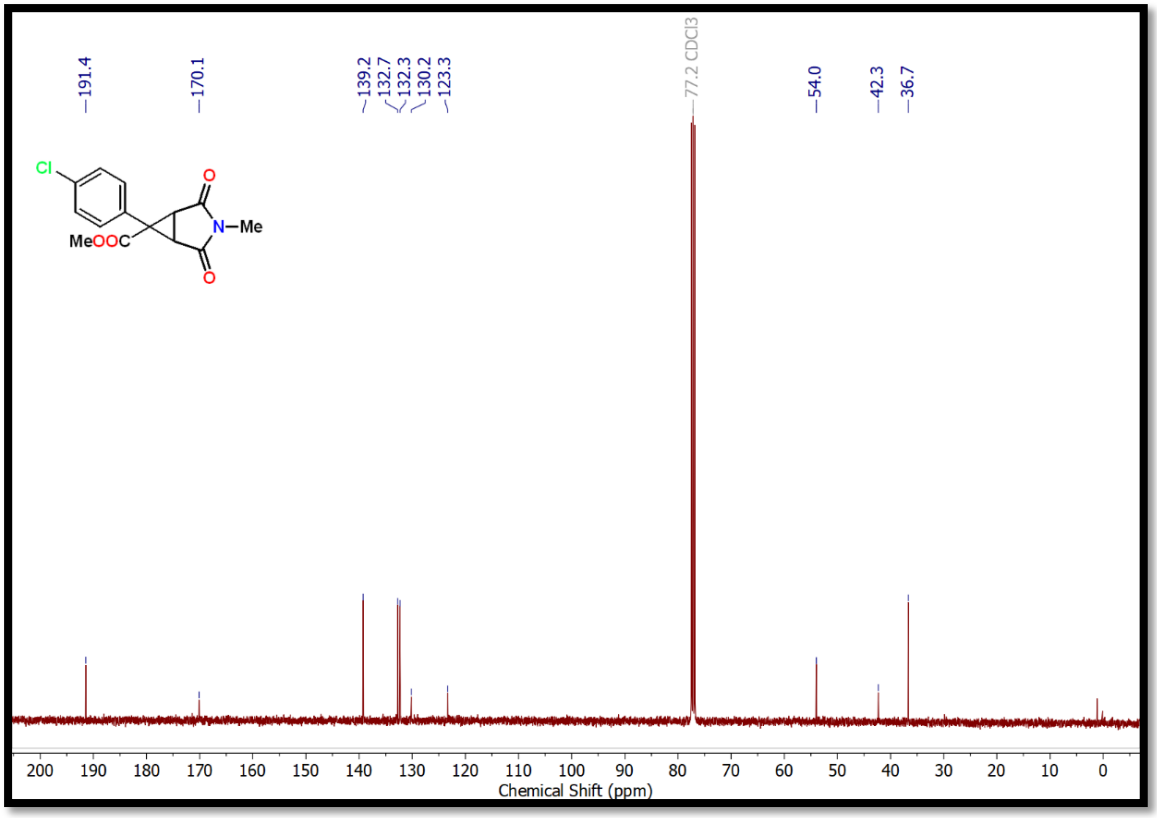
^{13}C NMR (100 MHz) of **7b** in $CDCl_3$



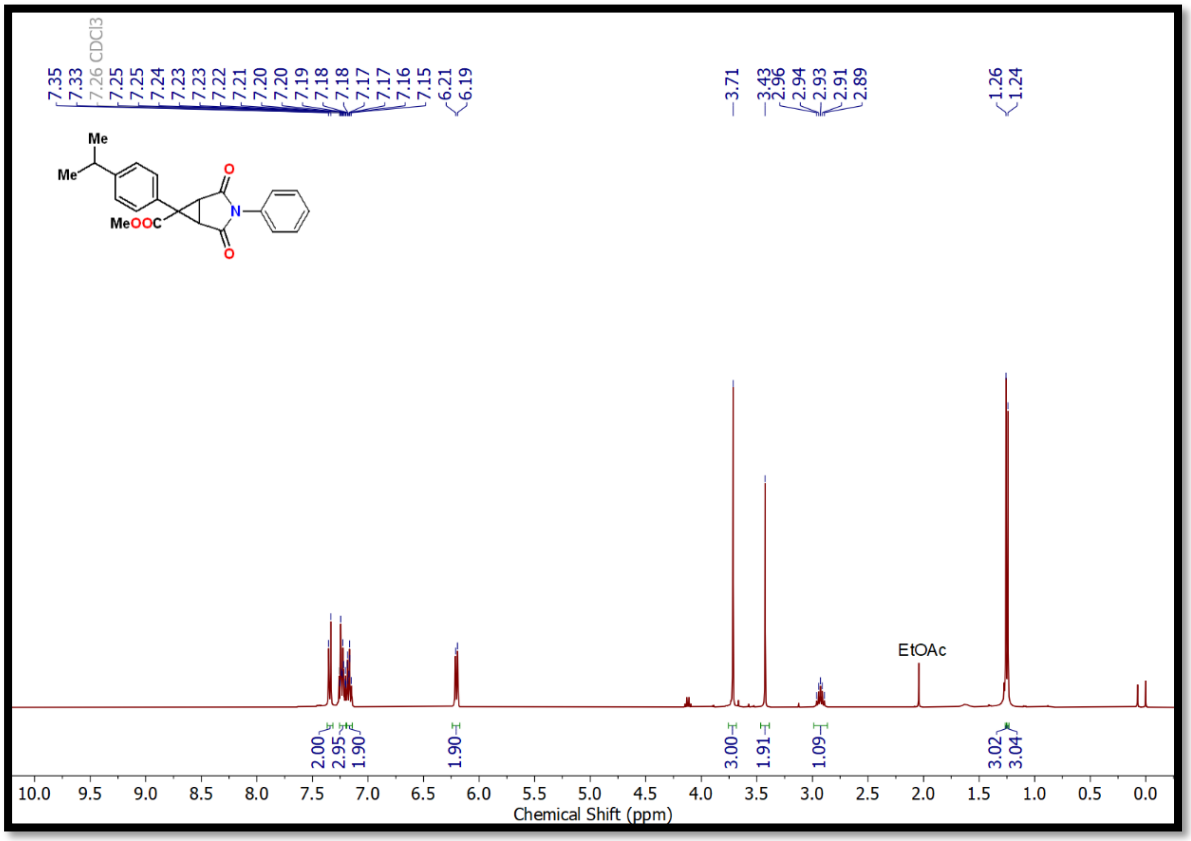
^{1}H NMR (400 MHz) of **7c** in $CDCl_3$



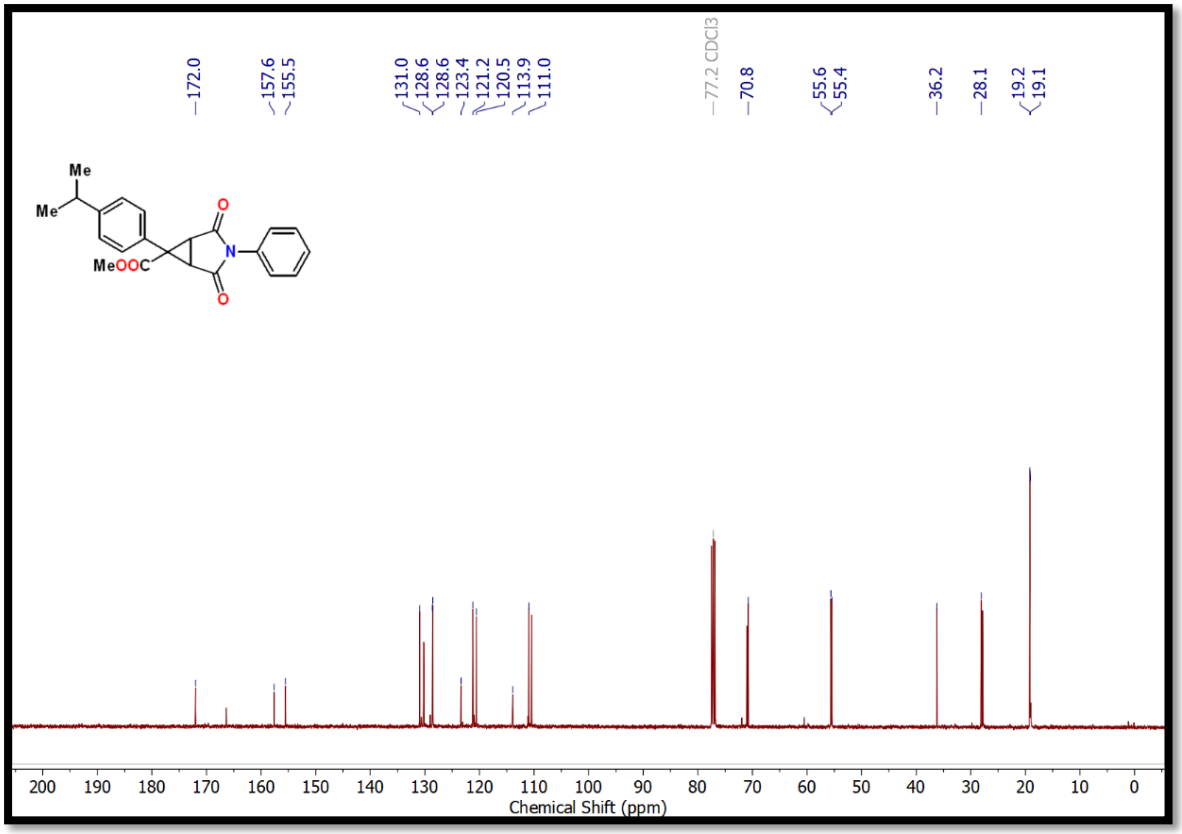
^{13}C NMR (100 MHz) of **7c** in $CDCl_3$



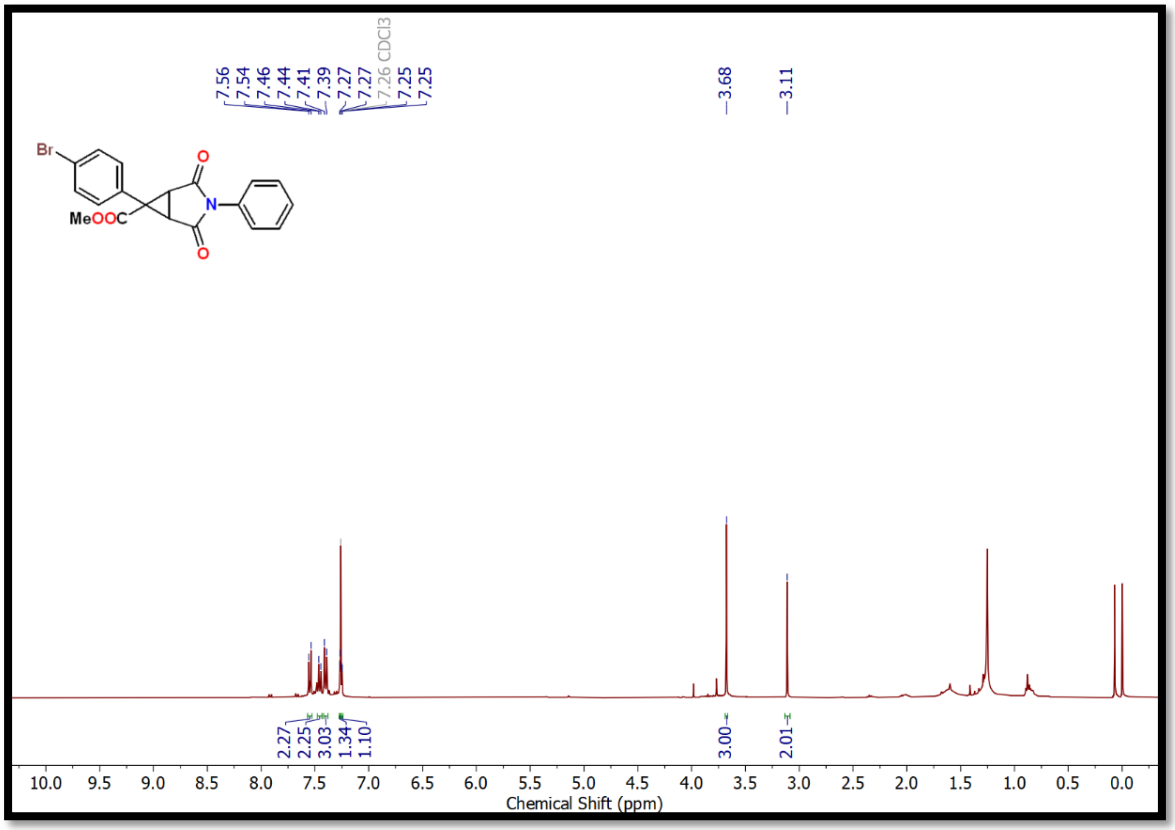
^{1}H NMR (400 MHz) of **7d** in $CDCl_3$



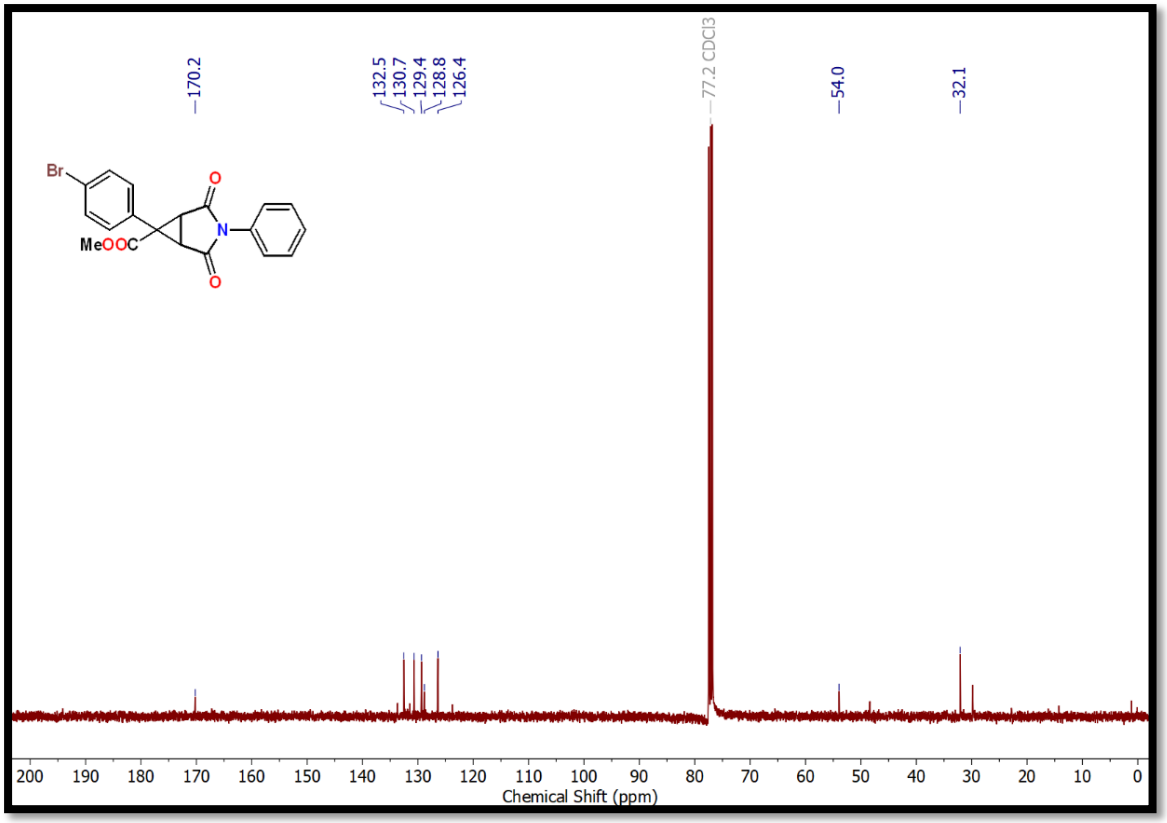
^{13}C NMR (100 MHz) of **7d** in $CDCl_3$



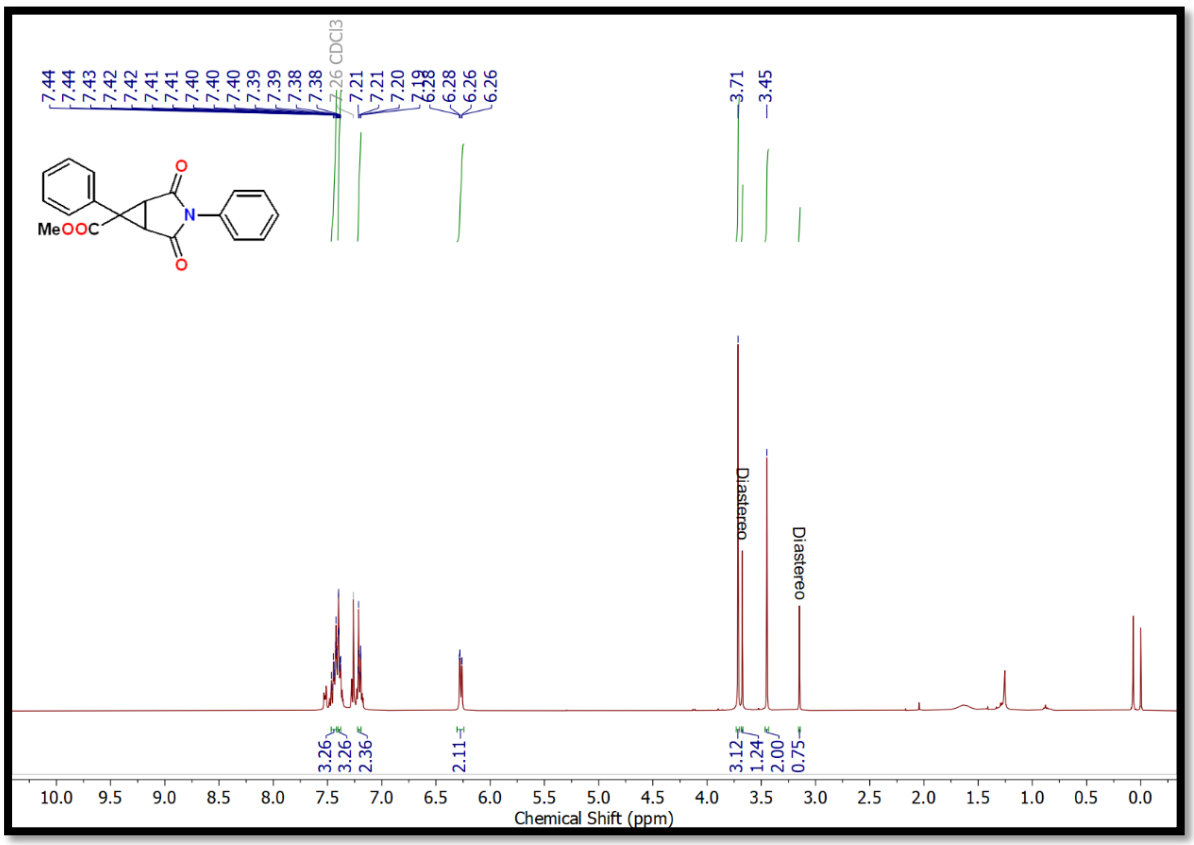
^{1}H NMR (400 MHz) of **7e** in $CDCl_3$



^{13}C NMR (100 MHz) of **7e** in $CDCl_3$



^{1}H NMR (400 MHz) of **7f** in $CDCl_3$



^{13}C NMR (100 MHz) of **7f** in $CDCl_3$